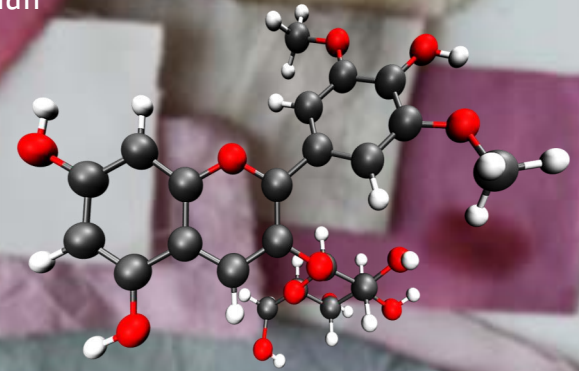


Non-Food Applications of Anthocyanins Extracted from Agro-Food Residues: a Combined Experimental and Theoretical Study

Kim Phan



Non-Food Applications of Anthocyanins Extracted from Agro-Food Residues: a Combined Experimental and Theoretical Study

Kim Phan

2021

Niet-Voedingstoepassingen van Anthocyaninen Geëxtraheerd uit Agrovoedingsresiduen: Een Gecombineerde Experimentele en Theoretische Studie

Non-Food Applications of Anthocyanins Extracted from Agro-Food Residues: a Combined Experimental and Theoretical Study

A dissertation submitted to Ghent University in partial fulfilment of the requirements for the degree of
Doctor of Bioscience Engineering: Chemistry and Bioprocess Technology
Academic Year: 2020-2021

Promoters:

prof. dr. ir. Steven De Meester

Laboratory for Circular Process Engineering (LCPE), Department of Green Chemistry and Technology, Ghent University

prof. dr. ir. Veronique Van Speybroeck

Center for Molecular Modeling, Ghent University

prof. dr. ir. Katleen Raes

Research Unit VEG-i-TEC, Department of Food Technology, Safety and Health, Ghent University

prof. dr. ir. Karen De Clerck

Department of Materials, Textiles and Chemical Engineering (MaTCh), Ghent University

Dean: prof. dr. ir. Marc Van Meirvenne

Rector: prof. dr. Rik Van de Walle



ISBN 978-94-6357-416-7

NUR 913

Wettelijk depot: D/2021/9873/032

Members of the examination committee:

Chairman:

prof. dr. ir. Stefaan De Smet (Ghent University)

Reading committee:

Prof. dr. ir. Matthias D'hooghe (Ghent University)

Prof. dr. ir. Ramon Ganigué (Ghent University)

Prof. dr. Dorien Derksen (AVANS Hogeschool & HZ University of Applied Sciences Breda)

Dr. ir. Sophie Roelants (Ghent University)

Dr. Mahmoud Hamzaoui (Celabor Scrl)

It's up to me now, turn on the bright lights

- Paul Banks

Voorwoord

Stof tot nadenken. Dat is het zeker en vast geweest, en nog steeds. Na vier jaar onderzoek op natuurlijke kleurstoffen is het voorwoord het ultieme sluitstuk over wat ik allemaal onderweg heb meegemaakt. Een “walk in the park” was het zeker niet, maar wel een mooi avontuur met belangrijke levenslessen die ik in mijn rugzak mag steken. Bizar genoeg is dit wel het moeilijkste stukje om te schrijven van gans het boekje. Misschien moet ik met de volgende quote beginnen:

“Je doet de kleurkes er gewoon bij en dat gaat wel lukken zeker.”

Een heerlijke quote van Steven, maar zo heb je er zoveel. Eerst wil ik je bedanken omdat je me deze unieke kans hebt gegeven. Een goede vier jaar geleden had je een bureau, wat geld en was je op zoek naar een chemist. Vier jaar later ben ik nog altijd vereerd om je chemist te mogen zijn. Dat ik hier mag staan, heb ik te danken aan je mensenkennis die je op cafés hebt opgedaan. Ik heb me vaak wat schuldig gevoeld als ik iets niet kon waarmaken tijdens mijn beginjaren. Mijn doorzettingsvermogen en zelfvertrouwen werden op de proef gesteld, maar je hebt me wel altijd gerustgesteld dat we nog op schema zaten. Het was een nieuw onderwerp voor ons allebei, maar je “out-of-the-box” denken vond ik heel inspirerend. Het was lang zoeken vooraleer ik op het rechte pad geraakte met deze natuurlijke kleurstoffen. Als de bovenstaande quote klopte, was er misschien geen sprake van een uitdaging. Verder was het leuk om vanop de eerste rij mee te maken hoe je onderzoeksgroep stelselmatig uitgroeide tot wat het nu geworden is. Je hebt veel gezaaid en dat werpt zijn vruchten af. Om de eerste te zijn die onder jouw leiding een doctoraat mag afleggen, kan ik enkel maar iets uit je lijflied (*The Smiths - There Is a Light That Never Goes Out*) citeren:

*And if a double-decker bus
Crashes into us
To die by your side
Is such a heavenly way to die
And if a ten ton truck
Kills the both of us
To die by your side
Well, the pleasure, the privilege is mine*

“Stronger through collaboration” is de slagzin aan het CMM en dit is zeer toepasselijk geweest tijdens mijn doctoraat. Naast Steven heb ik ook de privilege gehad om met drie ervaren promotoren te werken. Eerst en vooral wil ik Veronique heel hard bedanken voor haar tijd en ondersteuning. De voeling met het onderwerp is zeker niet vanzelfsprekend geweest, maar toch vond je altijd de juiste aanpak en oplossing. Je hebt me letterlijk onderdak geboden aan het CMM waar ik in een steile leercurve leerde modelleren dankzij de ondersteuning van de juiste mensen uit je team. Ik waardeer je professionele organisatie en de visie die je hebt over het CMM. De zoekklassen is daar het bewijs van. Dus om daarvan deel uit te maken is zeker iets om op trots te mogen zijn.

Verder wil ik ook Katleen bedanken voor haar bijdrage in dit hele verhaal. Je kennis van bioactieve componenten is voor dit verhaal van natuurlijke kleurstoffen zeer belangrijk geweest. Je oog voor detail komt heel goed van pas en het uitstippelen van werkplannen was zeker nodig in het begin van dit doctoraat. Dank je wel voor je steun!

Daarnaast wil ik ook Karen bedanken voor haar expertise en het openstellen van haar labo voor mijn experimenten. Ik ben blij dat je ook een van mijn promotoren bent geweest. Je kennis over textiel en kleurstoffen was zeker onmisbaar in dit verhaal, waarvoor veel dank!

De vele teamvergaderingen met jullie waren essentieel voor mij, want ik kreeg veel input vanuit verschillende invalshoeken van jullie diverse onderzoeksdomeinen. Het is letterlijk avontuur geweest, want soms was ik in een week bij al deze verschillende onderzoeksgroepen gepasseerd. Een evenwicht vinden tussen experimenteel werk en moleculair modelleren was soms op het nippertje, maar het resultaat kunnen jullie straks verder lezen of gewoon direct

naar de conclusie sectie gaan (p. 179).

De academische wereld is een komen en gaan, en zeker als je overal bij deze verschillende onderzoeksgroepen terechtkom, leer je snel nieuwe mensen. Ik ben hen ook dankbaar want ze waren allemaal vriendelijk en behulpzaam. Ik zal zeker enkele mensen vergeten waarvoor mijn excuses.

First of all I want to thank the people from LCPE, let's say the people with whom I spend most of my time. I want to thank them for their support during my research whether it is just about research or just for a banter. Some of my colleagues I can even call as true friends. Special thanks to Sibel. As you're a real chemist as well – even though Steven thinks you're not - it's nice how we both end up in the same research group. Thank you for your time, your help and entrusting my concerns about research and life. I also want to thank Martijn, Elisabetta (grazie mille), Ruben Demets, Kerstin, Benson, Rita,... for their support.

Verder wil ik ook de harde kern aan West-Vlamingen, en ook normale AN-ers, op UGent campus Kortrijk bedanken: Dave (bedankt voor jouw cynische humor waarmee ik altijd heerlijk om kan lachen), Pieter-Jan, Michael, Ellen, Pieter, Ruben, Tobias, Lies, Joël, Yannick, Isabel, Caroline, Ann,...

Daarnaast moet ik ook enkele personen bedanken van het CMM. Mijn bureaugenoten Pieter en Elias (paljas!). Zonder jullie kennis over modelleren zou ik hier ook niet gestaan hebben. Bedankt voor al jullie tijd om me het modelleren onder de knie te krijgen en bijhorende geduld. Verder wil ik ook Michael (ja, het is af!), Hannelore, Francesco, Toon, Massimo, Liesbeth,... bedanken voor hun hulp op al mijn vragen.

Mijn studenten over de jaren heen wil ook bedanken: Maxime, Tom, Maud (bedankt voor jouw mooie foto's die nu op de cover prijken ©), Clara en Pauline (waarschijnlijk mijn meest unieke ervaring ooit om een tweeling te begeleiden).

Thanks to the A&MS group, especially Frank and Lieve. I think performing my master thesis in your research group has inspired me to continue within the academic world. Eduardo, I'm really happy that you were my supervisor back then. Your warm human touch and care was very welcoming for me, you gave me much confidence, supported me, and tried opening doors for me. I'm really lucky

and thankful to know you and Ana.

Ook bedankt aan mijn bende chemisten met wie ik het universiteitsleven mee bewandelde: Stijn, Tineke, Emma, Judith, Sofie, Mien, Jonas en Sarah. Helaas hebben we elkaar nog niet veel kunnen zien de laatste jaren. Mijn tafeltennisvrienden heb ik ook moeten missen. Alhoewel dit eens beter uitdraaide in mijn laatste jaar, want dan kon ik mijn thesis schrijven, maar de wekelijkse training om eens de gedachten te verzetten en het bijhorende gezever is nog steeds voor mij de ideale ontspanning. Hopelijk kunnen we gauw weer op een balletje slaan.

De laatste en ook de meest belangrijke persoon die ik moet bedanken is mijn moeder. We hebben niet veel familie, maar we hebben wel elkaar. Om opeens je moederland te moeten verlaten door het regime en als immigrant naar België te komen was niet allemaal vanzelfsprekend geweest. Je hebt je leven op het spel gezet om jezelf een betere toekomst te geven, maar dan later ook voor mij. Je hebt me altijd gezegd dat studeren belangrijk is. Je wilde niet dat ik hetzelfde zware arbeid moet doen zoals jij. Dus dat ik hier mag staan, een doctoraat halen, heb ik grotendeels aan jou te danken. Je onvoorwaardelijke steun en liefde hebben me geholpen tijdens moeilijkere, maar ook mooie momenten. Je hebt me geleerd om te vallen, maar dan ook weer om op te staan en verder te gaan. Door hard te werken, kan je alles aan.

Kim Phan
Gent, 07 juni 2021

Contents

List of Abbreviations	xvii
List of Figures	xxi
List of Tables	xxvii
Samenvatting	xxxv
Summary	xl

I	General Introduction	1

1.	Introduction	3
1.1.	Context	3
1.2.	The Colorful Science Behind Light	9
1.2.1.	Anthocyanins	11
1.2.2.	Quinones	14
1.2.3.	Carotenoids	17
1.3.	Fruit and Vegetable By-Products Generated Within the Food Supply Chain	19
1.3.1.	Content of Natural Colorants Within Fruit and Vegetables	19
1.3.1.1.	Anthocyanins	20
1.3.1.2.	Quinones	22
1.3.1.3.	Carotenoids	22
1.4.	Natural Dyes in Practice	27
1.4.1.	Anthocyanins	28
1.4.2.	Quinones	32
1.4.2.1.	Benzoquinones	32
1.4.2.2.	Naphthoquinones	32
1.4.2.3.	Anthraquinones	34
1.4.3.	Carotenoids	36
1.5.	Conclusions	43

II Objectives of the PhD 45

III Major Research Results 51

2. An <i>In Silico</i> Study on The Solvent Dependency of Anthocyanin Extraction Profiles	55
2.1. Introduction	55
2.2. Materials and Methods	60
2.2.1. Theoretical Tools	60
2.2.1.1. Hansen Solubility Parameters	60
2.2.1.2. Flory-Huggins Interaction Parameter (χ_{12})	61
2.2.2. Computational Tools	61
2.2.2.1. Density Functional Theory: Static Calculations	61
2.2.2.2. Conductor-like Screening Model for Realistic Solvent (COSMO-RS)	62
2.2.3. Experimental Section	64
2.2.3.1. Reagents	64
2.2.3.2. Thermal Analyses	64
2.2.3.3. Statistical analysis	64
2.3. Results and Discussions	64
2.3.1. Hansen Solubility Parameters and Flory-Huggins Interaction Parameter (χ_{12})	64
2.3.2. Density Functional Theory: Static Calculations	67
2.3.3. Conductor-like Screening Model for Realistic Solvent (COSMO-RS)	67
2.3.4. Comparison of the Different Computational Models for Anthocyanidins and Anthocyanins Extraction	71
2.3.5. Binary Mixtures	76
2.4. Conclusions	79
3. The Potential of Anthocyanins from Blueberries as a Natural Dye for Cotton: a Combined Experimental and Theoretical Study	83
3.1. Introduction	83
3.2. Materials and Methods	86
3.2.1. Experimental Section	86
3.2.1.1. Scope of the Mordants	86
3.2.1.2. Samples and Reagents	87
3.2.1.3. Extraction Procedure	87

3.2.1.4.	Optimization of Dyeing Conditions	88
3.2.1.5.	Premordanting Procedure	88
3.2.1.6.	Metamordanting Procedure	89
3.2.1.7.	Fourier-Transform Infrared Spectrophotometer	89
3.2.1.8.	Spectrophotometric Data	90
3.2.1.9.	Fastness Tests of Dyed Fabrics	91
3.2.1.10.	Statistical Analysis	92
3.2.1.11.	Adsorption Models	92
3.2.2.	Molecular Modeling Details	94
3.2.2.1.	Static Calculations	94
3.2.2.2.	Molecular Dynamic Simulations	95
3.3.	Results and Discussion	96
3.3.1.	Optimization of the Dyeing Parameters	96
3.3.1.1.	Temperature	96
3.3.1.2.	Dyeing Time	97
3.3.1.3.	pH	98
3.3.1.4.	Concentration	99
3.3.1.5.	Esterification	100
3.3.2.	Dyeing Results with (Bio)mordants, Color Measurement and Fastness	100
3.3.2.1.	Metallic Mordants (Tin and Aluminium)	100
3.3.2.2.	Biomordant: Hydrogen Bonds	103
3.3.2.3.	Biomordant: Ionic Bond and π - π Interactions	104
3.3.3.	Modeling of Adsorption	110
3.3.4.	Molecular Modeling of Dye-Mordants Interaction	113
3.3.4.1.	Interaction Energies from Static Calculations	113
3.3.4.2.	Molecular Dynamics Simulations to Unravel Interactions between Tannic Acid, Dye Molecules and Solvent	115
3.4.	Conclusions	120
4.	A Comparative Study on the Photophysical Properties of Anthocyanins and Pyranoanthocyanins	123
4.1.	Introduction	123
4.2.	Computational Details	127
4.3.	Results and Discussion	129
4.3.1.	Photophysical Properties of Anthocyanins and their Derivatives by means of TD-DFT	129

4.3.1.1.	Influence of Solvation Model on UV-Vis Properties	129
4.3.1.2.	UV-Vis Properties of Anthocyanidins and Anthocyanins	130
4.3.1.3.	UV-Vis Properties of Acylated Anthocyanins . .	131
4.3.1.4.	UV-Vis Properties of Pyranoanthocyanins	136
4.3.1.5.	UV-Vis Properties of Acylated Pyranoanthocyanins	140
4.3.2.	A Tool for Food and Non-Food Applications	144
4.3.2.1.	Food Additives/Colorants and Analytical Standards	144
4.3.2.2.	Pyranoanthocyanins: New Natural Dyes on Textile Fibers with Better Fastness Properties? .	147
4.3.2.3.	Optical Transition Properties for DSSC	149
4.4.	Conclusions	153
5.	Toward industrial valorisation of natural dyes	155
5.1.	The Valorization Routes From Agro-Food Residues to Textile Application	155
5.1.1.	Valorization Route for Anthocyanins	156
5.1.2.	Valorization Route for Quinones	160
5.1.3.	Valorization Route for Carotenoids	162
5.2.	LCA of the Production of Naturally-Dyed Fabrics from Agro-Food Residues	165
5.2.1.	Methodology	165
5.2.2.	LCA Results	168
5.2.2.1.	Anthocyanins	168
5.2.2.2.	Naphthoquinones	168
5.2.2.3.	Anthraquinones	169
5.2.2.4.	Carotenoids	169
5.2.3.	Sensitivity analyses	173
5.3.	Conclusions	176
6.	General Conclusions and Future Perspectives	179
6.1.	Conclusions	179
6.2.	Future Perspectives	184
	Bibliography	187
	Appendix A. Introduction	239

Appendix B. An <i>In Silico</i> Study on the Solvent Dependency of Anthocyanin Extraction Profiles	263
Appendix C. The Potential of Anthocyanins from Blueberries as a Natural Dye for Cotton: a Combined Experimental and Theoretical Study	315
Appendix D. A Comparative Study on the Photophysical Properties of Anthocyanins and Pyranoanthocyanins	349
Appendix E. LCA of the Production of Naturally-Dyed Fabrics from Agro-Food Residues	533
Curriculum vitae	575

List of Abbreviations

Ap Apigeninidin 60, 74, 128, 132, 150

B3LYP Hybrid functional consisting of Becke's three-parameter combined with Lee-Yang-Parr correlation xv–xvii, xx, xxxii, 48, 62, 95, 117, 122, 131–134, 136, 138–141, 145–148, 150–152, 156, 157, 186

BSSE Basis Set Superposition Error 96, 116, 122

CAM-B3LYP B3LYP with the Coulomb-attenuating method xxxii, 48, 131, 132, 139, 140, 145, 146, 150, 157, 186

COSMO Conductor-like Screening Model 61, 62, 67, 131, 134

COSMO-RS Conductor-Like Screening Model For Real Solvents iv, xxx, xxxi, 47, 59, 60, 62–64, 67, 71, 74, 76, 77, 79, 80, 184, 185

CPCM Conductor-like Polarizable Continuum Model 131, 140

Cy Cyanidin 12, 60, 68, 71, 74, 76, 96, 116, 127, 128, 132, 148, 150

DFT Density Functional Theory xxx, 47, 60, 62, 71, 95, 96, 116, 130–132

Dp Delphinidin 12, 55, 56, 60, 74, 76, 96, 116, 127, 132, 150

DSSC Dye-Sensitized Solar Cell vi, xxxii, 55, 129, 130, 132, 148, 153, 154, 157

DW Dry Weight 19–23, 160, 161, 163, 164, 166

EtOH Ethanol xix, 57, 58

FT-IR Fourier Transform Infrared spectroscopy xxxi, 89, 101, 104, 105

FW Fresh Weight 19, 163

Glc Glucoside xix, 55, 57, 58, 68, 71, 74, 76, 96, 116, 148, 150, 189

HOMO Highest Occupied Molecular Orbital xvi, xvii, 132, 135, 137, 140, 142–145, 153, 156

HPLC High-Pressure Liquid Chromatography 59, 130, 134, 144, 149, 184

HSP Hansen Solubility Parameters 60, 61, 64, 65, 67, 68, 71, 76, 77

IEF-PCM Integral equation formalism (IEF) variant of the polarizable continuum model (PCM) 95, 131, 133

LCA Life Cycle Assessment xxxii, 8, 48, 169, 173, 177

LF Light Fastness xix, 30, 31, 167

Lt Luteolinidin 60, 74, 128, 132, 150

LUMO Lowest Unoccupied Molecular Orbital xvi, xvii, 132, 135, 137, 141–143, 145, 153, 156

MAE Mean Absolute Error xx, 133, 134, 138, 140, 141, 146, 148, 150, 157, 186

MD Molecular Dynamics 96, 97, 118, 119

MeOH Methanol xix, 57, 58, 132, 148

MS Mass Spectrometry 59, 130, 134, 144, 184

Mv Malvidin 12, 56, 60, 71, 74, 127, 132, 148, 150

Mv-3-Glc Malvidin-3-Glucoside xv, xvi, xx, 86, 88, 90, 92–97, 100, 106, 113–115, 117–122, 139, 145, 150, 154

M_w Molecular weight 90, 149

owf On the Weight of Fiber xviii, 89, 104, 163, 170, 173, 177–179

PBE0 Hybrid functional based on Perdew-Burke-Ernzerhof xxxii, 48, 131, 132, 140, 145, 146, 150, 157, 186

PCM Polarizable Continuum Model xv, 61, 96, 117, 122, 131, 133, 134

PEF Pulsed Electric Fields 161, 166

Pg Pelargonidin 12, 60, 74, 76, 127, 132, 150, 154, 189

PLA Polylactic acid 31, 36, 165

PLE Pressurized Liquid Extraction 161, 165, 166

Pn Peonidin 12, 60, 74, 76, 127, 132, 150

Pt Petunidin 12, 60, 74, 76, 96, 116, 127, 132, 150

SFE Supercritical Fluid Extraction 165, 166

SHP Sodium hypophosphite 87, 89, 101, 105

SMD Solvation Model based on Density xvi, xvii, xx, 61, 62, 74, 131, 133–136, 138, 140, 141, 146, 147, 152, 156

SPE Solid Phase Extraction 161, 167, 173

TD-DFT Time-Dependent Density Functional Theory v, xvii, xxxii, 86, 130, 132, 133, 139, 140, 148, 149, 151–155, 157, 186

UV-Vis Ultra-Violet and Visible light vi, xvi, 86, 90, 130–138, 140, 141, 144

WF Wash Fastness xix, 30, 31, 167

ΔC_p Change in heat capacity 63, 64

ΔE^* Color difference xx, 91, 100, 102–106, 108, 109, 123, 185

ΔG Change in Gibbs Free Energy 63, 64, 67, 107, 116, 122, 123, 153, 154, 186

ΔH Change in enthalpy 63

$\lambda_{\text{max,vis}}$ Maximal absorption wavelength at visible region xv, xvii, xx, 90, 98, 99, 128, 129, 133, 134, 140, 142, 145, 147–149, 151, 153, 157

χ_{12} Flory-Huggins interaction parameter iv, xxx, 47, 59–61, 64, 65, 71, 79, 184

List of Figures

1.1. The food supply chain of fruits and vegetables and the number of waste streams generated, in weight percentages and at each stage of the chain (European values [1]).	6
1.2. White light consists of a mixture of different wavelengths. When a light beam passes a glass prism, the different wavelengths or color components get dispersed due to refraction. The visible light, ranging from 400 - 700 nm, is the only light that is visible for human eye and takes a little part of the entire electromagnetic spectrum, i.e., from γ -rays till radiowaves.	10
1.3. The molecular structure of anthocyanin as a flavylium cation with its possible substitution patterns.	12
1.4. The common occurring naphthoquinones on top and below two naturally occurring benzoquinones.	14
1.5. The molecular representation of anthraquinones.	15
1.6. Most frequently occurring carotenoids. Acyclic carotenes: A: lycopene and B: ζ -carotene; Cyclic carotenes: C: α -carotene, D: β -carotene and E: γ -carotene; carotenols: F: lutein, G: zeaxanthin and H: β -cryptoxanthin; unique carotenoids: I: capsanthin, J: capsorubin, K: crocetin and L: bixin (Bechtold and Mussak, 2009; Rodriguez-Amaya, 2001).	18
1.7. These plots illustrate the number of by-products that are generated by processing within Europe as a function of the anthocyanin (A), quinone (B), or carotenoid (C) content within the different fruits and vegetables (Tables A.3 and A.4). The amount of by-products is derived from the percentage of waste to the primary production. This can be interpreted as a maximal value as the entire crop production will not be used for processing. The term 'raw' indicates the concentration found in the primary raw material. Additional figures on the amount of by-products produced locally can be found in the supporting information (Figures A.3 to A.9).	26
1.8. The fastness properties of anthocyanins on various fibers	39

1.9. The fastness properties of naphthoquinones on various fibers . . .	40
1.10. The fastness properties of anthraquinones on various fibers	41
1.11. The fastness properties of anthocyanins (A), naphthoquinones (B), anthraquinones (C), and carotenoids (D) on various fibers. The wash fastness is based on the color change on the grayscale, while it is expressed via blue wool standards. The scales of the fastness values are confined in boxes for the reader's convenience. The dotted lines represent the industrial-required fastness grades for general apparel. Only studies including both fastness properties were included in these plots; the reference labels are listed in Table A.5.	42
1.12. Overview of the various chapters within this dissertation.	49
2.1. The molecular structure and substitution pattern of anthocyanidins (ACDs) and anthocyanins (ACNs).	56
2.2. Hansen solubility parameters (δ_d , δ_p and δ_h) of the selected solvents (blue dots labelled as S1-S30), ACDs (magenta dots labelled as A1-A8) and ACNs (red dots labelled as A9-A14). Additional data on the distance R_a (MPa ^{1/2}) are illustrated and tabulated in the supporting information (Figure B.3 and Tables B.3 to B.6).	66
2.3. σ -profiles of Cy and Cy-3-Glc with the five most optimal solvents based on log S_{RS} (A) or σ -profile similarity (B, C). σ -values higher than 0.0081 e/Å ² show electron donor abilities, σ -values below 0.0081 e/Å ² show electron acceptor abilities and values in between indicate hydrophobic interactions.	70
2.4. (A) Normalized solubility values of ACDs and ACNs for the five most optimal solvents per computational method. The scale only shows the worst and best solvent from these five solvents to solubilize ACDs and ACNs as 0% and 100%, respectively. (B) The anthocyanin profiles in terms of log S_{RS} between the five most optimal solvents and the results of the traditional solvents used in anthocyanin extraction.	73
2.5. Normalized solubility values of ACDs and ACNs in water. The scale shows the worst and best solubility among ACDs and ACNs as 0% and 100%, respectively. The glycoside/aglycone pairs are indicated by the same color.	75

2.6. Relative solubility values (Log S_{RS}) calculated with COSMO-RS (A) and solubility parameter distances R_a (MPa ^{1/2}) (B) of aqueous mixtures (acetone-water, ethanol-water and methanol-water) for ACDs and ACNs extraction.	78
3.1. The four typically proposed types of intermolecular interactions between anthocyanins and (bio)mordants. This chapter therefore systematically compares: metal complexation: Sn(II) and Al(III), hydrogen bonds: sodium alginate, tannic acid and β -cyclodextrin; ionic bonding: oxalic acid; and π - π interactions: gallic acid and caffeic acid.	85
3.2. A: the optimization of the dyeing temperature in terms of relative dye uptake and amount of degradation, B: the relative dye uptake measured at 80 °C and the extent of degradation as a function of time, C: the $A_{440\text{ nm}}/A_{\lambda_{\text{max,vis}}}$ ratio representing the 3-glycosylation level of the dyebath over time and D: the absorbance ratio over time for two wavelengths (440 nm and 519 nm) of a blank dyebath and one containing the fabric.	98
3.3. Infrared spectra of esterification reactions with oxalic acid at different pH conditions.	101
3.4. The isotherm models: Langmuir (A), Freundlich (B), Redlich-Peterson (C) and Sips (D).	111
3.5. The kinetic models with from left to right: Lagergren (A), pseudo-second order (B) and intraparticle diffusion model (C). The blue data points were considered as outliers during fitting.	112
3.6. The 3D illustrations of tin and aluminium coordination complexes with cyanidin-3-glucoside: $\text{Sn}(\text{Cy}-3-\text{Glc})_2\text{Cl}_2$ (A), $[\text{Al}(\text{Cy}-3-\text{Glc})(\text{H}_2\text{O})_4]^{2+}$ (B), $[\text{Al}(\text{Cy}-3-\text{Glc})_2(\text{H}_2\text{O})_2]^+$ (C) and $\text{Al}(\text{Cy}-3-\text{Glc})_3$ (D) (B3LYP/DEF2TZVPP with PCM (water) and Grimme dispersion).	114
3.7. The time-averaged probability that a functional group of tannic acid (A) and Mv-3-Glc (B) forms a hydrogen bond interaction.	117
3.8. The visualisation of π - π interactions as interatomic distances between the aromatic groups of tannic acid and the A-ring (A), B-ring (B) or C-ring (C) of Mv-3-Glc.	118

3.9. 3D illustrations of simulation boxes in the gas phase wherein hydrogen bonds are observed (A) and within a water box wherein π - π interactions are highlighted between tannic acid (silver) and Mv-3-Glc (grey backbone with A-ring: magenta and B-ring: blue) (B).	118
4.1. The different substitution patterns of the studied anthocyanins and pyranoanthocyanins in their flavylum cation form.	124
4.2. The reaction mechanism between anthocyanins and yeast metabolites or vinyl compounds resulting in the formation of pyranoanthocyanins.	125
4.3. A comparison between experimentally measured (A) and calculated UV-Vis spectra of Mv-3-Glc derivatives, which are labeled according to Table D.1 (B3LYP/6-311++G(d,p) with SMD water) (B). . .	132
4.4. The molecular orbital composition of the HOMO and LUMO of Cy-3-Glc (A, 10), (Z)-caffeoyl acylated Cy-3-Glc (B, 22) and (E)-caffeoyl acylated Cy-3-Glc (C, 28). Generally, the highest contributions for the HOMO originate from the B-ring and caffeoyl moiety for anthocyanins and aromatic acylated anthocyanins, respectively (Figure 4.1).The analyses of the molecular orbital composition were carried out with Hirshfeld-I charges by calculating the atomic weight contribution to the HOMO and LUMO by means of Multiwfn [2, 3].	133
4.5. (Z)- (A, C) and (E)- (B, D) conformers of caffeoyl (Z: 26 and E: 32) and coumaroyl (Z: 38 and E: 44) acylated Mv-3-Glc (B3LYP/6-311++G(d,p), GD3, SMD solvation model and water as solvent).	135
4.6. 3D molecular structures of malvidin pyranoanthocyanin derivatives: 10-carboxy (A, 50), 10-H type (B, 56), vinylphenol adduct (C, 62) and vinylcatechol adduct (D, 68).	137
4.7. The molecular orbital composition of the HOMO and LUMO of pyranoanthocyanins 10-carboxy Cy-3-Glc (A, 46), 10-H Cy-3-Glc (B, 52), vinylphenol Cy-3-Glc (C, 58) and vinylcatechol Cy-3-Glc (D, 64). For the first two cases, the B-ring is the largest provider of the HOMO, while this contribution is shared with the 10-phenol or 10-catechol moiety for vinylphenol or vinylcatechol pyranoanthocyanins.	139

4.8.	The molecular orbital composition of the HOMO (left) and LUMO (right) of caffeoyl acylated vinylcatechol Cy-3-Glc (112). Similar to acylated anthocyanins, the caffeoyl acylated moiety takes the largest share of the HOMO.	141
4.9.	An overview of the various subclasses of anthocyanins and pyranoanthocyanins (in their flavylium cation form) based on their average $\lambda_{\text{max,vis}}$ -values and accompanying color, calculated with B3LYP/6-311++G(d,p) with SMD water solvation model. R^1 , R^2 and R^3 are according to the substitution pattern illustrated in Figure 4.1. The additional labels refer to the individual chemical structures shown in Table D.1.	143
4.10.	The color range attained for each anthocyanin-based subclass (in its flavylium cation form) based on TD-DFT calculations with B3LYP/6 311++G(d,p) and SMD water.	148
4.11.	Computed energy levels of acetyl (81-86), caffeoyl (105-110) and coumaroyl (129-134) acylated vinylphenol pyranoanthocyanins (B3LYP/6-311++G(d,p) with SMD water). The dotted lines represent the energy levels of TiO_2 conduction band and the iodide/triiodide (I^-/I_3^-) redox potential. The energy of the HOMO should be sufficiently lower compared to the electrolyte redox potential for dye regeneration, while the energy of the LUMO needs to be greater than the potential of the TiO_2 conduction band to induce charge injection. Energy levels of other anthocyanin-based compounds can be found in Figures D.33 to D.39.	152
5.1.	Examples of potential valorization routes summarized for each natural dye class.	164
5.2.	A general scheme of the different explorative scenarios for the LCA analysis of the extraction of and dyeing with natural dyes. The detailed schemes for each natural dye are illustrated in Figures E.1 to E.4.	167
5.3.	The environmental impact of dyeing one m^2 wool with anthocyanins (A), naphthoquinones (B), and anthraquinones (C), and one m^2 cotton with carotenoids (D). The horizontal bar is the synthetic dye reference. The environmental impact of dyeing one m^2 cotton and wool with each natural dye is shown in Figures E.5 to E.6, respectively.	171

- 5.4. These 3D surface plots display the influence of (A) the concentration of natural anthraquinone extracted and the amount of dye (% owf) required for dyeing and (B) the concentration extracted and transportation of the by-products from waste source to biorefinery (B) on the environmental impact of dyeing 1 m² wool with natural anthraquinone crude extract (scenario 2). The synthetic dye reference is indicated by the gray surface. 175

List of Tables

1.1. The percentage of by-products or waste streams generated at each stage of the fruit and vegetable supply chain and food in general (based on various studies).	6
1.2. An overview of the most naturally occurring anthocyanidins [4, 5].	12
1.3. An overview of naturally occurring anthraquinone structures. . . .	16
1.4. A summary table, based on Figure 1.11 and Figures A.11 to A.14, on the different dyeing methodologies and to what extent and effectiveness the methods are investigated with the following natural dyes. The performance of each dye class on cotton, protein fibers, and synthetic fibers has been evaluated against the industrial fastness requirements for general apparel (wash fastness (WF) ≥ 4 and light fastness (LF) ≥ 5). The ratios of studies are given between brackets.	31
2.1. The influence of solvent selection on the total anthocyanin content investigated by some studies. The content is usually expressed as cyanidin-3-glucoside (Cy-3-Glc) equivalents (EtOH: ethanol and MeOH: methanol).	57
2.2. A summary of studies in which the solvent dependency on the ACN composition is investigated on the individual concentration level (EtOH: ethanol and MeOH: methanol).	58
2.3. The selectivity between the glycoside-aglycone pairs in terms of solubility ratios obtained with COSMO-RS. The figures represent the number of times a glycoside is more soluble compared to the aglycone in a selection of solvents, with Dp and Dp-3-Glc as exception.	74
3.1. An overview of the isotherm and kinetic models applied.	93
3.2. Colorimetric values and color strength of fabrics dyed at different pH conditions and concentrations of the dye extract (uncertainties expressed as standard deviation ($n = 3$)).	99
3.3. The relative exhaustion levels ($E_{s,rel}$) and relative equilibrium adsorption capacities ($q_{e,s,rel}$) of the dyebaths (uncertainties expressed as standard deviation ($n = 3$)).	103

3.4.	The colorimetric properties (D65/10) and color strength of dyed (pre- and metamordanted), washed (according to ISO105-C06 and reimmersed cotton samples (uncertainties expressed as standard deviation ($n = 3$)). Color differences ΔE^*_1 and ΔE^*_2 are calculated with respect to dyed and washed fabrics, respectively. .	107
3.5.	The colorimetric properties (D65/10) and color strength of dyed (pre- and metamordanted, washed (according to ISO105-E01 and subjected by light test ISO105-B02 (uncertainties expressed as standard deviation ($n = 3$)).	108
3.6.	Fastness values of staining and color change (CC) of pre- and metamordanted cotton samples according to ISO105-C06 and ISO105-E01 and light test (ISO105-B02) (CDA: diacetate, CO: cotton, PA: nylon, PES: polyester, PC: polyacryl, WO: wool). . . .	109
3.7.	The isotherm parameters for the adsorption of Mv-3-Glc on cotton at 80 °C.	112
3.8.	The results for the parameters acquired from the adsorption kinetic models.	113
3.9.	The calculated counterpoise (CP) corrected complexation Gibbs free energy values (kJ mol^{-1}) of tin (Sn) and aluminium (Al) coordination complexes with the anthocyanin bidentate ligand. . .	119
4.1.	Mean absolute error (MAE) in nanometer (nm) and electronvolt (eV) of calculated $\lambda_{\text{max,vis}}$ -values of anthocyanidins, 3-deoxyanthocyanidins and anthocyanins (compounds 1-14 of Table D.1) (B3LYP/6-311++G(d,p)) in order to justify the correct implicit solvation model.	130
4.2.	Mean absolute error (MAE) of three different functionals (with a similar basis set 6 311++G(d,p)) applied for generating UV-VIS data of anthocyanidins, anthocyanins, acylated anthocyanins and pyranoanthocyanins with water and SMD solvation model. The error analyses were carried out for structures of which experimental values (n) were available. The calculations of the MAE for each anthocyanin subclass and functional are shown in Tables D.29 to D.36.	142
4.3.	The percent error between calculated and analytical standard molar absorption coefficients (ϵ) of anthocyanidins (1-8) and anthocyanins (9-14) with different levels of theories (B3LYP, PBE0 and CAM-B3LYP and 6-311++G(d,p) as basis set) in SMD methanol unless otherwise stated.	146

5.1. The potential European production scale of naturally-dyed fabric
that is derived from the most promising by-products containing
anthocyanins, quinones, or carotenoids. 159

Samenvatting

Kleur is alomtegenwoordig in ons dagelijks leven. De perceptie van verschillende kleuren wordt veroorzaakt door de aanwezigheid van organische moleculen die in een zeer specifieke wijze interageren met licht. Die moleculen worden ook wel kleurstoffen of pigmenten genoemd. Tegenwoordig zijn synthetische kleurstoffen en pigmenten de standaard in industrieën die instaan voor de productie textiel, verf en coatings, papier, voeding en dranken, inkt, cosmetica en persoonlijke verzorging, enz. Veel van deze toepassingen zijn gebaseerd op synthetische kleurstoffen doordat ze zeer goede echtheden of hechting vertonen, gemakkelijk en goedkoop te produceren zijn en een grote waaier aan kleuren kunnen aanbieden. Daartegenover staat dat de textiel kleuringsnijverheid en textielveredeling bekend staan als de grootste vervuilers van water door hun overmatig gebruik aan chemicaliën die al dan niet direct toxisch zijn voor de menselijke gezondheid. Daarbovenop focust de wereld zich alsmaar meer naar duurzaamheid en de inperking van vervuiling waardoor de aandacht zich terug op de natuurlijke kleurstoffen vestigt. Sommige van deze natuurlijke kleurstoffen zijn niet toxisch of carcinogeen. Daarnaast bezitten ze ook anti-UV en antimicrobiële eigenschappen en zijn ze biodegradeerbaar in natuurlijke omstandigheden. Fruit en groenten zijn een rijke bron aan natuurlijke kleurstoffen die het potentieel hebben om hun synthetische analogen te vervangen. De extractie van deze moleculen uit primaire bronnen zou een kostelijke zaak zijn en ook ethische discussies op vlak van voedselzekerheid teweegbrengen. Hierdoor vormen reststromen van groenten- en fruit verwerkende industrieën de ideale duurzame bron voor deze natuurlijke kleurstoffen, maar kwalitatieve en kwantitatieve eigenschappen van deze reststromen voor deze toepassing blijven schaars. In dit doctoraatproefschrift wordt eerst drie klassen van natuurlijke kleurstoffen (anthocyaninen, quinones en carotenoiden) besproken in combinatie met hun voorkomen, volumes en concentraties in reststromen die uit de landbouw en groenten- en fruit verwerkende industrieën komen. Het in kaart brengen van deze reststromen voor elke natuurlijke kleurstof klasse toont de grootschalige beschikbaarheid aan van agrovoedingsresiduen (>0.1 Mt jaarlijks in EU-28) met een maximale natuurlijke kleurstof gehalte van 56, 18 en 593 kg/t drooggewicht voor respectievelijk anthocyaninen, quinones en carotenoiden. Natuurlijke kleurstoffen vertonen ook maar middelmatige stabiliteit en affiniteit voor

textielvezels waardoor de haalbaarheid tot toepassing en duurzaamheid van het proces op dit gebied in vraag wordt gesteld. Verscheidene verf applicatiemethodes uit de literatuur werden beoordeeld om de tekortkomingen van natuurlijke kleurstoffen op te lossen. Metaalzouten of 'mordants' genieten de voorkeur om de fixatie van natuurlijke kleurstoffen te garanderen, maar brengen ook potentiële milieukwesties met zich mee. De meer duurzamere methodes zoals 'biomordants' en enzymen vertonen nog ruimte voor verbetering, terwijl chemische modificatie methoden de fixatie van kleur kunnen garanderen.

Anthocyanidinen en anthocyaninen zijn flavonoiden die in verscheidene planten, bloemen, fruit en groenten voorkomen. Ze staan bekend om hun antioxidatieve werking en therapeutische eigenschappen die de menselijke gezondheid ten goede komt. Deze positieve eigenschappen zijn aantrekkelijk voor (niet-)voedingstoepassingen. De chemische verscheidenheid tussen de moleculen leidt ook tot uiteenlopende affiniteiten en activiteiten. Deze kennis is belangrijk om de meest interessante anthocyanidinen en anthocyaninen te extraheren uit voedselreststromen. Om het volledige extractieprofiel te achterhalen, worden geavanceerde zuiveringsmethoden en gekoppelde technieken zoals HPLC-DAD-MS/MS aangehaald met de bijhorende kostbare analytische standaarden. Als alternatief kunnen computationele methoden en molecuair modelleren ingezet worden om de oplosbaarheid of bindingsaffiniteiten van moleculen te voorspellen in verschillende domeinen. In het tweede hoofdstuk van deze thesis werden de capaciteiten en beperkingen van verscheidene computationele methoden (i.e., Hansen oplosbaarheidsparameters (HSP), Flory-Huggins interactie parameter (χ_{12}), statische berekeningen gebaseerd op dichtheidsfunctionaaltheorie (DFT) en het COSMO-RS model) om de oplosbaarheid van anthocyanidinen en anthocyaninen te voorspellen geëvalueerd. COSMO-RS was in staat om kwantitatieve oplosbaarheidsgegevens te genereren voor verschillende zuivere solventen en de belangrijkste intermoleculaire interacties tussen kleurstof en solvent te beschrijven. Deze methode bleek echter niet geschikt te zijn om de oplosbaarheid te bepalen in mengsels van organisch solvent en water. De Flory-Huggins interactie parameter (χ_{12}) en solvatatie vrije energieën vertoonden middelmatige resultaten. De eerste methode overschatte de contributie van water, terwijl de laatstgenoemde methode in staat was om de grote lijnen van andere computationele methodes te reproduceren. Enkel de Hansen oplosbaarheidsparameters waren in staat om de meest optimale ratio te vinden voor mengsels van organisch solvent en water. Uit de solvent screening werd duidelijk dat oplosmiddelen met elektronenrijke aromatische ringen en

moleculen die over elektrondonoren beschikken zoals 1,4-dioxaan, diethylether, dimethylsulfoxide, chinoline of tetrahydrofuraan, die als waterstofbrug acceptoren fungeren, een betere oplosbaarheidsvermogen vertoonden dan de traditionele organische solventen (i.e., ethanol, methanol en aceton). De COSMO-RS resultaten illustreerden dat de oplosbaarheid van anthocyanidinen en anthocyaninen voornamelijk bestaan uit π - π interacties en intermoleculaire waterstofbruggen. Statistische analyses onthulden ook dat de relatieve molaire oplosbaarheidswaarden ($\log S_{RS}$) van waterige oplossingen met aceton, ethanol of methanol tot en met 40% v/v niet significant verschillend is in vergelijking met water. Hiermee werd aangetoond dat enig gebruik van de drie traditionele organische solventen voor anthocyanidinen en anthocyaninen extractie enkel winstgevend is voor waterige mengsels met een minimale volume fractie van 50% v/v. De Hansen oplosbaarheidsparameters toonden aan dat een waterige oplossing met een 50% v/v en een 40% v/v aan aceton optimaal is voor respectievelijk anthocyanidinen en anthocyaninen. Met ethanol is een 70% v/v waterige mengsel ideaal voor anthocyanidinen en 60% v/v voor anthocyaninen. De bekomen resultaten uit Hansen oplosbaarheidsparameters en COSMO-RS kunnen als referentiepunt gebruikt worden voor analiet-specifieke extracties die maximaal kunnen voldoen aan de vereisten van de gewenste toepassingen.

Eens het extractieprofiel van anthocyaninen gekend is, werd de haalbaarheid van anthocyaninen als natuurlijke kleurstof onderzocht op katoenvezels. Uit literatuur blijkt dat metaalzouten het vaakst worden toegepast om de affiniteit van de natuurlijke kleurstof op de vezel te verhogen, maar dit ligt in strijd met het 'groene' gedachtegoed in het verhaal. In Hoofdstuk 3 testen we het potentieel gebruik van anthocyaninen uit een blauwe bessen reststroom om katoen te kleuren met behulp van 'biomordants', die op maat uitgekozen zijn om intermoleculaire interacties zoals waterstofbruggen, ionische bindingen en π - π interacties aan te gaan met de kleurstof molecule. In het experimentele gedeelte werden extractie- en verfproces parameters geoptimaliseerd (vb. temperatuur, pH, verftijd en verfconcentratie). De invloed van '(bio)mordants' werd gemonitord aan de hand van Fourier-transformatie-infraroodspectroscopie (FT-IR), spectrofotometrische metingen en standaard ISO-testen op was- en lichtechtheden. Er werd aangetoond dat tin(II)chloride als beste metaalzout functioneert, terwijl geen enkele 'biomordant' in staat was om voldoende intermoleculair interacties te genereren aan het equivalent van dit metaalzout. De experimenten werden aangevuld met moleculaire modellering om inzicht te verkrijgen in de types van intermoleculaire interacties die plaatsvinden tussen

kleurstof molecule en '(bio)mordants'. Op dit vlak werden er statische DFT berekeningen en semi-empirische en krachtveld gebaseerde moleculaire dynamica simulaties uitgevoerd. In het algemeen bevestigden de resultaten dat de interactie energieën tussen 'biomordants' en kleurstof moleculen te klein waren, wat overeenstemt met de experimentele bevindingen. Dankzij het systematisch karakter van de experimenten in combinatie met het interpreteren van moleculaire modellen heeft dit hoofdstuk tot waardevolle inzichten geleid op vlak van ontwikkeling van duurzame routes om anthocyaninen als natuurlijke kleurstof te gebruiken op cellulose materialen.

De relatief matige chemische stabiliteit en affiniteit voor verscheidene toepassingen laten anthocyaninen niet toe om tot volledige exploitatie over te gaan. Daarom werden de pyranoanthocyaninen onderzocht in Hoofdstuk 4. De grote chemische diversiteit tussen anthocyaninen en pyranoanthocyaninen leidt tot molecuul specifieke eigenschappen zoals kleur en stabiliteit tegenover externe omstandigheden. De fotofysische experimentele karakterisatie is niet vanzelfsprekend aangezien dit in het algemeen geavanceerde analytische technieken vergt in combinatie met geoptimaliseerde opzuiveringsprocedures. Moleculaire modellering kan op een efficiënte computationele kost en uniforme manier voor een grote set van anthocyaninen gebaseerde moleculen fundamentele inzichten bijbrengen op vlak van fotofysische eigenschappen. De huidige literatuur over dit onderwerp is zeer versnipperd. Hierdoor is een grote set van 140 natuurlijk voorkomende anthocyaninen op systematische wijze onderzocht met behulp van drie functionalen B3LYP, PBE0, CAM-B3LYP. De accuraatheid van deze functionalen werd bepaald aan de hand van experimentele literatuur $\lambda_{\max, \text{vis}}$ -waarden. Naast de $\lambda_{\max, \text{vis}}$ -waarden, gaven de tijdsafhankelijke dichtheidsfunctionaaltheorie (TD-DFT) berekeningen ook oscillatorsterktes, molaire absorptiecoëfficiënten en orbitaal energieën, die uiteindelijk bepalen welke natuurlijk gebaseerde anthocyanine specifiek ingezet kan worden in voedings en niet-voedings toepassingen zoals voedingsadditieven/kleurstoffen, textielverf, analytische standaard en kleurstof gesensibiliseerde zonnecellen (DSSCs).

Natuurlijke kleurstoffen zijn tegenwoordig nog niet volledig geïmplementeerd in mainstream niet-voedings applicaties waaronder textielprocessen. Dit komt doordat er nog enkele technische uitdagingen voor de boeg liggen, zoals het verbeteren van een kosteneffectieve extractie en applicatie procedures, die eerst aangepakt moeten worden vooraleer er overgestapt kan worden naar grote (industriële) schaal. In Hoofdstuk 5 werd ook het techno-economisch potentieel

en de duurzaamheid van deze valorisatieroutes geanalyseerd. Voor het laatste werd een levenscyclusanalyse (LCA) opgesteld, op basis van de meest optimale valorisatieroute en de invloed van bijkomende processen zoals het drogen van biomassa en verschillende opzuiverings en encapsulatie technieken, om de milieu-impact te onderzoeken voor het extraheren van anthocyaninen, quinones en carotenoïden gaande van groenten- en fruitreststromen en de opvolgende applicatie tijdens het verfproces. Wat de toepassing betreft, is het kleuren met het ruwe extract voor elke natuurlijke kleurstof de milieuvriendelijkste aanpak.

Tot slot accentueert dit werk het interdisciplinaire aspect tussen moleculaire modellering en experimenteel werk voor het gebruik van anthocyaninen als natuurlijke kleurstof. Moleculaire modellering geeft inzicht in de onderliggende mechanismes die tijdens labo experimenten te zien zijn. Daarnaast functioneert het ook als voorspelling om experimenten specifiek te ontwerpen en oriënteren op maat van de uiteindelijke toepassing. Als gevolg hiervan heeft dit gecombineerde theoretisch en experimenteel werk geleid tot de afbakening van een operationeel kader waarin anthocyaninen toegepast kunnen worden in alledaagse toepassingen.

Summary

Color is omnipresent in our daily life. Different colors are caused by the presence of organic molecules that interact with light in a very specific manner, also called dyes or pigments. Nowadays, synthetic dyes and pigments are well established in industries producing textile, paints and coatings, paper, food and beverages, plastics, printing inks, cosmetics and personal care, and other industries. Many of these applications rely on synthetic dyes as they possess great fastness properties, low cost and ease of production and cover versatile color ranges. However, the textile dyeing and finishing industry for example, are renowned to be the largest polluter of clean water as this sector applies a vast range of chemicals, which are toxic for human health in an indirect or direct manner. Recently, global attention is shifting toward pollution control and environmental sustainability, which causes a renewed interest in natural dyes. They are believed to be safe due to their non-toxic and non-carcinogenic nature. Besides that, some of these natural dyes possess anti-UV and anti-microbial properties and they are more biodegradable in natural conditions. Many fruit and vegetables contain molecules with particular colors, which can potentially be an environmentally attractive substitute for their synthetic counterparts. Extracting these molecules from primary sources would be expensive and could induce discussions on food security. Therefore, the most sustainable source for such natural colorants would be to valorize them from by-products generated from fruit and vegetable processing industries. Yet, qualitative and quantitative characteristics of food by-products for this purpose still remain scarce.

Within this PhD thesis, first the three dye classes of natural dyes are discussed (i.e., anthocyanins, quinones and carotenoids) along with their occurrence, mass, and concentration in by-products that are generated from agricultural losses as well as the fruit and vegetable processing industries. Natural dyes also show mediocre stability and affinity toward textile fibers, which questions the potential feasibility for application and level of sustainability to overcome these issues in this sector. To tackle the shortcomings of natural dyes on fibers, several application techniques were reviewed from literature. The mapping of by-products for each natural dye class illustrates the vast availability of agro-food residues (>0.1 Mt annually in the EU-28) with a natural dye content up to 56, 18 and 593 kg/t dry weight for anthocyanins, quinones and carotenoids, respectively.

Metallic mordants are mostly preferred to improve the natural dyes' fixation, but entail potential environmental issues. The more greener approaches such as biomordants and enzymes still show room for improvement, while chemical modification methods might also guarantee dye fixation.

Anthocyanidins and anthocyanins are flavonoids that are present in various plants, flowers, fruits, and vegetables. They are known to be beneficial for human health due to their antioxidant activities and therapeutic effects. Their properties are attractive for food and non-food applications. The large chemical diversity amongst these molecules potentially leads to different affinities or activities. This is important to know when extracting anthocyanidins and anthocyanins from biomass, such as food waste. In order to characterize the extraction profile, highly advanced purification methods are required such as HPLC-DAD-MS/MS in combination with expensive analytical standards. Alternatively, computational tools and molecular modeling can be applied for predicting the solubility or binding affinity of molecules in different areas. In the second chapter of this thesis, the capabilities and limitations of several computational methods (i.e., Hansen solubility parameters, Flory-Huggins interaction parameter (χ_{12}), static calculations based on Density Functional Theory (DFT) and the COSMO-RS model) to predict the solubility of anthocyanidins and anthocyanins were evaluated. COSMO-RS was able to provide quantitative information on the solubility behavior within various pure solvents and describe the main intermolecular interactions between colorant and solvent. However, the method fell behind for characterizing the solubility within organic solvent-water mixtures. The Flory-Huggins interaction parameter (χ_{12}) and solvation free energies showed moderate results. The former overestimated the contribution of water and the latter was able to reproduce the general trends observed from other computational methods. Hansen solubility parameters were shown to be the most appropriate tool to find the most optimal organic solvent-water mixture ratio. Furthermore, the solvent screening showed that electron rich aromatic compounds and compounds containing electron donors such as 1,4-dioxane, diethylether, dimethyl sulfoxide, quinoline or tetrahydrofuran, acting as hydrogen bond acceptors, are favored over the more traditional organic solvents in this field (i.e., ethanol, methanol and acetone). The COSMO-RS results illustrated that the solubility of anthocyanidins and anthocyanins can be largely ascribed to π - π interactions and intermolecular hydrogen bonding, respectively. Statistical analyses also revealed that the relative molar solubilities ($\log S_{RS}$) of aqueous mixtures of acetone, ethanol or methanol till 40% v/v are not significantly

different compared to water. This indicated that the use of the three traditional organic solvents for anthocyanidins and anthocyanins extraction is most viable for aqueous mixtures of 50% v/v or higher. Hansen solubility parameters showed that an aqueous mixture of 50% v/v and 40% v/v of acetone is optimal for anthocyanidins and anthocyanins, respectively. For ethanol, a 70% v/v aqueous mixture is favored for anthocyanidins and a 60% v/v for anthocyanins. The results obtained from Hansen solubility parameters and COSMO-RS can be used as a benchmark for target specific extractions to maximize the applications' demands.

Once the extraction profile of anthocyanins had been analyzed, the capabilities of this natural dye were investigated on cotton fiber. In literature, typically, metallic mordants are used to improve the natural dye's affinity toward substrates, but this is not a suitable technique in a 'green story'. In Chapter 3, we tested the potential of using anthocyanins from blueberry waste streams for dyeing cotton with biomordants, which are selected to tailor the intermolecular interactions such as hydrogen bonds, ionic bonds and π - π interactions with the dye molecule. In the experimental part, parameters during extraction and dyeing were optimized (e.g., temperature, pH, dyeing time and concentration). The effect of the (bio)mordants was monitored by Fourier transform infrared spectroscopy (FT-IR), spectrophotometric measurements and standard ISO wash and light tests. It was shown that stannous chloride stands out as metallic mordant, while no biomordants showed sufficient intermolecular interactions to replace this metal salt. The experimental study has been corroborated with a series of molecular modeling calculations to obtain more insight into the intermolecular interactions between dye and (bio)mordants. To this end, both static DFT-based calculations as semi-empirical and force field based molecular dynamics simulations have been performed. The results indeed confirmed that, in general, too small interaction energies for the biomordants of interest with the dye molecules are found, in correspondence with experimental findings. Overall, by performing systematic experiments in combination with the interpretation of the molecular models, this chapter yields valuable insights into the development of green routes toward use of anthocyanins as a natural dye for cellulose-based materials.

The relative poor chemical stability and affinity for several applications still prevent the full exploitation. Therefore, the pyranoanthocyanins were investigated in Chapter 4. The large chemical diversity amongst anthocyanins and

pyranoanthocyanins leads to compound specific properties such as color and stability toward external conditions. The photophysical experimental characterization is not easy as this generally demands advanced analytical techniques along with optimized separation procedures. Molecular modeling can provide insights into the fundamental understanding of the photophysical properties of these compounds in a uniform way for a broad set of compounds. However, current literature is quite fragmented on this topic. Herein, a large set of 140 naturally derived anthocyanins was evaluated in a systematic way with three functionals (B3LYP, PBE0 and CAM-B3LYP). The accuracy of these functionals was determined with experimental literature $\lambda_{\text{max,vis}}$ -values. Next to $\lambda_{\text{max,vis}}$ -values, time-dependent density functional theory (TD-DFT) calculations also provided oscillator strengths, molar absorption coefficients and orbital energies, which define whether specific natural anthocyanin-based compounds can be deployed in food and non-food applications such as food additives/colorants, textile dyeing, analytical standards and dye sensitized solar cells (DSSCs).

Nowadays, natural dyes are not yet implemented in mainstream non-food applications such as textile processes, as several technical challenges, such as cost-effectively improving extraction and application procedures, must be resolved before heading to a large (industrial) scale. In Chapter 5, the techno-economic potential and environmental sustainability of these valorization routes were addressed. The latter is done by including a life cycle assessment (LCA), using different scenarios that are based on the most optimal valorization route and the influence of additional steps such as biomass drying and different purification and encapsulation techniques, to investigate the environmental impact of extracting anthocyanins, quinones and carotenoids from fruit and vegetable processing by-products and their subsequent application within the dyeing process. In terms of application, dyeing with the crude extract is, in all cases, the most environmentally friendly approach.

Concluding, this work highlights the interdisciplinary aspect between molecular modeling and experimental work for the application of anthocyanins as a natural dye. Molecular modeling provides insight into the experimental observations, but also functions as a predictive tool to design and orient the experiments to the specific needs of the final application. Consequently, this combined theoretical and experimental study confined the operating window of anthocyanins in real-life applications, which can be expanded to other natural dyes.

Part I

General Introduction

Introduction

1.1 Context

Nature is full of colors. The use of natural dyes dates back to 3500 BC, when several civilizations used plants, vegetables, fruits, flowers, and insects to color natural textiles, wood, or clay [6]. In 1856, the synthetic dye, mauveine, was created by Perkins, and by the end of 1910, most of the commercially available textiles were synthetically dyed [7]. Nowadays, synthetic dye and pigments are well-established in industries related to textiles, paints and coatings, paper, food and beverages, plastics, printing inks, cosmetics and personal care, and other industries [8]. The textile and paints as well as the coating industries accounted for 62.2% and 50.7% of the synthetic dye and pigment market in 2018, respectively [8]. The textile dyeing and finishing industry is renowned as the largest polluter of clean water, as it applies a vast range of chemicals that are toxic to human health, indirectly or directly [9]. Recently, global attention has shifted toward pollution control and environmental sustainability, which has caused a renewed interest in natural dyes. They are believed to be safe due to their non-toxic, non-carcinogenic, and biodegradable nature. Besides this, some of these dyes possess anti-UV and anti-microbial properties, and they neither cause pollution nor toxic wastewater effluents [9, 10]. Until now, the main application of natural colorants is for coloring food, which accounts for 36% of the global food colorant market [11, 12]. However, the textile and other industries, while in their pursuit of more sustainable production, may also have an interest in these natural dyes, although the competitiveness between natural dyes and synthetic dyes is complex in terms of price and the quality standards expressed as fastness properties. Furthermore, the dyeing process with natural dyes should be compatible with the technological equipment available in the modern textile industry [7].

The current textile industry operates linearly. Clothes are made from large amounts of non-renewable resources (98 Mt per year), such as oil for the production of synthetic fibers, fertilizers for growing cotton, and chemicals for

producing dyes and textile auxiliary products. Clothing is also massively underutilized, with garments even discarded after just seven to ten wears, after which the materials are mostly sent to the landfill or are incinerated. Despite the high collection rates for reuse and recycling textiles in some countries, only 13% of the material used for clothing ends up being recycled in lower-value applications (open-loop recycling), while even less than 1% results in a similar quality application (closed-loop recycling). Textiles can either be mechanically or chemically broken down into fiber for recycling, but fiber-recycling processes are scarcely able to separate blends or filter dyes and contaminants, leaving a poor color quality of shoddy [13, 14]. The transformation toward a new textiles economy requires a robust evidence base to create transparency regarding the current impacts of the system and convince stakeholders to change to a circular economy that is regenerative by design and beneficial for businesses, society, and the environment. The new textile economy should rely on the following four foundations: 1) phase out hazardous substances and microfiber release; 2) increase clothing utilization; 3) improve recycling by aligning clothing design collection and recycling processes; and 4) make effective use of resources and move to renewable inputs [13].

Natural dyes should be proven to be more sustainable compared to their synthetic counterparts. Indeed, natural dyes are extracted from biomass, which typically has a significant environmental impact both in the agricultural and extraction phases. When looking at the biomass from which natural dyes can be extracted, we see a whole range of flowers, leaves, fruits, vegetables, insects, etc. [7] The type and concentration of the dye depend on the biomass source. When looking at vegetables and fruit as a primary source of natural dyes, they typically contain high concentrations of these colorants, but extracting dyes from primary sources would be expensive and could induce discussions on food security and the danger of deforestation [15]. A more sustainable source of biomass might be food waste that occurs over the food industry's life cycle. Currently, 30% of all food, or about 1.3 Gt, is wasted worldwide [1], while the EU-28 generates an estimated 88 Mt of food waste per year [16]. Among all food types, fruits and vegetables encounter the largest losses and waste generation, which can reach up to 60% [17]. Figure 1.1 illustrates only the European amount of by-products that are generated during the different stages of fruits and vegetables' life cycle [1]. The first potential waste streams come from agriculture, where waste occurs on the field due to harvest failure because of bad weather conditions, diseases, or during post-harvest handling, which consists of grading the material by the quality standards set by retailers, and storage, awaiting distribution. The waste that is

generated during the first two steps accounts for 10–20% and 4–10%, respectively. As the consumption of fruits and vegetables comes with health benefits, many of the raw materials undergo processing to obtain various consumer-end products. The by-products that emerge from the production process typically contain high added-value compounds. For example, juice production, as well as the canning and freezing industries, generate around 5.5 and 6 million metric tons, respectively [18]. Wine production industries produce around 5 to 9 million metric tons of pomace [19]. Next to this, due to consumers' demand for fresh, healthy, convenient, and additive-free foods that are safe and nutritious, the European fresh-cut industry has grown exponentially since the 1980s [20]. For example, the production of fresh-cut iceberg salad generates at least 35.5% [21] of the waste; estimation of the UK alone leads to 6.7 Mt of food waste [20]. At this stage, there is also a significant difference in waste generation between industrialized and developing countries. While industrialized countries limit fruit and vegetable losses to 2%, developing countries attain 20–25% losses [1]. For the latter, this can be ascribed to the low level of handling techniques and poor infrastructure/facilities [17, 22]. The next stage of the supply chain is distribution at the retail store level, where 10 to 17% of fruit and vegetable waste emerges [1]. The last actors in the food-loss chain are households. This is influenced by households' socioeconomic and demographic characteristics [23]. Generally, in industrialized countries with medium-and high-income households, large amounts of human-edible produce are discarded (average 21 wt% fruit and vegetable waste of the purchased products) compared to developing countries (average 9 wt% fruit and vegetable waste) [1]. Insufficient planning, improper storage, and thus food spoilage, over-preparation, and confusion about expiration dates often lead to these food losses [24]. Besides this, (post-)consumer waste is commonly mixed and polluted, which generates difficulties for high-end applications [25]. These unavoidable agro-food residues represent mismanagement and inefficient use and should be reduced as much as is economically and technically possible. Implementing the proper policies could promote residues that are high in mass but low in value, toward a valuable and sought-after resource [26]. The lockdowns in 2020 and 2021 in many countries due to the COVID-19 pandemic have, from farm to fork, interrupted the food supply chain and complicated interactions. Due to the closedown of the catering industry, fresh produce remains on farms and is lost or wasted [27]. For these reasons, waste streams that are derived from agriculture or industry could be first considered for the extraction of valuable components [28]. This might also be interesting for other reasons, such as logistics or the fact that organic molecules

tend to degrade due to microbial activity when not properly handled, as is to be expected with putrescible, post-consumer waste [25].

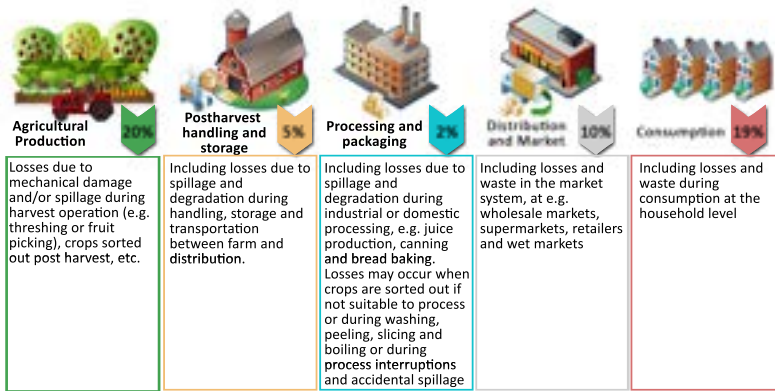


Figure 1.1: The food supply chain of fruits and vegetables and the number of waste streams generated, in weight percentages and at each stage of the chain (European values [1]).

Table 1.1: The percentage of by-products or waste streams generated at each stage of the fruit and vegetable supply chain and food in general (based on various studies).

	Agricultural production	Storage and handling	Processing & packaging	Distribution	Consumption or households	Reference
Fruit & vegetables	20	5	2	10 (f), 2 (p)	19 (f), 15 (p)	[1]
	20	3	1	12	28	[24]
	13	N/A	31.5	9	N/A	[29]
	23	12	5 ^(b)	9	52	[30]
Food ^(a)	20	7.32 ± 5.32	2	4.87 ± 2.49 (f)	19 (f)	[31]
	N/A	N/A	39	19	42	[32]
	11	N/A	19	17	53	[16]
	10.5	3.5	3.4	2.4	12.6	[22]

^(a) : food includes: grain products, fruits and vegetables, fish and seafood, meat and milk;

^(b) : by-products are not included; (f): fresh; (p): processed

Currently, by-products from the food processing industries go to animal feed, anaerobic digestion, energy production, the landfill, or an incineration facility for energy recovery [33]. It is worth mentioning that the use of food processing by-products as low-cost biosorbents for removing dyes, as well as heavy metals (e.g., Cd(II), Cr(III), Cr(VI), and Pb(II)) in wastewater effluents, is gaining more attention [34]. Meanwhile, the farmer or processor would rather give the by-products away for free instead of paying for anaerobic digestion (20-25 EUR/t

wet) or compost (10-70 EUR/t wet). The wet by-products from fruit- and vegetable processing industry for making animal fodder have a value of 3-50 EUR/t [35]. The Sustainable Development Goals (SDGs), set by the United Nations in 2015, demand the optimal utilization of all produced raw materials and associated activities throughout the food supply chain. This applies to the reduction of post-harvest losses, the implementation of technologies that ensure food safety and quality during processing and retailing, and the valorization and reutilization of bioactive compounds from food by-products [27]. Therefore, extracting valuable components such as biomolecules (e.g., antioxidants, phenolic compounds, and essential oils), polysaccharides, lignin, and proteins first could be an interesting gain to increase the added value of food waste/by-product management in a biorefinery approach [36]. The European Union's bio-based economy and circular economy initiatives with projects such as AWARENET [37], AGRIMAX [38], AGROCYCLE [39], FUSIONS [16], REFRESH [40], etc. aim to prevent food waste in and also stimulate the valorization of high added-value compounds from unavoidable EU food production by-products. They identified the main waste streams in Europe, developed policies to reduce food losses, performed consumer behavioral studies and evaluated environmental and cost dimensions of food waste [40]. On the technical side, they have investigated the favorable process conditions, the feasibility through techno-economic analyses and the obstacles for extracting high added-value compounds from food waste instead of traditional valorization practises such as animal feed [40]. The REFRESH report confirms the widely recognized perception that food processing waste streams are adequate sources for high value-added compounds can be realized in profitable business [36]. The Flemish agri-food chain, for instance, is considered as one of the best in Europe in terms of resource efficiency by investing heavily in limiting food losses and avoiding waste [33]. Also in this region, high end valorisation of biomolecules is limited whereas it is clear that the combination of a strong processing industry and investing more in high added-value compound valorization biorefining of the waste streams can be a game changer. Current European valorization processes are for instance pectin and limonene production from citrus peels, tomato seed oil and carotenoids from tomato pomace, various foodstuffs from whey, proteins from endive by-products, production of fuels, kernel oil, wood adhesive and activated carbon from olive stones, production of ethanol, resveratrol, bio-based packaging from grape pomace, etc. [15, 28, 36, 41, 42] One of these high added-value components are natural dyes, which come forward as a green alternative to synthetic dyes. When it comes to the implementation of natural dyes in non-food applications, such as with

textiles, research papers have assessed different types of applications and their properties. However, there is a lack of a general overview regarding in which waste sources the color molecules are present and their concentrations and to what extent different dyeing techniques are effective or demand more in-depth research to improve the natural dyes' stability and affinity to different fibers. Natural dyes are not yet implemented in mainstream textile processes, as several technical challenges, such as cost-effectively improving extraction and application procedures, must be resolved before heading to a large (industrial) scale [7]. The cottage industry accounts for the largest share of naturally-dyed fabric, which is only 1% of the total textiles produced [43].

For this reason, qualitative and quantitative characteristics of food by-products are one of the key features for designing valorization routes, as they indicate what types of fruit and vegetable processing waste streams would be most useful for industrial-level applications [44]. When suitable valorization opportunities are identified and applied to dyeing techniques, a sustainability performance should be performed to assess the environmental performance of novel pathways against current practices [44]. To date, studies on the environmental impact of deriving these natural dyes from food waste and subsequent dyeing are scarce. Within the aforementioned context, this chapter aims to provide more holistic insight into the potential of natural dyes that are extracted from food waste in non-food applications by: 1) providing the first detailed mapping of waste streams or by-products derived from the fruit and vegetable processing industry in Europe, along with the concentration levels of anthocyanins, quinones, and carotenoids, as these are the main colorants of fruit and vegetables; 2) investigating the performance of different application methodologies in terms of wash fastness and lightfastness properties of natural dyes into textile fibers, with regard to overcome the dyes' specific affinity and stability issues and identifying the potential emerging methods that require more in-depth research; 3) developing valorization process flowsheets through the evaluation of various conventional and emerging technologies for extraction, purification and encapsulation; this includes the potential pitfalls encountered with each natural dye; and 4) analyzing the environmental impacts of a naturally-dyed fiber by means of LCAs, using different scenarios that are based on the most optimal valorization route and the influence of additional steps such as biomass drying and different purification and encapsulation techniques. In the end, this study presents some examples of the most interesting valorization routes for each aforementioned natural dye, from fruit and vegetable processing waste to the non-food application field.

1.2 The Colorful Science Behind Light

The perception of color is an event of numerous complicated processes. It all starts with the absorption of colored light entering the eye, focusing on the light-sensitive cell covering at the back of the eye called the retina. The retina consists of two types of light-sensitive cells, i.e., rods and cones. Rods are cylindrical shaped cells and are not color-sensitive and detect light under conditions of weak illumination. Meanwhile, cones function at high level of illumination and are responsible for color vision due to the presence of three types of cones with wavelengths of maximum sensitivity in the red, green and blue regions of the visible spectrum. The photoreceptor proteins responsible for the color vision are called photopsins. Within rods, these opsin proteins are made light-sensitive with the chromophore retinal to form rhodopsin. Rhodopsins are responsible for the conversion of a photon into a signaling cascade. When light hits the photoreceptors (11-Z)-retinal is converted to (E)-retinal, which releases the opsin. In order for the cells to be stimulated again and sending electric signals to the brain, (E)-retinal is regenerated to (11-Z)-retinal via the retinoid cycle (Figure A.1). The optic nerves carry these electrical signals to the visual cortex in the brain [45]. Light consists of electromagnetic waves. When electromagnetic radiation strikes a matter, the molecule interacts with the individual photons of the incident light beam. Hereby, absorption takes place when the energy of the photon corresponds to the difference between two molecular energy levels, i.e., ground state and excited state. The electromagnetic spectrum covers all electromagnetic irradiation with a frequency from zero till infinity. The properties of the radiation is determined by the frequency, wavelength or wavenumber. Consequently, the spectrum, which in fact is a continuous band of radiation, is divided into multiple regions: γ -radiation, X-rays, ultraviolet light (UV), visible light (Vis), infrared light, microwaves and radiowaves (Figure 1.2). The human eye is only capable to detect electromagnetic waves from the visible light region: 400-700 nanometer (nm, 10^{-9} meter). An object will appear colored if selective absorption of some wavelengths takes place and reflection or transmission of the remaining wavelengths occur. Dye molecules that have an extensive conjugated system (also called chromophoric group), an alternating system of single and double bonds, are able to absorb wavelengths in the visible region.

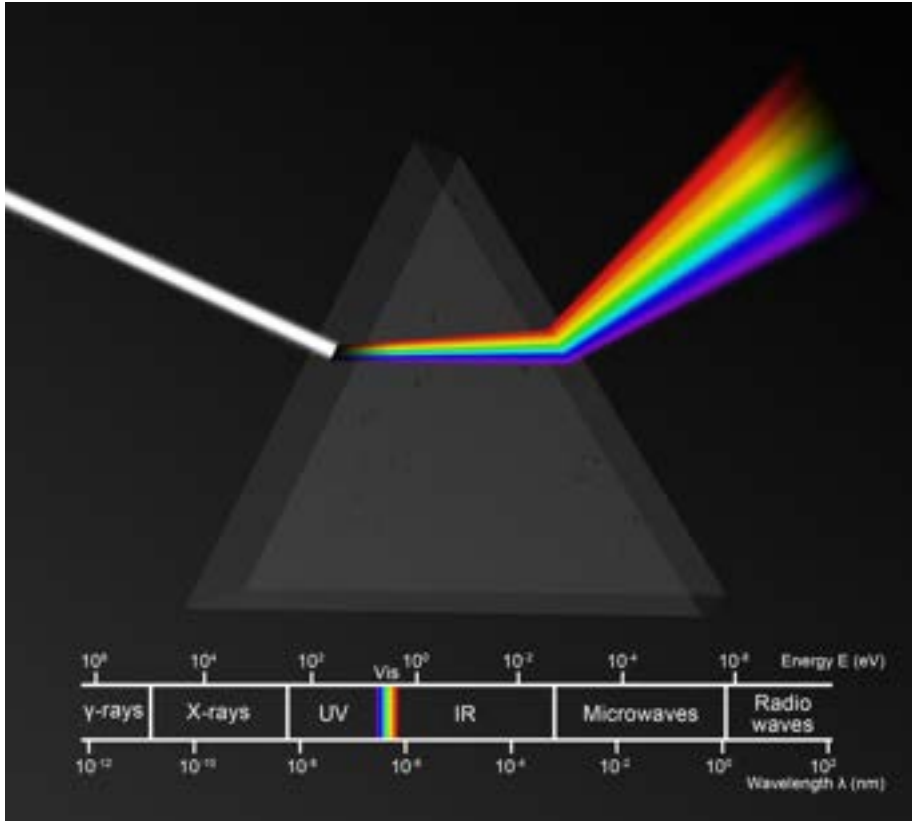


Figure 1.2: White light consists of a mixture of different wavelengths. When a light beam passes a glass prism, the different wavelengths or color components get dispersed due to refraction. The visible light, ranging from 400 - 700 nm, is the only light that is visible for human eye and takes a little part of the entire electromagnetic spectrum, i.e., from γ -rays till radiowaves.

As mentioned before, synthetic dyes are omnipresent in various industries. The most common synthetic dye classes are azo dyes, anthraquinones, indigoids, xanthenes, phthalocyanines, nitrated and nitrosated and triphenylmethanes. Azo dyes are the largest and most versatile dye class and takes about 70% of the world's annual production of synthetic dyes [46]. These dyes are chemically represented as $R-N=N-R'$, where $-N=N-$ represents the azo group, which can appear one or multiple times in a molecule, and R or R' depicts either aryl or alkyl groups. The versatility and vivid colors obtained with this single dye class also comes with a downside. Some azo dyes readily possess carcinogenic properties, but the real hazard of the majority of azo dyes arises due to reductive cleavage by human intestinal microflora, skin microflora, environmental microorganisms [47]. This results into toxic and carcinogenic compounds such as aromatic amines (benzidine), naphthalene and other aromatics. Consequently, the European Union has imposed restrictions, under REACH, Toy Safety Directive and EU Food Contact Material Framework, on the use of azo dyes for consumer products. Nowadays green chemistry, sustainability and ecology are gaining more attention and therefore natural colorants come in the picture again as alternatives. The following section describes the characteristics of three natural colorants' anthocyanins in terms of their (chemical) properties, quinones, and carotenoids. Anthocyanins depict the most colorful group among flavonoids and are responsible for red and purple hues. Quinones, and especially anthraquinones, are, after azo dyes, the second-largest dye class of textile colorants. Unlike azo dyes, synthetic quinones have natural counterparts that are mainly extracted from plants, nuts, and insects. This class of compounds displays various shades of brown, purple, red, orange, and yellow [48]. Carotenoids are found in many photosynthetic and nonphotosynthetic organisms and are responsible for their red, orange, and yellow color.

1.2.1 Anthocyanins

Anthocyanins are phenolic compounds that belong to one of six categories within the class of flavonoids (Figure 1.3) [49]. They are mainly present in higher plants, flowers, fruits, and vegetables and can be more specifically found in a cell's vacuoles. Anthocyanins consist of a C6-C3-C6 backbone, which mostly appears as a flavylium cation in acidic conditions and are glycosylated. In contrast, anthocyanidins are molecules that are without sugar moieties. At least 500 different anthocyanins have been identified and isolated from plants [4], while 90% of all anthocyanins are derived from these six common anthocyanidins:

cyanidin (Cy), delphinidin (Dp), malvidin (Mv), pelargonidin (Pg), peonidin (Pn) and petunidin (Pt), which are distributed in fruits and vegetables of 50%, 12%, 7%, 12%, 12%, and 7%, respectively (Table 1.2) [4, 50]. Other types of anthocyanidins, such as 3-deoxyanthocyanidins, rare methylated anthocyanidins, and 6-hydroxyanthocyanidins, account for only 2-3% each of the total anthocyanidin and anthocyanin varieties [4]. The anthocyanin content is highly varied and depends on several variables, such as genetic factors, light, temperature, and agronomic factors [4].

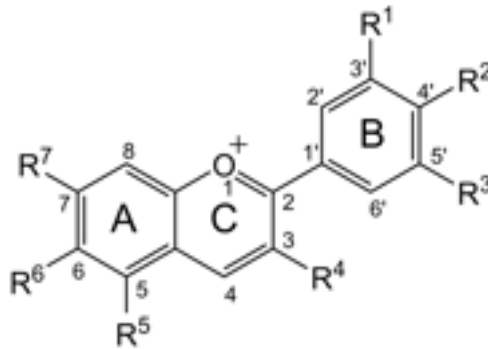


Figure 1.3: The molecular structure of anthocyanin as a flavylium cation with its possible substitution patterns.

Table 1.2: An overview of the most naturally occurring anthocyanidins [4, 5].

	Anthocyanidins	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	R ⁷
Most occurring anthocyanidins	Pelargonidin (Pg)	H	OH	H	OH	OH	H	OH
	Cyanidin (Cy)	OH	OH	H	OH	OH	H	OH
	Delphinidin (Dp)	OH	OH	OH	OH	OH	H	OH
	Peonidin (Pn)	OCH ₃	OH	H	OH	OH	H	OH
	Petunidin (Pt)	OH	OH	OCH ₃	OH	OH	H	OH
Rare methylated anthocyanidins	Malvidin (Mv)	OCH ₃	OH	OCH ₃	OH	OH	H	OH
	5-MethylCy	OH	OH	H	OH	OCH ₃	H	OH
	Pulchellidin	OH	OH	OH	OH	OCH ₃	H	OH
	Rosinidin	OCH ₃	OH	H	OH	OH	H	OCH ₃
	Europinidin	OCH ₃	OH	OH	OH	OCH ₃	H	OH
	Capensinidin	OCH ₃	OH	OCH ₃	OH	OCH ₃	H	OH
	Hirsutidin	OCH ₃	OH	OCH ₃	OH	OH	H	OCH ₃
6-hydroxylated anthocyanidins	6-HydroxyPg	H	OH	H	OH	OH	OH	OH
	6-HydroxyCy	OH	OH	H	OH	OH	OH	OH
	6-HydroxyDp	OH	OH	OH	OH	OH	OH	OH
3-deoxyanthocyanidins	Apigeninidin (Ap)	H	OH	H	H	OH	H	OH
	Luteolinidin (Lt)	OH	OH	H	H	OH	H	OH
	Tricetinidin (Tr)	OH	OH	OH	H	OH	H	OH
	Carajurone	H	OH	H	H	OCH ₃	OH	OH
	Carajurin	H	OCH ₃	H	H	OCH ₃	OH	OH

Anthocyanins, through reversible reactions, are known to undergo structural changes at different pH values (Figure A.2). The most stable species in acidic aqueous solutions (pH 1-3) is the red flavylum cation (A in Figure A.2). Anthocyanins are known as diacids with two pKa values at 4 and 7. When the flavylum cation loses its first acidic proton on one of the three phenolic OH groups (C7-OH, C4'-OH, or C5-OH), this will yield the neutral quinoidal base (B) (kinetic product). These neutral quinoidal bases could undergo a subsequent deprotonation step around neutrality and very high pH (pH > 11) to form the monoanionic (B⁻) and dianionic quinoidal bases (B²⁻), respectively [51, 52]. Another reaction that could occur with the flavylum cation is hydration. This is the case where a water molecule performs a nucleophilic attack at the C2 position of the flavylum cation, resulting in the colorless hemiketal structure, the thermodynamic product (C). Thereafter, a tautomerization reaction, with ring opening, results in the light-yellow (Z)-chalcone (D), which can possibly isomerize to (E)-chalcone (E) [53, 54, 55, 56]. The stability of the quinoidal base is aglycone dependent. Above pH 8, two groups of quinoidal bases can be distinguished. A first group, consisting of pelargonidin, peonidin and malvidin, only possessing one free hydroxy group on the B-ring resulted in a more stable blue color. The second group of petunidin and delphinidin shifts back from a blue to red color, while cyanidin constitutes an exception to this trend [57]. As mentioned above, anthocyanins are especially prone to pH fluctuations and also to temperature. Other factors that can affect their stability are concentration, light, oxygen, solvents, presence of enzymes, proteins, or copigments (e.g., phenolic compounds and metallic ions). The latter results in self-stacking configurations by intermolecular copigmentation and intramolecular copigmentation in the form of acylated anthocyanins [56, 58]. Intermolecular copigmentation exists via a weak association with alkaloids, amino acids, benzoic acids, coumarin, cinnamic acids, or other colorless (phenolic) compounds, such as flavonols. The higher the molar ratio copigment/pigment, the more stable the anthocyanins become [5, 56]. The acylated anthocyanins are known to be more stable toward different pH, light, and heat conditions [56, 58]. This is where an aliphatic or aromatic organic acid is acylated on the saccharide unit, mostly at the sixth position. Due to the free-rotatable bond of the saccharide unit at the C3 or C5 side, the planar aromatic acyl group can overlap with the planar benzopyrylium ion due to hydrophobic forces and π - π interactions. This protects the flavylum cation on both sides against nucleophilic attacks. The most ideal stacking "sandwich" configuration, which gives the lowest energy, is the one where the glycosyl-acyl groups are positioned at C3' and C7 sites [59].

1.2.2 Quinones

Quinones are organic compounds ($C_6H_4O_2$) that have a fully conjugated cyclic dione structure [49]. The simplest quinone molecules consist of a single benzene ring and are called benzoquinones (Figure 1.4). Due to the small size of the chromophore, it is frequently substituted with alkyl groups. Naphthoquinones, compared to benzoquinones, have an additional benzene ring. Lawsone and juglone are the most frequently occurring compounds.

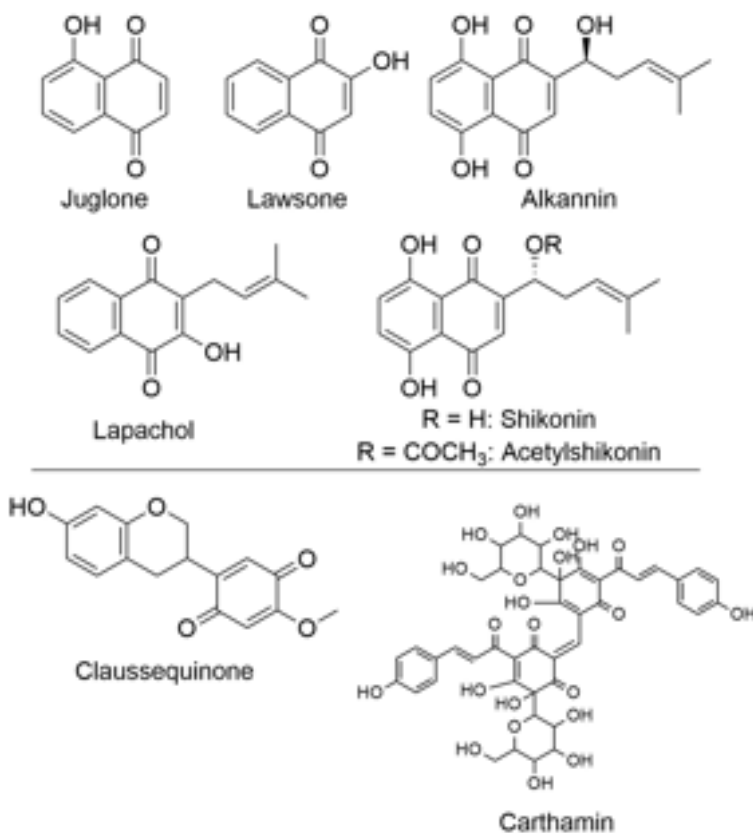


Figure 1.4: The common occurring naphthoquinones on top and below two naturally occurring benzoquinones.

Quinones that have a benzene ring on each side of the dione structure are classified as anthraquinones; they represent the largest fraction of naturally occurring quinones. In general, quinones are more present within plants, especially the roots (e.g., aloe, madder, senna, and rhubarb), fungi, mushrooms, lichens, and some insects rather than fruits or vegetables [60, 61]. The most frequently encountered anthraquinones are alizarin, catenarin, emodin, physcion,

and rhein, which are mostly glycosylated within the plant (Figure 1.5 and Table 1.3) [53, 60]. These compounds require hydrolysis before their dyeing applications. For dyeing purposes, Derksen et al. [62] succeeded in hydrolyzing ruberythric acid into the aglycone alizarin from madder. The aqueous method that was used could circumvent the simultaneous formation of unwanted mutagenic lucidin that is derived from the hydrolysis of lucidin primeveroside through endogenous enzymes.

Natural anthraquinones often appear as colorless compounds, but the color is provided due to the interaction with other molecules present within the matrix, or by transformation processes. The color is also affected by the number, types, and positions of the substituents. While electron-withdrawing groups (i.e., carbonyl groups) do not have an impact on the electronic spectrum, electron-donating groups (i.e., amino groups) can vary the dye's color from yellow, through red and blue, to green. The position of substituents also affects the intramolecular-hydrogen bond and possible steric hindrance [60]. Carminic acid, depending on the pH, can also change color [48].

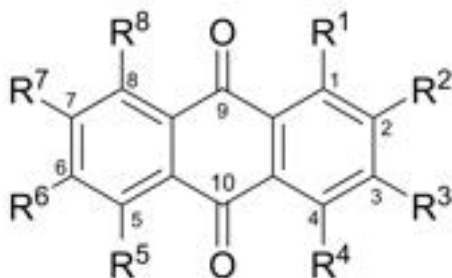


Figure 1.5: The molecular representation of anthraquinones.

Table 1.3: An overview of naturally occurring anthraquinone structures.

Anthraquinones	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	R ⁷	R ⁸
1-methylamino-4-(amino)anthraquinone	NHCH ₃	H	H	NH ₂	H	H	H	H
1-methylamino-4-(hydroxyethylamino)anthraquinone	NHCH ₃	H	H	NH(CH ₂) ₂ OH	H	H	H	H
Alizarin	OH	OH	H	H	H	H	H	H
Aloe-emodin	OH	H	CH ₂ OH	H	H	H	H	OH
Carminic acid	H	OH	COOH	CH ₃	OH	Glycosyl	OH	OH
Chrysophanol	OH	H	CH ₃	H	H	H	H	OH
Danthron	OH	H	H	H	H	H	H	OH
Dermocycin	OH	OH	OCH ₃	OH	H	CH ₃	H	OH
Emodin	OH	H	CH ₃	H	H	OH	H	OH
Laccaic acid A	COOH	COOH	OH	H	OH	OH	Ph-2-(OH)-5- -((CH ₂) ₂ NHC(O)CH ₃)	OH
Laccaic acid B	COOH	COOH	OH	H	OH	OH	Ph-2-(OH)-5- -((CH ₂) ₂ OH)	OH
Laccaic acid C	COOH	COOH	OH	H	OH	OH	Ph-2-(OH)-5- -(CH ₂ CHNH ₂ COOH)	OH
Laccaic acid D	CH ₃	COOH	OH	H	H	OH	H	OH
Laccaic acid E	COOH	COOH	OH	H	OH	OH	Ph-2-(OH)-5- ((CH ₂) ₂ NH ₂)	OH
Lucidin	OH	CH ₂ OH	OH	H	H	H	H	H
Munjistin	OH	COOH	OH	H	H	H	H	H
Physcion	OH	H	CH ₃	H	H	OCH ₃	H	OH
Pseudopurpurin	OH	COOH	OH	OH	H	H	H	H
Purpurin	OH	H	OH	OH	H	H	H	H
Quinizarin	OH	H	H	OH	H	H	H	H
Rhein	OH	H	COOH	H	H	H	H	OH
Ruberythric acid	OH	Primeverosyl	H	H	H	H	H	H
Tectoquinone	H	CH ₃	H	H	H	H	H	H
Xanthopurpurin	OH	H	OH	H	H	H	H	H

1.2.3 Carotenoids

Carotenoids belong to the class of tetraterpenes and are linear molecules, which consist of eight isoprenoid units that have an inversion center. Carotenoids are mainly lycopene derivatives ($C_{40}H_{56}$) that undergo reactions such as hydrogenation, dehydrogenation, cyclization, oxygen insertion, double-bond migration, methyl migration, chain shortening or extension, or combinations of these processes [5, 63]. Carotenoids can be divided into two subclasses: carotenes and xanthophylls (Figure 1.6). The former's molecules are comprised only of carbon and hydrogen atoms, whereas the latter additionally contains oxygen atoms. The extensive conjugated double-bond system, which acts as the light-absorbing chromophore, is responsible for the red, orange, and yellow color in fruits, vegetables, fungi, flowers, as well as in birds, insects, crustaceans (e.g., shrimp, lobster, and crab), and even fish (e.g., salmon and trout) [63]. Frequently encountered carotenes are lycopene and ζ -carotene. The former is mostly present in red-fleshed fruits and fruit vegetables, while the latter is more omnipresent, but at low levels. Other carotenes that are ubiquitous in food are bicyclic β -carotene, α -carotene and γ -carotene. For the carotenols or hydroxycarotenoids, lutein and zeaxanthin are present in leaves or green vegetables, while β -cryptoxanthin appears in most of the orange-fleshed fruits. Most carotenols in ripe fruit are esterified with fatty acids, which can be hydrolyzed through saponification. The saponification of the esters would release the esterified carotenoids from the mixture with fatty acids present within the matrix. The substitution of the more aliphatic chain by a hydroxy group makes carotenoids more polar and thus, introducing more possibilities for intermolecular interactions with polar. Some carotenoids are uniquely present in specific species. A few examples are capsanthin and capsorubin in red pepper, bixin in annatto, and crocetin in saffron [63]. The main disadvantage of carotenoids is their susceptibility to isomerization and oxidation. This depends on numerous factors, such as the presence of metals, enzymes, unsaturated lipids, pro-oxidants or antioxidants, light exposure, temperature variations, type of carotenoid, extraction procedure, packaging material, and storage conditions. Isomerization of the more stable (E)-isomer to the (Z)-isomer occurs by heating or exposure to direct sunlight or ultraviolet light and may lead to the photodestruction of carotenoids [63].

Carotenoids are also produced by microalgae, cyanobacteria and macroalgae. These are photosynthetic organisms that are capable of using sunlight (captured by the chlorophylls and other pigment groups) and inorganic nutrients to produce oxygen and organic matter by means of photosynthesis. Typical natural dye

classes, next to carotenoids, found in algae are chlorophylls (green) and phycobiliproteins (i.e., phycocyanin (blue) and phycoerythrin (red)). Chlorophylls are usually coextracted along with carotenoids. These green pigments are responsible for the photosynthesis process within plants and algae. However, these compounds are also highly instable to various external conditions such as heat, low pH, light, oxygen and enzymes, unless there are attached within the chloroplasts to carotenes, xanthophylls or thylakoids [53]. Chlorophylls are also widely used in the food (e.g., food colorants E140-E141) [7], biomordants in textile dyeing [64], cosmetics and pharmaceutical industry [65]. These chlorophylls will not be discussed in further detail within this dissertation.

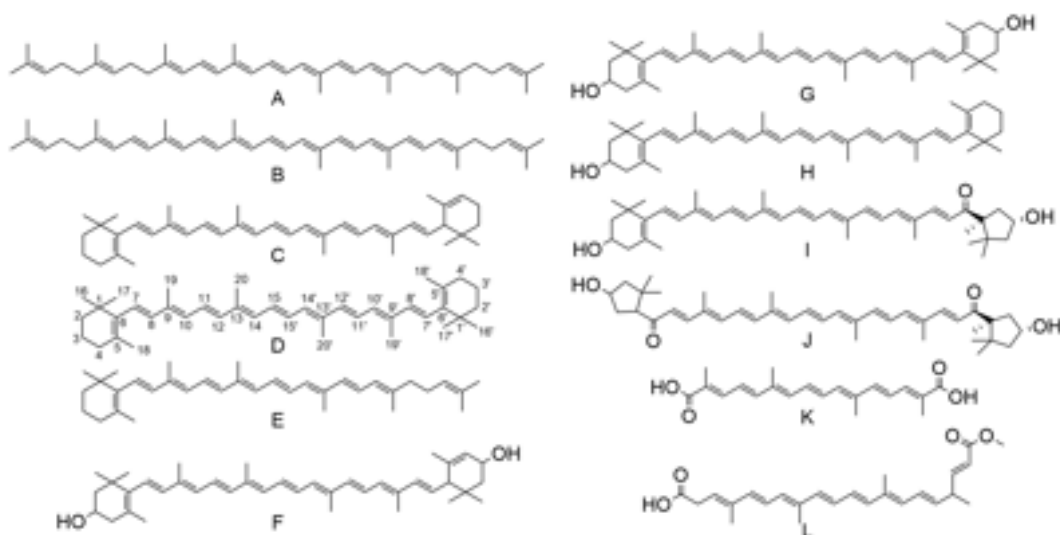


Figure 1.6: Most frequently occurring carotenoids. Acyclic carotenes: A: lycopene and B: ζ-carotene; Cyclic carotenes: C: α-carotene, D: β-carotene and E: γ-carotene; carotenols: F: lutein, G: zeaxanthin and H: β-cryptoxanthin; unique carotenoids: I: capsanthin, J: capsorubin, K: crocetin and L: bixin (Bechtold and Mussak, 2009; Rodriguez-Amaya, 2001).

1.3 Fruit and Vegetable By-Products Generated Within the Food Supply Chain

According to the European Commission, the product is defined as a material that is deliberately created in the production process. The material that is not deliberately produced during the process is called production residue, which may or may not be a waste. When the production residue is not treated as a waste, it is called a by-product [66]. When these definitions are applied to agricultural production and food processing industry, food is the product and by-products from agricultural production are for example, crops that were spoiled due to harvest failure because of bad weather conditions, diseases, or during post-harvest handling, which consists of grading the material by the quality standards set by retailers, and storage, awaiting distribution. By-products from fruit and vegetable processing industry consist of skins, seeds, peels and hulls, that could be considered unavoidable food waste because they are not intended for human consumption [30]. As previously mentioned, in the context of sustainable development, natural dyes are preferably extracted from waste biomass. In this section, we provide an overview of the amount of fruit and vegetable waste with the expected concentrations of natural dye molecules. To understand which fruit and vegetable by-products are interesting as a source for natural dyes, an overview is given of the pre-consumer generated waste for the most common fruit and vegetables, as well as the concentrations of anthocyanins, quinones, or carotenoids that are expected to be in these sources. Within this study, the data of Gustavsson et al. [1] were taken into account to estimate the amount of fruit and vegetable waste streams that are generated from agricultural practices and processing by-products in Europe (28 member states) (Table 1.1). Various authors also collected representative ratios of the by-products that are generated for specific fruits and vegetables [18, 28, 35, 39, 67, 68] (Table A.1). The amount of by-products is derived from the percentage of waste to the primary production [32]; this can be interpreted as a maximal value, as the entire crop production will not be used for processing. The following section elucidates the main by-product sources from which the aforementioned natural colorants can be withdrawn.

1.3.1 Content of Natural Colorants Within Fruit and Vegetables

This section is an overview of the content present in each natural colorant in specific fruits and vegetables. The concentrations are expressed in dry weight (DW), and fresh weight (FW) units were converted [69] to DW by taking into

account the moisture content of the specific fruit and vegetables (Table A.2) [70]. This data can be coupled with the number of by-products generated, which are illustrated in Figure 1.7 and within Tables A.3 and A.4. In general, it can be stated that the composition and concentrations of natural colorants within fruits and vegetables depend on the cultivation condition, ripeness, variety or cultivar, genotype, horticultural studies, geographic location, post-harvest storage conditions, processing method (machinery and/or techniques), the purpose of the end-product, and the extraction methods [71, 72, 73]. It was also noticed that the largest content of these natural dyes is present within the outer layers (skin/peel) of the fruit and vegetables. These parts usually form the base of the pomace and are ideal sources for obtaining these bioactive compounds. Based on the natural colorant content and the number of by-products available, it can be concluded that red grape pomace, walnut by-products, rhubarb by-products, and tomato pomace are the most interesting sources for the extraction of anthocyanins, naphthoquinones, anthraquinones, and carotenoids, respectively.

1.3.1.1 Anthocyanins

Figure 1.7A reveals that anthocyanins are largely present within red, black, or blue grape varieties, black raspberry, blackcurrant, and blueberry, with concentrations over 20 kg/t DW. For vegetables, onion red skin, rhubarb, and red varieties of cabbage and cauliflower show at least an anthocyanin content higher than 5 kg/t DW. Grapes abundantly consist of anthocyanins, especially within the skin. However, these compounds are only present within the blue, purple or red varieties, while white grapes only contain a ten-fold less to none. Red grape skin has the highest anthocyanin content (56.4 kg/t DW) [74] along with the highest available amount of by-products. Winery by-products such as red grape pomace and red wine lees are therefore appropriate sources due to their many by-products as well as their high anthocyanin content [75]. Among different berry varieties, raspberries are a rich source of anthocyanins (48.2 kg/t DW) [54]. As shown in Table A.3, black raspberries contain up to six times more anthocyanins compared to the red variety; meanwhile, blueberries also contain around 33.6 kg/t DW [54, 76]. The different anthocyanin distributions within these berries are represented by Welch et al. [57]. The beverage industry can extract 75% of the apple as juice, and the remaining by-products, after crushing and pressing, are solid apple pomace and apple pomace sludge (i.e., liquid waste). The pomace has the typical consistency of pulp (54%), peel (34%), seeds (7%), the seed core (4%), and stem (2%), with the peel containing the largest anthocyanin content

(Table A.4). Pomegranate also possesses anthocyanins, although in a six-fold smaller amount compared to apples. Pomegranate also possesses anthocyanins, although in a six-fold smaller amount compared to apples (3.86 kg/t DW) [77]. Stone fruits such as cherries, olives, plums, peaches, and nectarines are also rich in anthocyanins. Among stone fruits, cherries are the largest anthocyanin provider (32.4 kg/t DW) [54]. Olives mainly accommodate cyanidins (4.4 kg/t DW) [78]. The two main waste streams are crude olive cake and oil mill wastewater. The former is the remaining residue after the first olive pressing process and consists of olive pulp (30–50%), crushed stones (30–45%), olive skin (15–30%), water (~25%) and a small quantity of oil (4.5–9%) [39]. The composition of the latter varies along with the composition of the vegetation water, the olive oil extraction process, and the storage time. This source is also marked by a high content of polyphenols (0.5–24 g/L) [42, 79]. Red cultivars of plums attain a concentration of up to 5.3 kg/t DW within the peel, while nectarines and peaches contain around 1.5 to 1.7 kg/t DW within peels [57, 80]. While berries and red grape varieties are the major sources of anthocyanins in fruits, red cabbages are in vegetables. Red leaf varieties generally contain higher flavonoid levels than their green counterparts, although anthocyanins were only detected in red cultivars [81, 82]. Red cabbage and purple cauliflower contain similar anthocyanin levels [54, 83]. The flavonoid concentration of the by-products (e.g., leaves and stems) for the latter is much higher in comparison to the edible parts where only trace levels are present [84]. Albishi et al. [85] investigated the anthocyanin content between onion varieties and their parts. Quantification of the content reveals a higher anthocyanin level within the skin (63%) compared to the outer fleshy layer and, to a smaller extent, the edible part, which is limited to a single layer of cells of the epidermal tissue [85]. The same trend was visible in the study of Gennaro et al. [86], where the anthocyanin content decreased from the outer parts until the core of the red onion: red dry skin > red outer fleshy layer > red edible part. Despite the low anthocyanin content, the large amount of available waste stream (2000–4000 kt) makes this worth mentioning. Only red- or purple-fleshed varieties of potatoes contain anthocyanins. Purple tubers are more likely to have malvidin, petunidin, delphinidin, and peonidin, while pelargonidin is more likely to be found in red potatoes (Table A.3). During the recovery of anthocyanins in potato waste, toxic glycoalkaloids occur in high concentrations within the extracts, which can be circumvented by alkaline precipitation [87]. Will and Dietrich [88] measured the anthocyanin content in rhubarb (*Rheum rhabarbarum* L.) flesh, mash, skin and juice. Five anthocyanins were identified and it was observed that the highest concentration was found in the skin: 5013 g/t DW. The mash

contained only 379 g/t DW while the juice contained 11.3 to 14.8 mg/L. In terms of by-product availability as well as anthocyanin content, winery by-products such as red grape pomace and red wine lees are still the most recommended sources for valorization. The pomace provides various valorization purposes such as ethanol production, extraction of antioxidants (e.g., resveratrol) and pigments, production of grapeseed oil and grapeseed flour and production of bio-based packaging.

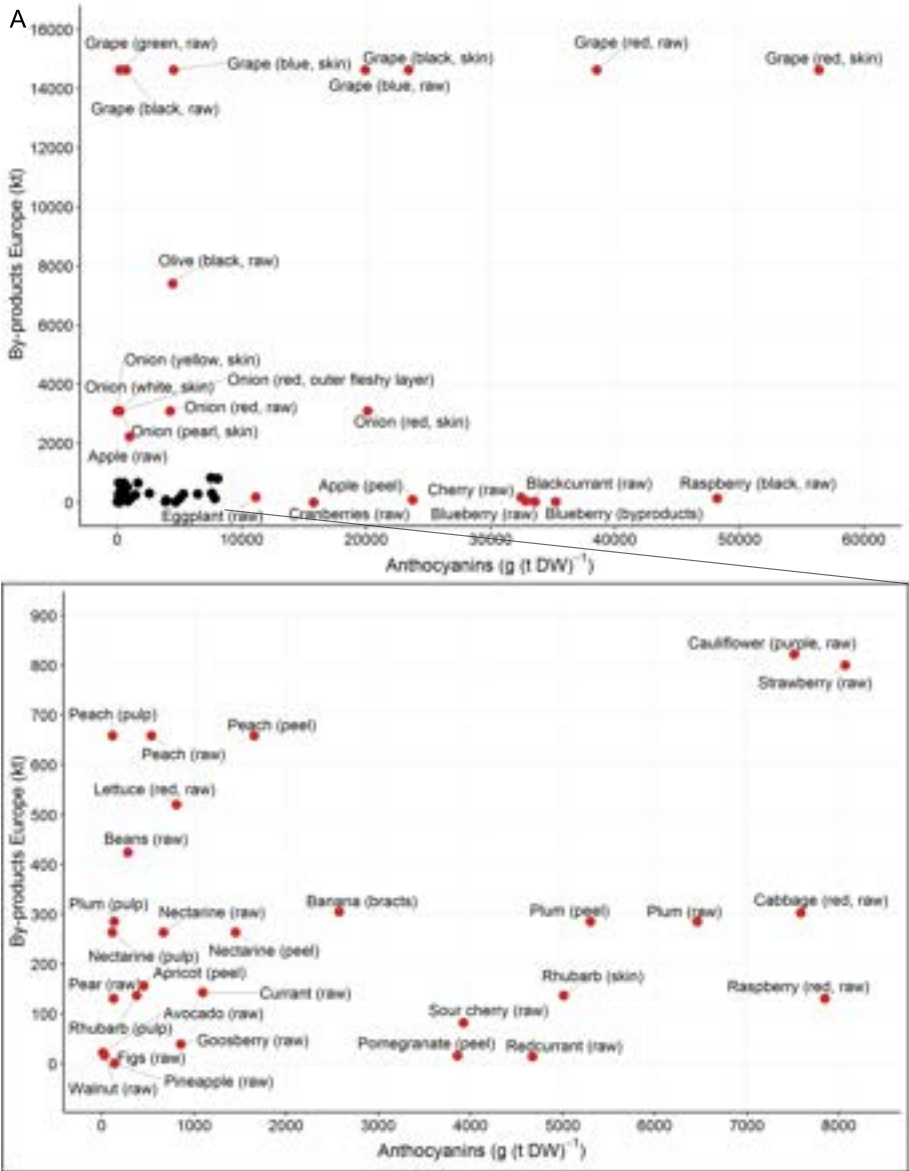
1.3.1.2 Quinones

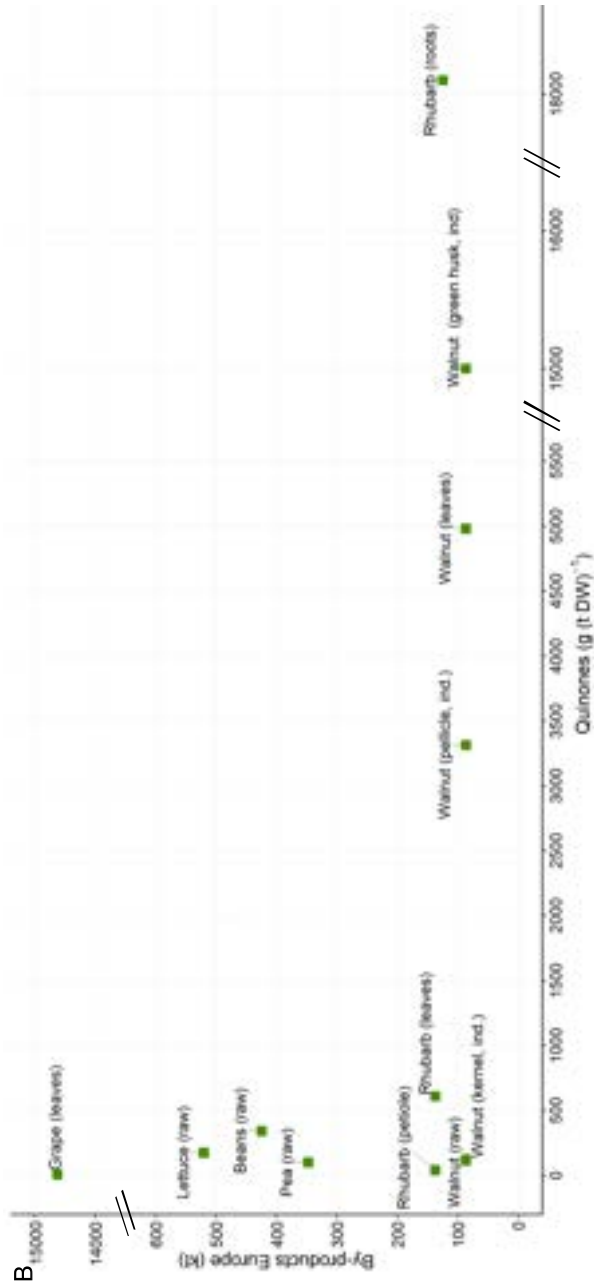
The number of natural quinone sources that are derived from fruits and vegetables appears to be limited in comparison with anthocyanin sources (Figure 1.7A). Walnut and its by-products (leaves and green husks) are a source of phenolic acids, syringaldehyde, and juglone that, due to their anti-inflammatory and anti-mutagenic properties, have been proven to positively enhance human health and wellbeing [89, 90]. Possible natural colorants that can be extracted from walnuts are naphthoquinone derivatives, such as 1,4-naphthoquinone, juglone (5-hydroxy-1,4-naphthoquinone), 2-methyl-1,4-naphthoquinone, and plumbagin (5-hydroxy-2-methyl-1,4-naphthoquinone) [91, 92]. Colaric et al. [89] quantified the juglone content in several walnut cultivars and reported 123 and 3313 g/t DW in kernel and pellicle, respectively. Its by-products, such as leaves and green husks, showed higher juglone concentrations [90, 93]. Anthraquinones could also be found within the *Polygonaceae* (*Rheum*) family [60]. Although many studies cover the Chinese herb, rhubarb, Paneitz and Westendorf [94] detected emodin, physcion and chrysophanol within the *Rheum rhabarbarum* petioles and leaves with a respective share of 50%, 30% and 20% of the total anthraquinone content. The concentrations found in the petioles and leaves reach up to 610 and 40 g/t DW, respectively [94]. Kosikowska et al. [95] obtained a total anthraquinone content of 18.1 kg/t DW rhubarb roots. Other natural anthraquinone sources were reported by Mueller et al. [81], who investigated lettuce, beans and peas for specific anthraquinones: emodin, chrysophanol and physcion, of which a total anthraquinone content of 174, 342, 21 g/t DW was found, respectively [81]. The most interesting sources for obtaining naphthoquinones and anthraquinones are walnuts and rhubarb, respectively.

1.3.1.3 Carotenoids

Carotenoids are known to be present within red, orange, and yellow fruits and vegetables. Tomato and pumpkin are the two largest carotenoid sources (Figure 1.7C). The main carotenoids found in tomato waste are lycopene, which

is the most abundant compound (66-84% of the total content), followed by β -carotene (13-28%) and lutein (<3-20%) [96]. Lycopene is more prominent within the water-insoluble fraction and the skin (72-92%). As a result, extracts from skins contain a five-fold higher concentration of lycopene compared to pulp extracts [97, 98]. Maximum carotenoid content of 593 kg/t DW tomato waste was obtained through soxhlet extraction [99]. Pumpkin is the second-largest carotenoid source, as illustrated in Figure 1.7C. The carotenoid content of pumpkins mainly consists of β -carotene (> 80%) [100]. Shi et al. [101] applied a conventional solvent extraction to obtain a total carotenoid content of 12.9 kg/t DW pumpkin. Carrots are also well-known sources of carotenoids, with β -carotene as the predominant carotenoid. The carrot peels (i.e., pomace), generated after the production process, are mostly discarded or used as fodder, as only 60–70% of the carrot is extracted into juice [102, 103, 104]. The peel contains 204.5 g β -carotene equivalent/t DW, although thermal processing such as hot-air drying could decrease the content by more than half [105]. Perrin et al. [106] investigated the carotenoid content in carrot leaves and roots and attained a maximum content of 4.6 kg/t DW in the leaves, with lutein as the main carotenoid (36-49% of total carotenoid content). The carotenoid level found in the roots was about 31 times lower. Spinach, red sweet pepper, and lettuce can still be considered as large carotenoid content sources. Citrus fruits contain somewhat lower carotenoid levels (156.23 g/t DW) [107] as Aravantinos-Zafiridis et al. [108] obtained 392 g β -carotene equivalent/t DW citrus peels, but the potential amount of by-products is still about 2000 kt. Potato by-products also come in high numbers, although potato peels only contain 3.77 g carotenoids/t DW [109].





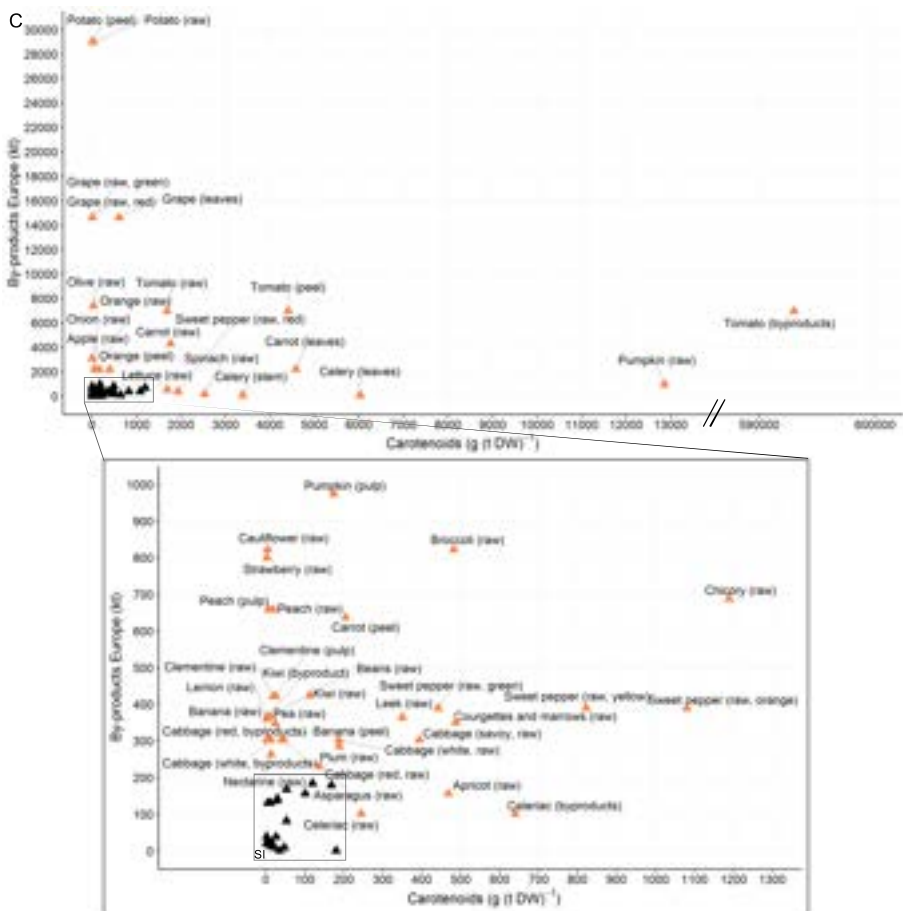


Figure 1.7: These plots illustrate the number of by-products that are generated by processing within Europe as a function of the anthocyanin (A), quinone (B), or carotenoid (C) content within the different fruits and vegetables (Tables A.3 and A.4). The amount of by-products is derived from the percentage of waste to the primary production. This can be interpreted as a maximal value as the entire crop production will not be used for processing. The term 'raw' indicates the concentration found in the primary raw material. Additional figures on the amount of by-products produced locally can be found in the supporting information (Figures A.3 to A.9).

1.4 Natural Dyes in Practice

The EU, after China, is the world's second-largest exporter of textiles and clothing [110]. Countries such as Austria, Belgium, France, Germany, Italy, Poland, Portugal, Romania, Spain, and the UK are top producers within the area of textiles and clothing, carpets, cellulosic fibers, and technical textiles, with 99% of the companies being qualified as SMEs [111]. The EU published article 68(2) to restrict substances classified as carcinogenic, mutagenic, or toxic for reproduction (CMR) in textiles for consumer purposes and emphasize the development of strategies in sustainability and a circular economy [110]. Dyeing with natural colorants, whether they originated from primary sources or by-products, has been trending over the last decades and steadily finds its way into non-food applications besides their use as food colorants. This part aims to review the studies performed for the aforementioned dye molecules on different fibers, including different attempts to improve affinity and stability. A literature review was performed by screening the databases, SCOPUS and the Web of Science, for “natural” AND “dye” within the article title and a timespan of two decades (starting from 2000). The search results were refined on two criteria that consider: 1) the presence of the natural dyes of interest (i.e., anthocyanins, quinones, or carotenoids) within the source or raw material used for dyeing purposes; and 2) the application on textile substrates (i.e., cotton, wool, silk, etc.). This resulted in 273 studies, of which 104 reported wash and lightfastness tests. Since natural dyes originate from natural sources and are not synthetically designed for non-food applications, they are typically less stable and have less affinity. The screened literature reveals several techniques to overcome the stability and affinity issues of natural dyes to textile substrates. These approaches can be grouped into four categories: mordants (metallic and bio) [112], enzymes, substrate modification, and dye modification.

- Metallic mordants rely on the formation of coordination complexes between the substrate, dye, and metal ions. The substrate and dye, the ligands, donate their free electron pairs of oxygen or nitrogen atoms to the free orbitals of the metal ion, which acts as an acceptor. This leads to a strong coordination bond with a covalent character. However, metal salts also possess potential toxicity and are not suitable for skin contact-related applications.
- Biomordants are possible alternatives. These are organic molecules, which should form stabilizing intermolecular interactions with hydrogen bonds, π - π interactions, inclusion, or Van der Waals interactions.

- Enzymes are considered a safe and “green” technology. The enzymes can be reused, are biodegradable, and have high chemo-, regio-, and stereospecificity; this means that fewer side products are generated. The disadvantages of enzymes are their instability toward extreme pH values, temperatures, and solvents [113].
- The last two techniques involve more synthetic steps: substrate and dye modification. The modification of the fiber alters the fiber's properties, such as improving the diffusivity of the dye into the fiber by plasma treatment, graft co-polymerization, gamma-ray irradiation, and ozonization, or creating ionic bonds with the dye by cationization agents or reactive group addition.

The following sections describe to what extent these aforementioned techniques were applied to each natural dye class, which is also summarized in Table 1.4. Figure 1.8 gives an illustrative overview of the various methods for anthocyanins, quinones (benzoquinones, naphthoquinones, and anthraquinones), and carotenoids for different fibers.

1.4.1 Anthocyanins

As shown in Figure 1.8, dyeing anthocyanins on textile substrates without mordant show rather mediocre wash fastness and poor lightfastness. Therefore, anthocyanins are predominantly combined with metallic mordants. Typical metal mordants that are tried are: Al(III)-, Ca(II)-, Co(II)-, Cr(VI)-, Cu(II)-, Fe(II)-, Fe(III)-, Mg(II)-, Mn(II)-, Sn(II)-, Sn(IV)-, and Zn(II) salts; the salts of the most frequent metal used alum ($\text{AlK}(\text{SO}_4)_2$) and ferrous sulfate (FeSO_4). The efficacy of the mordants depends on the applied substrate and source, which is represented by the wash- and lightfastness values. Stannous chloride is less commonly applied, but seems to be the most effective metal mordant on cotton [114, 115] and silk [116, 117], increasing the wash and lightfastness up to three and four grades, respectively, compared to the control [114, 118]. The application of multiple mordanting procedures, such as metal/metal [119] or metal/bio [120, 121], also leads to excellent wash and light fastnesses. Velmurugan et al. [122] investigated the effect of silver nanoparticles with purple sweet potato dye. The addition of the nanoparticles contributed only to the fabrics' antibacterial activity and did not significantly improve the properties. The use of biomordants is less common and consists mainly of tannins such as tannic acid or tartrate salts. The addition of gallic acid or tannic acid has been shown to improve the lightfastness of anthocyanins, as they carry UV-protective properties [123, 124]. This can be ascribed to the formation of a π -complex between the dye and

biomordant, as shown by various molecular dynamics simulations [52, 114]. Therefore, tannic acid is often combined with a metallic salt to improve the overall fastness. Two studies involved enzymatic application: protease enzymes such as trypsin, which hydrolyzes proteins at the C-terminal to arginine or lysine, and oxidoreductases such as laccase, which were used for pretreating the textile substrate. The use of protease enzymes did not result in any improvement compared to the control [117]. The use of laccase is hampered by the optimal conditions wherein enzymes operate. Process parameters such as temperature and solvent are easily adjustable parameters for anthocyanins, within margins of degradation. However, the difficulty lies in the pH. The optimal pH, for instance, for laccase is 5.5, which means that anthocyanins do not show their red color as in an acidic environment. Laccase aims to form a covalent bond through a radical-mediated reaction on polyphenolic compounds from gallnut, but this mechanism has not yet been proven to effectively work with anthocyanins [125]. Furthermore, the radical-mediated reaction could also interrupt the conjugated system of anthocyanins, which results in a typical yellow color of a polymeric polyphenolic compound. Laccase from *Bacillus subtilis* has an optimal pH of 3 and might be more suitable for the red flavylum cation. Coating films or thin-film sensors can be developed by mixing poly(acrylamide-co-acrylic acid)chitosan/nanocellulose solution [126], with anthocyanin extract, or by adding an epichlorohydrin coupling agent for a polyacrylonitrile application [127]. Due to the halochromic properties of anthocyanins, nanofibrous wound dressings can also be created through a mixture solution of sodium alginate and polyvinyl alcohol (PVA) [128]. Printing purposes with anthocyanins are done by adding a thickening agent such as gum tragacanth and guar gum, which results in the best printing silk, although with the addition of multiple metallic salts [129]. Cyanuric chloride has also been modified with 4-amino-benzenesulfonic acid to create more anionic sites that form ionic bonds with the flavylum cation, which increases the overall fastness by three grades [130]. In contrast to this, Gedik et al. [131] and Nakpathom et al. [132] used cationizing agents Laucol RW (a polyamine derivative) and 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHTAC), respectively, in combination with a metal salt, which also seemed to improve the overall properties. Other protein-based applications for anthocyanins are hair dyes [133, 134]. Upon adsorption, hair provides a neutralization environment, which shifts the equilibrium toward the anionic quinoidal base, resulting in a blue color [134]. Despite the hydrophilic property of anthocyanins, 54% of the studies were applied to protein fibers (silk and wool), while 40% were applied to cotton. Forty-one percent of the studies with anthocyanins applied to cotton and protein

fibers without mordant show a wash and lightfastness of 4 and 3 or higher, respectively (Figure A.11). Furthermore, protein fibers show one to two higher grades compared to cotton. The highest properties were obtained with ammonium ferrous sulfate and stannous chloride on silk and cotton [119]. While relatively effective, the use of metallic mordants hardly fits in a 'green story,' even though 36% of the studies applied metal salts, while only 16% worked with biomordants. The overall fastness for biomordants on protein fibers is two grades higher compared to cotton. As such, the use of tannic acid on silk and wool [116] or itaconic acid on silk [120] seem more justified in terms of environmental impact and also meet the industrial requirements for general apparel, i.e., $WF \geq 4$ and $LF \geq 5$ (Table 1.4) [135].

Table 1.4: A summary table, based on Figure 1.11 and Figures A.11 to A.14, on the different dyeing methodologies and to what extent and effectiveness the methods are investigated with the following natural dyes. The performance of each dye class on cotton, protein fibers, and synthetic fibers has been evaluated against the industrial fastness requirements for general apparel (wash fastness (WF) ≥ 4 and light fastness (LF) ≥ 5). The ratios of studies are given between brackets.

Methodology	Anthocyanins (n = 50)			Naphthoquinones (n = 64)			Antraquinones (n = 112)			Carotenoids (n = 46)		
	# studies WF ≥ 4 & LF ≥ 5			# studies WF ≥ 4 & LF ≥ 5			# studies WF ≥ 4 & LF ≥ 5			# studies WF ≥ 4 & LF ≥ 5		
	Cotton	Protein fibers ^a	Synthetic ^d	Cotton	Protein fibers ^a	Synthetic ^d	Cotton	Protein fibers ^a	Synthetic ^d	Cotton	Protein fibers ^a	Synthetic ^d
No mordant	36% (18/50)	10% (1/10)	41% (26/64)	33% (4/12)	41% (26/64)	41% (26/64)	0% (0/5)	23% (7/30)	33% (3/9)	39% (18/46)	0% (0/7)	0% (0/7)
Metallic mordants	36% (18/50)	36% (4/11)	36% (23/64)	64% (7/11)	36% (23/64)	31% (35/112)	43% (3/7)	50% (11/22)	25% (1/4)	33% (15/46)	22% (2/9)	20% (1/5)
Metallic + biomordants	6% (3/50)	0% (0/1)	6% (4/64)	100% (1/1)	6% (23/64)	5% (6/112)	100% (2/2)	67% (2/3)	-	4% (2/46)	-	-
Biomordants	16% (8/50)	75% (3/4)	9% (6/64)	50% (1/2)	9% (6/64)	6% (7/112)	0% (0/2)	40% (2/5)	-	9% (4/46)	67% (2/3)	0% (0/1)
Enzymes	0% (0/50)	-	3% (2/64)	0% (0/1)	3% (2/64)	1% (1/112)	0% (0/1)	-	-	0% (0/46)	-	-
Enzymes + mordants	0% (0/50)	-	0% (0/64)	-	0% (0/64)	4% (4/112)	100% (1/1)	67% (2/3)	-	2% (1/46)	-	0% (0/1)
Fiber modification	2% (1/50)	0% (0/1)	5% (3/64)	0% (0/2)	5% (3/64)	4% (5/112)	100% (2/2)	50% (1/2)	100% (1/1)	9% (4/46)	0% (0/2)	0% (0/1)
Fiber modification + mordants	4% (2/50)	0% (0/2)	0% (0/64)	-	0% (0/64)	5% (6/112)	-	100% (3/3)	100% (1/1)	4% (2/46)	-	-
Dye modification	0% (0/50)	-	0% (0/64)	-	0% (0/64)	2% (2/112)	-	-	100% (2/2)	0% (0/46)	-	-

^a : silk and wool, ^b : cotton and viscose, ^c : cotton and cotton/viscose blend,

^d : acrylic, nylon, PLA and polyester, ^e : cotton, cotton/viscose blend and lyocell

1.4.2 Quinones

The literature on naturally-derived quinones applied to textile fibers, compared to anthocyanins and carotenoids, is more abundant. The applications of this dye class are categorized according to their structure: benzoquinones, naphthoquinones, and anthraquinones. Anthraquinones, are, after azo dyes, the second-largest dye class of textile colorants. The adequate properties of anthraquinones have led to numerous profound studies.

1.4.2.1 Benzoquinones

The best-known benzoquinone-based dye is carthamin, which can be found in safflower [136] (Figure 1.4). By applying metallic mordants combined with carthamin, excellent wash fastness properties (grades 4/5-5) were obtained for cotton [137, 138], while on silk it also resulted in a lightfastness of grade 4/5 [138] (Figure A.10). The photofading property of carthamin was extended by the addition of UV absorbers, such as benzophenone-type containing a benzotriazolyl group [139], nickel sulphonate derivatives of phenyl esters [140], or naphthalene sulphonates derivatives ([141]). Another type of benzoquinone, claussequinone, which can be found in African coralwood (*Pterocarpus soyauxii*), was dyed with cotton, wood viscose, and bamboo viscose. It was shown that cotton is more appropriate for dyeing carthamin than the viscose types [142].

1.4.2.2 Naphthoquinones

The natural variety of naphthoquinones is quite limited in comparison to anthraquinones (Figure 1.4). Nevertheless, the literature reveals that three compounds are frequently reoccurring: juglone from various walnut materials, such as bark [143]; shells [144, 145]; leaves [146, 147] or mill waste [148]; lawsone from henna leaves [149]; and alkannin from alkanet roots [150, 151]. Other less known quinones are lapachol [152], shikonin and acetylshikonin [153]. Al(III)-, Cu(II)-, Fe(II)-, and Cr(VI)- salts are the most commonly applied metal salts for naphthoquinones. Figure 1.9 shows that applying naphthoquinones without mordant only acquires the industrial fastness properties. Forty-one percent of the studies were performed without mordant; within this category, 58% displayed excellent wash fastness (4-4/5), while 39% showed at least a lightfastness of grade 5 or higher (Figure A.12). The influence of adding metal salts, which account for 36% of the studies, is more of aesthetic value but is more negligible in terms of fastness properties. Next to that, Figure 1.9 also shows the small number of experiments conducted with biomordants: Indian gooseberry

(*Emblica officinalis* G.) [154], myrobalan (*Terminalia Chebula*) [155] or tamarind seed coat [156]. The combination of metallic mordant and biomordants as thickening agents yielded better wash fastness values for dyeing with ratanjot bark. Meanwhile, guar gum acts as the best natural thickener in terms of color yield and fastness property [157]. Pretreating cotton with an enzymatic mixture (glucoamylase, pectinase, and glucose oxidase) in combination with ultrasound resulted in a darker shade than when dyed with alkanet root or nutshell [158]. Cotton has also been pretreated with diasterease, lipase, and protease/amylase; this yielded a dye uptake of 56%, 49%, and 53%, respectively, while all fastness properties scored excellent [159]. The dyeing of enzymatically pretreated polyamide, by trypsin or pepsin, with walnut bark did not indicate any improvement compared to an untreated dyed sample [160]. Khattak et al. [161] applied different synthetic additives to modify the cotton's surface properties (cationizing agents, crosslinkers, and UV absorbers). The quaternary ammonium compound yielded better color strength, while UV absorbers (UV-SUN and Rayosan C) and finishing agents (Dicrylan) proved to be more effective during the post-mordanting procedure. Lin et al. [162] added a glucose-based surfactant, obtained by reacting glucose, n-tetradecanol, and glycidyl ether, on wool, which showed the highest color strength for the henna-based dye (lawsone), due to adduct formation within the wool fiber. Hebeish et al. [163] obtained a 46% increase in color strength with lawsone by modifying cotton with monochlorotriazinyl- β -cyclodextrin. The application of lawsone and octa(aminophenyl) polyhedral oligomeric silsesquioxane or N-phenyl aminopropyl polyhedral oligomeric silsesquioxane nanoparticles on polylactic acid showed similar fastness properties compared to the control sample [164]. Other synthetic fibers that were modified are polypropylene, which was modified with a hyperbranched poly(ester amide) (HPEA) for dyeing juglone before the spinning process. This showed a slight improvement in wash fastness [165]. Ozonization, which is a mild treatment, was also applied on polyamide fabrics [166]; the color strength increased without jeopardizing the wash fastness. The literature shows that naphthoquinones are mostly applied on protein fibers (44%) and cellulose fibers (38%), with no large differences between the overall fastness of both types of fibers (Table 1.4). Only a single combination of copper sulfate and juglone leads to the best possible fastness properties on cotton [167], though a more environmentally friendly procedure of applying naphthoquinones on wool is with tamarind seed coat, a by-product generated from the tamarind pulp industry [168] that is rich in polyphenolic compounds and condensed tannins [169].

1.4.2.3 Anthraquinones

As mentioned above, anthraquinone dyes form the second-largest group of synthetic dyes. For ecological purposes, naturally available sources from fruit or vegetables should be mapped to extract these dyes instead of using the industrial fossil-based approach. The most common natural sources are madder roots [170, 171], manjistha roots [172, 173], *rheum emodi* [174, 175] and *kerria lacca* [176], and cochineal insects [177, 178]. The molecular substitution patterns of these compounds can be found in Table 1.3. As illustrated in Figure 1.10, anthraquinones are mostly applied on wool and initially possess good wash and lightfastness properties and, in some cases, even very good to excellent lightfastness. The adsorption behavior of cochineal dye on polyamide revealed that dyeing at pH 3-4 is thermodynamically more preferable compared to pH 6. This can be ascribed to the significant role of electrostatic interactions between the anthraquinone molecules and the polyamide or wool fiber due to the availability of protonated amino groups, whereas only non-electrostatic hydrophobic interactions are present at pH 6 [179, 180]. Metal salts are also applied in large abundance, with alum ($\text{AlK}(\text{SO}_4)_2$), copper sulfate (CuSO_4) and ferrous sulfate (FeSO_4) as the most effective. This resulted in a half-grade increase until one grade in terms of wash fastness. This can be ascribed to the effective formation of metal-dye-fiber coordination complexes. Tin(II)chloride showed a marginal increase in color strength, but the light and wash fastness properties did not improve for the unmordanted wool fabric [181]. Similar to anthocyanins, silver nanoparticles contribute to the antibacterial activity of a fabric, but the formation of an insoluble anthraquinone complex improves wash fastness by one grade [182]. Studies about biomordants do exist, but they do not contain complete fastness data. The types of biomordants are limited to tannic acid, chitosan [183, 184] or tannin containing matter such as pomegranate rind [185, 186], myrobalan [172, 187], sohkhru leaves [188], *Acacia catechu* [189, 190], Indian gooseberry (*Emblica officinalis* G.) [154], eucalyptus [185], chestnut-leaved oak (*Quercus castaneifolia*) [185], Aleppo oak (*Quercus infectoria*) gall extract [124], Sicilian sumac (*Rhus coriaria*) [185], black myrobalan (*Terminalia chebula*) [175, 191] and gum Arabic tree (*Acacia nilotica*) [192]. Most biomordants are combined with a metal salt to improve the lightfastness properties of the dyed fabric, while *Acacia catechu* seems to be effectively working as a single biomordant for anthraquinones [193]. For the enzymatic approach, the pretreatment of wool by Savinase 16 L, a protease (hydrolyzing peptide bonds), resulted in increased absorption of madder and cochineal into the fabric [194].

The combination of potassium permanganate and an after-treatment with Savinase 16 L and microbial transglutaminase showed inferior fastness values compared to ferrous sulfate [195]. Vankar et al. [196] studied the effect of different enzymes with and without ultrasonication. It was observed that lipase is the most suitable enzyme for dyeing cotton and silk, with emodin over diastase and a protease-amylase mixture. Diastase seems to be the more appropriate enzyme to apply for dyeing cotton with tectoquinone. The dye uptake increased up to 28% with the use of ultrasonication compared to conventional dyeing [159]. The cavitation effect of ultrasonic dyeing also resulted in a 47% increase in dye uptake, compared to conventional heating, for lac dye with unmordanted wool [176]). A similar trend is observed for microwave-assisted dyeing with cochineal dye on wool fabric [197]. Several cationizing agents were also applied to improve the affinity to anthraquinones: Solfix E, a polyaminochlorohydrin quaternary ammonium polymer with epoxide functionality for reaction on the cotton fiber [198], 3-chloro-2-hydroxypropyltrimethyl ammonium chloride [199, 200], polypropylene imine dendrimer-modified chitosan (PPI) [201], chitosan-poly(amidoamine) dendrimer hybrid [202], chitosan-cyanuric chloride [203], polylactic acid with octa(aminophenyl) polyhedral oligomeric silsesquioxane or N-phenyl aminopropyl polyhedral oligomeric silsesquioxane nanoparticles [164], poly(ethyleneimine) (PEI) (cationic synthetic polymer) [204], Alpsfix (polyamino compound) [205, 206], cetrimide, cetrimonium bromide (CTAB), Sandofix HCF [207] and even ovalbumin [208], a protein. In order to overcome the hydrophobicity of wool, bentonite, an aluminum phyllosilicate, which is negatively charged, and bentonite modified with didecyldimethylammonium bromide (DDAB), polyethyleneglycol (PEG400), and lecithin were applied to create a more hydrophilic surface. The modified bentonite yielded at least a 22% increase in color strength [209]. Plasma treatment involves surface modification through erosion, etching, creation of microcraters, rounding of scale edges, or ablation [210]. This resulted in better fastness properties for dyeing cotton with madder roots [211]. The dyeability of cotton fibers with cochineal can also be improved by oxidizing the fabric with hydrogen peroxide followed by a chitosan biomordant treatment. The oxidation of primary alcohols of cellulose will result in aldehydes. When these aldehydes react with the amino groups of chitosan, imines are formed. However, in the presence of water, the aldehyde functional groups can form hydrates, which can be further oxidized to carboxylic acids. The reaction between a carboxyl acid with the amino group of chitosan will lead to amide bonds. This treatment increased rubbing and washing fastness by at least one grade [212]. Dye modification via the sol-gel process helps to immobilize and

stabilize the biomolecule or dye. The incorporation of (in)organic compounds occurs through hydrolysis and subsequent polycondensation with other organic or inorganic molecular precursors to form a sol, a dispersion of colloidal particles or polymers within a solvent. dos Santos et al. [213] and [214] encapsulated carminic acid through this process with tetraethylorthosilicate (TEOS), aluminum chloride, and hydrochloric acid, which showed a better wash fastness on bamboo viscose/PET/elastane, cotton, polyester, and wool, while other substrates such as polyacryl, polyamide, or PVC did not show any improvement. A more synthetic pathway is shown by Drivas et al. [215] who proved that alizarin and purpurin can be used as platform chemicals for improving the dyeing properties of polylactic acid by mono-alkylation. Better results were obtained when an ethoxy, benzyloxy, or methyl-4-butoanoate group was added to the starting anthraquinone compound. The additional presence of a 1-hydroxy group improves the photooxidative property of the compound by the formation of an intramolecular-hydrogen bond with the 9-ketone group. Wu et al. [216] also used alizarin as a platform molecule to graft alkyl and hydroxyalkyl groups with chain lengths from two to eight carbon atoms on the C2 position. Next to the hypsochromic shift, it was observed that supercritical CO₂ dyeing with the hydroxybutyl derivative showed the best performance. Fastness tests have indicated a higher preference for hydroxyalkyl derivatives over alkyl derivatives of alizarin. The studies showed a high application rate (61%) of natural anthraquinones on protein fibers. Eighteen percent of studies applied cellulose fibers, while 15% used synthetic fibers (Figure A.13). Forty-one percent of the case studies did not use a mordant, 31% used metal salts, and barely 6% used biomordants. Naturally-derived anthraquinones applied on protein fibers, polyester, and PLA are able to meet the industrial fastness requirements for general apparel without the addition of any type of mordant (Table 1.4). The addition of aluminum sulfate along with citric acid or potassium bitartrate can result in maximal fastness properties [177]. The use of black myrobalan (*Terminalia chebula*) as a biomordant also improves the fastness properties by two grades [175].

1.4.3 Carotenoids

Even though carotenoids are largely present in tomatoes and carrots, the literature shows that other sources are used to extract carotenoids, such as annatto seeds (bixin and norbixin [217, 218], marigold (*Tagetes erecta* L.) flowers (lutein) [219, 220] and *Gardenia* (crocin and crocetin) [221, 222]. Figure 1.11D shows that carotenoids possess good wash but poor lightfastness properties. It is

no secret that exposure to light is harmful to carotenoids, as it induces E-Z photoisomerization and photodestruction [63]. Once again, metal salts based on Al(III), Cu(II), and Fe(II) are frequently used for textile dyeing with carotenoids, which increases wash fastness by half a grade and lightfastness by at least two grades. The effectiveness of these metal salts can be ascribed to the aforementioned carotenoids. A similar trend in fastness properties is observed for rare earth metal salts such as lanthanum chloride and neodymium chloride, which are also able to form stable coordinative bonds between *Gardenia* dye and fiber [223]. The carotenoids found within the literature are xanthophylls (i.e., carotenoids containing oxygen atoms). This allows the metal ions to form effective metal-dye-fiber coordination complexes. Several biomordants were also investigated: tartaric acid [195, 224], myrobalan [155], pomegranate [186] and Indian gooseberry (*Emblica officinalis* G.) [186]. With enzymatic dyeing, the combination of pretreatment by using potassium permanganate and Savinase 16 L and an after-treatment of microbial transglutaminase did not render improved fastness properties compared to using aluminum sulfate or ferrous sulfate [195]. Fiber modification involved the addition of cationic dye fixing agents in the role of quaternary ammonium compounds: 3-chloro-2-hydroxypropyl trimethyl ammonium chloride [200, 225], CTAB, cetrimide, or Sandofix-HCF in combination with aluminum sulfate and myrobalan [207]. Additionally, other chemicals were used to break bonds, more specifically disulphide bonds within wool by tris(2-carboxyethyl)phosphine, which showed an increase in adsorption [226]. Improving lightfastness properties were found for annatto dyed silk in combination with a polydopamine (PDA) coating [227], benzotriazole on jute [207], and Rayosan PES resulted in PET improvement [217]. The gamma-ray pretreatment (30 kGy) of the cotton fabric increases the negative potential of the cellulosic fabric. The additional generation of carboxyl groups and a slightly acidic pH (5.0) improved the wash and lightfastness properties of lutein by at least one grade [228]. Lastly, dos Santos et al. [213] and Velho et al. [214] encapsulated annatto seed compounds through the sol gel process by using tetraethylorthosilicate (TEOS), aluminum chloride, and hydrochloric acid, which showed a better wash fastness on bamboo viscose/PET/elastane, cotton, and wool but worked less efficiently within a PVC matrix. In the end, 39% of the studies did not use any mordant, while 33% and 9% used metal salts or biomordants, respectively (Figure A.14). Only 44% of the purely applied carotenoids attained a wash fastness of 4, and 89% of those unmordanted carotenoid fibers scored poorly on lightfastness (below a grade of 3). The lightfastness property clearly improved when applying a metal salt, as 73% of all

metal mordanted carotenoid fiber showed at least a grade 4 or higher. Forty-four percent of the studies applied carotenoids on cellulose fibers, while 33% applied carotenoids on protein fibers, though only a grade difference was observed in the fastness properties for the no-mordant method. The best fastness properties ($WF = 4/5$ and $LF = 6-6/7$) on a cotton/viscose mixture or just cotton in the presence of a pomegranate rind as biomordant, which is a by-product generated by the pomegranate juice manufacturing industry and is rich in polyphenolic compounds [229].

The creation of new process inputs (e.g., natural dyes) to phase out hazardous substances is one of the four pillars for a new textile economy. Table 1.4 displays an overview of to what extent different application techniques for each natural dye achieved the industrial fastness requirements for general apparel and which methods still require more in-depth research and development. Metallic mordants are mostly favored to improve the affinity and stability of natural dyes but come along with potential environmental issues. The greener approaches, such as biomordants and enzymes, still indicate room for improvement. The former show that tannins positively contribute to wash and lightfastness properties, while the latter induces coupling reactions; this creates covalent bonds through radicalization or increases the diffusivity of the fabric by breaking linkages, although possibly jeopardizing the fabric's strength. For synthetic fibers specifically, heating above the glass transition temperature allows a higher mobility of the polymer chains, creating more available voids for dye diffusion. The other two modification methods for fiber and dye are more based on a synthetic nature that involves the addition of polymers or adding potentially toxic reactive groups (cyanuric chloride or vinylsulfone) to the dye. This synthesis approach guarantees dye fixation but might require more chemicals, which may not be preferable from a sustainability point of view. Encapsulating procedures via the sol-gel process or with biopolymers are promising techniques, as they potentially protect the dye from undesirable process conditions.

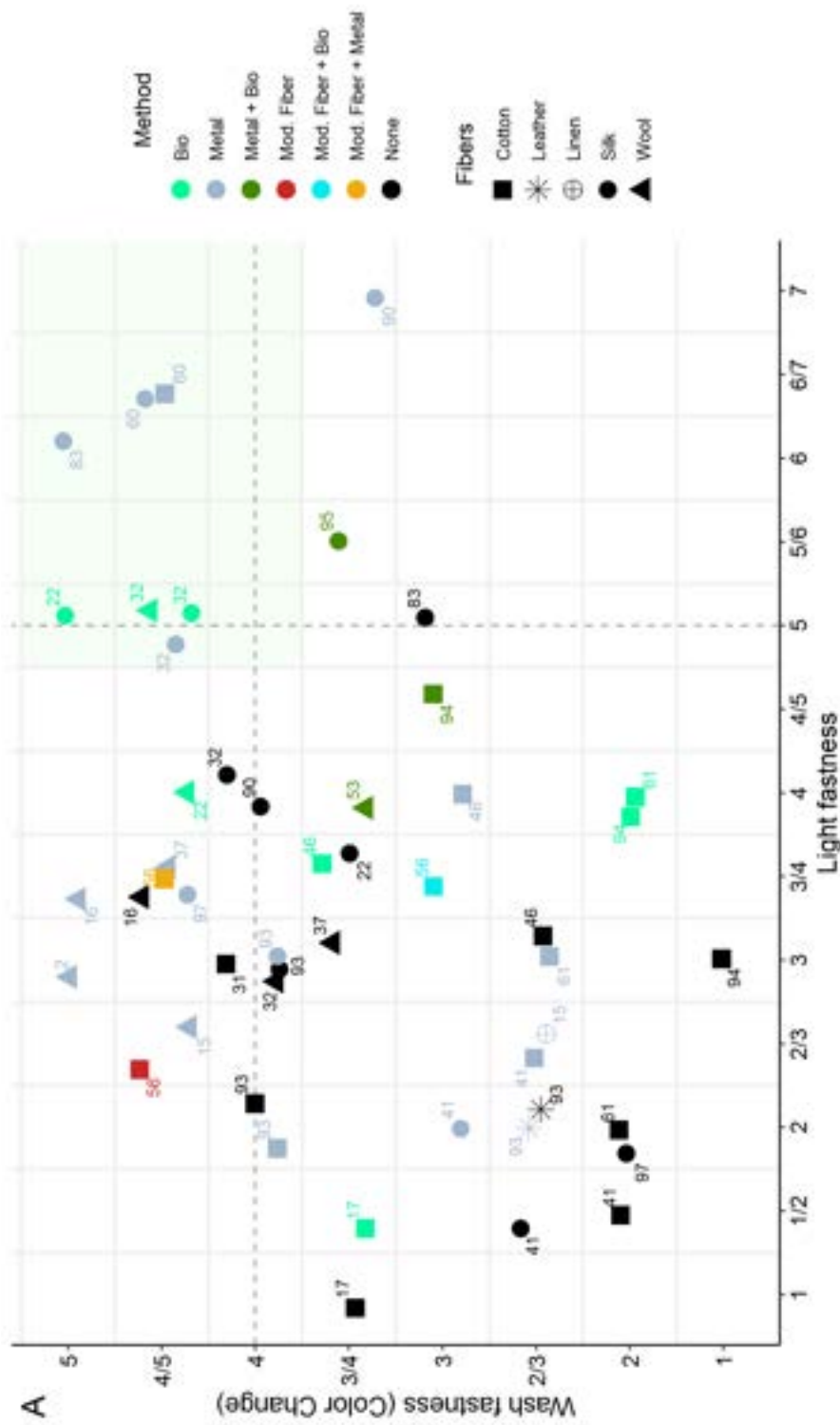


Figure 1.8

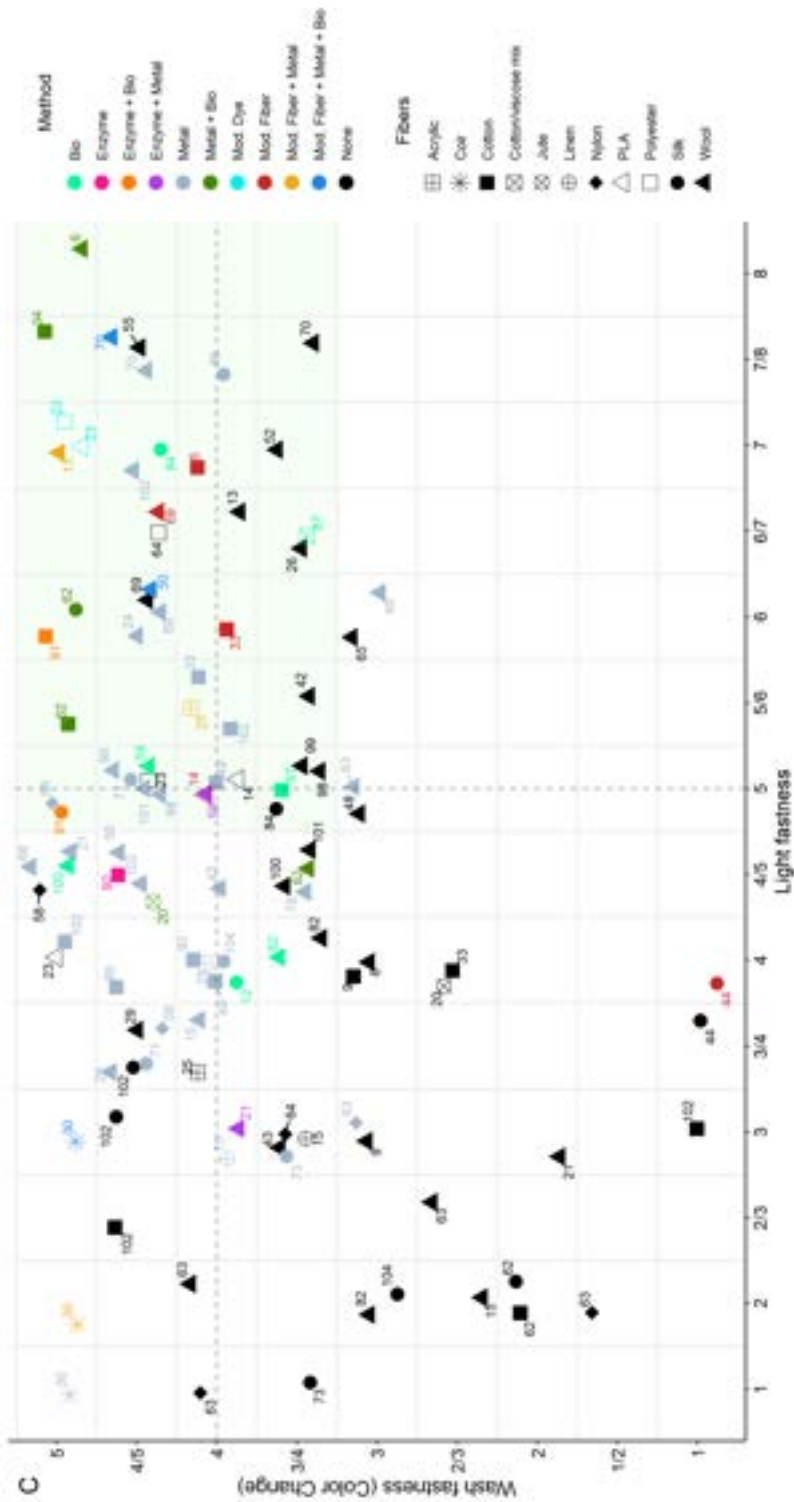


Figure 1.10

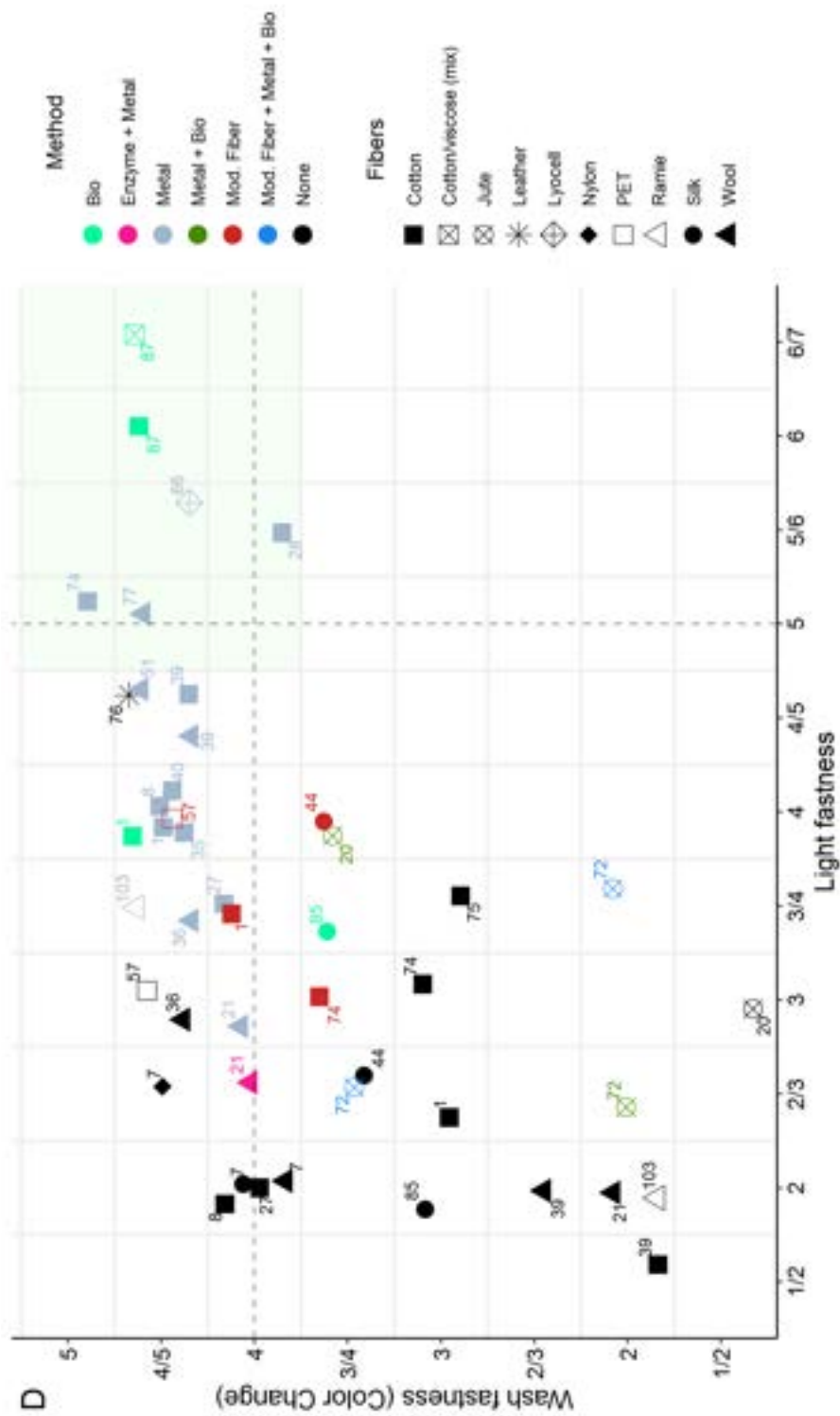


Figure 1.11: The fastness properties of anthocyanins (A), naphthoquinones (B), anthraquinones (C), and carotenoids (D) on various fibers. The wash fastness is based on the color change on the grayscale, while it is expressed via blue wool standards. The scales of the fastness values are confined in boxes for the reader's convenience. The dotted lines represent the industrial-required fastness grades for general apparel. Only studies including both fastness properties were included in these plots; the reference labels are listed in Table A.5.

1.5 Conclusions

Currently, much of the by-products produced by the fruit and vegetable supply chains are still further converted into a product with a relatively low economic value (e.g., fodder). To increase the value of these by-products, novel valorization routes should be developed, with an emphasis on high added-value bioactive compounds or fibers. This chapter contributes to one of the pillars for a new textile economy: the creation of renewable resource based coloring materials that phase out hazardous substances that are used within the industry. Natural dyes are one of those compounds that are of interest, as they have the potential to replace fossil-based synthetic dyes. Waste streams from the food processing industries are an affective source of natural dyes, as they are mostly composed of fruit and vegetables' outer parts that contain large amounts of natural dye. The mapping of agro-food residue quantities of anthocyanins, quinones, and carotenoids showed the vast availability of agro-food residues (>0.1 Mt annually) across the European Union (28 member states), with a natural dye content of up to 56 kg/t for anthocyanins (red grape pomace), 18 kg/t DW for quinones (walnut green husks and rhubarb roots), and 593 kg/t DW, for carotenoids (tomato pomace). These aforementioned fruit and vegetable processing waste streams are most interesting to come forth in (industrial) applications. However, the natural dye content extracted from biomass depends on many factors such as growing condition, ripeness, variety or cultivar, genotype, horticultural studies, geographic location, post-harvest storage conditions, the purpose of the end-product, and the extraction methods (i.e., technique and solvent). The literature shows that textile-related applications of natural dyes mostly constitute anthraquinones, compared to anthocyanins and carotenoids. This can be ascribed to the fact that anthraquinones, which have already proven their excellent fastness properties, form the second-largest dye class of textile colorants. Metallic mordants are mostly favored to improve the affinity and stability of natural dyes, but they also come along with potential environmental issues. The greener approaches, such as biomordants and enzymes, still show room for improvement; the last two modification methods on fiber and dye rely more on a technological and chemical synthesis approach, guaranteeing dye fixation, although they are questionable in terms of environmental sustainability. Encapsulating procedures via the sol-gel process or with biopolymers might be promising techniques, as they potentially protect the dye from undesirable process conditions.

Part II

Objectives of the PhD

Objectives of the PhD

Nowadays, synthetic dyes and pigments are well established in industries producing textile, paints and coatings, paper, food and beverages, plastics, printing inks, cosmetics and personal care, and other industries. These synthetic dyes possess great fastness properties, low cost and cover versatile color ranges. However, industries using these dyes and pigments such as the textile dyeing and finishing industry contribute to a large extent to pollution of clean water and furthermore, these molecules can be toxic for human health [13]. Recently, global attention is shifting toward pollution control and environmental sustainability, which causes a renewed interest in natural dyes. They are believed to be safe due to their non-toxic non-carcinogenic nature. Besides that, some of these natural dyes possess anti-UV and anti-microbial properties and they are more biodegradable in natural conditions.

In Chapter 1, the detailed mapping of by-products derived from the fruit and vegetable processing industry in Europe, along with the concentration levels of anthocyanins, quinones, and carotenoids illustrated the large availability of natural dye containing agrofood residues. Furthermore, the performance of different application methodologies in terms of fastness properties of natural dyes into textile fibers, with regard to overcome the dyes' specific affinity and stability issues and identifying the potential emerging methods were discussed. Based on this information, the main goal of this dissertation is to investigate the feasibility of implementing anthocyanins, with the aim of substituting their synthetic analogues, in non-food applications by means of combining molecular modeling and lab experiments.

For this purpose, first Chapter 2 applies and compares theoretical and computational modeling tools toward predicting the outcome of a solvent on the extraction process to achieve anthocyanidins and anthocyanins from biomass. The solubilities were screened toward in 30 solvents with the most common predictive models toward solubility, being the Hansen solubility parameters, Flory-Huggins interaction parameter (χ_{12}), static calculations based on Density Functional Theory (DFT) and the COSMO-RS hybrid solvent model. Furthermore, the best computational model was used to investigate the

anthocyanidins and anthocyanins profile in water-solvent mixtures.

Chapter 3 investigates the optimization of the dyeing procedure with anthocyanins for dyeing cotton and the investigation for effective (bio)mordants to improve the affinity of anthocyanins on cotton fibers by intermolecular interactions (e.g., metal-ligand, hydrogen bonds, ionic and π - π interactions), in combination with a modeling approach in the second part, presenting a profound understanding on the underlying mechanism between (bio)mordants, dye and substrate on molecular scale.

Chapter 4 explores the photophysical properties of a naturally derivatized subclass of anthocyanins, called pyranoanthocyanins. A systematic analysis was performed by evaluating three functionals (B3LYP, CAM-B3LYP and PBE0) for a large set of naturally occurring anthocyanin-based compounds along with structure elucidations to clarify the effect of structural changes between the different subclasses on the maximal absorption wavelength observed within the experimental literature data. Therefore, a library of 140 anthocyanin-based compounds is generated with their photophysical properties. The results obtained from this fundamental research provide insight in potential applications such as food additives/colorants, textile dyes, reference analytical standards and dye sensitizers (DSSCs).

Finally, Chapter 5 analyzes potential valorization process flowsheets including various conventional and emerging technologies for extraction, purification and encapsulation. This chapter includes the potential pitfalls encountered with each natural dye and it analyzes the environmental impacts of a naturally-dyed fiber by means of Life Cycle Assessment (LCA). The LCA assesses different scenarios that are based on the most optimal valorization route and the influence of additional steps such as biomass drying and different purification and encapsulation techniques.

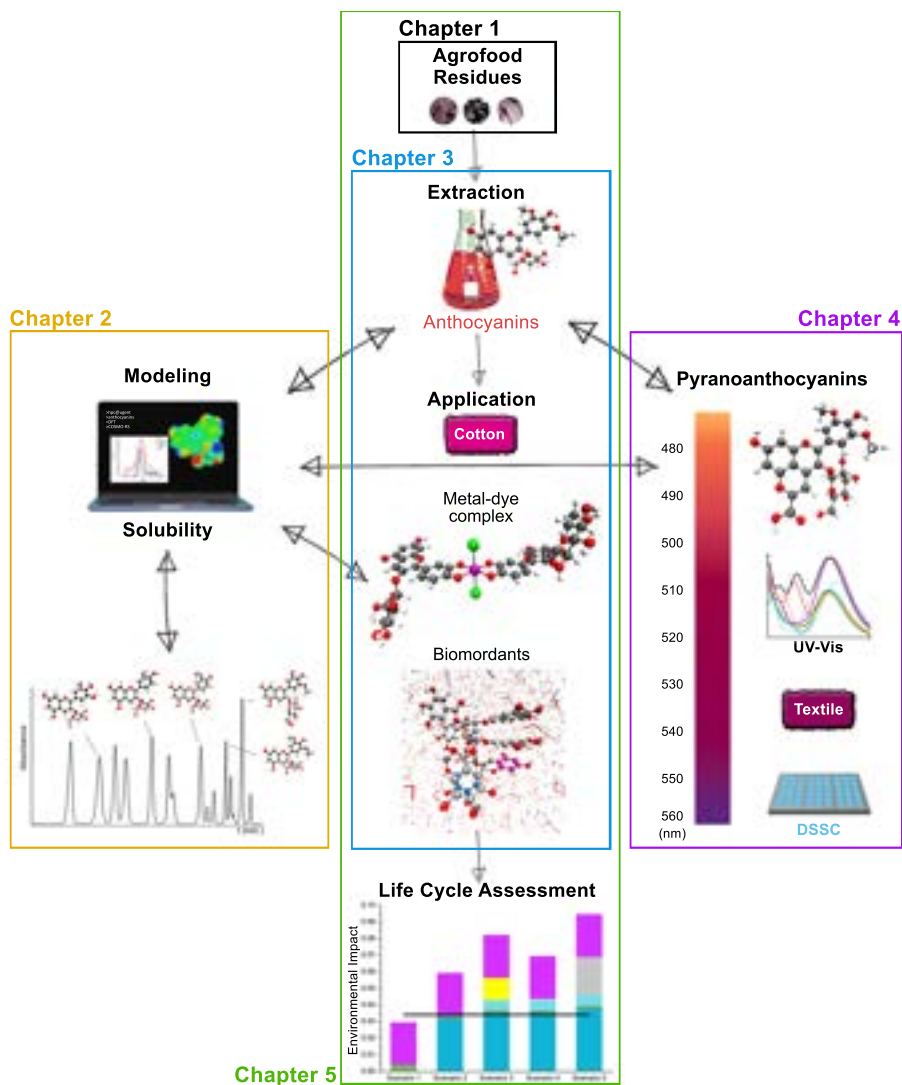


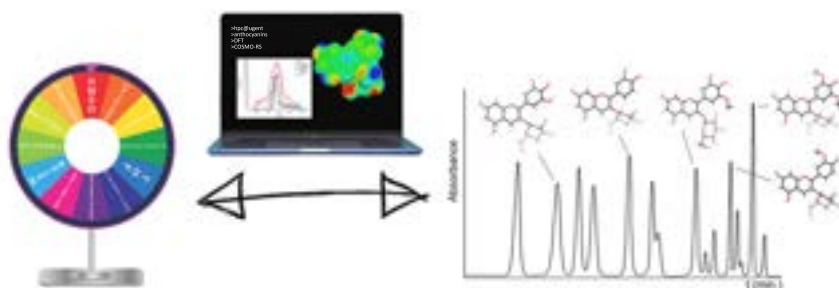
Figure 1.12: Overview of the various chapters within this dissertation.

Part III

Major Research Results

Chapter 2

***An in silico* Study on the Solvent Dependency of Anthocyanin Extraction Profiles**



Phan K., Van Den Broeck E., Raes K., De Clerck K., Van Speybroeck V., and De Meester, S. *To be submitted.*

An *In Silico* Study on The Solvent Dependency of Anthocyanin Extraction Profiles

2.1 Introduction

As concluded in Chapter 1, extracting anthocyanins can be performed by numerous procedures and techniques. Currently, several food products containing anthocyanins are frequently processed leading to a vast amount of by-products generated by food and vegetable processing industries, such as pomace during production of fruit juices or wine. Typically, anthocyanins are present within the outer layers (skin/peel) of fruit and vegetables. Those parts usually form the base of the pomace and are ideal sources for extraction to obtain these high added-value bioactive compounds. Next to their bioactivity, these molecules can also be applied as food colorants or in non-food applications such as pharmaceuticals, cosmetics, textiles and dye sensitized solar cells (DSSC) [7]. Anthocyanidins and anthocyanins (hereinafter referred to as **ACDs** and **ACNs**, respectively) are known to be beneficial for human health due to their antioxidant activities, but also have various therapeutic benefits such as cardioprotective, neuroprotective, anti-inflammatory, and anticarcinogenic properties [230]. For all these applications, they must be extracted from the solid biomass residues.

ACDs and **ACNs** are hydrophilic molecules (Figure 2.1), thus, in essence, water will suffice for a simple extraction to avoid remaining traces of potentially hazardous solvent in the extraction residue, but the yield is sometimes limited [231]. A 2.2% Dp-3-Glc w/w yield from blackcurrant pomace was obtained with a 0.01% HCl v/v aqueous extraction [231]. To maximize the extraction yield, organic solvents such as ethanol, methanol or acetone are commonly used or aqueous mixtures of the aforementioned solvents [50].

Hidalgo and Almajano [232] listed different extraction procedures along with the solvent composition for red fruits. Figure B.1 shows that pure solvents and

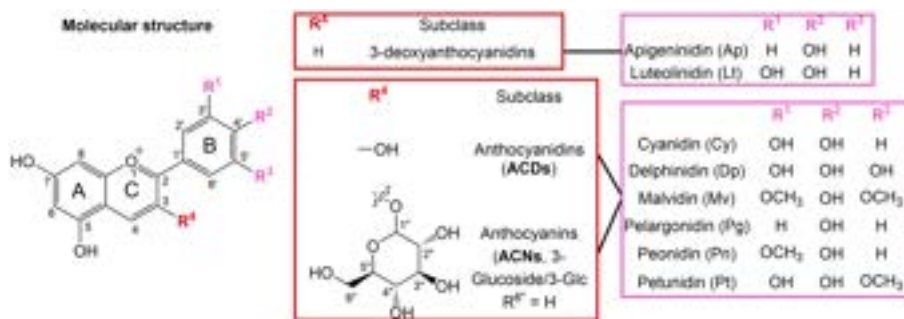


Figure 2.1: The molecular structure and substitution pattern of anthocyanidins (ACDs) and anthocyanins (ACNs).

aqueous mixtures containing 50, 70 and 80 volume percent (v/v) of organic solvent are favored. The most preferable organic solvent is ethanol (54.3%) followed by methanol (31.4%) and acetone (14.3%). A methanolic extraction from grape pulp is 20% and 73% more efficient compared to ethanol and water, respectively, but is less suitable for applications within the food industry due to the methanol toxicity [50]. In 30% of the cases the extraction solvent was acidified with acids such as hydrochloric acid (HCl), formic acid or acetic acid. Acidification of the extract comes with several gains: maintaining a low pH (<3.0) to secure stability and structural consistency, disrupting cell walls to increase accessibility of polyphenolic compounds and solvent transport, and inhibiting enzymes that catalyze polyphenol decomposition [231]. The amount of **ACDs** and **ACNs** extracted is then typically expressed as an equivalent of one specific anthocyanin rather than compound specific concentrations (Table 2.1), as analytical techniques to assess individual molecules within this group is difficult. Only a couple of studies investigated the solvent dependency on the **ACN** composition (Table 2.2). The overview within Tables 2.1 and 2.2 showed mixed trends in terms of most effective organic solvent between acetone, ethanol and methanol. It is noticed that a higher fraction of organic solvent within aqueous mixtures does not necessarily result into a higher extraction yield. Heffels et al. [233] revealed that individual **ACNs** behave differently with different extraction methods. In blueberries, it was found that Dp and Mv are largely affected by the variability of solvent and method used due to the highest polarity and highest abundance, respectively. All other aglycones seem more robust against method variability. It must be stressed that next to the extraction procedure, also the composition and concentrations of **ACNs** within fruits and vegetables depend on the growing condition, ripeness, variety or cultivar,

genotype, horticultural studies, geographic location, postharvest storage conditions, processing method (machinery and/or techniques) [4]. This makes comparisons between studies more difficult.

Table 2.1: The influence of solvent selection on the total anthocyanin content investigated by some studies. The content is usually expressed as cyanidin-3-glucoside (Cy-3-Glc) equivalents (EtOH: ethanol and MeOH: methanol).

Material	Solvent	Total anthocyanin content Ref.
Red cabbage leaves ^a [234]	Water/HCl: 99:1	0.56
	EtOH/Water/HCl: 20:79:1	0.66
	EtOH/Water/HCl: 40:59:1	0.69
	EtOH/Water/HCl: 50:49:1	0.77
	EtOH/Water/HCl: 60:39:1	0.71
	EtOH/Water/HCl: 80:19:1	0.64
Purple corn (<i>Zea mays</i> L.) ^b [235]	Water	6.80
	Water + 0.01% HCl	6.00
	EtOH + 0.01% HCl	1.40
	70% Acetone	9.80
Black currant ^b [236]	39% EtOH + acetic acid	12.76
	67% EtOH + acetic acid	13.33
	95% EtOH + acetic acid	12.87
Sweet cherries ^a [237]	Water + 0.1% HCl	1.70
	EtOH + 0.1% HCl	2.44
	MeOH + 0.1% HCl	2.49
Purple mashua (<i>Tropaeolum tuberosum</i>) ^b [238]	Water + 0.1% HCl	6.75
	10% MeOH + 0.1% HCl	6.45
	50% MeOH + 0.1% HCl	7.30
	90% MeOH + 0.1% HCl	8.00
	90% EtOH + 0.1% HCl	6.35
	90% Acetone + 0.1% HCl	7.45
	MeOH/Acetone/Water (45/45/10) + 0.1% HCl	7.35

^a : mg Cy-3-Glc/g FW, ^b : mg Cy-3-Glc/g DW

Table 2.2: A summary of studies in which the solvent dependency on the **ACN** composition is investigated on the individual concentration level (EtOH: ethanol and MeOH: methanol).

Material	Solvent	ACNs									
Grape skin extract ^a [74]	Water + 0.1% HCl	Cy-3-Glc	Dp-3-Glc	Mv-3-Glc	Pg-3-Glc	Pn-3-Glc	Pt-3-Glc				
		1.34	6.86	14.68	-	3.31	8.26				
	60% EtOH + 0.1% HCl	1.64	7.65	18.05	-	4.11	9.38				
	60% MeOH + 0.1% HCl	1.58	8.22	20.56	-	4.94	9.52				
	MeOH/Acetone/Water/HCl: 40:40:20:0.1	1.74	7.73	15.81	-	3.35	7.17				
Bilberry ^a [233]	70% MeOH + 7% acetic acid	1.52	7.96	19.20	-	3.78	9.08				
	70% MeOH + 0.1% TFA	1.58	8.34	19.74	-	3.91	9.46				
	MeOH/Water/Acetic acid 20:75:5	4.39	3.70	3.31	-	2.48	2.95				
	MeOH/Water/Acetic acid 80:15:5	4.51	4.53	4.03	-	2.75	3.50				
	MeOH/Water/Acetic acid 20:75:5	0.27	0.25	0.79	-	0.23	0.36				
Lowbush blueberry ^a [233]	MeOH/Water/Acetic acid 80:15:5	0.334	0.57	0.86	-	0.25	0.57				
	MeOH/Water/Acetic acid 20:75:5	0.029	-	-	-	0.074	-				
	MeOH/Water/Acetic acid 80:15:5	0.019	-	-	-	0.045	-				
Blueberry ^b [239]		Cy-3-Glc	Mv-3-Ara	Mv-3-Glc	Mv-3-Gal	Pn-3-Glc	Pn-3-Ara				
	60% Acetone	0.12	-	0.092	0.21	0.043	0.021				
	70% Acetone	0.14	-	0.11	0.26	0.059	0.035				
	80% Acetone	0.13	-	0.10	0.24	-	0.027				
	60% EtOH	0.067	-	0.062	0.16	0.026	0.018				
	70% EtOH	0.062	-	0.067	0.16	0.028	0.014				
	80% EtOH	0.064	-	-	0.019	0.012	0.098				
	60% MeOH	-	-	0.012	0.020	0.012	0.28				
	70% MeOH	0.082	0.057	-	0.015	0.32	0.11				
	80% MeOH	0.063	-	0.056	0.0043	0.26	0.019				

^a : mg/g DW, ^b : mg/g FW, TFA: trifluoroacetic acid,

Ara: arabinoside, Gal: galactoside and Glc: glucoside

Very little systematic information is available on the effect of solvent type on the subtype of **ACDs** and **ACNs** that are extracted. Knowing this is important, for example toward their bioactivity. **ACDs** have a higher Oxygen Radical Absorbance Capacity (ORAC) value compared to **ACN**, which is ascribed to the unstable aglycone resulting in a higher reactivity. Very specific **ACDs** or **ACNs** play a selective role in combating enemy cells or curing infections [51]. Therefore, a compound-specific extraction could be performed to maximize the yield of one particular compound, compared to total anthocyanin content. In order to characterize and quantify the exact anthocyanin profile starting from the extract, highly advanced analytical methods and hyphenated equipment are required such as HPLC-DAD-MS/MS in combination with a matrix clean-up and expensive or sometimes unavailable analytical standards [240]. The quantification of each individual anthocyanin starting from the extract requires a matrix clean-up, complete separation and identification. Besides that, a calibration curve is needed for each compound, while not all standards are commercially available.

Computational modeling tools, also called *in silico* tools, are frequently applied for predicting the solubility or binding affinity of drugs and additives and developing formulations. Common tools are phase-solubility studies, quantitative-structure property relationships [241], Hansen solubility parameter calculations via group contribution method [242, 243], Flory–Huggins interaction parameter (χ_{12}) [242], conductor-like screening model for real solvents (COSMO-RS), COSMO segment activity coefficient model (COSMO-SAC) [244], etc. In molecular modeling, solvation energies could be obtained via static calculations using an implicit solvation model or a more computationally expensive explicit solvation model by means of molecular dynamics in combination with the Free Energy Perturbation (FEP) method. The latter provides a better accuracy with errors in the range of -1 to 5.4 kJ mol⁻¹ compared to experimental data [245, 246]. The error with implicit solvation (PCM) for polar organic molecules goes beyond 13 kJ mol⁻¹ as the following phenomena are still challenging to be determined: hydrogen bonds, solvent entropy and non-electrostatic solvent effects for aprotic solvents [246]. These models could be applied on the extraction process of **ACDs** and **ACNs** to predict which solvent would be most effective toward which molecule. Yet, these models have different grades of complexity, and there is no literature available that assesses which model would be preferred for this purpose.

In this context, this chapter aims at using and comparing computational modeling tools toward predicting the outcome of a solvent on the extraction process. For

this purpose, the solubilities of 8 **ACDs** (i.e., 6 common **ACDs** (Cy, Dp, Mv, Pg, Pn and Pt) and 2 deoxyanthocyanins: apigeninidin (Ap) and luteolinidin Lt) and the 3-glycoside **ACN** form of the 6 main **ACDs** were screened toward their solubility in 30 solvents (Table B.1) with the most common predictive models toward solubility [247], being Hansen solubility parameters, Flory-Huggins interaction parameter (χ_{12}), static calculations based on Density Functional Theory (DFT) and the COSMO-RS hybrid solvent model. Furthermore, the best computational model was used to investigate the **ACDs** and **ACNs** profile in water and binary aqueous mixtures. The results can be used as a benchmark for target specific extractions to maximize the applications' demands.

2.2 Materials and Methods

2.2.1 Theoretical Tools

2.2.1.1 Hansen Solubility Parameters

There are various solubility theories such as Hildebrand and Scott, Burrell and Hansen. Hildebrand introduced the solubility parameter (δ) as the square root of the cohesive energy density (CED). The CED equals to the energy required to vaporize a mole of liquid per unit volume. The main shortcoming of this solubility parameter is the lack of describing polar and hydrogen bonding interactions. This is largely solved by accounting for the individual contributions for the calculation of the total energy of vaporization [242]. One of the most widely used approaches to calculate the solubility of drugs, solvents, polymers, oils and surfactants is the Hansen solubility parameters (HSP) [241]. The affinity between a solute and solvent is described by three types of interactions and thus, three partial solubility parameters: dispersion (δ_d), polar (δ_p) and hydrogen bonding (δ_h). The individual HSPs were calculated based on the group contribution method of Hoftyzer and Van-Krevelen [243]:

$$\delta_d = \frac{\sum_i F_{d_i}}{V_m} \quad (2.1)$$

$$\delta_p = \frac{\sqrt{(\sum_i F_{p_i})^2}}{V_m} \quad (2.2)$$

$$\delta_h = \sqrt{\frac{\sum_i F_{d_i}}{V_m}} \quad (2.3)$$

where i represents the structural moiety within the molecule, F_{d_i} and F_{p_i} are the total group contributions for dispersion ($\text{J}^{1/2} \text{ cm}^3/2 \text{ mole}^{-1}$) and polar ($\text{J}^{1/2}$

$\text{cm}^3/2 \text{ mole}^{-1}$), respectively, E_{hi} represents the group contribution to the hydrogen bonding energy (J mole^{-1}) and V_m is the molar volume of the molecule ($\text{cm}^3 \text{ mole}^{-1}$). The solubility parameter distance R_a gives a qualitative view for the miscibility between solute and solvent. The smaller R_a , the higher the miscibility between the two compounds of interest.

$$(R_a)^2 = 4(\delta_{d,A} - \delta_{d,S})^2 + (\delta_{p,A} - \delta_{p,S})^2 + (\delta_{h,A} - \delta_{h,S})^2 \quad (2.4)$$

where $\delta_{i,A}$ and $\delta_{i,S}$ ($\text{MPa}^{1/2}$) are the i^{th} component of **ACDs/ACNs** and solvent, respectively.

2.2.1.2 Flory-Huggins Interaction Parameter (χ_{12})

The Flory-Huggins “chi” parameter (χ) has been used for many years to define polymer blends. The χ_{12} interaction parameter, derived from the New Flory theory, is the successor of the χ -parameter and currently the standard for describing solute-solution behavior. This dimensionless parameter allows estimations where HSPs are known, but χ_{12} not. Hereby, the nonpolar Hildebrand solubility parameter for calculating χ_{12} is slightly modified by including HSPs containing polar and hydrogen bonding interactions, given by A_{12} ([242]):

$$A_{12} = (\delta_{d,A} - \delta_{d,S})^2 + 0.25(\delta_{p,A} - \delta_{p,S})^2 + 0.25(\delta_{h,A} - \delta_{h,S})^2 \quad (2.5)$$

This yields the following expression for calculating χ_{12} :

$$\chi_{12} = \frac{V_m A_{1,2}}{RT} \quad (2.6)$$

with V_m the molar volume of solvent (m^3/mol), R the gas constant (J/mol K) and T the temperature (K). The lower the χ_{12} -value, the better the miscibility between two compounds. χ_{12} -values ≤ 0.5 indicate miscibility, while χ_{12} -values > 0.5 show immiscibility.

2.2.2 Computational Tools

2.2.2.1 Density Functional Theory: Static Calculations

Continuum solvation models such as PCM, COSMO or SMD are cost-effective methods for describing the electrostatic interaction between solute and solvent. Hereby, the solvent is mainly represented as a dielectric medium [245]. All calculations were performed with Gaussian 16 [248] using density functional

theory (DFT). **ACDs** and **ACNs** were geometrically optimized with the B3LYP [249, 250] functional along with the 6-311++G(d,p) basis set, which already proven its reliability in describing organic systems [251]. SMD is applied as implicit solvation model as this yields the most accurate solvation energies, but still comes with a mean unsigned error of at least 10 kJ mol⁻¹ in solvation free energies for organic cations with B3LYP/6-31G*. The solvation energies were calculated in the following ways:

$$\Delta G_{s,intrinsic} = G_{solvent} - G_{gas} \quad (2.7)$$

In systems where solvent-induced changes in thermal motions are significant to the molecular structure, geometrical and thermal corrections are explicitly taken into account and the calculated Gibbs free energy of solvation is more accurate [252].

$$\Delta G_s = E_{solvent} - E_{gas} + G_{solvent}^{therm} - G_{gas}^{therm} + G_{nes} \quad (2.8)$$

where $E_{solution}$ and E_{gas} , represent the solute electronic energies of the optimized geometries in solution and gas, respectively. As such, the effect of geometrical relaxation is included in the free energy of solvation. G^{therm} and G_{nes} represent the thermal contributions and nonelectrostatic component to the Gibbs free energy [252].

2.2.2.2 Conductor-like Screening Model for Realistic Solvent (COSMO-RS)

This hybrid solvation model is based on conductor-like screening model (COSMO) calculations, introduced by Klamt [253] and is mostly applied for solubility prediction of drugs or formulations [254]. A COSMO-RS calculation starts with the COSMO implicit solvation model in which the molecule is surrounded by an infinite dielectric medium (perfect conductor). Afterward, the molecular surface of the molecule is divided arbitrarily into segments for which the charge density of each surface element (σ_m) are calculated in this perfect conductor. Once the averaged value of σ_m has been obtained for each segment m , the probability $p(\sigma)$ of finding a given segment with specified value of σ multiplied with the entire surface area of the molecule ($p(\sigma)A_i$) is obtained. The molecular interactions between solute and liquid are obtained by the statistical averaging of local pair wise interactions of surface segments. COSMO files were generated with Gaussian 16 and processed with Biovia Cosmotherm 20.0.0 (Dassault Systèmes). The accuracy for COSMO-RS calculations in determining the solubility for solid

compounds can be increased by including experimental information about the phase change of the compounds from solid to liquid. The most important thermodynamic parameters are the free energy of fusion ΔG_{fus} , the enthalpy of fusion (ΔH_{fus}) and the melting temperature (T_m) and the change in heat capacity (ΔC_p). The free energy change at constant temperature is described:

$$\Delta G = \Delta H - T\Delta S \quad (2.9)$$

Since at melting temperature, melting and crystallization processes are in equilibrium ΔG equals zero. As such

$$T_m = \frac{\Delta H_{fus}}{\Delta S_{fus}} \quad (2.10)$$

which yields:

$$\Delta G_{fus} = \Delta H_{fus} - T \frac{\Delta H_{fus}}{T_m} \quad (2.11)$$

The mole fraction solubility is calculated based on the free energy difference

$$\ln x_s = \frac{(\mu_{pure} - \mu_s - \Delta G_{fus})}{RT} \quad (2.12)$$

With μ_{pure} and μ_s representing the chemical potentials of the pure compound and the compound in solution, respectively; R the gas constant and T the temperature. The aforementioned chemical potentials can be derived by COSMO-RS. The reported COSMO-RS values are relative molar solubility values ($\log S_{RS}$ with $[S_{RS}] = \text{mol L}^{-1}$) obtained after conversion of the mole fraction solubility values ($\ln x_s$). ΔG_{fus} can be obtained by means of experiments, such as differential scanning calorimetry (DSC), via a combination of a reference solubility measurement and a COSMO-RS calculation or via quantitative structure property relationship (QSPR) model. Overall, COSMO-RS is able to obtain solvation free energies in pure and solvent mixtures and avoid the more lengthy explicit solvent treatments. However, this model makes use of approximate parameters for nonelectrostatic contributions from cavitation, dispersion and repulsion, that were designed for neutral compounds, but recent developments show promising results for ionic liquids and electrolytes [255].

2.2.3 Experimental Section

2.2.3.1 Reagents

Analytical standards of apigeninidin chloride ($\geq 97\%$), cyanidin chloride ($\geq 96\%$), delphinidin chloride ($\geq 97\%$), luteolinidin chloride ($\geq 95\%$), malvidin chloride ($\geq 97\%$), pelargonidin chloride ($\geq 97\%$), peonidin chloride ($\geq 97\%$), petunidin chloride ($\geq 95\%$), cyanidin-3-O-glucoside chloride ($\geq 96\%$), delphinidin-3-O-glucoside chloride ($\geq 95\%$), malvidin-3-O-glucoside chloride ($\geq 95\%$), pelargonidin-3-O-glucoside chloride ($\geq 95\%$), peonidin-3-O-glucoside chloride ($\geq 95\%$) and petunidin-3-O-glucoside chloride ($\geq 95\%$) were obtained from Extrasynthese (Genay, France).

2.2.3.2 Thermal Analyses

In order to obtain the melting properties of 14 **ACDs** and **ACNs** (ΔG_{fus} , T_m and ΔC_p), Differential scanning calorimetry (DSC) measurements were performed with the DSC 204 F1 system (NETZSCH). Samples of 2-4 mg were weighted in an aluminum crucible (25 μL) and subsequently sealed. The samples were heated from room temperature (25 $^{\circ}\text{C}$) up to 400 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under constant flow of nitrogen, 20 mL min^{-1} . The thermograms were analyzed with NETZSCH Proteus Thermal Analysis (8.0.2) software to obtain the melting properties and are used as experimental input for COSMO-RS (Table B.2, Figure B.2).

2.2.3.3 Statistical analysis

The one-way analysis of variance (ANOVA) was carried out to investigate the added value of the organic solvent of interest to the solubility compared to water. The significance level (α) for the statistical analyses is 0.05. The p-values obtained lower than 0.05 are regarded as significantly different. All statistical analyses were performed with SPSS Statistics Version 25 (IBM) software.

2.3 Results and Discussions

2.3.1 Hansen Solubility Parameters and Flory-Huggins Interaction Parameter (χ_{12})

HSPs commonly display the smallest distances R_a ($\text{MPa}^{1/2}$) for solvents that are most likely to solvate **ACDs** and **ACNs** (Figures 2.2 and B.3). 1,2-ethanediol ($R_{a,\text{avg}} = 20.88$), m-cresol (22.41), benzylalcohol (22.64) dimethyl sulfoxide (DMSO) (22.92) and ethanol (24.23) are the preferred solvents for **ACDs** by

applying the group contribution method. 1,2-ethanediol ($R_{a,avg} = 19.68$) is also the best solvent for **ACNs** followed by DMSO (22.84), m-cresol (23.23), benzylalcohol (23.46) and ethanol (23.85). It is clear that the most optimal solvents for **ACN** extraction put forward by the HSP method show a high structural resemblance with the natural dyes (i.e., aromatic rings and hydroxy groups). As this group contribution method is based on the structural fragments within a molecule, there are shortcomings for describing complex molecules wherein hydrogen bonds or electrostatic interactions occur [256]. The χ_{12} -values showed more polar solvents (i.e., alcohols) rather than aromatic solvents compared to HSPs. This model recommends water; 1,2-ethanediol; methanol, ethanol or DMSO as the five most optimal solvents for both **ACDs** ($\chi_{12} = 1.54, 2.54, 2.67, 3.59$ and 3.90 , respectively) and **ACNs** ($\chi_{12} = 1.22, 2.18, 2.36, 3.40$ and 3.80 , respectively), known their hydrophilic nature (Figure B.4). This contradicts the experimental concept of adding organic solvents to improve the anthocyanin solubility.

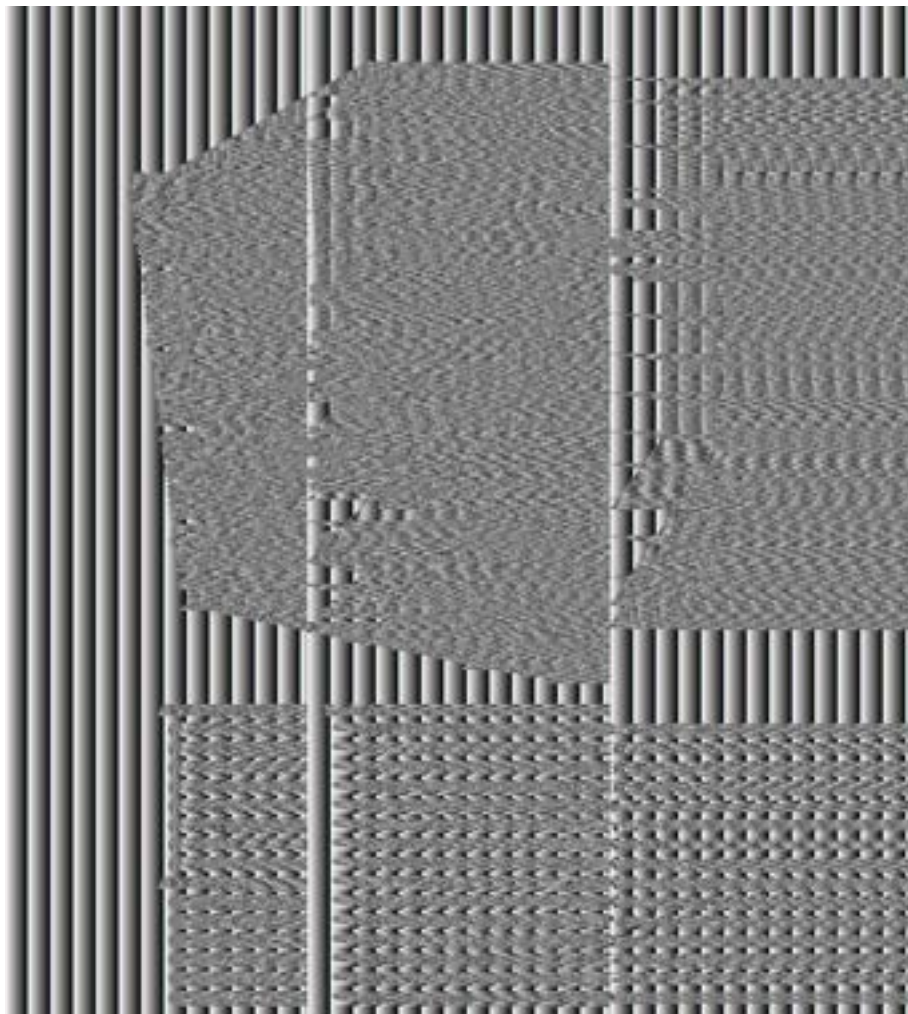


Figure 2.2: Hansen solubility parameters (δ_d , δ_p and δ_h) of the selected solvents (blue dots labelled as S1-S30), **ACDs** (magenta dots labelled as A1-A8) and **ACNs** (red dots labelled as A9-A14). Additional data on the distance R_a ($\text{MPa}^{1/2}$) are illustrated and tabulated in the supporting information (Figure B.3 and Tables B.3 to B.6).

2.3.2 Density Functional Theory: Static Calculations

Static calculations based on intrinsic Gibbs free energies of solvation recommend alcohols: methanol ($\Delta G_{\text{avg,s,intrinsic}} = -251.03 \text{ kJ mol}^{-1}$) > ethanol ($-249.42 \text{ kJ mol}^{-1}$) > 2-propanol ($-248.15 \text{ kJ mol}^{-1}$) > 1-propanol ($-246.20 \text{ kJ mol}^{-1}$) > 1-butanol ($-242.48 \text{ kJ mol}^{-1}$) for **ACDs** (Figure B.5). The ranking for **ACNs** does not differ much compared to **ACDs** with methanol ($-310.95 \text{ kJ mol}^{-1}$) and ethanol ($-308.54 \text{ kJ mol}^{-1}$) being most efficient solvents, followed by water ($-305.07 \text{ kJ mol}^{-1}$), 2-propanol ($-302.36 \text{ kJ mol}^{-1}$) and 1-propanol ($-302.04 \text{ kJ mol}^{-1}$). The occurrence of water in the list confirms that additional hydroxy groups from the glucose moiety allows a better stabilization in water. The calculated Gibbs free energies of solvation also displayed smaller values for **ACNs** compared to **ACDs** with an extra 60 kJ mol^{-1} stabilizing energy in favor of **ACNs** for alcohols.

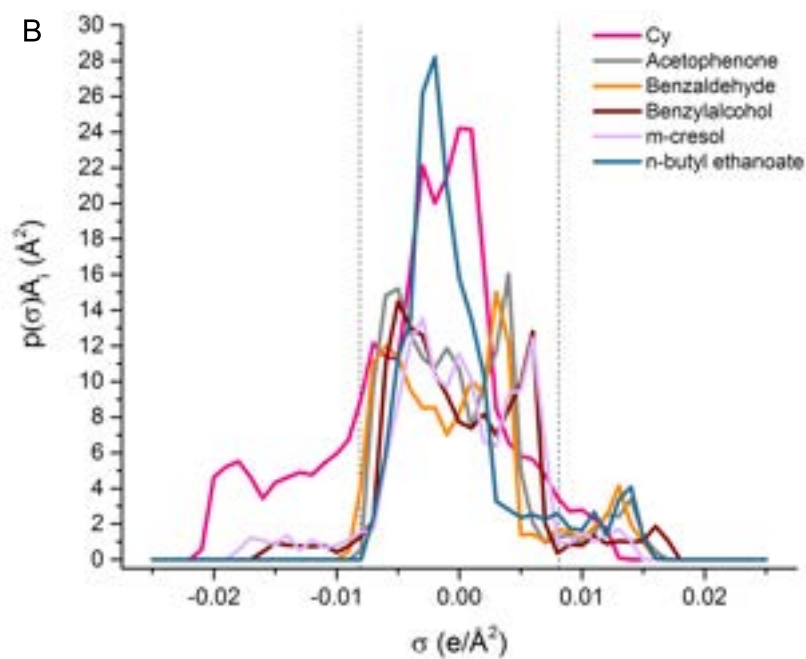
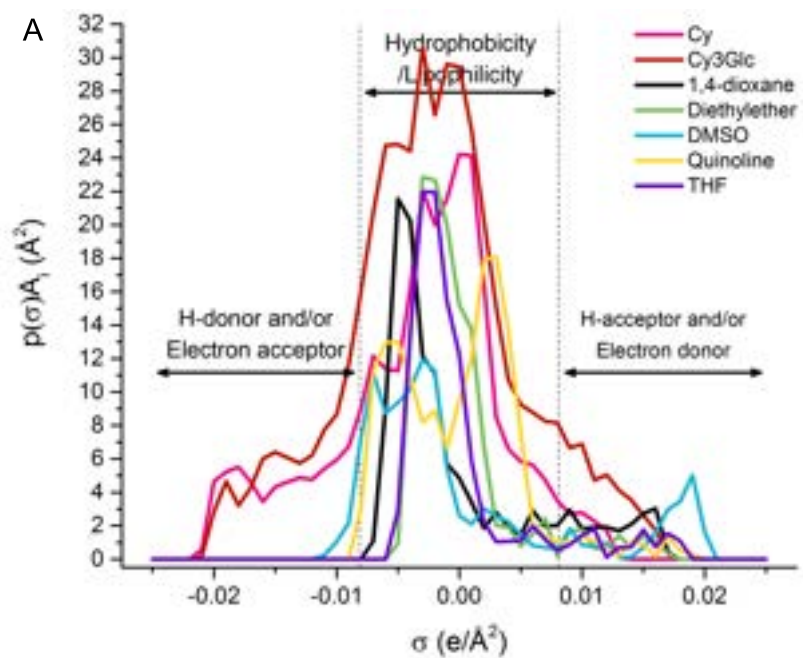
When thermal contributions and nonelectrostatic components are included for the Gibbs free energies of solvation (Equation (2.8)), solvents with electron-rich aromatics appear as most optimal solvents in the case of **ACDs**: benzaldehyde ($\Delta G_{\text{avg,s,intrinsic}} = -252.97 \text{ kJ mol}^{-1}$) > acetone ($-251.88 \text{ kJ mol}^{-1}$) > acetonitrile ($-251.67 \text{ kJ mol}^{-1}$) > quinoline ($-251.62 \text{ kJ mol}^{-1}$) > acetophenone ($-246.36 \text{ kJ mol}^{-1}$) (Figure B.6). For **ACNs**, the solubilizing power is as follows: acetone ($-298.19 \text{ kJ mol}^{-1}$) > 2-propanol ($-294.48 \text{ kJ mol}^{-1}$) > benzaldehyde ($-293.41 \text{ kJ mol}^{-1}$) > ethanol ($-291.93 \text{ kJ mol}^{-1}$) > acetonitrile ($-290.09 \text{ kJ mol}^{-1}$). Acetonitrile is an aprotic solvent, but contains π -electrons, which are also able to interact with the **ACDs** or **ACNs** π -systems.

2.3.3 Conductor-like Screening Model for Realistic Solvent (COSMO-RS)

The results of COSMO-RS indicate the most optimal solvents for solubilizing **ACDs** as follows: tetrahydrofuran (THF) ($\log S_{\text{avg,RS}} = 15.30$) > quinoline (14.79) > DMSO (14.73) > diethylether (14.51) > 1,4-dioxane (14.42) and for **ACNs**: DMSO (17.53) > 1,4-dioxane (16.29) > tetrahydrofuran (15.93) > quinoline (15.50) > diethylether (13.52) (Figure B.7). These results can be described as a combination of the results obtained with HSP and the static calculations. This can be ascribed to the fact that COSMO-RS calculations start with the COSMO implicit solvation model, but combined with the post-processing method of breaking down the molecular surface into infinitesimal charge density areas, which leans more toward the HSP method. More remarkably is the absence of any alcohol solvents for both natural dye subclasses.

The selected alcohols (Table B.1) only showed an average $\log S_{RS}$ values of 9.98 and 11.22 for **ACDs** and **ACNs**, respectively. This indicates that **ACDs** and **ACNs** would be about 5.32 and 6.32 times less soluble ($\log S_{RS}$ difference), respectively, compared to the best solvent from the screening (**ACDs**: THF and **ACNs**: DMSO). It can be noticed that these most optimal solvents are solely hydrogen bond acceptors and cannot act as hydrogen bond donors.

The aforementioned conclusion can be validated by superimposing σ -profiles of the solvents and **ACDs** or **ACNs**. Figure 2.3A compares the σ -profiles of Cy and Cy-3-Glc based on the results obtained via the relative solubility screening ($\log S_{avg,RS}$). The difference in σ -profiles between Cy and Cy-3-Glc is the higher intensity at the positive σ -values. This can be ascribed to the presence of four additional hydroxy groups of the glucose moiety. The profiles also showed the hydrogen acceptor ability ($\sigma > 0.0081 \text{ e}/\text{\AA}^2$) of the optimal solvents, i.e., lone electron pairs of oxygen or nitrogen that serve as electron donors, which improves the hydrogen bonding between solvent and dye. Furthermore, the hydrophobic part of the solvents' σ -profiles also showed good overlap with Cy's profile. When the σ -profiles were evaluated by using the normalized "sigma match similarity" method, the highest similarity values with **ACDs** were found for m-cresol (0.104) > n-butylacetate (0.0874) > benzylalcohol (0.0835) > acetophenone (0.0819) > benzaldehyde (0.0775) and for **ACNs**: DMSO (0.0711) > 1,2-ethanediol (0.0672) > 2-methoxyethanol (0.0477) > 1,4-dioxane (0.0350) > water (0.0331). Figures 2.3A to 2.3A illustrate the σ -profiles of the five best solvents based on the degree of similarity with the Cy and Cy-3-Glc σ -profiles. It shows that the most optimal solvents for dissolving Cy are mainly based on hydrophobic interactions via electron rich aromatic systems and in a lesser amount via hydrogen bonds. In the case of Cy-3-Glc, solvents with both electron donor ($\sigma > 0.0081 \text{ e}/\text{\AA}^2$) and electron acceptor ($\sigma < 0.0081 \text{ e}/\text{\AA}^2$) abilities are highly ranked such as 1,2-ethanediol, 2-methoxyethanol and water. Based on the "sigma match similarity" method, the results correlate closer to HSPs and follows the "like dissolves like" principle, but the highest solubility values are still obtained via the relative molar solubility method ($\log S_{avg,RS}$).



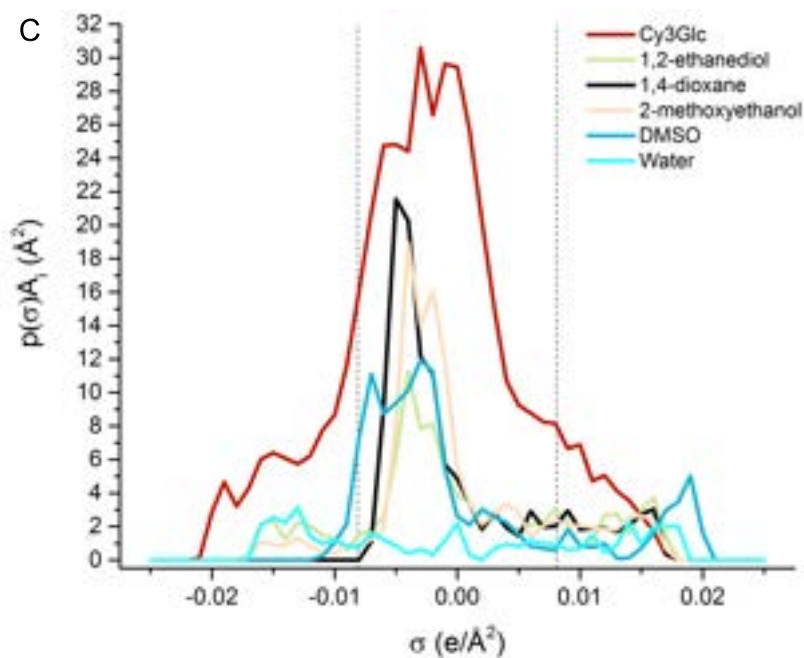


Figure 2.3: σ -profiles of Cy and Cy-3-Glc with the five most optimal solvents based on $\log S_{RS}$ (A) or σ -profile similarity (B, C). σ -values higher than $0.0081 \text{ e}/\text{\AA}^2$ show electron donor abilities, σ -values below $0.0081 \text{ e}/\text{\AA}^2$ show electron acceptor abilities and values in between indicate hydrophobic interactions.

2.3.4 Comparison of the Different Computational Models for Anthocyanidins and Anthocyanins Extraction

In Figure 2.4A, we visualize in a relative comparison the most promising solvents for the solubilization **ACDs** and **ACNs** as predicted by the different models (100% means it is predicted as best solvent by that method). After evaluating four predictive models (HSP, χ_{12} , DFT and COSMO-RS), it can be concluded that the different models predict different optimal solvents. Both group contribution based methods (HSP and χ_{12}) displayed similar reoccurring solvents such as 1,2-ethanediol, ethanol and DMSO, but the χ_{12} -values also showed water as the best solvent for **ACDs** and **ACNs** extraction. This contradicts the experimental concept that adding organic solvents improves the anthocyanin solubility. However, Hong et al. [257] have found a good correlation between the chromaticity analyses of *Gardenia* extracts, which contain crocin, and the χ_{12} parameter. A higher color absorbance was observed for smaller χ_{12} -values. Solvation free energies based on DFT calculations favor alcohols and electron rich systems (e.g., aromatic rings and acetonitrile), while COSMO-RS recommends solvents with hydrogen bond acceptor abilities such as DMSO and ethers. COSMO-RS has been successfully applied for the solubility prediction of flavonoids in a wide variety of ionic liquids [258]. Therefore, further in-depth analyses of individual **ACDs** and **ACNs** solubilities obtained with COSMO-RS were carried out. Whilst Figure 2.4A focuses on the overall extraction efficiency, Figure 2.4B focuses on the type of **ACD** and **ACN** extracted with a range of solvents as predicted by COSMO-RS. It includes the most optimal solvents for **ACDs/ACNs** extraction based on the results discussed above. DMSO is an ideal solvent for extracting Cy-3-Glc, but for Mv THF would be more recommended. From the traditional organic solvents, acetone is a better solvent in general to solubilize both **ACDs** ($\log S_{\text{avg,RS}}=11.60$) and **ACNs** (12.51). The difference between ethanol and methanol lies in the fact that the former shows a 3-fold higher average solubility value (S_{RS}) for **ACDs**, while the latter is a better solvent for solubilizing **ACNs** with a 33% higher S_{RS} -value (Table 2.3). This confirms the results of Ju and Howard [74], who found that extraction of **ACNs** with methanol is 10% and 30% more effective than ethanol and water, respectively; and Metivier et al. [259] who obtained a 20% and 73% more effective **ACNs** extraction with methanol compared to ethanol and water, respectively. The solubility gap between the organic solvents acetone ($F(1,26) = 72.691$, $p < 0.001$), ethanol ($F(1,26) = 45.714$, $p < 0.001$) and methanol ($F(1,26) = 39.934$, $p < 0.001$) with water is already significant. This extends even more for the most



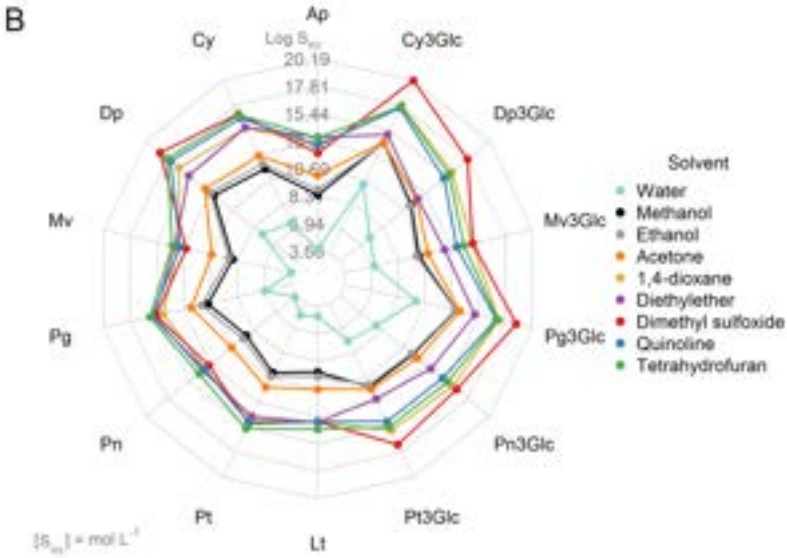


Figure 2.4: (A) Normalized solubility values of **ACDs** and **ACNs** for the five most optimal solvents per computational method. The scale only shows the worst and best solvent from these five solvents to solubilize **ACDs** and **ACNs** as 0% and 100%, respectively. (B) The anthocyanin profiles in terms of log S_{RS} between the five most optimal solvents and the results of the traditional solvents used in anthocyanin extraction.

Table 2.3 illustrates the selectivity, displayed in Figure 2.4B, between the glycoside-aglycone pairs within these traditional solvents and DMSO. It shows that the highest selectivity can be obtained with pure water. The glycosides of Cy, Mv, Pg, Pn, Pt are at least one order of magnitude more soluble in water compared to acetone, ethanol and methanol. Only the solubility ratio of Dp is smaller in water compared to ethanol. The claim in literature about higher solubilities for **ACDs** in alcohols than **ACNs** (glucosides) and the latter being highly soluble in water is valid for all **ACDs** and **ACNs** except for the pair Dp and Dp-3-Glc [51]. This underlines again the significant role of the glucose moiety in the solvation process via hydrogen bonds.

Table 2.3: The selectivity between the glycoside-aglycone pairs in terms of solubility ratios obtained with COSMO-RS. The figures represent the number of times a glycoside is more soluble compared to the aglycone in a selection of solvents, with Dp and Dp-3-Glc as exception.

Solubility ratio	DMSO	Ethanol	Methanol	Acetone	Water
$\log(S_{RS,Cy-3-Glc}/S_{RS,Cy})$	3.20	1.95	2.50	1.31	3.67
$\log(S_{RS,Dp}/S_{RS,Dp-3-Glc})$	0.91	1.73	1.21	1.57	0.47
$\log(S_{RS,Mv-3-Glc}/S_{RS,Mv})$	2.03	0.83	1.39	0.33	2.63
$\log(S_{RS,Pg-3-Glc}/S_{RS,Pg})$	3.22	1.89	2.49	1.34	4.01
$\log(S_{RS,Pn-3-Glc}/S_{RS,Pn})$	1.44	2.05	2.59	1.48	3.90
$\log(S_{RS,Pt-3-Glc}/S_{RS,Pt})$	2.38	0.81	1.36	0.23	2.47

In literature, the polarity of **ACDs** and **ACNs**, based on retention indices, show a decreasing trend in the order of Dp, Cy, Pt, Pg, Pn, and Mv [263]. In the case of **ACDs**, this correlates best with the solubility predicted with COSMO-RS, while the group contribution methods showed Lt and Pn as the **ACDs** with the highest polarities (Figure 2.5). The normalized data highlight the influence of each moiety of the molecule on the solubility. The number of hydroxy groups on the B-ring has clearly got the highest impact on the solubility (Dp: 3 OH groups, Cy: 2 OH groups and Pg: 1 OH group). Pt, having 2 OH groups and 1 methoxy group showed higher water solubility than the 3-deoxyanthocyanidins (Ap and Lt). The increasing number of methoxy groups on the B-ring is unfavorable for water solubility. The polarity trend for **ACNs** can be closely described by the SMD solvation model than the COSMO-RS model.

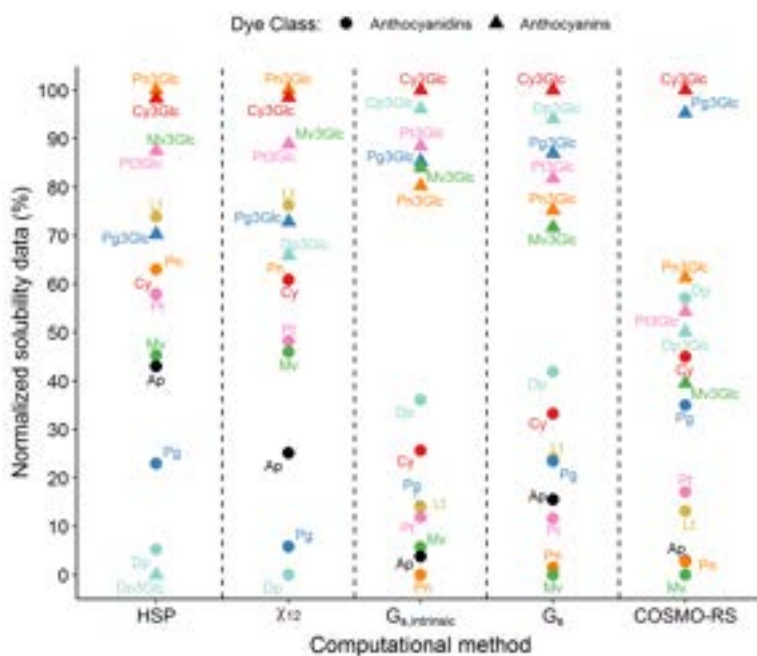


Figure 2.5: Normalized solubility values of **ACDs** and **ACNs** in water. The scale shows the worst and best solubility among **ACDs** and **ACNs** as 0% and 100%, respectively. The glycoside/aglycone pairs are indicated by the same color.

2.3.5 Binary Mixtures

Mixed solvents play important roles in chemical syntheses and applications. Their change in polarity and Brønsted acidity and basicity can be decisive in the extraction outcome [255]. However, mixed solvents are difficult to describe as a homogenous medium in implicit solvation models. The preferential solvation behavior, which represents the complex ordering of co-solvents near the solute, is still challenging to include in implicit solvation model for polar or ionic compounds. Hybrid solvation models such as COSMO-RS are closest to describe mixed solvents without the need of an explicit solvent model that requires a higher degree of parametrization and are computationally more costly [255]. As previously mentioned, acetone, ethanol and methanol are the main organic solvents applied for **ACDs** and **ACNs** extraction within experiments. Figure B.1 showed that pure organic solvents or aqueous mixtures containing 50, 70 and 80 volume percentage of organic solvent are mostly favored. However, higher fractions of organic solvent do not guarantee higher **ACN** content (Tables 2.1 and 2.2). Figure 2.6A illustrates the relative solubility values of **ACDs** and **ACNs** for the aforementioned ratios, determined with COSMO-RS, in acetone-water, ethanol-water and methanol-water mixtures. The solubility in binary mixtures follows the same trend as in pure solvents: acetone > methanol > ethanol. A detailed look on the **ACDs** and **ACNs** profile for acetone-water mixtures shows that for Cy-3-Glc, Dp-3-Glc, Pg-3-Glc, Pn-3-Glc and Pt-3-Glc pure acetone performs more inefficient compared to an aqueous mixture of 90% v/v acetone (Figures 2.6A and B.8). The anthocyanin profiles between ethanol and methanol are relatively similar and both alcohol systems show a linear increase in solubility with increasing volume fraction of organic solvent, which contradicts the trends observed within literature experiments (Tables 2.1 and 2.2). Catena et al. [264] also observed this linear correlation with COSMO-RS for the investigation of phenolic and anthocyanin compounds from *Oryza sativa* L. in ethanol-water mixtures. Therefore, additional solubility parameter distances, based on HSPs, with increasing volume fraction of organic solvent, were calculated. Figure 2.6B clearly illustrates the optimal ratio of binary aqueous mixtures for **ACDs** and **ACNs**. It was found that an aqueous mixture of acetone showed the shortest distance with **ACDs** at 50% v/v and **ACNs** at 40% v/v. For ethanol, a 70% v/v mixture is favored for **ACDs** and a 60% v/v for **ACNs**. The shortest HSPs distances between **ACDs** and methanol-water mixtures are found at 70-80% v/v and in the case of **ACNs**, 60%-70% v/v. The presence of these HSPs distance minima for organic solvent-water mixtures provides a better picture of the literature values (Tables 2.1 and 2.2). Furthermore, statistical analyses also displayed that relative

molar solubility ($\log S_{RS}$) of aqueous mixtures of acetone till 40% v/v are not significantly different compared to water (40% v/v acetone: $F(1,26) = 3.046$, $p = 0.093$; 50% v/v acetone: $F(1,26) = 5.940$, $p = 0.022$; 60% v/v acetone: $F(1,26) = 10.415$, $p = 0.003$) (Figure B.8). The same trend is observed for aqueous mixtures ethanol and methanol (40% v/v ethanol or methanol: $F(1,26) = 2.643$, $p = 0.116$; 50% v/v ethanol or methanol: $F(1,26) = 4.613$, $p = 0.041$; 60% v/v ethanol or methanol: $F(1,26) = 7.559$, $p = 0.011$; 70% v/v ethanol or methanol: $F(1,26) = 10.415$, $p = 0.002$). Whereas COSMO-RS is able to provide quantitative information on the solubility behavior within various pure solvents, it is unable to accurately describe the solubility behavior within organic solvent-water mixtures. Therefore, HSPs is a more appropriate tool to find the most optimal mixture ratio. These results were calculated for pure anthocyanidins and anthocyanins, but during experiments, matrix compounds such as flavonoids, alkaloids, amino acids, organic acids, nucleotides, polysaccharides are potentially coextracted. Wang et al. [265] analyzed the fruit quality of blueberries and obtained a sugar content (fructose and glucose) of 62.89 mg/g FW, organic acids (citric acid and malic acid) of 1.67 mg/g FW, a total phenolic content of 1.07 mg/g FW and total anthocyanin content of 2.55 mg/g FW. These copigments have a stabilizing factor for **ACDs** and **ACNs** and could potentially influence the extraction process [50].

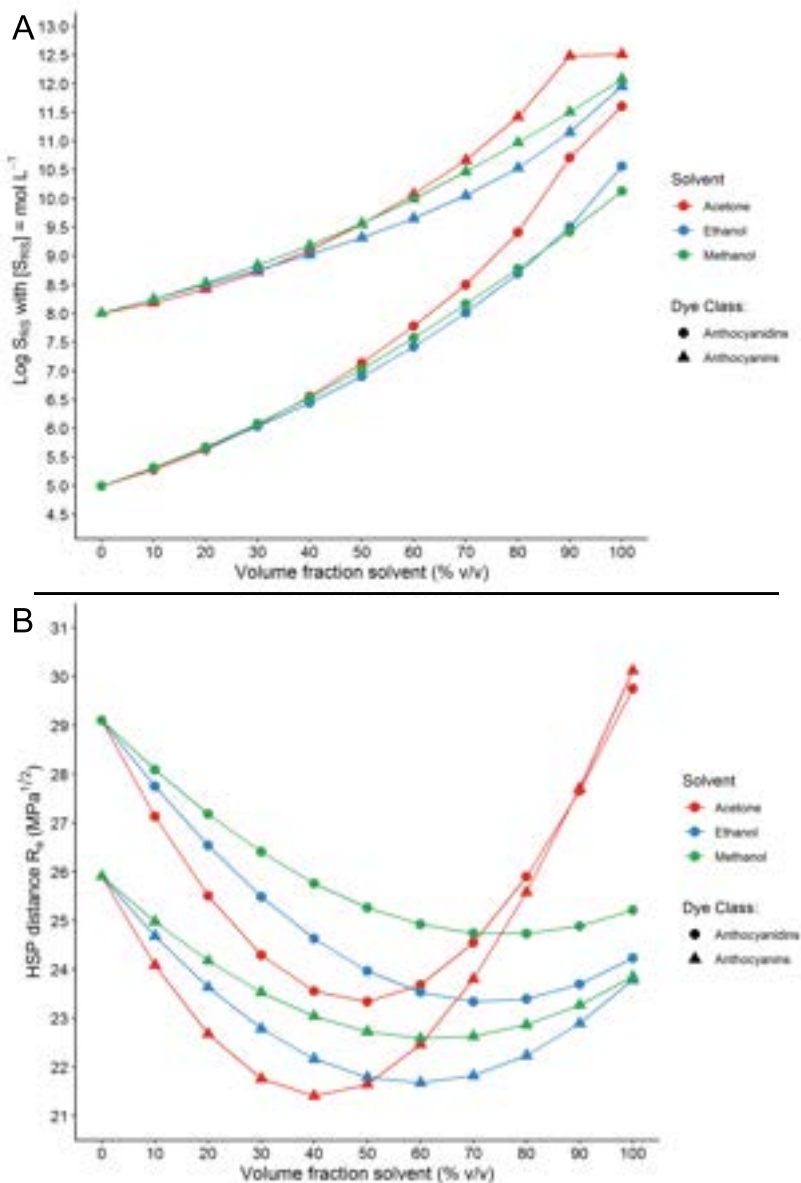


Figure 2.6: Relative solubility values ($\text{Log } S_{RS}$) calculated with COSMO-RS (A) and solubility parameter distances R_a ($\text{MPa}^{1/2}$) (B) of aqueous mixtures (acetone-water, ethanol-water and methanol-water) for **ACDs** and **ACNs** extraction.

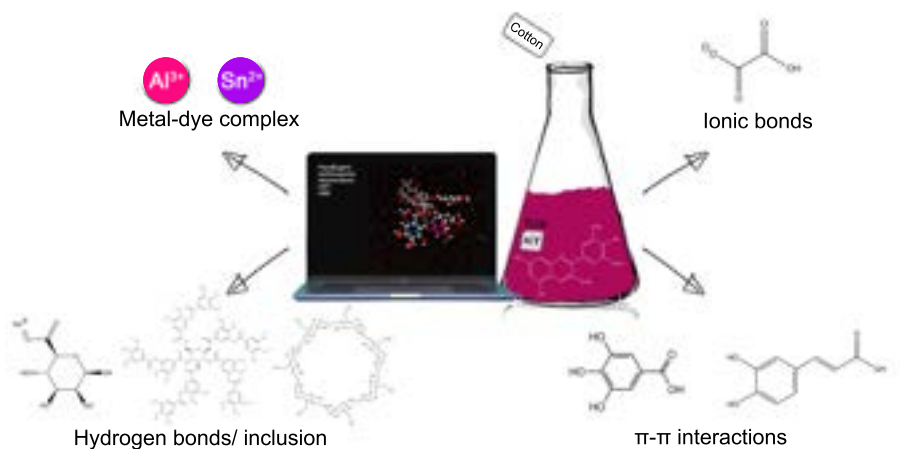
2.4 Conclusions

In this work, the capabilities and limitations of computational methods for the solubility determination of anthocyanidins and anthocyanins were evaluated. COSMO-RS was able to provide quantitative information on the solubility behavior within various pure solvents and describe the main intermolecular interactions between colorant and solvent. However, the method fell behind for characterizing the solubility within organic solvent-water mixtures. The Flory-Huggins interaction parameter (χ_{12}) and solvation free energies showed moderate results. The former overestimated the contribution of water and the latter was able to reproduce the general trends observed from other computational methods. Only Hansen solubility parameters were the most appropriate tool to find the most optimal organic solvent-water mixture ratio. Acetone, ethanol and methanol or aqueous mixtures of the aforementioned solvents are commonly used within experiments to increase the anthocyanidins and anthocyanins extraction yield. The relative molar solubility values showed that acetone is a better solvent to solubilize both anthocyanidins ($\log S_{\text{avg,RS}}=11.60$) and anthocyanins (12.51). The difference between ethanol and methanol lies in the fact that the former shows a 3-fold higher average solubility value (S_{RS}) for anthocyanidins, while the latter is a better solvent for solubilizing anthocyanins with a 33% higher S_{RS} -value. Furthermore, the solvent screening showed that electron rich aromatic compounds and compounds containing electron donors such as 1,4-dioxane, diethylether, DMSO, quinoline or tetrahydrofuran, acting as hydrogen bond acceptors, are favored over the more traditional organic solvents in this field. However, for environmental, health and safety issues, DMSO would be most applicable in anthocyanidins and anthocyanins extraction. The COSMO-RS results illustrate that the solubility of anthocyanidins and anthocyanins can be largely ascribed to π - π interactions and intermolecular hydrogen bonding, respectively. Statistical analyses also revealed that the relative molar solubilities ($\log S_{\text{RS}}$) of aqueous mixtures of acetone, ethanol or methanol till 40% v/v are not significantly different compared to water. This indicated that the use of the three traditional organic solvents for anthocyanidins and anthocyanins extraction is most viable for aqueous mixtures of 50% v/v or higher. Hansen solubility parameters showed that an aqueous mixture of 50% v/v and 40% v/v of acetone is optimal for anthocyanidins and anthocyanins, respectively. For ethanol, a 70% v/v aqueous mixture is favored for anthocyanidins and a 60% v/v for anthocyanins. The shortest Hansen solubility parameter distances between anthocyanidins and methanol-water mixtures is

found at 70-80% v/v and in the case of anthocyanins at 60%-70% v/v. The results obtained from Hansen solubility parameters and COSMO-RS can be used as a benchmark for target specific extractions to maximize the applications' demands. Future solubility studies can include explicit solvation model by means of molecular dynamics in combination with the Free Energy Perturbation (FEP) method. The application of computational modeling tools contributes significantly to the fundamental understanding of the solubility behavior of anthocyanidins and anthocyanins, which is of added value for experimental studies.

Chapter 3

The Potential of Anthocyanins from Blueberries as a Natural Dye for Cotton: a Combined Experimental and Theoretical Study



Phan K., Van Den Broeck E., Van Speybroeck V., De Clerck K., Raes K., and De Meester, S. *Dyes and Pigments*, **176**, 108180 (2020).

The Potential of Anthocyanins from Blueberries as a Natural Dye for Cotton: a Combined Experimental and Theoretical Study

3.1 Introduction

In Chapter 1, it was demonstrated that waste streams or by-products generated from food processing industries contain high-added value compounds including natural dyes, so there is sustainable feedstock available on the market at relatively low cost [28]. For instance, approximately 20% of the raw blueberries remain as pomace during juice processing [266]. However, natural dyes have some shortcomings in terms of stability and affinity for substrates. Therefore, they require dye procedures or fixatives such as mordants [112]. Most of the time, these mordants are metal salts, which could form coordination complexes with the natural dye molecule. This improves the stability, but (heavy) metallic mordants also come along with potential pollution and waste water issues [112]. Biomordants, often tannin rich compounds, which are responsible for the formation of hydrogen bonds, might be able to substitute these metallic equivalents as they fit better in a shift toward sustainability [267]. This chapter focuses on anthocyanins, which is a subclass within the class of flavonoids and, which are responsible for red till bluish colors in most flowers, higher plants, fruit and vegetables. The chemistry behind anthocyanins is described in section 1.2.1.

Anthocyanins are mostly applied as food colorant [268], but also have potential to find their way into non-food applications (e.g., textile substrates and dye sensitized solar cells). Cotton [115, 122, 130, 269, 270, 271], leather [122], wool [116, 269, 272, 273, 274], silk [118, 121, 122, 270, 271, 275] and human hair [134] were dyed with several by-products such as fruit and vegetable pressed

and liquid residues [274]. Examples are: blackcurrant fruit waste [134, 271, 273], sunflower seed [272], red cabbage extract [116], onion outer skins [121], grape pomace [269], purple sweet potato [122, 275], black cowpea seed coat [270] and mulberry fruits [115, 118, 130]. Several approaches to improve the affinity of anthocyanins were already tested. From section 1.4, four mechanisms are distinguished to improve the affinity of anthocyanins on textile fibers: (i) metal salts, (ii) biomordants based on hydrogen bonds, (iii) ionic interactions and (iv) π - π interactions (Figure 3.1).

Various metal salts were applied within the aforementioned studies, it appeared that the following mordants improved the wash and light fastness values compared to the control sample: alum [269, 270, 272, 274, 275], alum in combination with ferrous sulfate [121], antimony potassium tartrate [273], ferrous chloride [271], ferrous sulfate [121, 269, 270, 274], stannous chloride [115, 116, 118, 270] and silver nanoparticles [122]. The main reason why metal salts are frequently used to improve the dye affinity is due to their ability to form metal-dye coordination complexes. Since anthocyanins and cellulose contain many hydroxy groups with free electron pairs on the oxygen atoms, they could act as donors and fill the free orbitals of the metal ions. This induces a deprotonation upon forming the metal-ligand complex. Within literature, it has been stated that anthocyanins perform as bidentate ligands within metal complexation. The most important requirement for that, is the presence of hydroxy groups at the C3' and C4' positions [50, 276]. This leads to the conclusion that only three types of anthocyanins are able to form a coordination complex, i.e., cyanidin, delphinidin and petunidin. Furthermore, the formation of coordination complexes usually comes along with a bathochromic shift [276].

Meanwhile, research on the use of biomordants with anthocyanins increases gradually: tannic acid, a mixture of polygalloyl glucoses [116, 130], and tannin [269] would increase the affinity of the substrate by means of van der Waals forces and hydrogen bonds [269]. These interactions originate from their large molecular size (500–3000 g mol⁻¹) and availability of hydroxy groups, respectively. Next to that, the interaction between polysaccharides and anthocyanins has also emerged as one of the stabilizing mechanisms, e.g., gelation by alginate [277] or molecular inclusion [278]. The latter leads to cyclodextrins, which appear to possess promising properties for pigment inclusion via hydrogen bonding, van der Waals and electrostatic interactions [278, 279].

The third mechanism involves developing anionic sites by cotton pretreatment. The generation of additional anionic sites is necessary as dyeing with an acidic dyebath includes a low pH. Hereby, the cellulosic hydroxy groups

are not sufficiently negatively charged to adsorb the flavylium cation. Therefore, dicarboxylic acids such as succinic acid [115] or a reactive anionic agent, based on 4-amino-benzenesulfonic acid and cyanuric chloride [130], are applied to establish ionic bonds with the flavylium cation.

The fourth mordanting method is based on copigmentation. This process is defined as the formation of noncovalent complexes by π - π interactions consisting of an anthocyanin and a copigment compound present within the source, and the accompanying changes in spectral properties such as absorption intensity and wavelength [50, 52, 59]. The major natural copigments are hydrolysable tannins, flavonoids and phenolic acids [52]. Within nature, anthocyanins exist as their acylated forms. Due to intramolecular copigmentation, these acylated anthocyanins gain more stability in comparison to their unacylated forms. Diacylated anthocyanins result in a “sandwich” structure as the aromatic acyl moieties overlap with the benzopyrylium structure, which improves the resistance to physicochemical and biochemical factors such as heat, light, pH changes, hydrogen peroxide and nucleophilic attack of water.

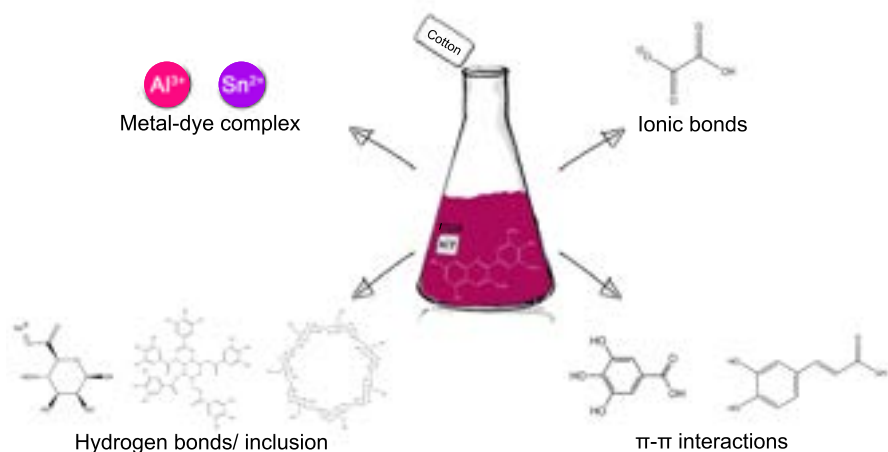


Figure 3.1: The four typically proposed types of intermolecular interactions between anthocyanins and (bio)mordants. This chapter therefore systematically compares: metal complexation: Sn(II) and Al(III) , hydrogen bonds: sodium alginate, tannic acid and β -cyclodextrin; ionic bonding: oxalic acid; and π - π interactions: gallic acid and caffeic acid.

Apart from this diversity in mordanting techniques, little is known on the optimal conditions for dyeing with anthocyanins. In literature, different dyeing conditions were applied such as temperatures ranging from room temperature till 100 °C, different pH values between 2 and 5, dyeing time from 60 min till 24

hours and different liquor ratios. Such a lack of consistency makes it difficult to compare literature, and furthermore it seems that there is a lack of evidence related to the optimized anthocyanin dyeing procedures. For this purpose, this chapter contains an extensive experimental part on (i) the optimization of the dyeing procedure with anthocyanins for dyeing cotton and (ii) the investigation for effective (bio)mordants to improve the affinity of anthocyanins on cotton fibers by intermolecular interactions (e.g., metal-ligand, hydrogen bonds, ionic and π - π interactions), (iii) in combination with a modeling approach in the second part, presenting a profound understanding on the underlying mechanism between (bio)mordants, dye and substrate on molecular scale. Through mathematical modeling, insight can be obtained in the sorption mechanisms and molecular modeling can greatly help in unravelling the underlying mechanisms governing the interactions between the dye and the (bio)mordant. Adsorption modeling with anthocyanin are frequently applied within purification methods. Hereby, different resins were compared for their adsorption and elution capacities [280]. Molecular modeling studies between metal-ions and anthocyanins involve a series of 12 common metallic cations in nature, where complexes of Co(III), Fe(III), Cr(III), and Al(III) were thermodynamically more favored [281, 282]. Furthermore, the influence of the oxidation state of iron was investigated between malvidin-3-glucoside (Mv-3-Glc) and ellagic acid. Calculations show that Fe(II) preferably undergoes cation- π interactions, which are stronger than π -stacking [283]. Other studies based on anthocyanins were on conformational analyses [284, 285, 286, 287], copigmentation effects of π - π interactions [52, 288, 289, 290] and generation of UV-Vis spectra by time dependent-density functional theory (TD-DFT) [285, 288]. Hereby, the behavior of anthocyanins on intermolecular interactions and accompanying spectral changes due to copigmentation were clarified, but a systematic analysis of the four dyeing mechanisms is not available yet.

3.2 Materials and Methods

3.2.1 Experimental Section

3.2.1.1 Scope of the Mordants

In this study, eight mordants were investigated to improve the affinity and stability of anthocyanins to cotton based on the four proposed types of intermolecular interactions as described above. Two metallic mordants were selected, supported by the successful application within literature, SnCl_2 and $\text{AlK}(\text{SO}_4)_2$. Other biomordants were selected according to the aforementioned

intermolecular interactions they could undergo with anthocyanins. Tannic acid and sodium alginate for their hydrogen bonding. β -cyclodextrin is a funnel-shaped cyclic oligosaccharide with seven glucose moieties linked by α -(1-4) glycosidic bonds, and is particularly known for its inclusion capability of organic molecules. Oxalic acid was preferred for its low pKa values to form ionic bonds. Gallic acid and caffeic acid were selected to reproduce the stability obtained by copigmentation or π - π interactions.

3.2.1.2 Samples and Reagents

Metallic mordants consist of tin chloride dihydrate (VEL) and potassium aluminium sulphate dodecahydrate (alum) (MERCK). The biomordants were oxalic acid dihydrate (Chem-lab), sodium alginate (PanReac Applichem), β -cyclodextrin (Acros organics), tannic acid (Sigma Aldrich), gallic acid (97.5 – 102.5% (titration), Sigma Aldrich) and caffeic acid (predominantly (E)-isomer $\geq$ 99%, Acros organics). Hydrochloric acid (37% analytical reagent, Chem-lab) was used to acidify the extraction solvent. Sodiumhypophosphite (SHP) (Merck) was applied as a catalyst during the esterification reaction. A 50% sodium hydroxide solution (Sigma Aldrich) was used to adjust the pH of the dyebath. Potassium chloride (Chem-lab) and sodium acetate trihydrate (Chem-lab) were applied within the pH-differential method for determining the anthocyanin content. Spectrophotometric solutions are prepared in polystyrene macrocuvettes (VWR) with a path length of 1 cm. Cotton, with a density of 190 g m⁻² and prepared for dyeing, was supplied by Utexbel NV and cut into samples, each weighing 1 gram.

3.2.1.3 Extraction Procedure

Blueberry waste would preferably be used if one is using the anthocyanins as natural colorant within the dyeing industry. However, for the experiments conducted, the use of blueberries as such or blueberry waste will not influence our results as the anthocyanins present are the same in both matrices. As for practical reasons, it was much easier to obtain blueberries as a rich source of anthocyanins than the blueberry waste. Therefore, the anthocyanins were extracted from the fruit itself. Frozen blueberries were crushed with pestle and mortar and extracted in acidic environment. The extraction made use of a material-to-liquor ratio (further referred to as M:L) of 1:3, i.e., 1 g of blueberry for 3 mL of solvent. The solvent consisted of a 1% (v/v) aqueous hydrochloric acid solution as dyeing occurs in aqueous environment. The extraction time and temperature were 1 hour and 60 °C, respectively [291]. The solution was filtered with a Büchner funnel and filter paper

with a 40 μm particle retention (VWR). The concentration of the filtrate obtained was 510.7 ± 9.5 mg malvidin-3-glucoside equivalents L^{-1} (hereinafter referred to as Mv-3-Glc equiv) and was used as dyebath (pH: 1.47). These conditions were made constant by dilution with the above-mentioned solvent to ensure consistent results. A simple cost-effective aqueous extraction was favored over methanol as dyeing commonly occurs within aqueous conditions and maximizing yield was not the main objective (Chapter 2). Moreover, this avoids an additional evaporation or clean-up step to remove the organic solvent. A more in-depth investigation on the influence of physicochemical parameters (e.g., particle size, moisture content, temperature, solid-liquid ratio) on the extraction process was not considered in this dissertation.

3.2.1.4 Optimization of Dyeing Conditions

The dyeing parameters, temperature, time, pH and concentration, were optimized for dyeing cotton without applying any mordant. The temperature was varied from 30 $^{\circ}\text{C}$ till 100 $^{\circ}\text{C}$ to find an optimum between dye uptake, color strength, degradation of the colorant and wash fastness. The duration time of dyeing was analyzed through adsorption kinetics whereby (0.5 mL) samples of the 100 mL dyebath were taken with a syringe for anthocyanin measurements at a 5-minute interval from the beginning till 20 min, a 10-min interval till 60 min and a 30-minute interval till 180 min. A blank dyebath was included to monitor the degradation at each stage. The pH optimization experiment consists of the dyebath being varied from the filtrate's pH till 11 by a 50% NaOH solution. The optimal concentration of the dyebath was also checked, and dilutions were carried out with a 1% HCl solution. From preliminary tests, it was clear that only pre- and metamordanting dyeing procedures were taken into account as postmordanting or after treatment of the dyed fabric resulted into leaching of the dye back into solution. Furthermore, as the optimal temperature and pH, which are the most vulnerable parameters for a natural dye, were obtained from the sequential approach, a design of experiments (DOE) was not further considered. The optimal conditions for each mordant were not explored as anthocyanins have a very limited operating range due to their thermolability and pH-sensitivity. Therefore, the dyeing conditions were optimized for anthocyanins specifically rather than for the different types of mordants.

3.2.1.5 Premordanting Procedure

The cotton samples were premordanted in a M:L of 1:50, i.e., 1 g of cotton fabric and 50 mL of distilled water. For both metallic mordants (coordination

complexes), tin and alum and both polysaccharides (hydrogen bond interactions), sodium alginate and β -cyclodextrin, a concentration of 2 g L^{-1} was used, based on literature [115] and solubility restraints. The solutions used for the esterification reactions consisted of the (di)carboxylic acid and sodium hypophosphite (SHP, catalyst). For oxalic acid, gallic acid and caffeic acid, the concentrations were 50 g L^{-1} , 20 g L^{-1} and 2 g L^{-1} , respectively. An equal amount of SHP, 1:1 (w/w), was added and the pH of the solutions was adjusted to the optimal pH for this reaction (pH=3), which was only necessary for oxalic acid. The optimal premordanting condition for tannic acid was 25 g L^{-1} (50% owf and M:L of 1:20) at pH 7 [130], which was adjusted with a 50% sodium hydroxide solution. The temperature profile for premordanting was performed as described by Burkinshaw and Kumar [292]. The premordanted cotton samples were left air-dried overnight. These dried cotton samples were placed in 100 mL stainless steel beakers. The dye extract was added at a M:L ratio of 1:50 and placed within the Mathis Labomat BFA8 (40 rpm, auto reverse: 555). A temperature gradient of $2.0 \text{ }^{\circ}\text{C min}^{-1}$ was applied to obtain the optimal dyeing temperature of $80 \text{ }^{\circ}\text{C}$, which continued to dye for 1 hour. The samples were left air-dried for further analysis and testing. This premordanting procedure was performed in triplicate and each run was accompanied with a blank sample to monitor the potential compound specific degradation.

3.2.1.6 Metamordanting Procedure

The mordant concentrations were similar compared to the premordanting procedure, but within metamordanting the distilled water has been replaced by the dye extract. The conditions for tannic acid remained similar except the pH of 7, which cannot be applied in this method as it would alter the dye's property. The biomordants requiring esterification were dyed at pH 3, which was the optimal pH for esterification. This metamordanting procedure was performed in triplicate and each individual mordant was accompanied with a blank sample to monitor the degradation.

3.2.1.7 Fourier-Transform Infrared Spectrophotometer

The effectiveness of the mordants was investigated by infrared measurements (Figures C.1 to C.2). Premordanted, dyed, wash- and light tested cotton samples were analyzed with the Nicolet iS50 ATR FT-IR spectrometer (Thermo Scientific). Each measurement consisted of 32 replicates and the wavenumber region ranged from 400 cm^{-1} till 4000 cm^{-1} with a wavenumber resolution setting

of 4. The measured spectra were corrected for the baseline and normalized to the highest peak.

3.2.1.8 Spectrophotometric Data

All spectrophotometric data (absorption and reflectance spectra) were measured with the Perkin Elmer Lambda 900 UV/VIS/NIR Spectrometer. The dye uptake was monitored by measuring the anthocyanin concentration before and after dyeing by means of the pH-differential method [293]. Due to the high available content of Mv-3-Glc within blueberries [291, 294, 295] and the matching wavelength of maximum absorbance observed within the recorded UV-Vis absorption spectra, Mv-3-Glc was selected to express the anthocyanin concentration.

$$\text{Anthocyanin concentration} \left(\frac{\text{mg}}{\text{L}} \right) = \frac{A \cdot M_w \cdot DF \cdot 1000}{\varepsilon \cdot b} \quad (3.1)$$

with absorbance $A = (A_{\lambda_{max}} - A_{700nm})_{pH=1.0} - (A_{\lambda_{max}} - A_{700nm})_{pH=4.5}$, $\lambda_{\text{max,vis}}$ at 519 nm and the measurement at $\lambda = 700$ nm corrects for the haze within the solution. M_w displays the molecular weight of Mv-3-Glc (493.44 g mol⁻¹), DF the dilution factor applied for the measurement, ε the molecular attenuation coefficient (28000 L mol⁻¹ cm⁻¹) and b the path length of the cuvette (1 cm). This quantification method has been used to determine the (relative) exhaustion (E%) and the equilibrium adsorption capacity q_e :

$$E\% = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (3.2)$$

$$q_e = (C_0 - C_e) \cdot \frac{V_{\text{solution}}}{m_{\text{fabric}}} \quad (3.3)$$

in which, C_0 and C_e , the initial and equilibrium dye concentration (mg Mv-3-Glc equiv L⁻¹), respectively, q_e represents the amount of adsorbate per unit mass of adsorbent (mg Mv-3-Glc (g cotton)⁻¹), V , the volume of the dyebath (L) and m , the mass of the fabric (g). Due to the mediocre thermostability of anthocyanins, blank dyebaths were included along with the dyeing experiments. Hereby, the degradation factor can be assessed to correct the exhaustion and equilibrium adsorption capacity values (Figure C.3). Next to that, structural properties of anthocyanins can be derived from the UV-Vis spectra such as the glycosylation level at the C3 position, appearing as a shoulder in the 400–440 nm region [58, 296]. This amount is defined by the ratio of absorbance values at 440 nm and $\lambda_{\text{max,vis}}$ ($A_{440 \text{ nm}}/A_{\lambda_{\text{max,vis}}}$), which accounts for $34.9 \pm 0.6\%$ within the dye extract. Furthermore, the half-life value $t_{1/2}$ was calculated by plotting the natural logarithm of the ratio of the

anthocyanin concentration of the blank dyebath at specific times, as described within the optimization of the dyeing time, over the initial dye extract (C_t/C_0) as a function of time [297, 298]. The slope of this plot yields the first-order rate constant k for which the half-life value can be determined with $t_{1/2} = (\ln 2)/k$. Reflectance spectra were recorded, in triplicate, for dyed and wash- and light tested samples from 380 nm till 700 nm to obtain the color strength, which was calculated by the Kubelka–Munk equation:

$$\frac{K}{S} = \frac{(1 - R)^2}{2 \cdot R} \quad (3.4)$$

with K the absorption coefficient, S the scattering coefficient and R the reflectance. The K/S values were calculated by the integrated wavelength method. Furthermore, these reflectance spectra were converted into the corresponding CIELAB coordinate system (L^* , a^* , b^* , C^* and h), with properties of a D65 illuminant and an observer angle of 10° , by OptLab-SPX software (Ascanis). L^* represents the lightness of the sample, a^* the red-green axis with $a^* > 0$ red and $a^* < 0$ green, b^* the yellow-blue axis with $b^* > 0$ yellow and $b^* < 0$ blue, C^* the chromaticity ($C^* = \sqrt{(a^{*2} + b^{*2})}$) and h the hue angle ($h_{ab} = \arctan \frac{b^*}{a^*}$). The hue angle, which defines the color, around 0° (or 360°), 90° , 180° (or -180°) and 270° (or -90°) describes red, yellow, green and blue, respectively. The color difference, ΔE^* , is calculated between the tested sample and the dyed sample.

$$\Delta E^* = \sqrt{(L_{tested}^* - L_{dyed}^*)^2 + (a_{tested}^* - a_{dyed}^*)^2 + (b_{tested}^* - b_{dyed}^*)^2} \quad (3.5)$$

3.2.1.9 Fastness Tests of Dyed Fabrics

Two standard methods of wash tests were applied on the cotton dyed samples: ISO105-C06 and ISO105-E01. The former is based on the use of detergent (ECE formulation phosphate reference detergent (B) without optical brightening agent, pH=9.4), while the latter is only based on water. The assessment whether the natural dye had completely been washed away after the ISO105-C06 test or was still present within the fabric, includes the reimmersion of the washed cotton sample in a 1% HCl solution at a similar liquor ratio as dyeing, for one minute. In order to assess staining, James Heal multifibers were stitched to the dyed cotton samples prior to testing. The ISO105-C06 tests were carried out in a James Heal Gyrowash 815/8. Afterward, the washed samples were left air-dried. The color fastness to light was tested with ISO105-B02, using a Xenotest Alpha instrument. The

samples were irradiated for 22 hours and had an radiant exposure H of 3350 kJ m^{-2} . All fastness values of the tested fabrics were examined by a James Heal grey scale for assessing staining ISO105-A03 and grey scale change in color ISO105-A02 (1-5) in a light box with D65 illumination. The fastness values of the light test for color change were evaluated by blue wool standards (1-8).

3.2.1.10 Statistical Analysis

The one-way analysis of variance (ANOVA) was carried out to investigate the influence of the (bio)mordants with respect to the control sample by comparison of means. The significance level (α) for the statistical analyses is 0.05. The p -values obtained lower than 0.05 are regarded as significantly different. All statistical analyses were performed with SPSS Statistics Version 25 (IBM) software.

3.2.1.11 Adsorption Models

Adsorption isotherms describe the mobility and affinity of an adsorbate within an aqueous environment to a solid-phase at constant temperature and pH [299]. The experimental adsorption equilibrium data were collected as mg Mv-3-Glc equiv per gram of cotton, which is the most abundant compound within blueberries, under optimized dyeing conditions and without mordant. These single component data were fitted with two two-parameter models, Langmuir and Freundlich, and two three-parameter models, Redlich-Peterson and Sips. Describing multicomponent adsorption is frequently performed by means of ideal adsorbed solute theory (IAST). This multicomponent adsorption model generates good predictions for mixtures that are close to ideal and mixtures containing compounds with similar adsorption affinities. However, the main shortcomings of this model are predicting adsorption equilibria of mixtures containing molecules of different size, polarity or adsorption interactions (affinities) such as the blueberry extract, and the poor predictions due to adsorbent heterogeneity [300]. Table 3.1 contains the mathematical expressions of the models applied, q_e and C_e represent the amount of adsorbate per unit mass of adsorbent ($\text{mg Mv-3-Glc equiv (g cotton)}^{-1}$) and the equilibrium dye concentration ($\text{mg Mv-3-Glc equiv L}^{-1}$), respectively. The isotherm parameters for Langmuir are K_L , the isotherm constant ($\text{L (mg Mv-3-Glc equiv)}^{-1}$), and Q_L , the maximum monolayer adsorption capacity ($\text{mg Mv-3-Glc equiv (g cotton)}^{-1}$); for Freundlich: K_F the adsorption capacity ($\text{mg Mv-3-Glc equiv}^{1-1/n} \text{ L}^{1/n} \text{ (g cotton)}^{-1}$) and n_F , the adsorption intensity; for Redlich-Peterson: K_R Redlich-Peterson isotherm constant as L (g cotton)^{-1} , a_R , Redlich-Peterson isotherm constant as ($\text{L (mg Mv-3-Glc equiv)}^{-1}$) $^\beta$ and β , the exponential variable; and for Sips model: K_s (L (g cotton)^{-1}),

a_5 (L (mg Mv-3-Glc equiv)⁻¹) and n_5 the Sips model exponent.

Table 3.1: An overview of the isotherm and kinetic models applied.

Adsorption model	Definition	Plot	Assumed mechanisms	Reference
Isotherm				
Langmuir	$q_e = \frac{Q_L \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$	$\frac{1}{q_e}$ vs $\frac{1}{C_e}$	Monolayer adsorption, identical sites and no mutual interactions between neighboring adsorbed molecules	[299, 301]
Freundlich	$q_e = K_F \cdot C_e^{\frac{1}{n_F}}$	$\ln q_e$ vs $\ln C_e$	Multilayer adsorption of the molecules on a heterogeneous surface	[299, 302]
Redlich-Peterson	$q_e = \frac{K_R \cdot C_e}{1 + a_R \cdot C_e^b}$	q_e vs $C_e^{(a)}$	Describe wide concentration range for homogenous and heterogeneous systems	[299, 303]
Sips	$q_e = \frac{K_S \cdot C_e^{n_S}}{1 + a_S \cdot C_e^{n_S}}$	q_e vs $C_e^{(a)}$	Low adsorbate concentrations: Freundlich, while high concentrations: Langmuir	[299, 304]
<i>(a)</i> : Iterative fitting was performed for this model				
Kinetics				
Lagergren	$\frac{dq_t}{dt} = k_1 \cdot (q_e - q_t)$	$\ln q_e - q_t$ vs t	Adsorption reaction model	[305, 306, 307]
Pseudo-second order	$\frac{dq_t}{dt} = k_2 \cdot (q_e - q_t)^2$	$\frac{t}{q_t}$ vs t	Adsorption diffusion model	[305, 306, 307, 308, 309]
Intraparticle diffusion model (IPD)	$q_t = k_P \cdot t^{\frac{1}{2}} + C$	q_t vs $t^{\frac{1}{2}}$	Three-step process: 1) external surface adsorption, 2) gradual adsorption step where intraparticle diffusion is controlled and 3) equilibrium stage	[305, 306, 310]

These nonlinear isotherm models were solved by iteration in Origin (OriginLab, Northampton, MA). In order to determine the best isotherm model to describe the uptake of anthocyanins on cotton, the Chi-square analysis was carried out as goodness of fit next to R^2 -values. The Chi-square test is calculated as the sum of squares of the differences between the experimental data and the data fitted by the model:

$$\chi^2 = \sum \frac{(q_{e,exp} - q_{e,m})^2}{q_{e,m}} \quad (3.6)$$

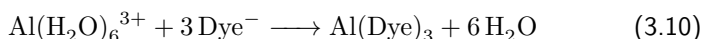
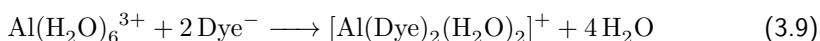
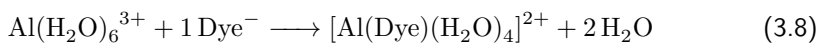
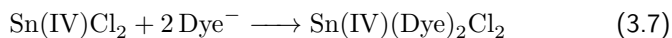
with $q_{e,exp}$ (mg Mv-3-Glc (g cotton)⁻¹) and $q_{e,m}$ (mg Mv-3-Glc (g cotton)⁻¹) the equilibrium adsorption capacity from the experimental data and the isotherm model, respectively [311]. A small χ^2 value is obtained when the data of the model is similar to the experimental data, when they differ χ^2 will be large.

3.2.2 Molecular Modeling Details

3.2.2.1 Static Calculations

In order to study the metal-dye coordination complexes and ionic interactions between oxalic acid and Mv-3-Glc, static calculations were carried out with Gaussian 16 [248] by means of DFT. Geometrical optimizations were performed with the B3LYP functional, with a 6-311++G(d,p) basis set [249, 250], as it has proven its reliability for a broad set of chemical systems [281, 312]. Furthermore, Grimme's third-generation dispersion corrections were also added to account for the dispersion interactions [313]. As dyeing occurs in an aqueous environment, implicit solvation was taken into account by the standard self-consistent reaction field using the integral equation formalism variant of the polarisable continuum model (IEF-PCM) with water as solvent ($\epsilon_{\text{dip}} = 78.3553$) [314].

Static calculations were performed to investigate the interaction of the dye with a series of metal coordination complexes. Both complexes with aluminium and tin were considered, which were modelled using an effective core potential DEF2TZVPP basis set. The following systems were considered:



In the literature, it has been shown that stannic chloride (Sn(IV)) will be formed by oxidation at the expense of stannous chloride (Sn(II)) and hydrochloric acid [315]. The structural organotin(IV) complexes are potentially tetrahedral, trigonal pyramidal, or octahedral, following the $\text{R}_n\text{SnX}_{4-n}$ formula ($n = 1-3$, $\text{X} =$ halide, carboxylate, dithiocarbamate etc.) [316, 317]. The typical coordination geometry observed between diorganotin(IV) $^{2+}$ and flavonoids containing vicinal hydroxy groups is the octahedral configuration (O_6) [318]. Therefore, the octahedral SnCl_2 complex consists of the metal salt attached to two bidentate dye ligands (Equation (3.7)). The aluminium ion is represented as a metal aquo complex, i.e., an Al(III) cation surrounded by six water molecules in an octahedral fashion. To investigate the stability of the aluminium-anthocyanin complex, two water molecules from the initial metal aquo complex have been exchanged by one bidentate anthocyanin (Equations (3.8) to (3.10)) till all water molecules were

substituted by the natural dyes [281]. As mentioned earlier, Mv-3-Glc is the most abundant compound among other anthocyanins present within blueberries [295]. The anthocyanins eligible for complexation are cyanidin-3-glucoside, delphinidin-3-glucoside and petunidin-3-glucoside (hereinafter referred to as Cy-3-Glc, Dp-3-Glc and Pt-3-Glc, respectively), due to the presence of vicinal hydroxy groups at the B-ring. The global charge of the ligands used within these coordination complexes is -1. This is obtained after deprotonation of two hydroxy groups at the 3' and 4' positions of the flavylium cation. Intermolecular interactions between oxalic acid and Mv-3-Glc were investigated under the same conditions as the geometrical optimizations. The resulting interaction energies from these static calculations were corrected for Basis Set Superposition Error (BSSE). For these static PCM calculations, counterpoise correction was applied to the PCM optimized structures in separate calculations without implicit solvation, as the aforementioned correction cannot be implemented during PCM calculations [319]. Furthermore, charge distribution and atomic population analyses of the flavylium cation, Mv-3-Glc and oxalic acid were carried out with Hirshfeld I (HI) [2] and Minimal Basis Iterative Stockholder (MBIS), an expanded variant of the Hirshfeld AIM method [320]. HI is able to create a good estimate of the electrostatic potential of organic molecules [321]. Both were performed using the in-house software package HORTON 2.1.1 [322].

3.2.2.2 Molecular Dynamic Simulations

In addition to static calculations based on DFT, semi-empirical molecular dynamic (MD) simulations were carried out to investigate the intermolecular behavior between tannic acid and Mv-3-Glc by using the CP2K software [323] as tannic acid is a considerably large system, it was not feasible to treat this system at the DFT level. The unit cell, measuring 40 Å x 40 Å x 40 Å, contained tannic acid and Mv-3-Glc and was simulated by PM6 with Grimme D3 dispersion corrections [324]. For these simulations, the canonical ensemble was applied at 353 K controlled by a CSVR thermostat with a time constant of 300 fs. A time-step of 0.5 fs is used for the integration of the equation of motion. The self-consistent field (SCF) convergence criterion was fixed at 10⁻⁵ eV. The total run time for this simulation was 305 ps, the initial 50 ps were omitted by cause of equilibration. In a second stage, as solvent effects could highly influence the interaction patterns between mordant and dye, solvation has been taken into account in an explicit manner in order to match the experimental conditions more realistically. To this end, classical molecular dynamics simulations are performed

on a GPU cluster. Therefore, both tannic acid and the Mv-3-Glc dye were solvated with water molecules to reproduce the experimental density and accounting two solvent layers of water to each molecule (based on the experimental radial distribution function of water) [325]. This resulted in a solute-water box of 53 Å x 53 Å x 53 Å counting 4892 water molecules per solvation layer, generated with PACKMOL [326]. Both compounds were parameterized with the GAFF2 force field using AmberTools [327, 328] and the TIP3P water model [329], which has proven its accountability in several researches [330]. The simulation was performed in the NpT ensemble, which was controlled by the Langevin integrator and Monte Carlo barostat (1 bar) [331]. The total duration of the simulation was 2294.5 ns and analysis of the trajectory files was accomplished, by using the last 1657.6 ns of the MD simulation, with the MDTraj python package [332] and PLUMED software package [333].

3.3 Results and Discussion

This section will first discuss the optimization of the dyeing procedure for anthocyanins on cotton without applying any mordant. Next, the experimental data on the influence of the (bio)mordants are described, which are elaborated according to the interaction mechanism. Finally, observations from the dyeing experiments are clarified with the results obtained from modeling.

3.3.1 Optimization of the Dyeing Parameters

3.3.1.1 Temperature

Firstly, the influence of the temperature has been studied. Hereby, the dye uptake has been monitored over a temperature range between 30 °C till 100 °C. As anthocyanins are susceptible to degradation at higher temperatures [334], a compromise should be found between dye uptake, color strength, degradation of the colorant and wash fastness (Table C.1). From Figure 3.2A, it can be seen that dyeing at 80 °C resulted into the highest dye uptake. Table C.1 shows that dyeing at temperatures lower than 60 °C resulted in a high color strength and a negligible amount of degradation, but had a larger color loss after washing. The dyeing properties at 70 °C and 80 °C were very similar, with the dye uptake as the most determining factor for the latter even though a small amount of degradation is present. In general, the thermal stability of anthocyanins is determined by the grade of methoxylation, glycosylation, and acylation [335, 336]. This is advantageous for the high content of Mv-3-Glc present within blueberries, while other anthocyanin derivatives are more prone to thermal

degradation. This implies that dyeing at 80 °C just reached the equilibrium between maximum dye uptake and the initial steps of anthocyanin degradation, which are the successive deglycosylation reactions. This results into their respective aglycones, which still possess color and eventually lead to cleavage into a phenolic acid and a phenolic aldehyde [297]. These two latter stages are more pronounced at 90 and 100 °C dyeing. Dyeing at 90 °C still resulted in a high dye uptake, however, a color loss on the fabric was observed due to the degradation of anthocyanins, that was already taken up within the fabric, leading to a lower a^* and higher L^* value compared to lower dyeing temperatures. This decline in color loss was larger for the sample dyed at 100 °C. Therefore, 80 °C has been applied in further experiments.

3.3.1.2 Dyeing Time

The dyeing time was monitored by performing an adsorption kinetics experiment whereby the dye uptake has been investigated in function of time. Hereby, Figure 3.2B illustrates that the dye uptake reached a plateau after 60 min of dyeing at 80 °C, indicating that dyeing reaches equilibrium and longer dyeing times are not required. As mentioned above, the blueberry extract consists of glycosides and aglycones. The former shows higher solubility within water, while the latter is more soluble in alcohol [51]. Through this experiment, the amount of 3-glycosides within the blueberry extract was determined by the $A_{440\text{ nm}}/A_{\lambda_{\text{max,vis}}}$ ratio as a function of time. Figure 3.2C illustrates the increase of this ratio over time. As the optimal dyeing time is 60 min, the ratio is barely 3% higher compared to the initial dyebath, while it reaches up to 14% at the end of this experiment. Two processes can occur within the blank dyebath: the 3-glycosides are degraded by losing their sugar moiety and become aglycones and the degradation of aglycones into their corresponding phenolic constituents. Both aforementioned processes also occur within the sample beaker, with the additional factor of the uptake of anthocyanins and anthocyanidins into the fabric. The increase of 3% after dyeing is too low to draw any conclusion. However, the 14% increase of the ratio at the end of the kinetic experiment can be ascribed to the higher rate of degradation of aglycones compared to 3-glycosides, meaning the latter being more stable despite the acidic conditions and elevated temperature. This is also indicated in Figure 3.2D, which displays the change of absorbance at the wavelength of maximal absorption (519 nm) and the wavelength determining the fraction of 3-glycosides (440 nm) as a function of time. Even though a decline is noticed for both peaks, the absorbance value at

440 nm decreases more slowly compared to the total anthocyanin peak, while the ratio between them increases. Furthermore, the half-life value of the dyebath, 1.88 h, determined by first-order reaction kinetics (Figure C.4), showed the same order of magnitude as the half-life values obtained by Yue and Xu [298] with bilberry extract heating at 80 °C and Sadilova et al. [297] for strawberry and elderberry at pH 3.5 and a temperature of 95 °C.

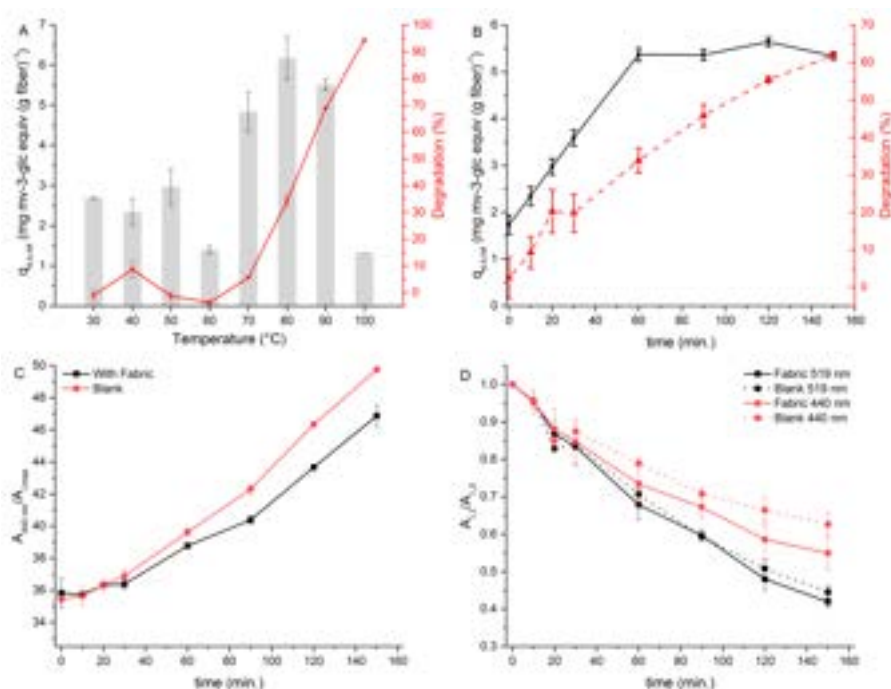


Figure 3.2: A: the optimization of the dyeing temperature in terms of relative dye uptake and amount of degradation, B: the relative dye uptake measured at 80 °C and the extent of degradation as a function of time, C: the $A_{440 \text{ nm}}/A_{\lambda_{\text{max,vis}}}$ ratio representing the 3-glycosylation level of the dyebath over time and D: the absorbance ratio over time for two wavelengths (440 nm and 519 nm) of a blank dyebath and one containing the fabric.

3.3.1.3 pH

The stability of anthocyanins for dyeing was also studied. Due to the fact that anthocyanins are pH-sensitive, the pH of the dyebath was altered from 1.47 till 11 and dyed at 80 °C for 60 min. Hereby, Table 3.2 shows that the color strength is highest for the pH of the original extract (pH = 1.47), followed by dyeing at pH 3. At increasing pH, the dyebath consisted of a mixture of different anthocyanin isomers and not exclusively the flavylum cation. At pH 5, the a^* value decreased

significantly and the fabric displays a bluish tint. Dyeing at pH 7 and beyond, the degradation of these isomers occurs more rapidly at higher temperatures. This resulted into yellow degradation products of anthocyanins, hence the positive b^* color value. This was evidenced by the fact that no color change was visible when the fabrics were placed in a 1% HCl solution, indicating the presence of degradation products (i.e., phenolic acid and phenolic aldehyde) rather than the chalcone isomer [297, 337]. Therefore, the pH of the original extract remains unadjusted for further dyeing experiments.

Table 3.2: Colorimetric values and color strength of fabrics dyed at different pH conditions and concentrations of the dye extract (uncertainties expressed as standard deviation ($n = 3$)).

pH	After dyeing						Samples	After washing ISO105-C06								Samples
	L*	a*	b*	C*	h	K/S		L*	a*	b*	C*	h	K/S	ΔE*		
1.47	47.9	26.4	-5.3 ±	26.9	348.7	1.8 ±		72.1	2.0 ±	1.7 ±	2.6 ±	44.3	0.3 ±	35.1		
	±0.9	±0.6	0.2	±0.6	±0.7	0.1		±0.2	0.2	0.6	±0.5	±8.8	0.1	±1.1		
3	49.9	22.4	-6.7 ±	23.3	343.4	1.5 ±		73.8	1.7 ±	1.6 ±	2.4 ±	51.5	0.3 ±	32.7		
	±0.6	±0.8	0.2	±0.9	±0.1	0.1		±0.7	0.1	1.0	0.7	±1.1	0.1	±1.3		
5	62.6	3.5	-2.5 ±	4.3	324.6	0.7 ±		74.8	1.3 ±	0.7 ±	1.5 ±	29.4	0.3 ±	12.7		
	±0.1	0.1	0.2	0.2	±1.2	0.1		±0.2	0.1	0.1	0.1	±1.9	0.1	±0.2		
7	72.9	3.7 ±	18.1	18.4	78.6	0.5 ±		82.4	3.3 ±	8.3 ±	9.0 ±	68.6	0.1 ±	13.6		
	±1.3	0.6	±1	±1.1	±1.2	0.1		±0.7	0.4	0.6	0.7	±1.0	0.1	±0.7		
9	72.5	2.0 ±	14.6	14.7	82.4	0.5 ±		84.1	2.5 ±	6.9 ±	7.3 ±	70.3	0.1 ±	14.0		
	±0.3	0.4	±1.1	±1.2	±1.0	0.1		±0.6	0.2	0.5	0.5	±0.3	0.1	±1.0		
11	79.5	3.5 ±	14.5	14.9	76.3	0.2 ±		89.3	1.2 ±	5.9 ±	6.0 ±	78.5	0.1 ±	13.2		
	±0.6	0.2	±0.9	±0.9	±0.2	0.1		±0.1	0.1	0.1	0.1	±0.0	0.1	±1.0		
Dilution																
Original ^a	47.4	26.6	-5.6 ±	27.2	348.2	1.9 ±		69.3	-1.8 ±	0.1 ±	1.9 ±	179.9	0.5 ±	36.3		
	±0.9	±0.6	0.4	±0.5	±0.9	0.1		±0.3	0.4	0.6	0.4	±19.4	0.1	±0.8		
2-fold ^a	53.5	24.8	-7.0 ±	25.8	344.2	1.2 ±		73.2	-2.1 ±	-0.1 ±	2.2 ±	184.1	0.3 ±	34.1		
	±0.3	±0.2	0.1	±0.2	±0.3	0.1		±0.1	0.2	0.5	0.2	±12.1	0.1	±0.4		
5-fold ^a	63.1	21.2	-7.5 ±	22.5	340.4	0.6 ±		78.9	-2 ±	0.2 ±	2 ±	174.7	0.2 ±	29.1		
	±0.3	±0.3	0.1	±0.3	±0.3	0.1		±0.2	0.3	0.2	0.3	±4.6	0.1	±0.2		
10-fold ^a	68.5	19.1	-7.3 ±	20.4	339	0.4 ±		82.2	-2.1 ±	0.7 ±	2.2 ±	161.0	0.1 ±	26.4		
	±0.1	±0.3	0.1	±0.3	±0.1	0.1		±0.5	0.2	0.3	0.3	±5.6	0.1	±0.5		

^a: the concentrations for the original, 2-, 5- and 10-fold diluted extract were: 510.7 ± 9.5 , 257.1 ± 7.7 , 69.3 ± 1.1 and 40 ± 0.4 mg Mv-3-Glc L⁻¹, respectively.

3.3.1.4 Concentration

The concentration of the dyebath was also optimized in terms of color strength. Dilutions of the original extract were made with a 1% HCl solution. It was observed that a higher dilution factor results in a decline of redness (a^*), an increase in L^* and lower K/S values (Table 3.2). The smaller color differences (ΔE^*) are due to the fact that the initial dyed cotton samples already possess high lightness values. This experiment showed that lower concentrations of the dyebath were not sufficient to saturate the cotton fabrics with the dye, hence the lower color strength.

3.3.1.5 Esterification

In order to create anionic sites on the cotton fabrics, an optimal esterification reaction was developed with oxalic acid. Literature shows that SHP is the most efficient catalyst for this reaction [338, 339]. To effectively verify the formation of the ester peak, the premordanted fabrics were rinsed with grade 3 water in the same M:L ratio. The FT-IR spectra showed that rinsing reduced the amount of ester bonds formed, but they still remain within the cotton (Figure C.5). The anionic sites formed can potentially attract the dye molecule through ionic bonds and strengthen its affinity. The effect of the pH for this reaction was investigated as oxalic acid has two pKa values, 1.25 and 4.14. The most interesting peaks of cellulose to investigate are at 3326 cm^{-1} (O-H stretch), 2888 cm^{-1} (symmetric C-H stretch), 1632 cm^{-1} (OH bend of absorbed water), and in the fingerprint region: 1423 cm^{-1} (in-plane HCH and OCH bending vibration), 1368 cm^{-1} (in-plane CH bending), 1313 cm^{-1} (CH_2 rocking vibration at C6), 1157 cm^{-1} (C-O-C asymmetrical stretch) and 1020 cm^{-1} (C-C, C-OH, C-H ring and side group vibrations) (Figure 3.3) [340]. At pH 1, the peak at 1735 cm^{-1} (C=O stretch) and an increased peak 1157 cm^{-1} (C-C-O stretch of an ester bond) indicate that oxalic acid, as a dicarboxylic acid, was able to form an ester bond. At pH 3, oxalic acid exists as hydrogen oxalate and several variations in peak intensities illustrate the increased formation of ester bonds with the availability of anionic sites: an increase at 1735 cm^{-1} (ester bond), a decrease of vacant hydroxy groups shown by 3326 cm^{-1} and 1020 cm^{-1} (primary alcohol), and an increase for the bands in the fingerprint region at 1414 cm^{-1} and 1600 cm^{-1} (symmetric and asymmetric CO_2 stretch, respectively). Beyond pH 5, oxalic acid exists entirely as dicarboxylate, which could be seen around 1600 cm^{-1} (asymmetric CO_2 stretch) and 1313 cm^{-1} (C-O stretch). Both peaks intensify with increasing pH. The C=O stretch is small at pH 5 and absent at pH 7 and 9. From this FT-IR analysis, it can be concluded that pH 3 offers the most effective esterification. This is in good agreement to the optimal pH found by Yang [338] for ester crosslinking of cellulose with a polycarboxylic acid.

3.3.2 Dyeing Results with (Bio)mordants, Color Measurement and Fastness

3.3.2.1 Metallic Mordants (Tin and Aluminium)

The first approach to improve the affinity of anthocyanins for cellulose, which could be seen as a non-preferable reference, is the application of metallic mordants. The

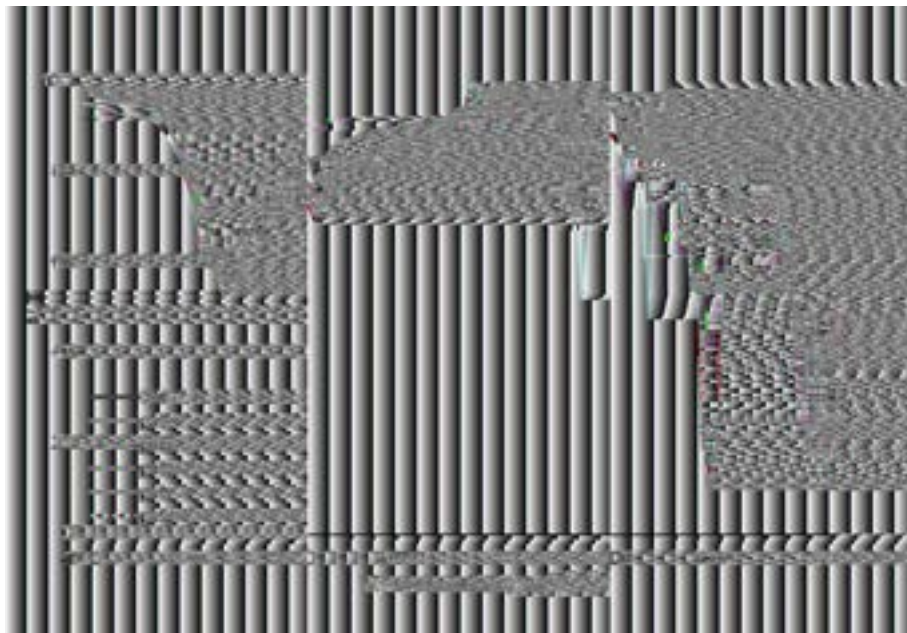


Figure 3.3: Infrared spectra of esterification reactions with oxalic acid at different pH conditions.

mordants of interest were stannous chloride and alum. Under optimized dyeing conditions, the dye uptake, q_e , for the premordanted tin sample is 27% more compared to the control sample (Table 3.3). This higher dye uptake can also be translated toward the colorimetric coordinates whereby the premordanted stannous chloride cotton sample showed a significant darker purple color, lower L^* , a^* and more negative b^* values, compared to the control sample ($F(1,4) = 75.81$, $p = 0.0010$; $F(1,4) = 11.80$, $p = 0.026$ and $F(1,4) = 7.97$, $p = 0.048$; respectively). Furthermore, the largest color strength is also notable for the premordanted tin sample, 5.2 compared to 2.1 for the control sample ($F(1,4) = 34.52$, $p = 0.004$). Within metamordanting, tin resulted in a lighter purple shade compared to the premordanted sample. This was also visible at the maximum absorption peak that was bathochromatically shifted to 528 nm compared to the blank (Figure C.6). The aluminium mordant did not show any color difference in pre- or metamordanting dyeing compared to the blank in every aspect ($p > 0.05$). During the wash tests, most of the samples turned bluish/grey due to the alkaline detergent of the ISO105-C06, explained by the dye's pH sensitivity, but the premordanted tin sample still maintains an intense purple tint (L^* : 48.9, a^* : 2.2 and b^* : -5.9). The color difference, ΔE^*_1 , is also lower compared to the control, assuming the main effect

is related to the pH of the detergent rather than washing off. An indicator of the presence of the dye within the fabric, is by performing the reimmersion test (Table 3.4). It can be seen that both tin mordanted samples still holds a significant amount of anthocyanins (pre: L^* 50.6, a^* 17.3 and b^* -13.2 ($F(1,4) = 122601$, $p < 0.001$; $F(1,4) = 21952$, $p < 0.001$; $F(1,4) = 18336$, $p < 0.01$; respectively); meta: L^* 71.7, a^* 8.5 and b^* -4.7 ($F(1,4) = 268$, $p < 0.001$; $F(1,4) = 5547$, $p < 0.001$; $F(1,4) = 8192$, $p < 0.001$; respectively)). This also resulted into a higher color strength and a higher color difference, ΔE^*_2 (relative to washed samples), which is mainly contributed by the a^* value. The reimmersed alum samples did not show any significant differences compared to the reimmersed control sample as the dyed samples did not show any added value after dyeing in the first place. In Table 3.5, the color fastness to water is displayed. In general, it can be seen that the colors are better retained on the fabrics, now the detergent has been omitted, but it still marks the hydrophilicity of the dye. Both tin mordanted samples retain their color more strongly compared to the control sample (pre: L^* 30.7, a^* 14.3 and b^* -13.1 ($F(1,4) = 1780$, $p < 0.001$; $F(1,4) = 0.10$, $p = 0.766$; $F(1,4) = 697$, $p < 0.001$; respectively); meta: L^* 46.4, a^* 15.0 and b^* -13.5 ($F(1,4) = 30$, $p = 0.005$; $F(1,4) = 0.67$, $p = 0.46$; $F(1,4) = 1853$, $p < 0.001$; respectively)), although the lightness (L^*) of the metamordanted sample is slightly higher. The water test on alum mordanted samples show comparable properties to the control sample. The general trend in fastness values are low staining on the multifiber and a high color change for ISO105-C06 and the opposite for ISO105-E01, larger staining on the multifiber and smaller color change were observed. The metamordanted alum shows a better fastness than its premordanted analogue. The best result for color change is the premordanted tin sample in both wash tests (Table 3.6). Next to that, the light test results also show that the premordanted tin sample is capable to retain its color better than the aluminium and control sample, based on the ΔE^* and fastness value. This is in good agreement with the observations made by Wang et al. [115], where SnCl_2 retained its color better and slightly better after one washing cycle in neutral and alkaline soapy solution, respectively, in comparison to the control sample. The use of alum in other studies resulted in a more greyish and lightly blue tinted samples, however different pH and fibers were used [269, 270, 274]. Next to that, the fastness values with alum were comparable with the control samples. From this section, it can be concluded that tin improves the stability and affinity of anthocyanins for cotton, although it is not likely to be first choice for application purposes due to its potential health and environmental hazards.

Table 3.3: The relative exhaustion levels ($E_{s,rel}$) and relative equilibrium adsorption capacities ($q_{e,s,rel}$) of the dyebaths (uncertainties expressed as standard deviation ($n = 3$)).

	Premordanting		Metamordanting	
	$E_{s,rel}$ (%)	$q_{e,s,rel}$ (mg dye/g fiber)	$E_{s,rel}$ (%)	$q_{e,s,rel}$ (mg dye/g fiber)
Control	25.1 ± 1.2	6.1 ± 0.2	25.1 ± 1.2	6.1 ± 0.2
SnCl ₂	33.4 ± 0.7	7.8 ± 0.3	20.9 ± 0.9	5.5 ± 1.0
Alum	25.6 ± 0.1	5.9 ± 0.9	23.5 ± 1.2	6.2 ± 1.3
Tannic acid	23.5 ± 1.7	5.5 ± 0.6	26.7 ± 0.7	7.0 ± 1.2
β-CD	24.5 ± 0.8	6.0 ± 0.7	22.9 ± 1.1	5.9 ± 0.7
Alginate	24.2 ± 1.2	5.9 ± 0.6	22.7 ± 1.2	5.9 ± 1.1
Oxalic acid	22.1 ± 0.2	4.5 ± 0.8	31.0 ± 0.1	6.9 ± 0.1
Gallic acid	22.6 ± 1.0	5.2 ± 0.3	14.1 ± 0.5	4.1 ± 0.2
Caffeic acid	24.9 ± 1.3	5.8 ± 0.7	33.2 ± 1.4	8.4 ± 1.3

3.3.2.2 Biomordant: Hydrogen Bonds

Three biomordants, tannic acid, sodium alginate and β-cyclodextrin, were investigated for their potential intermolecular interactions through hydrogen bonding as these compounds contain vast amounts of hydroxy groups. The dye uptake of these compounds did not indicate any significant improvement compared to the control sample (Table 3.3). Premordanted tannic acid cotton sample showed a yellowish color after the pretreatment, which indicates the successful application on it. The FT-IR spectra verified the presence of tannic acid with increments visible at the at 3325 cm⁻¹ (OH-stretch), 2888 cm⁻¹ (symmetric C-H stretch), 1700 cm⁻¹ (conjugated aromatic ester C=O stretch), 1610 cm⁻¹ (aromatic C=C stretch), 1313 cm⁻¹ (CH₂ rocking vibration at C6) and 1200 cm⁻¹ (C-C-O conjugated aromatic ester stretch) (Figures C.1B and C.2B). The dyed premordanted tannic acid sample produces a better color strength (K/S = 2.7). Meanwhile, the metamordanted tannic acid sample produces a very bright color, which is indicated by a combination of slightly higher L* value and a more positive a* value (a*: 38.3). The λ_{max}-value shifted toward a higher wavelength (524 nm) as a consequence of the copigmentation effect (Figure C.6). After the detergent wash step, the pre- and metamordanted tannic acid sample still shows a feeble yellow tint, which still holds during the reimmersion step (positive b* value) (Table 3.4). For the fastness to water, the metamordanted sample still displays a more intense red color as it was initially more brighter than the other mordants. However, this decay (ΔE*) is situated in the same range compared to the other mordants. The increased redness (a* value) and K/S value of the premordanted 30% and 50% owf tannic acid dyed cotton samples

were also observed within Bechtold et al. [269] and Wang et al. [115]. In terms of fastness levels, tannic acid matches the control sample and marks a half grade better for color change after the water-based wash test. Additionally, tannic acid showed very good fastness values for the light test in both dyeing procedures $\Delta E^* = \pm 15.0$ (Table 3.5), which confirms the observations found in Wang et al. [115]. This could be ascribed to the gallic acid moieties within tannic acid, which carry antioxidant properties and act as a copigment. It is generally known that tannins or compounds containing aromatic moieties (e.g., phenolic compounds) are able to absorb ultraviolet rays, especially UVA and UVB radiation, which cover the wavelength region between 280 to 400 nm, and thus they might be useful as UV-protectors [124, 341]. Furthermore, the type of copigment and pH also play a role within the formation of π - π complexes. Bąkowska et al. [342] show that several anthocyanin-polyphenol copigment complexes were less prone to degradation by UV-irradiation at pH 2.5 where the flavylium ion is exclusively present in solution. The other two biomordants did not show any significant differences compared to the control sample in both dyeing procedures. The FT-IR spectra did show more intense peaks for O-H stretch, symmetric C-H stretch, HCH and OCH in-plane bending vibration (1423 cm^{-1}) and in-the-plane CH bending (1368 cm^{-1}), which indicates the effective application within premordanting, but this was less pronounced in metamordanting (Figures C.1B and C.2B). However, no increased binding by hydrogen bonds or inclusion of anthocyanins were experimentally noticed from the colorimetric data. The results from the fastness tests did not indicate an improved affinity as well. The lack of inclusion by β -cyclodextrin might be assigned to the preferential uptake of the colorless anthocyanin isomers, also called anti-copigmentation effect. The presence of a tetrahedral carbon atom within the hemiketal and chalcone forms, allows a larger flexibility, which makes adaptation to the cyclodextrin cavity far easier, in comparison to the more rigid planar flavylium cation [343]. From the data analyzed, tannic acid shows promising properties as a biomordant, though still inferior to stannous chloride with exception to light fastness.

3.3.2.3 Biomordant: Ionic Bond and π - π Interactions

After optimizing the esterification procedure, oxalic acid, gallic acid and caffeic acid and an equal amount of SHP was used to fix these biomordants on cellulose. The first to improve the affinity by ionic bonds, the last two by means of π - π interactions. The IR spectrum of oxalic acid was already described in section 3.3.1.5, the gallic acid spectrum have corresponding peaks to that of tannic acid

as its aromatic moieties also consist of gallic acid. The main notable peak of caffeic acid is a doublet at 1638 cm^{-1} and 1615 cm^{-1} , which shows the (E)- and vinyl substitution pattern of the alkene (Figures C.1A and C.2A). From Table 3.4, no major differences were visible compared to the control sample in this three-step procedure (i.e., premordanting, dyeing and ISO105-C06 wash fastness). Meanwhile, within metamordanting, intermolecular interactions were clearly visible during the spectrophotometric measurement of the dye uptake. The maximum absorption wavelengths for oxalic, gallic and caffeic acid are shown at 521 nm, 523 and 519 nm, respectively (Figure C.6). Moreover, the dye uptakes of oxalic acid and caffeic acid were at least 15% and 20% higher compared to the control sample, respectively. The oxalic acid sample showed a light purplish tint, similar to stannous chloride. Gallic acid gave cotton a very bright pink color (L^* : 54.7) due to copigmentation, which comes along with a smaller color strength value and in Table 3.5, the sample lost a lot of its color strength after the water wash test. The effect of caffeic acid is more distinct during the ISO105-C06 wash step, at which the cotton showed a darker shade (L^* : 67.4), during the reimmersion step where the a^* value is three times higher compared to the control sample (L^* : 69.8, a^* = 14.1 and b^* : 3.2 ($F(1,4) = 266$, $p < 0.001$; $F(1,4) = 5881$, $p < 0.001$; $F(1,4) = 432$, $p < 0.001$; respectively)) and during the water wash test where the red color is still very strong (a^* : 22.0). This can be indicated from the amount of dye that was taken up ($q_e \geq 7.1\text{ mg Mv-3-Glc equiv (g cotton)}^{-1}$) and smaller wash off by this procedure. The ISO105-C06 fastness values for these compounds were only rated poor for color change for both dyeing procedures. A very minor decrease in color change was visible between oxalic acid and the control sample whereas Wang et al. [115] obtained an increase of 0.5 till 2 grades with increasing succinic acid concentration, implying effective ionic bonds between the treated cotton and dye. One particular issue arises from the use of this acidic environment ($\text{pH} < 3$), which is necessary to obtain the, most stable isomer of anthocyanins, red flavylium cation. This acidic condition jeopardizes the ester bond formed during the premordanting step through acid-catalyzed hydrolysis, explaining the loss of the ester peak after dyeing (Figure C.1B). The color change for the metamordanted samples withstands the water wash test better than the premordanted samples. The results of the light test showed that oxalic acid could not inhibit the color deterioration, whereas a very good light fastness was observed for gallic acid, especially when dyed by metamordanting ($\Delta E^* = 11.3$ compared to 18.8 by premordanting). Caffeic acid also showed a good light fastness within pre- and metamordanting as shown in Table 3.6. Concluding, neither oxalic acid nor both

aromatic compounds were capable to improve the affinity of the dye for cellulose via ionic bonds or π - π stacking, respectively. However, the latter was able to prevent light induced degradation of anthocyanins by their antioxidant capabilities to some extent due to copigmentation, which is in fact an exothermic process. This phenomenon is more pronounced during metamordanting than the premordanting procedure. In most of those complexes experimentally studied, the negative enthalpy factor favors copigmentation while the entropic factor is also negative. The latter refers to the ordering of two compounds within this process, and therefore, limiting the rotational and translational contributions to entropy [52]. For instance, the copigmentation complex between malvin and caffeic acid resulted in a standard Gibbs Free Energy (ΔG°) of $-13.6 \text{ kJ mol}^{-1}$ (with $\Delta H^\circ = -25.6 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = 46.0 \text{ J mol}^{-1} \text{ K}^{-1}$), which decreases more at elevated temperatures [344].

Table 3.4: The colorimetric properties (D65/10) and color strength of dyed (pre- and metamordanted), washed (according to ISO105-C06 and reimmersed cotton samples (uncertainties expressed as standard deviation ($n = 3$)). Color differences ΔE^*_{11} and ΔE^*_{22} are calculated with respect to dyed and washed fabrics, respectively.

	After Dyeing						After Washing ISO105-C06						After washing ISO105-C06 and reimmersion in a 1% HCl solution										
	L*	a*	b*	C*	h	K/S	Samples	L*	a*	b*	C*	h	K/S	ΔE*	Samples	L*	a*	b*	C*	h	K/S	ΔE*	Samples
Premord.	46.2	29.1	-4.7	± 29.5	350.7	2.1 ±		70.7	0.2	0.7	1.7	± 42.1	0.4	± 36.2		75.6	4.2	-0.5	± 4.2	± 353.7	0.4	± 6.5	
Control	± 1.3	± 3.0	0.8	± 2.8	± 2.5	0.2		± 1.4	1.9	0.8	1.0	± 4.1	0.1	± 1.1		± 0.4	0.1	0.1	0.1	± 0.8	0.1	± 2.3	
SnCl ₂	31.1	20.5	-6.5	± 21.6	342.3	5.2 ±		48.9	2.2	-5.9	± 6.3	± 289.1	1.6	± 26.2		50.6	17.3	-13.2	± 21.8	322.5	1.3	± 15.3	
	± 2.7	± 3.1	0.7	± 3	± 2.5	1.2		± 2.5	1.8	0.9	1.5	± 13.1	0.3	± 0.5		± 0.2	± 0.1	± 0.2	± 0.2	± 0.2	0.1	± 0.3	
Alum	46.8	28.4	-5.3	± 28.9	349.4	2.0 ±		72.2	-1.4	-0.2	± 1.7	± 188.1	0.4	± 40.4		75.8	4.4	-0.6	± 4.4	± 352.6	0.2	± 6.4	
	± 1.6	± 1.7	0.9	± 1.5	± 2.4	0.2		± 2.7	0.3	1.2	0.1	± 44.9	0.1	± 1.1		± 0.3	0.1	0.1	0.1	± 0.7	0.1	± 0.2	
Tannic acid	42.5	29.9	-5.4	± 30.4	349.7	2.7 ±		69.8	0.3	3.2	± 3.2	± 83.5	0.5	± 41.6		75.7	2.5	4.3	± 4.9	± 420	0.3	± 4.4	
	± 2.0	± 1.3	0.5	± 1.2	± 1.2	0.4		± 3.2	0.1	1.4	1.4	± 5.4	0.1	± 0.8		± 0.1	0.1	0.1	0.0	± 0.8	0.1	± 0.5	
β-CD	46.2	28.4	-5.1	± 28.9	349.8	2.1 ±		71.7	-1.2	-0.7	± 1.5	± 294.9	0.4	± 40.2		76	4.1	-0.4	± 4.1	± 353.9	0.2	± 5.9	
	± 1.5	± 1.7	0.9	± 1.6	± 2.3	0.2		± 3.1	0.1	0.9	0.3	± 92.1	0.1	± 1.3		± 0.1	0.1	0.1	0.1	± 0.9	0.1	± 0.2	
Alginate	45.7	28.4	-5.1	± 28.9	349.8	2.2 ±		71.5	-1	-0.5	± 1.5	± 201.2	0.4	± 40.1		75.3	4.2	-0.5	± 4.2	± 353.6	0.2	± 5.8	
	± 1.6	± 1.3	1.2	± 1.1	± 2.8	0.2		± 3.3	0.4	1.4	0.3	± 61.9	0.1	± 1.5		± 0.2	0.1	0.1	0.1	± 0.9	0.1	± 0.3	
Oxalic acid	46.2	28.5	-5.1	± 29	349.7	2.1 ±		71.8	-1.5	-0.8	± 1.7	± 206.5	0.4	± 40.3		75.9	4.3	-0.9	± 4.4	± 348.3	0.2	± 6.1	
	± 1.9	± 1.6	1.0	± 1.4	± 2.4	0.3		± 3.4	0.1	0.5	0.2	± 16.4	0.1	± 1.1		± 0.2	0.1	0.1	0.1	± 0.2	0.1	± 0.4	
Gallic acid	46.9	27.9	-6.2	± 28.6	347.4	2.0 ±		71.7	-1.8	-0.5	± 2.1	± 192.8	0.4	± 40.0		75.3	4.4	-1	± 4.5	± 347.5	0.2	± 6.6	
	± 1.1	± 1.8	1.1	± 1.6	± 2.6	0.1		± 2.6	0.2	1.5	0.1	± 42.9	0.1	± 1.9		± 0.2	0.1	0.1	0.1	± 0.8	0.1	± 0.4	
Caffeic acid	46.4	28.2	-5.3	± 28.7	349.3	2.1 ±		70.4	-0.9	-0.8	± 1.2	± 214.5	0.4	± 39.0		73.7	6.4	0.3	± 6.4	± 363	0.3	± 7.2	
	± 1.6	± 1.8	1.2	± 1.6	± 2.9	0.2		2.0	0.6	0.8	1.0	± 17.9	0.1	± 0.3		± 0.3	0.1	0.1	0.0	± 0.5	0.0	± 0.1	
Metamord.	44.6	22.1	-9.1	± 23.9	350.7	1.9 ±		71.9	-0.8	0.3	± 1.0	± 42.1	0.3	± 36.9		71.7	8.5	-4.7	± 9.7	± 353.7	0.3	± 10.6	
SnCl ₂	± 1.0	± 0.9	0.4	± 0.8	± 2.5	0.1		± 0.8	0.2	0.7	0.3	± 4.1	0.0	± 1.9		± 0.2	0.0	0.1	0.0	± 0.8	0.0	± 0.4	
Alum	45.6	31.5	-3.3	± 31.7	337.7	2.2 ±		71.2	-0.8	1.9	± 2.1	± 285.1	0.4	± 41.6		73.5	5.2	1.8	± 5.5	± 330.9	0.3	± 6.5	
	± 0.8	± 0.4	0.5	± 0.4	± 1.3	0.1		± 0.2	0.1	0.7	0.6	± 79.4	0.0	± 0.6		± 0.3	0.1	0.2	0.1	± 0.3	0.1	± 0.2	
Tannic acid	48.4	38.3	-7.6	± 39.1	354	1.8 ±		76.5	-1.1	4.3	± 4.5	± 116.2	0.3	± 49.9		77.6	2.5	3.3	± 4.2	± 19.3	0.2	± 4.3	
	± 0.4	± 0.6	0.1	± 0.6	± 0.9	0.1		± 0.1	0.4	2.2	2.1	± 11.7	0.0	± 0.5		± 0.1	0.1	0.1	0.1	± 1.9	0.1	± 0.5	
β-CD	45.1	32.1	-3.6	± 32.3	353.6	2.3 ±		71.8	-0.5	1.9	± 1.9	± 109.7	0.4	± 42.4		74.2	5.1	2.0	± 5.4	± 24.1	0.3	± 6.1	
	± 0.3	± 0.4	0.2	± 0.4	± 0.9	0.0		± 0.2	0.1	1.0	0.9	± 9.6	0.0	± 0.6		± 0.2	0.1	0.1	0.0	± 2.3	0.1	± 0.2	
Alginate	45.3	31.9	-3.6	± 32.1	348.7	2.3 ±		71.6	-0.6	1.8	± 1.9	± 107.3	0.4	± 42.2		74.1	5.2	2.3	± 5.7	± 52.5	0.3	± 6.4	
	± 1.0	± 0.7	0.4	± 0.7	± 0.2	0.2		± 0.4	0.2	0.5	0.5	± 10.7	0.0	± 0.8		± 0.2	0.0	0.3	0.1	± 1.0	0.1	± 0.1	
Oxalic acid	45.8	23.6	-7.7	± 24.8	353.5	2.2 ±		72.9	-0.9	2.7	± 2.9	± 106.5	0.4	± 38.0		73.3	3.3	0.9	± 3.4	± 21.2	0.3	± 4.7	
	± 0.6	± 0.8	0.1	± 0.7	± 0.5	0.1		± 0.6	0.2	1.1	1.0	± 8.6	0.0	± 1.4		± 0.5	0.1	0.1	0.1	± 0.7	0.1	± 0.4	
Gallic acid	54.7	30.1	-9.3	± 31.5	342.0	1.0 ±		71.6	-0.7	1.9	± 2.0	± 110.3	0.4	± 36.9		74.0	5.1	2.0	± 5.5	± 14.9	0.3	± 6.3	
	± 0.1	± 0.2	0.3	± 0.2	± 0.7	0.0		± 0.3	0.2	0.9	0.8	± 9.6	0.0	± 0.3		± 0.3	0.1	0.1	0.1	± 1.1	0.0	± 0.4	
Caffeic acid	49.7	32.3	-4.8	± 32.7	342.8	1.6 ±		67.4	1.9	0.7	± 2.1	± 113.7	0.5	± 35.7		69.8	14.1	3.2	± 14.5	± 21.4	0.5	± 12.7	
	± 0.5	± 0.2	0.5	± 0.1	± 0.4	0.1		± 0.6	0.4	0.7	0.7	± 12.7	0.0	± 0.5		± 0.5	± 0.2	0.3	± 0.2	± 0.6	0.1	± 0.4	

Table 3.5: The colorimetric properties (D65/10) and color strength of dyed (pre- and metamordanted, washed (according to ISO105-E01 and subjected by light test ISO105-B02 (uncertainties expressed as standard deviation ($n = 3$)).

	After Washing ISO105-E01							After light test ISO105-B02						
	L*	a*	b*	C*	h	K/S	ΔE^*	L*	a*	b*	C*	h	K/S	ΔE^*
Premord.														
Control	56.6 ± 0.9	13.9 ± 2.3	-5.1 ± 0.1	15.0 ± 2.1	339.5 ± 3.5	1.1 ± 0.1	18.9 ± 3.0	61.9 ± 0.1	14.0 ± 0.1	-3.9 ± 0.0	14.5 ± 0.1	344.4 ± 0.1	0.7 ± 0.0	22.0 ± 1.2
SnCl ₂	30.7 ± 0.6	14.3 ± 0.5	-13.1 ± 0.5	19.4 ± 0.6	317.6 ± 1.1	4.9 ± 0.2	9.7 ± 2.3	40.7 ± 0.1	15.0 ± 0.1	-14.3 ± 0.1	20.7 ± 0.1	316.4 ± 0.2	2.5 ± 0.0	14.0 ± 0.7
Alum	57.8 ± 0.6	12.0 ± 1.1	-5.1 ± 0.1	13.1 ± 1.0	336.9 ± 2.1	1.0 ± 0.0	19.8 ± 0.7	62.4 ± 0.3	13.3 ± 0.1	-3.5 ± 0.0	13.8 ± 0.1	345.3 ± 0.1	0.7 ± 0.0	21.8 ± 1.5
Tannic acid	51.9 ± 1.0	14.7 ± 1.0	-4.2 ± 0.5	15.3 ± 1.1	344 ± 0.7	1.4 ± 0.1	18.0 ± 2.2	54.7 ± 0.1	21.2 ± 0.1	-6.1 ± 0.1	22.1 ± 0.1	344.1 ± 0.2	1.1 ± 0.0	15.0 ± 1.5
β -CD	56.6 ± 1.3	12.9 ± 1.6	-5.3 ± 0.2	14 ± 1.4	337.3 ± 3.1	1.1 ± 0.1	18.7 ± 3.0	63.2 ± 0.1	13.5 ± 0.1	-3.5 ± 0.0	13.9 ± 0.1	345.4 ± 0.1	0.7 ± 0.0	22.7 ± 1.6
Alginate	56.2 ± 1.4	14.0 ± 2.2	-5.0 ± 0.1	14.9 ± 2.1	339.9 ± 3.1	1.1 ± 0.1	17.9 ± 3.2	63.2 ± 0.1	13 ± 0.1	-3.5 ± 0.1	13.5 ± 0.1	344.8 ± 0.2	0.7 ± 0.0	23.4 ± 1.4
Oxalic acid	57.8 ± 1.0	11.4 ± 1.0	-5.3 ± 0.1	12.6 ± 0.9	334.9 ± 1.8	1.0 ± 0.1	19.8 ± 2.2	63.1 ± 0.2	13.7 ± 0.1	-3.2 ± 0.0	14.1 ± 0.1	346.9 ± 0.1	0.7 ± 0.0	22.5 ± 1.4
Gallic acid	56.7 ± 0.9	13.0 ± 1.1	-4.4 ± 0.2	13.8 ± 1.0	341.4 ± 2.5	1.0 ± 0.1	18.4 ± 1.1	60.9 ± 0.2	15.5 ± 0.2	-4.4 ± 0.0	16.1 ± 0.1	344.2 ± 0.1	0.8 ± 0.0	18.8 ± 1.7
Caffeic acid	56.7 ± 1.0	13.0 ± 0.8	-4.4 ± 0.3	13.8 ± 0.7	341.4 ± 2.3	1.0 ± 0.1	18.4 ± 2.6	60.1 ± 0.2	16.9 ± 0.2	-3.2 ± 0.1	17.2 ± 0.2	349.2 ± 0.1	0.8 ± 0.0	17.9 ± 1.5
Metamord.														
SnCl ₂	46.4 ± 3.1	15.0 ± 0.3	-13.5 ± 0.3	20.2 ± 0.5	339.5 ± 3.5	1.7 ± 0.4	9.0 ± 1.1	66.7 ± 0.2	10.2 ± 0.1	-5.7 ± 0.1	11.6 ± 0.0	330.9 ± 0.3	0.4 ± 0.0	25.4 ± 1.1
Alum	56.2 ± 0.8	17.4 ± 1.4	-6.0 ± 0.5	18.4 ± 1.2	318.1 ± 0.1	1.0 ± 0.1	17.8 ± 2.4	59.1 ± 0.0	17.6 ± 0.1	-3.7 ± 0.0	18.0 ± 0.1	348.1 ± 0.0	0.8 ± 0.0	19.4 ± 0.8
Tannic acid	56.8 ± 0.1	24.0 ± 0.8	-7.2 ± 0.2	25.0 ± 0.8	340.8 ± 3.0	1.0 ± 0.1	16.7 ± 0.4	56.8 ± 0.1	25.3 ± 0.0	-7.6 ± 0.0	26.4 ± 0.0	343.3 ± 0.0	0.9 ± 0.0	15.5 ± 0.8
β -CD	55.3 ± 1.1	18.7 ± 1.4	-5.4 ± 0.7	19.5 ± 1.1	343.1 ± 2.0	1.1 ± 0.1	16.9 ± 1.9	61.9 ± 0.1	14.6 ± 0.1	-4.4 ± 0.0	15.2 ± 0.1	343.2 ± 0.1	0.7 ± 0.0	24.2 ± 0.4
Alginate	53.9 ± 1.5	19.0 ± 1.1	-5.8 ± 0.4	19.9 ± 0.9	343.3 ± 0.1	1.2 ± 0.1	15.7 ± 2.9	63.0 ± 0.1	14.2 ± 0.1	-4.2 ± 0.1	14.8 ± 0.1	343.4 ± 0.2	0.6 ± 0.0	25.0 ± 1.1
Oxalic acid	54.5 ± 1.3	17.8 ± 0.9	-9.2 ± 0.4	20.1 ± 0.8	343.7 ± 3.2	1.1 ± 0.1	10.5 ± 2.4	66.4 ± 0.2	11.4 ± 0.2	-5.9 ± 0.1	12.9 ± 0.2	332.6 ± 0.1	0.5 ± 0.0	24.0 ± 0.7
Gallic acid	65.4 ± 0.8	17.6 ± 0.8	-8.3 ± 0.4	19.5 ± 0.7	332.8 ± 1.6	0.5 ± 0.1	16.5 ± 1.3	62.5 ± 0.1	22.3 ± 0.1	-6.9 ± 0.0	23.3 ± 0.1	342.8 ± 0.0	0.6 ± 0.0	11.3 ± 0.2
Caffeic acid	59.1 ± 0.6	22.0 ± 0.3	-5.7 ± 0.3	22.8 ± 0.2	334.9 ± 1.4	0.8 ± 0.1	14.0 ± 0.6	65.4 ± 0.1	19.7 ± 0.1	0.7 ± 0.1	19.7 ± 0.1	2.1 ± 0.2	0.6 ± 0.0	21.0 ± 0.3

Table 3.6: Fastness values of staining and color change (CC) of pre- and metamordanted cotton samples according to ISO105-C06 and ISO105-E01 and light test (ISO105-B02) (CDA: diacetate, CO: cotton, PA: nylon, PES: polyester, PC: polyacryl, WO: wool).

ISO105-C06														ISO105-E01														ISO105-B01													
Premord.	CDA	CO	PA	PES	PAN	WO	CC	CDA	CO	PA	PES	PAN	WO	CC	CDA	CO	PA	PES	PAN	WO	CC	CDA	CO	PA	PES	PAN	WO	CC													
Control	4/5	4	5	5	5	4	2	3/4	2/3	2/3	3	3	3/4	3	3/4	2/3	2/3	3	3	3/4	3	3	3/4	3	3	3	3/4	3	1/2												
SnCl ₂	5	4/5	5	5	5	5	2/3	3/4	3	4	4/5	4	5	4/5	3/4	3	4	4/5	4	5	4/5	3	3	4	4/5	4	5	4/5	3												
Alum	5	4	4/5	5	5	4/5	1/2	3/4	2/3	2	3	3/4	4	2	3/4	2/3	2	3	3/4	4	2	3/4	2/3	2	3	3/4	4	2	1/2												
Tannic acid	5	4/5	5	5	5	5	2	3/4	2/3	2/3	4	4	3	3	3/4	2/3	2/3	4	4	3	3	3	3/4	2/3	4	4	3	3	3												
β-CD	5	4/5	4/5	5	5	4/5	1/2	4	3	2/3	4	4	3/4	2/3	4	3	2/3	4	4	3/4	2/3	4	3	2/3	4	4	3/4	2/3	1/2												
Alginate	5	4/5	4/5	5	5	4/5	1/2	4	3	2/3	4	4	3/4	2/3	4	3	2/3	4	4	3/4	2/3	4	3	2/3	4	4	3/4	2/3	1/2												
Oxalic acid	5	4/5	4/5	5	5	4/5	1/2	4	3	2/3	4	4	3/4	2/3	4	3	2/3	4	4	3/4	2/3	4	3	2/3	4	4	3/4	2/3	1/2												
Gallic acid	5	4/5	4/5	5	5	4/5	1/2	4	3	2/3	4	4	3/4	2/3	4	3	2/3	4	4	3/4	2/3	4	3	2/3	4	4	3/4	2	2/3												
Caffeic acid	5	4/5	4/5	5	5	4/5	1/2	4	3	3	4	4	3/4	1/2	4	3	3	4	4	3/4	1/2	4	3	3	4	4	3/4	1/2	2/3												
Metamord.																																									
SnCl ₂	5	4/5	4/5	5	5	4/5	2	4	2/3	4	3/4	3/4	4/5	4	4	2/3	4	3/4	3/4	4/5	4	4	2/3	4	3/4	3/4	4/5	4	2												
Alum	5	4	4/5	5	5	4/5	2	3/4	2	3	3/4	3	3	3	3/4	2	3	3/4	3	3	3	3	3/4	2	3	3/4	3	2	2												
Tannic acid	5	4/5	4/5	5	5	4/5	1	3	1/2	3	3	2	3	3	3	1/2	3	3	2	3	3	3	1/2	3	3	2	3	3	4												
β-CD	5	4/5	5	5	5	4/5	1/2	3/4	1/2	2/3	3	3	3	3	3/4	1/2	2/3	3	3	3	3	3	3/4	1/2	2/3	3	3	3	2	2											
Alginate	5	4	4/5	5	5	4/5	1/2-2	3/4	2	2	3	2/3	3	3/4	3/4	2	2	3	2/3	3	3/4	2	2	3	2/3	3	3/4	2	2												
Oxalic acid	4/5	3/4	5	5	5	4/5	1/2	3	2	2/3	3	2/3	2	3	3	2	2/3	3	2/3	2	3	3	2	2/3	3	2	2	2/3-3	1	1											
Gallic acid	4/5	3	5	5	5	4/5	1/2	3	1/2	3	3	2	3	3	3	1/2	3	3	2	3	3	3	1/2	3	3	2	3	2-2/3	4	4											
Caffeic acid	4/5	4	4/5	5	4/5	4/5	2	3	1/2	3	3	2	3	2	3	1/2	3	3	2	3	2	3	1/2	3	3	2	3	2/3	3	3											

3.3.3 Modeling of Adsorption

The following section describes the results obtained for modeling of adsorption isotherm systems, which represents the event associated with the mobility of a substance from aqueous environments to a solid material at constant temperature and pH.

Adsorption isotherms

The data obtained from the dilution experiment (section 3.3.1.4) allows the fitting of isotherm models to study the adsorption mechanism (Figures 3.4A to 3.4C), the important parameters derived from the different isotherm models are described in Table 3.7. The Langmuir separation factor R_L ($= \frac{1}{1+K_L C_0}$) is 0.97, which means adsorption is favorable. The saturation level is theoretically fitted by Langmuir's Q_L -value in Table 3.7. This value can be validated if more concentrated blueberry extracts are used for dyeing cotton till the maximum saturation level is attained. In this dyeing study, a simple cost-effective aqueous extraction was applied over organic solvents as dyeing commonly occurs within aqueous conditions and maximizing yield was not the main objective. The Freundlich heterogeneity factor n shows a slightly higher value than one, indicating a linear adsorption. The two three-parameter models yield similar results for their corresponding isotherm parameters. The χ^2 values were lower compared to Langmuir and Freundlich isotherms, providing the best fit to the experimental data. However, the standard deviations for two Redlich-Peterson's variables, a_R and β , were too large for correct interpretation, while the Sips model yields smaller standard deviations and thus, representing the best isotherm model for these data. The exponential parameter n_s , also indicates that the Sips model reduces to the Langmuir model. The solid solute adsorption isotherms can also be classified into different classes: S, L, H and C curves. This classification is useful for interpreting the adsorption mechanism and solute orientation, identifying any impurities or associated solute within the solution and measuring the specific surface area of a solid [345]. From Figures 3.4C and 3.4D, the q_e vs C_e plot resembles the C curve with a less steep slope visible after the inflection point. The C curve is characterized by a constant partition of solute between the dyebath solution and the cellulose substrate. The derived parameter K_s represents the partition coefficient and this low value obtained results in a negative $\log P$ (-1.3), indicating the hydrophilicity of this dye molecule, which was evidenced by the ISO105-E01 wash test. Bhat et al. [346] calculated $\log P$ values of 86 arylamine dyes from the color index (CI) and found a distribution where 75% of these dyes attained values between 3 to 6 and 35% were above 5, illustrating the

more hydrophobic character of synthetic dyes.

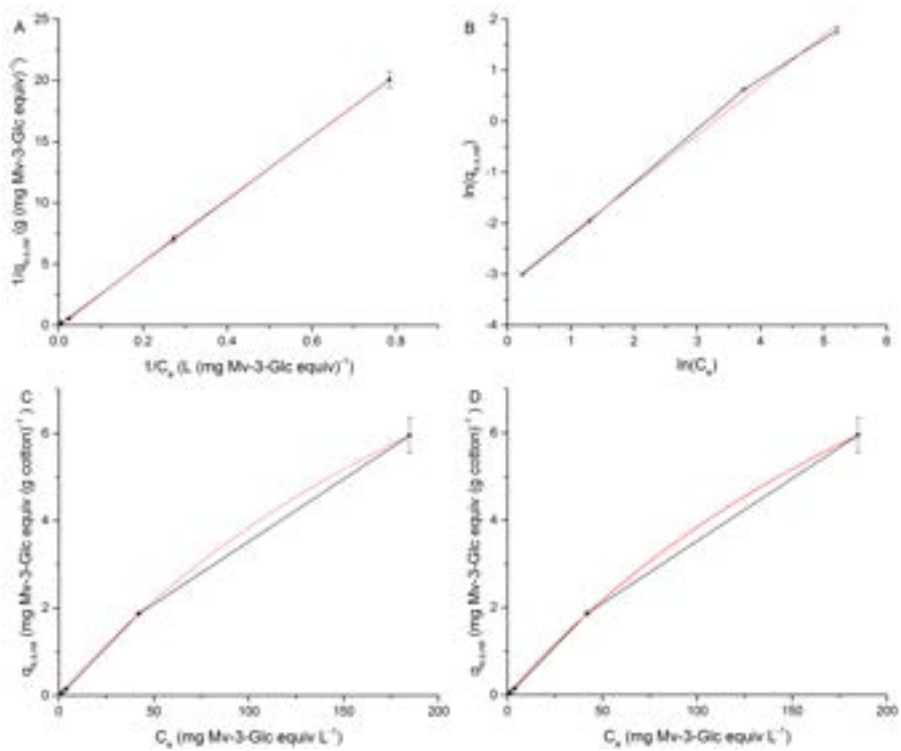


Figure 3.4: The isotherm models: Langmuir (A), Freundlich (B), Redlich-Peterson (C) and Sips (D).

Adsorption Kinetics

In order to study the adsorption kinetics of Mv-3-Glc, mathematical models were fitted to the experimental data from the dyeing time (section 3.3.1.2) to find the most optimal correlation between the adsorbed amounts of dye and time. The equations used were Lagergren, pseudo-second order and intraparticle diffusion (Table 3.1). Table 3.8 describes the results for the adsorption kinetic models applied for the adsorption of Mv-3-Glc at optimized conditions on cotton. The calculated equilibrium adsorption capacities from both models are also slightly deviated from the real value ($q_e = 6.1 \pm 0.2$ mg Mv-3-Glc (g cotton)⁻¹) as no appropriate correlation coefficients can be attained with the complete dataset. The intraparticle diffusion model can be depicted by plotting q_t as a function of $t_{1/2}$, which yields a multilinear plot referring to the three stage process of this model. As displayed in Figure 3.5C, the first part of the plot displays the mass transfer of the dye through the solution toward the external surface of the adsorbent, also called

Table 3.7: The isotherm parameters for the adsorption of Mv-3-Glc on cotton at 80 °C.

Two-parameter model	Parameters	Value	Three-parameter model	Parameters	Value
Langmuir	Q_L (mg g ⁻¹)	244.73 ± 425.32	Redlich-Peterson	a_R (L mg ⁻¹) ^β	0.0029 ± 0.020
	K_L (L mg ⁻¹)	0.047 ± 1.9		β	1 ± 1.14
	R_L	0.97 ± 0.51		K_R (L g ⁻¹)	0.050 ± 0.013
	R^2	0.99996		R^2	0.99993
	χ^2	0.22		χ^2	0.012
Freundlich	K_F (mg ^{1-$\frac{1}{n}$} L ^{$\frac{1}{n}$} g ⁻¹)	0.041 ± 0.0051	Sips	a_S (L mg ⁻¹) ^{n_s}	0.0029 ± 0.00029
	n_F	1.024 ± 0.040		K_S (L g ⁻¹)	0.050 ± 0.016
	R^2	0.99699		n_s	1.0 ± 0.10
	χ^2	0.14		R^2	0.99993
				χ^2	0.012

boundary layer diffusion. The last two parts could be described as intraparticle diffusion for which the last part is accounted to the final equilibrium stage. The slope of each linear part describes the rate of adsorption. It could be seen that the second part of adsorption is the fastest, which refers to the intraparticle diffusion of the dye through macro- and mesopores, while the third part displays the lowest slope and is related to the diffusion into the micropores of the substrate due to the saturation of the cotton fabric with the anthocyanin dye [347]. The latter is in this case also the rate-limiting step. From the adsorption modeling of anthocyanins on cotton, it can be concluded that this dyeing procedure is a pore size dependent diffusion process. The main interactions between cellulose and anthocyanins will be mainly governed by hydrogen bonding. The pore size distribution for cotton fabrics showed that majority of pores around 50 nm radius is present within cotton fabrics [348] and thus, explaining the higher adsorption rate in the second part of this model. The rate constants in this study are within the same order of magnitude as the study of Cheung et al. [347] on the adsorption of acid dyes onto chitosan, which also followed a pore size dependent mechanism.

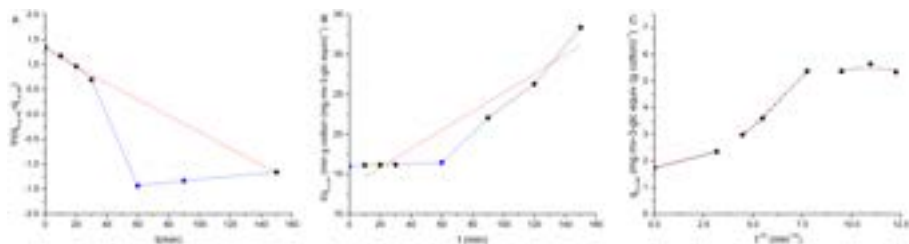
**Figure 3.5:** The kinetic models with from left to right: Lagergren (A), pseudo-second order (B) and intraparticle diffusion model (C). The blue data points were considered as outliers during fitting.

Table 3.8: The results for the parameters acquired from the adsorption kinetic models.

	Lagergren	Pseudo-second order	
q_e (mg Mv-3-Glc (g cotton) ⁻¹)	3.64	8.48	
k (^a : min ⁻¹ , ^b : g mg ⁻¹ min ⁻¹)	0.017 ^a	0.0010 ^b	
h (mg g ⁻¹ min ⁻¹)	-	0.074	
R^2	0.996	0.95	
χ^2	0.018	0.46	
Intraparticle diffusion model			
	Part1	Part2	Part3
k (mg g ⁻¹ min ^{$-\frac{1}{2}$})	0.19	0.74	-0.0048
C (mg g ⁻¹)	1.73	-0.39	5.5
R^2	1	0.997	0.0016
χ^2	0	0.0016	0.010

3.3.4 Molecular Modeling of Dye-Mordants Interaction

3.3.4.1 Interaction Energies from Static Calculations

In this section, static DFT calculations are performed to obtain insight into the strength of the intermolecular interactions between dye and mordant and to further explain the experimental observations. As mentioned earlier, it has been studied that stannous chloride, Sn(II)Cl₂, oxidizes to the +IV state in acidic environment [315], while diorganotin(IV)²⁺ compounds preferably forms octahedral complexes with flavonoids containing vicinal hydroxy moieties [318]. Consequently, the tin(IV) coordination complexes were built as octahedral complexes with the chlorine atoms positioned in the (E)-configuration and two bidentate anthocyanins, as anionic quinoidal bases optimized in appendix C, arranged within the same plane (Figure 3.6A). The aluminium salt was modelled as a metal-aquo complex, i.e., an Al(III) cation surrounded by six water molecules in an octahedral fashion whereby the bidentate anthocyanin ligand gradually substitutes two water molecules [281, 349]. For Cy-3-Glc, this yields the following complexes: [Al(Cy-3-Glc)(H₂O)₄]₂⁺, [Al(Cy-3-Glc)₂(H₂O)₂]⁺ and Al(Cy-3-Glc)₃ (Figures 3.6B to 3.6D). The Gibbs free energies of the coordination complexes, displayed in Table 3.9, reveal that tin is able to form the most stable complex with the dye molecules. There were no significant differences visible between the three types of anthocyanins (Cy-3-Glc, Dp-3-Glc and Pt-3-Glc), thus, preferential complexation could be excluded. The aluminium coordination complexes also form stable complexes, which is indicated by the negative Gibbs free complexation energy. Estévez et al. [281] obtained greater

complexation values for the aluminium complexes with cyanidin, but this might be ascribed to the approximations made within their calculations and lack of corrections for dispersion and BSSE. The same researchers performed a more thorough investigation (including the correction factors described above) with the anionic cyanidin-3,5-di-O-methyl molecule and multiple metal ions, and found that Co(III), Fe(III), Cr(III), and Al(III) are more favored to form a complex, but the values obtained are still high [282]. In general, the aluminium interaction energies obtained remain smaller compared to the tin complexes ($\Delta G_{\text{Sn-complex, avg}} = -952.83 \text{ kJ mol}^{-1}$). It is also worth mentioning that these Gibbs Free Energies obtained are indicative of nature as more detailed numbers can be obtained when hydration free energies would be included for each ionic compound through explicit solvation. Until now, researchers are able to parametrize hydration energies for neutral molecules, which match the experimental values, though elaboration to ionic compounds is more challenging [350]. In the end, these observations match the experimental findings where stabilizing properties of tin were superior to aluminium (section 3.3.2.1).

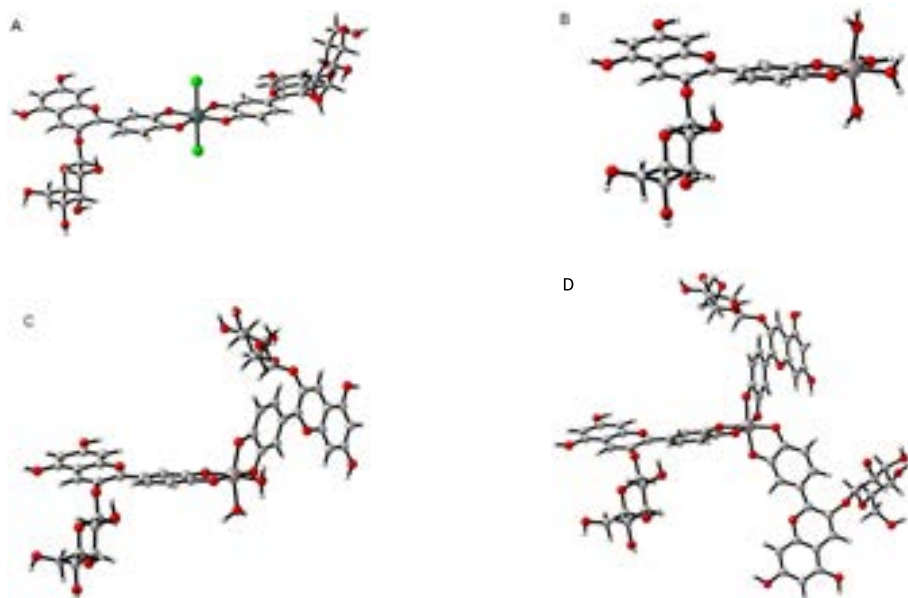


Figure 3.6: The 3D illustrations of tin and aluminium coordination complexes with cyanidin-3-glucoside: $\text{Sn}(\text{Cy}-3-\text{Glc})_2\text{Cl}_2$ (A), $[\text{Al}(\text{Cy}-3-\text{Glc})(\text{H}_2\text{O})_4]^{2+}$ (B), $[\text{Al}(\text{Cy}-3-\text{Glc})_2(\text{H}_2\text{O})_2]^+$ (C) and $\text{Al}(\text{Cy}-3-\text{Glc})_3$ (D) (B3LYP/DEF2TZVPP with PCM (water) and Grimme dispersion).

The second mechanism to improve the dye's affinity is the creation of anionic

sites on cotton, which could attract the positively charged dye molecule. Succinic acid was applied within literature [115], but due to the high pKa value of succinic acid, oxalic acid was opted within this study. Within experiments, the pH of the dyebath is set as such that oxalic acid is present as hydrogen oxalate, i.e., single negatively charged. Firstly, charge and population analyses were performed on hydrogen oxalate and Mv-3-Glc with Hirshfeld I and MBIS charges (Table C.2 and Figure C.10). According to the resonance structure of the flavylum cation, the positive charge is located on the oxygen of the pyrylium ring (compound A in Figure C.12). However, from the charge analysis, it can be shown that the pyrylium oxygen carries a partial negative charge (-0.20), while both carbon atoms on each side of the oxygen carry a partial positive charge (C2: 0.3 and C9: 0.45), which corresponds to the delocalized positive charge throughout the flavylum cation system. Consequently, ionic interactions are likely not to occur as described within literature. To prove this concept, nine different initial guess complexes containing hydrogen oxalate and Mv-3-Glc, in close proximity to each other, were investigated for potential intermolecular interactions, i.e., hydrogen bonding and ionic interactions. Only two conformations resulted into a negative complexation Gibbs Free Energy (Table 3.9 and Figure C.13). As illustrated in Table C.4, this can be ascribed to the large negative entropic contribution as complexation comes with the ordering of two compounds. Hence from these calculations, it was concluded that preferential associations between hydrogen oxalate and Mv-3-Glc are based on hydrogen bonds instead of ionic bonds. Overall, the interaction between the dye and hydrogen oxalate is relatively weak, confirming the experimental results where the application of this biomordant showed similar properties to the control sample.

3.3.4.2 Molecular Dynamics Simulations to Unravel Interactions between Tannic Acid, Dye Molecules and Solvent

Molecular dynamics simulations were performed to cope with the large and flexible structure of tannic acid, dye and interactions with the aqueous environment. A first MD simulation was applied on a simulation box wherein three dye molecules were positioned around the biomordant in a way that mutual interactions between the dyes were ruled out. It was noticed that one dye molecule diffused away from the complex. A second MD simulations was set up to investigate the interaction of tannic acid with a single dye molecule. Hydrogen bonds were visible between biomordant and dye. The most occurring state is a hydrogen bond interaction between the carbonyl oxygen of the ester function and the OH group at the C5

or C7 position or one of the glucose moiety. The combination of two H-bond interactions described above was also observed during certain portions of the MD simulation (Figure 3.9A).

However, in order to more realistically mimic the dyeing experiment, a more complex model was set up where also water was added in the simulation box, together with Mv-3-Glc and tannic acid. It is interesting to investigate in how far water will compete with Mv-3-Glc or tannic acid. Therefore, a solvent environment has been created in an explicit manner whereby two solvation layers of water molecules surround tannic acid and Mv-3-Glc molecule. The resulting H-bond interactions were calculated and expressed as a time average of the MD simulation for which a hydrogen bond was formed between dye or tannic acid with water molecules according to the geometrical criteria of Baker and Hubbard [351] ($\Theta_{H\cdots acceptor} > 120^\circ$ and $r_{H\cdots acceptor} < 2.5 \text{ \AA}$), while hydrogen bonds between water molecules were excluded. It was observed that the hydroxy groups of the aromatic moieties of tannic acid were largely forming hydrogen bonds with water molecules. Some of the carbonyl oxygen of the ester functions were also continuously undergoing hydrogen bonds with water, making those sites now unavailable for H-bond interactions with the dye (Figure 3.7A). Meanwhile, the C5 and C7 hydroxy groups of the dye were barely forming hydrogen bonds compared to the first MD simulation, this could be attributed to a local hydrophobic effect (Figure 3.7B). By visualizing the distance between the two molecules in terms of center of mass as a function of time, it can be seen that the A-ring is continuously covered by an aromatic moiety of tannic acid by a characteristic distance of π - π interactions of $3.5 \text{ \AA}$ (Figure 3.8A) [52]. The same trend was also visible for the B-ring (Figure 3.8B), while the C-ring did not show any overlap as the dye is aligned to the aforementioned π - π interactions (Figure 3.8C). The simulation also showed that when one aromatic moiety of tannic acid leaves the π - π stacking complex, another aromatic moiety fills in that position. Next to that, tannic acid also displays intramolecular π - π interactions (Figure 3.9B). Two optional MD simulations within a water box were performed with two and three dye molecules, but taking the concentration effect into consideration, it is the solvent based MD simulation with one tannic acid molecule and one dye that most closely represents the experimental dyeing conditions for tannic acid (Table C.5). From these solvent based MD simulations, we have demonstrated, in a qualitative manner, that the main intermolecular interactions between tannic acid and Mv-3-Glc are π - π interactions rather than hydrogen bonds. This is in agreement with studies conducted by Kunsági-Máté et al. [352, 353], wherein π - π interactions were the main intermolecular

interactions between malvidin-3-glucoside and other polyphenolic compounds. In general the number of π - π interactions made between tannic acid and the dye molecule, may be anticipated too low to effectively induce strong interactions as described by experimental studies (section 3.3.2.3). However, the higher color strength and a^* value obtained during pre- and metamordanting, respectively, and the good light fastness tests observed within experiments indicated a potential copigmentation effect, which is hereby confirmed.

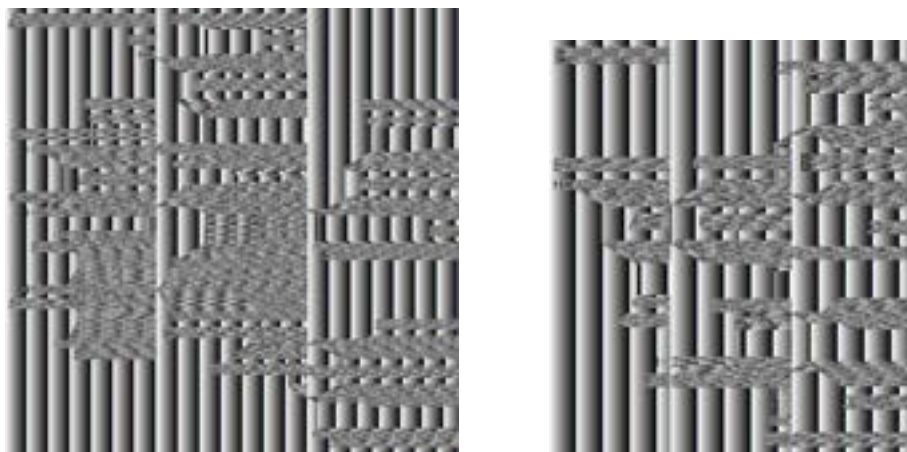


Figure 3.7: The time-averaged probability that a functional group of tannic acid (A) and Mv-3-Glc (B) forms a hydrogen bond interaction.

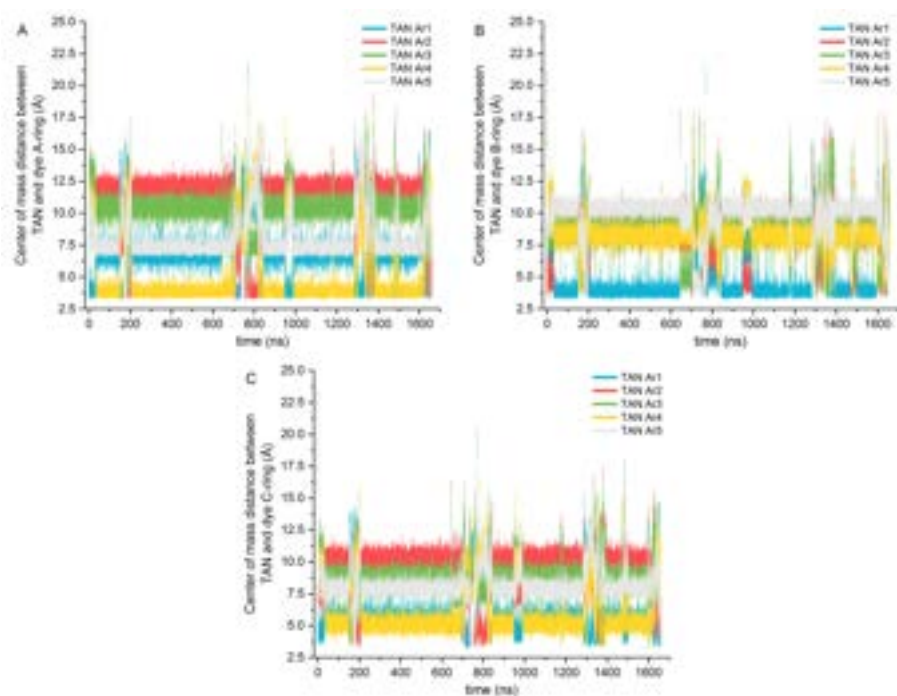


Figure 3.8: The visualisation of π - π interactions as interatomic distances between the aromatic groups of tannic acid and the A-ring (A), B-ring (B) or C-ring (C) of Mv-3-Glc.

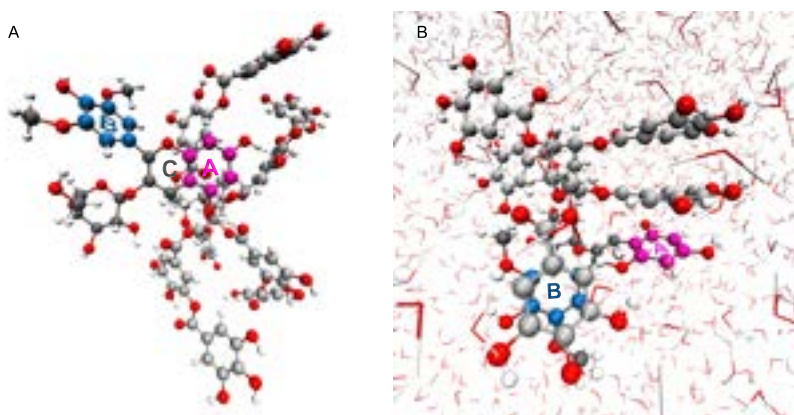


Figure 3.9: 3D illustrations of simulation boxes in the gas phase wherein hydrogen bonds are observed (A) and within a water box wherein π - π interactions are highlighted between tannic acid (silver) and Mv-3-Glc (grey backbone with A-ring: magenta and B-ring: blue) (B).

Table 3.9: The calculated counterpoise (CP) corrected complexation Gibbs free energy values (kJ mol^{-1}) of tin (Sn) and aluminium (Al) coordination complexes with the anthocyanin bidentate ligand.

Conformation	CP corrected $\Delta G_{\text{complex}}$ (kJ mol ⁻¹) ^a	BSSE (kJ mol ⁻¹)	Type of interactions	Figures
Static calculations				
Metal-ligand complexation ^b				
Sn(Cy-3-Glc) ₂ Cl ₂	-954.45	17.57	A Sn(IV) octahedral complex consisting of two anionic quinoidal base molecules with each attached as a bidentate ligand	Figure 3.6A
Sn(Dp-3-Glc) ₂ Cl ₂	-951.28	17.48		Figure C.8A
Sn(Pt-3-Glc) ₂ Cl ₂	-952.77	17.38		Figure C.9A
[Al(Cy-3-Glc)(H ₂ O) ₄] ⁺	-295.33	29.76	An Al(III) octahedral complex with one anionic quinoidal base molecule and 4 water molecules	Figure 3.6B
[Al(Dp-3-Glc)(H ₂ O) ₄] ⁺	-295.92	29.79		Figure C.8B
[Al(Pt-3-Glc)(H ₂ O) ₄] ⁺	-291.58	29.65		Figure C.9B
[Al(Cy-3-Glc) ₂ (H ₂ O) ₂] ⁺	-524.99	26.78	An Al(III) octahedral complex with two anionic quinoidal base molecules and 2 water molecules	Figure 3.6C
[Al(Dp-3-Glc) ₂ (H ₂ O) ₂] ⁺	-519.55	26.80		Figure C.8C
[Al(Pt-3-Glc) ₂ (H ₂ O) ₂] ⁺	-516.32	26.61		Figure C.9C
[Al(Cy-3-Glc) ₃]	-684.96	23.35	An Al(III) octahedral complex with three anionic quinoidal base molecules	Figure 3.6D
[Al(Dp-3-Glc) ₃]	-689.80	22.99		Figure C.8D
[Al(Pt-3-Glc) ₃]	-675.58	23.08		Figure C.9D
Biomordant ^c				
Mv-3-Glc & hydrogen oxalate ^d	-17.81	3.89	Dye-H(8) . . . O(6) (1.58 Å)	Figure C.13A
			Dye-H(7) . . . O(5) (2.17 Å)	
	2.17	3.35	Dye-H(8) . . . O(4) (1.70 Å)	Figure C.13B
			Dye-H(7) . . . O(5) (2.07 Å)	
	-9.33	4.22	Dye-H(12) . . . O(5) (1.53 Å)	Figure C.13C
			Dye-O(18) . . . H(7) (2.11 Å)	
	23.10	6.89	Dye-H(34) . . . O(3) (1.98 Å)	Figure C.13D
			Dye-H(14) . . . O(5) (2.33 Å)	
	15.09	5.74	Dye-H(53) . . . O(5) (1.60 Å)	Figure C.13E
	23.37	8.73	Dye-O(57) . . . H(7) (1.86 Å)	Figure C.13F
Dynamic simulations			Dye-O(15) . . . H(7) (2.90 Å)	Figure C.13G
	18.82	10.48	Dye-H(26) . . . O(4) (2.44 Å)	Figure C.13G
	15.17	11.01	Dye-H(32) . . . O(4) (2.30 Å)	Figure C.13H
			Dye-H(32) . . . O(6) (2.57 Å)	Figure C.13H
	23.88	10.67	Dye-O(24) . . . H(7) (2.49 Å)	Figure C.13I
Tannic acid	Qualitative		π - π interactions aromatic moieties Tannic acid aromatic moiety 4 and Mv-3-Glc A ring Tannic acid aromatic moiety 1 and Mv-3-Glc B-ring	Figure 3.9B

^a : ΔG values at 298.15 K, ^b : B3LYP/DEF2TZVPP with PCM and Grimme dispersion, ^c : B3LYP/6-311++G(d,p) with PCM and Grimme dispersion, ^d : labels are based on Figure C.10.

3.4 Conclusions

This chapter has explored the capabilities of anthocyanins as a natural dye on cellulose-based materials and considered 3 main objectives: to optimize the dyeing procedure with anthocyanins for cotton fibers, to investigate the potential of different types of biomordants, which might be equally or more effective compared to metal mordants and to interpret these experimental results by (molecular) modeling approaches. First, optimized dyeing conditions were based on finding an optimum between dye uptake, color strength, degradation of the natural dye and wash fastness. Therefore, dyeing cotton with anthocyanins is preferred at 80 °C for 60 min at a pH of 1.47 and a concentration 510.7 ± 9.5 mg malvidin-3-glucoside equivalents L^{-1} . Furthermore, fixation of oxalic acid on cotton through esterification was favored at pH 3.

Second, the use of metallic mordants was only successful for stannous chloride with premordanting, which successfully endured the wash- and light tests. The biomordants of interest did not seem to have the required properties to substitute this metal salt. The pH-sensitivity of anthocyanins could not be prevented by any of the biomordants, although it has been proven that the anthocyanins were still slightly present within the fabric when it has been reintroduced within acidic conditions, thus, the main effect is related to the pH of the detergent rather than washing off. This was observed with the wash test of water where a slight to large color loss was visible instead of an alteration. Whereas the biomordants did not show promising results related to the washing tests (ISO105-C06: $\Delta E^*_{Sn, pre} = 26.2$ and $\Delta E^*_{biomordants, pre} \geq 39.0$, ISO105-E01: $\Delta E^*_{Sn, pre} = 9.7$ and $\Delta E^*_{biomordants, pre} \geq 17.6$), the biomordants consisting of phenolic moieties, such as gallic acid and tannic acid, showed their added value in terms of antioxidant property in the light tests (ISO105-B02: $\Delta E^*_{control} = 22.0$, $\Delta E^*_{tannic\ acid, meta} = 15.5$ and $\Delta E^*_{gallic\ acid, meta} = 11.3$).

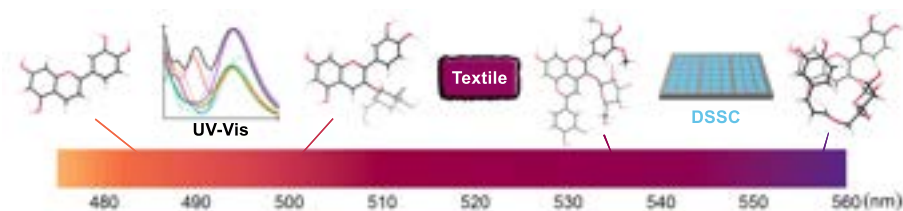
Previous findings were corroborated with molecular modeling simulations at different levels of complexity, to obtain insight into strength and type of interactions between the dye and the (bio)mordants. It can be concluded that the intermolecular interactions, hydrogen bonds and π - π interactions, were too weak in comparison to metal-ligand complexation ($\Delta G_{Sn, avg} = -953$ kJ mol^{-1} , $\Delta G_{Al} = [-690$ kJ mol^{-1} , -282 kJ $mol^{-1}]$). It was found that anthocyanins are not able to establish ionic bonds with oxalic acid, but only hydrogen bonds ($\Delta G_{hydrogen\ oxalate} = -17.8$ kJ mol^{-1}). Furthermore from the molecular dynamics simulations, it was concluded that the main intermolecular interactions between tannic acid and anthocyanins are governed by π - π interactions and not on hydrogen bonds, which

are overall also too weak to yield an efficient dying process.

With this combined experimental and theoretical work, the boundaries of anthocyanins in non-food applications on cotton were established. It is clear that it will be difficult for biomordants to be a real game changer for improving the affinity of natural dyes for textile substrates, despite some 'positive' stories in literature. The stability and affinity of a natural dye initially stands or falls by its molecular structure, notwithstanding analogous "Sn-anthocyanin" complexes can be explored via sustainable building blocks to fit the 'green story'. Currently, applications with anthocyanins can be deployed in aqueous environment provided that alkaline substances should be avoided and therefore, are relevant within short life cycle products (e.g., biodegradable products, pH indicator). Future approaches for anthocyanin dyeing could therefore involve enzymatic dyeing or reactive dyeing, by chemical modification. These pathways allow the formation of a covalent bond between dye and substrate, and might potentially be interesting due to the stronger interactions between various components.

Chapter 4

A Comparative Study on The Photophysical Properties of Anthocyanins and Pyranoanthocyanins



Phan K., De Meester S., Raes K., De Clerck K., and Van Speybroeck V.
Chemistry - A European Journal, **27**, 5956 – 5971 (2021).

A Comparative Study on the Photophysical Properties of Anthocyanins and Pyranoanthocyanins

4.1 Introduction

Anthocyanins depict the most colorful group amongst flavonoids and are known for their antioxidant properties and red till bluish colors in most flowers, higher plants, fruit and vegetables [4]. The variety of substitution patterns on the B-ring lead to six frequently occurring anthocyanidins, i.e., cyanidin (Cy), delphinidin (Dp), malvidin (Mv), pelargonidin (Pg), peonidin (Pn) and petunidin (Pt) (Figure 4.1). The most stable form of anthocyanins, the flavylium cation, commonly appears between pH 1 to 3 and displays the red color. Increasing the pH leads to isomerization via kinetic or thermodynamic pathways as described in section 1.2.1.

Anthocyanins are of high interest in various cosmetic, food, pharmaceutical and textile industries, mainly due to the potential health and sensorial benefits [354]. However, their relative poor chemical stability and affinity for several applications still prevent the full exploitation of these compounds (Chapter 3). They are especially prone to external conditions such as pH-fluctuations and temperature. Other factors that can affect their stability are concentration, light, oxygen, solvents, presence of enzymes, proteins or copigments (e.g., phenolic compounds and metallic ions) [50, 337]. Within fruits and plants, anthocyanins appear as acylated variants, which contribute to the chemical stability of the compound through intramolecular copigmentation. This induces a decrease in polarity and creates steric hindrance that prevents nucleophilic attack of the anthocyanins [59]. Several methods and strategies of stabilizing anthocyanins,



Figure 4.1: The different substitution patterns of the studied anthocyanins and pyranoanthocyanins in their flavylium cation form.

including copigmentation and encapsulation, are described by Cortez et al. [355]. Two peculiar classes of anthocyanins have attracted attention as they possess unique properties that could mainly overcome the aforementioned chemical instability: 3-deoxyanthocyanidins and pyranoanthocyanins (Figure 4.1). Apigeninidin (Ap) and luteolinidin (Lt) are the most common 3-deoxyanthocyanidins and consist up to 50% of the total anthocyanin content in black and brown sorghum [356]. They distinguish themselves from common anthocyanidins by the lack of a hydroxy substituent at the C3 position. This results in an improved protection against pH fluctuations, bleaching by food additives (e.g., ascorbic acid and sulphites) and thermal degradation [357]. Ap and Lt, displaying a yellow ($\lambda_{\max, \text{vis}} = 472.7 \text{ nm}$) and orange color ($\lambda_{\max, \text{vis}} = 489.8 \text{ nm}$) in acidic conditions, respectively, retain 51% of the original absorbance (measured at pH=1) at pH 4, while Cy still only possesses 12% of its initial absorbance. At pH 7, the 3-deoxyanthocyanidins and cyanidin still show an absorbance retention of 41% and 17%, respectively [356]. The pH change in combination with the addition of an acidulant at pH 5 in a watery extract leads to the precipitation of Ap [357], which limits the application in acidic drinks, but shows more potential as a natural dye or pigment.

Pyrananthocyanins are anthocyanin-derived compounds that are mainly formed during the ageing and maturation of red wines and port. These polyphenolic pigments are a result of a condensation reaction between anthocyanins and secondary metabolites derived from yeast fermentation such as pyruvic acid,

acetaldehyde and acetone (Figure 4.2). Pyranoanthocyanins can also be formed with other compounds that contain a polarizable double bond, e.g., cinnamic acids or vinylphenols. The reaction involves the formation of an additional D-ring between the C4 position of the flavylum cation and the C5-OH group. This newly formed D-ring causes a steric hindrance as such that pyranoanthocyanins exhibit a higher color intensity and greater stability to pH fluctuations, temperature, oxidative degradation and SO₂ bleaching [358]. The type of pyranoanthocyanins formed depends on a lot of factors such as wine-making techniques, composition, pH, storage temperature and time, acetaldehyde concentration, SO₂ concentration and aeration during storage [359]. This leads to a vast color range from yellow ($\lambda_{\max, \text{vis}} = 373 \text{ nm}$, oxovitisins) till turquoise blue ($\lambda_{\max, \text{vis}} = 676 \text{ nm}$, pyranoanthocyanin dimers) [358].

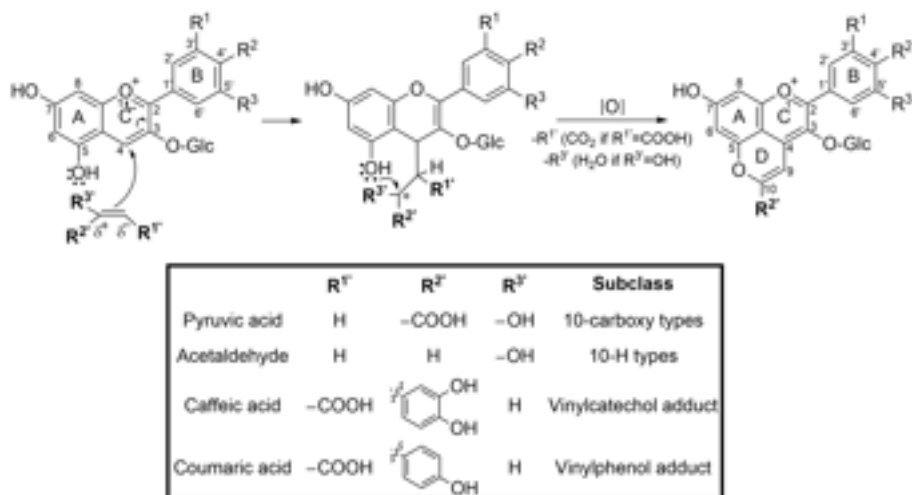


Figure 4.2: The reaction mechanism between anthocyanins and yeast metabolites or vinyl compounds resulting in the formation of pyranoanthocyanins.

Anthocyanins have furthermore gained importance in a variety of applications, for example as food additive to replace artificial colorants as they also carry beneficial health effects as antioxidants, antimicrobials and prevention of chronic diseases. Generally, anthocyanidins have a higher oxygen radical absorbance capacity (ORAC) compared to anthocyanins, and orthohydroxylation, methoxylation or acylation with phenolic acid of anthocyanins also contribute to a higher antioxidant effect [51]. In the non-food area, anthocyanins could substitute potentially allergenic and toxic synthetic dyes for textile industries [360], or as transition dye complexes for dye sensitized solar cells (DSSC) [361]. The working principle of DSSCs, based on TiO₂ as semiconductor and I⁻/I₃⁻ as redox couple,

consists of the light absorption of the dye, which provides photon-excited electrons that are transferred into the conduction band of the semiconductor. These injected electrons move further through the external circuit (load) to meet the platinum coated conductive glass counter electrode. The oxidized dye is regenerated through electron donation from the redox couple [362, 363, 364]. The cell performance mainly depends on the dye's absorption capacity and charge injection properties. Anthocyanins are already experimentally evaluated in DSSCs, reaching efficiencies up to 2.9% [361]. However, this is only about 24% of the efficiency obtained with conventional Ru(II)-based dye complexes [365]. The main requirement for a DSSC sensitizer material is photostability, i.e., the capability to undergo many redox cycles without decomposition, the ability to carry co-absorbents and having good chelating properties onto the TiO₂ surface such as the presence of a catechol group or carboxylic acid [361, 366, 367].

Within such applications, anthocyanins and pyranoanthocyanins are frequently identified and subjected to structure elucidation by means of high-pressure liquid chromatography (HPLC) or capillary electrophoresis coupled to various detection systems such as diode array detector, mass spectrometry (MS) and ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy [368, 369]. This, in order to analyse the composition in various food materials, but also to give quantitative information. A more simple and economical method to quantify the total anthocyanin content can be done with UV-Vis spectroscopy. It has been proven that a high correlation exists between UV-Vis, based on the pH differential method, and HPLC [370]. Furthermore, UV-Vis can also be used to experimentally determine the acidity constants [371]. Chemical analysis and quantification of the vast range of anthocyanin derivatives, however, is still a very complex challenge due to the costly and sometimes unavailable analytical standards. Molecular modeling approaches such as Density Functional Theory (DFT) and its time-dependent variant (TD-DFT) can reliably describe the optical or halochromic properties of such molecules at low computational cost and more importantly in a systematic way for a large group of compounds providing a standard for detection purposes [372]. Some modeling studies are already available on anthocyanins and pyranoanthocyanins. The geometrical structure, the formation of noncovalent charge transfer complexes due to copigmentation effects, acidity constants and antioxidant capacity, were investigated at DFT level for anthocyanins [367]. Similar topics are also studied for pyranoanthocyanins: geometry [373], antioxidant activity [374, 375], UV-Vis spectra [376, 377] and acidity constants [378].

However, the current literature about the photophysical properties of anthocyanins and pyranoanthocyanins is quite scattered using a variety of methods such as calculations within the gas phase [285] or different solvation models (i.e., PCM, CPCM, COSMO or SMD), different levels of theory, and scattered datasets such as single compound data [379] or synthetically modified anthocyanins to investigate the influence of the substituent on the color change [377, 380]. Herein, a systematic analysis was performed by evaluating three functionals (B3LYP, CAM-B3LYP and PBE0) for a large set of naturally occurring anthocyanin-based compounds along with structure elucidations to clarify the hypso- or bathochromic shifts observed within the experimental literature data. The data obtained from this fundamental approach provide target-specific solutions in real-life applications such as food additives/colorants, textile dyes, reference analytical standards and dye sensitizers.

This chapter is organized as follows: first of all an appropriate level of theory and effect of solvent is tested on anthocyanidins and anthocyanins. With the selected methodology, a library of 140 anthocyanin-based compounds are computed to generate the UV-Vis spectra. We systematically discuss the effect of structural changes between the different subclasses on the maximal absorption wavelength. In the last part of the chapter the results are used to link with the aforementioned applications, to show the potential use of the generated standard library of photophysical properties.

4.2 Computational Details

All calculations were performed with Gaussian 16 [248] using density functional theory (DFT), as this method offers the best computational efficiency and accuracy to study the spectral properties of medium and large dye molecules [372]. Geometry optimizations and frequency calculations were carried out to find the absolute minimum for each system. This was performed with the B3LYP [249, 250] (20% Hartree Fock (HF) exchange) functional along with the 6-311++G(d,p) basis set [381], which already proven its reliability in describing organic systems [251]. Furthermore, Grimme's third-generation dispersion corrections (GD3) were also added to account for the dispersion interactions [313]. Additional conformational analyses were carried out for B-ring rotamers of anthocyanins, E/Z-configurations of caffeoyl and coumaroyl acylated anthocyanins and B- and D-ring rotamers of pyranoanthocyanins (Figures D.5, D.6 and D.11 to D.14). Two solvation models were investigated to obtain the best accuracy: integral equation formalism polarisable continuum model (IEF-PCM) and its SMD variant, the latter showing smaller mean unsigned errors

in solvation free energies of neutrals and ions [382]. Furthermore, two solvents were considered for this study, i.e., methanol (MeOH, $\epsilon_{\text{dip}}=32.613$) and water ($\epsilon_{\text{dip}}=78.3553$). Methanol is a common and effective extraction solvent for anthocyanins, while an aqueous environment is also frequently applied (e.g., food-based products, dyeing and DSSC). UV-Vis spectra were generated with TD-DFT using 50 excited states. These calculations are based on the optimized ground state geometries, hence, vertical excitation energies are obtained. Two hybrid exchange-correlation functionals, B3LYP and PBE0[383] (20 and 25% HF exchange, respectively) were applied to evaluate the influence of the DFT functional on the UV-Vis spectra as it also showed good accuracy for dyes described by vertical transition energies [372]. Furthermore, a range-separated hybrid functional, CAM-B3LYP[384] (19% HF exchange for short-range and 65% for long-range interactions) was included to investigate the intramolecular π - π interactions that are involved in acylated anthocyanins as intramolecular charge transfer phenomena are often difficult to describe with common hybrid functionals [372]. The 6-311++G(d,p) basis set has been applied for TD-DFT calculations at all times. The anthocyanins studied are represented in the form of the flavylium cation (Figure 4.1), which is the most stable anthocyanin isomer. A schematic overview of the different substitution patterns that were considered is shown in Figure 4.1 and **labeled** according to Table D.1. The library consists of two 3 deoxyanthocyanidins (apigeninidin (Ap) and luteolinidin (Lt), (**1-2**)), the six most occurring anthocyanidins (cyanidin (Cy), delphinidin (Dp), malvidin (Mv), pelargonidin (Pg), peonidin (Pn) and petunidin (Pt), (**3-8**)), anthocyanins (3-glucosides of the six anthocyanidins, **9-14**), acylated anthocyanins (acylation at the glucose moiety with acetic acid (**15-20**), caffeic acid (**21-32**) and coumaric acid (**33-44**)), pyranoanthocyanins (pyruvic acid (**45-50**), acetaldehyde (**51-56**), vinylphenol (**57-62**) and vinylcatechol (**63-68**) derivatives of the six anthocyanins) and their acylated variants (**69-140**). The total number of anthocyanin-based compounds studied is 140. The analyses of the molecular orbital composition were carried out with Hirshfeld-I charges by calculating the atomic weight contribution to the HOMO and LUMO by means of Multiwfn [2, 3]. The software was also applied to calculate the net charge transfer between fragments upon the first two excited states using the Becke partition.

4.3 Results and Discussion

4.3.1 Photophysical Properties of Anthocyanins and their Derivatives by means of TD-DFT

4.3.1.1 Influence of Solvation Model on UV-Vis Properties

Due to the fact that many anthocyanin-based processing practices frequently include aqueous or solvent-related environment, a first screening on solvation model was performed. IEF-PCM and SMD implicit solvation models were applied, in which the solvent is modelled as an infinite continuous medium, characterized by a dielectric constant, surrounding the anthocyanin by a cavity. Additionally, the SMD model also considers short-range polarization and nonelectrostatic interactions such as cavitation, dispersion, and solvent structural effects (CDS) [382]. Firstly, UV-Vis data for this initial set of fourteen molecules, comprising 3-deoxyanthocyanidins, anthocyanidins and anthocyanins (**1-14**), were generated in the gas phase, water and methanol with two types of solvation model, i.e., IEF-PCM and SMD at the B3LYP level. The accuracy of the model was evaluated with experimental wavelength of maximal absorption in the visible region ($\lambda_{\text{max,vis}}$) from literature and certified analytical standards. The calculated UV-VIS spectra generally consist of two distinctive absorption bands: one located at the visible region, from 480 nm for 3-deoxyanthocyanidins to about 530 nm for anthocyanidins and anthocyanins, while the other manifests in the UV-region between 200 and 280 nm (or 260 till 280 nm experimentally) [293] (Figure D.1). As shown in Table 4.1, the mean absolute error (MAE) on $\lambda_{\text{max,vis}}$ is used as a measure for accuracy and includes only compounds for which experimental literature values are available (n values). Hereby, it could be observed that the inclusion of a solvent model is required as gas phase values showed a MAE of 34.62 nm or 0.18 eV with respect to the experimental literature values in water (Tables 4.1 and D.2). Among the solvation models, the SMD model attained smaller deviations (MAE: 0.061 eV) compared to PCM (MAE: 0.074 eV) (Table 4.1). Eilmes [385] also performed TD-DFT calculation for N,N-diethyl-4-nitroaniline in four common solvents using implicit, explicit and a combined solvation model and retrieved the best results with SMD. Kantchev et al. [386] also found the SMD model in combination with the B3LYP functional better performing compared to IEF-PCM for Pechmann dyes. The additional parametrized term, describing short-range interactions between solute and solvent molecules in the first solvation shell, within the SMD model is found more favorable for these positively charged anthocyanins compared to IEF-PCM [382].

Therefore, the SMD will be applied as main implicit solvation model in further calculations within this study.

Table 4.1: Mean absolute error (MAE) in nanometer (nm) and electronvolt (eV) of calculated $\lambda_{\max, \text{vis}}$ -values of anthocyanidins, 3-deoxyanthocyanidins and anthocyanins (compounds **1-14** of Table D.1) (B3LYP/6-311++G(d,p)) in order to justify the correct implicit solvation model.

		Gas ^a	Methanol		Water	
			PCM	SMD	PCM	SMD
Anthocyanidins + 3 deoxyanthocyanidins (1-8)	MAE (nm)	28.49 ^b	11.97 ^c	5.94 ^c	6.49 ^b	12.22 ^b
	MAE (eV)	0.15 ^b	0.056 ^c	0.027 ^c	0.031 ^b	0.058 ^b
Anthocyanins (9-14)	MAE (nm)	39.74 ^d	28.47 ^d	24.60 ^d	15.07 ^d	11.33 ^d
	MAE (eV)	0.20 ^d	0.13 ^d	0.11 ^d	0.073 ^d	0.055 ^d
Overall gas phase			MAE (nm)		34.62 ^e	
			MAE (eV)		0.18 ^e	
Overall PCM-model			MAE (nm)		15.58 ^f	
			MAE (eV)		0.074 ^f	
Overall SMD model			MAE (nm)		12.97 ^f	
			MAE (eV)		0.061 ^f	

^a: MAE with respect to experimental values in water, ^b: n=5, ^c: n=8, ^d: n=6, ^e: n=11, ^f: n=25

4.3.1.2 UV-Vis Properties of Anthocyanidins and Anthocyanins

From Table 4.1, it could be seen that the method applied corresponds very well to the experimental values from standards or from HPLC-MS identified fractions and therefore, attain smaller errors compared to the static calculations from Rustioni et al. [387] (MAE = 0.25 eV) with PCM and COSMO as solvation models. The trends observed in experimental literature values for this initial set were well reproduced by the calculations performed with the B3LYP functional and including the SMD implicit solvation model (Figure D.3). The main difference between anthocyanidins (**3-8**) and anthocyanins (**9-14**) on the one hand and 3-deoxyanthocyanins (**1-2**) on the other is the presence of a hydroxy group at the C3 position (R⁴ in Figure 4.1), which is responsible for a bathochromic shift of ± 40 nm (Figures D.1 and 4.9). This shift is reproduced by our calculations. The additional presence of a hydroxy group at C3' (R¹ in Figure 4.1) next to existing C4' (R² in Figure 4.1) hydroxy shows bathochromic shift of around 14 nm within experiments, the calculations revealed a similar shift of 11 to 20 nm (Table D.3). Adding another hydroxy group at C5' next to the hydroxy substituted C3' and C4' induces an 11 nm bathochromic shift, while the

calculations also showed a bathochromic shift of 3 to 9 nm. The influence of a methoxygroup on the B-ring remains limited with a small shifts of 1-5 nm in both ways. This small shift could not be reproduced accurately as the calculations showed a bathochromic shift from 5 up to 25 nm. The main difference between anthocyanidins (**3-8**) and anthocyanins (**9-14**) is the glycosylation. In this study, only the glycosylation at the C3 hydroxy group (R^4 in Figure 4.1) was taken into account. The different positions of glycosylation and the multiple appearances of different sugar moieties were not considered as they do not directly influence the chromophore, and hence, showing negligible shifts. The most important trend derives from the presence of the glucose moiety at the C3 position in anthocyanins, which leads to a 7 to 14 nm hypsochromic shift compared to the anthocyanidins (Figures 4.3, D.1 and D.2). The calculations display a higher hypsochromic shift of 28.84 ± 8.54 nm and 30.72 ± 4.69 nm for water and methanol with SMD implicit solvation, respectively (Figure 4.3, Table D.4). This can be ascribed to the deviation of the B-ring from planarity, which leads to reduction of delocalization efficiency with the B-ring [373]. The obtained dihedral deviation for anthocyanidins and anthocyanins in water and SMD solvation model are $11.95 \pm 6.01^\circ$ and $27.76 \pm 5.91^\circ$, respectively (Table D.5). This is in line with the dihedral angles obtained for anthocyanidins from Carvalho et al. [373].

The molecular orbital composition analysis of anthocyanins showed the electronic transition between the electron-rich B-ring (64% of the HOMO) to the electron-poor AC rings (80% of the LUMO) (Figure 4.4 and Table D.6). The analysis also clearly shows the effect of the substituents on the B-ring. The share of the B-ring to the HOMO ranges from 46% to 74%. The additional presence of a C3'-OH group next to the C4'-OH group increases the fragment's contribution by 22%. However, an additional OH group at the C5' position next to C3' and C4' hydroxy groups, only changes the percentage by 0.6, while a methoxygroup at that similar position will decrease the contribution by 8%. Meanwhile, a methoxygroup at the C3' position increases the contribution by 1%. The highest B-ring contribution (74%) was observed when two electron-donating methoxy groups were present.

4.3.1.3 UV-Vis Properties of Acylated Anthocyanins

As mentioned above, anthocyanin glycosyl acylation contributes to the chemical stability of anthocyanins. Acylated anthocyanins (**15-44**) have a lower polarity and higher molecular size, which creates extra steric hindrance that prevents a nucleophilic attack on anthocyanins. Two types of compounds are able to esterify

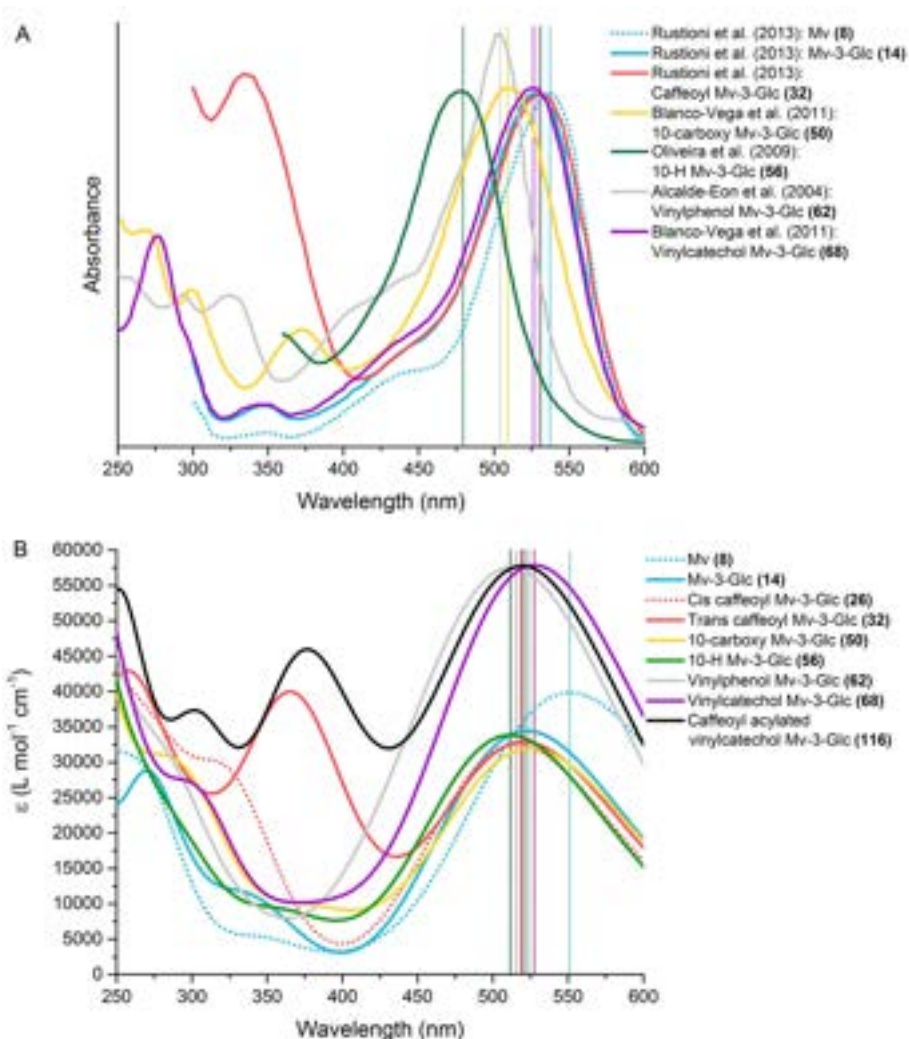


Figure 4.3: A comparison between experimentally measured (A) and calculated UV-Vis spectra of Mv-3-Glc derivatives, which are labeled according to Table D.1 (B3LYP/6-311++G(d,p) with SMD water) (B).

the glucose moiety at the C6'' position: aliphatic and aromatic acids. The latter are able to form intramolecular copigmentation complexes by π - π interactions. These aromatic copigments possess UV-absorbing and electron-donating properties, which improve the compounds' light stability [59]. In this section, the influence of acylation ($R^{6''}$ in Figure 4.1) by acetic acid (**15-20**), caffeic acid (**21-32**) and p-coumaric acid (**33-44**) as copigments will be discussed. Furthermore, the effect of E/Z-isomerization of the two aromatic acids on the UV

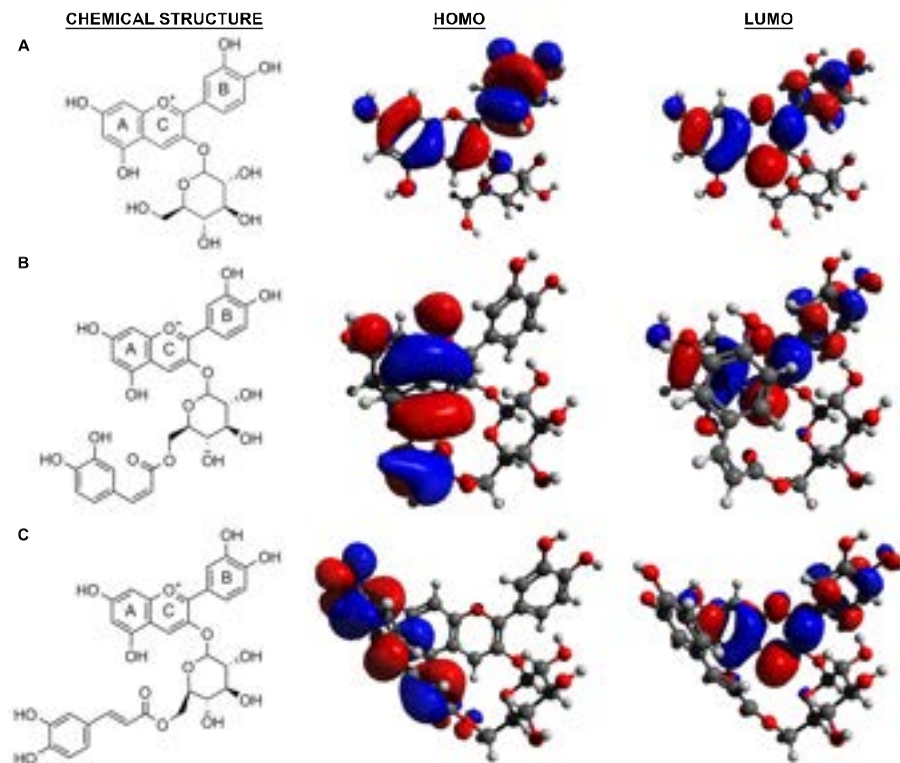


Figure 4.4: The molecular orbital composition of the HOMO and LUMO of Cy-3-Glc (A, **10**), (Z)-caffeoyl acylated Cy-3-Glc (B, **22**) and (E)-caffeoyl acylated Cy-3-Glc (C, **28**). Generally, the highest contributions for the HOMO originate from the B-ring and caffeoyl moiety for anthocyanins and aromatic acylated anthocyanins, respectively (Figure 4.1). The analyses of the molecular orbital composition were carried out with Hirshfeld-I charges by calculating the atomic weight contribution to the HOMO and LUMO by means of Multiwfn [2, 3].

Vis spectra is also considered.

Acylation with acetic acid

From analytical literature studies, aliphatic acylated anthocyanins with acetic acid (**15-20**) were mostly found. Therefore, UV-Vis properties of acetyl acylated structures were investigated. As acetic acid does not contain any conjugated bonds, no strong interaction and thus, large shifts are expected in the spectra compared to anthocyanins (**9-14**). The analysis of the molecular orbital composition confirmed this chemical intuition as the contribution to the HOMO of the AC fused rings, B-ring, glycosyl and acetyl group are 35%, 62%, 2% and 0.1%, respectively (Table D.7). The main intramolecular interaction is the

hydrogen bond between the carbonyl oxygen of acetyl acylated group and the C5 hydroxy group of the flavylum ion (Figure D.4). The experimental values display a bathochromic shift between 3-7 nm (Table D.8). The calculations show small hypsochromic shifts of 3 to 7 nm in water (SMD), with an exception of 23 nm for petundin. Overall, a comparison with six experimental literature values has lead to a MAE of 22.39 nm or 0.10 eV for this procedure. Generally, aromatic acyls have a stronger ability to stabilize acylated anthocyanins compared to aliphatic acyls due to the formation of intramolecular copigmented complexes [59].

Acylation with caffeic acid and coumaric acid

As aromatic acyls induce intramolecular copigmentation within acylated anthocyanins, the different types and strengths of the intramolecular interactions are further investigated. In order to find the minima between E/Z-isomerization, the rotational barriers of each individual caffeoyl (**21-32**) or coumaroyl (**33-44**) acylated anthocyanin were determined. In the gas phase, the E/Z barrier for caffeoyl acylated anthocyanins is less than 6 kJ mol⁻¹ (Figure D.5), while the barrier for coumaroyl acylated anthocyanins is 11 kJ mol⁻¹ (Figure D.6), both in favor of the (E)-conformer. The barriers for caffeoyl and coumaroyl acylated anthocyanins in methanol with SMD as solvation model were about 10 kJ mol⁻¹, while in water the caffeoyl and coumaroyl acylated conformers showed an average gap of 4.4 kJ mol⁻¹ and 11 kJ mol⁻¹, respectively (Table D.9). Both conformers do show an internal hydrogen bond between the C5-OH and the carbonyl oxygen of the ester function as a consequence of acylation (Figure 4.5). Internal hydrogen bonds are the main interactions observed within the (E)-conformers, while (Z)-conformers showed a better overlap of aromatic systems, which leads to stabilizing π - π interactions. Furthermore, it was proven that hydrogen bonds did not occur in the neighborhood of π - π stacking interactions [114]. However, these π - π interactions could not fully compensate the internal hydrogen bonding present in (E)-conformers. The smaller barrier for caffeoyl acylated anthocyanins than coumaroyl acylated anthocyanins can be ascribed to the presence of the additional hydroxy group, next to the phenol hydroxy group, which allows a more efficient formation of an internal hydrogen bond.

The calculated UV-Vis spectra of these compounds showed an increase in absorptivity within the region of 300-400 nm compared to non-acylated anthocyanins. For (Z)-caffeoyl or (Z)-coumaroyl acylated anthocyanins, this was more situated around 325 nm with the B3LYP functional. The same (E)-conformers displayed peaks at 360 and 370 nm for (E)-coumaroyl and (E)-caffeoyl acylated anthocyanins, respectively. This additional peak could be

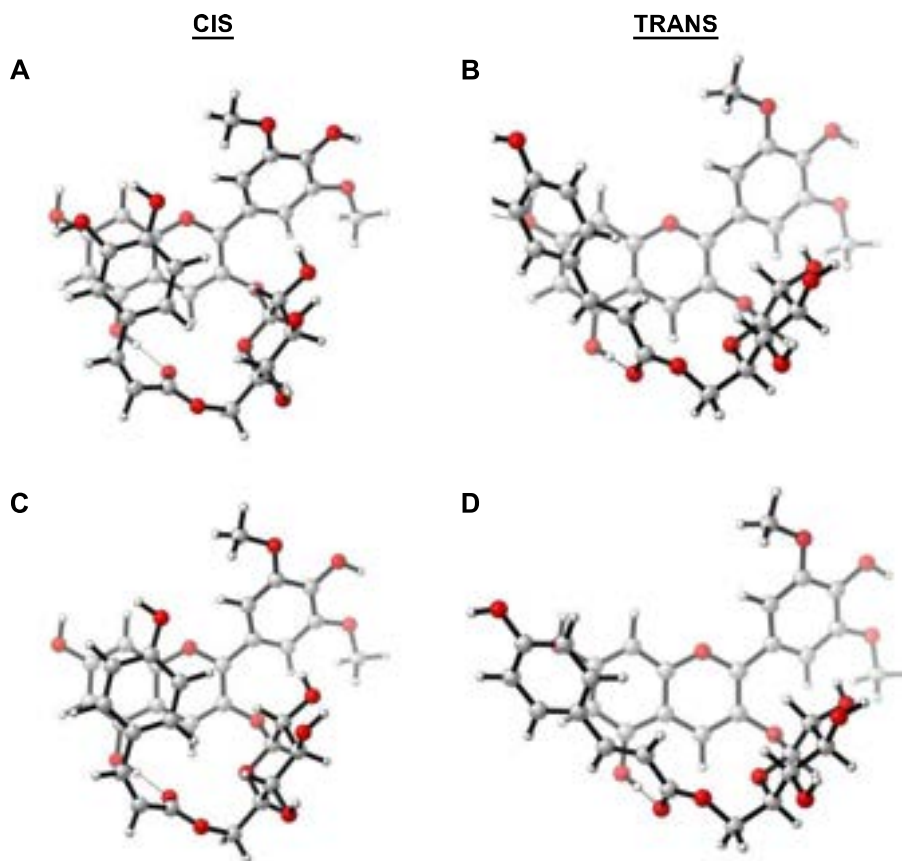


Figure 4.5: (Z)- (A, C) and (E)- (B, D) conformers of caffeoyl (Z: **26** and E: **32**) and coumaroyl (Z: **38** and E: **44**) acylated Mv-3-Glc (B3LYP/6-311++G(d,p), GD3, SMD solvation model and water as solvent).

ascribed to the absorbance maxima obtained from pure cinnamic acid based compounds, which is situated in the 310-325 nm region (Figures 4.3 and D.7 to D.10) [388]. The UV-VIS data generated with B3LYP showed that the functional is good for locating the energy of the first transition, also called the optical gap, which corresponds very well with the experimental values. However, the accompanying oscillator strength (f) suggests that this $S_0 \rightarrow S_1$ transition is not allowed ($f \approx 0$), but rather the $S_0 \rightarrow S_2$ (Table D.10). This intramolecular charge transfer transitions, described by the π - π interactions between the aromatic moiety of the acylated function and mainly the AC rings of the flavylum cation, has always been a drawback in TD-DFT [389]. Therefore, calculations with CAM-B3LYP, which could potentially better describe this phenomenon, were

also carried out, but the results showed even larger deviations of the S_1 transition (Table 4.2). The π - π overlap is clearly visible when analyzing the composition of the molecular orbital. Whereas the B-ring normally is the largest donor to the HOMO for anthocyanins, the caffeoyl moiety of these acylated anthocyanins contributes for 97% of the HOMO (Figure 4.4 and Table D.11). This phenomenon also induces a bathochromic shift of 5-18 nm as shown by experimental literature values (Table D.8). Generally, bathochromic shifts are larger with caffeic acid compared to p-coumaric acid, which is in agreement with Rustioni et al. [387]. Besides that, (Z)-caffeoyl also showed larger shifts compared to (E)-caffeoyl due to a better overlap with the AC-rings. This effect is less pronounced for p-coumaric acylated compounds.

4.3.1.4 UV-Vis Properties of Pyranoanthocyanins

This section describes the TD-DFT results of four types of pyranoanthocyanins (10-carboxy types (**45-50**), 10-H types (**51-56**), vinylphenol- (**57-62**) and vinylcatechol (**63-68**) derivatives) for each anthocyanin in water and methanol with the SMD implicit solvation model. Table 4.2 contains the results of the MAE of different functionals on 19 pyranoanthocyanins for which experimental literature $\lambda_{\text{max,vis}}$ -values were available. Looking at pyranoanthocyanins alone, PBE0 outperformed B3LYP by a small margin, while calculated values for CAM-B3LYP are about one order of magnitude higher (Table 4.2). The accuracy obtained is also better compared to Quartarolo and Russo [376] who applied the PBE0 functional on eight pyranoanthocyanins and obtained a total MAD of 0.12 eV in water (CPCM) for their calculations. Table D.12 displays mixed trends compared to experimental literature values. The trends were determined with own calculated values generated by means of B3LYP/6-311++G(d,p) with water and SMD as implicit solvation model. Literature study revealed that the extended conjugated system, due to the formation of an additional D-ring, did not result in a bathochromic shift compared to its precursors, the anthocyanins. On the contrary, pyranoanthocyanins showed lower wavelength of maximal absorption (Figures 4.3 and 4.9). This may be caused by the newly formed D-ring that creates a larger electron deficient ACD fragment, balancing with the contribution of the B-ring, which deviates from the coplanar conjugated system consisting of the A-, B-, and D-rings (Figure 4.6) [373]. The pyranoanthocyanins' dihedral deviation of the B-ring from planarity is 28° on average over the different pyranoanthocyanin derivatives (Table D.5). This is slightly higher in comparison to the angle of 20° for 10-carboxy types and 10-H types from Carvalho et al.

[373] that was calculated with MP2/cc-pVDZ and by substituting the sugar moiety with a methyl group.

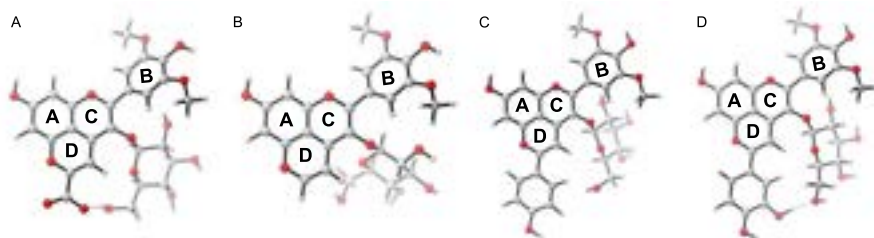


Figure 4.6: 3D molecular structures of malvidin pyranoanthocyanin derivatives: 10-carboxy (A, **50**), 10-H type (B, **56**), vinylphenol adduct (C, **62**) and vinylcatechol adduct (D, **68**).

Due to the deviations between experimental and the B3LYP-calculated anthocyanin values, the trends mainly showed small bathochromic shifts for 10-carboxy (**45-50**) and vinylphenol (**57-62**) types (Table D.12). Similar larger shifts were observed for vinylcatechol (**63-68**) types. The hypsochromic shifts for 10-H pyranoanthocyanins (**51-56**) were smaller than the experimental literature values, but showed good correspondence. Especially the 10-carboxy pyranoanthocyanins produced a MAE of 60 nm (0.25 eV with B3LYP and SMD water), which was also found by Quartarolo and Russo [376]. A closer study on the equilibrium forms of vitisin A by means of NMR titration and UV-Vis spectroscopy revealed that the first pKa of this compound lies around 1.09 ± 0.09 , which was associated with the proton of the 10 carboxyl group [390]. The second and third pKa values at 4.93 and 9.14 were connected to the 7-OH group and 4'-OH group, respectively. As these pyranoanthocyanins are formed at wine pH (≈ 3.6) [391], the complex mixture predominantly consists of the orange quinoidal 10-carboxyl form, which is truly measured instead of the fully protonated flavylum form. The calculations of these neutral 10-carboxyl compounds (**45-50**) corresponded better with these experimental values, resulting into a MAE of 5.73 nm (0.027 eV) (Table 4.2). The 10-carboxy types showed an average bathochromic shift of 14 nm with respect to 10-H-types (Table D.12 and Figures D.15 and D.16). This would be ascribed to the greater LUMO energy stabilization by the carboxylic substituent, which is absent in the 10-H types [376]. For the molecular orbital composition, pyranoanthocyanins were divided into four fragments: the central pyrilium containing fused rings (A, C and D), B-ring, glycosyl moiety and the fragment at the C10 position (R^5 in Figure 4.1) (Figure 4.7 and Tables D.13 to D.16). For the 10-carboxy types

(**45-50**), the B-ring showed the highest contribution (68%) to the HOMO, followed by the pyrilium containing fragment, the glycosyl and carboxylate group with 30%, 1.5% and 0.4%, respectively. The LUMO orbital composition displayed 80%, 13% and 6% for the central fused ring, B-ring and carboxylate group, respectively. The 10-H types (**51-56**) described a similar HOMO-LUMO composition with the lack of LUMO stabilization by the C10-fragment, which is only 1.2%. This closely matches the molecular orbital analysis, based on Mulliken charges, performed by Quartarolo and Russo [376]. The larger bathochromic shifts for vinyl adducts (**57-68**) can firstly be ascribed to the discrepancy between experimental and B3LYP-calculated $\lambda_{\text{max,vis}}$ -values as mentioned earlier, but also to the shared contribution between the B-ring and the phenol or catechol moiety at the 10-position to the HOMO for vinylphenol (**57-63**) and vinylcatechol adducts (**63-68**), respectively (Tables D.15 and D.16). Besides that, the dihedral angle between the catechol (21° on average with SMD water) and phenol (6° on average with SMD water) moiety to the ACD ring is smaller compared the B-ring dihedral angle, which causes a more efficient electron delocalization (Table D.5). Meanwhile for anthocyanins (**3-8**), 10-carboxy (**45-50**) and 10-H (**51-56**) pyranoanthocyanins, the main contribution comes solely from the B-ring.

Experimentally, there was also a small bathochromic shift of 6-8 nm (6.8 nm on average) noticed within the vinyl adducts (**57-68**) (Table D.12 and Figures D.17 and D.18). The additional ortho-positioned hydroxy group of vinylcatechol adducts (**63-68**) compared to vinylphenol adducts (**57-62**) is responsible for creating a larger electron rich moiety at the 10-position. This results in a larger net charge transfer to the ACD moiety, hence, a larger displacement to higher wavelengths. This bathochromic shift was well reproduced with our calculations (6-12 nm, 9.3 nm on average) (Table D.12). The contribution to the HOMO for vinylphenol types are highest for the B-ring (48%) followed by the ACD fused rings (35%) and the phenol moiety at the 10-position (15%). When looking at the vinylcatechol types the fragments' contributions were more evenly distributed with ACD fused rings, B-ring and catechol moiety accounting for 30%, 36% and 33% of the HOMO on average, respectively.

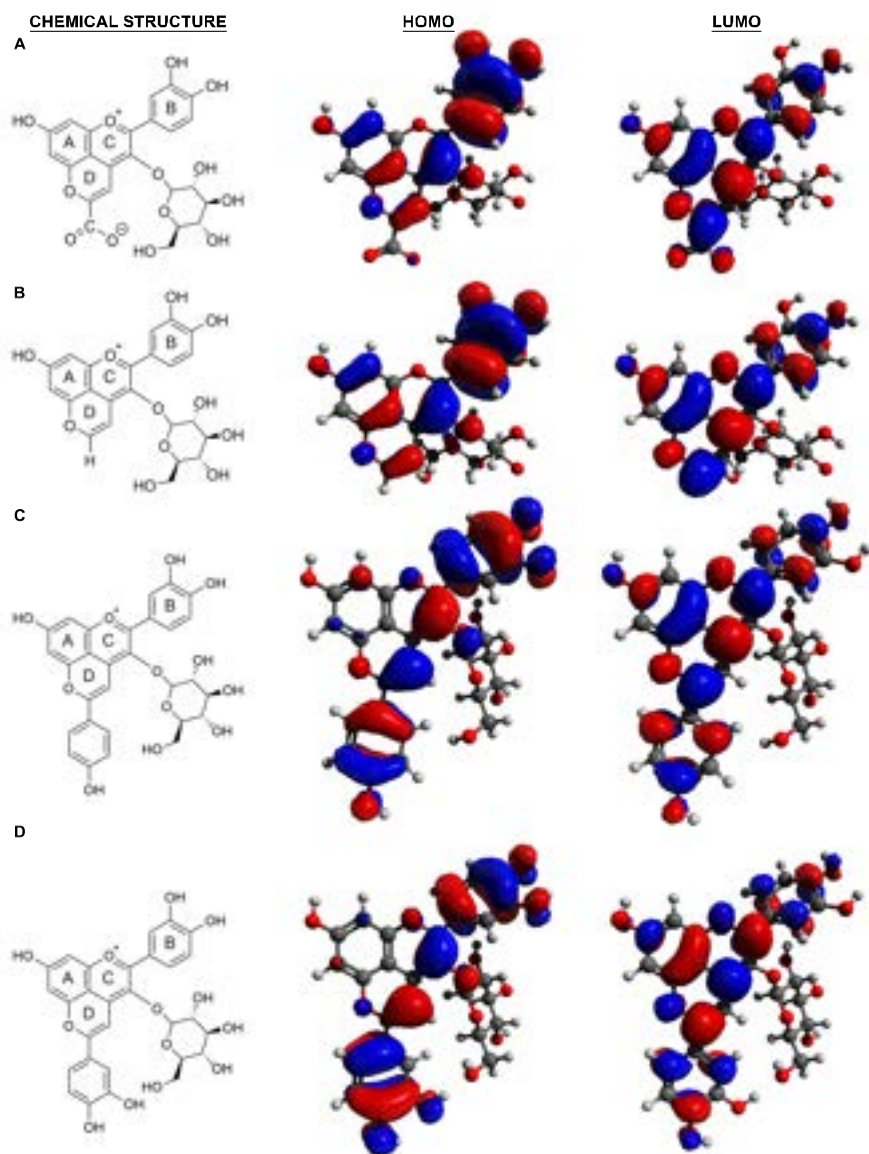


Figure 4.7: The molecular orbital composition of the HOMO and LUMO of pyranoanthocyanins 10-carboxy Cy-3-Glc (A, **46**), 10-H Cy-3-Glc (B, **52**), vinylphenol Cy-3-Glc (C, **58**) and vinylcatechol Cy-3-Glc (D, **64**). For the first two cases, the B-ring is the largest provider of the HOMO, while this contribution is shared with the 10-phenol or 10-catechol moiety for vinylphenol or vinylcatechol pyranoanthocyanins.

4.3.1.5 UV-Vis Properties of Acylated Pyranoanthocyanins

Blanco-Vega et al. [392] investigated the formation of wine pyranoanthocyanins through wine model reactions. The structure elucidation was performed by means of HPLC-DAD, which was further equipped with an electrospray ionization mass spectrometry (ESI-MS/MS). This ion trap mass spectrometer allows further fragmentation of pyranoanthocyanins with the loss of the glycosidic moiety, whether it was acylated or not. As such, this study also investigated the influence of acetyl, caffeoyl and coumaroyl acylation ($R^{6''}$ in Figure 4.1) on the four pyranoanthocyanin types (R^5 in Figure 4.1) discussed earlier. The trends from experimental literature values generally display small bathochromic shifts of 1-8 nm for acylated pyranoanthocyanins (**69-140**) with respect to pyranoanthocyanins (**45-68**) (Table D.18). The shifts between aliphatic and aromatic acyl groups are in the same range, which put to the conclusion that only (E)-conformers of aromatic acylated pyranoanthocyanins (**93-140**) were observed. The calculations displayed comparable shifts with experimental values for acetyl acylated pyranoanthocyanins (**69-92**). Only the acetyl acylated vinylphenol types (**81-86**) showed larger hypsochromic shifts (8-15 nm) (Table D.20). Caffeoyl acylated compounds (**93-116**) produced generally hypsochromic shifts between 1 and 20 nm compared to common pyranoanthocyanins (**45-68**). The coumaroyl acylated structures (**117-140**) generally displayed bathochromic shifts (4-26 nm) for the 10-carboxy (**117-122**) and 10-H (**123-128**) types, while the same vinylphenol (**129-134**) and vinylcatechol (**135-140**) derivatives showed hypsochromic shifts of 2-20 nm with respect to non-acylated pyranoanthocyanins (**45-68**). When experimental literature values of acylated pyranoanthocyanins (**69-140**) and acylated anthocyanins (**15-44**) were placed next to each other, hypsochromic shifts between 15 and 41 nm were observed for the former with respect to the latter (Table D.22). From our calculations, the acetyl acylated pyranoanthocyanins (**69-92**) showed mixed trends within the different pyranoanthocyanin types (Table D.24). Acetyl acylated 10-carboxy (**69-74**) and acetyl acylated vinylcatechol (**87-92**) types displayed bathochromic shifts of 7-12 nm and 12-31 nm, respectively. Meanwhile, acetyl acylated 10-H (**75-80**) and vinylphenol (**81-86**) types resulted in hypsochromic shifts of 3-10 and shifts of -7 till 7 nm, respectively. (E)-caffeoyl (**93-116**) and (E)-coumaroyl (**117-140**) acylated pyranoanthocyanins generally followed the same experimental trend with average hypsochromic shifts of 25 nm and 10 nm with regard to (E)-caffeoyl (**27-32**) and (E)-coumaroyl (**39-44**) acylated anthocyanins, respectively. As it was shown that acetyl moieties do not contribute to the HOMO, an in-depth

analysis of the molecular orbitals was performed for caffeoyl acylated vinylcatechol (**111-116**) and caffeoyl acylated (**105-110**) vinylphenol pyranoanthocyanins to investigate the different contributions from the different parts within the molecule. A similar dominant contribution was observed of the caffeoyl acylated group to the HOMO (87-97%) as for caffeoyl acylated anthocyanins (Figure 4.8 and Table D.25). Only for the Mv-3-Glc type the main contribution to the HOMO leaned more toward the B-ring (56%), ACD fused rings (26%) and 10-catechol moiety (17%). As illustrated in Table 4.2, the B3LYP functional also outperformed other functionals in these subclasses in terms of accuracy.

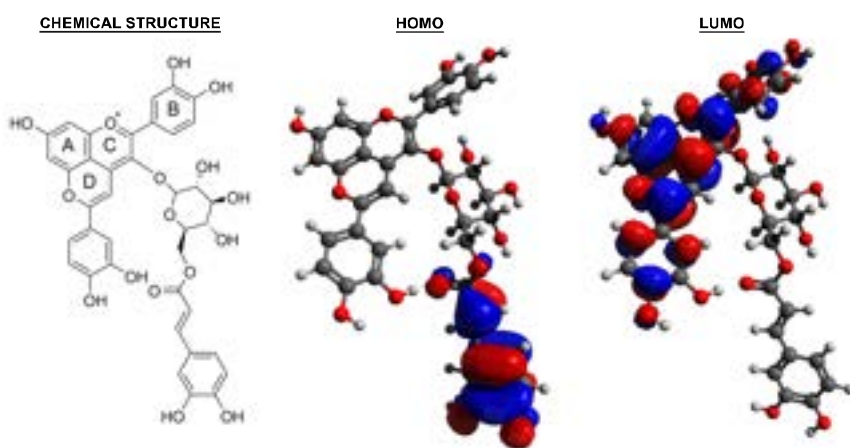


Figure 4.8: The molecular orbital composition of the HOMO (left) and LUMO (right) of caffeoyl acylated vinylcatechol Cy-3-Glc (**112**). Similar to acylated anthocyanins, the caffeoyl acylated moiety takes the largest share of the HOMO.

The optical properties of 140 natural anthocyanin-based compounds were evaluated with three functionals B3LYP, PBE0 and CAM-B3LYP (Table 4.2 and Figures 4.9 and D.3). From the large dataset, 101 compounds could be compared directly with experimental literature values (Tables D.2, D.27 and D.28). It could be stated that B3LYP is the most accurate functional to describe the photophysical properties of anthocyanin-based compounds. Even for acylated compounds where charge-transfer transitions were observed, the functional was able to locate the $\lambda_{\text{max,vis}}$ -values. The PBE0 functional is only more suitable to describe the non-acylated pyranoanthocyanins. Meanwhile, the long-range CAM-B3LYP functional overestimated the excitation energies leading to a blue shift of the $\lambda_{\text{max,vis}}$ -values. This can be ascribed to the higher percentage of long-range HF exchange. The color differences between the various anthocyanin subclasses are illustrated in Figure 4.9.

Table 4.2: Mean absolute error (MAE) of three different functionals (with a similar basis set 6 311++G(d,p)) applied for generating UV-VIS data of anthocyanidins, anthocyanins, acylated anthocyanins and pyranoanthocyanins with water and SMD solvation model. The error analyses were carried out for structures of which experimental values (n) were available. The calculations of the MAE for each anthocyanin subclass and functional are shown in Tables D.29 to D.36.

Compound class	Labels Table D.1	B3LYP		PBE0		CAM-B3LYP	
		MAE (nm)	MAE (eV)	MAE (nm)	MAE (eV)	MAE (nm)	MAE (eV)
Anthocyanidins	1-8	8.36 ^a	0.039 ^a	12.64 ^a	0.060 ^a	42.19 ^a	0.22 ^a
Anthocyanins	9-14	17.96 ^b	0.085 ^b	28.15 ^b	0.16 ^b	74.56 ^b	0.39 ^b
Acetyl acylated anthocyanins	15-20	22.39 ^c	0.10 ^c	38.58 ^c	0.19 ^c	83.36 ^c	0.44 ^c
(E)-caffeoyl acylated anthocyanins	27-32	10.56 ^{d, m}	0.045 ^{d, m}	24.67 ^{d, n}	0.11 ^{d, m}	87.82 ^d	0.46 ^d
(Z)-coumaroyl acylated anthocyanins	33-38	5.58 ^{e, m}	0.025 ^{e, m}	34.86 ^{e, n}	0.16 ^{e, m}	86.09 ^e	0.45 ^e
(E)-coumaroyl acylated anthocyanins	39-44	6.05 ^{e, m}	0.027 ^{e, m}	30.79 ^{e, n}	0.14 ^{e, m}	87.00 ^e	0.46 ^e
∑ Acylated anthocyanins		11.74 ^f	0.053 ^f	32.92 ^f	0.16 ^f	85.84 ^f	0.45 ^f
10-carboxy types	45-50	5.73 ^e	0.027 ^e	13.69 ^e	0.068 ^e	68.29 ^e	0.38 ^e
10-H types	51-56	10.91 ^d	0.055 ^d	8.61 ^d	0.046 ^d	59.13 ^d	0.35 ^d
Vinylphenol types	57-62	12.53 ^e	0.060 ^e	4.85 ^e	0.024 ^e	50.13 ^e	0.27 ^e
Vinylcatechol types	63-68	14.93 ^e	0.069 ^e	4.80 ^e	0.023 ^e	53.04 ^e	0.28 ^e
∑ Pyranoanthocyanins		10.71 ^g	0.051 ^g	8.27 ^g	0.042 ^g	57.89 ^g	0.32 ^g
Acetyl acylated pyranoanthocyanins	69-92	8.33 ^h	0.040 ^h	10.59 ^h	0.053 ^h	61.78 ^h	0.34 ^h
Caffeoyl acylated pyranoanthocyanins	93-116	6.07 ⁱ	0.029 ⁱ	8.95 ⁱ	0.058 ⁱ	65.75 ⁱ	0.37 ⁱ
Coumaroyl acylated pyranoanthocyanins	117-140	10.07 ^j	0.048 ^j	11.68 ^j	0.058 ^j	65.21 ^j	0.36 ^j
∑ Acylated pyranoanthocyanins		8.56 ^k	0.042 ^k	10.69 ^k	0.061 ^k	63.83 ^k	0.36 ^k
Total		10.75 ^l	0.049 ^l	17.49 ^l	0.085 ^l	65.50 ^l	0.35 ^l

^a : n=13, ^b : n=12, ^c : n=6, ^d : n=4, ^e : n=5, ^f : n=20, ^g : n=19, ^h : n=16, ⁱ : n=7, ^j : n=14, ^k : n=37, ^l : n=101
^m : with values from first excited state (S₀ → S₁), ⁿ : with values from second excited state (S₀ → S₂)

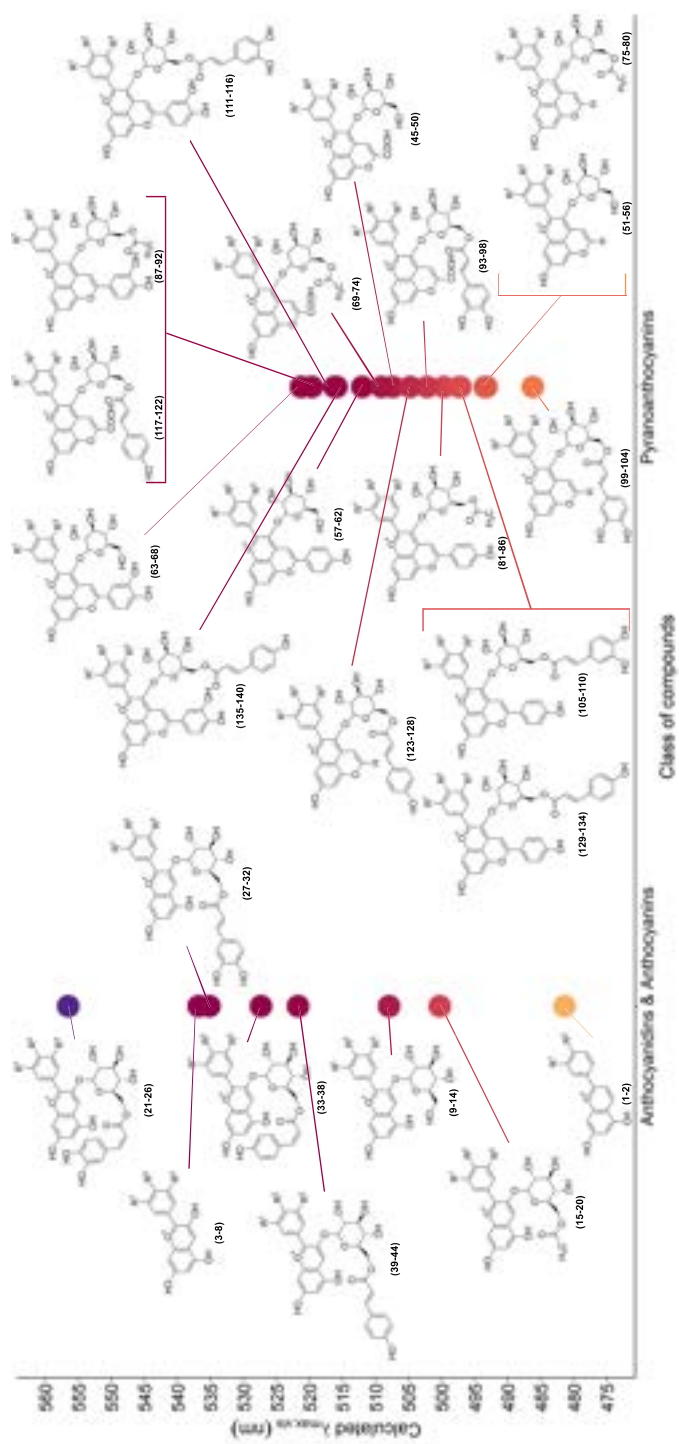


Figure 4.9: An overview of the various subclasses of anthocyanins and pyranoanthocyanins (in their flavylium cation form) based on their average $\lambda_{\text{max,vis}}$ -values and accompanying color, calculated with B3LYP/6-311++G(d,p) with SMD water solvation model. R^1 , R^2 and R^3 are according to the substitution pattern illustrated in Figure 4.1. The additional labels refer to the individual chemical structures shown in Table D.1.

4.3.2 A Tool for Food and Non-Food Applications

In this section, we highlight three applications for which the library of $\lambda_{\max, \text{vis}}$ -values and other photophysical properties obtained from theory can be used as a tool in providing target specific solutions: food chemistry for characterization and quantification purposes that rely on $\lambda_{\max, \text{vis}}$ -values and molar absorption coefficients (ϵ), natural dyes producing similar colors as established synthetic dyes in textiles, described by $\lambda_{\max, \text{vis}}$ -values and natural dye sensitizers for DSSCs, defined by orbital energy levels.

4.3.2.1 Food Additives/Colorants and Analytical Standards

Analytical standards are highly pure compounds and provide experimentalists certified reference data for quantification purposes. However, these compounds can be expensive and are not widely available. Therefore, $\lambda_{\max, \text{vis}}$ -values and molar absorption coefficients (ϵ), which is related to the oscillator strength (f), obtained from TD-DFT can be an alternative method providing the same information at low computational cost and in a pure environment [393]. The ϵ -values for anthocyanidins (**1-8**) and anthocyanins (**9-14**) extracted from the calculated UV-VIS spectra at $\lambda_{\max, \text{vis}}$ were compared to the certified reference standards for which the B3LYP functional offered the best accuracy for these ϵ -values compared to other functionals (Table 4.3). Besides that, the MAE remains within the standard deviations from the reference standards, which go from 1000-4000 L/(mol cm) and 2000-3000 L/(mol cm) for anthocyanidins and anthocyanins, respectively. Giusti et al. [58] reported for p-coumaroyl acylated Mv-3-Glc (**44**) an ϵ -value of 30200 L/(mol cm) in 0.1% HCl in MeOH, which corresponds to the calculated value of 32594 and 32992 L/(mol cm) for the (E)- (**44**) and (Z)- (**38**) conformer in methanol, respectively. Ahmadiani et al. [388] obtained ϵ -values of 23147 and 20259 L/(mol cm) for p-coumaroyl acylated Cy-3-diGlc-5-Glc in acidified methanol and pH 1 buffer, respectively, which lies in the same range of the calculated value of 29716 L/(mol cm) for (E)-coumaroyl acylated Cy-3-Glc (**40**). Currently, pyranoanthocyanins lack certified values, which makes comparison more difficult. Jordheim et al. [394] obtained ϵ -values for two 10 carboxy pyranoanthocyanins (**45-46**) from 21000-22000 L/(mol cm) in acidified methanol, which are basically similar to the values obtained for normal anthocyanins in the same study. Håkansson et al. [395] reported ϵ -values for malvidin-3-glucoside (**14**) and its vinylphenol type (**62**), which are 27600 and 12200 L/(mol cm) in model wine at pH 1.5, respectively. Quijada-Morín et al. [396] obtained only 4496 L/(mol cm) for malvidin 3-glucoside-vinylcatechol (**68**)

at pH 0.8. Meanwhile, the ϵ -values obtained from our calculations for 10-carboxy (**45-50**) and 10-H (**51-56**) types were 33569 and 34764 L/(mol cm) on average, while vinylphenol (**57-62**) and vinylcatechol (**63-68**) types showed average coefficients around 59066 and 54173 L/(mol cm). These skewed experimentally molar absorptivity coefficients can be a result of the method used for its determination as it is based on dissolving purified dried pigments to obtain concentrations of 10^{-4} - 10^{-6} M and include a chloride counterion or a water molecule to take hydration into account next to the molecular weight of the anthocyanin (Equation (4.1)) [58, 394].

$$A = \epsilon \cdot b \cdot c = \frac{\epsilon \cdot b \cdot n}{V} = \frac{\epsilon \cdot b \cdot m}{M_w \cdot V} \Leftrightarrow \epsilon = \frac{A \cdot M_w \cdot V}{b \cdot m} \quad (4.1)$$

with A measured absorbance, ϵ molar absorption coefficient (L/(mol cm)), b pathlength (cm), n mole, V volume (L), m mass (g) and M_w molecular weight (g/mol).

Anthocyanins carry beneficial health effects in terms of antioxidant activities, which is a structurally dependent property. Generally, anthocyanidins have a higher oxygen radical absorbance capacity (ORAC) compared to anthocyanins, and orthohydroxylation, methoxylation or acylation with phenolic acid of anthocyanins also contribute to a higher antioxidant effect [51]. The TD-DFT generated ϵ -values showed good correspondence for anthocyanins and acylated anthocyanins (Table D.37). For pyranoanthocyanins, these calculated values could be used as benchmark values. In the end, the $\lambda_{\max, \text{vis}}$ -values and molar absorption coefficients (ϵ) obtained by TD-DFT allow the experimental HPLC quantification for more complex anthocyanins derivatives.

Table 4.3: The percent error between calculated and analytical standard molar absorption coefficients (ϵ) of anthocyanidins (**1-8**) and anthocyanins (**9-14**) with different levels of theories (B3LYP, PBE0 and CAM-B3LYP and 6-311++G(d,p) as basis set) in SMD methanol unless otherwise stated.

Anthocyanidins	$\epsilon_{\text{STANDARD}}$ (L/mol cm)	ϵ_{B3LYP} (L/mol cm)	Percent error (%)	ϵ_{PBE0} (L/mol cm)	Percent error (%)	$\epsilon_{\text{CAM-B3LYP}}$ (L/mol cm)	Percent error (%)
Ap (1)	33110	41922	27	43048	30	45660	38
Cy (4)	35900	37074	3	38349	7	40611	13
Dp (6)	41000	37770	8	38839	5	40163	2
Lt (2)	35000	40782	17	42495	21	46196	32
Mv (8)	38750	39658	2	40850	5	42673	10
Pg (3)	32400	36511	13	37568	16	40310	24
Pn (5)	37000	37567	2	38875	5	41390	12
Pt (7)	39200	37801	4	38922	1	40382	3
MAE ^a		3248		3933		5837	
Anthocyanins							
Cy-3-Glc (10)	35000	32974	6	34980	0	39852	14
Dp-3-Glc (12)	37300	35412	5	36977	1	39680	6
Mv-3-Glc (14)	35000	36187	3	37935	8	41878	20
Pg-3-Glc (9)	28500	37018	30	38034	33	40452	42
Pn-3-Glc (11)	32370	34595	7	36596	13	41696	29
Pt-3-Glc (13)	35000	36410	4	38051	9	41044	17
MAE ^b		2881		3348		6905	
Acylated anthocyanins	$\epsilon_{\text{LITERATURE}}$ (L/mol cm)	ϵ_{B3LYP} (L/mol cm)	Percent error (%)	ϵ_{PBE0} (L/mol cm)	Percent error (%)	$\epsilon_{\text{CAM-B3LYP}}$ (L/mol cm)	Percent error (%)
p-coumaroyl acylated Mv-3-Glc (44)	30200 ^c [58]	32594	8	34643	15	39552	31
p-coumaroyl acylated Cy3diGlc-5-Glc*	23147 ^d [388]	29716	28	31278	35	36641	58
p-coumaroyl acylated Cy3diGlc-5-Glc*	20259 ^e [388]	29716	47	30133	49	36324	79
Pyrananthocyanins							
10-carboxy Pg-3-Glc (45)	22000 ^f [394]	36709	67	38059	73	40777	85
10-carboxypyranoc Cy-3-Gal**	21000 ^f [394]	32908	57	35200	68	40749	94
Vinylphenol Mv-3-Glc (62)	12200 ^g [395]	55025	351	57734	373	62632	413
Vinylcatechol Mv-3-Glc (68)	4496 ^h [396]	56321 ⁱ	1153	60096 ⁱ	1237	63024 ⁱ	1302

^a: n=8, ^b: n=6, ^c: 0.1% HCl in MeOH, ^d: acidified MeOH, ^e: pH=1 buffer,
^f: 1% HCl/MeOH, ^g: model wine pH=1.5, ^h: citrate buffer pH=0.8, ⁱ: SMD Water

*: p-coumaroyl acylated Cy-3-Glc (**40**) was taken as comparison

:: 10-carboxypyranoc Cy-3-Glc (46**) was taken as comparison

4.3.2.2 Pyranoanthocyanins: New Natural Dyes on Textile Fibers with Better Fastness Properties?

Nowadays, synthetic dye and pigments find their way in industries related to textile, paints and coatings, paper, food and beverages, plastics, printing inks, cosmetics and personal care, and other industries [8]. However, these dyes potentially possess toxic, allergic and even carcinogenic properties. Along with growing concerns about sustainability and ecology, natural dyes emerge as promising alternatives. However, these dyes have a couple of shortcomings compared to their synthetic analogues in terms of stability and affinity for textile substrates. Our previous study (Chapter 3) showed that applications with anthocyanins in the form of the red stable flavylum cation, can be deployed in aqueous environment provided that alkaline substances should be avoided and therefore, are relevant within short life cycle products (e.g., biodegradable products, pH indicator, paper-based coffee cups, etc.) [114]. In order to test the applicability of anthocyanins and pyranoanthocyanins, it is essential to know the color range that can be obtained with these compounds. The generally accessible color range, based on $\lambda_{\text{max,vis}}$ -values obtained with the B3LYP functional, is visualized in Figure 4.10. It is immediately clear that anthocyanidins (**3-8**) and anthocyanins (**9-14**) are generally strong red colors in at $\text{pH} < 3$, while 3-deoxyanthocyanidins (**1-2**) rather show yellow to orange colors [356]. 10-H pyranoanthocyanins (**51-56**) and their acetyl (**75-80**) and caffeoyl acylated (**99-104**) derivatives display a similar orange color as those 3-deoxyanthocyanidins [397] and 10-carboxy pyranoanthocyanin (**45-50**) showed a comparable color range as anthocyanins. Marquez et al. [358] mentioned a reddish-orange color for vinylphenol (**57-62**) and vinylcatechol (**63-68**) adducts with a $\lambda_{\text{max,vis}}$ at 505-508 nm, which corresponds better to the calculated 10 vinylphenol $\lambda_{\text{max,vis}}$ -values as the additional OH group of the catechol moiety results in a small bathochromic shift as mentioned earlier. The more voluminous caffeoyl, coumaroyl vinylcatechol or vinylphenol pyranoanthocyanins are potentially suitable as textile dyes as they are lower in polarity and larger in size compared to common anthocyanins and hence, possess lower water solubility. Till date, dyeing studies involving pyranoanthocyanins are not yet available, but the $\lambda_{\text{max,vis}}$ -values obtained from TD-DFT show that pyranoanthocyanins have great potential for dyeing purposes which could be interesting to validate in future experimental studies.

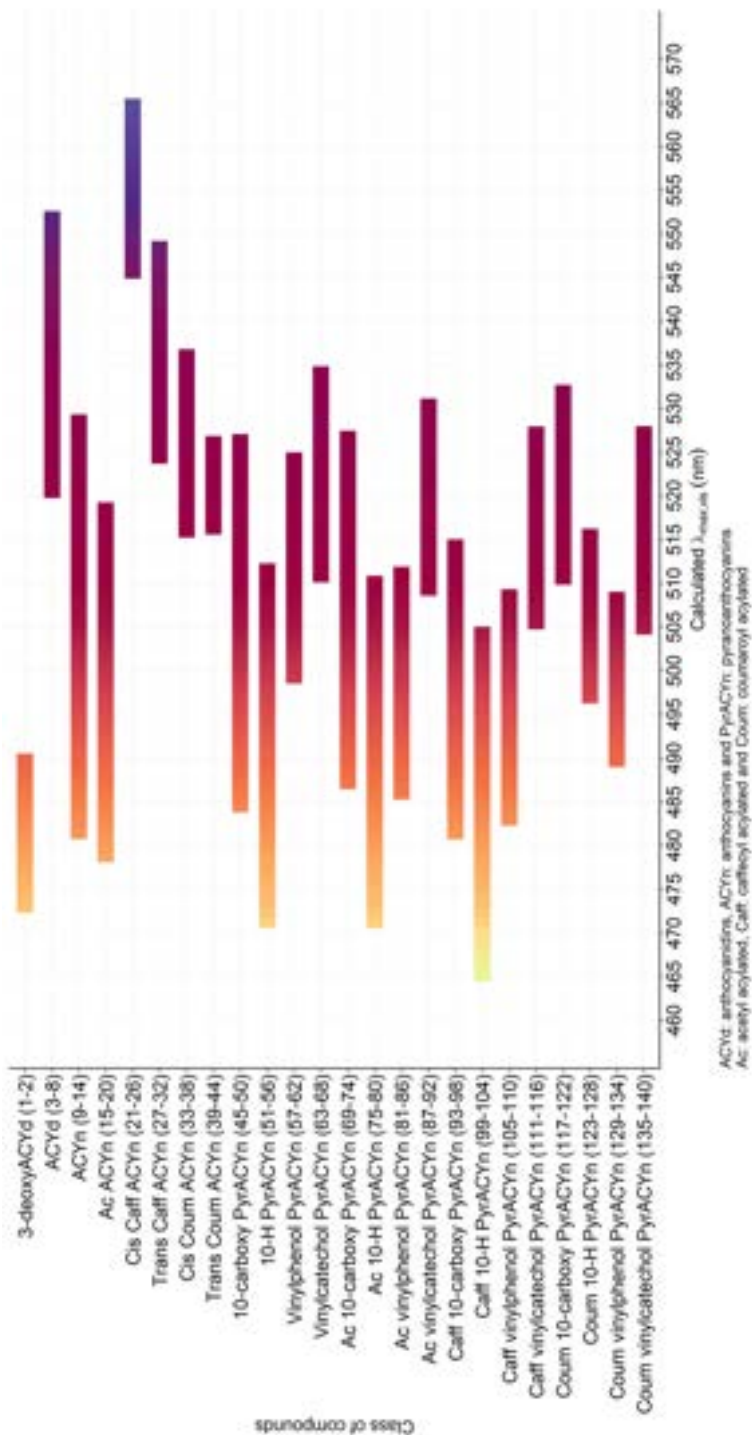


Figure 4.10: The color range attained for each anthocyanin-based subclass (in its flavylium cation form) based on TD-DFT calculations with B3LYP/6 311++G(d,p) and SMD water.

4.3.2.3 Optical Transition Properties for DSSC

The choice of natural dye sensitizer is characterized by the most favorable structural and optical properties (e.g., $\lambda_{\max, \text{vis}}$, ϵ , color stability) [361]. In order to fulfill the energy requirements for photo-energy generation, the energy of the HOMO should be sufficiently lower compared to the electrolyte redox potential for dye regeneration ($E(I^-/I_3^-) = -4.8 \text{ eV}$), while the energy of the LUMO needs to be greater than the potential of the TiO_2 conduction band to promote charge injection ($E_{CB} = -4.0 \text{ eV}$) (Figure 4.11) [363]. These orbital energies can be extracted from vertical excitations obtained from TD-DFT calculations [398]. The cell's efficiency is commonly evaluated by short-circuit photocurrent density (J_{SC}), which can be theoretically estimated in terms of the Gibbs free energy change of electron injection (ΔG_{inj}), estimated open circuit voltage (eV_{oc}), the regeneration efficiency (ΔG_{reg}) and the light harvesting efficiency (LHE) [399]. These efficiencies also depend on the substitution patterns of specific anthocyanins or pyranoanthocyanins with the electron density of the LUMO ideally delocalized across the anchoring site to improve the charge injection process [363]. The Gibbs free energy change for electron injection ΔG_{inj} is expressed as [367]:

$$\Delta G_{inj} = E_{ox}^{dye*} - E_{CB}^{TiO_2} \quad (4.2)$$

where E_{ox}^{dye*} is the oxidation potential energy of the dye in the excited state and $E_{CB}^{TiO_2}$ the potential of the TiO_2 conduction band. The former can be calculated as the difference between the oxidation potential energy of the dye in the ground state (E_{ox}^{dye}), which corresponds to $-E_{HOMO}$ according to Koopman's theorem, and the vertical excitation energy gap λ_{max}^{ICT} , if the entropy change during the light absorption is neglected [363, 398].

$$E_{ox}^{dye*} = E_{ox}^{dye} - \lambda_{max}^{ICT} \quad (4.3)$$

The V_{oc} and LHE values are described by the following equations:

$$V_{oc} = E_{LUMO} - E_{CB}^{TiO_2} \quad (4.4)$$

$$LHE = 1 - 10^{-f} \quad (4.5)$$

With f the oscillator strength associated with the vertical excitation energy gap. And lastly, the regeneration efficiency η_{reg} is based on the Gibbs free energy change of regeneration (ΔG_{reg}) and involves the electrolyte redox potential for

dye regeneration (I^-/I_3^-):

$$\Delta G_{reg} = E_{ox}^{dye} - E_{redox}^{I_3^-} \quad (4.6)$$

Table D.37 displays negative values for injection and regeneration Gibbs free energies of anthocyanins and pyranoanthocyanins, which indicate the thermodynamic feasibility for both electron transfer processes within DSSCs. The LHE values are more ambiguous due to the charge transfer phenomena within acylated structures. For anthocyanidins (**1-8**) and anthocyanins (**9-14**), malvidin (**8, 14**) showed the largest ΔG_{inj} due to the presence of two methoxy groups. Caffeoyl (**21-32**) and coumaroyl (**33-44**) acylated anthocyanins showed a higher injection performance compared to anthocyanins. Additionally, (E)-caffeoyl (**27-32**) and coumaroyl (**39-44**) anthocyanins resulted into an increase of 32-56% and 24-37% for ΔG_{inj} on average compared to (Z)-configurations (**21-26** and **33-38**), respectively. Pyranoanthocyanins generally show at least a 54% higher electron donation capacity compared to anthocyanins in aqueous environment. Furthermore, 10-H types (**51-56**), vinylphenol (**57-62**) and vinylcatechol (**63-68**) adducts offer averagely 29-33% better electron injection free energy compared to 10-carboxy types (**45-50**) in the same medium. A comparable trend was also observed for V_{oc} values where pyranoanthocyanins without carboxyl group claimed the largest values. This corresponds to the study of Pinto et al. [400] where carboxylic groups were found to have a detrimental effect on the electron injection due to the electron withdrawing character, while dyes containing only electron-donating groups (i.e., hydroxy, methoxy, methyl) contribute to higher J_{SC} and V_{OC} values. The highest ΔG_{inj} -values were found for caffeoyl acylated vinylphenol adducts (**105-110**), especially the Pg type (**105**) (-0.429 eV), which are 59% and 215% higher compared to vinylphenol adducts (**57-62**) and anthocyanins (**9-14**) on average in water, respectively. Besides that, the presence of a catechol unit offers an anchoring site for the TiO_2 , although the caffeoyl moiety would only contribute to structural features rather than to electron injection capacity (Figure 4.8 and Table D.38). In conclusion, the orbital energies obtained from vertical excitations in TD-DFT calculations on the library of anthocyanin based compounds lead to the fact that pyranoanthocyanins could potentially perform better as dye sensitizer than anthocyanins, while caffeoyl acylated vinylphenol adducts specifically would lead to high cell efficiencies due to their high injection rates and ϵ -value. Pinto et al. [400] obtained an overall cell efficiency of 1.51% for vinylcatechol Mv-3-Glc (**68**) without further optimization, while anthocyanins reach an efficiency of 0.73% on average over a period of 16

years [361]. Generally, this proves that orbital energies obtained from vertical excitations in TD-DFT calculations can be applied as a screening method for anthocyanin dye sensitizers and providing complementary information to experimental data.

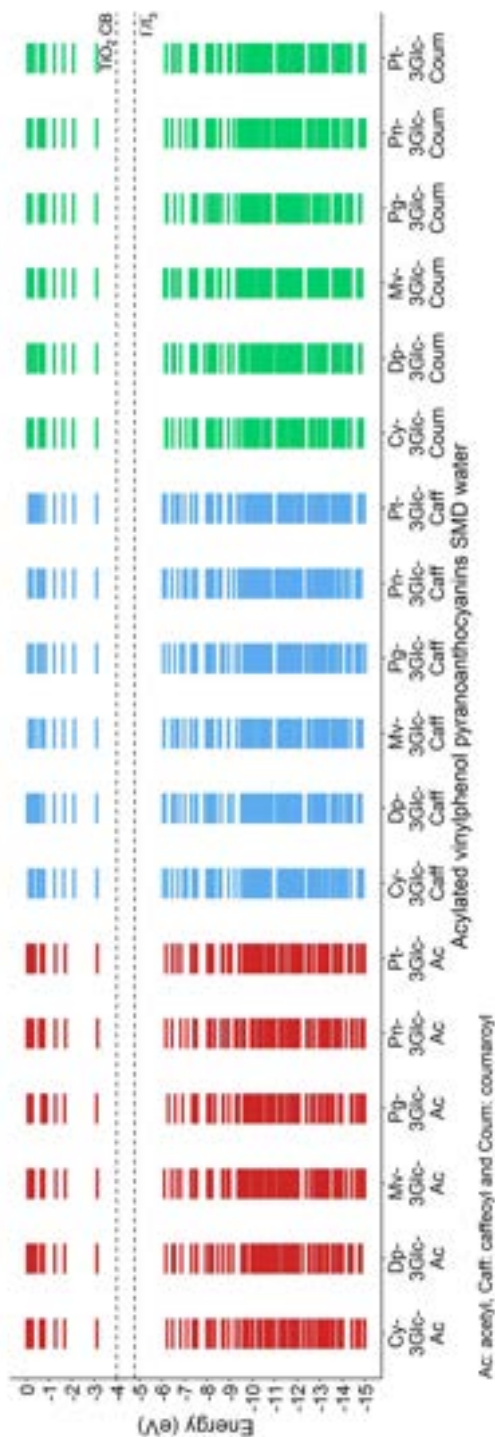


Figure 4.11: Computed energy levels of acetyl (**81-86**), caffeoyl (**105-110**) and coumaroyl (**129-134**) acylated vinylphenol pyrananthocyanins (B3LYP/6-311++G(d,p) with SMD water). The dotted lines represent the energy levels of TiO_2 conduction band and the iodide/triiodide (I^-/I_3^-) redox potential. The energy of the HOMO should be sufficiently lower compared to the electrolyte redox potential for dye regeneration, while the energy of the LUMO needs to be greater than the potential of the TiO_2 conduction band to induce charge injection. Energy levels of other anthocyanin-based compounds can be found in Figures D.33 to D.39.

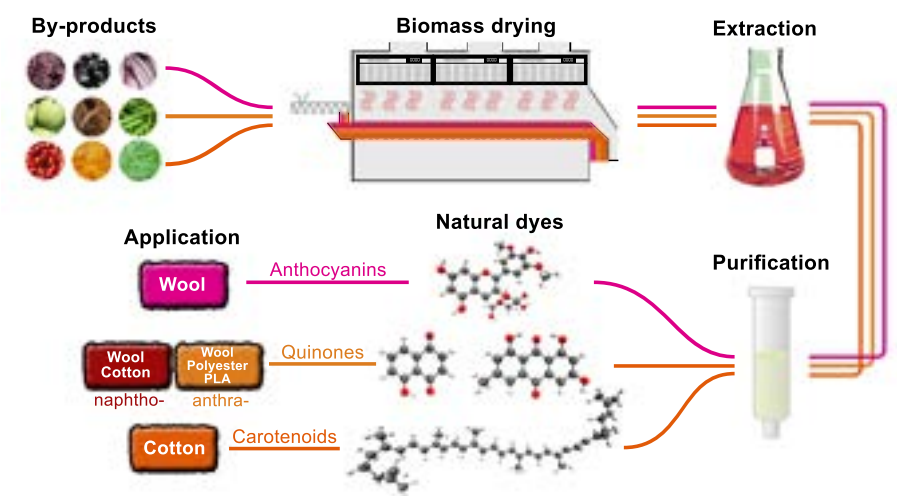
4.4 Conclusions

Anthocyanin-based compounds are providing color in flowers, higher plants, fruit and vegetables and are interesting components in food and non-food applications. Within this contribution, we have provided insight into the photophysical properties of these compounds. 140 compounds of natural occurring anthocyanin-based colorants were analyzed by means of TD-DFT with various functionals B3LYP, PBE0 and CAM-B3LYP. It showed that B3LYP results in the best overall accuracy ($MAE_{B3LYP} = 0.049 \text{ eV} < MAE_{PBE0} = 0.085 \text{ eV} < MAE_{CAM-B3LYP} = 0.35 \text{ eV}$), even in long-range charge transfer transitions, this hybrid functional was capable in locating $\lambda_{\text{max,vis}}$. The library of $\lambda_{\text{max,vis}}$ -values and other photophysical properties obtained from TD-DFT can be used as a tool providing target specific solutions at low computational cost in a pure environment. This is beneficial for characterizing and quantifying complex anthocyanin derivatives, applied as food additives/colorants, for which reference analytical standards are unavailable. The molar absorption coefficients for anthocyanins are corresponding well with reference standards, the extrapolation to pyranoanthocyanins could be used as a benchmark as there is some inconsistency within experimental ϵ -values. In terms of color shades, pyranoanthocyanins cover similar shades as anthocyanins, while the former would provide better stability against external conditions such as pH fluctuations and temperature. Furthermore, the evaluation of orbital energies also proves that all naturally derived pyranoanthocyanins studied are interesting compounds for DSSCs applications. In conclusion, TD-DFT calculations can provide us insight into the potential utilization of specific natural anthocyanin-based compounds in various applications.

Chapter 5

Non-Food Applications of Natural Dyes Extracted from Agro-Food Residues: a Critical Review

Partim Valorization Routes & Life Cycle Assessment



Phan K., Raes K., Van Speybroeck V., Roosen M., De Clerck K., and De Meester, S. *Journal of Cleaner Production*, **301**, 126920 (2021).

Toward industrial valorisation of natural dyes

5.1 The Valorization Routes From Agro-Food Residues to Textile Application

This section summarizes the main conclusions from sections 1.3 and 1.4. In section 1.3, the number of by-products generated from fruit and vegetable processing industries and the adjoining anthocyanin, quinone, and carotenoid content was evaluated, while section 1.4 provided insight into the best possible application methods, assessed in terms of the wash and lightfastness properties for each of these natural dyes on the different fiber types. The following sections evaluate the most interesting process chains for each of the natural dyes based on “5-stage universal recovery processing,” which includes macroscopic pretreatment, macro-and micro-molecule separation, extraction, isolation-purification, and product formation or encapsulation [401]. The final purified product is then applied to the textile fiber. Conventional and emerging technologies are discussed below, as the latter have technological and scale-up boundaries that restrict their efficiency for commercial implementation. However at lab scale, non-conventional technologies can shorten the extraction time, operate at a lower temperature and with reduced solvent consumption, and obtain a higher extraction yield with lower energy consumption [402]. Extraction methods such as solid-liquid extraction are easily possible at industrial scale. Others such as ultrasonic assisted extraction, microwave assisted extraction and supercritical fluid extraction have potential towards scaling up, but this is less straightforward compared to conventional solid-liquid extraction. Typical barriers for non-conventional technologies are increased energy consumption for membrane processes, the higher operational cost for chromatography systems, or reduced control over thermal processes [403].

5.1.1 Valorization Route for Anthocyanins

The most interesting waste source for obtaining anthocyanins is red grape pomace, which is derived from the wine or juice manufacturing industries, resulting in an estimated 15 Mt of by-products in Europe alone. The pomace consists mainly of grape skins, which have an anthocyanin content of 56.4 kg/t DW [74]. Other interesting sources are black olive pomace and red onion skins, both of which have a minimum of two times lower anthocyanin content and by-product quantity. Anthocyanin-containing by-products are more prominent in southern parts of Europe, such as France, Spain, or Italy, where olives are cultivated and 74% of Europe's vineyards are located (representing 32% of the global vineyard surface area) [404]. These three anthocyanin-containing by-products mainly emerge as side streams at manufacturing plants. As these by-products contain at least 50% moisture (Table 5.1), dehydration of these residues is important to prevent chemical deterioration (oxidation) and microbial spoilage by yeasts and molds [405, 406]. The residual moisture content of a by-product depends on the fruit or vegetable variety, the processing conditions applied, and any depectinization of the mash [405]. Microwave and dielectric drying systems could be recommended as they would be able to safeguard the drying process of thermolabile materials without degrading the product [407]. However, dielectric heating typically attains an energy transfer of 60% from the generator to the product. The major part of the emitted energy must be absorbed evenly by the matrix, which is more difficult in by-products due to their varying matrix composition [403]. The process conditions for extracting anthocyanins should take into account that these compounds are susceptible to degradation by light, pH, and temperature, resulting in pigment loss [57]. The degradation rate of anthocyanins increases proportionally from 65 °C onward, so a short time/high-temperature process is recommended for the best pigment retention [408]. As anthocyanins are water-soluble compounds, extraction can be simply performed with acidified water to avoid potentially hazardous solvent residues, which may limit potential commercial applications [231, 409]. Acidification of the extract comes with several gains: maintaining a low pH (<3.0) to secure stability and structural consistency, disrupting cell walls to increase the accessibility of polyphenolic compounds and solvent transport, and inhibiting enzymes that catalyze polyphenol decomposition [231]. Organic solvents, mostly methanol or ethanol, are frequently added to water in various ratios to maximize the extraction yield [410]. Lapornik et al. [411] revealed that the concentration was at least ten-fold higher with a 70% methanol or 70% ethanol mixture compared

to pure water. This can be ascribed to the less polar character of methanol and ethanol compared to water, improving the efficiency of extraction in cell walls and seeds [411]. The use of methanol or ethanol also involves additional evaporation or clean-up steps to remove the organic solvent, as dyeing frequently occurs in an aqueous environment. Besides that, the extraction technique also influences the yield. Corrales et al. [412] evaluated the anthocyanin extraction yield with three novel extraction techniques: ultrasonication, high hydrostatic pressure (HHP), and pulsed electric fields (PEF). It was shown that PEF is the preferred technique, as the total anthocyanin content increased by 58% compared to the control sample. The high voltage electric pulses induce the formation of pores in the membrane (electroporation), which increases the cell permeability, allowing molecules to be released into the extraction medium [413]. However, the highest extraction yield from red grape skin is obtained through pressurized liquid extraction (PLE). This technique allows the total anthocyanin content to reach up to 41.3 kg/t DW with acidified water at 50 °C and increases by 22% and 37% with an acidified 60% ethanol and 60% methanol mixture, respectively [74]. The crude extract can be used in two ways: apply it on the substrate of interest or include an additional purification step usually performed with solid-phase extraction (SPE) [409]. This preparative method can clean up the matrix (i.e., sugars, acids, proteins, pectin, etc.). Performing solid-phase extraction (SPE) on industrial scale requires the optimization of more variables such as the particle size of the resin (i.e., lower particle size means high pressure of flow for loading), possibility of regenerating and recycling the solid phase resin without loss of recovery efficiency and the recovery of extraction solvent and solvents used during one SPE cycle (washing and reactivation of resin) [231, 414]. The anthocyanins are concentrated through elution with an organic solvent, for example, ethanol [409]. This requires an additional drying step to obtain a dye powder or liquid concentrate. The following three drying methods are commonly used: spray drying, vacuum drying (e.g., rotary evaporator), and freeze drying [43]. Freeze drying comes with high equipment and operating costs but is the most recommended strategy for heat-sensitive dyes [43], although 80–90% of anthocyanin encapsulates are spray-dried [415]. Despite the hydrophilic property of anthocyanins, the overall fastness for biomordants on protein fibers is two grades higher compared to cotton. The highest fastness properties were obtained with ammonium ferrous sulfate and stannous chloride on silk and cotton [119] but the use of metal is generally not preferred. The use of tannic acid on silk and wool [116] or itaconic acid on silk [120] also meets the industrial requirements for general apparel [135]. Tannins also carry UV-protection properties, which are

certainly of added value for these light-prone anthocyanins [124]. In general, applications with anthocyanins in the form of the red stable flavylium cation can be deployed in an aqueous environment, provided that alkaline substances should be avoided and are relevant within short life cycle products (e.g., biodegradable products, pH indicator, paper-based coffee cups, etc.) [114]. With the amount of red grape pomace generated in Europe, the woven fabrics produced there could be dyed approximately five times (Table 5.1) [416]. Hereby, the amount of by-products required for dyeing 1 m² of naturally-dyed fabric was considered (*vide infra*). Anthocyanin dyes produced from black olive pomace and red onion skins would be able to dye 10% and 48% of the woven fabrics produced in Europe, respectively.

Table 5.1: The potential European production scale of naturally-dyed fabric that is derived from the most promising by-products containing anthocyanins, quinones, or carotenoids.

	Amount of by-products (Mt) in Europe	Moisture content (%)	Concentration	Amount of dye (kt)	Amount of by-products required for 1 m ² naturally-dyed fabric (kg)	Estimated European production of naturally-dyed fabric (km ²)
Anthocyanins					cotton	wool
Wet red grape pomace	14.6	81.7 (w)	20.5 ^a [74]	299	1.16 ^{c,e}	12603 ^e
Dried red grape pomace	3.3	4.5 (d)	106.8 ^b	356	0.31 ^{d,e}	10663 ^e
Wet red onion skins	3.1	58.2 (w)	9.2 ^a [86]	28.4	2.59 ^{c,e}	1194 ^e
Dried red onion skins	1.4	3.8 (d)	20.1 ^b [86]	28.3	1.40 ^{d,e}	1010 ^e
Wet black olive pomace	7.4	68.0 (w)	0.83 ^a [78]	6.1	28.62 ^{c,e}	258 ^e
Dried black olive pomace	3.0	8.0 (d)	2.4 ^b	7.1	13.53 ^{d,e}	218 ^e
Quinones						
Wet walnut green husks	0.086	87.7 (w)	23.0 ^a [417]	2.0	1.03 ^{c,e}	84 ^e
Dried walnut green husks	0.018	8.0 (d)	172.0 ^b	3.0	0.23 ^{d,e}	75 ^e
Wet rhubarb roots	0.12	75.0 (w)	4.5 ^a [95]	0.56	0.84 ^{c,f}	225 ^f
Dried rhubarb roots	0.041	8.0 (d)	16.7 ^b	0.68	0.31 ^{d,f}	133 ^f
Wet bean waste	0.42	90.32 (w)	36.0 ^a [81]	0.015	115.15 ^{c,f}	5.60 ^f
Dried bean waste	0.10	14.0 (d)	0.34 ^b [81]	0.034	30.32 ^{d,f}	5.04 ^f
Carotenoids						
Wet tomato pomace	7.0	84.0 (w)	103.8 ^a	723	0.23 ^{c,e}	30453 ^e
Dried tomato pomace	1.9	10.7 (d)	579.2 ^b [99]	1078	0.067 ^{d,e}	27862 ^e
Wet pumpkin pomace	1.0	91.6 (w)	1.1 ^a	1.1	21.16 ^{c,e}	46 ^e
Dried pumpkin pomace	0.13	4.6 (d)	12.9 ^b [418]	1.6	3.01 ^{d,e}	42 ^e
Wet carrot leaves	2.2	80.89 (w)	0.95 ^a	2.1	24.96 ^{c,e}	89 ^e
Dried carrot leaves	0.60	8.0 (d)	4.6b [106]	2.7	7.40 ^{d,e}	81 ^e

(w): wet, (d): dry

^a : kg/t FW, ^b : kg/t DW, ^c : mass wet by-product from scenario 1,^d : mass dried by-product from scenario 5, ^e : dyed at 12.5% owf, ^f : dyed at 2% owf

5.1.2 Valorization Route for Quinones

As previously mentioned, quinones are not widely found in fruits and vegetables but are more frequently encountered within plants and insects. The main sources of quinones are walnuts, which specifically contain naphthoquinones, while rhubarb and beans contain anthraquinones. The juglone content within walnut green husks attained 15.0 kg/t DW [90]. Rhubarb parts (e.g., petioles, leaves, and roots) showed the presence of anthraquinones (e.g., emodin, physcion, and chrysophanol). Concentrations found in the petioles, leaves, and roots reach up to 610, 40, and 18100 g/t DW, respectively [94, 95]. The amount of quinone-containing by-products differs by two orders of magnitude compared to anthocyanin- and carotenoid-containing by-products. Quinone by-products are more likely to be found through agricultural losses or post-harvest handling; only rhubarb is further processed to become juice but is rather new on an industrial scale [88]. Nuts that have fallen to the ground before harvesting are dryer compared to the less mature nuts that must be shaken from the trees. They also require drying to a storage safe moisture content of 8% to prevent mold development [419]. There are no restrictions on drying techniques, as 1,4-naphthoquinones are thermally stable up to 600 °C [420], while anthraquinones such as emodin, chrysophanol, and physcion only start to decompose at 281 °C, 189 °C, and 200 °C, respectively [48]. The most suitable solvents for extracting phytochemicals from walnut green husk and leaves are water, methanol, and ethanol [421]. It has also been noticed that the phenolic content in the extract increases by optimizing the ratio of the aforementioned solvents [421]. A 60% ethanol-water mixture at a temperature of 60 °C for 30 minutes in combination with ultrasonication seems to yield the highest total phenolic content from the walnut green husk [422]. Nour et al. [423] optimized the extraction conditions of walnut leaves by using ultrasonication in a hydroalcoholic medium. The optimized parameters were 62.82% (v/v) ethanol concentration, a solid-liquid ratio of 4.96 v/w, and an extraction time of 48.75 min., with the first two parameters as the most determining factors for extraction efficiency. Anthraquinones from *Rheum* species are frequently extracted through ultrasonication and a 50-80% ethanol-water mixture [95, 424]. The anthraquinone extraction yield depends on the type of solvent, which is highest for acetone > acetonitrile > methanol > ethanol. Acetone displayed the best results in both maceration and ultrasonication. This can be ascribed to its structural similarity with anthraquinones (i.e., carbonyl functional group) [60, 424]. Generally, a compromise should be found between yield and the

environmental impact of the extraction procedure. For ultrasonication, Duval et al. [60] recommend a temperature between 55 and 67 °C for 30 to 60 min. Other extraction techniques for anthraquinones are microwave assisted extraction (MAE), PLE or supercritical fluid extraction (SFE), each with its advantages and drawbacks in terms of extraction time, ease of use, solvent consumption, operation cost, etc. [60]. The extract should be subjected to mutagenicity studies, as 1,3-dihydroxyanthraquinones having a methyl (rubiadin) or hydroxymethyl (lucidin) group on the C2 position can form covalent adducts with nucleobases [53]. The engineering of efficient power ultrasonic systems (e.g., generators and reactors) for industrial processing can be a possible issue, although ultrasonic systems are frequently and successfully applied in the food sector [38]. An additional fast and straightforward purification step for quinones is not yet available, as flash chromatography based on silica gel is the only method applied for naphthoquinones [425, 426], while countercurrent chromatography (CCC) or centrifugal partition chromatography (CPC) is the preparative method of choice for separating and purifying anthraquinones from the crude extract [60]. This chromatographic technique is based on two liquid phases, as one is kept stationary by a centrifugal force while the other acts as a mobile phase that flows in the opposite direction. The main advantages are its high sample recoveries, large loading capacities, and thus processing large sample volumes that allow for an industrial-scale-up [60]. The drawback of this technique is that the stationary phase is still a liquid, which is difficult to maintain inside the column with the mobile phase flowing through it [427]. The use of the entire extract after drying the organic solvent can be seen as the most practical solution. Naphthoquinones are mostly applied on protein fibers (44%) and cotton (34%), leaving a dark reddish to brown color. Furthermore, 41% of the studies were performed without mordant; within this, 58% displayed excellent wash fastness (4-4/5), while 39% showed at least a lightfastness of grade 5 or higher. In essence, naphthoquinones met the industrial fastness requirements for both protein and cotton fibers, without the addition of any mordant. In the meantime, natural anthraquinones show a high application rate on protein fibers (61%), while 17% were applied on cotton. When these anthraquinones were applied to protein fibers, polyester, and PLA without any mordant, the industrial fastness requirements for general apparel were met. As emodin, chrysophanol, and physcion are the main natural anthraquinones found in rhubarb and bean by-products, the fibers will display yellow to orange colors [11]. The anthraquinones from rhubarb waste and bean by-products are suitable for dyeing only 6% and 0.15% of Europe's entire woven fabric production, respectively, while

naphthoquinones from walnut husks are just good for 3% (Table 5.1).

5.1.3 Valorization Route for Carotenoids

Tomatoes are among the world's most popular vegetables. They are consumed fresh and are also frequently processed into paste, juice, ketchup, or puree [36]. This results in many by-products, estimated at 7 Mt in Europe per year (Figure 1.7A). The pomace, mostly consisting of skins and seeds, is also a rich source of carotenoids, which reach up to 593 kg/t DW via soxhlet extraction, with a 96 (v/v %) ethanol-hexane mixture [99]. There is a difference in consistency between wet pomace (i.e., 33% seed, 27% skin, and 40% pulp) and dry pomace (i.e., 44% seed and 56% pulp and skin), which could lead to various extraction profiles [67, 428]. Next to tomato pomace, carrot leaves and pumpkin by-products are two carotenoid sources, though the waste streams are three and seven times lower in quantity, respectively. Carrot leaves mostly emerge after post-harvest handling, while tomato pomace and pumpkin are more likely derived from processing side streams. Drying is certainly mandatory for these thermolabile carotenoid-containing by-products, as they rapidly spoil due to high moisture and nutrient content (Table 5.1) [36]. Hernández-Ortega et al. [429] retained 2.5 times more β -carotene in carrot pomace that was microwave-dried compared to hot-air-dried. As most carotenoids in tomato are lipid-soluble, extraction procedures depend on the use of organic solvents (e.g., hexane, acetone, ethanol, ethyl acetate, ethyl lactate, chloroform, petroleum ether, or mixtures of these aforementioned solvents) [430]. Extraction with ethanol releases more xanthophylls and a ten-fold lower contribution of lycopene [99]. It is noteworthy to remark that ethyl lactate, which is an environmentally friendly solvent that is derived from the fermentation of carbohydrate feedstocks available from corn and soybean industries, produces good results in the carotenoids' extraction [431], but its high boiling point (150 °C) makes solvent recovery more costly compared to lower boiling solvents such as ethyl acetate and hexane [36, 38]. Besides obtaining carotenoids via soxhlet extraction, other conventional and more unconventional extraction methods were applied, such as ultrasonication, MAE, PEF, PLE, SFE and enzyme assisted extraction (EAE), which makes use of hydrolytic enzymes (cellulase and pectinase) for disrupting the cell wall [432]. After extraction, when chromatographic analysis is desired, saponification is carried out as an additional step. The purpose of this procedure is to remove xanthophylls that are acylated with saturated and unsaturated fatty acids along with chlorophylls and lipids. This will give rise to an interference-free

chromatographic analysis; however, this would be redundant for application purposes, as this extra step induces quantitative losses, artefact formation, and carotenoid degradation [432]. The purification of carotenoids from the matrix can be simply performed with SPE [433]. When carotenoid dye powder or concentrate needs to be obtained, concentrating carotenoid extracts by rotary evaporation is possible at reduced pressure and a temperature below 40 °C [63], although freeze drying is the most advisable technique due to the thermolability of carotenoids. In terms of applications, only 44% of the purely applied carotenoids attain a wash fastness of 4, and 89% of those unmordanted carotenoid fibers score poorly on lightfastness (below a grade of 3). Thirty-nine percent of the studies applied carotenoids to cotton fibers, while 33% applied them to protein fibers. Carotenoids show the best fastness properties ($WF = 4/5$ and $LF = 6-6/7$) on a cotton/viscose mixture or cotton in the presence of a pomegranate rind as a biomordant containing polyphenolic compounds that are protecting the carotenoids from photodestruction. The dyed fabric will vary in color from yellow/orange to red, depending on the polarity of the solvents used during extraction. Xanthophylls are mostly yellow-orange colored pigments, while β -carotene and lycopene have orange and red colors, respectively [434]. Due to the vast amount of tomato by-products and their large carotenoid content, the woven fabrics produced in Europe could be approximately dyed 12 times, while carrot leaves and pumpkin pomace only allow dyeing 4% and 2% of the entire production, respectively (Table 5.1).

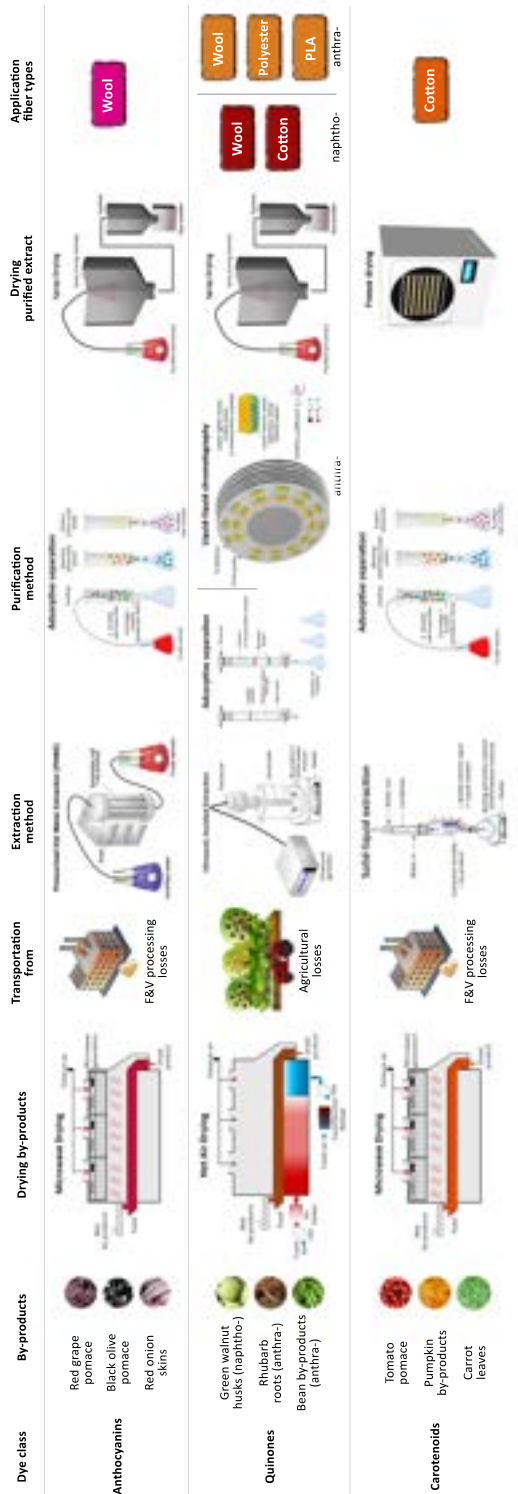


Figure 5.1: Examples of potential valorization routes summarized for each natural dye class.

5.2 LCA of the Production of Naturally-Dyed Fabrics from Agro-Food Residues

As shown in the previous section (e.g., Figure 5.1), the main challenge with finding a suitable extraction procedure for application, and to improve dyes' stability and fastness by one level, offering the same product service compared to synthetic dyes, is not straightforward. It is not easy to match the performance of synthetic dyes; the main driver to choose natural dyes will be the potential environmental performance. However, bio-based products are not necessarily 'greener.' Therefore, we have, by Life Cycle Assessment LCA, determined the environmental impact of suitable natural dye scenarios, starting from the waste stream until the dyed end-product.

5.2.1 Methodology

The goal of the studied systems is to determine how environmentally friendly it is to dye one m² of cotton or wool fabric with a natural dye (Functional Unit) that is derived from the waste stream, compared to dyeing one m² with a synthetic anthraquinone dye (i.e., 9,10-anthracenedione building block displaying a yellow color). Data for the production chain was collected from the literature and comprises the natural dyes' concentration, waste's moisture content, transportation logistics (± 115 km), extraction conditions, filtration process, purification method, recovery losses, drying methods, dyeing methods, and wastewater treatment. Complementary data, as well as data of the entire production and dyeing process with the synthetic anthraquinone dye, were collected from the ecoinvent version 3.1 database, using OpenLCA software [435]. The full data inventories can be found in Tables E.1 to E.16. Furthermore, different strategies can be applied to obtain naturally-dyed goods. Therefore, five explorative scenarios were studied for anthocyanins, naphthoquinones, anthraquinones, and carotenoids to investigate the influence of various extraction and purification pathways (Figure 5.2) [436].

- The first scenario consists of a simple extraction from the wet waste stream and a subsequent batch dyeing procedure at a single site.
- The second scenario involves a drying step of the biomass at the manufacturer, as this would reduce the transport costs before moving the by-products to the extraction and dyeing site.
- The other three scenarios include the impact of an additional purification

step of the crude extract in combination with one of three common drying methods:

- Spray drying (scenario 3)
- Vacuum drying (e.g., rotary evaporator) (scenario 4)
- Freeze drying (scenario 5)

Hereby, the natural dye is converted into a batch of dye powder or liquid concentrate for long-term storage and ease of transport while guaranteeing shade uniformity [43]. To protect these sensitive compounds against process conditions, maltodextrin was considered as a drying agent during the spray and freeze-drying step. This compound increases the glass transition temperature, reduces the hygroscopicity of the powder, and assures pigment retention through encapsulation [437]. As natural dyes show lower substantivity to textile fibers, a dye amount of 12.5% on weight fiber (owf) was calculated as the worst-case scenario (except for anthraquinones) [114]. Next to that, tannic acid (50% owf) was also taken into account as a biomordant in both natural anthocyanins [114] and carotenoids as well as synthetic dyeing processes. For the latter, the additional contribution of the biomordant can also be interpreted as an approximation for the additional chemical modification of the synthetic 9,10-anthracenedione building block. The zero-burden approach was applied in all cases, as the environmental impact of the waste stream was not allocated. The solid residue after extraction can still be applied to other integrated or coupled processes, which allows the subsequent recovery of each residue. The residue can also be deployed after the required post-treatments with a desolventizer and dryer to remove the solvent residue, in low economic valorization purposes depending on its chemical and functional properties [36]. Due to these complex factors, neither contribution was taken into account in this study. Ecopoints are calculated with the ReCiPe endpoint method as the sum of the impact categories: resources, human health, and ecosystems. The results are illustrated in Figure 5.3.

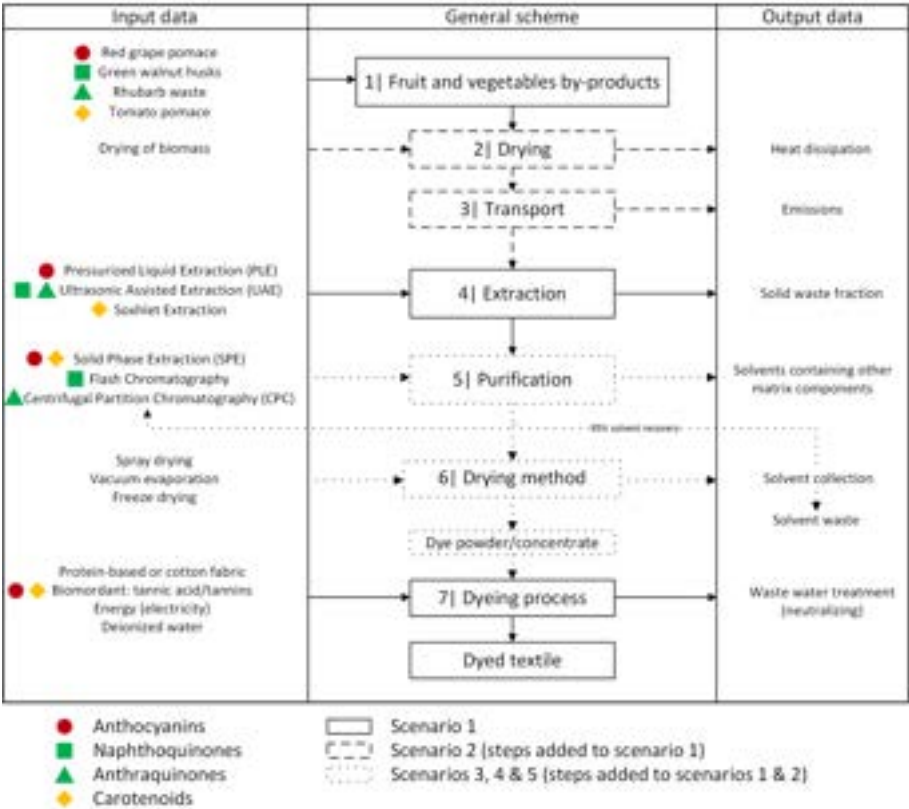


Figure 5.2: A general scheme of the different explorative scenarios for the LCA analysis of the extraction of and dyeing with natural dyes. The detailed schemes for each natural dye are illustrated in Figures E.1 to E.4.

5.2.2 LCA Results

5.2.2.1 Anthocyanins

The first two scenarios (Figure 5.3A) differ regarding whether the red grape pomace has been dried before extraction or not. The aqueous extraction from the dry pomace showed a lower impact compared to the wet pomace. The drying of the biomass accounts for 55% of the total environmental impact (Figure 5.3A). In the following scenarios, which include a purification step, biomass drying still accounts for at least 40% of the total impact. Afterward, to obtain a dye concentrate or powder, three drying procedures, after purification of the crude extract, were compared to each other. As shown in Figure 5.3A, drying in a vacuum has the lowest environmental impact, followed by spray drying and freeze drying. Even though spray drying might degrade temperature-sensitive compounds, up to 90% of the anthocyanins encapsulated are spray-dried [415]. Freeze drying guarantees more careful handling of temperature-sensitive compounds but comes with higher operating costs and a 15% higher environmental impact. Due to the green extraction method, the total environmental impact of dyeing 1 m² of wool with an anthocyanin crude extract is better compared to the synthetic dye.

5.2.2.2 Naphthoquinones

Figure E.2 depicts the five different scenarios for obtaining natural quinone from walnut green husks with ultrasound-assisted extraction (UAE). As dyeing frequently occurs in an aqueous environment, pervaporation, a membrane separation technique, was applied to separate binary azeotropic mixtures. Membranes with wide pores can efficiently separate macro- and micro-molecules. The molecular cut-off becomes more stringent for narrower membrane pores, and the separation is mainly based on compounds' solubility, membrane hydrophobicity, and polarity resistance [401]. This technique is competitive with conventional high energy-consuming methods such as distillation, extraction, or drying, as it is proven to be more economical, safe, and eco-friendly [438]. This leads to a 21% lower impact for the first scenario compared to the synthetic dye reference. The drying of biomass shows yet again a large contribution to the overall impact (55–71%) (Figure 5.3B). As was previously mentioned, the only preparative purification method for naphthoquinones is flash chromatography [425], which is not the most practical procedure and shows an average contribution of 13% to the total impact. In terms of the drying method, vacuum

evaporation is again the most efficient method, which is allowed due to the great thermostability of 1,4-naphthoquinones. In the end, dyeing with crude extract produces a better environmental impact compared to the synthetic dye.

5.2.2.3 Anthraquinones

This is the most interesting case, as a one-to-one comparison is possible. Natural anthraquinones are more present in plant- and insect-based sources. For this reason, only rhubarb by-products form the base of this LCA. Due to the good fastness properties of these dyes, calculations were based on a 2% owf. This resulted in a small number of by-products and lower amounts of consumables. The direct application of the extract, after pervaporation, on wool fiber showed a 21% lower impact on the reference synthetic anthraquinone dye (Figure 5.3C). The scenario involving the drying of biomass is 2.5 times higher in impact compared to the first scenario. This could be ascribed to the drying process, which accounts for 81% of the total impact. The purification method with CPC is the most applied method for separating anthraquinones from the crude extract [60]. This purification system consists of a n-hexane/ethyl acetate/methanol/water mixture and comprises up to 46% of the total impact [439]. Afterward, the purified anthraquinones could be spray-dried, as these dyes only start to decompose from 189 °C onward [48] and this method is 43% lower in total impact compared to vacuum evaporation. The application of crude extract is the most environmentally friendly approach for dyeing with natural anthraquinones. Agnhage et al. [440] performed an LCA analysis from the cultivation of the madder plant, dye extraction, and dyeing of 1 kg of polyester with 3% owf concentration. The results showed that the dye extraction phase (solvent and energy use) and the dyeing phase (liquor ratio) have the largest environmental impact of the entire process, but this study lacks a comparison with the synthetic dye equivalent.

5.2.2.4 Carotenoids

The LCA scenarios of a naturally-dyed carotenoid cotton from tomato pomace are shown in Figure E.4. Despite this by-product's high carotenoid content, the environmental impact is at least 72% higher than the synthetic anthraquinone dye (Figure 5.3D), which could be ascribed to the use of organic solvents and the required clean-up step afterward. The additional SPE purification procedure was taken from Shen et al. [433]. Due to the use of many organic solvents during purification, the environmental impact of this step takes about 28% to 47% of the total impact. When carotenoid dye powder or concentrate is desired,

concentrating carotenoid extracts by rotary evaporation is possible at reduced pressure and a temperature below 40 °C [63]. Spray drying is not recommended as this would degrade the carotenoids by both increasing residence time and temperature [441]. Furthermore, the stability of the spray-dried carotenoid powder granules may decline at high processing temperatures [441]. For these reasons, freeze drying is the most advisable technique to obtain a stable carotenoid powder, even though freeze drying is the costliest drying technique and contributes to a larger environmental impact (Figure 5.3D). Broeze et al. [36] performed a techno-economic analysis of tomato seed oil's production costs, which is further refined to carotenoids from tomato by-products. The revenues and production costs are nearly break-even on a small scale; however, on a ten times larger production scale, these production costs could decrease by 40%.

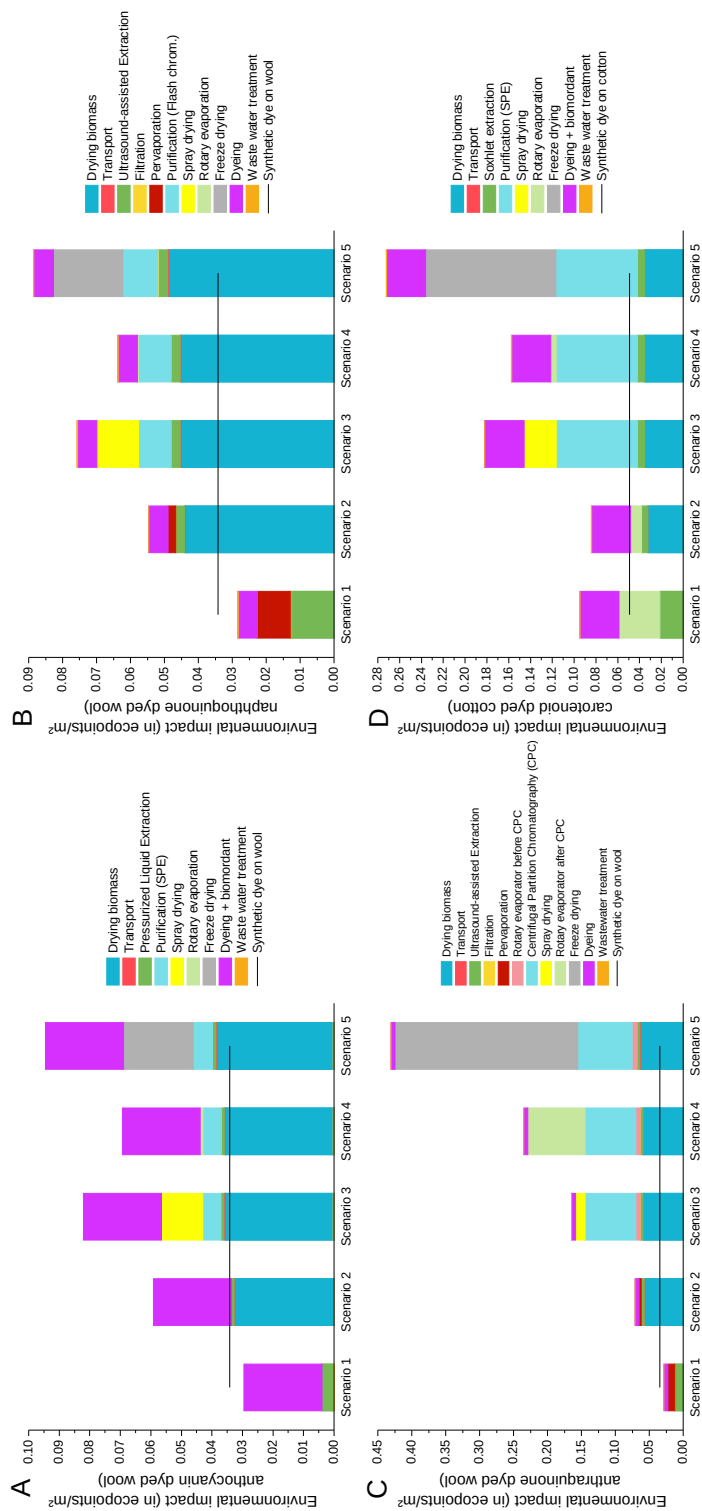


Figure 5.3: The environmental impact of dyeing one m² wool with anthocyanins (A), naphthoquinones (B), and anthraquinones (C), and one m² cotton with carotenoids (D). The horizontal bar is the synthetic dye reference. The environmental impact of dyeing one m² cotton and wool with each natural dye is shown in Figures E.5 to E.6, respectively.

The valorization routes were designed with the natural dye as the target compound, but by-products also contain other high added-value substances. To remain competitive in processing costs, the EU RESFOOD project advises the co-production of multiple compounds. This means that by-products should first be valorized toward a major bulk compound (e.g., protein, fat, carbohydrate, or fiber), while the minor compounds can be separated from the crude extract afterward [15]. Even though dyeing with the crude extract is in all cases the most competitive and environmentally friendly approach, this is recommended only when the extract is depleted of the main valuable substances or their extraction is not economically viable. Otherwise, purification is justified; the purified dye extract can be processed to a concentrate via vacuum evaporation. This has the lowest impact on the three types of drying techniques. For a dye powder, spray drying should be balanced against freeze drying, depending on the natural dye's properties, cost efficiency, and, for further application purposes, encapsulates its quality. In theory, there could be a competition of other phenolic compounds with anthocyanins when dyeing with a crude extract. However, with the dye amount of 12.5% on weight fiber the saturation level would be attained for every scenario, but a more pure naturally dyed fabric would be obtained in scenarios (3-5) and thus, potentially higher product quality. Despite the high environmental impact of these purified natural dyes, there is still room for optimization, just as synthetic dyes were chemically modified and optimized throughout the years. The aspect of post-consumer textile waste also needs to be considered, as in lower-value applications only 13% of the material used for clothing ends up being recycled, while even less than 1% results in a similar quality application (closed-loop recycling) [13]. The goal during the chemical recycling of textiles is to obtain pulp that is free from impurities such as additives and synthetic dyes. The removal of these compounds is crucial, as this increases the fiber's solubility as well as simplifies and stabilizes the regeneration process [442]. From this point of view, natural dyes can contribute to an easier recycling process, leading to a higher recycling rate and quality.

5.2.3 Sensitivity analyses

Sensitivity analyses were conducted to explore the variables that can be encountered during the process chains. The LCA analyses mentioned above were based on the maximal extractable amount of dye from the by-products; the largest amount of dye that can be used for dyeing (12.5% owf) to have a comparable shade depth, with respect to the synthetic dye, was also analyzed. The concentration of natural dye obtained depends largely on the type of by-product and extraction technique. For the same amount of dye required for the application, a smaller extracted dye content would lead to a higher amount of by-products. Hence, more consumables are needed. The influence of the natural dye content extracted on the environmental impact of a 1 m² naturally-dyed fabric is displayed in Figures E.7A and E.8A, for wool and cotton, respectively. This case could also refer to the use of other by-products that contain smaller natural dye concentrations (Figure 1.7). A general trend is visible between the direct application of the crude extract and the purified dye. The increase in the environmental impact at a lower extraction content is higher for scenarios that involve a purification step than those with the direct crude extraction application. The plots show an increase of at least 14%, 200%, 200%, and 75% in the environmental impact when the natural dye content extracted for anthocyanins, naphthoquinones, anthraquinones, and carotenoids drops in half, respectively. The shade depth can vary depending on the type of application and its desired quality. A lower amount of dye can be used, which leads to lower amounts of consumables (Figure 5.4A). This environmental impact as a function of the required dye amount (taking into account the natural dye's maximal extraction content) is shown in Figures E.7B and E.8B. Convergence is observed at the lowest dye amount, although this amount might be too low for proper coloration. Again, the first two scenarios were more competitive to the synthetic dye (2% owf) reference impact compared to the scenarios that included a purification and drying step. For anthocyanin dyed wool, scenarios two and four revealed a similar environmental impact compared to the synthetic dye at 3.2% owf and 2.4% owf, respectively. Naphthoquinone dyed wool fabrics showed a better impact with scenario one and exhibited identical environmental impacts to the synthetic dye, at 7.2% owf and 6.1% owf for the crude extract method with the drying of the by-products and purified dye concentrate, respectively. The carotenoid crude extract dyeing on cotton displayed an equal impact at 3.4% owf. For anthraquinones, the environmental impact of one 1 m² of naturally anthraquinone dyed wool outperformed the synthetic analog when using the crude extract

(scenario 1). If the drying step of the bio-products (scenario 2) was included, the impact matched the synthetic dye at 0.9% owf, and the spray-dried natural anthraquinone (scenario 3) only became competitive at 0.27% owf. The effect that transportation has on the overall impact depends on the natural content of the by-product and its density. For carotenoids, only small increments in the impact were observed due to the large carotenoid content in tomato pomace, which results in lower amounts of by-products required for dyeing 1 m² of fabric (Figures E.7C and E.8C). Red grape pomace and walnut green husks contain proportionally lower amounts of anthocyanins and naphthoquinones, respectively, and show a linear increase in impact at larger transport distances. The capacity of a semi-trailer for foodstuff logistics (30000 L) would contain lower loads of by-products for anthocyanin or naphthoquinone dye production compared to tomato pomace, despite their varying densities. This sensitivity analysis is also related to the regional availability of the fruits and vegetables and the derived by-products across the different EU member states. To feed a large-scale plant, sufficient supply from regional waste streams is crucial [36]. However, environmental impact and production costs will increase when larger distances need to be covered between the processing industry unit and biorefinery (Figure 5.4B). The average cost of road freight transport by truck is 0.14 EUR/tkm [443]. Consequently, the extraction of high added-value bioactive compounds and their application should be encouraged to be maximally exploited at locations where a strong agricultural production of specific fruits and vegetables exists, leading to potential agricultural losses and where large amounts of by-products arise to minimize the number of steps in the valorization route. This is in line with the concept of the distributed bio-based economy Luoma et al. [444]. This concept suggests the simultaneous development of a global bio-based economy and distributed production models at a local level. This “glocal” economy emphasizes the proximity between sites where raw materials are obtained and production and consumption sites; this leads to closed-loop value networks of local plants that produce and use by-products from neighboring plants in different processes [444, 445].

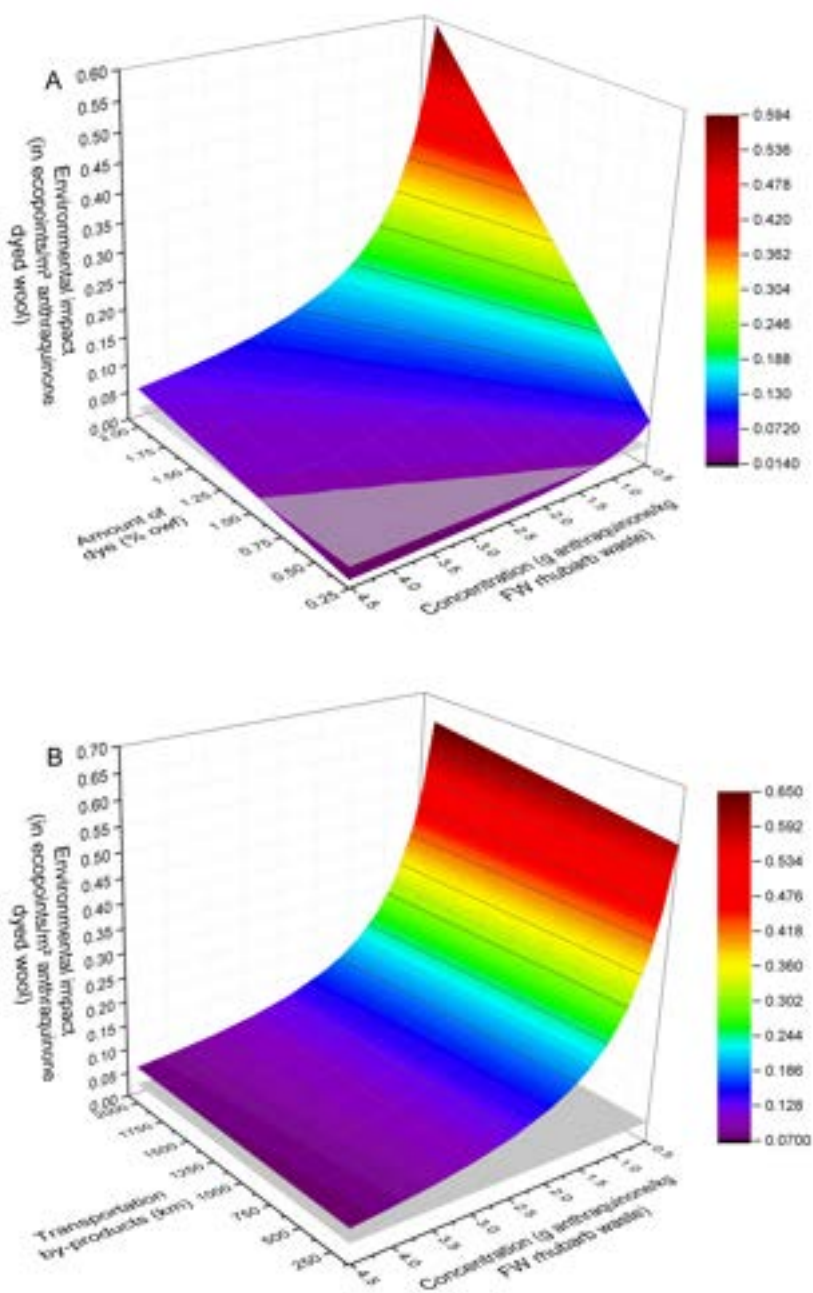


Figure 5.4: These 3D surface plots display the influence of (A) the concentration of natural anthraquinone extracted and the amount of dye (% owf) required for dyeing and (B) the concentration extracted and transportation of the by-products from waste source to biorefinery (B) on the environmental impact of dyeing 1 m² wool with natural anthraquinone crude extract (scenario 2). The synthetic dye reference is indicated by the gray surface.

5.3 Conclusions

The most recommended valorization routes, from agro-food residues to application on textile fiber, of three natural dye classes were discussed in this chapter. The valorization routes have taken into account conventional and emerging technologies for extraction, purification, and encapsulation for each specific natural dye; they also addressed the potential pitfalls that are encountered, such as thermolability, matrix clean-up, the formation of side products, cost efficiency, etc. To examine the environmental impact compared to a reference synthetic anthraquinone dye, an LCA with different scenarios that are based on the most optimal valorization route for each natural dye was carried out. It was observed that the by-products drying process has a significant influence on the total environmental impact, although this step is essential for safeguarding by-products from mold development and microbial spoilage. In terms of application, dyeing with the crude extract is, in all cases, the most environmentally friendly approach. It produces a lower or competitive environmental impact compared to the synthetic dye if an equal depth of the shade is desired. This impact decreases when lower dye amounts are required for the application and the desired quality, as this would lead to a lighter shade of the product. By-products also contain other high added-value substances, to remain competitive in processing costs, the co-production of multiple compounds is an interesting option. Even though dyeing with the crude extract is the most environmentally friendly approach, this means that it is only recommended when the extract is depleted of other valuable substances, such as proteins or other phenolics.

As only 1% of textiles are naturally dyed, the potential for commercializing this product also comes with a few obstacles, such as the variable quality of the waste stream due to deterioration, which eventually affects the end-product in terms of homogeneity and product characteristics. The moisture content is an important parameter to keep an eye on as organic molecules tend to degrade due to microbial activity. Therefore, biomass drying is essential to safeguard by-products from mold development and microbial spoilage. Furthermore, the region-dependent and seasonal availability of a waste stream hampers the continuous supply of the biorefinery and, the production of large quantities and the difficulty in reproducing shades with certified fastness properties. Nevertheless, the valorization routes analyzed in this chapter revealed that agricultural losses and food processing waste streams can indeed be adequate sources of natural dyes, and methodological

and technological aspects are available to overcome the natural dyes' obstacles for niche scale applications.

General Conclusions and Future Perspectives

6.1 Conclusions

Currently, much of the by-products of fruit and vegetable supply chains are further converted into a product with a relatively low economic value (e.g., animal feed, anaerobic digestion, energy production, landfill or an incineration facility for energy recovery). To increase the value of these by-products, novel valorization routes should be developed, with an emphasis on high added-value compounds. Natural dyes such as anthocyanins are one of those compounds that are of interest as they would replace fossil-based synthetic dyes. The textile dyeing and finishing industry are renowned to be the largest polluter of clean water as it applies a vast range of chemicals, which are toxic for human health and ecosystems [13]. The goal of this thesis was to find sustainable pathways to implement natural dyes or anthocyanins specifically in non-food applications.

Waste streams from food processing industries are an interesting source of natural dyes as they mostly contain outer parts of fruit and vegetables that contain large amounts of natural dye. The mapping of agro-food residue quantities of anthocyanins, quinones and carotenoids in Chapter 1 showed the vast availability of agro-food residues (>0.1 Mt annually) across the European Union (28 member states) with a natural dye content up to 56, 18 and 593 kg/t dry weight for anthocyanins, quinones and carotenoids, respectively. This allowed to conclude which by-products are most interesting to start from, as they show a combination of high natural dye content as well as a high availability of by-products.

Next, the mapping of the dyeing methods for the different natural dyes in terms of fastness properties showed that metallic mordants are mostly preferred to improve the affinity and stability of natural dyes, but also come along with potential environmental issues. The more greener approaches such as biomordants and enzymes still show room for improvement. Alternatively,

chemical modification of the dye molecules and encapsulating procedures via sol-gel process or with biopolymers might be promising techniques as they potentially protect the dye from process conditions.

Anthocyanidins and anthocyanins are flavonoids that are present in various plants, flowers, fruits, and vegetables. They are known to be beneficial for human health due to their antioxidant activities and therapeutic effects. Their properties are attractive for food and non-food applications. The large chemical diversity amongst these molecules potentially leads to different affinities or activities. This is important to know when extracting anthocyanidins and anthocyanins from waste streams. In order to characterize the extraction profile, highly advanced purification methods are required such as HPLC-DAD-MS/MS in combination with expensive analytical standards. Alternatively, the solubility of anthocyanidins and anthocyanins was analyzed in Chapter 2 by various *in silico* tools. The capabilities and limitations of several computational methods (i.e., Hansen solubility parameters, Flory-Huggins interaction parameter (χ_{12}), static calculations based on Density Functional Theory (DFT) and the COSMO-RS model) for the solubility determination of anthocyanidins and anthocyanins were evaluated. COSMO-RS was able to provide quantitative information on the solubility behavior within various solvents and describe the main intermolecular interactions between colorant and solvent. However, the method fell behind for characterizing the solubility within organic solvent-water mixtures. The Flory-Huggins interaction parameter (χ_{12}) and solvation free energies showed moderate results. The former overestimated the contribution of water and the latter was able to reproduce the general trends observed from other computational methods. Hansen solubility parameters were shown to be the most appropriate tool to find the most optimal organic solvent-water mixture ratio. Acetone, ethanol and methanol or aqueous mixtures of the aforementioned solvents are commonly used within experiments to increase the anthocyanidins and anthocyanins extraction yield. Furthermore, the solvent screening showed that electron rich aromatic compounds and compounds containing electron donors such as 1,4-dioxane, diethylether, dimethyl sulfoxide, quinoline or tetrahydrofuran, acting as hydrogen bond acceptors, are favored over the more traditional organic solvents in this field. However, for environmental, health and safety issues, dimethyl sulfoxide would be most applicable in anthocyanidins and anthocyanins extraction. The COSMO-RS results illustrated that the solubility of anthocyanidins and anthocyanins can be largely ascribed to π - π interactions and intermolecular hydrogen bonding, respectively. Statistical analyses also revealed

that the relative molar solubilities ($\log S_{RS}$) of aqueous mixtures of acetone, ethanol or methanol till 40% v/v are not significantly different compared to water. This indicated that the use of the three traditional organic solvents for anthocyanidins and anthocyanins extraction is most viable for aqueous mixtures of 50% v/v or higher. Hansen solubility parameters showed that an aqueous mixture of 50% v/v and 40% v/v of acetone is optimal for anthocyanidins and anthocyanins, respectively. For ethanol, a 70% v/v aqueous mixture is favored for anthocyanidins and a 60% v/v for anthocyanins. The shortest distances between anthocyanidins and methanol-water mixtures are found at 70-80% v/v and in the case of anthocyanins, 60%-70% v/v. The results obtained from Hansen solubility parameters and COSMO-RS can be used as a guidance for target specific extractions to maximize the applications' demands.

With the composition of the anthocyanin dye extract investigated, the capabilities of anthocyanins as a natural dye were explored on cellulose-based materials in Chapter 3 and considered three main objectives: to optimize the dyeing procedure with anthocyanins for cotton fibers, to investigate the potential of different types of biomordants and to interpret these experimental results by (molecular) modeling approaches. First, optimized dyeing conditions were based on finding an optimum between dye uptake, color strength, degradation of the natural dye and wash fastness. Therefore, dyeing cotton with anthocyanins is preferred at 80 °C for 60 min. at a pH of 1.47 and a concentration 510.7 ± 9.5 mg malvidin-3-glucoside equivalents L^{-1} . Furthermore, fixation of oxalic acid on cotton through esterification was favored at pH 3. Second, the use of metallic mordants was only successful for stannous chloride with premordanting, which successfully endured the wash- and light tests. The biomordants of interest did not seem to have the required properties to substitute this metal salt. The pH-sensitivity of anthocyanins could not be prevented by any of the biomordants, although it has been proven that the anthocyanins were still slightly present within the fabric when it has been reintroduced within acidic conditions, thus, the main effect is related to the pH of the detergent rather than washing off. This was observed with the wash test of water where color loss was visible. Whereas the biomordants did not show promising results related to the washing tests (ISO150-C06: $\Delta E^*_{S_n, pre} = 26.2$ and $\Delta E^*_{biomordants, pre} \geq 39.0$, ISO105-E01: $\Delta E^*_{S_n, pre} = 9.7$ and $\Delta E^*_{biomordants, pre} \geq 17.6$), the biomordants consisting of phenolic moieties, such as gallic acid and tannic acid, showed their added value in terms of antioxidant property in the light tests (ISO105-B02: $\Delta E^*_{control} = 22.0$, $\Delta E^*_{tannic\ acid, meta} = 15.5$ and $\Delta E^*_{gallic\ acid, meta} = 11.3$).

Previous findings were corroborated with molecular modeling simulations at different levels of complexity, to obtain insight into strength and type of interactions between the dye and the (bio)mordants. It can be concluded that the intermolecular interactions, hydrogen bonds and π - π interactions, were too weak in comparison to metal-ligand complexation ($\Delta G_{\text{Sn,avg}} = -953 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta G_{\text{Al}} = [-690 \text{ kJ} \cdot \text{mol}^{-1}, -282 \text{ kJ} \cdot \text{mol}^{-1}]$). It was found that anthocyanins are not able to establish ionic bonds with oxalic acid, but only hydrogen bonds ($\Delta G_{\text{hydrogen oxalate}} = -17.8 \text{ kJ} \cdot \text{mol}^{-1}$). Furthermore from the molecular dynamics simulations, it was concluded that the main intermolecular interactions between tannic acid and anthocyanins are governed by π - π interactions and not on hydrogen bonds, which are overall also too weak to yield an efficient dying process. Currently, applications with anthocyanins can be deployed in moderate environments, especially in those that do are not prone to alkaline conditions, or specific niche applications (e.g., biodegradable products, pH indicator).

With the operating area of anthocyanin on cellulose-based materials defined, the question arises if anthocyanin derivatives, pyranoanthocyanins, would be more stable for non-food applications while maintaining similar color properties. Therefore, the photophysical properties of a 140 compounds of natural occurring anthocyanin-based colorants were analyzed in Chapter 4 by means of TD-DFT with various functionals B3LYP, PBE0 and CAM-B3LYP. It showed that B3LYP results in the best overall accuracy ($\text{MAE}_{\text{B3LYP}} = 0.048 \text{ eV} < \text{MAE}_{\text{PBE0}} = 0.085 \text{ eV} < \text{MAE}_{\text{CAM-B3LYP}} = 0.35 \text{ eV}$), even in long-range charge transfer transitions, this hybrid functional was capable in locating $\lambda_{\text{max,vis}}$.

The library of $\lambda_{\text{max,vis}}$ -values and other photophysical properties obtained from TD-DFT can be used as a tool providing target specific compositions at low computational cost. This is beneficial for characterizing and quantifying complex anthocyanin derivatives, applied as food additives/colorants, for which reference analytical standards are unavailable. The molar absorption coefficients for anthocyanins are corresponding well with reference standards, whereas the extrapolation to pyranoanthocyanins induced some inconsistencies within experimental ϵ -values. In terms of color shades, pyranoanthocyanins cover similar shades as anthocyanins, while the former would provide better stability against external conditions such as pH fluctuations and temperature. Furthermore, the evaluation of orbital energies also proves that all naturally derived pyranoanthocyanins studied are interesting compounds for dye-sensitized solar cell applications. In conclusion, TD-DFT calculations can provide us insight into the potential utilization of specific natural anthocyanin-based compounds in various

applications.

Natural dyes are not yet implemented in mainstream non-food applications such as textile processes, as several technical challenges, such as cost-effectively improving extraction and application procedures, must be resolved before heading to a large (industrial) scale. In Chapter 5, the valorization routes of natural dyes from agro-food residues to application on textile fiber were analyzed. This analysis included both conventional and emerging technologies for extraction, purification, and encapsulation for specific natural dyes. The analysis also addressed the potential pitfalls, such as thermolability, matrix clean-up, the formation of side products, cost efficiency, etc.

A life cycle assessment with different scenarios based on the most optimal valorization route was carried out for each natural dye to examine the environmental impact compared to a reference synthetic anthraquinone dye. It was observed that drying of the by-products had a significant influence on the total environmental impact, although this step is essential to safeguard by-products from mold development and microbial spoilage. In terms of application, dyeing with the crude extract was in all cases the most environmentally friendly approach showing a lower or competitive environmental impact compared to the synthetic dye. This impact decreased more when lower dye amounts would be required for the application and the desired quality as this would lead to a lighter shade of the product. However, by-products also contain other high added-value substances and in order to remain competitive in processing costs, the co-production of multiple compounds is an interesting option. Even though dyeing with the crude extract is in all cases the most environmentally friendly approach, still other valuable substances such as proteins or other phenolics can be valorized.

As only 1% of the total textiles is naturally dyed, the potential to commercialize this also comes with a few bottlenecks such as a variable quality of the waste stream due to deterioration, eventually affecting the end-product in terms of homogeneity and product characteristics; the limited region-dependent and seasonal availability of a waste stream and the difficulty in reproducing shades with certified fastness properties. Yet, by implementing the right policies, these unavoidable agro-food residues could be promoted to a valuable feedstock for valorization in biorefineries. Nevertheless, the valorization routes analyzed in Chapter 5 showed that agricultural losses and food processing waste streams can indeed be adequate sources of natural dyes, and the methodological and technological aspects are available to overcome the natural dyes' obstacles for

niche scale applications.

Next to its practical implications, this work highlights the interdisciplinary aspect between molecular modeling and experimental work for the application of anthocyanins in non-food applications. Molecular modeling provides insight into the experimental observations, but also functions as a predictive tool to design and orient the experiments to the specific needs of the final application. Consequently, this combined theoretical and experimental approach confined the operating window of anthocyanins in real-life applications.

6.2 Future Perspectives

Even though anthocyanins show mediocre stability and affinity toward textile fibers, this work has highlighted the potential feasibility for application and level of sustainability to overcome these issues. Metallic mordants are mostly preferred from a chemical perspective, but entail potential environmental issues. The more greener approaches such as biomordants and enzymes are two pathways that still require more in-depth research. The selection of the most appropriate biomordant should be based on stronger intermolecular interactions (i.e., hydrogen bonds and π - π interactions) with anthocyanins. Currently, these interactions were found too little to form a stable complex. The use of enzymes is often hampered by the optimal conditions wherein enzymes operate. As such, unsynchronized process conditions can emerge in combination with anthocyanins. Due to fact that anthocyanins are very sensitive to various process conditions (e.g., temperature and pH), three methods can be explored to circumvent these issues. The first method would be the encapsulation of anthocyanins, which would protect these anthocyanins from these fluctuating external conditions while offering pigment retention. Preliminary tests in our lab showed that the sol-gel process is able to protect anthocyanins against the aforementioned process conditions. The second method would entail chemical modification of the dye molecules to guarantee dye fixation. Natural derivatization methods for anthocyanins would be the third method to improve the stability properties. The potential use of a natural derived compound class from anthocyanins, called pyranoanthocyanins, was investigated in this work. In terms of color shades, pyranoanthocyanins cover similar shades as anthocyanins. Literature study on pyranoanthocyanins already showed a better stability against pH fluctuations and temperature, but this should be further explored in future work.

The relative poor chemical stability and affinity for several applications still prevent the full exploitation of anthocyanins and are currently only relevant within short life cycle products (e.g., biodegradable or sensorial products). Plastic

packaging is an example of short life cycle products. This type of material relies on full chemical recyclability and the efficient removal of additives and colorants is essential for the recycling process. The main colors used in printing inks commonly consist of magenta (e.g., anthocyanins), yellow (e.g., quinones or carotenoids) and cyan (e.g., phycocyanin or anthocyanins). The question arises if these natural dyes can be captured and stabilized in typical ink formulations and if not, how the process or molecules can be adjusted to achieve the required specifications (e.g., color strength, gloss, transparency) and resistance properties. The natural dyes might be an interesting option also for biodegradable plastic. As the main polymer degrades, also additives such as the inks should biodegrade, which is currently a bottleneck for industry active in this field. Furthermore, the pH dependence of anthocyanins is sometimes regarded as the dye's Achilles' heel, but this property is very attractive for sensorial materials. Since the pH value is often a direct indicator of the food's freshness, an indicator sensor based on anthocyanins and biodegradable polymers such as polysaccharides, chitosan, or starch would be a non-destructive and visual method for monitoring potential food spoilage (e.g., shelf life of milk) [446, 447]. Other applications that could take advantage of this halochromic property are wound dressing materials. In order to resolve the stability or affinity issues of anthocyanins, microbial cell factories can also be deployed for anthocyanin production, allowing the creation of novel anthocyanins with unique properties. At least 11 transgenes of the anthocyanin biosynthetic pathway need to be introduced in microorganisms such as yeast or *E. coli* to produce the simplest anthocyanin (Pg-3-Glc) from phenylalanine [448]. This metabolic engineering approach is already applied and commercialized by the French biotech start-up company PILI [449]. Hereby, enzymatic cascade reactions are used to produce textile dyes from renewable resources based such as sugar.

Many dyeing studies are based on trial-and-error experiments, which are laborious and costly. The added value of computational tools is to provide (predictive) information, which is useful for experimental design, and vice versa. In this work, experimental studies have been corroborated with a series of molecular modeling calculations to obtain more insight into the intermolecular interactions between dye and (bio)mordants. These affinity studies can be performed between dyes and various textile substrates or polymers, but also for investigating the natural dye behavior within broader formulations such as ink varnishes, which include solvents, binders and additives. This would require extensive molecular dynamics simulations containing explicit solvation molecules

for accurate description. More in-depth investigation on the solubility behavior of anthocyanins or pyranoanthocyanins can also be conducted via molecular dynamics in combination with the Free Energy Perturbation (FEP) method.

In general, the mapping of by-products for each natural dye class showed the vast availability of agro-food residues (>0.1 Mt annually in the EU-28) with a natural dye content of up to 56 kg/t for anthocyanins (red grape pomace), 18 kg/t DW for quinones (walnut green husks and rhubarb roots), and 593 kg/t DW, for carotenoids (tomato pomace). This work has only covered the potential use of anthocyanins in non-food applications, but there is still a wide variety of natural dyes such as quinones, carotenoids, chlorophylls and phycobiliproteins (e.g., phycocyanins and phycoerythrins) from microalgae and seaweed, to be explored along with their properties and affinities. This work can serve as a guide to explore the properties of other natural dyes by combining molecular modeling tools and laboratory experiments.

Bibliography

- [1] J. Gustavsson, C. Cederberg, U. Sonesson, R. van Otterdijk, and M. Alexandre, "Global food losses and food waste – Extent, causes and prevention," Report, 2011.
- [2] P. Bultinck, P. W. Ayers, S. Fias, K. Tiels, and C. Van Alsenoy, "Uniqueness and basis set dependence of iterative Hirshfeld charges," *Chemical Physics Letters*, vol. 444, no. 1, pp. 205–208, 2007.
- [3] T. Lu and F. Chen, "Multiwfn: a multifunctional wavefunction analyzer," *Journal of computational chemistry*, vol. 33, no. 5, pp. 580–592, 2012.
- [4] K. R. Andersen, Ø. M. Markham, *Flavonoids : chemistry, biochemistry, and applications*, Taylor & Francis Group, LLC, 2006.
- [5] F. Delgado-Vargas, A. R. Jiménez, and O. Paredes-López, "Natural Pigments: Carotenoids, Anthocyanins, and Betalains — Characteristics, Biosynthesis, Processing, and Stability," *Critical Reviews in Food Science and Nutrition*, vol. 40, no. 3, pp. 173–289, 2000.
- [6] S. Kadolph, "Natural Dyes: A Traditional Craft Experiencing New Attention," *Delta Kappa Gamma Bulletin*, vol. 75, no. 1, pp. 14–17, 2008.
- [7] M. Shahid, I. Shahid ul, and F. Mohammad, "Recent advancements in natural dye applications: a review," *Journal of Cleaner Production*, vol. 53, pp. 310–331, 2013.
- [8] The Business Research Company, "Synthetic Dyes And Pigments Global Market Opportunities And Strategies To 2022," Report, 2019.
- [9] M. Mirjalili, K. Nazarpour, and L. Karimi, "Eco-friendly dyeing of wool using natural dye from weld as co-partner with synthetic dye," *Journal of Cleaner Production*, vol. 19, no. 9–10, pp. 1045–1051, 2011.
- [10] R. Singh, A. Jain, S. Panwar, D. Gupta, and S. K. Khare, "Antimicrobial activity of some natural dyes," *Dyes and Pigments*, vol. 66, no. 2, pp. 99–102, 2005.
- [11] Y. Caro, L. Anamale, M. Fouillaud, P. Laurent, T. Petit, and L. Dufosse, "Natural hydroxyanthraquinoid pigments as potent food grade colorants: an overview," *Natural Products and Bioprospecting*, vol. 2, no. 5, pp. 174–193, 2012.
- [12] A. Mortensen, "Carotenoids and other pigments as natural colorants," *Pure and Applied Chemistry*, vol. 78, no. 8, pp. 1477–1491, 2006.

-
- [13] A. Morlet, R. Opsomer, S. Herrmann, L. Balmond, C. Gillet, and L. Fuchs, "A New Textiles Economy: Redesigning fashion's future," Report, Ellen MacArthur Foundation, 2017.
- [14] A. Payne, *6 - Open- and closed-loop recycling of textile and apparel products*, pp. 103–123, Woodhead Publishing, 2015.
- [15] Resource efficient and safe food production and processing (RESFOOD), "Project Final Report, Update 03 05 2016," Report, European Union, 2016.
- [16] A. Stenmarck, C. Jensen, T. Quested, G. Moates, M. Buksti, B. Cseh, S. Juul, A. Parry, A. Politano, and B. Redlingshofer, "Estimates of European food waste levels.-FUSIONS: Reducing food waste through social innovation, Stockholm," 2016.
- [17] N. A. Sagar, S. Pareek, S. Sharma, E. M. Yahia, and M. G. Lobo, "Fruit and Vegetable Waste: Bioactive Compounds, Their Extraction, and Possible Utilization," *Comprehensive Reviews in Food Science and Food Safety*, vol. 17, no. 3, pp. 512–531, 2018.
- [18] K. Waldron, *Handbook of waste management and co-product recovery in food processing*, vol. 1, Elsevier, 2009.
- [19] A. Schieber, F. Stintzing, and R. Carle, "By-products of plant food processing as a source of functional compounds-recent developments," *Trends in Food Science & Technology*, vol. 12, no. 11, pp. 401–413, 2001.
- [20] Food and Agriculture Organization of the United Nations (FAO), "Processing of fresh-cut tropical fruits and vegetables: A technical guide," Report, 2010.
- [21] S. Plazzotta, L. Manzocco, and M. C. Nicoli, "Fruit and vegetable waste management and the challenge of fresh-cut salad," *Trends in Food Science & Technology*, vol. 63, pp. 51–59, 2017.
- [22] Food and Agriculture Organization of the United Nations (FAO), "The future of food and agriculture - Trends and challenges," Report, 2017.
- [23] A. Close, G. Stewart, M. Masotti, M. Setti, and M. Vittuari, "A roadmap to reduce food waste in Europe. REFRESH Deliverable 4.8," Report, European Union, 2019.
- [24] D. Gunders and J. Bloom, *Wasted: How America is losing up to 40 percent of its food from farm to fork to landfill*, Natural Resources Defense Council New York, 2017.
- [25] J. Wain, K. Waldron, G. Moates, and P. Metcalfe, "Viability of bio-based chemicals from food waste. REFRESH Deliverable 6.8," Report, European Union, 2019.
- [26] E. White and T. Oldfield, "Report on the holistic analysis of AWCB chains and logistics of AWCB valorisation systems," Report, European Union, 2016.

- [27] C. M. Galanakis, "The Food Systems in the Era of the Coronavirus (COVID-19) Pandemic Crisis," *Foods*, vol. 9, no. 4, p. 523, 2020.
- [28] N. Mirabella, V. Castellani, and S. Sala, "Current options for the valorization of food manufacturing waste: a review," *Journal of Cleaner Production*, vol. 65, pp. 28–41, 2014.
- [29] A. Braekevelt and N. Vanaken, "Aanbod en bestemming biomassa(rest)stromen voor de circulaire economie in Vlaanderen," Report, Openbare Vlaamse Afvalstoffenmaatschappij (OVAM), 2017.
- [30] B. Lipinski, C. Hanson, J. Lomax, L. Kitinoja, R. Waite, and T. Searchinger, "Reducing food loss and waste," *World Resources Institute Working Paper*, pp. 1–40, 2013.
- [31] S. D. Porter, D. S. Reay, P. Higgins, and E. Bomberg, "A half-century of production-phase greenhouse gas emissions from food loss & waste in the global food supply chain," *Science of the Total Environment*, vol. 571, pp. 721–729, 2016.
- [32] V. Monier, S. Mudgal, V. Escalon, C. O'Connor, G. Anderson, H. Montoux, H. Reisinger, P. Dolley, S. Ogilvie, and G. Gareth Morton, "Preparatory Study on Food Waste across EU 27," Report, 2010.
- [33] K. Roels and D. Van Gijseghe, "Voedselreststromen en voedselverliezen: preventie en valorisatie - monitoring Vlaanderen 2015," Report, 2017.
- [34] H. E. M. El-Sayed and M. M. H. El-Sayed, "Assessment of Food Processing and Pharmaceutical Industrial Wastes as Potential Biosorbents: A Review," *Journal of Biomedicine and Biotechnology*, vol. 2014, p. 146769, 2014.
- [35] L. Kips and B. Van Droogenbroeck, "Valorisatie van groente- en fruitreststromen: opportuniteiten en knelpunten," 2014.
- [36] J. Broeze, P. Geerdink, and J. Voogt, "Food waste high value exploitation hypothesis testing. REFRESH Deliverable D6.12," Report, European Union, 2019.
- [37] L. De las Fuentes, "AWARENET: Agro-food wastes minimisation and reduction network," *WIT Transactions on Ecology and the Environment*, vol. 56, 2002.
- [38] C. Fritsch, S. Andreas, A. Happel, M. A. Cubero, G. Belotti, I. Aguiló, M. Abadias, M. Gallur, I. Maria Cigognini, A. Montanari, M. J. Lopez, F. Suarez-Estrella, N. Brunton, L. Sisti, and M. Ferri, "Agri and food waste valorisation co-ops based on flexible multi-feedstocks biorefinery processing technologies for new high added value applications," Report, European Union, 2017.
- [39] S. I. Patsios, K. N. Kontogiannopoulos, S. T. Mitrouli, K. V. Plakas, and

- A. J. Karabelas, "Characterisation of agricultural waste co- and by-products," Report, European Union, 2016.
- [40] S. Wunder, E. van Herpen, K. Bygrave, H. Bos-Brouwers, F. Colin, K. Östergren, M. Vittuari, H. Pinchen, and M. Kemper, "REFRESH Final Results Brochure," Report, European Union, 2020.
- [41] G. Moates, N. Sweet, K. Bygrave, and K. Waldron, "Top 20 Food waste streams. REFRESH Deliverable 6.9," Report, European Union, 2016.
- [42] E. Rosello-Soto, M. Koubaa, A. Moubarik, R. P. Lopes, J. A. Saraiva, N. Boussetta, N. Grimi, and F. J. Barba, "Emerging opportunities for the effective valorization of wastes and by-products generated during olive oil production process: Non-conventional methods for the recovery of high-added value compounds," *Trends in Food Science & Technology*, vol. 45, no. 2, pp. 296–310, 2015.
- [43] S. S. Muthu, *Roadmap to sustainable textiles and clothing: Eco-friendly raw materials, technologies, and processing methods*, Springer, 2014.
- [44] G. Garcia-Garcia, J. Stone, and S. Rahimifard, "Opportunities for waste valorisation in the food industry – A case study with four UK food manufacturers," *Journal of Cleaner Production*, vol. 211, pp. 1339–1356, 2019.
- [45] P. D. Kiser, M. Golczak, A. Maeda, and K. Palczewski, "Key enzymes of the retinoid (visual) cycle in vertebrate retina," *Biochimica et Biophysica Acta (BBA) - Molecular and Cell Biology of Lipids*, vol. 1821, no. 1, pp. 137–151, 2012.
- [46] D. Rawat, V. Mishra, and R. S. Sharma, "Detoxification of azo dyes in the context of environmental processes," *Chemosphere*, vol. 155, pp. 591–605, 2016.
- [47] K.-T. Chung, "Azo dyes and human health: A review," *Journal of Environmental Science and Health, Part C*, vol. 34, no. 4, pp. 233–261, 2016.
- [48] M. Fouillaud, Y. Caro, M. Venkatachalam, I. Grondin, and L. Dufossé, *Anthraquinones*, pp. 130–170, CRC Press, 2018.
- [49] A. D. McNaught and A. Wilkinson, *IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book")*, Wiley-Blackwell, 1997.
- [50] A. Castaneda-Ovando, M. D. Pacheco-Hernandez, M. E. Paez-Hernandez, J. A. Rodriguez, and C. A. Galan-Vidal, "Chemical studies of anthocyanins: A review," *Food Chemistry*, vol. 113, no. 4, pp. 859–871, 2009.
- [51] H. E. Khoo, A. Azlan, S. T. Tang, and S. M. Lim, "Anthocyanidins and anthocyanins: colored pigments as food, pharmaceutical ingredients, and

- the potential health benefits," *Food & Nutrition Research*, vol. 61, no. 1, pp. 1361779–1361779, 2017.
- [52] P. Trouillas, J. C. Sancho-Garcia, V. De Freitas, J. Gierschner, M. Otyepka, and O. Dangles, "Stabilizing and Modulating Color by Copigmentation: Insights from Review Theory and Experiment," *Chemical Reviews*, vol. 116, no. 9, pp. 4937–4982, 2016.
- [53] T. Bechtold and R. Mussak, *Handbook of Natural Colorants*, Wiley, 2009.
- [54] M. Horbowicz, R. Kosson, A. Grzesiuk, and H. Dębski, "Anthocyanins of Fruits and Vegetables - Their Occurrence, Analysis and Role in Human Nutrition," 2008.
- [55] M. P. Kähkönen and M. Heinonen, "Antioxidant Activity of Anthocyanins and Their Aglycons," *Journal of Agricultural and Food Chemistry*, vol. 51, no. 3, pp. 628–633, 2003.
- [56] C. Malien-Aubert, O. Dangles, and M. J. Amiot, "Color stability of commercial anthocyanin-based extracts in relation to the phenolic composition. Protective effects by intra and intermolecular copigmentation," *Journal of Agricultural and Food Chemistry*, vol. 49, no. 1, pp. 170–176, 2001.
- [57] C. R. Welch, Q. Wu, and J. E. Simon, "Recent advances in anthocyanin analysis and characterization," *Current Analytical Chemistry*, vol. 4, no. 2, pp. 75–101, 2008.
- [58] M. M. Giusti, L. E. Rodriguez-Saona, and R. E. Wrolstad, "Molar absorptivity and color characteristics of acylated and non-acylated pelargonidin-based anthocyanins," *Journal of Agricultural and Food Chemistry*, vol. 47, no. 11, pp. 4631–4637, 1999.
- [59] C. L. Zhao, Y. Q. Yu, Z. J. Chen, G. S. Wen, F. G. Wei, Q. Zheng, C. D. Wang, and X. L. Xiao, "Stability-increasing effects of anthocyanin glycosyl acylation," *Food Chemistry*, vol. 214, pp. 119–128, 2017.
- [60] J. Duval, V. Pecher, M. Poujol, and E. Lesellier, "Research advances for the extraction, analysis and uses of anthraquinones: A review," *Industrial Crops and Products*, vol. 94, pp. 812–833, 2016.
- [61] H. Sakakibara, Y. Honda, S. Nakagawa, H. Ashida, and K. Kanazawa, "Simultaneous determination of all polyphenols in vegetables, fruits, and teas," *Journal of Agricultural and Food Chemistry*, vol. 51, no. 3, pp. 571–581, 2003.
- [62] G. C. H. Derksen, M. Naayer, T. A. van Beek, A. Capelle, I. K. Haaksman, H. A. van Doren, and A. E. de Groot, "Chemical and enzymatic hydrolysis

- of anthraquinone glycosides from madder roots," *Phytochemical Analysis*, vol. 14, no. 3, pp. 137–144, 2003.
- [63] D. B. Rodriguez-Amaya, *A guide to carotenoid analysis in foods*, ILSI press Washington, DC, 2001.
- [64] A. Guesmi, N. Ladhari, N. B. Hamadi, M. Msaddek, and F. Sakli, "First application of chlorophyll-a as biomordant: sonicator dyeing of wool with betanin dye," *Journal of cleaner production*, vol. 39, pp. 97–104, 2013.
- [65] V. da Silva Ferreira and C. Sant'Anna, "Impact of culture conditions on the chlorophyll content of microalgae for biotechnological applications," *World Journal of Microbiology and Biotechnology*, vol. 33, no. 1, p. 20, 2016.
- [66] European Commission, "Communication from the Commission To The Council and the European Parliament on the Interpretative Communication On Waste And By-Products," *COM*, p. 13, 2007.
- [67] A. Barbulova, G. Colucci, and F. Apone, "New trends in cosmetics: By-products of plant origin and their potential use as cosmetic active ingredients," *Cosmetics*, vol. 2, no. 2, pp. 82–92, 2015.
- [68] I. Goñi and D. Hervet-Hernández, *By-products from plant foods are sources of dietary fibre and antioxidants*, pp. 95–116, InTech, 2011.
- [69] U.S. Environmental Protection Agency, *Exposure Factors Handbook Chapter 9 (Update): Intake of Fruits and Vegetables*, vol. EPA/600/R-18/098F, U.S. EPA Office of Research and Development, Washington, DC, 2018.
- [70] U.S. Department of Agriculture, "USDA National Nutrient Database for Standard Reference Release v.3.9.5.3_2019-06-13," 2019.
- [71] H. Arvayo-Enríquez, I. Mondaca-Fernández, P. Gortáñez-Moroyoqui, J. López-Cervantes, and R. Rodríguez-Ramírez, "Carotenoids extraction and quantification: a review," *Analytical Methods*, vol. 5, no. 12, pp. 2916–2924, 2013.
- [72] A. Freitas, M. Moldão-Martins, H. S. Costa, T. G. Albuquerque, A. Valente, and A. Sanches-Silva, "Effect of UV-C radiation on bioactive compounds of pineapple (*Ananas comosus* L. Merr.) by-products," *Journal of the Science of Food and Agriculture*, vol. 95, no. 1, pp. 44–52, 2015.
- [73] H. Liu, J. K. Cao, and W. B. Jiang, "Evaluation and comparison of vitamin C, phenolic compounds, antioxidant properties and metal chelating activity of pulp and peel from selected peach cultivars," *LWT - Food Science and Technology*, vol. 63, no. 2, pp. 1042–1048, 2015.
- [74] Z. Y. Ju and L. R. Howard, "Effects of solvent and temperature on pressurized liquid extraction of anthocyanins and total phenolics from dried red grape

- skin," *Journal of Agricultural and Food Chemistry*, vol. 51, no. 18, pp. 5207–13, 2003.
- [75] F. G. Braga, F. Silva, and A. Alves, "Recovery of winery by-products in the Douro Demarcated Region: Production of calcium tartrate and grape pigments," *American Journal of Enology and Viticulture*, vol. 53, no. 1, pp. 41–45, 2002.
- [76] R. Bobinaitė, G. Pataro, N. Lamanauskas, S. Šatkauskas, P. Viškelis, and G. Ferrari, "Application of pulsed electric field in the production of juice and extraction of bioactive compounds from blueberry fruits and their by-products," *Journal of Food Science and Technology*, vol. 52, no. 9, pp. 5898–5905, 2015.
- [77] X. Zhao, Z. Yuan, Y. Fang, Y. Yin, and L. Feng, "Characterization and evaluation of major anthocyanins in pomegranate (*Punica granatum* L.) peel of different cultivars and their development phases," *European Food Research and Technology*, vol. 236, no. 1, pp. 109–117, 2013.
- [78] V. Neveu, J. Perez-Jiménez, F. Vos, V. Crespy, L. du Chaffaut, L. Mennen, C. Knox, R. Eisner, J. Cruz, D. Wishart, and A. Scalbert, "Phenol-Explorer: an online comprehensive database on polyphenol contents in foods," *Database*, vol. 2010, pp. bap024–bap024, 2010.
- [79] V. R. W. Oreopoulou, *Utilization of by-products and treatment of waste in the food industry*, Springer, New York, 2007.
- [80] F. A. Tomás-Barberán, M. I. Gil, P. Cremin, A. L. Waterhouse, B. Hess-Pierce, and A. A. Kader, "HPLC-DAD-ESIMS analysis of phenolic compounds in nectarines, peaches, and plums," *Journal of Agricultural and Food Chemistry*, vol. 49, no. 10, pp. 4748–4760, 2001.
- [81] S. O. Mueller, M. Schmitt, W. Dekant, H. Stopper, J. Schlatter, P. Schreier, and W. K. Lutz, "Occurrence of Emodin, Chrysophanol and Physcion in Vegetables, Herbs and Liquors. Genotoxicity and Anti-genotoxicity of the Anthraquinones and of the Whole Plants," *Food and Chemical Toxicology*, vol. 37, no. 5, pp. 481–491, 1999.
- [82] C. Reif, E. Arrigoni, H. Schärer, L. Nyström, and R. F. Hurrell, "Carotenoid database of commonly eaten Swiss vegetables and their estimated contribution to carotenoid intake," *Journal of Food Composition and Analysis*, vol. 29, no. 1, pp. 64–72, 2013.
- [83] J. Volden, G. B. Bengtsson, and T. Wicklund, "Glucosinolates, L-ascorbic acid, total phenols, anthocyanins, antioxidant capacities and colour in cauliflower (*Brassica oleracea* L. ssp. botrytis); effects of long-term freezer storage," *Food Chemistry*, vol. 112, no. 4, pp. 967–976, 2009.

- [84] R. Llorach, J. C. Espín, F. A. Tomás-Barberán, and F. Ferreres, "Valorization of Cauliflower (*Brassica oleracea* L. var. botrytis) By-Products as a Source of Antioxidant Phenolics," *Journal of Agricultural and Food Chemistry*, vol. 51, no. 8, pp. 2181–2187, 2003.
- [85] T. Albishi, J. A. John, A. S. Al-Khalifa, and F. Shahidi, "Antioxidative phenolic constituents of skins of onion varieties and their activities," *Journal of Functional Foods*, vol. 5, no. 3, pp. 1191–1203, 2013.
- [86] L. Gennaro, C. Leonardi, F. Esposito, M. Salucci, G. Maiani, G. Quaglia, and V. Fogliano, "Flavonoid and Carbohydrate Contents in Tropea Red Onions: Effects of Homelike Peeling and Storage," *Journal of Agricultural and Food Chemistry*, vol. 50, no. 7, pp. 1904–1910, 2002.
- [87] A. Schieber and M. D. A. Saldaña, "Potato peels: a source of nutritionally and pharmacologically interesting compounds-a review," *Food*, vol. 3, no. 2, pp. 23–29, 2009.
- [88] F. Will and H. Dietrich, "Processing and chemical composition of rhubarb (*Rheum rhabarbarum*) juice," *LWT - Food Science and Technology*, vol. 50, no. 2, pp. 673–678, 2013.
- [89] M. Colaric, R. Veberic, A. Solar, M. Hudina, and F. Stampar, "Phenolic Acids, Syringaldehyde, and Juglone in Fruits of Different Cultivars of *Juglans regia* L.," *Journal of Agricultural and Food Chemistry*, vol. 53, no. 16, pp. 6390–6396, 2005.
- [90] F. Stampar, A. Solar, M. Hudina, R. Veberic, and M. Colaric, "Traditional walnut liqueur – cocktail of phenolics," *Food Chemistry*, vol. 95, no. 4, pp. 627–631, 2006.
- [91] W.-U. Müller and E. Leistner, "Aglycones and glycosides of oxygenated naphthalenes and a glycosyltransferase from *Juglans*," *Phytochemistry*, vol. 17, no. 10, pp. 1739–1742, 1978.
- [92] F. Shahidi and P. Ambigaipalan, "Phenolics and polyphenolics in foods, beverages and spices: Antioxidant activity and health effects – A review," *Journal of Functional Foods*, vol. 18, Part B, pp. 820–897, 2015.
- [93] S. N. Cosmulescu, I. Trandafir, G. Achim, and A. Baci, "Juglone Content in Leaf and Green Husk of Five Walnut (*Juglans regia* L.) Cultivars," *Notulae Botanicae Horti Agrobotanici Cluj-Napoca*, vol. 39, no. 1, pp. 237–240, 2011.
- [94] A. Paneitz and J. Westendorf, "Anthranoid contents of rhubarb (*Rheum undulatum* L.) and other *Rheum* species and their toxicological relevance," *European Food Research and Technology*, vol. 210, no. 2, pp. 97–101, 1999.
- [95] U. Kosikowska, H. D. Smolarz, and A. Malm, "Antimicrobial activity and

- total content of polyphenols of *Rheum* L. species growing in Poland," *Central European Journal of Biology*, vol. 5, no. 6, pp. 814–820, 2010.
- [96] I. F. Strati and V. Oreopoulou, "Process optimisation for recovery of carotenoids from tomato waste," *Food Chemistry*, vol. 129, no. 3, pp. 747–752, 2011.
- [97] D. Kaur, D. S. Sogi, S. K. Garg, and A. S. Bawa, "Flotation-cum-sedimentation system for skin and seed separation from tomato pomace," *Journal of Food Engineering*, vol. 71, no. 4, pp. 341–344, 2005.
- [98] E. H. Papaioannou and A. J. Karabelas, "Lycopene recovery from tomato peel under mild conditions assisted by enzymatic pre-treatment and non-ionic surfactants," *Acta Biochimica Polonica*, vol. 59, no. 1, pp. 71–74, 2012.
- [99] E. Vági, B. Simándi, K. P. Vászrhelyiné, H. Daoood, . Kéry, F. Doleschall, and B. Nagy, "Supercritical carbon dioxide extraction of carotenoids, tocopherols and sitosterols from industrial tomato by-products," *Journal of Supercritical Fluids*, vol. 40, no. 2, pp. 218–226, 2007.
- [100] J. S. Seo, B. J. Burri, Z. Quan, and T. R. Neidlinger, "Extraction and chromatography of carotenoids from pumpkin," *Journal of Chromatography A*, vol. 1073, no. 1, pp. 371–375, 2005.
- [101] X. Shi, H. Wu, J. Shi, S. J. Xue, D. Wang, W. Wang, A. Cheng, Z. Gong, X. Chen, and C. Wang, "Effect of modifier on the composition and antioxidant activity of carotenoid extracts from pumpkin (*Cucurbita maxima*) by supercritical CO₂," *LWT - Food Science and Technology*, vol. 51, no. 2, pp. 433–440, 2013.
- [102] B. Chen and Y. Tang, "Processing and stability of carotenoid powder from carrot pulp waste," *Journal of Agricultural and Food Chemistry*, vol. 46, no. 6, pp. 2312–2318, 1998.
- [103] B. Ćosić, T. Pukšec, G. Krajačić, N. Duić, N. Markovska, H. Mikulčić, and M. Vujanović, "Agrocycle: Database/inventory of the current agricultural value chains - Vegetable AWCB value chain," 2016.
- [104] M. Wadhwa and M. Bakshi, "Utilization of fruit and vegetable wastes as livestock feed and as substrates for generation of other value-added products," Report, Food and Agriculture Organization (FAO), 2013.
- [105] P. Chantaro, S. Devahastin, and N. Chiewchan, "Production of antioxidant high dietary fiber powder from carrot peels," *LWT - Food Science and Technology*, vol. 41, no. 10, pp. 1987–1994, 2008.
- [106] F. Perrin, M. Brahem, C. Dubois-Laurent, S. Huet, M. Jourdan, E. Geoffriau, D. Peltier, and S. Gagné, "Differential Pigment Accumulation in Carrot

- Leaves and Roots during Two Growing Periods," *Journal of Agricultural and Food Chemistry*, vol. 64, no. 4, pp. 906–912, 2016.
- [107] E. Biehler, F. Mayer, L. Hoffmann, E. Krause, and T. Bohn, "Comparison of 3 Spectrophotometric Methods for Carotenoid Determination in Frequently Consumed Fruits and Vegetables," *Journal of Food Science*, vol. 75, no. 1, pp. C55–C61, 2010.
- [108] G. Aravantinos-Zafirios, V. Oreopoulou, C. Tzia, and C. Thomopoulos, "Utilisation of orange by-products—orange peel carotenoids," *Journal of the Science of Food and Agriculture*, vol. 59, no. 1, pp. 77–79, 1992.
- [109] M. d. C. Robles-Ramírez, R. Monterrubio-López, R. Mora-Escobedo, and M. del Carmen Beltrán-Orozco, "Evaluation of extracts from potato and tomato wastes as natural antioxidant additives," *Archivos Latinoamericanos De Nutricion*, vol. 66, no. 1, pp. 66–73, 2016.
- [110] European Apparel and Textile Confederation (EURATEX), "Annual Report 2018," Report, 2018.
- [111] European Apparel and Textile Confederation (EURATEX), "Annual Report 2017," Report, 2017.
- [112] I. Shahid ul and F. Mohammad, "Natural Colorants in the Presence of Anchors So-Called Mordants as Promising Coloring and Antimicrobial Agents for Textile Materials," *ACS Sustainable Chemistry & Engineering*, vol. 3, no. 10, pp. 2361–2375, 2015.
- [113] K. Buchholz, V. Kasche, and U. T. Bornscheuer, *Biocatalysts and enzyme technology*, John Wiley & Sons, 2012.
- [114] K. Phan, E. Van Den Broeck, V. Van Speybroeck, K. De Clerck, K. Raes, and S. De Meester, "The potential of anthocyanins from blueberries as a natural dye for cotton: A combined experimental and theoretical study," *Dyes and Pigments*, vol. 176, pp. 1–19, 2020.
- [115] H. Wang, Z. Tang, and W. Zhou, "A method for dyeing cotton fabric with anthocyanin dyes extracted from mulberry (*Morus rubra*) fruits," *Coloration Technology*, vol. 132, no. 3, pp. 222–231, 2016.
- [116] W. Haddar, M. Ben Ticha, N. Meksi, and A. Guesmi, "Application of anthocyanins as natural dye extracted from *Brassica oleracea* L-var. capitata f. rubra: dyeing studies of wool and silk fibres," *Natural Product Research*, vol. 32, no. 2, pp. 141–148, 2018.
- [117] D. Shukla and P. S. Vankar, "Natural dyeing with black carrot: new source for newer shades on silk," *Journal of Natural Fibers*, vol. 10, no. 3, pp. 207–218, 2013.
- [118] H. Wang, P. Li, and W. Zhou, "Dyeing of Silk with Anthocyanins Dyes

- Extract from *Liriope platyphylla* Fruits," *Journal of Textiles*, vol. 2014, p. 9, 2014.
- [119] N. N. Patil and A. G. Datar, "Applications of natural dye from *Ixora coccinea* L. in the field of textiles and cosmetics," *Coloration Technology*, vol. 132, no. 1, pp. 98–103, 2016.
- [120] D. Das, D. B. Datta, and P. Bhattacharya, "Simultaneous dyeing and finishing of silk fabric with natural color and itaconic acid," *Clothing and Textiles Research Journal*, vol. 32, no. 2, pp. 93–106, 2014.
- [121] M. G. Uddin, "Effects of different mordants on silk fabric dyed with onion outer skin extracts," *Journal of Textiles*, vol. 2014, p. 8, 2014.
- [122] P. Velmurugan, J. I. Kim, K. Kim, J. H. Park, K. J. Lee, W. S. Chang, Y. J. Park, M. Cho, and B. T. Oh, "Extraction of natural colorant from purple sweet potato and dyeing of fabrics with silver nanoparticles for augmented antibacterial activity against skin pathogens," *Journal of Photochemistry and Photobiology B-Biology*, vol. 173, pp. 571–579, 2017.
- [123] M. Chairat, S. Rattanaphani, J. B. Bremner, and V. Rattanaphani, "Adsorption kinetic study of lac dyeing on cotton," *Dyes and Pigments*, vol. 76, no. 2, pp. 435–439, 2008.
- [124] D. Grifoni, L. Bacci, G. Zipoli, L. Albanese, and F. Sabatini, "The role of natural dyes in the UV protection of fabrics made of vegetable fibres," *Dyes and Pigments*, vol. 91, no. 3, pp. 279–285, 2011.
- [125] R. B. Bai, Y. Y. Yu, Q. Wang, J. G. Yuan, and X. R. Fan, "Effect of laccase on dyeing properties of polyphenol-based natural dye for wool fabric," *Fibers and Polymers*, vol. 17, no. 10, pp. 1613–1620, 2016.
- [126] Z. H. Z. Abidin, "The colour stability of natural blue dye extracted from *Clitoria ternatea* L. in poly(acrylamide-co-acrylic acid) coating film," *Pigment & Resin Technology*, vol. 48, no. 4, pp. 265–271, 2019.
- [127] M. M. Fares and K. H. Masadeh, "Natural dye cyanidin-based polyacrylonitrile conjugate as environmental-friendly thin film sensor," *Advances in Polymer Technology*, vol. 37, no. 4, pp. 977–984, 2018.
- [128] A. Pakolpakcil, E. Karaca, and B. Becerir, "Investigation of a natural pH-indicator dye for nanofibrous wound dressings," in "IOP Conference Series: Materials Science and Engineering," vol. 460, pp. 1–5, 2018.
- [129] P. Yadav, E. Grover, and N. Fatima, "Printing of silk with natural red cabbage dye," *Textile Trends*, vol. 53, no. 4, pp. 36–40, 2010.
- [130] H. Wang, M. Hussain, and W. Zhou, "A novel method for natural dyeing of cotton fabrics with anthocyanin pigments from *Morus rubra* fruits," *Textile Research Journal*, vol. 87, no. 15, pp. 1896–1911, 2017.

- [131] G. Gedik, A. Yavas, O. Avinc, and O. Simsek, "Cationized natural dyeing of cotton fabrics with Corn Poppy (*Papaver rhoeas*) and investigation of antibacterial activity," *Asian Journal of Chemistry*, vol. 25, no. 15, pp. 8475–8483, 2013.
- [132] M. Nakpathom, B. Somboon, N. Narumol, and R. Mongkholrattanasit, "Dyeing of cationized cotton with natural colorant from purple corncob," *Journal of Natural Fibers*, vol. 15, no. 5, pp. 668–679, 2018.
- [133] P. Pipattanamomgkol, N. Lourith, and M. Kanlayavattanakul, "The natural approach to hair dyeing product with *Cleistocalyx nervosum* var. *paniala*," *Sustainable Chemistry and Pharmacy*, vol. 8, pp. 88–93, 2018.
- [134] P. M. Rose, V. Cantrill, M. Benohoud, A. Tidder, C. M. Rayner, and R. S. Blackburn, "Application of anthocyanins from blackcurrant (*Ribes nigrum* L.) fruit waste as renewable hair dyes," *Journal of Agricultural and Food Chemistry*, vol. 66, no. 26, pp. 6790–6798, 2018.
- [135] P. R. Richards, *Chapter 19 - Fabric Finishing: Dyeing and Colouring*, pp. 475–505, Woodhead Publishing, 2015.
- [136] B. Pavlišić, L. Černe, S. Bračko, and V. F. Savec, "Influence of UV radiation on cotton fabrics dyed with natural dyes," *Tekstilec*, vol. 54, no. 4-6, pp. 69–79, 2011.
- [137] Y. M. Jia and H. W. Jiang, *Dyeing of mulberry silk using natural safflower yellow pigment*, vol. 670-671 of *Applied Mechanics and Materials*, pp. 197–200, Trans Tech Publications Ltd, Stafa-Zurich, 2014.
- [138] M. Zarkogianni, E. Mikropoulou, E. Varella, and E. Tsatsaroni, "Colour and fastness of natural dyes: revival of traditional dyeing techniques," *Coloration Technology*, vol. 127, no. 1, pp. 18–27, 2011.
- [139] H. Oda, "Improvement of light fastness of natural dye: Effect of ultraviolet absorbers containing benzotriazolyl moiety on the photofading of red carthamin," *Coloration Technology*, vol. 128, no. 2, pp. 108–113, 2012.
- [140] H. Oda, "Improvement of light fastness of natural dyes. Part 2: Effect of functional phenyl esters on the photofading of carthamin in polymeric substrate," *Coloration Technology*, vol. 117, no. 5, pp. 257–261, 2001.
- [141] H. Oda, "Improvement of the light fastness of natural dyes: The action of single oxygen quenchers on the photofading of red carthamin," *Coloration Technology*, vol. 117, no. 4, pp. 204–208, 2001.
- [142] J. B. Saha Tchinda, A. Pétrissans, S. Molina, M. K. Ndikontar, S. MOUNGUENGUI, S. Dumarçay, and P. Gérardin, "Study of the feasibility of a natural dye on cellulosic textile supports by red padouk (*Pterocarpus*

- soyauxii) and yellow movingui (*Distemonanthus benthamianus*) extracts," *Industrial Crops and Products*, vol. 60, pp. 291–297, 2014.
- [143] M. A. Khan, I. Shahid Ul, and F. Mohammad, "Extraction of natural dye from walnut bark and its dyeing properties on wool yarn," *Journal of Natural Fibers*, vol. 13, no. 4, pp. 458–469, 2016.
- [144] D. Coman, N. Vrinceanu, and S. Oancea, "Investigation of ecofriendly ultrasonic coloring with natural dyes," *Academic Journal of Manufacturing Engineering*, vol. 14, no. 2, pp. 40–45, 2016.
- [145] M. Mirjalili and L. Karimi, "Extraction and characterization of natural dye from green walnut shells and its use in dyeing polyamide: Focus on antibacterial properties," *Journal of Chemistry*, vol. 2013, no. 1, pp. 1–9, 2013.
- [146] A. Onal, N. Camci, and A. Sari, "Extraction of total dyestuff from walnut leaves (*Juglans regia* L.) and its dyeing conditions for natural fibres," *Asian Journal of Chemistry*, vol. 16, no. 3-4, pp. 1533–1539, 2004.
- [147] A. Onal and B. Demir, "Preparation of Dyeing Prescription and Investigation of Natural Hair Dyeing Properties of Walnut (*Juglans regia* L.), Logwood (*Alnus glutinosa* L.), Alkanet (*Alkanna tinctoria* L.) Madder red (*Rubai tinctorum* L.) and Wouw (*Reseda luteola* L.) Extracts," *Asian Journal of Chemistry*, vol. 21, no. 2, pp. 1449–1452, 2009.
- [148] K. Doty, S. Haar, and J. Kim, "Black walnut, Osage orange and eastern redcedar sawmill waste as natural dyes: effect of aluminum mordant on color parameters," *Fashion and Textiles*, vol. 3, no. 1, p. 22, 2016.
- [149] M. A. Rahman Bhuiyan, A. Ali, A. Islam, M. A. Hannan, S. M. Fijul Kabir, and M. N. Islam, "Coloration of polyester fiber with natural dye henna (*Lawsonia inermis* L.) without using mordant: a new approach towards a cleaner production," *Fashion and Textiles*, vol. 5, no. 1, pp. 1–11, 2018.
- [150] M. I. Bahtiyari, H. Benli, A. Yavas, and C. Akca, "Use of different natural dye sources for printing of cotton fabrics," *Tekstil Ve Konfeksiyon*, vol. 27, no. 3, pp. 259–265, 2017.
- [151] M. Rekaby, A. A. Salem, and S. H. Nassar, "Eco-friendly printing of natural fabrics using natural dyes from alkanet and rhubarb," *Journal of the Textile Institute*, vol. 100, no. 6, pp. 486–495, 2009.
- [152] K. K. Sharma, P. K. Pareek, A. S. M. Raja, P. Temani, A. Kumar, D. B. Shakyawar, and M. C. Sharma, "Extraction of natural dye from *Kigelia pinnata* and Its application on Pashmina (Cashmere) fabric," *Research Journal of Textile and Apparel*, vol. 17, no. 2, pp. 28–32, 2013.
- [153] H. Wang and C. Chen, "Formulation studies and properties evaluation of

- natural semi-permanent hair dye made from Gromwell Root and Sappan Wood," *Journal of Fiber Science and Technology*, vol. 65, no. 10, pp. 276–281, 2009.
- [154] K. H. Prabhu, M. D. Teli, and N. G. Waghmare, "Eco-Friendly Dyeing Using Natural Mordant Extracted from *Emblica officinalis* G. Fruit on Cotton and Silk Fabrics with Antibacterial Activity," *Fibers and Polymers*, vol. 12, no. 6, pp. 753–759, 2011.
- [155] S. N. Chattopadhyay, N. C. Pan, and A. Khan, "Printing of jute fabric with natural dyes extracted from manjistha, annatto and ratanjot," *Indian Journal of Fibre & Textile Research*, vol. 43, no. 3, pp. 352–356, 2018.
- [156] J. Sheikh, P. S. Jagtap, and M. D. Teli, "Ultrasound assisted extraction of natural dyes and natural mordants vis a vis dyeing," *Fibers and Polymers*, vol. 17, no. 5, pp. 738–743, 2016.
- [157] S. N. Chattopadhyay and N. C. Pan, "Ecofriendly printing of jute fabric with natural dyes and thickener," *Journal of Natural Fibers*, pp. 1–12, 2018.
- [158] H. Benli and M. I. Bahtiyari, "Use of ultrasound in biopreparation and natural dyeing of cotton fabric in a single bath," *Cellulose*, vol. 22, no. 1, pp. 867–877, 2015.
- [159] P. S. Vankar and R. Shanker, "Ecofriendly ultrasonic natural dyeing of cotton fabric with enzyme pretreatments," *Desalination*, vol. 230, no. 1-3, pp. 62–69, 2008.
- [160] M. I. Bahtiyari and H. Benli, "Dyeing of enzymatically modified polyamide fabrics with natural dyes," *Industria Textila*, vol. 67, no. 2, pp. 114–120, 2016.
- [161] S. P. Khattak, S. Rafique, T. Hussain, F. Inayat, and B. Ahmad, "Colour fastness and tensile strength of cotton fabric dyed with natural extracts of *alkanna tinctoria* by continuous dyeing technique," *Journal of the Chemical Society of Pakistan*, vol. 37, no. 5, pp. 903–909, 2015.
- [162] L. H. Lin, H. C. Chu, K. M. Chen, and S. C. Chen, "Surface properties of glucose-based surfactants and their application in textile dyeing with natural dyes," *Journal of Surfactants and Detergents*, vol. 22, no. 1, pp. 73–83, 2019.
- [163] A. A. Hebeish, A. A. Ragheb, S. H. Nassar, E. E. Allam, and J. I. Abd El Thalouth, "Technological evaluation of reactive cyclodextrin in cotton printing with reactive and natural dyes," *Journal of Applied Polymer Science*, vol. 102, no. 1, pp. 338–347, 2006.
- [164] O. Baykus, I. T. Celik, S. D. Dogan, A. Davulcu, and M. Dogan, "Enhancing

- the dyeability of poly(lactic acid) fiber with natural dyes of alizarin, lawsone, and indigo," *Fibers and Polymers*, vol. 18, no. 10, pp. 1906–1914, 2017.
- [165] A. Davulcu, "Investigation the dyeability of hyperbranched polymer modified polypropylene fibers with natural dyes," *Tekstil Ve Konfeksiyon*, vol. 25, no. 1, pp. 73–79, 2015.
- [166] R. Atav and O. Namirti, "Effect of ozonation process on dyeing of polyamide fabrics with a natural dye: Walnut rind," *Industria Textila*, vol. 67, no. 4, pp. 233–237, 2016.
- [167] A. Sharma and E. Grover, "Colour fastness of walnut dye on cotton," *Indian Journal of Natural Products and Resources*, vol. 2, no. 2, pp. 164–169, 2011.
- [168] C. S. Kumar and S. Bhattacharya, "Tamarind Seed: Properties, Processing and Utilization," *Critical Reviews in Food Science and Nutrition*, vol. 48, no. 1, pp. 1–20, 2008.
- [169] K. H. Prabhu and M. D. Teli, "Eco-dyeing using *Tamarindus indica* L. seed coat tannin as a natural mordant for textiles with antibacterial activity," *Journal of Saudi Chemical Society*, vol. 18, no. 6, pp. 864–872, 2014.
- [170] M. Sadeghi-Kiakhani, "Eco-friendly dyeing of wool and nylon using madder as a natural dye: kinetic and adsorption isotherm studies," *International Journal of Environmental Science and Technology*, vol. 12, no. 7, pp. 2363–2370, 2015.
- [171] M. Yusuf, F. Mohammad, and M. Shabbir, "Eco-friendly and effective dyeing of wool with anthraquinone colorants extracted from *Rubia cordifolia* roots: Optimization, colorimetric and fastness assay," *Journal of King Saud University - Science*, vol. 29, no. 2, pp. 137–144, 2017.
- [172] A. K. Samanta, A. Konar, S. Chakraborty, and S. Datta, "Effect of different mordants, extraction conditions and dyeing process variables on colour interaction parameters and colour fastness properties in dyeing of jute fabric with manjistha, a natural dye," *Journal of the Institution of Engineers (India), Part TX: Textile Engineering Division*, vol. 91, no. AUG, pp. 7–15, 2010.
- [173] N. Vedaraman, K. V. Sandhya, N. R. B. Charukesh, B. Venkatakrishnan, K. Haribabu, M. R. Sridharan, and R. Nagarajan, "Ultrasonic extraction of natural dye from *Rubia Cordifolia*, optimisation using response surface methodology (RSM) & comparison with artificial neural network (ANN) model and its dyeing properties on different substrates," *Chemical Engineering and Processing*, vol. 114, pp. 46–54, 2017.
- [174] A. Sharma, E. Grover, and S. Paul, "Development of suitable process for dyeing of silk with natural dye *Rheum Emodi*," *Indian Silk*, vol. 50, no. 4, pp. 24–26, 2011.

- [175] M. Srivastava, P. Udawat, P. Gupta, S. K. Mishra, and K. C. Gupta, "Dyeing of silk with natural dye extracted from *Rheum emodi* with different mordants," *Man-Made Textiles in India*, vol. 39, no. 8, pp. 273–278, 2011.
- [176] M. M. Kamel, R. M. El-Shishtawy, B. M. Yussef, and H. Mashaly, "Ultrasonic assisted dyeing - III. Dyeing of wool with lac as a natural dye," *Dyes and Pigments*, vol. 65, no. 2, pp. 103–110, 2005.
- [177] L. Ammayappan and D. B. B. Shakyawar, "Dyeing of carpet woolen yarn using natural dye from Cochineal," *Journal of Natural Fibers*, vol. 13, no. 1, pp. 42–53, 2016.
- [178] B. Y. Sahinbaskan, R. Karadag, and E. Torgan, "Dyeing of silk fabric with natural dyes extracted from cochineal (*Dactylopius coccus* Costa) and gall oak (*Quercus infectoria* Olivier)," *Journal of Natural Fibers*, vol. 15, no. 4, pp. 559–574, 2018.
- [179] S. Mirnezhad, S. Safapour, and M. Sadeghi-Kiakhani, "Dual-mode adsorption of cochineal natural dye on wool fibers: Kinetic, equilibrium, and thermodynamic studies," *Fibers and Polymers*, vol. 18, no. 6, pp. 1134–1145, 2017.
- [180] M. Sadeghi-Kiakhani, S. Safapour, and S. Mirnezhad, "Thermodynamic and kinetic studies of the adsorption behaviour of the natural dye cochineal on polyamide 66," *Coloration Technology*, vol. 134, no. 4, pp. 308–314, 2018.
- [181] M. Yusuf, M. Shahid, M. I. Khan, S. A. Khan, M. A. Khan, and F. Mohammad, "Dyeing studies with henna and madder: A research on effect of tin (II) chloride mordant," *Journal of Saudi Chemical Society*, vol. 19, no. 1, pp. 64–72, 2015.
- [182] H. Barani, M. N. Boroumand, and S. Rafiei, "Application of silver nanoparticles as an antibacterial mordant in wool natural dyeing: synthesis, antibacterial activity, and color characteristics," *Fibers and Polymers*, vol. 18, no. 4, pp. 658–665, 2017.
- [183] L. Liu, J. Zhang, and R. C. Tang, "Adsorption and functional properties of natural lac dye on chitosan fiber," *Reactive and Functional Polymers*, vol. 73, no. 11, pp. 1559–1566, 2013.
- [184] M. Yadav, N. Singh, A. Kaur, and O. Sahu, "Antibacterial activity assessment of woolen fabric treated with natural dyes and chitosan," *Agriculture and Natural Resources*, vol. 53, no. 2, pp. 188–196, 2019.
- [185] A. Jahangiri, S. M. Ghoreishian, A. Akbari, M. Norouzi, M. Ghasemi, M. Ghoreishian, and E. Shafiabadi, "Natural dyeing of wool by Madder (*Rubia tinctorum* L.) root extract using tannin-based biomordants:

- colorimetric, fastness and tensile assay," *Fibers and Polymers*, vol. 19, no. 10, pp. 2139–2148, 2018.
- [186] M. D. Teli and P. Ambre, "Discharge printing of compound shades from natural dyes using mordants," *Asian Dyer*, vol. 15, no. 1, pp. 30–35, 2018.
- [187] A. K. Samanta, P. Agarwal, and S. Datta, "Studies on color-strength-related parameters and compatibility for dyeing of cotton fabric with binary mixtures of Jackfruit wood and other natural dyes," *Journal of Natural Fibers*, vol. 6, no. 1, pp. 27–45, 2009.
- [188] A. N. Banerjee, O. P. Kotnala, and S. R. Maulik, "Dyeing of Eri silk with natural dyes in presence of natural mordants," *Indian Journal of Traditional Knowledge*, vol. 17, no. 2, pp. 396–399, 2018.
- [189] A. Sen, A. Bhowal, and S. Datta, "Application of natural dye on polytrimethylene terephthalate fiber," *Research Journal of Textile and Apparel*, vol. 23, no. 1, pp. 71–90, 2019.
- [190] M. Yusuf, M. Shahid, S. A. Khan, M. I. Khan, I. Shahid Ul, F. Mohammad, and M. A. Khan, "Eco-dyeing of wool using aqueous extract of the roots of indian madder (*Rubia cordifolia*) as natural dye," *Journal of Natural Fibers*, vol. 10, no. 1, pp. 14–28, 2013.
- [191] M. A. Khan, I. Shahid ul, and F. Mohammad, "Investigating the combined effect of natural and metal salt mordants on coloring potential of Indian Rhubarb (*Rheum emodi*) natural dye," *Journal of Natural Fibers*, vol. 14, no. 2, pp. 196–204, 2017.
- [192] L. J. Rather, M. A. Khan, and F. Mohammad, "Biomordanting potential of *Acacia nilotica* (Babul) in conjunction with *Kerria lacca* and *Rheum emodi* natural dyes," *Journal of Natural Fibers*, vol. 16, no. 2, pp. 275–286, 2019.
- [193] M. Yusuf, F. Mohammad, M. Shabbir, and M. A. Khan, "Eco-dyeing of wool with *Rubia cordifolia* root extract: Assessment of the effect of *Acacia catechu* as biomordant on color and fastness properties," *Textiles and Clothing Sustainability*, vol. 2, no. 1, p. 10, 2016.
- [194] A. Nazari, M. Montazer, F. Afzali, and A. Sheibani, "Optimization of proteases pretreatment on natural dyeing of wool using response surface methodology," *Clean Technologies and Environmental Policy*, vol. 16, no. 6, pp. 1081–1093, 2014.
- [195] L. Cui, G. C. Du, J. Chen, Q. Wang, P. Wang, and X. R. Fan, "Effect of microbial transglutaminase on dyeing properties of natural dyes on wool fabric," *Biocatalysis and Biotransformation*, vol. 26, no. 5, pp. 399–404, 2008.
- [196] P. S. Vankar, R. Shanker, and A. Verma, "Enzymatic natural dyeing of cotton

- and silk fabrics without metal mordants," *Journal of Cleaner Production*, vol. 15, no. 15, pp. 1441–1450, 2007.
- [197] N. S. Elshemy, "Unconventional natural dyeing using microwave heating with Cochineal as natural dyes," *Research Journal of Textile and Apparel*, vol. 15, no. 4, pp. 26–36, 2011.
- [198] M. M. Kamel, M. M. El Zawahry, N. S. E. Ahmed, and F. Abdelghaffar, "Ultrasonic dyeing of cationized cotton fabric with natural dye. Part 1: Cationization of cotton using Solfix E," *Ultrasonics Sonochemistry*, vol. 16, no. 2, pp. 243–249, 2009.
- [199] M. M. Kamel, M. M. El Zawahry, N. S. E. Ahmed, and F. Abdelghaffar, "Ultrasonic dyeing of cationized cotton fabric with natural dye. Part 2: Cationization of cotton using Quat 188," *Industrial Crops and Products*, vol. 34, no. 3, pp. 1410–1417, 2011.
- [200] L. Zhou, J. Z. Shao, and L. Q. Chai, "Study on the UV-protective Performance of cotton fabrics dyed with natural dyes," *Advanced Materials Research*, vol. 332-334, pp. 1408–1413, 2011.
- [201] L. Mehrparvar, S. Safapour, M. Sadeghi-Kiakhani, and K. Gharanjig, "A cleaner and eco-benign process for wool dyeing with madder, *Rubia tinctorum* L., root natural dye," *International Journal of Environmental Science and Technology*, vol. 13, no. 11, pp. 2569–2578, 2016.
- [202] M. Sadeghi-Kiakhani, S. Safapour, and Y. Golpazir-Sorkheh, "Impact of chitosan-poly(amidoamine) dendreimer hybrid treatment on dyeing and color fastness properties of wool yarn with madder natural dye," *Progress in Color, Colorants and Coatings*, vol. 12, no. 4, pp. 241–250, 2019.
- [203] S. Safapour, M. Sadeghi-Kiakhani, and S. Doustmohammadi, "Chitosan-cyanuric chloride hybrid as an efficient novel bio-mordant for improvement of cochineal natural dye absorption on wool yarns," *Journal of the Textile Institute*, vol. 110, no. 1, pp. 81–88, 2019.
- [204] S. Janhom, R. Watanesk, S. Watanesk, P. Griffiths, O. A. Arquero, and W. Naksata, "Comparative study of lac dye adsorption on cotton fibre surface modified by synthetic and natural polymers," *Dyes and Pigments*, vol. 71, no. 3, pp. 188–193, 2006.
- [205] M. L. Gulrajani, D. Gupta, and P. Gupta, "Application of natural dyes on bleached coir yarn," *Indian Journal of Fibre & Textile Research*, vol. 28, no. 4, pp. 466–470, 2003.
- [206] M. L. Gulrajani, R. C. Srivastava, and M. Goel, "Colour gamut of natural dyes on cotton yarns," *Coloration Technology*, vol. 117, no. 4, pp. 225–228, 2001.

- [207] A. K. Samanta, P. Agarwal, D. Singhee, and S. Datta, "Application of single and mixtures of red sandalwood and other natural dyes for dyeing of jute fabric: studies on colour parameters/colour fastness and compatibility," *Journal of the Textile Institute*, vol. 100, no. 7, pp. 565–587, 2009.
- [208] F. Giacomini, A. A. U. de Souza, and M. A. S. D. de Barros, "Cationization of cotton with ovalbumin to improve dyeing of modified cotton with cochineal natural dye," *Textile Research Journal*, vol. 90, no. 15-16, pp. 1–18, 2020.
- [209] H. Barani, "Modification of bentonite with different surfactants and substitute as a mordant in wool natural dyeing," *Chiang Mai Journal of Science*, vol. 45, no. 1, pp. 492–504, 2018.
- [210] D. M. Lewis and J. A. Rippon, *The coloration of wool and other keratin fibres*, John Wiley & Sons, 2013.
- [211] A. Haji, "Dyeing of cotton fabric with natural dyes improved by mordants and plasma treatment," *Progress in Color, Colorants and Coatings*, vol. 12, no. 3, pp. 191–201, 2019.
- [212] G. Ke, K. Zhu, and M. H. Chowdhury, "Dyeing of Cochineal natural dye on cotton fabrics treated with oxidant and chitosan," *Journal of Natural Fibers*, pp. 1–13, 2019.
- [213] C. dos Santos, L. F. W. Brum, R. D. Vasconcelos, S. K. Velho, and J. H. Z. dos Santos, "Color and fastness of natural dyes encapsulated by a sol-gel process for dyeing natural and synthetic fibers," *Journal of Sol-Gel Science and Technology*, vol. 86, no. 2, pp. 351–364, 2018.
- [214] S. R. K. Velho, L. F. W. Brum, C. O. Petter, J. H. Z. dos Santos, . Šimunić, and W. H. Kappa, "Development of structured natural dyes for use into plastics," *Dyes and Pigments*, vol. 136, pp. 248–254, 2017.
- [215] I. Drivas, R. S. Blackburn, and C. M. Rayner, "Natural anthraquinonoid colorants as platform chemicals in the synthesis of sustainable disperse dyes for polyesters," *Dyes and Pigments*, vol. 88, no. 1, pp. 7–17, 2011.
- [216] J. Wu, H. Zhao, M. Wang, W. Zhi, X. Xiong, and L. Zheng, "A novel natural dye derivative for natural fabric supercritical carbon dioxide dyeing technology," *Fibers and Polymers*, vol. 20, no. 11, pp. 2376–2382, 2019.
- [217] M. Nakpathom, B. Somboon, N. Narumol, and R. Mongkhlorattanasit, "High temperature dyeing of PET fabric with natural colourants extracted from annatto seeds," *Pigment & Resin Technology*, vol. 48, no. 2, pp. 129–136, 2019.
- [218] G. Savvidis, M. Zarkogianni, E. Karanikas, N. Lazaridis, N. Nikolaidis, and E. Tsatsaroni, "Digital and conventional printing and dyeing with the natural

- dye annatto: optimisation and standardisation processes to meet future demands," *Coloration Technology*, vol. 129, no. 1, pp. 55–63, 2013.
- [219] D. Jothi, "Extraction of natural dyes from African marigold flower (*Tagetes Erecta* L.) for textile coloration," *Autex Research Journal*, vol. 8, no. 2, pp. 49–53, 2008.
- [220] S. Y. Rashdi, T. Naveed, N. Sanbhal, S. Almani, P. Lin, and W. Wei, "Lyocell fabric dyed with natural dye extracted from marigold flower using metallic salts," *Autex Research Journal*, vol. 20, no. 3, pp. 352–358, 2019.
- [221] M. O. Park and S. L. Yoon, "Properties of natural dyeing of bast fiber (Part 1): Properties of dye and extraction condition of sappan wood, gardenia and gallnut," *Palpu Chongi Gisul/Journal of Korea Technical Association of the Pulp and Paper Industry*, vol. 41, no. 3, pp. 49–59, 2009.
- [222] Y. Zhou, J. Zhang, R.-C. Tang, and J. Zhang, "Simultaneous dyeing and functionalization of silk with three natural yellow dyes," *Industrial Crops and Products*, vol. 64, pp. 224–232, 2015.
- [223] G. H. Zheng, H. B. Fu, and G. P. Liu, "Application of rare earth as mordant for the dyeing of ramie fabrics with natural dyes," *Korean Journal of Chemical Engineering*, vol. 28, no. 11, pp. 2148–2155, 2011.
- [224] V. N. Swamy, K. Gowda, and R. Sudhakar, "Dyeing of silk using *Madhuca longifolia* as natural dye source," *Indian Journal of Fibre & Textile Research*, vol. 40, no. 4, pp. 419–424, 2015.
- [225] S. I. Yoo, U. M. Oh, Y. R. Min, and T. H. Choi, "Improvement on dyeability of Hanji with natural dyes using a (3-chloro-2-hydroxypropyl) trimethyl ammonium chloride," *Palpu Chongi Gisul/Journal of Korea Technical Association of the Pulp and Paper Industry*, vol. 43, no. 3, pp. 88–97, 2011.
- [226] J. J. Shen, P. Gao, and H. Ma, "The effect of tris(2-carboxyethyl)phosphine on the dyeing of wool fabrics with natural dyes," *Dyes and Pigments*, vol. 108, pp. 70–75, 2014.
- [227] S. Kesornsit, P. Jitjankarn, W. Sajomsang, P. Gonil, J. B. Bremner, and M. Chairat, "Polydopamine-coated silk yarn for improving the light fastness of natural dyes," *Coloration Technology*, vol. 135, no. 2, pp. 143–151, 2019.
- [228] S. Adeel, T. Gulzar, M. Azeem, R. Fazal ur, M. Saeed, I. Hanif, and N. Iqbal, "Appraisal of marigold flower based lutein as natural colourant for textile dyeing under the influence of gamma radiations," *Radiation Physics and Chemistry*, vol. 130, pp. 35–39, 2017.
- [229] M. Shahamirian, M. H. Eskandari, M. Niakousari, S. Esteghlal, H. Hashemi Gahruei, and A. Mousavi Khaneghah, "Incorporation of pomegranate rind powder extract and pomegranate juice into frozen burgers:

- oxidative stability, sensorial and microbiological characteristics," *Journal of Food Science and Technology*, vol. 56, no. 3, pp. 1174–1183, 2019.
- [230] S. Zafra-Stone, T. Yasmin, M. Bagchi, A. Chatterjee, J. A. Vinson, and D. Bagchi, "Berry anthocyanins as novel antioxidants in human health and disease prevention," *Molecular Nutrition & Food Research*, vol. 51, no. 6, pp. 675–683, 2007.
- [231] S. Farooque, P. M. Rose, M. Benohoud, R. S. Blackburn, and C. M. Rayner, "Enhancing the Potential Exploitation of Food Waste: Extraction, Purification, and Characterization of Renewable Specialty Chemicals from Blackcurrants (*Ribes nigrum* L.)," *Journal of Agricultural and Food Chemistry*, vol. 66, no. 46, pp. 12265–12273, 2018.
- [232] G.-I. Hidalgo and M. Almajano, "Red Fruits: Extraction of Antioxidants, Phenolic Content, and Radical Scavenging Determination: A Review," *Antioxidants*, vol. 6, no. 1, p. 7, 2017.
- [233] P. Heffels, F. Weber, and A. Schieber, "Influence of Accelerated Solvent Extraction and Ultrasound-Assisted Extraction on the Anthocyanin Profile of Different *Vaccinium* Species in the Context of Statistical Models for Authentication," *Journal of Agricultural and Food Chemistry*, vol. 63, no. 34, pp. 7532–7538, 2015.
- [234] J. Chandrasekhar, M. Madhusudhan, and K. Raghavarao, "Extraction of anthocyanins from red cabbage and purification using adsorption," *Food and bioproducts processing*, vol. 90, no. 4, pp. 615–623, 2012.
- [235] P. Jing and M. Giusti, "Effects of Extraction Conditions on Improving the Yield and Quality of an Anthocyanin-Rich Purple Corn (*Zea mays* L.) Color Extract," *Journal of Food Science*, vol. 72, no. 7, pp. C363–C368, 2007.
- [236] J. Cacace and G. Mazza, "Optimization of Extraction of Anthocyanins from Black Currants with Aqueous Ethanol," *Journal of Food Science*, vol. 68, no. 1, pp. 240–248, 2003.
- [237] M. L. Blackhall, R. Berry, N. W. Davies, and J. T. Walls, "Optimized extraction of anthocyanins from Reid Fruits' *Prunus avium* 'Lapins' cherries," *Food Chemistry*, vol. 256, pp. 280–285, 2018.
- [238] R. Chirinos, H. Rogez, D. Campos, R. Pedreschi, and Y. Larondelle, "Optimization of extraction conditions of antioxidant phenolic compounds from mashua (*Tropaeolum tuberosum* Ruiz & Pavón) tubers," *Separation and Purification Technology*, vol. 55, no. 2, pp. 217–225, 2007.
- [239] W. Wang, J. Jung, E. Tomasino, and Y. Zhao, "Optimization of solvent and ultrasound-assisted extraction for different anthocyanin rich fruit and their

- effects on anthocyanin compositions," *LWT - Food Science and Technology*, vol. 72, pp. 229–238, 2016.
- [240] W. Wiczowski, D. Szawara-Nowak, and J. Topolska, "Red cabbage anthocyanins: Profile, isolation, identification, and antioxidant activity," *Food Research International*, vol. 51, no. 1, pp. 303–309, 2013.
- [241] T. Das, C. H. Mehta, and U. Y. Nayak, "Multiple approaches for achieving drug solubility: an in silico perspective," *Drug Discovery Today*, vol. 25, no. 7, pp. 1206–1212, 2020.
- [242] C. M. Hansen, *Hansen solubility parameters: a user's handbook*, CRC press, 2007.
- [243] D. W. Van Krevelen and K. Te Nijenhuis, *Properties of polymers: their correlation with chemical structure; their numerical estimation and prediction from additive group contributions*, Elsevier, 2009.
- [244] I. H. Bell, E. Mickoleit, C.-M. Hsieh, S.-T. Lin, J. Vrabec, C. Breitkopf, and A. Jäger, "A Benchmark Open-Source Implementation of COSMO-SAC," *Journal of Chemical Theory and Computation*, vol. 16, no. 4, pp. 2635–2646, 2020.
- [245] R. Skyner, J. McDonagh, C. Groom, T. Van Mourik, and J. Mitchell, "A review of methods for the calculation of solution free energies and the modelling of systems in solution," *Physical Chemistry Chemical Physics*, vol. 17, no. 9, pp. 6174–6191, 2015.
- [246] S. N. Steinmann, P. Sautet, and C. Michel, "Solvation free energies for periodic surfaces: comparison of implicit and explicit solvation models," *Physical Chemistry Chemical Physics*, vol. 18, no. 46, pp. 31850–31861, 2016.
- [247] C. M. Hansen, "50 Years with solubility parameters—past and future," *Progress in Organic Coatings*, vol. 51, no. 1, pp. 77–84, 2004.
- [248] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant,

- S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, "Gaussian 16 Rev. B.01," 2016.
- [249] A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *The Journal of chemical physics*, vol. 98, no. 7, pp. 5648–5652, 1993.
- [250] C. Lee, W. Yang, and R. G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density," *Physical Review B*, vol. 37, no. 2, pp. 785–789, 1988.
- [251] J. Tirado-Rives and W. L. Jorgensen, "Performance of B3LYP Density Functional Methods for a Large Set of Organic Molecules," *Journal of Chemical Theory and Computation*, vol. 4, no. 2, pp. 297–306, 2008.
- [252] J. Ho and M. Z. Ertem, "Calculating Free Energy Changes in Continuum Solvation Models," *The Journal of Physical Chemistry B*, vol. 120, no. 7, pp. 1319–1329, 2016.
- [253] A. Klamt, "Conductor-like Screening Model for Real Solvents: A New Approach to the Quantitative Calculation of Solvation Phenomena," *The Journal of Physical Chemistry*, vol. 99, no. 7, pp. 2224–2235, 1995.
- [254] A. Benazzouz, L. Moity, C. Pierlot, V. Molinier, and J.-M. Aubry, "Hansen approach versus COSMO-RS for predicting the solubility of an organic UV filter in cosmetic solvents," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 458, pp. 101–109, 2014.
- [255] A. M. Maldonado, Y. Basdogan, J. T. Berryman, S. B. Rempe, and J. A. Keith, "First-principles modeling of chemistry in mixed solvents: Where to go from here?" *The Journal of Chemical Physics*, vol. 152, no. 13, p. 130902, 2020.
- [256] J. Gupta, C. Nunes, S. Vyas, and S. Jonnalagadda, "Prediction of Solubility Parameters and Miscibility of Pharmaceutical Compounds by Molecular Dynamics Simulations," *The Journal of Physical Chemistry B*, vol. 115, no. 9, pp. 2014–2023, 2011.
- [257] I. K. Hong, H. Jeon, and S. B. Lee, "Extraction of natural dye from Gardenia and chromaticity analysis according to chi parameter," *Journal of Industrial and Engineering Chemistry*, vol. 24, pp. 326–332, 2015.
- [258] Z. Guo, B.-M. Lue, K. Thomasen, A. S. Meyer, and X. Xu, "Predictions of flavonoid solubility in ionic liquids by COSMO-RS: experimental verification, structural elucidation, and solvation characterization," *Green Chemistry*, vol. 9, no. 12, pp. 1362–1373, 2007.
- [259] R. Metivier, F. Francis, and F. Clydesdale, "Solvent extraction of

- anthocyanins from wine pomace," *Journal of Food Science*, vol. 45, no. 4, pp. 1099–1100, 1980.
- [260] R. K. Henderson, C. Jiménez-González, D. J. C. Constable, S. R. Alston, G. G. A. Inglis, G. Fisher, J. Sherwood, S. P. Binks, and A. D. Curzons, "Expanding GSK's solvent selection guide – embedding sustainability into solvent selection starting at medicinal chemistry," *Green Chemistry*, vol. 13, no. 4, pp. 854–862, 2011.
- [261] A. Nalaparaju and J. Jiang, "Recovery of Dimethyl Sulfoxide from Aqueous Solutions by Highly Selective Adsorption in Hydrophobic Metal–Organic Frameworks," *Langmuir*, vol. 28, no. 43, pp. 15305–15312, 2012.
- [262] D. Prat, A. Wells, J. Hayler, H. Sneddon, C. R. McElroy, S. Abou-Shehada, and P. J. Dunn, "CHEM21 selection guide of classical- and less classical-solvents," *Green Chemistry*, vol. 18, no. 1, pp. 288–296, 2016.
- [263] D. Amić, D. Davidović-Amić, and N. Trinajstić, "Application of topological indices to chromatographic data: Calculation of the retention indices of anthocyanins," *Journal of Chromatography A*, vol. 653, no. 1, pp. 115–121, 1993.
- [264] S. Catena, N. Rakotomanomana, P. Zunin, R. Boggia, F. Turrini, and F. Chemat, "Solubility study and intensification of extraction of phenolic and anthocyanin compounds from *Oryza sativa* L. 'Violet Nori'," *Ultrasonics Sonochemistry*, vol. 68, p. 105231, 2020.
- [265] S. Y. Wang, C.-T. Chen, W. Sciarappa, C. Y. Wang, and M. J. Camp, "Fruit Quality, Antioxidant Capacity, and Flavonoid Content of Organically and Conventionally Grown Blueberries," *Journal of Agricultural and Food Chemistry*, vol. 56, no. 14, pp. 5788–5794, 2008.
- [266] H. Rohm, C. Brennan, C. Turner, E. Gunther, G. Campbell, I. Hernando, S. Struck, and V. Kontogiorgos, "Adding Value to Fruit Processing Waste: Innovative Ways to Incorporate Fibers from Berry Pomace in Baked and Extruded Cereal-based Foods-A SUSFOOD Project," *Foods*, vol. 4, no. 4, pp. 690–697, 2015.
- [267] O. E. İsmal, "Greener natural dyeing pathway using a by-product of olive oil; prina and biomordants," *Fibers and Polymers*, vol. 18, no. 4, pp. 773–785, 2017.
- [268] F. J. Francis and P. C. Markakis, "Food colorants: anthocyanins," *Critical Reviews in Food Science & Nutrition*, vol. 28, no. 4, pp. 273–314, 1989.
- [269] T. Bechtold, A. Mahmud-Ali, and R. Mussak, "Anthocyanin dyes extracted from grape pomace for the purpose of textile dyeing," *Journal of the Science of Food and Agriculture*, vol. 87, no. 14, pp. 2589–2595, 2007.

- [270] Y. S. Jung and D. G. Bae, "Natural dyeing with black Cowpea Seed Coat. I. dyeing properties of cotton and silk fabrics," *Fibers and Polymers*, vol. 15, no. 1, pp. 138–144, 2014.
- [271] A. Yasukawa, A. Chida, Y. Kato, and M. Kasai, "Dyeing silk and cotton fabrics using natural blackcurrants," *Textile Research Journal*, vol. 87, no. 19, pp. 2379–2387, 2017.
- [272] Z. Ahmadi and F. G. Houjehgan, "Evaluation of color sensitivity to dyeing parameters in natural dyeing with anthocyanin," *J Textil Polym*, vol. 5, no. 2, pp. 97–102, 2017.
- [273] C. X. Wang, M. Li, L. P. Zhang, S. H. Fu, and C. X. Wang, "Extraction of natural dyes from *Cinnamomum camphora* (L.) presl fruit and their application on wool fabric," *Textile Research Journal*, vol. 87, no. 20, pp. 2550–2560, 2017.
- [274] T. Bechtold, R. Mussak, A. Mahmud-Ali, E. Ganglberger, and S. Geissler, "Extraction of natural dyes for textile dyeing from coloured plant wastes released from the food and beverage industry," *Journal of the Science of Food and Agriculture*, vol. 86, no. 2, pp. 233–242, 2006.
- [275] Y. J. Yin, J. R. Jia, T. Wang, and C. X. Wang, "Optimization of natural anthocyanin efficient extracting from purple sweet potato for silk fabric dyeing," *Journal of Cleaner Production*, vol. 149, pp. 673–679, 2017.
- [276] R. Boulton, "The copigmentation of anthocyanins and its role in the color of red wine: A critical review," *American journal of enology and viticulture*, vol. 52, no. 2, pp. 67–87, 2001.
- [277] D. T. Santos, J. Q. Albarelli, M. M. Beppu, and M. A. A. Meireles, "Stabilization of anthocyanin extract from jabuticaba skins by encapsulation using supercritical CO₂ as solvent," *Food Research International*, vol. 50, no. 2, pp. 617–624, 2013.
- [278] A. Fernandes, M. A. A. Rocha, L. M. N. B. F. Santos, J. Brás, J. Oliveira, N. Mateus, and V. de Freitas, "Blackberry anthocyanins: β -Cyclodextrin fortification for thermal and gastrointestinal stabilization," *Food Chemistry*, vol. 245, pp. 426–431, 2018.
- [279] L. R. Howard, C. Brownmiller, R. L. Prior, and A. Mauromoustakos, "Improved Stability of Chokeberry Juice Anthocyanins by β -Cyclodextrin Addition and Refrigeration," *Journal of Agricultural and Food Chemistry*, vol. 61, no. 3, pp. 693–699, 2013.
- [280] T. J. Buran, A. K. Sandhu, Z. Li, C. R. Rock, W. W. Yang, and L. Gu, "Adsorption/desorption characteristics and separation of anthocyanins and

- polyphenols from blueberries using macroporous adsorbent resins," *Journal of Food Engineering*, vol. 128, pp. 167–173, 2014.
- [281] L. Estévez, N. Otero, and R. A. Mosquera, "Molecular structure of cyanidin metal complexes: Al(III) versus Mg(II)," *Theoretical Chemistry Accounts*, vol. 128, no. 4, pp. 485–495, 2011.
- [282] L. Estévez, M. Sánchez-Lozano, and R. A. Mosquera, "Complexation of common metal cations by cyanins: Binding affinity and molecular structure," *International Journal of Quantum Chemistry*, vol. 119, no. 6, p. e25834, 2019.
- [283] S. Kunsági-Máté, E. Ortmann, L. Kollár, K. Szabó, and M. P. Nikfardjam, "Effect of ferrous and ferric ions on copigmentation in model solutions," *Journal of Molecular Structure*, vol. 891, no. 1, pp. 471–474, 2008.
- [284] L. Estévez and R. A. Mosquera, "Where is the positive charge of flavylum cations?" *Chemical Physics Letters*, vol. 451, no. 1, pp. 121–126, 2008.
- [285] J. N. Woodford, "A DFT investigation of anthocyanidins," *Chemical physics letters*, vol. 410, no. 4-6, pp. 182–187, 2005.
- [286] L. Estévez and R. A. Mosquera, "A density functional theory study on pelargonidin," *The Journal of Physical Chemistry A*, vol. 111, no. 43, pp. 11100–11109, 2007.
- [287] L. Estévez and R. A. Mosquera, "Molecular structure and antioxidant properties of delphinidin," *The Journal of Physical Chemistry A*, vol. 112, no. 42, pp. 10614–10623, 2008.
- [288] F. Di Meo, J. C. Sancho Garcia, O. Dangles, and P. Trouillas, "Highlights on Anthocyanin Pigmentation and Copigmentation: A Matter of Flavonoid π -Stacking Complexation To Be Described by DFT-D," *Journal of Chemical Theory and Computation*, vol. 8, no. 6, pp. 2034–2043, 2012.
- [289] B.-J. Qian, J.-H. Liu, S.-J. Zhao, J.-X. Cai, and P. Jing, "The effects of gallic/ferulic/caffeic acids on colour intensification and anthocyanin stability," *Food Chemistry*, vol. 228, pp. 526–532, 2017.
- [290] P. Ferreira da Silva, J. C. Lima, A. A. Freitas, K. Shimizu, A. L. Maçanita, and F. H. Quina, "Charge-Transfer Complexation as a General Phenomenon in the Copigmentation of Anthocyanins," *The Journal of Physical Chemistry A*, vol. 109, no. 32, pp. 7329–7338, 2005.
- [291] W. Kalt, J. E. McDonald, and H. Donner, "Anthocyanins, Phenolics, and Antioxidant Capacity of Processed Lowbush Blueberry Products," *Journal of Food Science*, vol. 65, no. 3, pp. 390–393, 2000.
- [292] S. M. Burkinshaw and N. Kumar, "Polyvinyl alcohol as an aftertreatment:

- Part 3 direct dyes on cotton," *Dyes and Pigments*, vol. 85, no. 3, pp. 124–132, 2010.
- [293] M. M. Giusti and R. E. Wrolstad, *Characterization and Measurement of Anthocyanins by UV-Visible Spectroscopy*, John Wiley & Sons, Inc., 2001.
- [294] G. Skrede, R. Wrolstad, and R. Durst, "Changes in anthocyanins and polyphenolics during juice processing of highbush blueberries (*Vaccinium corymbosum* L.)," *Journal of food science*, vol. 65, no. 2, pp. 357–364, 2000.
- [295] J. Lee, R. Durst, and R. Wrolstad, "Impact of Juice Processing on Blueberry Anthocyanins and Polyphenolics: Comparison of Two Pretreatments," *Journal of Food Science*, vol. 67, no. 5, pp. 1660–1667, 2002.
- [296] V. Hong and R. E. Wrolstad, "Use of HPLC separation/photodiode array detection for characterization of anthocyanins," *Journal of Agricultural and Food Chemistry*, vol. 38, no. 3, pp. 708–715, 1990.
- [297] E. Sadilova, R. Carle, and F. C. Stintzing, "Thermal degradation of anthocyanins and its impact on color and in vitro antioxidant capacity," *Molecular nutrition & food research*, vol. 51, no. 12, pp. 1461–1471, 2007.
- [298] X. Yue and Z. Xu, "Changes of Anthocyanins, Anthocyanidins, and Antioxidant Activity in Bilberry Extract during Dry Heating," *Journal of Food Science*, vol. 73, no. 6, pp. C494–C499, 2008.
- [299] K. Y. Foo and B. H. Hameed, "Insights into the modeling of adsorption isotherm systems," *Chemical Engineering Journal*, vol. 156, no. 1, pp. 2–10, 2010.
- [300] K. S. Walton and D. S. Sholl, "Predicting multicomponent adsorption: 50 years of the ideal adsorbed solution theory," *AIChE Journal*, vol. 61, no. 9, pp. 2757–2762, 2015.
- [301] I. Langmuir, "The constitution and fundamental properties of solids and liquids. Part I. Solids," *Journal of the American Chemical Society*, vol. 38, no. 11, pp. 2221–2295, 1916.
- [302] H. Freundlich, "Over the adsorption in solution," *J. Phys. Chem*, vol. 57, no. 385471, pp. 1100–1107, 1906.
- [303] O. Redlich and D. Peterson, "A useful adsorption isotherm," *Journal of Physical Chemistry*, vol. 63, no. 6, pp. 1024–1024, 1959.
- [304] R. Sips, "Combined form of Langmuir and Freundlich equations," *J. Chem. Phys*, vol. 16, no. 429, pp. 490–495, 1948.
- [305] M. Arshadi, M. J. Amiri, and S. Mousavi, "Kinetic, equilibrium and thermodynamic investigations of Ni(II), Cd(II), Cu(II) and Co(II) adsorption on barley straw ash," *Water Resources and Industry*, vol. 6, pp. 1–17, 2014.

- [306] V. Fierro, V. Torné-Fernández, D. Montané, and A. Celzard, "Adsorption of phenol onto activated carbons having different textural and surface properties," *Microporous and Mesoporous Materials*, vol. 111, no. 1, pp. 276–284, 2008.
- [307] P. R. Piergiovanni, "Adsorption Kinetics and Isotherms: A Safe, Simple, and Inexpensive Experiment for Three Levels of Students," *Journal of Chemical Education*, vol. 91, no. 4, pp. 560–565, 2014.
- [308] Y.-S. Ho and G. McKay, "Pseudo-second order model for sorption processes," *Process biochemistry*, vol. 34, no. 5, pp. 451–465, 1999.
- [309] Y. S. Ho and G. McKay, "A Comparison of Chemisorption Kinetic Models Applied to Pollutant Removal on Various Sorbents," *Process Safety and Environmental Protection*, vol. 76, no. 4, pp. 332–340, 1998.
- [310] F.-C. Wu, R.-L. Tseng, and R.-S. Juang, "Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics," *Chemical Engineering Journal*, vol. 153, no. 1, pp. 1–8, 2009.
- [311] Y.-S. Ho, "Selection of optimum sorption isotherm," *Carbon*, vol. 42, no. 10, pp. 2115–2116, 2004.
- [312] J. M. Mercero, J. M. Matxain, X. Lopez, D. M. York, A. Largo, L. A. Eriksson, and J. M. Ugalde, "Theoretical methods that help understanding the structure and reactivity of gas phase ions," *International Journal of Mass Spectrometry*, vol. 240, no. 1, pp. 37–99, 2005.
- [313] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, "A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu," *The Journal of chemical physics*, vol. 132, no. 15, p. 154104, 2010.
- [314] T. De Meyer, K. Hemelsoet, L. Van der Schueren, E. Pauwels, K. De Clerck, and V. Van Speybroeck, "Investigating the Halochromic Properties of Azo Dyes in an Aqueous Environment by Using a Combined Experimental and Theoretical Approach," *Chemistry – A European Journal*, vol. 18, no. 26, pp. 8120–8129, 2012.
- [315] S. W. Young, "Studies on solutions of stannous salts. II. The oxidation of solutions of stannous chloride by means of free oxygen," *Journal of the American Chemical Society*, vol. 23, no. 3, pp. 119–147, 1901.
- [316] J. O. Adeyemi and D. C. Onwudiwe, "Organotin(IV) Dithiocarbamate Complexes: Chemistry and Biological Activity," *Molecules (Basel, Switzerland)*, vol. 23, no. 10, p. 2571, 2018.
- [317] L. Pellerito and L. Nagy, "Organotin(IV) n^{+} complexes formed with biologically active ligands: equilibrium and structural studies, and some

- biological aspects," *Coordination Chemistry Reviews*, vol. 224, no. 1, pp. 111–150, 2002.
- [318] L. Nagy, H. Mehner, A. A. Christy, E. Sletten, F. T. Edelmann, and Q. M. Andersen, "Preparation and structural studies on organotin(IV) complexes with flavonoids," *Journal of Radioanalytical and Nuclear Chemistry*, vol. 227, no. 1, pp. 89–99, 1998.
- [319] L. F. Holroyd and T. van Mourik, "Stacking of the mutagenic DNA base analog 5-bromouracil," *Theoretical Chemistry Accounts*, vol. 133, no. 2, p. 1431, 2013.
- [320] T. Verstraelen, S. Vandenbrande, F. Heidar-Zadeh, L. Vanduyfhuys, V. Van Speybroeck, M. Waroquier, and P. W. Ayers, "Minimal basis iterative stockholder: atoms in molecules for force-field development," *Journal of chemical theory and computation*, vol. 12, no. 8, pp. 3894–3912, 2016.
- [321] S. Van Damme, P. Bultinck, and S. Fias, "Electrostatic Potentials from Self-Consistent Hirshfeld Atomic Charges," *Journal of Chemical Theory and Computation*, vol. 5, no. 2, pp. 334–340, 2009.
- [322] T. Verstraelen, P. Tecmer, F. Heidar-Zadeh, C. E. González-Espinoza, M. Chan, T. D. Kim, K. Boguslawski, S. Fias, S. Vandenbrande, D. Berrocal, and P. W. Ayers, "HORTON 2.1.1," 2017.
- [323] J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, and J. Hutter, "Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach," *Computer Physics Communications*, vol. 167, no. 2, pp. 103–128, 2005.
- [324] J. C. Kromann, A. S. Christensen, C. Steinmann, M. Korth, and J. H. Jensen, "A third-generation dispersion and third-generation hydrogen bonding corrected PM6 method: PM6-D3H+," *PeerJ*, vol. 2, pp. e449–e449, 2014.
- [325] A. K. Soper, "The radial distribution functions of water and ice from 220 to 673 K and at pressures up to 400 MPa," *Chemical Physics*, vol. 258, no. 2, pp. 121–137, 2000.
- [326] L. Martínez, R. Andrade, E. G. Birgin, and J. M. Martínez, "PACKMOL: a package for building initial configurations for molecular dynamics simulations," *Journal of computational chemistry*, vol. 30, no. 13, pp. 2157–2164, 2009.
- [327] J. Wang, W. Wang, P. A. Kollman, and D. A. Case, "Automatic atom type and bond type perception in molecular mechanical calculations," *Journal of molecular graphics and modelling*, vol. 25, no. 2, pp. 247–260, 2006.
- [328] J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman, and D. A. Case,

- "Development and testing of a general amber force field," *Journal of computational chemistry*, vol. 25, no. 9, pp. 1157–1174, 2004.
- [329] D. J. Price and C. L. Brooks III, "A modified TIP3P water potential for simulation with Ewald summation," *The Journal of chemical physics*, vol. 121, no. 20, pp. 10096–10103, 2004.
- [330] P. Florová, P. Sklenovský, P. Banáš, and M. Otyepka, "Explicit Water Models Affect the Specific Solvation and Dynamics of Unfolded Peptides While the Conformational Behavior and Flexibility of Folded Peptides Remain Intact," *Journal of Chemical Theory and Computation*, vol. 6, no. 11, pp. 3569–3579, 2010.
- [331] P. Eastman, J. Swails, J. D. Chodera, R. T. McGibbon, Y. Zhao, K. A. Beauchamp, L.-P. Wang, A. C. Simmonett, M. P. Harrigan, C. D. Stern, R. P. Wiewiora, B. R. Brooks, and V. S. Pande, "OpenMM 7: Rapid development of high performance algorithms for molecular dynamics," *PLoS computational biology*, vol. 13, no. 7, pp. e1005659–e1005659, 2017.
- [332] R. T. McGibbon, K. A. Beauchamp, M. P. Harrigan, C. Klein, J. M. Swails, C. X. Hernández, C. R. Schwantes, L.-P. Wang, T. J. Lane, and V. S. Pande, "MDTraj: A Modern Open Library for the Analysis of Molecular Dynamics Trajectories," *Biophysical Journal*, vol. 109, no. 8, pp. 1528–1532, 2015.
- [333] G. A. Tribello, M. Bonomi, D. Branduardi, C. Camilloni, and G. Bussi, "PLUMED 2: New feathers for an old bird," *Computer Physics Communications*, vol. 185, no. 2, pp. 604–613, 2014.
- [334] A. Patras, N. P. Brunton, C. O'Donnell, and B. K. Tiwari, "Effect of thermal processing on anthocyanin stability in foods; mechanisms and kinetics of degradation," *Trends in Food Science & Technology*, vol. 21, no. 1, pp. 3–11, 2010.
- [335] R. Jackman and J. Smith, *Anthocyanins and betalains*, pp. 244–309, Springer, 1996.
- [336] K. Mori, N. Goto-Yamamoto, M. Kitayama, and K. Hashizume, "Loss of anthocyanins in red-wine grape under high temperature," *Journal of Experimental Botany*, vol. 58, no. 8, pp. 1935–1945, 2007.
- [337] E. Sadilova, F. C. Stintzing, and R. Carle, "Thermal Degradation of Acylated and Nonacylated Anthocyanins," *Journal of Food Science*, vol. 71, no. 8, pp. C504–C512, 2006.
- [338] C. Q. Yang, "Effect of pH on Nonformaldehyde Durable Press Finishing of Cotton Fabric: FT-IR Spectroscopy Study:Part II: Formation of the Anhydride Intermediate," *Textile Research Journal*, vol. 63, no. 12, pp. 706–711, 1993.

- [339] C. Q. Yang, "FTIR spectroscopy study of ester crosslinking of cotton cellulose catalyzed by sodium hypophosphite," *Textile Research Journal*, vol. 71, no. 3, pp. 201–206, 2001.
- [340] M. Fan, D. Dai, and B. Huang, *Fourier transform infrared spectroscopy for natural fibres*, IntechOpen, 2012.
- [341] L. C. Cefali, J. A. Ataide, P. Moriel, M. A. Foglio, and P. G. Mazzola, "Plant-based active photoprotectants for sunscreens," *International Journal of Cosmetic Science*, vol. 38, no. 4, pp. 346–353, 2016.
- [342] A. Bąkowska, A. Z. Kucharska, and J. Oszmiański, "The effects of heating, UV irradiation, and storage on stability of the anthocyanin–polyphenol copigment complex," *Food Chemistry*, vol. 81, no. 3, pp. 349–355, 2003.
- [343] O. Dangles, N. Saito, and R. Brouillard, "Anthocyanin intramolecular copigment effect," *Phytochemistry*, vol. 34, no. 1, pp. 119–124, 1993.
- [344] S. Galland, N. Mora, M. Abert-Vian, N. Rakotomanomana, and O. Dangles, "Chemical Synthesis of Hydroxycinnamic Acid Glucosides and Evaluation of Their Ability To Stabilize Natural Colors via Anthocyanin Copigmentation," *Journal of Agricultural and Food Chemistry*, vol. 55, no. 18, pp. 7573–7579, 2007.
- [345] C. H. Giles, A. P. D'Silva, and I. A. Easton, "A general treatment and classification of the solute adsorption isotherm part. II. Experimental interpretation," *Journal of Colloid and Interface Science*, vol. 47, no. 3, pp. 766–778, 1974.
- [346] K. L. Bhat, A. Garg, and C. W. Bock, "Calculated values of the octanol–water partition coefficient and aqueous solubility for aminoazobenzene dyes and related structures," *Dyes and Pigments*, vol. 52, no. 2, pp. 145–159, 2002.
- [347] W. H. Cheung, Y. S. Szeto, and G. McKay, "Intraparticle diffusion processes during acid dye adsorption onto chitosan," *Bioresource Technology*, vol. 98, no. 15, pp. 2897–904, 2007.
- [348] Z. Mao, H. Yu, Y. Wang, L. Zhang, Y. Zhong, and H. Xu, "States of water and pore size distribution of cotton fibers with different moisture ratios," *Industrial & Engineering Chemistry Research*, vol. 53, no. 21, pp. 8927–8934, 2014.
- [349] M. Shiono, N. Matsugaki, and K. Takeda, "Structure of the blue cornflower pigment," *Nature*, vol. 436, no. 7052, pp. 791–791, 2005.
- [350] M. Riquelme, A. Lara, D. L. Mobley, T. Verstraelen, A. R. Matamala, and E. Vöhringer-Martinez, "Hydration Free Energies in the FreeSolv Database

- Calculated with Polarized Iterative Hirshfeld Charges," *Journal of Chemical Information and Modeling*, vol. 58, no. 9, pp. 1779–1797, 2018.
- [351] E. N. Baker and R. E. Hubbard, "Hydrogen bonding in globular proteins," *Progress in Biophysics and Molecular Biology*, vol. 44, no. 2, pp. 97–179, 1984.
- [352] S. Kunsági-Máté, K. Szabó, M. P. Nikfardjam, and L. Kollár, "Determination of the thermodynamic parameters of the complex formation between malvidin-3-O-glucoside and polyphenols. Copigmentation effect in red wines," *Journal of Biochemical and Biophysical Methods*, vol. 69, no. 1, pp. 113–119, 2006.
- [353] S. Kunsági-Máté, E. Ortmann, L. Kollár, and M. P. Nikfardjam, "Effect of the Solvation Shell Exchange on the Formation of Malvidin- 3-O-Glucoside-Ellagic Acid Complexes," *The Journal of Physical Chemistry B*, vol. 111, no. 40, pp. 11750–11755, 2007.
- [354] M. Esti, L. Cinquanta, F. Sinesio, E. Moneta, and M. Di Matteo, "Physicochemical and sensory fruit characteristics of two sweet cherry cultivars after cool storage," *Food Chemistry*, vol. 76, no. 4, pp. 399–405, 2002.
- [355] R. Cortez, D. A. Luna-Vital, D. Margulis, and E. Gonzalez de Mejia, "Natural Pigments: Stabilization Methods of Anthocyanins for Food Applications," *Comprehensive Reviews in Food Science and Food Safety*, vol. 16, no. 1, pp. 180–198, 2017.
- [356] J. M. Awika, L. W. Rooney, and R. D. Waniska, "Properties of 3-Deoxyanthocyanins from Sorghum," *Journal of Agricultural and Food Chemistry*, vol. 52, no. 14, pp. 4388–4394, 2004.
- [357] F. U. G. Akogou, A. P. P. Kayodé, H. M. W. den Besten, A. R. Linnemann, and V. Fogliano, "Effects of processing and storage on the stability of the red biocolorant apigeninidin from sorghum," *LWT*, vol. 90, pp. 592–597, 2018.
- [358] A. Marquez, M. Serratos, and J. Merida, *Pyrananthocyanin Derived Pigments in Wine: Structure and Formation during Winemaking*, vol. 2013, 2013.
- [359] C. Romero and J. Bakker, "Interactions between grape anthocyanins and pyruvic acid, with effect of pH and acid concentration on anthocyanin composition and color in model solutions," *J Agric Food Chem*, vol. 47, no. 8, pp. 3130–9, 1999.
- [360] S. Saxena and A. Raja, *Natural dyes: sources, chemistry, application and sustainability issues*, pp. 37–80, Springer, 2014.
- [361] G. Calogero, A. Bartolotta, G. Di Marco, A. Di Carlo, and F. Bonaccorso,

- "Vegetable-based dye-sensitized solar cells," *Chemical Society Reviews*, vol. 44, no. 10, pp. 3244–3294, 2015.
- [362] K. Gong, Y. Pan, L. J. Rather, W. C. Wang, Q. Zhou, T. H. Zhang, and Q. Li, "Natural pigment during flora leaf senescence and its application in dyeing and UV protection finish of silk and wool - a case study of *Cinnamomum Camphora*," *Dyes and Pigments*, vol. 166, pp. 114–121, 2019.
- [363] A. Sinopoli, I. Citro, G. Calogero, and A. Bartolotta, "Combined experimental and DFT-TDDFT investigation on anthocyanidins for application in dye-sensitised solar cells," *Dyes and Pigments*, vol. 143, pp. 291–300, 2017.
- [364] K. Wongcharee, V. Meeyoo, and S. Chavadej, "Dye-sensitized solar cell using natural dyes extracted from rosella and blue pea flowers," *Solar Energy Materials and Solar Cells*, vol. 91, no. 7, pp. 566–571, 2007.
- [365] K. Sharma, V. Sharma, and S. S. Sharma, "Dye-Sensitized Solar Cells: Fundamentals and Current Status," *Nanoscale Research Letters*, vol. 13, no. 1, p. 381, 2018.
- [366] N. A. Ludin, A. M. Al-Alwani Mahmoud, A. Bakar Mohamad, A. A. H. Kadhum, K. Sopian, and N. S. Abdul Karim, "Review on the development of natural dye photosensitizer for dye-sensitized solar cells," *Renewable and Sustainable Energy Reviews*, vol. 31, pp. 386–396, 2014.
- [367] A. Sinopoli, G. Calogero, and A. Bartolotta, "Computational aspects of anthocyanidins and anthocyanins: A review," *Food Chemistry*, vol. 297, p. 124898, 2019.
- [368] S. Hillebrand, M. Schwarz, and P. Winterhalter, "Characterization of Anthocyanins and Pyranoanthocyanins from Blood Orange [*Citrus sinensis* (L.) Osbeck] Juice," *Journal of Agricultural and Food Chemistry*, vol. 52, no. 24, pp. 7331–7338, 2004.
- [369] A. d. Villiers, G. Vanhoenacker, P. Majek, and P. Sandra, "Determination of anthocyanins in wine by direct injection liquid chromatography–diode array detection–mass spectrometry and classification of wines using discriminant analysis," *Journal of Chromatography A*, vol. 1054, no. 1, pp. 195–204, 2004.
- [370] J. Lee, C. Rennaker, and R. E. Wrolstad, "Correlation of two anthocyanin quantification methods: HPLC and spectrophotometric methods," *Food Chemistry*, vol. 110, no. 3, pp. 782–786, 2008.
- [371] R. Brouillard, G. A. Iacobucci, and J. G. Sweeny, "Chemistry of anthocyanin pigments. 9. UV-visible spectrophotometric determination of the acidity constants of apigeninidin and three related 3-deoxyflavylium salts," *Journal of the American Chemical Society*, vol. 104, no. 26, pp. 7585–7590, 1982.

- [372] A. D. Laurent, C. Adamo, and D. Jacquemin, "Dye chemistry with time-dependent density functional theory," *Physical Chemistry Chemical Physics*, vol. 16, no. 28, pp. 14334–14356, 2014.
- [373] A. R. F. Carvalho, J. Oliveira, V. d. Freitas, N. Mateus, and A. Melo, "A theoretical interpretation of the color of two classes of pyranoanthocyanins," *Journal of Molecular Structure: THEOCHEM*, vol. 948, no. 1, pp. 61–64, 2010.
- [374] J. Azevedo, J. Oliveira, L. Cruz, N. Teixeira, N. F. Brás, V. De Freitas, and N. Mateus, "Antioxidant Features of Red Wine Pyranoanthocyanins: Experimental and Theoretical Approaches," *Journal of Agricultural and Food Chemistry*, vol. 62, no. 29, pp. 7002–7009, 2014.
- [375] M. Leopoldini, F. Rondinelli, N. Russo, and M. Toscano, "Pyranoanthocyanins: A Theoretical Investigation on Their Antioxidant Activity," *Journal of Agricultural and Food Chemistry*, vol. 58, no. 15, pp. 8862–8871, 2010.
- [376] A. D. Quartarolo and N. Russo, "A Computational Study (TDDFT and RICC2) of the Electronic Spectra of Pyranoanthocyanins in the Gas Phase and Solution," *Journal of Chemical Theory and Computation*, vol. 7, no. 4, pp. 1073–1081, 2011.
- [377] F. Siddique, C. Silva, G. Silva, H. Lischka, F. Quina, and A. Aquino, *The Electronic Transitions of Analogs of Red Wine Pyranoanthocyanin Pigments*, vol. 18, 2018.
- [378] J. Oliveira, V. Petrov, A. J. Parola, F. Pina, J. Azevedo, N. Teixeira, N. F. Brás, P. A. Fernandes, N. Mateus, M. J. Ramos, and V. de Freitas, "Chemical Behavior of Methylpyranomalvidin-3-O-glucoside in Aqueous Solution Studied by NMR and UV-Visible Spectroscopy," *The Journal of Physical Chemistry B*, vol. 115, no. 6, pp. 1538–1545, 2011.
- [379] R. Soto-Rajo, J. Baldenebro-Lopez, N. Flores-Holguin, and D. Glossman-Mitnik, "Comparison of several protocols for the computational prediction of the maximum absorption wavelength of chrysanthemin," *J Mol Model*, vol. 20, no. 8, p. 2378, 2014.
- [380] A. A. Freitas, K. Shimizu, L. G. Dias, and F. H. Quina, "A computational study of substituted flavylum salts and their quinonoidal conjugate-bases: S0 → S1 electronic transition, absolute pKa and reduction potential calculations by DFT and semiempirical methods," *Journal of the Brazilian Chemical Society*, vol. 18, no. 8, pp. 1537–1546, 2007.
- [381] K. B. Wiberg, "Basis set effects on calculated geometries: 6-311++G** vs.

- aug-cc-pVDZ," *Journal of Computational Chemistry*, vol. 25, no. 11, pp. 1342–1346, 2004.
- [382] A. V. Marenich, C. J. Cramer, and D. G. Truhlar, "Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions," *The Journal of Physical Chemistry B*, vol. 113, no. 18, pp. 6378–6396, 2009.
- [383] C. Adamo and V. Barone, "Toward reliable density functional methods without adjustable parameters: The PBE0 model," *The Journal of Chemical Physics*, vol. 110, no. 13, pp. 6158–6170, 1999.
- [384] T. Yanai, D. P. Tew, and N. C. Handy, "A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP)," *Chemical Physics Letters*, vol. 393, no. 1, pp. 51–57, 2004.
- [385] A. Eilmes, "Solvatochromic probe in molecular solvents: implicit versus explicit solvent model," *Theoretical Chemistry Accounts*, vol. 133, no. 9, p. 1538, 2014.
- [386] E. A. Kantchev, T. B. Norsten, and M. B. Sullivan, "Time-dependent density functional theory (TDDFT) modelling of Pechmann dyes: from accurate absorption maximum prediction to virtual dye screening," *Org Biomol Chem*, vol. 10, no. 33, pp. 6682–92, 2012.
- [387] L. Rustioni, F. Di Meo, M. Guillaume, O. Failla, and P. Trouillas, "Tuning color variation in grape anthocyanins at the molecular scale," *Food Chemistry*, vol. 141, no. 4, pp. 4349–4357, 2013.
- [388] N. Ahmadiani, R. J. Robbins, T. M. Collins, and M. M. Giusti, "Molar absorptivity (ϵ) and spectral characteristics of cyanidin-based anthocyanins from red cabbage," *Food Chemistry*, vol. 197, pp. 900–906, 2016.
- [389] C. Adamo and D. Jacquemin, "The calculations of excited-state properties with Time-Dependent Density Functional Theory," *Chemical Society Reviews*, vol. 42, no. 3, pp. 845–856, 2013.
- [390] J. Oliveira, N. Mateus, and V. de Freitas, "Network of carboxypyranomalvidin-3-O-glucoside (vitisin A) equilibrium forms in aqueous solution," *Tetrahedron Letters*, vol. 54, no. 37, pp. 5106–5110, 2013.
- [391] V. de Freitas and N. Mateus, "Formation of pyranoanthocyanins in red wines: a new and diverse class of anthocyanin derivatives," *Anal Bioanal Chem*, vol. 401, no. 5, pp. 1463–73, 2011.
- [392] D. Blanco-Vega, F. J. López-Bellido, J. M. Alía-Robledo, and I. Hermosín-Gutiérrez, "HPLC–DAD–ESI–MS/MS characterization of

- pyranoanthocyanins pigments formed in model wine," *Journal of Agricultural and Food Chemistry*, vol. 59, no. 17, pp. 9523–9531, 2011.
- [393] E. J. Beard, G. Sivaraman, I. Vázquez-Mayagoitia, V. Vishwanath, and J. M. Cole, "Comparative dataset of experimental and computational attributes of UV/vis absorption spectra," *Scientific Data*, vol. 6, no. 1, p. 307, 2019.
- [394] M. Jordheim, K. Aaby, T. Fossen, G. Skrede, and y. M. Andersen, "Molar absorptivities and reducing capacity of pyranoanthocyanins and other anthocyanins," *Journal of agricultural and food chemistry*, vol. 55, no. 26, pp. 10591–10598, 2007.
- [395] A. E. Håkansson, K. Pardon, Y. Hayasaka, M. de Sa, and M. Herderich, "Structures and colour properties of new red wine pigments," *Tetrahedron Letters*, vol. 44, no. 26, pp. 4887–4891, 2003.
- [396] N. Quijada-Morín, O. Dangles, J. C. Rivas-Gonzalo, and M. T. Escribano-Bailón, "Physico-Chemical and Chromatic Characterization of Malvidin 3-Glucoside-vinylcatechol and Malvidin 3-Glucoside-vinylguaiacol Wine Pigments," *Journal of Agricultural and Food Chemistry*, vol. 58, no. 17, pp. 9744–9752, 2010.
- [397] J. Bakker and C. F. Timberlake, "Isolation, Identification, and Characterization of New Color-Stable Anthocyanins Occurring in Some Red Wines," *Journal of Agricultural and Food Chemistry*, vol. 45, no. 1, pp. 35–43, 1997.
- [398] J. Preat, C. Michaux, D. Jacquemin, and E. A. Perpète, "Enhanced Efficiency of Organic Dye-Sensitized Solar Cells: Triphenylamine Derivatives," *The Journal of Physical Chemistry C*, vol. 113, no. 38, pp. 16821–16833, 2009.
- [399] J. K. Roy, S. Kar, and J. Leszczynski, "Insight into the optoelectronic properties of designed solar cells efficient tetrahydroquinoline dye-sensitizers on TiO₂ (101) surface: first principles approach," *Scientific reports*, vol. 8, no. 1, pp. 1–12, 2018.
- [400] A. L. Pinto, L. Cruz, V. Gomes, H. Cruz, G. Calogero, V. de Freitas, F. Pina, A. J. Parola, and J. Carlos Lima, "Catechol versus carboxyl linkage impact on DSSC performance of synthetic pyranoflavylum salts," *Dyes and Pigments*, vol. 170, p. 107577, 2019.
- [401] C. M. Galanakis, "Separation of functional macromolecules and micromolecules: From ultrafiltration to the border of nanofiltration," *Trends in Food Science & Technology*, vol. 42, no. 1, pp. 44–63, 2015.
- [402] Q. Deng, K. G. Zinoviadou, C. M. Galanakis, V. Orlie, N. Grimi, E. Vorobiev, N. Lebovka, and F. J. Barba, "The Effects of Conventional and Non-conventional Processing on Glucosinolates and Its Derived

- Forms, Isothiocyanates: Extraction, Degradation, and Applications," *Food Engineering Reviews*, vol. 7, no. 3, pp. 357–381, 2015.
- [403] C. M. Galanakis, "Emerging technologies for the production of nutraceuticals from agricultural by-products: A viewpoint of opportunities and challenges," *Food and Bioproducts Processing*, vol. 91, no. 4, pp. 575–579, 2013.
- [404] Eurostat, "Wine-grower holdings by production," 2015.
- [405] C. M. Galanakis, *Valorization of Fruit Processing By-products*, Academic Press, 2020.
- [406] M. A. Pedroza, M. R. Salinas, G. L. Alonso, and A. Zalacain, *9 - Oenological Applications of Winemaking By-Products*, pp. 215–232, Academic Press, 2017.
- [407] A. Mujumdar, *Handbook of Industrial Drying, Fourth Edition*, Taylor & Francis, 2014.
- [408] P. Markakis, *Anthocyanins as food colors*, New York (N.Y.) : Academic press, 1982.
- [409] P. Denev, M. Ciz, G. Ambrozova, A. Lojek, I. Yanakieva, and M. Kratchanova, "Solid-phase extraction of berries' anthocyanins and evaluation of their antioxidative properties," *Food Chemistry*, vol. 123, no. 4, pp. 1055–1061, 2010.
- [410] I. Ignat, I. Volf, and V. I. Popa, "A critical review of methods for characterisation of polyphenolic compounds in fruits and vegetables," *Food Chemistry*, vol. 126, no. 4, pp. 1821–1835, 2011.
- [411] B. Lapornik, M. Prošek, and A. Golc Wondra, "Comparison of extracts prepared from plant by-products using different solvents and extraction time," *Journal of Food Engineering*, vol. 71, no. 2, pp. 214–222, 2005.
- [412] M. Corrales, S. Toepfl, P. Butz, D. Knorr, and B. Tauscher, "Extraction of anthocyanins from grape by-products assisted by ultrasonics, high hydrostatic pressure or pulsed electric fields: A comparison," *Innovative Food Science & Emerging Technologies*, vol. 9, no. 1, pp. 85–91, 2008.
- [413] A. Baiano, "Recovery of biomolecules from food wastes-a review," *Molecules*, vol. 19, no. 9, pp. 14821–42, 2014.
- [414] A. Scoma, C. Pintucci, L. Bertin, P. Carlozzi, and F. Fava, "Increasing the large scale feasibility of a solid phase extraction procedure for the recovery of natural antioxidants from olive mill wastewaters," *Chemical Engineering Journal*, vol. 198-199, pp. 103–109, 2012.
- [415] S. A. Mahdavi, S. M. Jafari, M. Ghorbani, and E. Assadpoor, "Spray-Drying Microencapsulation of Anthocyanins by Natural Biopolymers: A Review," *Drying Technology*, vol. 32, no. 5, pp. 509–518, 2014.

- [416] Eurostat, "Total production by PRODCOM list (NACE Rev. 2) - annual data," 2018.
- [417] J. Jakopic and R. Veberic, "Extraction of phenolic compounds from green walnut fruits in different solvents," *Acta Agriculturae Slovenica*, vol. 93, no. 1, pp. 11–15, 2009.
- [418] M. Durante, M. S. Lenucci, and G. Mita, "Supercritical Carbon Dioxide Extraction of Carotenoids from Pumpkin (*Cucurbita* spp.): A Review," *International Journal of Molecular Sciences*, vol. 15, no. 4, pp. 6725–6740, 2014.
- [419] R. Khir, Z. Pan, G. G. Atungulu, J. F. Thompson, and D. Shao, "Size and Moisture Distribution Characteristics of Walnuts and Their Components," *Food and Bioprocess Technology*, vol. 6, no. 3, pp. 771–782, 2013.
- [420] R. D. McWhinney, S. Zhou, and J. P. D. Abbatt, "Naphthalene SOA: redox activity and naphthoquinone gas–particle partitioning," *Atmos. Chem. Phys.*, vol. 13, no. 19, pp. 9731–9744, 2013.
- [421] A. Jahanban-Esfahlan, A. Ostadrahimi, M. Tabibiazar, and R. Amarowicz, "A Comprehensive Review on the Chemical Constituents and Functional Uses of Walnut (*Juglans* spp.) Husk," *International Journal of Molecular Sciences*, vol. 20, no. 16, 2019.
- [422] R. Tabaraki and S. Rastgoo, "Comparison between conventional and ultrasound-assisted extractions of natural antioxidants from walnut green husk," *Korean Journal of Chemical Engineering*, vol. 31, no. 4, pp. 676–683, 2014.
- [423] V. Nour, I. Trandafir, and S. Cosmulescu, "Optimization of ultrasound-assisted hydroalcoholic extraction of phenolic compounds from walnut leaves using response surface methodology," *Pharmaceutical Biology*, vol. 54, no. 10, pp. 2176–2187, 2016.
- [424] L. Wang, D. Li, C. Bao, J. You, Z. Wang, Y. Shi, and H. Zhang, "Ultrasonic extraction and separation of anthraquinones from *Rheum palmatum* L." *Ultrasonics Sonochemistry*, vol. 15, no. 5, pp. 738–746, 2008.
- [425] K. Mathiyazhagan, A. Kumaran, and P. Arjun, "Isolation of Natural Naphthoquinones from *Juglans regia* and In Vitro Antioxidant and Cytotoxic Studies of Naphthoquinones and the Synthetic Naphthofuran Derivatives," *Russian Journal of Bioorganic Chemistry*, vol. 44, no. 3, pp. 346–353, 2018.
- [426] X.-B. Zhang, C.-L. Zou, Y.-X. Duan, F. Wu, and G. Li, "Activity guided isolation and modification of juglone from *Juglans regia* as potent cytotoxic agent against lung cancer cell lines," *BMC Complementary and Alternative Medicine*, vol. 15, 2015.

- [427] A. Berthod, T. Maryutina, B. Spivakov, O. Shpigun, and I. A. Sutherland, "Countercurrent chromatography in analytical chemistry (IUPAC Technical Report)," *Pure and Applied chemistry*, vol. 81, no. 2, pp. 355–387, 2009.
- [428] D. S. Sogi and A. S. Bawa, "Dehydration of tomato processing waste," *Indian Food Packer*, vol. 52, no. 2, pp. 26–29, 1998.
- [429] M. Hernández-Ortega, G. Kissangou, H. Necoechea-Mondragón, M. E. Sánchez-Pardo, and A. Ortiz-Moreno, "Microwave dried carrot pomace as a source of fiber and carotenoids," *Food and Nutrition Sciences*, vol. 4, no. 10, 2013.
- [430] I. F. Strati and V. Oreopoulou, "Recovery of carotenoids from tomato processing by-products – a review," *Food Research International*, vol. 65, pp. 311–321, 2014.
- [431] I. F. Strati and V. Oreopoulou, "Effect of extraction parameters on the carotenoid recovery from tomato waste," *International Journal of Food Science & Technology*, vol. 46, no. 1, pp. 23–29, 2011.
- [432] R. K. Saini and Y.-S. Keum, "Carotenoid extraction methods: A review of recent developments," *Food Chemistry*, vol. 240, pp. 90–103, 2018.
- [433] Y. Shen, Y. Hu, K. Huang, S. Yin, B. Chen, and S. Yao, "Solid-phase extraction of carotenoids," *Journal of Chromatography A*, vol. 1216, no. 30, pp. 5763–5768, 2009.
- [434] H.-E. Khoo, K. N. Prasad, K.-W. Kong, Y. Jiang, and A. Ismail, "Carotenoids and their isomers: color pigments in fruits and vegetables," *Molecules (Basel, Switzerland)*, vol. 16, no. 2, pp. 1710–1738, 2011.
- [435] G. Wernet, C. Bauer, B. Steubing, J. Reinhard, E. Moreno-Ruiz, and B. Weidema, "The ecoinvent database version 3 (part I): overview and methodology," *The International Journal of Life Cycle Assessment*, vol. 21, no. 9, pp. 1218–1230, 2016.
- [436] G. Finnveden, M. Z. Hauschild, T. Ekvall, J. Guinée, R. Heijungs, S. Hellweg, A. Koehler, D. Pennington, and S. Suh, "Recent developments in Life Cycle Assessment," *Journal of Environmental Management*, vol. 91, no. 1, pp. 1–21, 2009.
- [437] S. S. Costa, B. A. S. Machado, A. R. Martin, F. Bagnara, S. A. Ragadalli, and A. R. C. Alves, "Drying by spray drying in the food industry: Micro-encapsulation, process parameters and main carriers used," *African Journal of Food Science*, vol. 9, no. 9, pp. 462–470, 2015.
- [438] A. Verhoef, J. Degreë, B. Huybrechts, H. van Veen, P. Pex, and B. Van der Bruggen, "Simulation of a hybrid pervaporation–distillation

- process," *Computers & Chemical Engineering*, vol. 32, no. 6, pp. 1135–1146, 2008.
- [439] K. Skalicka-Woźniak and I. Garrard, "A comprehensive classification of solvent systems used for natural product purifications in countercurrent and centrifugal partition chromatography," *Natural Product Reports*, vol. 32, no. 11, pp. 1556–1561, 2015.
- [440] T. Agnhage, A. Perwuelz, and N. Behary, "Towards sustainable Rubia tinctorum L. dyeing of woven fabric: How life cycle assessment can contribute," *Journal of Cleaner Production*, vol. 141, pp. 1221–1230, 2017.
- [441] Y. C. Tang and B. H. Chen, "Pigment change of freeze-dried carotenoid powder during storage," *Food Chemistry*, vol. 69, no. 1, pp. 11–17, 2000.
- [442] H. Wedin, B. Källman, A. R. Kristinsdottir, E. Niit, Z. Mansoor, C. Lindgren, and H. Rammsy, "Evaluation of dyeing and finishing components in recycling and regeneration of coloured textiles," Report, Research Institute of Sweden, 2018.
- [443] W. Schade, C. Doll, M. Maibach, M. Peter, F. Crespo, D. Carvalho, G. Caiado, M. Conti, A. Lilico, and N. Afraz, "COMPETE Final Report: Analysis of the contribution of transport policies to the competitiveness of the EU economy and comparison with the United States," Report, 2006.
- [444] P. Luoma, J. Vanhanen, and P. Tommila, "Distributed Bio-Based Economy: Driving Sustainable Growth," *Finnish Innovation Fund (SITRA): Helsinki, Finland*, p. 24, 2011.
- [445] K. McCormick and N. Kautto, "The bioeconomy in Europe: An overview," *Sustainability*, vol. 5, no. 6, pp. 2589–2608, 2013.
- [446] S. Roy and J.-W. Rhim, "Anthocyanin food colorant and its application in pH-responsive color change indicator films," *Critical Reviews in Food Science and Nutrition*, pp. 1–29, 2020.
- [447] M. Weston, M. A. T. Phan, J. Arcot, and R. Chandrawati, "Anthocyanin-based sensors derived from food waste as an active use-by date indicator for milk," *Food Chemistry*, vol. 326, p. 127017, 2020.
- [448] I. Appelhagen, A. K. Wulff-Vester, M. Wendell, A.-K. Hvoslef-Eide, J. Russell, A. Oertel, S. Martens, H.-P. Mock, C. Martin, and A. Matros, "Colour bio-factories: Towards scale-up production of anthocyanins in plant cell cultures," *Metabolic Engineering*, vol. 48, pp. 218–232, 2018.
- [449] PILI, 2021.
- [450] M. Henríquez, S. Almonacid, M. Lutz, R. Simpson, and M. Valdenegro, "Comparison of three drying processes to obtain an apple peel food ingredient," *CyTA - Journal of Food*, vol. 11, no. 2, pp. 127–135, 2013.

- [451] H. Hamid, M. F. B. Abdollah, N. A. Masripan, and R. Hasan, "Characterization of Raw and Ripen of Banana Peel wastes and It's Oils extraction using Soxhlet Method," *International Journal of Applied Chemistry*, vol. 12, pp. 1–5, 2016.
- [452] C. Tagliani, C. Perez, A. Curutchet, P. Arcia, and S. Cozzano, "Blueberry pomace, valorization of an industry by-product source of fibre with antioxidant capacity," *Food Science and Technology*, vol. 39, no. 3, pp. 644–651, 2019.
- [453] Eurostat, "Crop production in EU standard humidity (apro_cpsh1)," 2018.
- [454] J. M. Holden, A. L. Eldridge, G. R. Beecher, I. Marilyn Buzzard, S. Bhagwat, C. S. Davis, L. W. Douglass, S. Gebhardt, D. Haytowitz, and S. Schakel, "Carotenoid Content of U.S. Foods: An Update of the Database," *Journal of Food Composition and Analysis*, vol. 12, no. 3, pp. 169–196, 1999.
- [455] H. Müller, "Determination of the carotenoid content in selected vegetables and fruit by HPLC and photodiode array detection," *Zeitschrift für Lebensmitteluntersuchung und -Forschung A*, vol. 204, no. 2, pp. 88–94, 1997.
- [456] C. E. West and E. J. Poortvliet, *The carotenoid content of foods with special reference to developing countries*, Arlington, VA (USA) International Science and Technology Inst. for Agency for International Development, 1993.
- [457] S. Bhagwat, D. B. Haytowitz, and J. M. Holden, "USDA database for the flavonoid content of selected foods, Release 3.1," *US Department of Agriculture: Beltsville, MD, USA*, 2014.
- [458] G. Gremaud, I. Schmid, and R. Sieber, "Estimation de l'utilisation des denrées alimentaires en Suisse pour les années 2001/2002," *Fünfter Schweizerischer Ernährungsbericht/Cinquième rapport sur la nutrition en Suisse*, pp. 7–23, 2005.
- [459] M. O'Neill, Y. Carroll, B. Corridan, B. Olmedilla, F. Granado, I. Blanco, H. Van den Berg, I. Hininger, A.-M. Rousell, and M. Chopra, "A European carotenoid database to assess carotenoid intakes and its use in a five-country comparative study," *British Journal of Nutrition*, vol. 85, no. 04, pp. 499–507, 2001.
- [460] P. Bridle and C. F. Timberlake, "Anthocyanins as natural food colours - selected aspects," *Food Chemistry*, vol. 58, no. 1, pp. 103–109, 1997.
- [461] A. A. Franke, L. J. Custer, C. Arakaki, and S. P. Murphy, "Vitamin C and flavonoid levels of fruits and vegetables consumed in Hawaii," *Journal of Food Composition and Analysis*, vol. 17, no. 1, pp. 1–35, 2004.
- [462] H. Wang, G. Cao, and R. L. Prior, "Oxygen Radical Absorbing Capacity of

- Anthocyanins," *Journal of Agricultural and Food Chemistry*, vol. 45, no. 2, pp. 304–309, 1997.
- [463] X. Wu, G. R. Beecher, J. M. Holden, D. B. Haytowitz, S. E. Gebhardt, and R. L. Prior, "Concentrations of Anthocyanins in Common Foods in the United States and Estimation of Normal Consumption," *Journal of Agricultural and Food Chemistry*, vol. 54, no. 11, pp. 4069–4075, 2006.
- [464] K. Elst and I. Geyskens, "Overzicht van de Organisch-biologische Nevenstromen in Vlaanderen," Report, 2013.
- [465] L. C. R. dos Reis, V. R. de Oliveira, M. E. K. Hagen, A. Jablonski, S. H. Flôres, and A. de Oliveira Rios, "Carotenoids, flavonoids, chlorophylls, phenolic compounds and antioxidant activity in fresh and cooked broccoli (*Brassica oleracea* var. Avenger) and cauliflower (*Brassica oleracea* var. Alphina F1)," *LWT - Food Science and Technology*, vol. 63, no. 1, pp. 177–183, 2015.
- [466] J.-C. Favier, J. Ireland-Ripert, C. Laussucq, and M. Feinberg, "Répertoire général des aliments(Tome 3, Table de composition des fruits exotiques, fruits de cueillette d'Afrique)," p. 242, 1993.
- [467] M. S. DuPont, Z. Mondin, G. Williamson, and K. R. Price, "Effect of Variety, Processing, and Storage on the Flavonoid Glycoside Content and Composition of Lettuce and Endive," *Journal of Agricultural and Food Chemistry*, vol. 48, no. 9, pp. 3957–3964, 2000.
- [468] F. Ren, K. Reilly, J. P. Kerry, M. Gaffney, M. Hossain, and D. K. Rai, "Higher Antioxidant Activity, Total Flavonols, and Specific Quercetin Glucosides in Two Different Onion (*Allium cepa* L.) Varieties Grown under Organic Production: Results from a 6-Year Field Study," *Journal of Agricultural and Food Chemistry*, vol. 65, no. 25, pp. 5122–5132, 2017.
- [469] H. Akyol, Y. Riciputi, E. Capanoglu, M. F. Caboni, and V. Verardo, "Phenolic Compounds in the Potato and Its Byproducts: An Overview," *International Journal of Molecular Sciences*, vol. 17, no. 6, p. 835, 2016.
- [470] Eurostat, "Crop production in EU standard humidity (apro_cpsh1)," 2019.
- [471] Landbouw Vlaanderen Departement Landbouw en Visserij, "Akkerbouw," 2017.
- [472] Food and Agriculture Organization of the United Nations (FAO), "Production, Crops," 2018.
- [473] D. Hofstrand, "Agricultural Marketing Resource Center," 2018.
- [474] D. I. Onwude, N. Hashim, R. Janius, N. Nawi, and K. Ebdan, "Color Change Kinetics and Total Carotenoid Content of Pumpkin as Affected by Drying

- Temperature," *Italian Journal of Food Science*, vol. 29, no. 1, pp. 1–18, 2016.
- [475] R. Pokluda, "Selected Nutritional Aspects of Field Grown Root Vegetables in the Czech Republic," pp. 315–322, International Society for Horticultural Science (ISHS), Leuven, Belgium, 2013.
- [476] R. Lavecchia and A. Zuorro, "Improved lycopene extraction from tomato peels using cell-wall degrading enzymes," *European Food Research and Technology*, vol. 228, no. 1, pp. 153–158, 2008.
- [477] E. Luengo, I. Alvarez, and J. Raso, "Improving carotenoid extraction from tomato waste by pulsed electric fields," *Frontiers in Nutrition*, vol. 1, pp. 1–10, 2014.
- [478] B. Ćosić, T. Pukšec, G. Krajačić, N. Duić, N. Markovska, H. Mikulčić, and M. Vujanović, "Agrocycle: Database/inventory of the current agricultural value chains - Fruit AWCB value chain," 2016.
- [479] R. Tsao, R. Yang, J. C. Young, and H. Zhu, "Polyphenolic Profiles in Eight Apple Cultivars Using High-Performance Liquid Chromatography (HPLC)," *Journal of Agricultural and Food Chemistry*, vol. 51, no. 21, pp. 6347–6353, 2003.
- [480] K. L. Wolfe and R. H. Liu, "Apple peels as a value-added food ingredient," *Journal of Agricultural and Food Chemistry*, vol. 51, no. 6, pp. 1676–83, 2003.
- [481] D. Ruiz, J. Egea, M. I. Gil, and F. A. Tomás-Barberán, "Characterization and Quantitation of Phenolic Compounds in New Apricot (*Prunus armeniaca* L.) Varieties," *Journal of Agricultural and Food Chemistry*, vol. 53, no. 24, pp. 9544–9552, 2005.
- [482] I. S. Şanal, E. Bayraktar, . Mehmetoğlu, and A. Çalimli, "Determination of optimum conditions for SC-(CO₂ + ethanol) extraction of β-carotene from apricot pomace using response surface methodology," *Journal of Supercritical Fluids*, vol. 34, no. 3, pp. 331–338, 2005.
- [483] J. M. Harnly, R. F. Doherty, G. R. Beecher, J. M. Holden, D. B. Haytowitz, S. Bhagwat, and S. Gebhardt, "Flavonoid Content of U.S. Fruits, Vegetables, and Nuts," *Journal of Agricultural and Food Chemistry*, vol. 54, no. 26, pp. 9966–9977, 2006.
- [484] E. A. Pazmino-Duran, M. M. Giusti, R. E. Wrolstad, and M. B. A. Gloria, "Anthocyanins from banana bracts (*Musa X paradisiaca*) as potential food colorants," *Food Chemistry*, vol. 73, no. 3, pp. 327–332, 2001.
- [485] A. Subagio, N. Morita, and S. Sawada, "Carotenoids and their fatty-acid

- esters in banana peel," *Journal of Nutritional Science and Vitaminology*, vol. 42, no. 6, pp. 553–566, 1996.
- [486] X. Wu, L. Gu, R. L. Prior, and S. McKay, "Characterization of anthocyanins and proanthocyanidins in some cultivars of Ribes, Aronia, and Sambucus and their antioxidant capacity," *Journal of Agricultural and Food Chemistry*, vol. 52, no. 26, pp. 7846–56, 2004.
- [487] M. Jordheim, F. Måge, and y. M. Andersen, "Anthocyanins in Berries of Ribes Including Gooseberry Cultivars with a High Content of Acylated Pigments," *Journal of Agricultural and Food Chemistry*, vol. 55, no. 14, pp. 5529–5535, 2007.
- [488] E. Revilla, J. M. Ryan, and G. Martin-Ortega, "Comparison of several procedures used for the extraction of anthocyanins from red grapes," *Journal of Agricultural and Food Chemistry*, vol. 46, no. 11, pp. 4592–4597, 1998.
- [489] Z. Li, Q. Pan, X. Cui, and C. Duan, "Optimization on anthocyanins extraction from wine grape skins using orthogonal test design," *Food Science and Biotechnology*, vol. 19, no. 4, pp. 1047–1053, 2010.
- [490] A. Liazid, R. F. Guerrero, E. Cantos, M. Palma, and C. G. Barroso, "Microwave assisted extraction of anthocyanins from grape skins," *Food Chemistry*, vol. 124, no. 3, pp. 1238–1243, 2011.
- [491] D. M. Segantini, S. Leonel, G. P. P. Lima, S. M. Costa, and A. R. P. Ramos, "Caracterização da polpa de pêssegos produzidos em São Manuel-SP," *Ciência Rural*, vol. 42, pp. 52–57, 2012.
- [492] L. M. R. d. Silva, E. A. T. d. Figueiredo, N. M. P. S. Ricardo, I. G. P. Vieira, R. W. d. Figueiredo, I. M. Brasil, and C. L. Gomes, "Quantification of bioactive compounds in pulps and by-products of tropical fruits from Brazil," *Food Chemistry*, vol. 143, pp. 398–404, 2014.
- [493] D. Loeillet, "The world pineapple market: the importance of europe," pp. 37–48, International Society for Horticultural Science (ISHS), Leuven, Belgium, 1997.
- [494] O. K. Chun, D.-O. Kim, H. Y. Moon, H. G. Kang, and C. Y. Lee, "Contribution of individual polyphenolics to total antioxidant capacity of plums," *Journal of Agricultural and Food Chemistry*, vol. 51, no. 25, pp. 7240–7245, 2003.
- [495] V. Usenik, F. Štampar, and R. Veberič, "Anthocyanins and fruit colour in plums (*Prunus domestica* L.) during ripening," *Food Chemistry*, vol. 114, no. 2, pp. 529–534, 2009.
- [496] D. de Origen Protegida Granada Mollar de Elche, "The pomegranate," 2016.
- [497] U. A. Fischer, R. Carle, and D. R. Kammerer, "Identification and

- quantification of phenolic compounds from pomegranate (*Punica granatum* L.) peel, mesocarp, aril and differently produced juices by HPLC-DAD-ESI/MSⁿ," *Food Chemistry*, vol. 127, no. 2, pp. 807–821, 2011.
- [498] F. A. Nagia and R. S. R. El-Mohamedy, "Dyeing of wool with natural anthraquinone dyes from *Fusarium oxysporum*," *Dyes and Pigments*, vol. 75, no. 3, pp. 550–555, 2007.
- [499] O. K. Alebeid, Z. Tao, and A. I. Seedahmed, "New approach for dyeing and UV protection properties of cotton fabric using natural dye extracted from Henna leaves," *Fibres & Textiles in Eastern Europe*, vol. 23, no. 5, pp. 60–65, 2015.
- [500] S. Ali, T. Hussain, and R. Nawaz, "Optimization of alkaline extraction of natural dye from Henna leaves and its dyeing on cotton by exhaust method," *Journal of Cleaner Production*, vol. 17, no. 1, pp. 61–66, 2009.
- [501] A. S. Nateri, E. Dehnavi, A. Hajipour, and E. Ekrami, "Dyeing of polyamide fibre with cochineal natural dye," *Pigment & Resin Technology*, vol. 45, no. 4, pp. 252–258, 2016.
- [502] N. F. Ali and R. S. R. El. Mohamedy, "Cationization of cotton fabric for dyeing with natural anthraquinone dyes from *Fusarium Oxysporum*," *Research Journal of Textile and Apparel*, vol. 14, no. 2, pp. 21–29, 2010.
- [503] N. Baaka, I. El Ksibi, and M. F. Mhenni, "Optimisation of the recovery of carotenoids from tomato processing wastes: application on textile dyeing and assessment of its antioxidant activity," *Natural Product Research*, vol. 31, no. 2, pp. 196–203, 2017.
- [504] N. Baaka, A. Mahfoudhi, and M. F. Mhenni, "Orange peels waste as a low cost cotton natural dye," *Moroccan Journal of Chemistry*, vol. 5, no. 2, pp. 259–265, 2017.
- [505] M. I. Bahtiyari, H. Benli, and A. Yavas, "Printing of wool and cotton fabrics with natural dyes," *Asian Journal of Chemistry*, vol. 25, no. 6, pp. 3220–3224, 2013.
- [506] R. Raisanen, P. Nousiainen, and P. H. Hynninen, "Emodin and dermocybin natural anthraquinones as mordant dyes for wool and polyamide," *Textile Research Journal*, vol. 71, no. 11, pp. 1016–1022, 2001.
- [507] R. Raisanen, P. Nousiainen, and P. H. Hynninen, "Emodin and dermocybin natural anthraquinones as high-temperature disperse dyes for polyester and polyamide," *Textile Research Journal*, vol. 71, no. 10, pp. 922–927, 2001.
- [508] R. Raisanen, P. Nousiainen, and P. H. Hynninen, "Dermorubin and 5-chlorodermorubin natural anthraquinone carboxylic acids as dyes for wool," *Textile Research Journal*, vol. 72, no. 11, pp. 973–976, 2002.

- [509] T. Bechtold, A. Turcanu, E. Ganglberger, and S. Geissler, "Natural dyes in modern textile dyehouses - How to combine experiences of two centuries to meet the demands of the future?" *Journal of Cleaner Production*, vol. 11, no. 5, pp. 499–509, 2003.
- [510] M. N. Bukhari, I. Shahid ul, M. Shabbir, L. J. Rather, M. Shahid, M. A. Khan, and F. Mohammad, "Effect of binary and ternary combination of metal salt mordants on dyeing and fastness properties of natural protein fibre with *Juglans regia* L. dye," *Journal of Natural Fibers*, vol. 14, no. 4, pp. 519–529, 2017.
- [511] P. Sasivatchutikool and M. Nakpathom, "Application of natural dye extracted from *Cassia Fistula* ripe pods for dyeing of silk fabric," *Fibers and Polymers*, vol. 20, no. 9, pp. 1841–1849, 2019.
- [512] S. N. Chattopadhyay, N. C. Pan, A. K. Roy, S. Saxena, and A. Khan, "Development of natural dyed jute fabric with improved colour yield and UV protection characteristics," *Journal of the Textile Institute*, vol. 104, no. 8, pp. 808–818, 2013.
- [513] G. Savvidis, E. Karanikas, N. Nikolaidis, I. Eleftheriadis, and E. Tsatsaroni, "Ink-jet printing of cotton with natural dyes," *Coloration Technology*, vol. 130, no. 3, pp. 200–204, 2014.
- [514] A. T. Selvi, R. Aravindhan, B. Madhan, and J. R. Rao, "Studies on the application of natural dye extract from *Bixa orellana* seeds for dyeing and finishing of leather," *Industrial Crops and Products*, vol. 43, pp. 84–86, 2013.
- [515] I. Shahid ul, L. J. Rather, M. Shabbir, M. N. Bukhari, M. A. Khan, and F. Mohammad, "First application of mix metallic salt mordant combinations to develop newer shades on wool with *Bixa orellana* natural dye using reflectance spectroscopy," *Journal of Natural Fibers*, vol. 15, no. 3, pp. 363–372, 2018.
- [516] A. Shams-Nateri, "Reusing wastewater of madder natural dye for wool dyeing," *Journal of Cleaner Production*, vol. 19, no. 6-7, pp. 775–781, 2011.
- [517] R. M. El-Shishtawy, G. M. Shokry, N. S. E. Ahmed, and M. M. Kamel, "Dyeing of modified acrylic fibers with curcumin and madder natural dyes," *Fibers and Polymers*, vol. 10, no. 5, pp. 617–624, 2009.
- [518] A. Etemadifar, H. Dehghanizadeh, N. Nasirizadeh, and M. Rohani-Moghadam, "Statistical optimization of wool dyeing with Alizarin Red S as a natural dye via central composite design," *Fibers and Polymers*, vol. 15, no. 2, pp. 254–260, 2014.
- [519] K. Faidei, N. Baaka, S. Hammami, R. E. Mokni, Z. Mighri, and M. F. Mhenni, "Extraction of carotenoids from *Lycium ferocissimum* fruits for cotton dyeing:

- Optimization survey based on a central composite design method," *Fibers and Polymers*, vol. 17, no. 1, pp. 36–43, 2016.
- [520] A. Farooq, S. Ali, N. Abbas, N. Zahoor, and M. A. Ashraf, "Optimization of extraction and dyeing parameters for natural dyeing of cotton fabric using Marigold (*Tagetes erecta*)," *Asian Journal of Chemistry*, vol. 25, no. 11, pp. 5955–5959, 2013.
- [521] S. R. Shukla and S. M. Patil, "Colour matching on wool using natural and synthetic dyes," *Indian Journal of Fibre & Textile Research*, vol. 25, no. 4, pp. 303–308, 2000.
- [522] M. P. Gashti, B. Katozian, M. Shaver, and A. Kiumarsi, "Clay nanoadsorbent as an environmentally friendly substitute for mordants in the natural dyeing of carpet piles," *Coloration Technology*, vol. 130, no. 1, pp. 54–61, 2014.
- [523] C. Singh and E. Grover, "Red Cabbage - A natural dye for silk," *Man-Made Textiles in India*, vol. 52, no. 5, pp. 157–160, 2009.
- [524] W. Haddar, M. Ben Ticha, A. Guesmi, F. Khoffi, and B. Durand, "A novel approach for a natural dyeing process of cotton fabric with *Hibiscus mutabilis* (Gulzuba): process development and optimization using statistical analysis," *Journal of Cleaner Production*, vol. 68, pp. 114–120, 2014.
- [525] P. B. Tayade and R. V. Adivarekar, "Colour gamut with easy sources of natural dyes," *International Journal of Clothing Science and Technology*, vol. 28, no. 5, pp. 558–569, 2016.
- [526] O. A. Hakeim, "Application of tannic acid-metal salt combination in cotton printing with natural dye," *Journal of the Textile Association*, vol. 63, no. 6, pp. 281–286, 2003.
- [527] M. Tutak and H. Benli, "Colour and fastness of fabrics dyed with walnut (*Juglans regia* L.) base natural dyes," *Asian Journal of Chemistry*, vol. 23, no. 2, pp. 566–568, 2011.
- [528] S. F. Harlapur and H. P. Nagaswarupa, "Marigold: eco-friendly natural dye for fabrics," in "Materials Today: Proceedings," vol. 5, pp. 22350–22354, 2018.
- [529] M. Tutak and N. E. Korkmaz, "Environmentally friendly natural dyeing of organic cotton," *Journal of Natural Fibers*, vol. 9, no. 1, pp. 51–59, 2012.
- [530] X. Hou, X. Chen, Y. Cheng, H. Xu, L. Chen, and Y. Yang, "Dyeing and UV-protection properties of water extracts from orange peel," *Journal of Cleaner Production*, vol. 52, pp. 410–419, 2013.
- [531] X. Hou, F. Fang, X. Guo, J. Wizi, B. Ma, Y. Tao, and Y. Yang, "Potential of sorghum husk extracts as a natural functional dye for wool fabrics," *ACS Sustainable Chemistry & Engineering*, vol. 5, no. 6, pp. 4589–4597, 2017.

- [532] S. Jabeen, S. Ali, M. Nadeem, K. Arif, N. Qureshi, G. A. Shar, G. A. Soomro, M. Iqbal, A. Nazir, and U. H. Siddiqua, "Statistical modeling for the extraction of dye from natural source and industrial applications," *Polish Journal of Environmental Studies*, vol. 28, no. 4, pp. 2145–2150, 2019.
- [533] C. K. Jha, R. Kumar, S. Venkat Kumar, and V. Devi Rajeswari, "Extraction of natural dye from marigold flower (*Tagetes Erecta* L.) and dyeing of fabric and yarns: A focus on colorimetric analysis and fastness properties," *Der Pharmacia Lettre*, vol. 7, no. 1, pp. 185–195, 2015.
- [534] R. Yadav, Anubhav, P. Mathur, and J. Sheikh, "Antibacterial, UV protective and antioxidant linen obtained by natural dyeing with henna," *Cellulose Chemistry and Technology*, vol. 53, no. 3-4, pp. 357–362, 2019.
- [535] M. M. Kamel, F. Abdelghaffar, and M. M. El-Zawahry, "Eco-friendly dyeing of wool with a mixture of natural dyes," *Journal of Natural Fibers*, vol. 8, no. 4, pp. 289–307, 2011.
- [536] A. A. Khan, N. Iqbal, S. Adeel, M. Azeem, F. Batool, and I. A. Bhatti, "Extraction of natural dye from red calico leaves: Gamma ray assisted improvements in colour strength and fastness properties," *Dyes and Pigments*, vol. 103, pp. 50–54, 2014.
- [537] L. Ledwani, S. Sehgal, and K. C. Gupta, "Anthraquinone glycoside from stem bark of *Cassia reingera* and use of aqueous bark extracts as an eco-friendly natural dye on wool," *Asian Journal of Chemistry*, vol. 21, no. 7, pp. 5179–5183, 2009.
- [538] S. R. Maulik, L. Bhowmik, and K. Agarwal, "Batik on handloom cotton fabric with natural dye," *Indian Journal of Traditional Knowledge*, vol. 13, no. 4, pp. 788–794, 2014.
- [539] B. Meryemoglu, "Natural dyes from lignocellulosic biomass hydrolysates," *Indian Journal of Fibre & Textile Research*, vol. 43, no. 1, pp. 92–97, 2018.
- [540] P. K. Mishra, P. Singh, K. K. Gupta, H. Tiwari, and P. Srivastava, "Extraction of natural dye from *Dahlia variabilis* using ultrasound," *Indian Journal of Fibre & Textile Research*, vol. 37, no. 1, pp. 83–86, 2012.
- [541] F. A. Mohamed, "Eco-friendly dyeing of wool and silk fabrics using mixed synthesized acid and natural dyes and antibacterial activity for the dyed fabrics," *Bioscience Research*, vol. 15, no. 3, pp. 1480–1486, 2018.
- [542] C. J. Cramer and D. G. Truhlar, "Quantum chemical conformational analysis of glucose in aqueous solution," *Journal of the American Chemical Society*, vol. 115, no. 13, pp. 5745–5753, 1993.
- [543] J. B. Harborne, "Spectral methods of characterizing anthocyanins," *The Biochemical journal*, vol. 70, no. 1, pp. 22–28, 1958.

- [544] F. L. da Silva, M. T. Escribano-Bailón, J. J. Pérez Alonso, J. C. Rivas-Gonzalo, and C. Santos-Buelga, "Anthocyanin pigments in strawberry," *LWT - Food Science and Technology*, vol. 40, no. 2, pp. 374–382, 2007.
- [545] C. Alcalde-Eon, M. T. Escribano-Bailón, C. Santos-Buelga, and J. C. Rivas-Gonzalo, "Changes in the detailed pigment composition of red wine during maturity and ageing: A comprehensive study," *Analytica Chimica Acta*, vol. 563, no. 1, pp. 238–254, 2006.
- [546] C. Alcalde-Eon, M. T. Escribano-Bailón, C. Santos-Buelga, and J. C. Rivas-Gonzalo, "Separation of pyranoanthocyanins from red wine by column chromatography," *Analytica Chimica Acta*, vol. 513, no. 1, pp. 305–318, 2004.
- [547] Extrasynthese, "Specification (January 2020 (version 11.1))," 2020.
- [548] HM Revenue & Customs, "Wines and Spirits - of Chapter 22: UK,EU & Non-EU Imports: General Trade," 2014.
- [549] A. M. Goula, K. Thymiatidis, and K. Kaderides, "Valorization of grape pomace: Drying behavior and ultrasound extraction of phenolics," *Food and Bioprocesses Processing*, vol. 100, pp. 132–144, 2016.
- [550] E. Bernaerts, E. Demuynck, J. Platteau, V. Samborski, and D. Vervloet, "Groenten en Fruit," 2016.
- [551] Büchi, "Pure Chromatography Instruments Technical data sheet," 2019.
- [552] K. Mathiyazhagan, A. Kumaran, and P. Arjun, "Isolation of Natural Naphthoquinones from *Juglans regia* and In Vitro Antioxidant and Cytotoxic Studies of Naphthoquinones and the Synthetic Naphthofuran Derivatives," *Russian Journal of Bioorganic Chemistry*, vol. 44, no. 3, pp. 346–353, 2018.
- [553] C. G. J. Baker and K. A. McKenzie, "Energy Consumption of Industrial Spray Dryers," *Drying Technology*, vol. 23, no. 1-2, pp. 365–386, 2005.
- [554] VITO/InfoMil, "Fact sheets on air emission abatement techniques," Report, 2009.
- [555] K. Lim, M. Ma, and K. D. Dolan, "Effects of Spray Drying on Antioxidant Capacity and Anthocyanidin Content of Blueberry By-Products," *Journal of Food Science*, vol. 76, no. 7, pp. H156–H164, 2011.
- [556] C. Fredes, C. Becerra, J. Parada, and P. Robert, "The Microencapsulation of Maqui (*Aristotelia chilensis* (Mol.) Stuntz) Juice by Spray-Drying and Freeze-Drying Produces Powders with Similar Anthocyanin Stability and Bioaccessibility," *Molecules*, vol. 23, no. 5, pp. 1227–1242, 2018.
- [557] L. S. Limited, "Labocon Advance Freeze Dryer 300 series," 2014.
- [558] A. Hasanbeigi and L. Price, "A review of energy use and energy efficiency

- technologies for the textile industry," *Renewable and Sustainable Energy Reviews*, vol. 16, no. 6, pp. 3648–3665, 2012.
- [559] Büchi, "SpeedExtractor E-916 / E-916XL / E-914 Technical data sheet," 2019.
- [560] A. Gallo-Cordova, M. d. M. Silva-Gordillo, G. A. Muñoz, X. Arboleda-Faini, and D. Almeida Streitwieser, "Comparison of the adsorption capacity of organic compounds present in produced water with commercially obtained walnut shell and residual biomass," *Journal of Environmental Chemical Engineering*, vol. 5, no. 4, pp. 4041–4050, 2017.
- [561] S. De Meester, *Life cycle assessment in biorefineries: case studies and methodological development*, Thesis, 2013.
- [562] H.-L. Huang and S. Yang, "Filtration characteristics of polysulfone membrane filters," *Journal of Aerosol Science*, vol. 37, no. 10, pp. 1198–1208, 2006.
- [563] M. Mulder, J. O. Hendrickman, H. Hegeman, and C. Smolders, "Ethanol-water separation by pervaporation," *Journal of Membrane Science*, vol. 16, pp. 269–284, 1983.
- [564] W. Ho and K. Sirkar, *Membrane handbook*, Springer Science & Business Media, 2012.
- [565] H. Panda, *Handbook on chemical industries (alcohol based)*, Asia Pacific Business Press Inc., 2002.
- [566] P. Ghosh and A. Katiyar, "Densitometric HPTLC analysis of juglone, quercetin, myricetin, rutin, caffeic acid, and gallic acid in *Juglans regia* L," *JPC Journal of Planar Chromatography Modern TLC*, vol. 25, no. 5, pp. 420–425, 2012.
- [567] Machine and Process Design, "Bulk Density Values For Food Processing," 2020.
- [568] T.-Y. Zhang, L. K. Pannell, Q.-L. Pu, D.-G. Cai, and Y. Ito, "Separation of hydroxyanthraquinone derivatives extracted from *rheum* with analytical high-speed counter-current chromatography," *Journal of Chromatography A*, vol. 442, pp. 455–458, 1988.
- [569] S. Guo, B. Feng, R. Zhu, J. Ma, and W. Wang, "Preparative isolation of three anthraquinones from *Rumex japonicus* by high-speed counter-current chromatography," *Molecules*, vol. 16, no. 2, pp. 1201–1210, 2011.
- [570] Gilson Purification S.A.S., "User's guide Gilson CPC Systems," 2020.
- [571] B. Yegorov and I. Malaki, "Technological foundations of processing tomato pomace in feed additives," *Ukrainian Food Journal*, vol. 3, no. 2, pp. 228–236, 2014.

- [572] A. Zuorro, R. Lavecchia, F. Medici, and L. Piga, "Use of cell wall degrading enzymes for the production of high-quality functional products from tomato processing waste," *Chemical Engineering Transactions*, vol. 38, pp. 355–360, 2014.

Introduction

The Retinoid Cycle

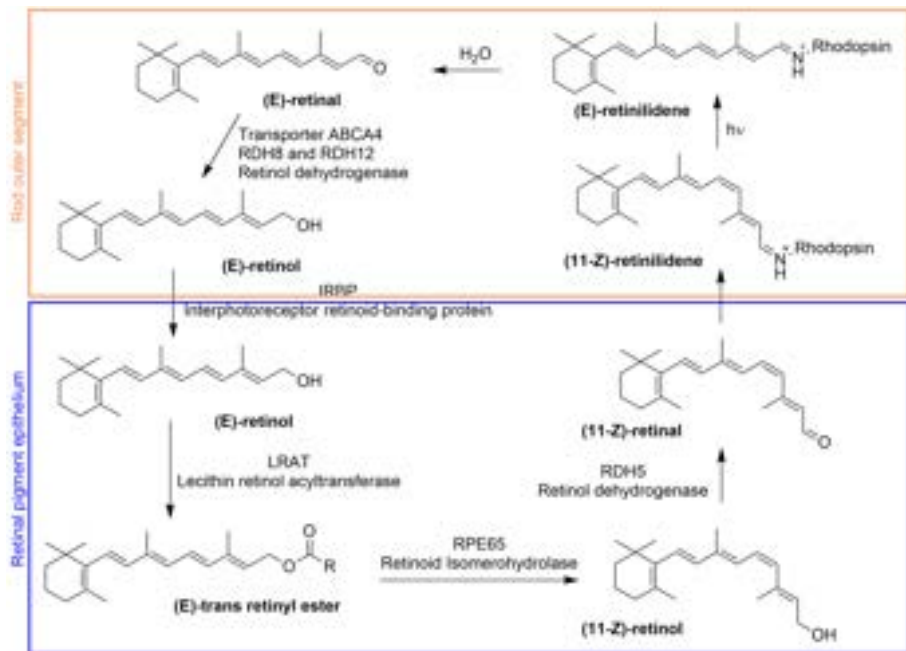


Figure A.1: The chemistry behind the retinoid cycle.

The Influence of pH on Anthocyanins

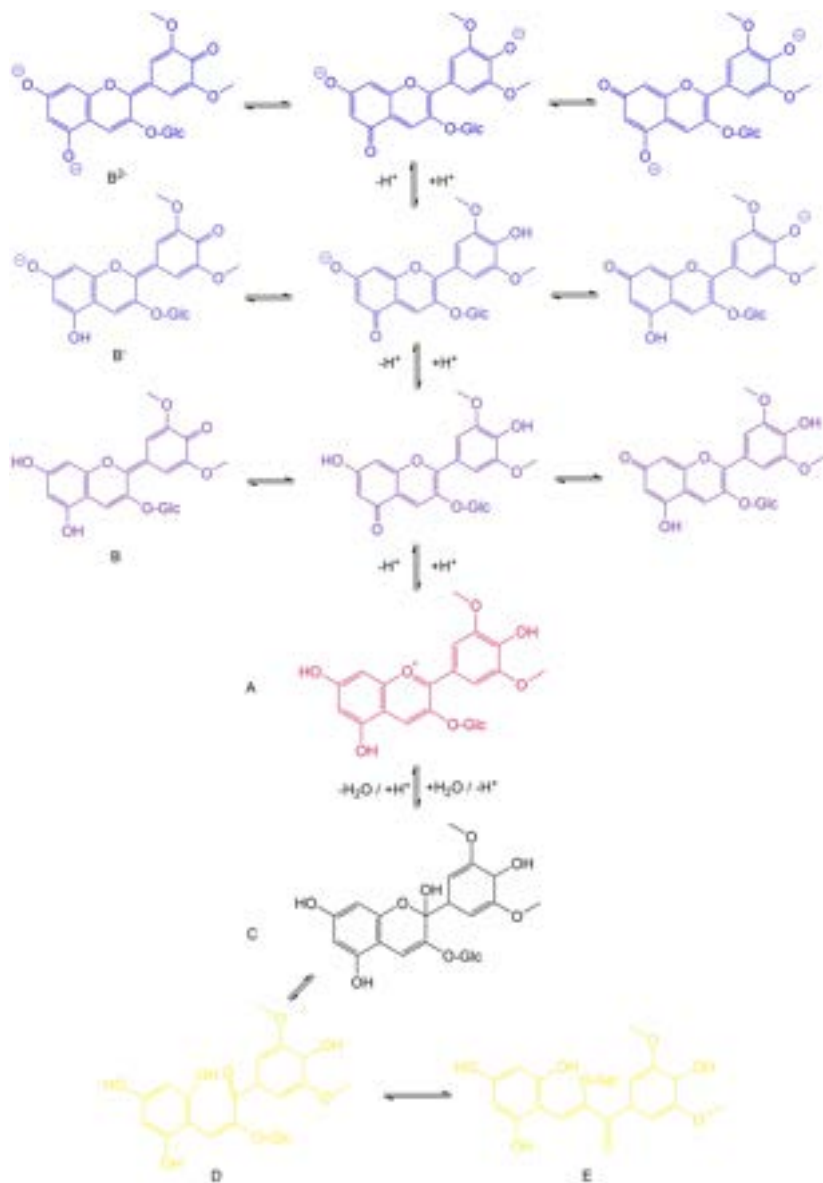


Figure A.2: The influence of pH on anthocyanins. Molecule A represents the flavylium cation, which exists exclusively below pH 3. B is the quinoidal base (B) obtained after deprotonation. A second and third deprotonation step around neutrality and pH 8.5 yields the anionic (B⁻) and dianionic (B²⁻) quinoidal bases. C illustrates the hemiketal isomer after hydration at the C2 position of the flavylium cation. After tautomerization, light-yellow (Z)-chalcone (D) and (E)-chalcone (E) isomers can be formed.

Specific Percentages of By-Products Generation

Source	Type of by-products	Amount (in %)
Asparagus	Spear	40-50
Banana	Peel	30
Bean	Poor quality	20
Cabbage	Leaves and cabbage juice	30
Carrot	Pomace and peel	5-12
Cauliflower	Suspended solid	0.25 - 5
Chicory	Poor quality	11
Kiwi	Pomace	19
Leek	Poor quality	5
Onion	Solid waste	8.2 - 25
Pea	Poor quality	18
Peach	Pulp	10
Pineapple	Core	9.1
Pineapple	Peels	13.5
Pineapple	Pulp	14.5
Pineapple	Top	14.9
Spinach	Poor quality	5

Table A.1: Specific amounts of by-products generated from fruit and vegetable processing industries [35, 68].

Moisture Content of Fruits and Vegetables

Table A.2: The moisture content of fruits and vegetables for the conversion of fresh weight units to dry weight units [70].

Vegetables	Value (g per 100 g)	Fruits	Value (g per 100 g)
Asparagus	93.22	Apple	85.56
Beans	90.32	Apple (peel) [450]	90.9
Brussels sprout	87.07	Apricot	86.35
Cabbage (red)	90.39	Avocado	73.23
Cabbage (savoy)	91.0	Banana	74.91
Cabbage (white)	92.18	Banana (peel) [451]	87.58
Cabbage waste	93.0	Blackcurrant	81.96
Carrot	88.29	Blueberry	84.21
Broccoli	89.3	Blueberry pomace [452]	50.0
Cauliflower	89.79	Cherry	86.13
Celeriac	88.0	Clementine	86.58
Celery (<i>Allium graveolens</i>)	95.43	Cranberries (<i>Vaccinium macrocarpon</i>)	87.32
Chicory	94.52	Currants	83.95
Courgettes and marrows	94.79	Figs (<i>Ficus carica</i>)	79.11
Cucumber	95.23	Gooseberry	87.87
Eggplant	92.3	Grape (red or green)	80.54
Leek	83.0	Grape (leaves)	73.32
Lettuce (<i>Lactuca sativa</i> L.)	94.98	Kiwi	83.07
Lettuce (red)	95.64	Lemons	88.98
Onion	89.11	Limes	88.26
Onion (red)	88.6	Nectarine	87.59
Pea	78.86	Olive (black)	81.3
Potato	81.58	Olive (green)	75.28
Potato (red)	80.96	Orange	86.75
Pumpkin	91.6	Peach (<i>Prunus persica</i>)	88.87
Rhubarb	93.61	Pear	83.96
Rhubarb root	75.0	Pineapple	86.0
Salsify (<i>Scorzonera hispanica</i>)	77.0	Plum	87.23
Spinach	91.4	Pomegranate	70.3
Sweet pepper (green)	93.89	Raspberry (<i>Rubus idaeus</i>)	85.75
Sweet pepper (orange)	92.21	Redcurrant	83.95
Sweet pepper (red)	92.21	Sour cherry	86.13
Sweet pepper (yellow)	92.02	Strawberry	90.95
Turnip (<i>Brassica rapa subsp. rapa</i>)	91.87	Sweet cherry	82.25
Turnip greens (leaves)	89.67	Tomato	94.52
		Tomato pomace [99]	10.7
		Walnut	4.07
		Walnut leaves	80.00

Additional Figures about the Amount of By-Products

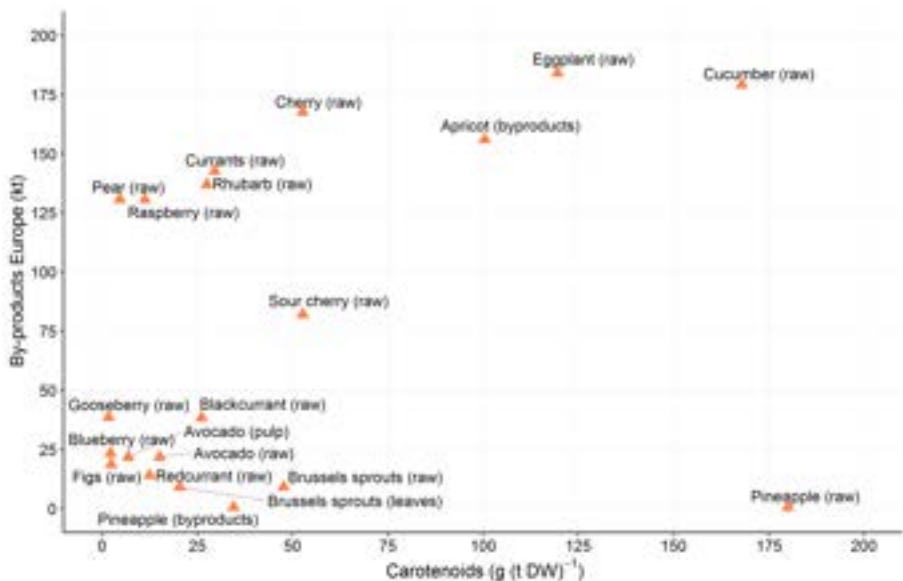


Figure A.3: Part 3 of the amount of by-products as a function of the carotenoids concentration, within Europe (Fig 7C).

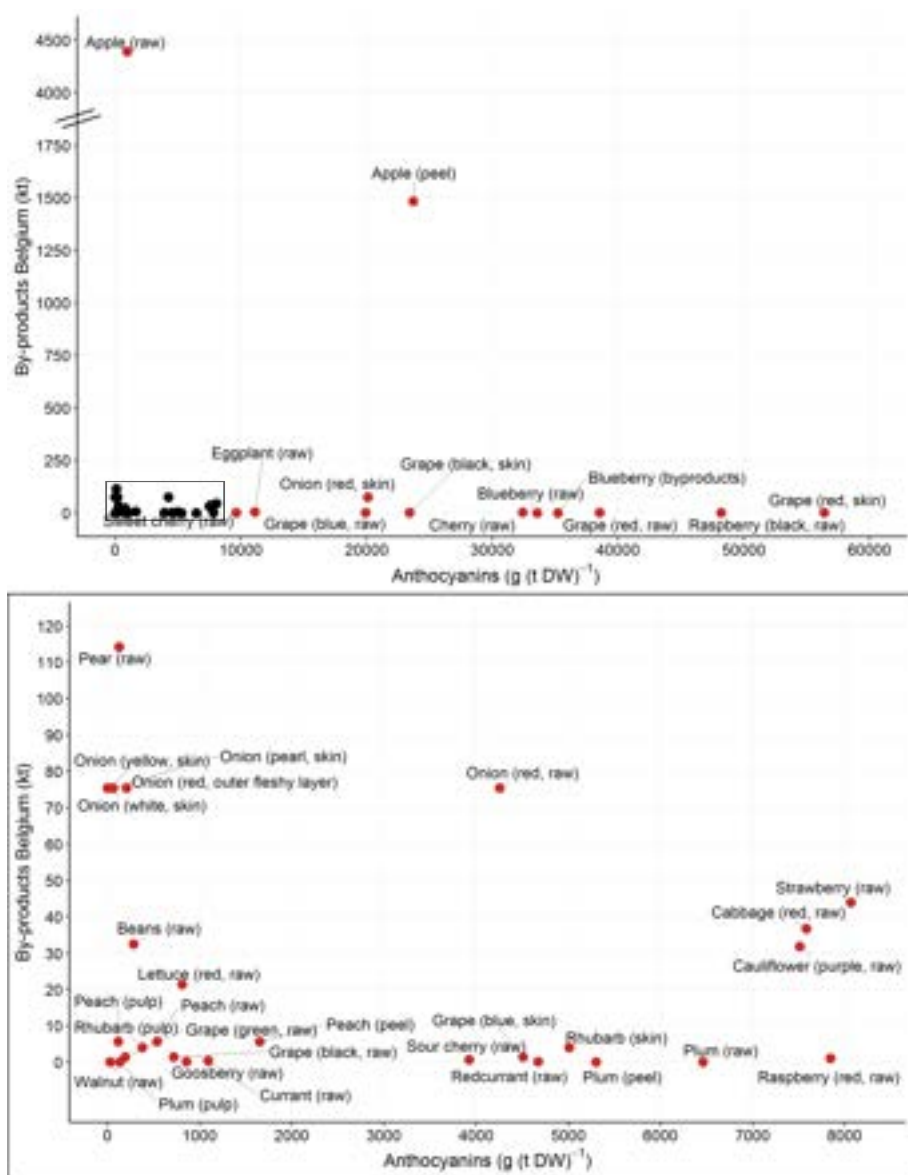


Figure A.4: The amount of by-products as a function of the anthocyanin concentration, within Belgium.

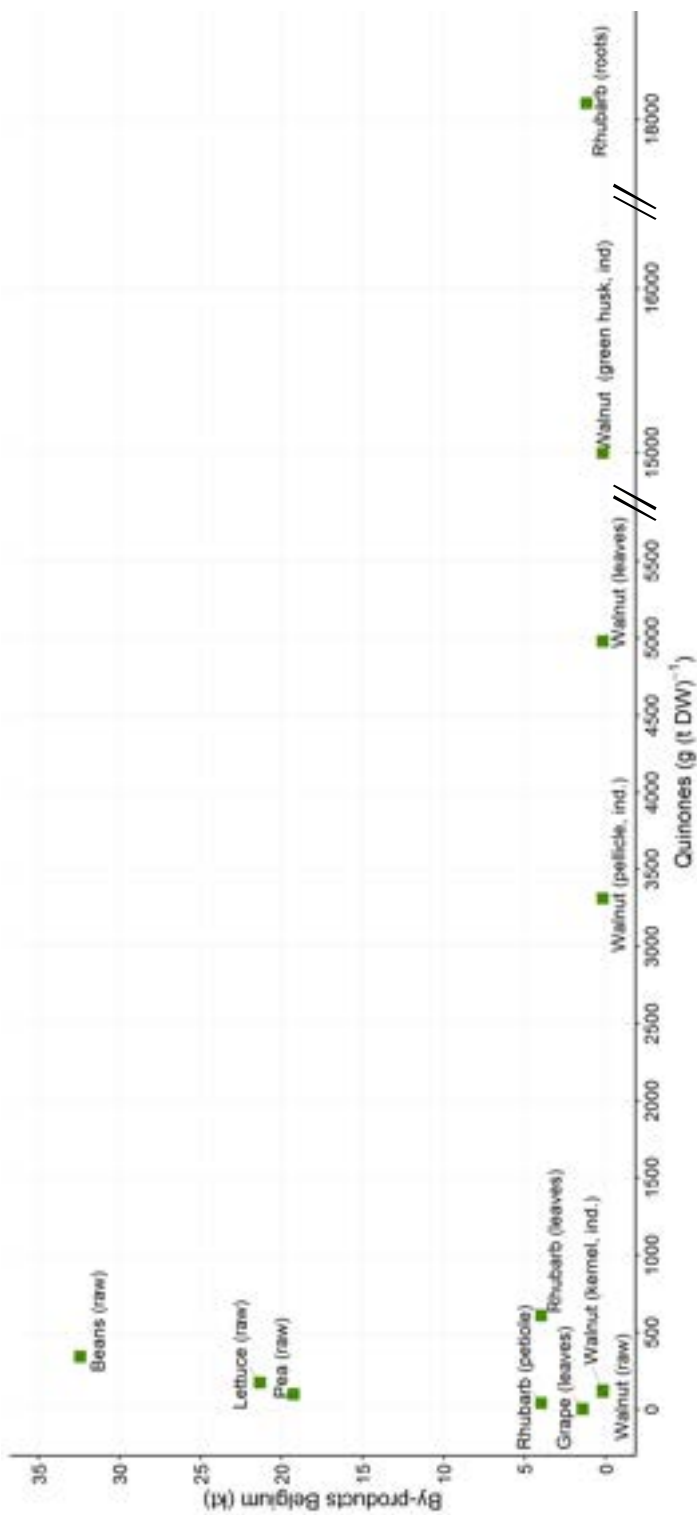
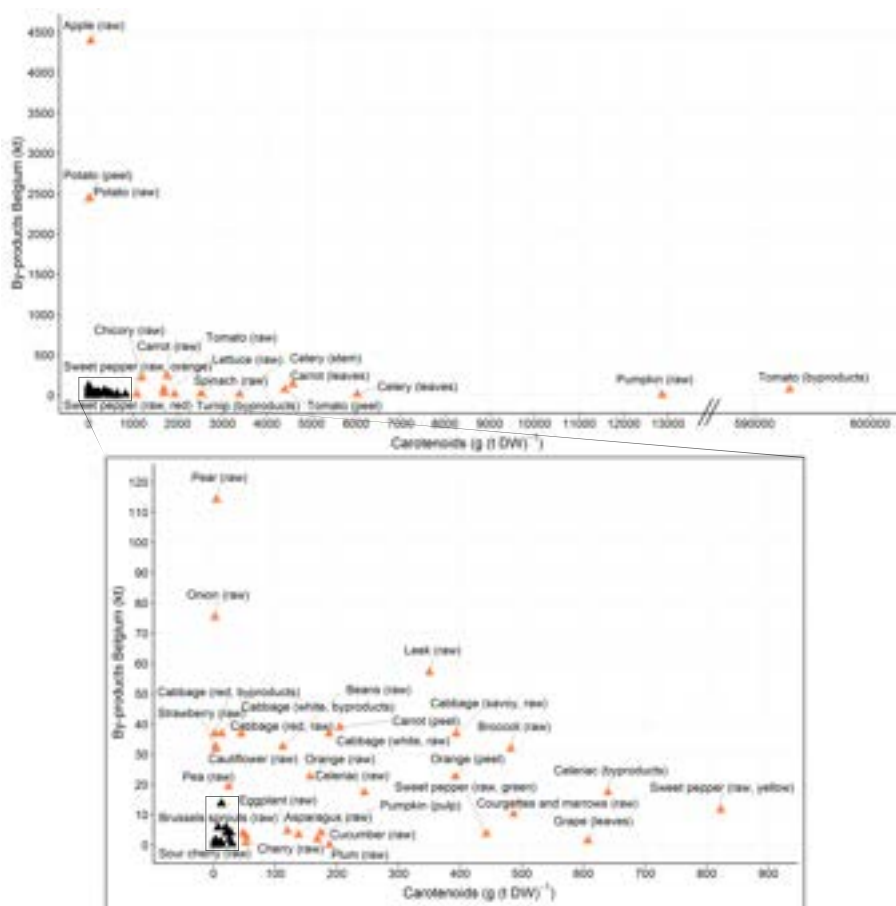


Figure A.5: The amount of by-products as a function of the quinone concentration, within Belgium.



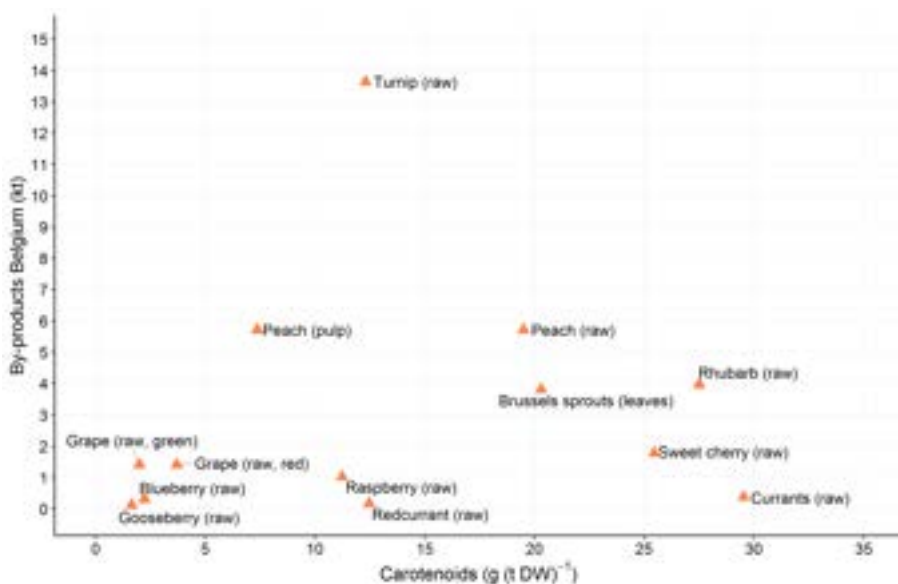


Figure A.6: The amount of by-products as a function of the carotenoid concentration, within Belgium.

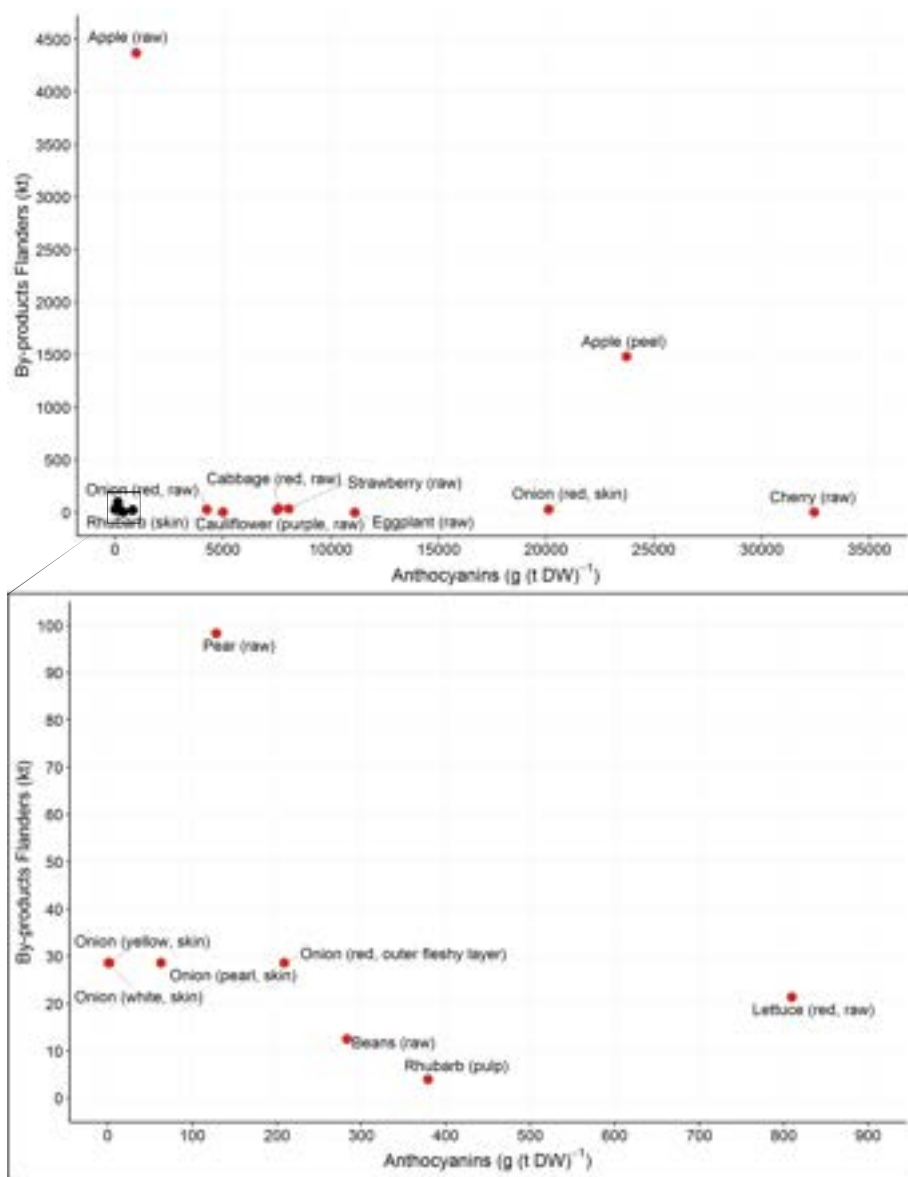


Figure A.7: The amount of by-products as a function of the anthocyanin concentration within Flanders.

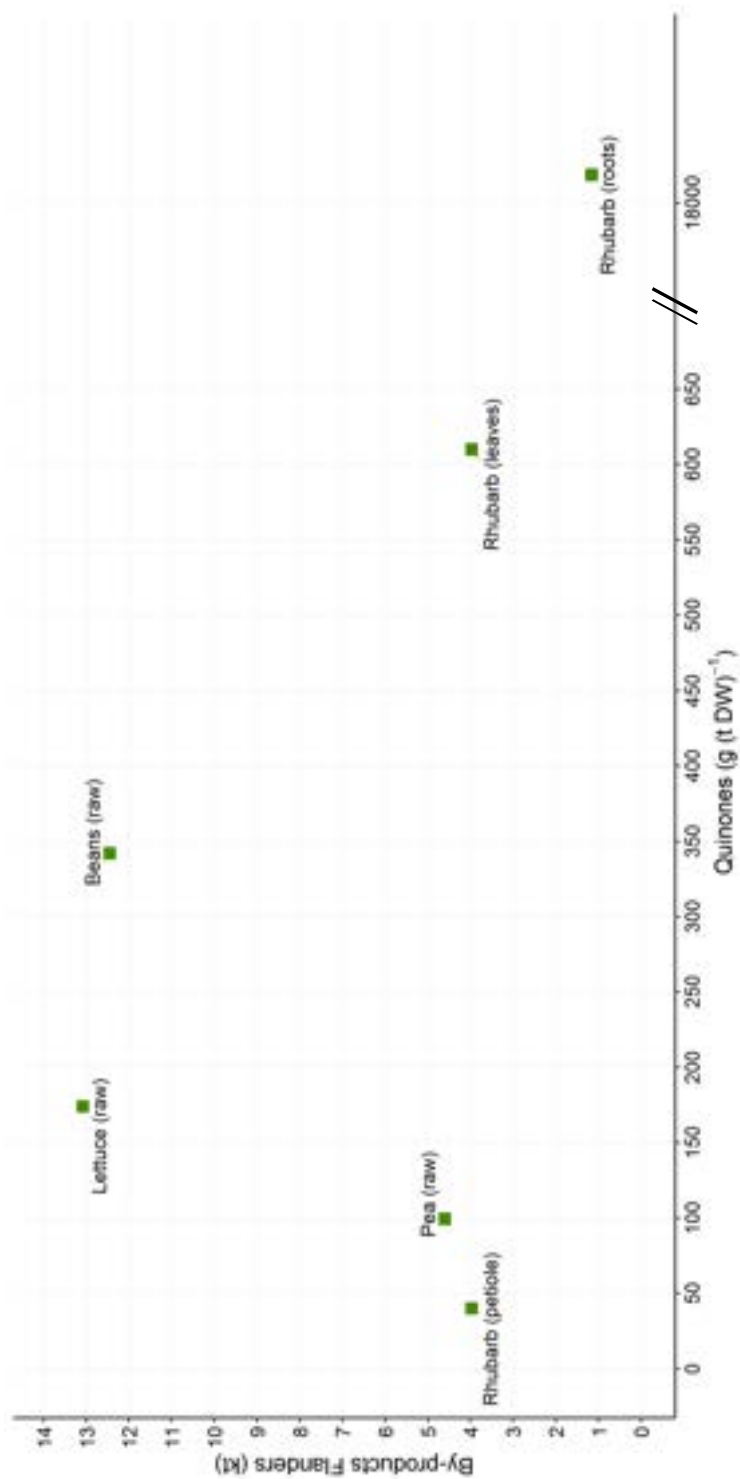


Figure A.8: The amount of by-products as a function of the quinone concentration within Flanders.

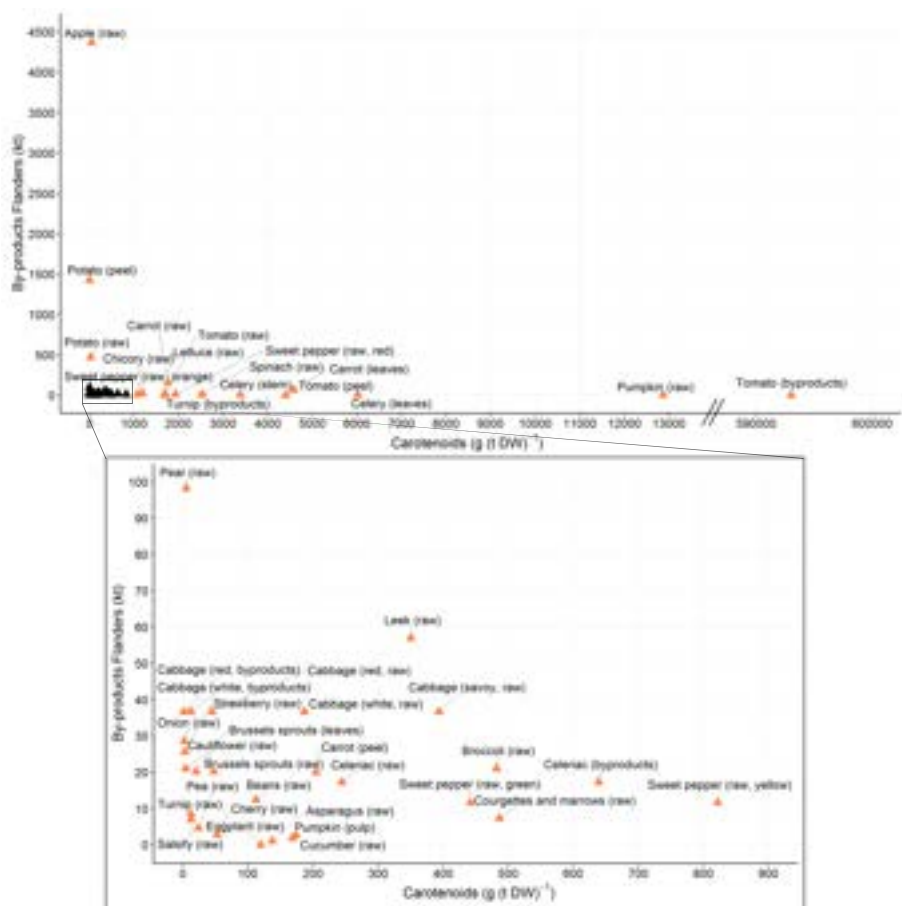


Figure A.9: The amount of by-products as a function of the carotenoid concentration, within Flanders.

The Occurrence, Masses and Concentrations of Natural Dyes in Fruit and Vegetables By-Products

Table A.3: An overview of the vegetables containing the natural colorants of interest. Raw refers to the primary raw material and its concentration, Agri. and A&I refer to the agricultural by-products and the combined agricultural and industrial by-products along with its specific content within this by-product, respectively. (EU: Europe, BE: Belgium, FL: Flanders, ACN: anthocyanins, QUI: quinones and CAR: carotenoids)

Vegetables	Primary production (tonne)				Source	Total amount of waste stream (tonne)			Components (g/tonne DW)			References
	EU	BE	FL			EU	BE	FL	ACN	QUI	CAR	
Asparagus	331580	5340	1680		Raw						8.9 - 137	[453, 454, 455, 456]
					A&I	232106	3364	1058				[1, 29, 68]
Beans, common	98250	37730	98250		Raw				283	0.4 - 342	36.1 - 112	[107, 453, 454, 457]
					A&I	424436	32423	12451				[35, 69, 81, 456]
					A&I	424436	32423	12451				[1, 29, 68]
Brussels sprout	211410	54550	45400		Raw						3.6 - 47.6	[35, 453, 454, 458]
					A&I	46510	24275	20203		20.3 ^(c)		[82, 455, 456, 459]
					A&I	46510	24275	20203				[1, 29, 35, 456]
Cabbage	3396970	52900	52900 ^(d,e,f)		Raw				3351 - 7586 ^(d)		2.4 - 44.8 ^(d) , 307 - 393 ^(e) , 2.6 - 187 ^(f)	[453, 458, 460, 461]
					A&I	302645	36710	36710 ^(e,f)			1.6 ^(d) , 12.4 ^(f)	[35, 54, 454, 455]
					A&I	302645	36710	36710 ^(e,f)				[69, 82, 459, 462]
					A&I	302645	36710	36710 ^(e,f)				[240, 456, 463]
					A&I	302645	36710	36710 ^(e,f)				[1, 29, 68, 103]
					A&I	302645	36710	36710 ^(e,f)				[35, 456]
Carrot	5309550	323500	166800		Raw						588 - 1757	[107, 453, 454, 458]
					A&I	4291548	238805	156236			205 ^(a)	[35, 82, 455, 459]
					A&I	4291548	238805	156236				[29, 103, 105, 464]
					A&I	4291548	238805	156236				[1, 35, 68, 106]
					A&I	4291548	238805	156236				[69]
Cauliflower* and broccoli	2375950	122340	81920		Raw				6964 - 7512 ⁽ⁱ⁾		2880 - 4580 ^(c) , 1.7 - 3.9 ^(k) , 146 - 482 ^(l)	[106]
					Agri	2214082	134900	69500				[453, 454, 458, 465]
					Raw							[69, 455, 456]

		A&I	347502	19267	4600				[1, 29, 68, 464]
Potato*	51846030	4058700	2377705			Raw			[35]
								0.3 - 24.4	[453, 469, 470, 471]
Pumpkin	4427871	9200	6000			A&I	28997490	2433026	1425338
						Raw			[103, 109, 464]
									[35, 418, 472]
						A&I	974132	4094	2670
									[418, 472, 473, 474]
Rhubarb*	622720	8920	8920			Raw			[456]
									[94, 453]
						A&I	136998	3969	3969
									[1, 88, 94]
Salsify			13300			Agri	124544	1160	1160
						Raw			[1, 29, 95]
						A&I		7000	[35, 475]
									[29, 35]
Spinach	680210	82350	78750			Raw			[35, 453, 454, 458]
									[82, 455, 456]
						A&I	171553	14823	14175
									[6, 88, 97, 454]
									36 - 442 (e), 382 -
Sweet pepper	2584240	26040	26040			Raw			1926 (d), 779 -
									[35, 107, 453, 454]
									1080 (h), 15 - 822
									(i)
						A&I	389703	≥ 11631	11631
									[35]
Tomato	16730540	258680				Raw			[453, 454, 458, 459]
									[82]
						A&I	6969380	72460	501
									[35, 103, 109, 476]
						Raw			[69, 96, 477]
Turnip		43300	15500						[35, 453, 456]
						A&I	13640	8583	[29, 35]

^a : peel/skin, ^b : pulp, ^c : leaves, ^d : red, ^e : savory, ^f : white, ^g : green, ^h : orange, ⁱ : yellow, ^j : purple cauliflower, ^k : cauliflower, ^l : broccoli,
^m : stem, ⁿ : dry skin, ^o : outer fleshy layer, ^p : pearl, ^q : purple potato, ^r : roots * : production of purple cauliflower, purple potatoes and rhubarb are
overestimated

Table A.4: An overview of the fruits containing the natural colorants of interest. Raw refers to the primary raw material and its concentration and A&I refers to the combined agricultural and industrial by-products along with its specific content within this by-product. (EU: Europe, BE: Belgium, FL: Flanders, ACN: anthocyanins, QUI: quinones and CAR: carotenoids)

Fruits	Primary production (tonne)			Source	Total amount of waste stream (tonne)			Components (g/tonne DW)			References
	EU	BE	FL		EU	BE	FL	ACN	QUI	CAR	
Apple	13836380	229160	86236	Raw				41.6 - 983.4		2.1 - 47.8	[107, 453, 478] [35, 454, 463, 470]
				A&I	2228028	4389096	4368254	604 - 23736 ^(a)			[1, 29, 464, 478] [35, 54, 479, 480]
Apricot	709260			Raw						86.9 - 468.1	[107, 453, 454, 466] [459]
				A&I	156037			29.3 - 454.2 ^(a)		55 - 100.4	[1, 481, 482]
Avocado	99300			Raw				12.3		4.5 - 15.1	[107, 453, 454, 483] [459]
				A&I	21846					6.9 ^(b)	[1, 466]
Banana	609530			Raw						4.0 - 4.8	[453, 459]
				A&I	304765			2577 ^(c)		24.2 - 40.3 ^(a)	[68, 484, 485]
Blackcurrant	174250			Raw				7206 - 32828		5.5 - 26.1	[54, 78, 453, 456] [463, 486]
				A&I	38335						[1]
Blueberry	106420	700		Raw				5225 - 33566		2.2	[54, 453, 454, 483]
				A&I	23412	312		15496 - 35246			[1, 29, 76] [35, 54, 107, 453]
Cherry	985320	5500	≤ 5500	Raw				3996 - 32444		3.6 - 52.6	[78, 456, 459, 463] [1, 29, 35]
				A&I	167504	2866	2866			5.8 - 24.9	[453, 456, 466]
Clementine	1917400			Raw							[1]
				A&I	421828						[54, 463, 472, 483]
Cranberry	1863			Raw				3628 - 15773			

			A&I	410					[1]
Currant(d)	648114	863	Raw			6829		3.6 - 29.5	[54, 78, 472, 487] [456, 463, 486]
			A&I	142585	384				[1, 29]
Figs	85280		Raw			24.4		2.2 - 2.4	[453, 456, 457, 466]
			A&I	18762					[1]
Gooseberry	176235	272	Raw			540.8 - 857.4		1.65	[78, 456, 457, 472] [463]
			A&I	38772	121				[1, 29]
Grape	29845052	2881	Raw			1542 - 38541 ^(f) , 3705 ^(g) , 411 - 19938 ^(h) , 194 ⁽ⁱ⁾		3.7 ^(f) , 2.0 ⁽ⁱ⁾	[454, 460, 472, 478] [54, 78, 459, 488] [69, 463]
			A&I	14624075	1412	1139 - 56400 ^(a, f) , 19305 - 23421 ^(a, g) , 3752 - 4510 ^(a, h)		1.5 - 3.0 ⁽ⁱ⁾	[74, 412, 454, 478] [81, 488, 489, 490] [453, 459]
Kiwi	939450		Raw					9.92	
			A&I	366386				3.0 - 5.3	[1, 68, 456, 466]
Lemon and acid limes	1638450		Raw					0.9 - 1.1	[453, 466]
			A&I	360459					[1]
Nectarine	1198110		Raw			24.2 - 669		6.5 - 13.1	[54, 453, 454, 483] [459, 463]
			A&I	263584		54 - 114 ^(e) , 938 - 1450 ^(a) 4437 ^(b)			[1, 29, 80]
Olive	13664750		Raw					27.1	[78, 107, 453, 456] [103]
			A&I	7391759					
Orange	6517900		Raw					9.1 - 156	[107, 453, 466, 478] [454, 459]
			A&I	2184711	22498			392 ^(a)	[69, 108, 478]
Peach	2639620		Raw			173 - 539		16.1 - 20.0	[453, 454, 478, 483] [459, 463]
			A&I	658236	5720	7.6 - 118 ^(b) , 900 - 1654 ^(a)		2.6 - 7.4 ^(b)	[1, 29, 68, 478] [80, 491]
Pear	2612590	330890	Raw			128		2.1 - 4.6	[453, 454, 470, 483] [35, 459]

Pineapple	948	A&I Raw	130630	114157	98266	0.386 - 180	[1, 29, 35] [456, 472, 492]
		A&I	683			1.4 - 34.5	[67, 68, 492, 493] [69]
Plum	1297250	30	Raw			8.9 - 188	[54, 453, 454, 494] [78, 456, 463, 495]
							[1, 29, 80]
Pomegranate	5000	A&I	285395	13			[496]
		Raw					
		A&I	16000				[1, 69, 497]
Raspberry	593746	2304	Raw			1.4 - 11.2	[54, 78, 454, 472] [456, 463]
							[1, 29]
Redcurrant	64300	380	Raw			3.6 - 12.5	[54, 78, 453, 487] [456, 463]
							[1, 29]
Sour cherry	372910	1500	A&I	14146	169		[78, 453, 456]
			Raw			32.8 - 52.6	[1, 29]
			A&I	82040	668		[1, 29]
Strawberry	1290500	48000	37500	Raw		0.55 - 2.8	[54, 453, 454, 483] [35, 78, 459, 463]
							[1, 29, 35]
Sweet cherry	4000	A&I	800110	43920	34313	13.0 - 25.5	[78, 453, 456]
		Raw					[29]
		A&I		1780			[472]
Walnut	337766	364	Raw			34 - 114	
						1000 - 4980 ^(j)	
			A&I	86338	162	28.3 ^(k, l)	[1, 29, 89, 93] [90, 417, 483]

^a : peel, ^b : pulp, ^c : bracts, ^d : golden, ^e : flesh, ^f : red, ^g : black, ^h : blue, ⁱ : white, ^j : leaves, ^k : kernel, ^l : pellicle, ^m : green husk

Fastness Properties of Benzoquinones

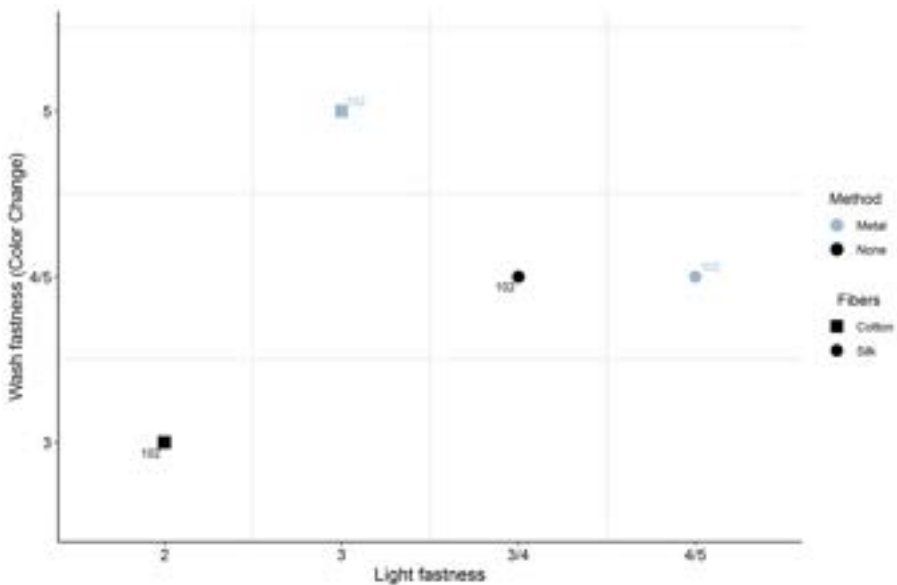


Figure A.10: The fastness properties of benzoquinones on various fibers. The wash fastness are based on the color change on grey scale, while the light fastness are expressed via blue wool standards (ref. 102: [138]).

Trend Analyses of Applied Natural Dyes on Textile Fibers

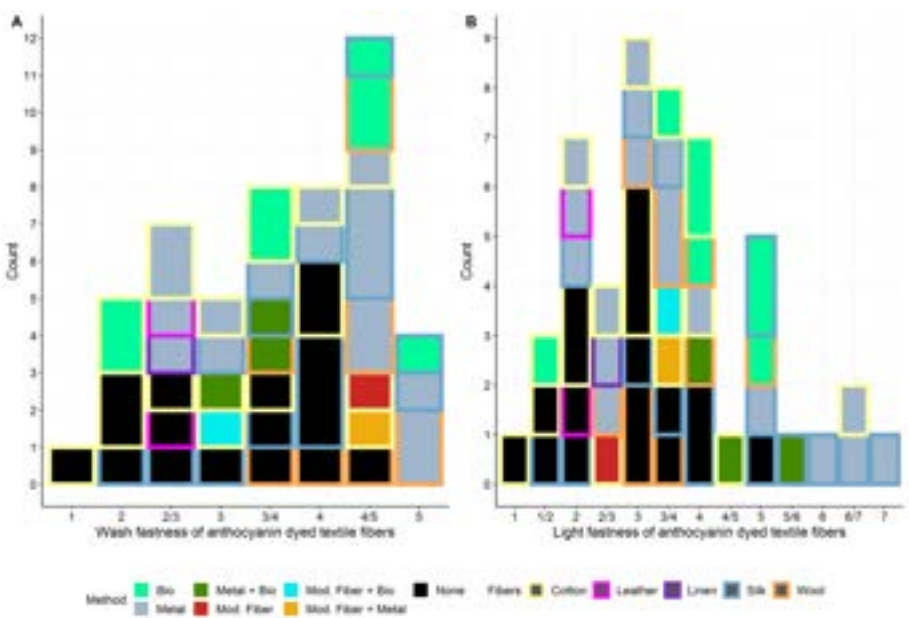


Figure A.11: Stacked histograms of wash (A) and light (B) fastness levels obtained with anthocyanin dyed textile fibers (n=50).

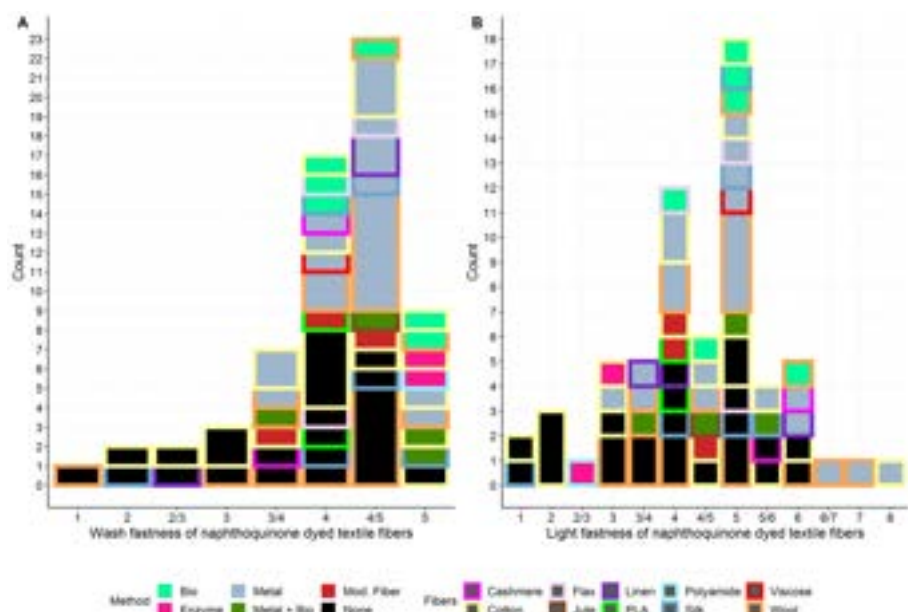


Figure A.12: Stacked histograms of wash (A) and light (B) fastness levels obtained with naphthoquinone dyed textile fibers (n=64).

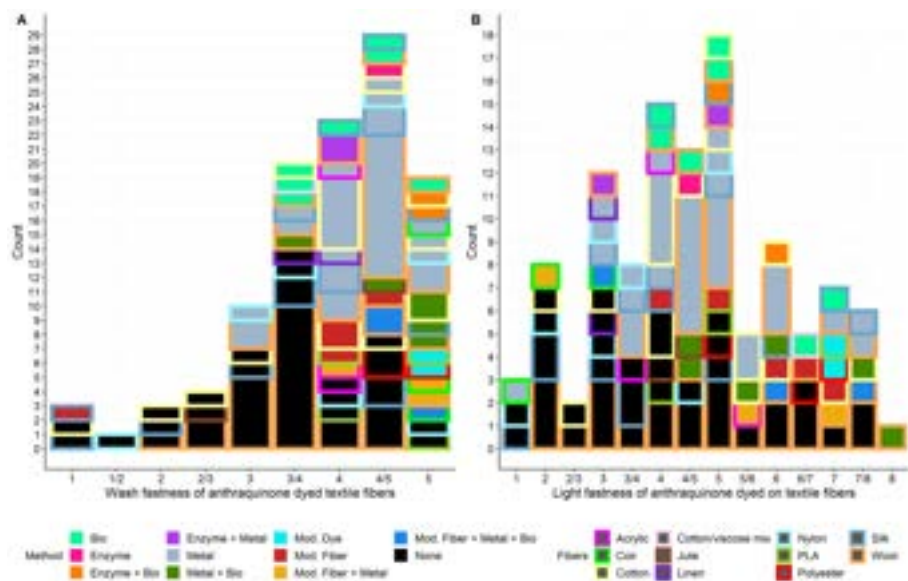


Figure A.13: Stacked histograms of wash (A) and light (B) fastness levels obtained with anthraquinone dyed textile fibers (n=112).

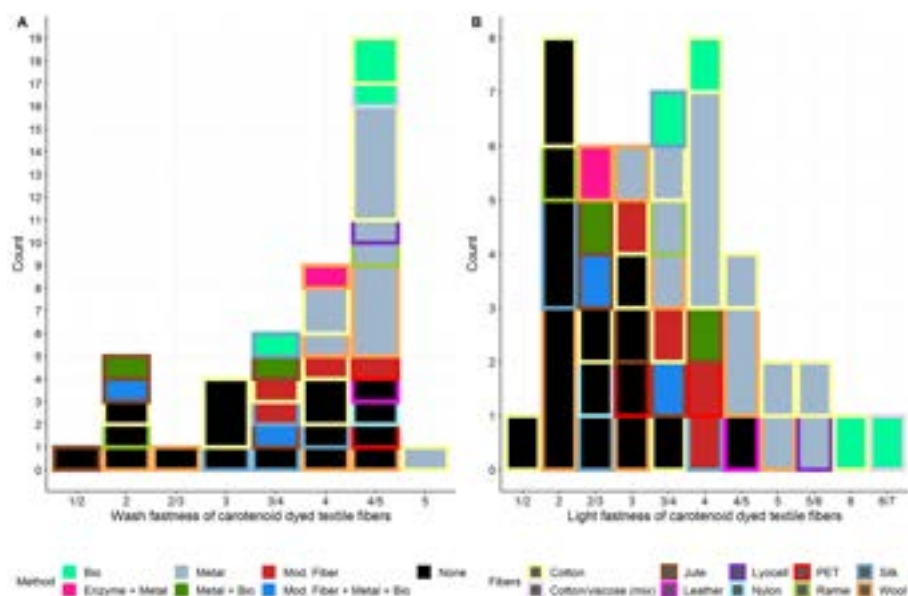


Figure A.14: Stacked histograms of wash (A) and light (B) fastness levels obtained with carotenoid dyed textile fibers (n=46).

The List of Studies used for Mapping the Fastness Properties

Table A.5: The labels assigned to the selection of studies for which fastness properties are available and mapped in Figure 1.11.

Label in Figure 1.11	Reference	Label in Figure 1.11	Reference
1	Adeel et al. [228]	55	Nagia and El-Mohamedy [498]
2	Ahmadi and Houjeghan [272]	56	Nakpathom et al. [132]
3	Alebeid et al. [499]	57	Nakpathom et al. [217]
4	Ali et al. [500]	58	Nateri et al. [501]
5	Ali and El. Mohamedy [502]	59	Nazari et al. [194]
6	Ammayappan and Shakyawar [177]	60	Patil and Datar [119]
7	Baaka et al. [503]	61	Phan et al. [114]
8	Baaka et al. [504]	62	Prabhu et al. [154]
9	Bahtiyari et al. [505]	63	Raisanen et al. [506]
10	Bahtiyari and Benli [160]	64	Raisanen et al. [507]
11	Bahtiyari et al. [150]	65	Raisanen et al. [508]
12	Banerjee et al. [188]	66	Rashdi et al. [220]
13	Barani [209]	67	Rekaby et al. [151]
14	Baykus et al. [164]	68	Sadeghi-Kiakhani [170]
15	Bechtold et al. [509]	69	Sadeghi-Kiakhani et al. [202]
16	Bechtold et al. [274]	70	Safapour et al. [203]
17	Bechtold et al. [269]	71	Sahinbaskan et al. [178]
18	Benli and Bahtiyari [158]	72	Samanta et al. [207]
19	Bukhari et al. [510]	73	Sasivatchutikool and Nakpathom [511]
20	Chattopadhyay et al. [512]	74	Savvidis et al. [218]
21	Cui et al. [195]	75	Savvidis et al. [513]
22	Das et al. [120]	76	Selvi et al. [514]
23	Drivas et al. [215]	77	Shahid ul et al. [515]
24	Elshehy [197]	78	Shams-Nateri [516]
25	El-Shishtawy et al. [517]	79	Sharma and Grover [167]
26	Etemadifar et al. [518]	80	Sharma et al. [152]
27	Faidi et al. [519]	81	Sheikh et al. [156]
28	Farooq et al. [520]	82	Shukla and Patil [521]
29	Gashti et al. [522]	83	Singh and Grover [523]
30	Gulrajani et al. [205]	84	Srivastava et al. [175]
31	Haddar et al. [524]	85	Swamy et al. [224]
32	Haddar et al. [116]	86	Tayade and Adivarekar [525]
33	Haji [211]	87	Teli and Ambre [186]
34	Hakeim [526]	88	Tutak and Benli [527]
35	Harlapur and Nagaswarupa [528]	89	Tutak and Korkmaz [529]
36	Hou et al. [530]	90	Uddin [121]
37	Hou et al. [531]	91	Vankar et al. [196]
38	Jabeen et al. [532]	92	Vankar and Shanker [159]
39	Jha et al. [533]	93	Velmurugan et al. [122]
40	Jothi [219]	94	Wang et al. [115]
41	Jung and Bae [270]	95	Yadav et al. [129]
42	Kamel et al. [176]	96	Yadav et al. [534]
43	Kamel et al. [535]	97	Yasukawa et al. [271]
44	Kesornsit et al. [227]	98	Yusuf et al. [190]
45	Khan et al. [143]	99	Yusuf et al. [181]
46	Khan et al. [536]	100	Yusuf et al. [193]
47	Khattak et al. [161]	101	Yusuf et al. [171]
48	Ledwani et al. [537]	102	Zarkogianni et al. [138]
49	Maulik et al. [538]	103	Zheng et al. [223]
50	Mehrpavar et al. [201]	104	Zhou et al. [222]
51	Meryemoglu [539]		
52	Mirnezhad et al. [179]		
53	Mishra et al. [540]		
54	Mohamed [541]		

B

An *In Silico* Study on the Solvent Dependency of Anthocyanin Extraction Profiles

Trend Analysis in Literature

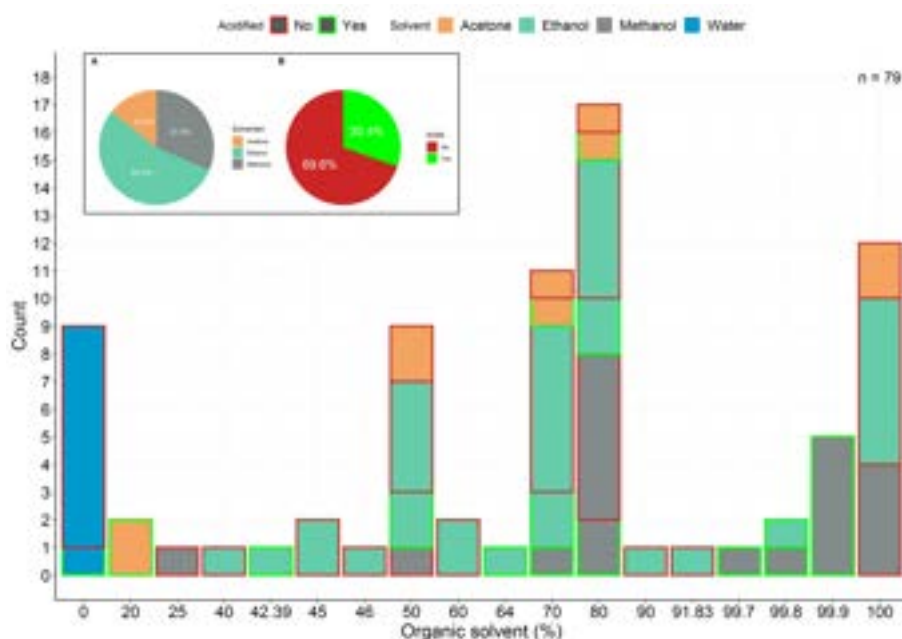


Figure B.1: The different extraction procedures from a selection of studies [232].

Solvent Selection for Screening

Table B.1: The 30 selected solvents categorized into various subclasses.

Solvent	Dielectric constant ϵ
1,2-ethanediol	40.245
1-butanol	17.332
1-propanol	20.524
2-propanol	19.264
Benzylalcohol	12.457
Ethanol	24.852
Methanol	32.613
Methoxyethanol	17.2
Esters	
Butyl ethanoate	4.9941
Ethyl ethanoate	5.9867
Ethyl methanoate	8.331
Methyl ethanoate	6.8615
Methyl propanoate	6.0777
Propyl ethanoate	5.5205
Ketones	
Acetone	20.493
Acetophenone	17.44
Acids	
Acetic acid	6.2528
Aromatics	
Benzaldehyde	18.22
m-Cresol	12.44
Quinoline	9.16
Toluene	2.3741
Ethers	
1,4-dioxane	2.2099
Anisole	4.2247
Diethylether	4.24
Tetrahydrofuran	7.4257
Alkanes	
Hexane	1.8819
Dipolar aprotic	
Acetonitrile	35.688
Dimethylsulfoxide	46.826
Halogenated	
Dichloromethane	8.93
Water	
Water	78.3553

Data Differential Scanning Calorimetry (DSC)

Table B.2: Melting properties of **ACDs** and **ACNs** (ΔH_{fus} : enthalpy of fusion, ΔS_{fus} : entropy of fusion, T_m : melting temperature and ΔC_p : change in heat capacity)

Compound	T_m ($^{\circ}\text{C}$)	T_m (K)	ΔH_{fus} (kJ/mol)	ΔS_{fus} (J/mol K)	ΔC_p (kJ/mol K)
Apigeninidin (Ap)	255.0	528.15	33.837	64.07	0.078
Cyanidin (Cy)	265.6	538.75	46.824	86.91	0.303
Delphinidin (Dp)	291.4	564.55	47.858	84.77	0.666
Luteolinidin (Lt)	244.0	517.15	19.095	36.92	0.172
Malvidin (Mv)	250.2	523.35	66.015	126.14	0.515
Pelargonidin (Pg)	289.3	562.45	37.816	67.23	0.159
Peonidin (Pn)	253.8	526.95	47.410	89.97	0.085
Petunidin (Pt)	250.8	523.95	31.893	60.87	0.299
Cyanidin-3-glucoside (Cy-3-Glc)	223.8	496.95	38.123	76.71	0.350
Delphinidin-3-glucoside (Dp-3-Glc)	233.6	506.75	41.800	82.49	0.079
Malvidin-3-glucoside (Mv-3-Glc)	255.4	528.55	12.614	23.87	0.716
Pelargonidin-3-glucoside (Pg-3-Glc)	293.3	566.45	31.801	56.14	0.227
Peonidin-3-glucoside (Pn-3-Glc)	265.6	538.75	21.661	40.21	0.369
Petunidin-3-glucoside (Pt-3-Glc)	195.8	468.95	19.379	41.32	0.059

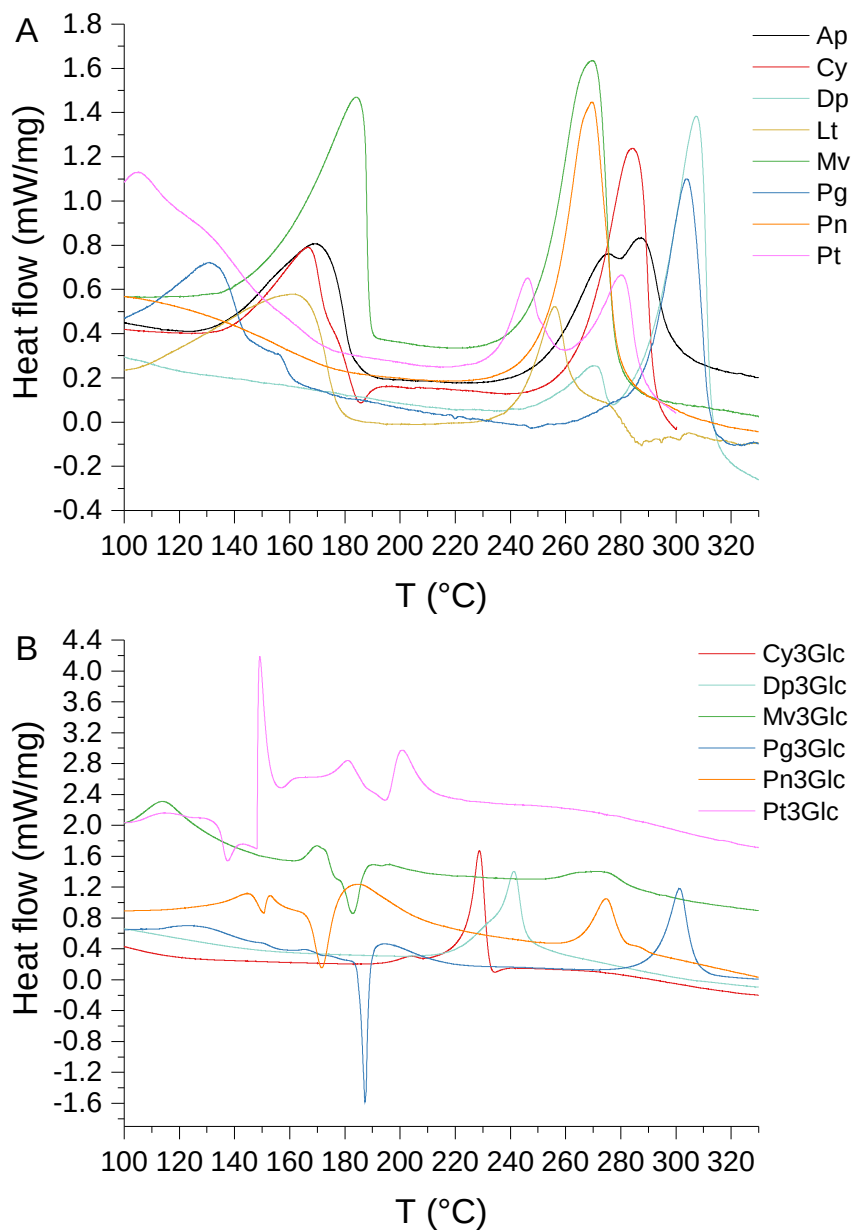


Figure B.2: DSC thermograms of anthocyanidins and anthocyanins.

Hansen Solubility Parameters

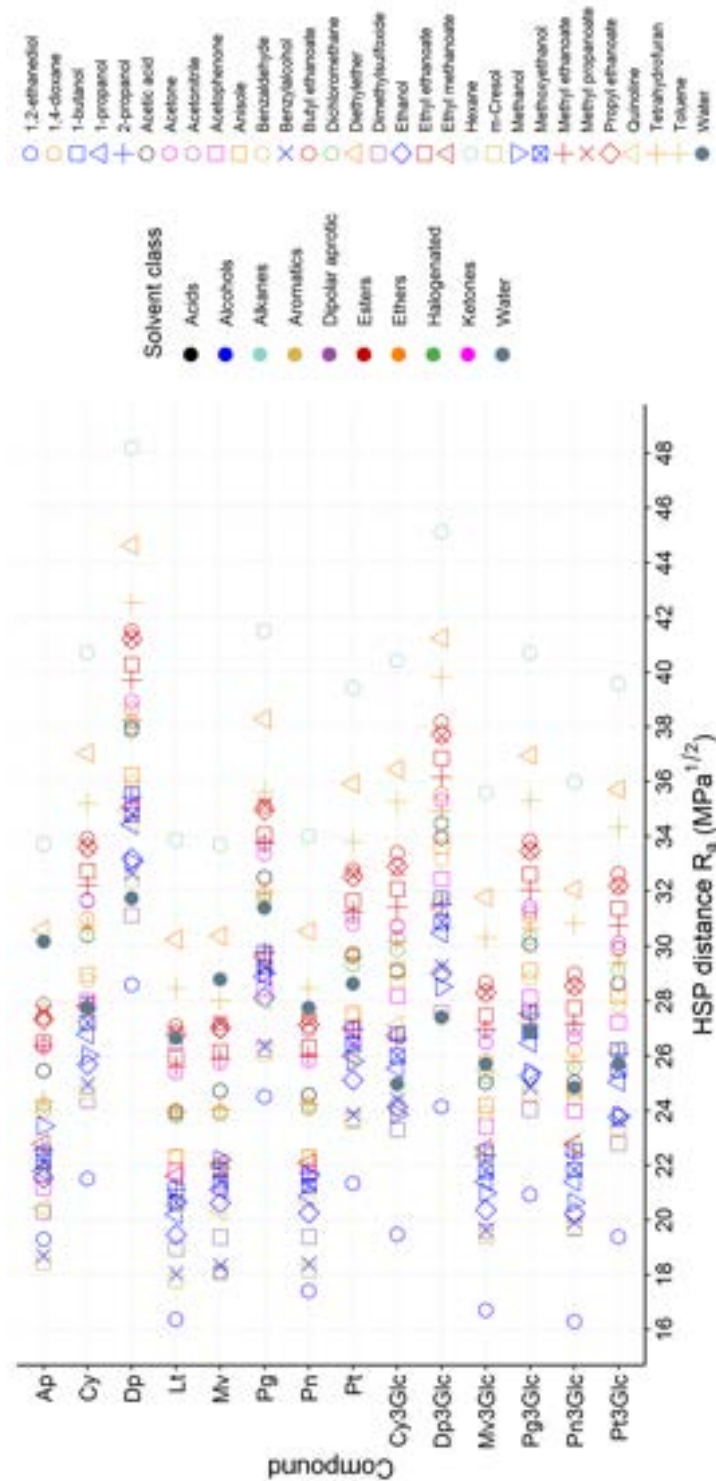


Figure B.3: Distance R_a ($\text{MPa}^{1/2}$) between anthocyanidins, anthocyanins and selected solvents based on Hansen solubility parameters.

Table B.3: Hansen solubility parameters for anthocyanidins and anthocyanins.

Anthocyanidins	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	Anthocyanins	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})
Apigeninidin (Ap)	26.40	11.64	21.71	Cyanidin-3-glucoside (Cy-3-Glc)	25.70	19.48	28.08
Cyanidin (Cy)	27.15	18.01	27.06	Delphinidin-3-glucoside (Dp-3-Glc)	27.45	22.35	30.11
Delphinidin (Dp)	29.92	22.48	30.22	Malvidin-3-glucoside (Mv-3-Glc)	24.96	15.88	24.70
Luteolinidin (Lt)	24.98	13.64	23.55	Pelargonidin-3-glucoside (Pg-3-Glc)	26.71	18.66	27.40
Malvidin (Mv)	25.79	12.95	22.22	Peonidin-3-glucoside (Pn-3-Glc)	24.69	16.33	25.39
Pelargonidin (Pg)	28.95	16.38	25.80	Petunidin-3-glucoside (Pt-3-Glc)	25.91	18.52	27.19
Peonidin (Pn)	25.49	13.31	23.04				
Petunidin (Pt)	27.30	16.52	25.82				

Table B.4: Hansen solubility parameters for the selected solvents.

Label	Solvents	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	Molar volume (cm ³ /mol)
S1	1,2-ethanediol	17	11	26	55.9
S2	1,4-dioxane	17.5	1.8	9	85.7
S3	1-butanol	16	5.7	15.8	92
S4	1-propanol	16	6.8	17.4	75.1
S5	2-propanol	15.8	6.1	16.4	76.9
S6	Acetic acid	14.5	8	13.5	62
S7	Acetone	15.5	10.4	7	73.8
S8	Acetonitrile	15.3	18	6.1	52.9
S9	Acetophenone	20.48	8.04	4.55	96.7
S10	Anisole	19.96	4.62	5.78	89.7
S11	Benzaldehyde	19.4	7.4	5.3	74.7
S12	Benzylalcohol	18.4	6.3	13.7	103.8
S13	Butyl ethanoate	15.8	3.7	6.3	132.6
S14	Dichloromethane	17	7.3	7.1	64.4
S15	Diethylether	14.5	2.9	4.6	104.7
S16	Dimethyl sulfoxide	18.4	16.4	10.2	71.3
S17	Ethanol	15.8	8.8	19.4	58.6
S18	Ethyl ethanoate	15.8	5.3	7.2	98.6
S19	Ethyl methanoate	16.65	11.82	9.95	75.7
S20	Hexane	14.9	0	0	131.4
S21	m-cresol	18.5	6.5	13.7	105
S22	Methanol	14.7	12.3	22.3	40.6
S23	Methoxyethanol	16	8.2	15	79.3
S24	Methyl ethanoate	15.5	7.2	7.6	79.8
S25	Methyl propanoate	14.8	4.85	8.32	101.1
S26	Propyl ethanoate	15.3	4.3	7.6	115.8
S27	Quinoline	19.4	7	7.6	109.5
S28	Tetrahydrofuran	16.8	5.7	8	81.9
S29	Toluene	18	1.4	2	106.6
S30	Water	15.6	16	42.3	18

Table B.5: Distance R_a ($\text{MPa}^{1/2}$) between anthocyanidins and selected solvents based on Hansen solubility parameters.

Anthocyanidins	Apigeninidin (Ap)	Cyanidin (Cy)	Delphinidin (Dp)	Luteolinidin (Lt)	Malvidin (Mv)	Pelargonidin (Pg)	Peonidin (Pn)	Petunidin (Pt)
1,2-ethanediol	19.30	21.50	28.59	16.37	18.09	24.50	17.40	21.32
1,4-dioxane	23.99	31.01	38.66	24.00	23.96	31.92	24.19	29.72
1-butanol	22.43	27.85	35.56	21.12	21.84	29.75	21.70	26.98
1-propanol	21.79	26.76	34.43	20.18	21.08	28.86	20.85	26.00
2-propanol	22.55	27.76	35.45	21.10	21.91	29.76	21.73	26.94
Acetic acid	25.44	30.40	37.95	23.92	24.71	32.51	24.55	29.65
Acetone	26.33	31.67	38.94	25.38	25.72	33.36	25.79	30.79
Acetonitrile	27.88	31.64	38.17	26.43	26.93	33.70	26.92	31.09
Acetophenone	21.16	28.00	34.99	21.76	21.20	28.43	21.69	26.65
Anisole	21.66	28.96	36.24	22.32	21.81	29.37	22.27	27.54
Benzaldehyde	21.98	28.74	35.93	22.29	21.92	29.42	22.32	27.45
Benzylalcohol	18.68	24.94	32.64	18.01	18.31	26.33	18.38	23.83
Butylacetate	27.39	33.93	41.50	27.09	27.17	35.11	27.36	32.77
Dichloromethane	24.20	30.42	37.85	23.78	23.87	31.67	24.06	29.32
Diethylether	30.59	37.05	44.62	30.23	30.35	38.29	30.53	35.93
Dimethyl sulfoxide	20.28	24.35	31.12	18.95	19.36	26.24	19.38	23.68
Ethanol	21.52	25.67	33.19	19.44	20.60	28.11	20.24	25.09
Ethyl ethanoate	26.46	32.73	40.28	25.96	26.14	34.06	26.29	31.64
Ethyl methanoate	22.78	27.79	35.06	21.59	22.05	29.62	22.06	26.98
Hexane	33.70	40.70	48.18	33.87	33.70	41.51	34.02	39.42
m-cresol	18.45	24.70	32.40	17.78	18.08	26.09	18.15	23.60
Methanol	23.42	25.99	33.06	20.65	22.19	29.00	21.62	25.78
Methoxyethanol	22.13	27.18	34.79	20.63	21.40	29.23	21.24	26.40
Methyl ethanoate	26.35	32.22	39.71	25.60	25.89	33.75	25.99	31.23
Methyl propanoate	27.58	33.63	41.24	26.85	27.18	35.15	27.25	32.61
Propyl ethanoate	27.31	33.59	41.19	26.77	26.99	34.96	27.12	32.51
Quinoline	20.41	27.20	34.55	20.57	20.31	28.00	20.66	25.92
Tetrahydrofuran	24.33	30.71	38.26	23.93	24.04	31.96	24.22	29.59
Toluene	27.85	35.19	42.53	28.45	28.02	35.64	28.45	33.79
Water	30.16	27.75	31.75	26.64	28.77	31.39	27.74	28.62

Table B.6: Distance R_a ($\text{MPa}^{1/2}$) between anthocyanins and selected solvents based on Hansen solubility parameters.

Anthocyanins	Cyanidin-3-glucoside (Cy-3-Glc)	Delphinidin-3-glucoside (Dp-3Glc)	Malvidin-3-glucoside (Mv-3-Glc)	Pelargonidin-3-glucoside (Pg-3-Glc)	Peonidin-3-glucoside (Pn-3-Glc)	Petunidin-3-glucoside (Pt-3-Glc)
1,2-ethanediol	19.47	24.13	16.70	20.93	16.29	19.38
1,4-dioxane	30.75	35.55	25.83	31.02	26.21	29.89
1-butanol	26.78	31.72	22.45	27.60	22.52	26.21
1-propanol	25.52	30.46	21.37	26.45	21.38	25.02
2-propanol	26.60	31.54	22.36	27.48	22.40	26.07
Acetic acid	29.09	33.95	25.00	30.06	25.03	28.62
Acetone	30.71	35.33	26.48	31.42	26.68	30.12
Acetonitrile	30.29	34.44	26.91	31.23	26.98	29.92
Acetophenone	28.17	32.45	23.41	28.12	23.97	27.21
Anisole	29.15	33.63	24.18	29.10	24.73	28.16
Benzaldehyde	28.70	33.14	23.92	28.80	24.41	27.79
Benzylalcohol	24.36	29.23	19.62	24.84	19.90	23.60
Butylacetate	33.40	38.18	28.68	33.85	28.99	32.63
Dichloromethane	29.85	34.54	25.24	30.31	25.55	29.11
Diethylether	36.44	41.23	31.78	36.95	32.07	35.71
Dimethyl sulfoxide	23.29	27.56	19.56	24.03	19.73	22.78
Ethanol	24.11	29.00	20.34	25.25	20.22	23.75
Ethyl ethanoate	32.08	36.86	27.46	32.60	27.73	31.36
Ethyl methanoate	26.74	31.37	22.60	27.51	22.76	26.18
Hexane	40.43	45.13	35.60	40.71	35.99	39.59
m-cresol	24.14	29.00	19.39	24.61	19.67	23.37
Methanol	23.85	28.50	20.97	25.37	20.62	23.78
Methoxyethanol	25.97	30.87	21.78	26.88	21.83	25.46
Methyl ethanoate	31.41	36.16	26.94	32.04	27.17	30.75
Methyl propanoate	32.81	37.65	28.28	33.45	28.50	32.15
Propyl ethanoate	32.90	37.72	28.28	33.46	28.54	32.19
Quinoline	27.09	31.65	22.25	27.24	22.71	26.19
Tetrahydrofuran	30.16	34.93	25.47	30.62	25.78	29.41
Toluene	35.27	39.83	30.31	35.31	30.81	34.32
Water	24.95	27.39	25.69	26.89	24.83	25.69

Flory-Huggins Interaction Parameter (χ_{12})

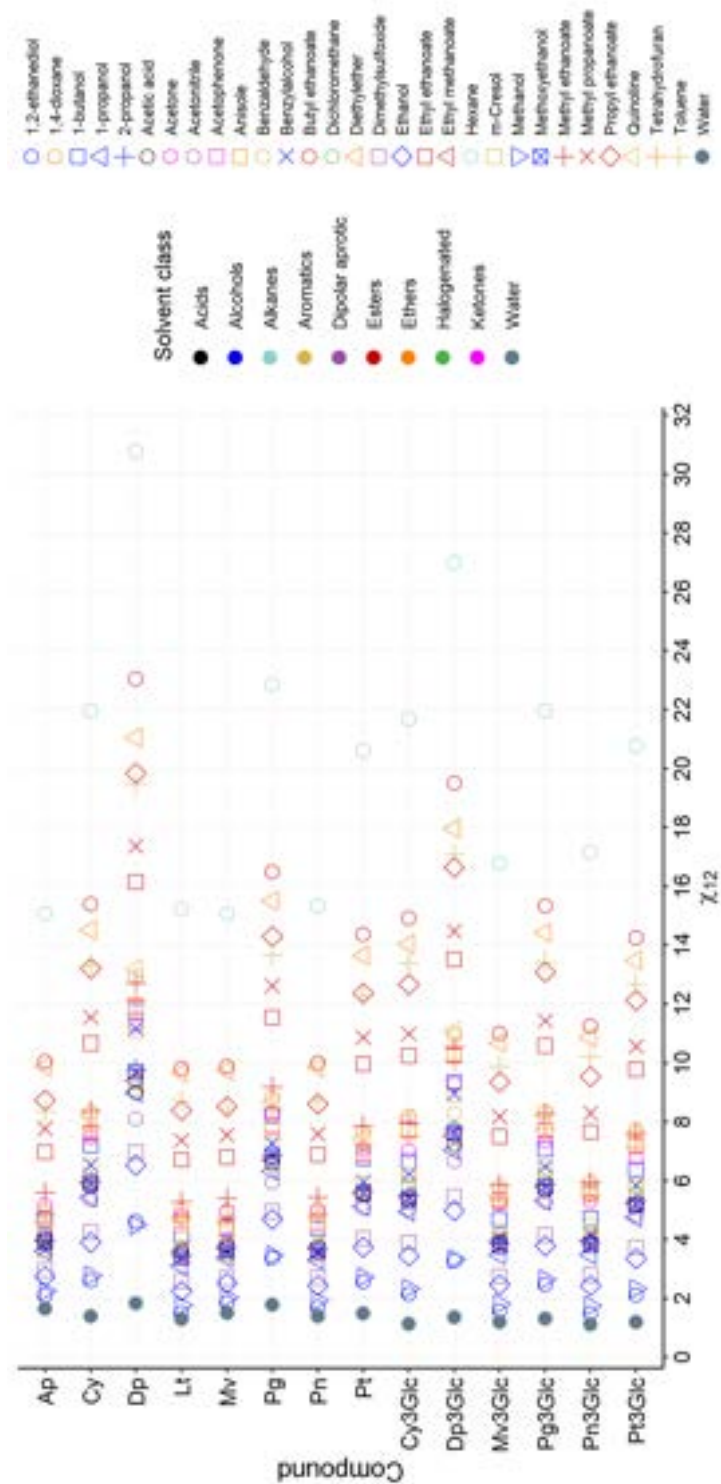


Figure B.4: Flory-Huggins interactions parameters (χ_{12}) for anthocyanidins, anthocyanins in the selected solvents.

Table B.7: Flory-Huggins interaction parameters (χ_{12}) anthocyanidins and selected solvents.

Anthocyanidins	Apigeninidin (Ap)	Cyanidin (Cy)	Delphinidin (Dp)	Luteolinidin (Lt)	Malvidin (Mv)	Pelargonidin (Pg)	Peonidin (Pn)	Petunidin (Pt)
1,2-ethanediol	2.10	2.61	4.61	1.51	1.85	3.39	1.71	2.56
1,4-dioxane	4.97	8.31	12.93	4.98	4.96	8.81	5.06	7.64
1-butanol	4.67	7.20	11.74	4.14	4.43	8.21	4.37	6.76
1-propanol	3.60	5.43	8.98	3.09	3.37	6.31	3.29	5.12
2-propanol	3.95	5.98	9.75	3.46	3.72	6.87	3.66	5.63
Acetic acid	4.05	5.78	9.01	3.58	3.82	6.61	3.77	5.50
Acetone	5.16	7.47	11.29	4.80	4.93	8.29	4.95	7.06
Acetonitrile	4.15	5.35	8.10	3.44	3.53	5.94	3.55	5.06
Acetophenone	4.37	7.65	11.94	4.62	4.38	7.89	4.59	6.93
Anisole	4.25	7.59	11.88	4.51	4.30	7.81	4.49	6.87
Benzaldehyde	3.64	6.23	9.73	3.74	3.62	6.52	3.76	5.68
Benzylalcohol	3.65	6.51	11.16	3.40	3.51	7.26	3.54	5.95
Butylacetate	10.04	15.40	23.04	9.82	9.88	16.49	10.02	14.37
Dichloromethane	3.81	6.01	9.31	3.68	3.70	6.52	3.76	5.59
Diethylether	9.89	14.50	21.03	9.66	9.73	15.49	9.85	13.64
Dimethyl sulfoxide	2.96	4.27	6.97	2.58	2.70	4.95	2.70	4.03
Ethanol	2.74	3.90	6.51	2.24	2.51	4.67	2.42	3.72
Ethyl ethanoate	6.97	10.66	16.14	6.71	6.80	11.54	6.88	9.96
Ethyl methanoate	3.96	5.90	9.39	3.56	3.71	6.70	3.72	5.56
Hexane	15.06	21.97	30.77	15.21	15.06	22.85	15.34	20.61
m-cresol	3.61	6.46	11.12	3.35	3.46	7.21	3.49	5.90
Methanol	2.25	2.77	4.48	1.75	2.02	3.45	1.92	2.72
Methoxyethanol	3.92	5.91	9.69	3.40	3.67	6.84	3.61	5.57
Methyl ethanoate	5.59	8.36	12.70	5.28	5.40	9.17	5.44	7.85
Methyl propanoate	7.76	11.54	17.35	7.36	7.54	12.60	7.58	10.85
Propyl ethanoate	8.72	13.18	19.83	8.37	8.51	14.28	8.59	12.35
Quinoline	4.60	8.18	13.19	4.68	4.56	8.66	4.72	7.43
Tetrahydrofuran	4.89	7.79	12.10	4.73	4.78	8.44	4.85	7.23
Toluene	8.34	13.32	19.46	8.70	8.44	13.66	8.70	12.28
Water	1.65	1.40	1.83	1.29	1.50	1.79	1.40	1.49

Table B.8: Flory-Huggins interaction parameters (χ_{12}) anthocyanins and selected solvents.

Anthocyanins	Cyanidin-3-glucoside (Cy-3-Glc)	Delphinidin-3-glucoside (Dp-3-Glc)	Malvidin-3-glucoside (Mv-3-Glc)	Pelargonidin-3-glucoside (Pg-3-Glc)	Peonidin-3-glucoside (Pn-3-Glc)	Petunidin-3-glucoside (Pt-3-Glc)
1,2-ethanediol	2.14	3.29	1.57	2.47	1.50	2.12
1,4-dioxane	8.18	10.93	5.77	8.32	5.94	7.73
1-butanol	6.66	9.34	4.68	7.07	4.71	6.38
1-propanol	4.93	7.03	3.46	5.30	3.46	4.75
2-propanol	5.49	7.72	3.88	5.86	3.89	5.27
Acetic acid	5.29	7.21	3.91	5.65	3.92	5.12
Acetone	7.02	9.29	5.22	7.35	5.30	6.76
Acetonitrile	5.03	6.66	3.74	5.27	3.80	4.84
Acetophenone	7.74	10.27	5.35	7.72	5.61	7.23
Anisole	7.69	10.24	5.29	7.67	5.53	7.18
Benzaldehyde	6.21	8.28	4.31	6.25	4.49	5.82
Benzylalcohol	6.22	8.95	4.03	6.46	4.15	5.83
Butylacetate	14.92	19.50	11.01	15.33	11.25	14.25
Dichloromethane	5.79	7.75	4.14	5.97	4.24	5.50
Diethylether	14.03	17.96	10.67	14.42	10.86	13.47
Dimethyl sulfoxide	3.90	5.46	2.75	4.16	2.80	3.73
Ethanol	3.44	4.97	2.45	3.77	2.42	3.34
Ethyl ethanoate	10.24	13.52	7.50	10.58	7.65	9.78
Ethyl methanoate	5.46	7.52	3.90	5.78	3.96	5.24
Hexane	21.67	27.00	16.80	21.97	17.17	20.78
m-cresol	6.17	8.91	3.98	6.41	4.10	5.79
Methanol	2.33	3.33	1.80	2.64	1.74	2.32
Methoxyethanol	5.40	7.63	3.79	5.78	3.81	5.19
Methyl ethanoate	7.94	10.53	5.84	8.27	5.94	7.61
Methyl propanoate	10.98	14.46	8.16	11.42	8.28	10.54
Propyl ethanoate	12.65	16.63	9.35	13.08	9.52	12.11
Quinoline	8.11	11.07	5.47	8.20	5.70	7.58
Tetrahydrofuran	7.52	10.08	5.36	7.75	5.49	7.15
Toluene	13.38	17.06	9.88	13.41	10.21	12.67
Water	1.13	1.36	1.20	1.31	1.12	1.20

Density Functional Theory: Static Calculations

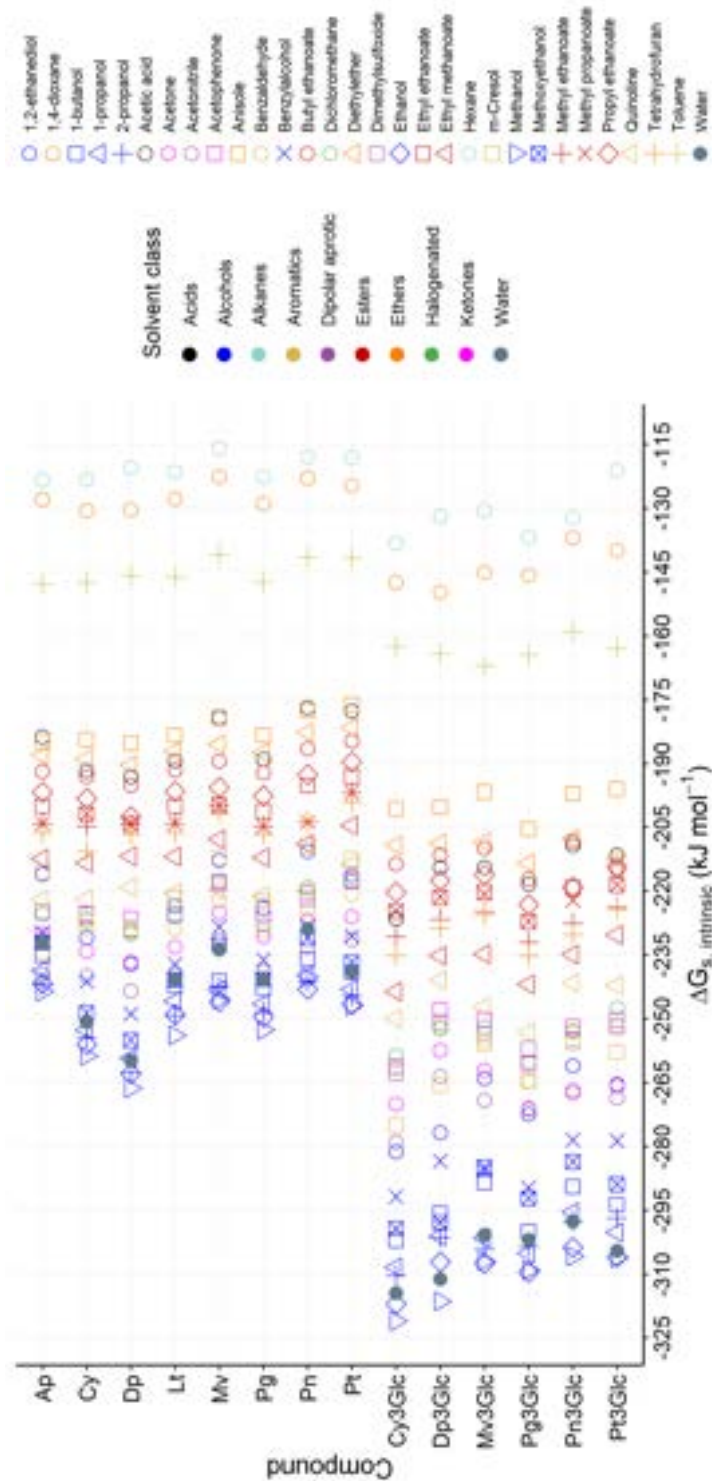


Figure B.5: Intrinsic Gibbs free energies of solvation (kJ mol⁻¹) of anthocyanidins and anthocyanins in the selected solvents. (B3LYP/6-311++G(d,p) + SMD solvation model).

Table B.9: Free energies (hartree), electronic energies (E_{gas}) and thermal contributions G^{therm} to the Gibbs free energy of anthocyanidins and anthocyanins in the gas phase.

Anthocyanidins	Apigeninidin (Ap)	Cyanidin (Cy)	Delphinidin (Dp)	Luteolinidin (Lt)	Malvidin (Mv)	Pelargonidin (Pg)	Peonidin (Pn)	Petunidin (Pt)
G_{gas} (hartree)	-878.97	-1029.46	-1104.70	-954.22	-1183.27	-954.21	-1068.75	-1143.99
E_{gas} (hartree)	-879.156	-1029.648	-1104.897	-954.406	-1183.520	-954.397	-1068.963	-1144.213
$G^{\text{therm}}_{\text{gas}}$ (hartree)	0.185	0.190	0.193	0.188	0.246	0.187	0.217	0.219
Anthocyanins	Cyanidin-3-glucoside (Cy-3-Glc)	Delphinidin-3-glucoside (Dp-3-Glc)	Malvidin-3-glucoside (Mv-3-Glc)	Pelargonidin-3-glucoside (Pg-3-Glc)	Peonidin-3-glucoside (Pn-3-Glc)	Petunidin-3-glucoside (Pt-3-Glc)		
G_{gas} (hartree)	-1640.271	-1715.523	-1794.088	-1565.024	-1679.559	-1754.807		
E_{gas} (hartree)	-1640.619	-1715.876	-1794.492	-1565.369	-1679.934	-1755.185		
$G^{\text{therm}}_{\text{gas}}$ (hartree)	0.348	0.353	0.405	0.345	0.375	0.378		

Table B.10: Free energies (hartree) of anthocyanidins in solution at 298.15 K.

Anthocyanidins	Apigeninidin (Ap)	Cyanidin (Cy)	Delphinidin (Dp)	Luteolinidin (Lt)	Malvidin (Mv)	Pelargonidin (Pg)	Peonidin (Pn)	Petunidin (Pt)
1,2-ethanediol	-879.0528	-1029.545	-1104.795	-954.303	-1183.356	-954.295	-1068.826	-1144.0759
1,4-dioxane	-879.0193	-1029.507	-1104.754	-954.266	-1183.321	-954.259	-1068.793	-1144.0410
1-butanol	-879.0600	-1029.552	-1104.801	-954.310	-1183.366	-954.303	-1068.836	-1144.0846
1-propanol	-879.0614	-1029.554	-1104.803	-954.311	-1183.367	-954.304	-1068.838	-1144.0861
2-propanol	-879.0627	-1029.554	-1104.804	-954.313	-1183.367	-954.305	-1068.838	-1144.0867
Acetic acid	-879.0405	-1029.531	-1104.778	-954.290	-1183.343	-954.282	-1068.814	-1144.0612
Acetone	-879.0586	-1029.547	-1104.795	-954.306	-1183.360	-954.298	-1068.833	-1144.0796
Acetonitrile	-879.0618	-1029.549	-1104.797	-954.309	-1183.363	-954.301	-1068.835	-1144.0817
Acetophenone	-879.0582	-1029.543	-1104.791	-954.304	-1183.358	-954.296	-1068.830	-1144.0763
Anisole	-879.0410	-1029.528	-1104.775	-954.288	-1183.343	-954.280	-1068.814	-1144.0606
Benzaldehyde	-879.0599	-1029.545	-1104.792	-954.305	-1183.359	-954.297	-1068.832	-1144.0776
Benzylalcohol	-879.0581	-1029.549	-1104.799	-954.308	-1183.362	-954.300	-1068.833	-1144.0814
Butyl ethanoate	-879.0436	-1029.531	-1104.779	-954.291	-1183.347	-954.283	-1068.817	-1144.0639
Dichloromethane	-879.0564	-1029.544	-1104.792	-954.304	-1183.357	-954.297	-1068.830	-1144.0764
Diethylether	-879.0422	-1029.529	-1104.777	-954.289	-1183.345	-954.281	-1068.816	-1144.0627
Dimethyl sulfoxide	-879.0562	-1029.543	-1104.792	-954.304	-1183.357	-954.295	-1068.831	-1144.0764
Ethanol	-879.0626	-1029.555	-1104.804	-954.313	-1183.368	-954.305	-1068.839	-1144.0874
Ethyl ethanoate	-879.0467	-1029.534	-1104.782	-954.294	-1183.351	-954.287	-1068.821	-1144.0671
Ethyl methanoate	-879.0514	-1029.539	-1104.785	-954.298	-1183.354	-954.291	-1068.826	-1144.0715
Hexane	-879.0175	-1029.504	-1104.750	-954.264	-1183.319	-954.257	-1068.791	-1144.0385
m-cresol	-879.0526	-1029.544	-1104.791	-954.302	-1183.355	-954.295	-1068.826	-1144.0745
Methanol	-879.0634	-1029.556	-1104.806	-954.314	-1183.368	-954.306	-1068.838	-1144.0876
Methoxyethanol	-879.0589	-1029.552	-1104.801	-954.309	-1183.363	-954.302	-1068.834	-1144.0837
Methyl ethanoate	-879.0483	-1029.535	-1104.782	-954.295	-1183.351	-954.288	-1068.824	-1144.0685
Methyl propanoate	-879.0483	-1029.534	-1104.782	-954.295	-1183.351	-954.288	-1068.824	-1144.0685
Propyl ethanoate	-879.0455	-1029.533	-1104.781	-954.293	-1183.349	-954.285	-1068.820	-1144.0658
Quinoline	-879.0551	-1029.542	-1104.788	-954.302	-1183.358	-954.294	-1068.830	-1144.0750
Tetrahydrofuran	-879.0492	-1029.538	-1104.783	-954.296	-1183.351	-954.289	-1068.824	-1144.0693
Toluene	-879.0269	-1029.514	-1104.760	-954.273	-1183.328	-954.266	-1068.800	-1144.0475
Water	-879.0589	-1029.553	-1104.803	-954.309	-1183.364	-954.302	-1068.833	-1144.0845

Table B.11: Intrinsic Gibbs free energies of solvation (kJ mol^{-1}) of anthocyanidins in the selected solvents. (B3LYP/6-311++G(d,p) + SMD solvation model).

Anthocyanidins	Apigeninidin (Ap)	Cyanidin (Cy)	Delphinidin (Dp)	Luteolinidin (Lt)	Malvidin (Mv)	Pelargonidin (Pg)	Peonidin (Pn)	Petunidin (Pt)
1,2-ethanediol	-216.03	-230.91	-237.10	-223.42	-212.89	-223.93	-210.64	-216.26
1,4-dioxane	-128.00	-130.53	-130.29	-127.80	-122.70	-128.94	-122.93	-124.72
1-butanol	-234.96	-248.60	-255.04	-242.23	-241.04	-242.94	-235.91	-239.08
1-propanol	-238.66	-252.67	-259.30	-245.97	-243.30	-246.63	-239.89	-243.15
2-propanol	-242.02	-254.46	-262.62	-249.22	-242.52	-248.51	-241.28	-244.53
Acetic acid	-183.75	-191.75	-193.04	-189.33	-179.21	-188.98	-176.89	-177.71
Acetone	-231.10	-234.18	-236.71	-233.09	-225.03	-230.72	-226.83	-226.05
Acetonitrile	-239.71	-239.95	-243.46	-239.59	-231.40	-238.76	-233.11	-231.38
Acetophenone	-230.16	-225.34	-226.34	-225.48	-218.19	-225.56	-220.48	-217.22
Anisole	-184.89	-184.36	-185.19	-183.31	-179.20	-183.33	-177.57	-176.16
Benzaldehyde	-234.49	-228.82	-229.58	-229.05	-222.16	-229.27	-224.40	-220.74
Benzylalcohol	-229.85	-241.29	-248.93	-237.30	-228.46	-236.19	-228.13	-230.64
Butylacetate	-191.84	-193.12	-195.14	-191.51	-189.51	-192.16	-186.58	-184.75
Dichloromethane	-225.34	-226.65	-230.00	-225.88	-217.71	-227.85	-219.19	-217.70
Diethylether	-188.16	-188.89	-190.40	-187.24	-185.52	-187.44	-182.70	-181.70
Dimethyl sulfoxide	-224.84	-225.58	-229.00	-225.43	-217.70	-223.72	-221.81	-217.66
Ethanol	-241.76	-256.13	-262.92	-249.11	-246.08	-249.66	-243.13	-246.58
Ethyl ethanoate	-200.02	-201.82	-204.25	-200.05	-199.71	-201.20	-195.17	-193.06
Ethyl methanoate	-212.37	-213.41	-211.87	-211.95	-207.87	-212.16	-208.98	-204.61
Hexane	-123.32	-123.18	-120.53	-121.51	-115.92	-122.64	-117.86	-118.16
m-cresol	-215.49	-227.06	-228.68	-221.63	-212.12	-222.38	-209.40	-212.49
Methanol	-243.70	-258.74	-266.40	-253.94	-245.46	-252.65	-240.30	-247.08
Methoxyethanol	-232.10	-248.62	-255.05	-240.85	-232.59	-240.69	-231.07	-236.73
Methyl ethanoate	-204.21	-204.67	-204.30	-204.16	-199.97	-204.80	-203.77	-196.92
Methyl propanoate	-204.21	-201.90	-204.30	-204.16	-199.97	-204.80	-203.77	-196.92
Propyl ethanoate	-196.77	-198.32	-202.52	-196.64	-195.73	-197.57	-192.66	-189.75
Quinoline	-222.12	-221.90	-219.13	-220.54	-219.62	-221.24	-219.93	-213.87
Tetrahydrofuran	-206.45	-210.75	-206.70	-206.43	-201.80	-206.65	-203.66	-199.06
Toluene	-147.87	-147.49	-145.97	-146.22	-140.88	-147.37	-141.47	-141.68
Water	-232.04	-250.78	-259.76	-240.81	-233.72	-240.86	-228.83	-238.96

Table B.12: Free energies (hartree) of anthocyanins in solution at 298.15 K.

Anthocyanins	Cyanidin-3-glucoside (Cy-3-Glc)	Delphinidin-3-glucoside (Dp-3-Glc)	Malvidin-3-glucoside (Mv-3-Glc)	Pelargonidin-3-glucoside (Pg-3-Glc)	Peonidin-3-glucoside (Pn-3-Glc)	Petunidin-3-glucoside (Pt-3-Glc)
1,2-ethanediol	-1640.378	-1715.629	-1794.188	-1565.128	-1679.659	-1754.908
1,4-dioxane	-1640.327	-1715.580	-1794.143	-1565.079	-1679.612	-1754.860
1-butanol	-1640.386	-1715.636	-1794.198	-1565.138	-1679.670	-1754.919
1-propanol	-1640.388	-1715.638	-1794.203	-1565.140	-1679.672	-1754.921
2-propanol	-1640.389	-1715.638	-1794.204	-1565.139	-1679.673	-1754.920
Acetic acid	-1640.357	-1715.604	-1794.169	-1565.107	-1679.639	-1754.887
Acetone	-1640.374	-1715.621	-1794.187	-1565.127	-1679.661	-1754.908
Acetonitrile	-1640.377	-1715.624	-1794.190	-1565.127	-1679.661	-1754.909
Acetophenone	-1640.370	-1715.618	-1794.183	-1565.123	-1679.655	-1754.902
Anisole	-1640.347	-1715.600	-1794.163	-1565.102	-1679.635	-1754.881
Benzaldehyde	-1640.371	-1715.619	-1794.185	-1565.125	-1679.656	-1754.903
Benzylalcohol	-1640.382	-1715.631	-1794.196	-1565.134	-1679.666	-1754.913
Butyl ethanoate	-1640.352	-1715.604	-1794.168	-1565.106	-1679.639	-1754.889
Dichloromethane	-1640.369	-1715.619	-1794.184	-1565.123	-1679.656	-1754.901
Diethylether	-1640.351	-1715.603	-1794.167	-1565.105	-1679.639	-1754.888
Dimethyl sulfoxide	-1640.371	-1715.619	-1794.184	-1565.122	-1679.657	-1754.903
Ethanol	-1640.392	-1715.640	-1794.205	-1565.142	-1679.675	-1754.923
Ethyl ethanoate	-1640.357	-1715.608	-1794.172	-1565.110	-1679.643	-1754.890
Ethyl methanoate	-1640.364	-1715.613	-1794.177	-1565.116	-1679.649	-1754.894
Hexane	-1640.324	-1715.574	-1794.137	-1565.076	-1679.610	-1754.853
m-cresol	-1640.376	-1715.624	-1794.185	-1565.125	-1679.657	-1754.905
Methanol	-1640.393	-1715.644	-1794.205	-1565.142	-1679.676	-1754.923
Methoxyethanol	-1640.385	-1715.637	-1794.196	-1565.135	-1679.668	-1754.917
Methyl ethanoate	-1640.359	-1715.610	-1794.173	-1565.112	-1679.646	-1754.892
Methyl propanoate	-1640.357	-1715.608	-1794.172	-1565.110	-1679.644	-1754.890
Propyl ethanoate	-1640.355	-1715.606	-1794.170	-1565.109	-1679.643	-1754.888
Quinoline	-1640.366	-1715.615	-1794.182	-1565.120	-1679.652	-1754.899
Tetrahydrofuran	-1640.361	-1715.610	-1794.174	-1565.113	-1679.647	-1754.892
Toluene	-1640.333	-1715.586	-1794.151	-1565.086	-1679.620	-1754.869
Water	-1640.391	-1715.642	-1794.202	-1565.139	-1679.673	-1754.923

Table B.13: Intrinsic Gibbs free energies of solvation (kJ mol^{-1}) anthocyanins and selected solvents. (B3LYP/6-311++G(d,p) + SMD solvation model).

Anthocyanins	Cyanidin-3-glucoside (Cy-3-Glc)	Delphinidin-3-glucoside (Dp-3-Glc)	Malvidin-3-glucoside (Mv-3-Glc)	Pelargonidin-3-glucoside (Pg-3-Glc)	Peonidin-3-glucoside (Pn-3-Glc)	Petunidin-3-glucoside (Pt-3-Glc)
1,2-ethanediol	-281.21	-276.71	-263.97	-272.50	-261.09	-265.46
1,4-dioxane	-147.40	-149.69	-145.09	-145.76	-136.96	-139.93
1-butanol	-302.05	-295.73	-288.50	-300.02	-289.43	-293.72
1-propanol	-308.51	-301.16	-301.57	-305.19	-295.52	-300.26
2-propanol	-310.40	-301.43	-304.21	-303.60	-297.64	-296.88
Acetic acid	-226.48	-210.91	-214.42	-218.43	-209.23	-211.47
Acetone	-270.08	-257.45	-262.06	-271.13	-266.76	-265.84
Acetonitrile	-278.98	-263.52	-269.12	-271.36	-267.43	-268.60
Acetophenone	-261.18	-247.90	-250.24	-260.53	-251.85	-250.19
Anisole	-200.64	-200.25	-196.70	-205.46	-197.11	-196.05
Benzaldehyde	-261.67	-251.77	-255.30	-264.65	-253.15	-251.69
Benzylalcohol	-291.86	-283.49	-285.79	-289.82	-278.58	-278.79
Butylacetate	-213.62	-211.51	-209.88	-217.09	-208.30	-215.04
Dichloromethane	-258.69	-252.39	-252.02	-260.12	-252.89	-247.55
Diethylether	-209.28	-208.80	-208.56	-213.47	-207.80	-212.56
Dimethyl sulfoxide	-262.78	-250.78	-253.65	-257.02	-254.88	-251.84
Ethanol	-317.05	-307.26	-307.56	-309.57	-303.78	-306.04
Ethyl ethanoate	-224.82	-221.56	-220.20	-227.20	-219.14	-218.63
Ethyl methanoate	-243.68	-235.25	-234.87	-241.98	-235.02	-230.31
Hexane	-138.18	-131.91	-130.50	-136.79	-132.09	-121.14
m-cresol	-275.05	-265.54	-256.02	-264.58	-255.70	-257.79
Methanol	-321.09	-316.42	-306.95	-309.18	-305.86	-306.21
Methoxyethanol	-299.28	-297.87	-284.89	-292.18	-283.65	-288.93
Methyl ethanoate	-230.65	-226.61	-224.77	-232.00	-227.60	-223.84
Methyl propanoate	-224.85	-221.44	-220.68	-227.09	-222.25	-218.53
Propyl ethanoate	-220.31	-217.53	-216.27	-223.19	-219.21	-214.33
Quinoline	-250.03	-240.97	-247.24	-253.28	-241.68	-242.18
Tetrahydrofuran	-235.23	-228.73	-225.62	-235.17	-230.27	-224.28
Toluene	-162.52	-164.18	-167.04	-164.46	-158.98	-162.98
Water	-314.46	-311.14	-300.78	-301.86	-297.61	-304.55

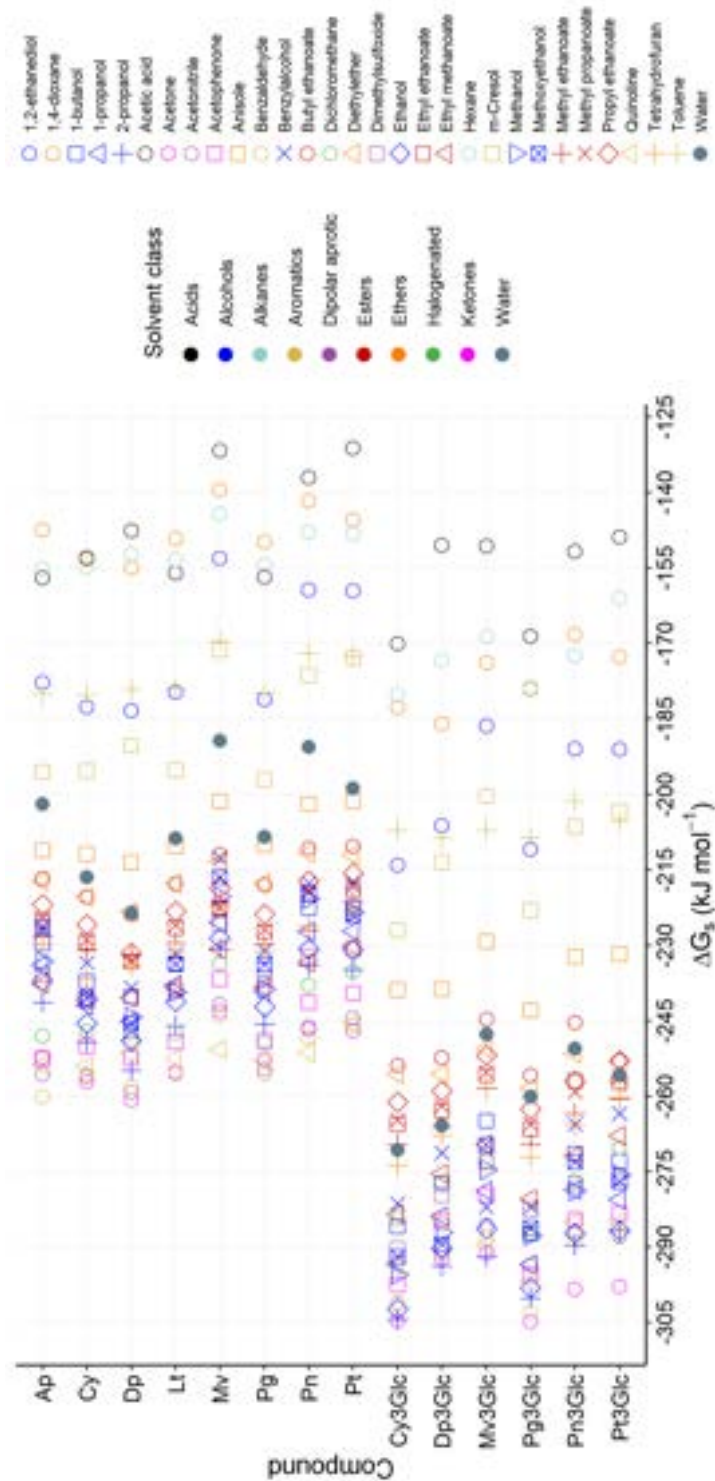


Figure B.6: Gibbs free energies of solvation including thermal contributions and nonelectrostatic component (kJ mol^{-1}) of anthocyanidins in the selected solvents. (B3LYP/6-311++G(d,p) + SMD solvation model).

Table B.14: Electronic energies (E_{solution} (hartree)), G^{therm} (hartree) and G_{nes} (kcal/mol) represent the thermal contributions and nonelectrostatic component to the Gibbs free energy of anthocyanidins in solution.

Solvent	Apigeninidin (Ap)	Cyanidin (Cy)	Delphinidin (Dp)	Luteolinidin (Lt)	Malvidin (Mv)	Pelargonidin (Pg)	Peonidin (Pn)	Petunidin (Pt)
1,2-ethanediol	E_{solution} -879.239	-1029.736	-1104.988	-954.491	-1183.602	-954.485	-1069.045	-1144.296
	$G_{\text{solution}}^{\text{therm}}$ 0.187	0.191	0.193	0.188	0.247	0.189	0.218	0.220
	G_{nes} 9.140	11.530	12.840	10.440	14.300	10.230	12.260	13.560
1,4-dioxane	E_{solution} -879.206	-1029.698	-1104.949	-954.457	-1183.568	-954.448	-1069.012	-1144.262
	$G_{\text{solution}}^{\text{therm}}$ 0.187	0.191	0.195	0.190	0.247	0.188	0.219	0.221
	G_{nes} -4.640	-5.430	-5.890	-5.100	-4.010	-4.980	-4.480	-4.950
1-butanol	E_{solution} -879.247	-1029.744	-1104.996	-954.499	-1183.612	-954.492	-1069.053	-1144.305
	$G_{\text{solution}}^{\text{therm}}$ 0.187	0.192	0.195	0.189	0.245	0.190	0.217	0.221
	G_{nes} 1.260	2.720	3.530	2.060	4.440	1.930	3.180	3.980
1-propanol	E_{solution} -879.248	-1029.746	-1104.998	-954.500	-1183.613	-954.494	-1069.055	-1144.307
	$G_{\text{solution}}^{\text{therm}}$ 0.187	0.192	0.195	0.189	0.246	0.190	0.217	0.220
	G_{nes} 1.120	2.570	3.370	1.910	4.240	1.780	3.000	3.790
2-propanol	E_{solution} -879.248	-1029.746	-1104.998	-954.501	-1183.614	-954.494	-1069.055	-1144.307
	$G_{\text{solution}}^{\text{therm}}$ 0.186	0.192	0.194	0.188	0.247	0.189	0.217	0.220
	G_{nes} 0.160	1.240	1.830	0.750	2.800	0.650	1.720	2.310
Acetic acid	E_{solution} -879.228	-1029.722	-1104.973	-954.479	-1183.589	-954.472	-1069.032	-1144.282
	$G_{\text{solution}}^{\text{therm}}$ 0.188	0.192	0.195	0.189	0.246	0.189	0.219	0.221
	G_{nes} 6.390	9.260	10.860	7.960	11.370	7.690	9.530	11.110
Acetone	E_{solution} -879.244	-1029.737	-1104.987	-954.495	-1183.608	-954.486	-1069.049	-1144.299
	$G_{\text{solution}}^{\text{therm}}$ 0.185	0.190	0.193	0.188	0.247	0.188	0.217	0.220
	G_{nes} -5.060	-5.490	-5.740	-5.300	-4.320	-5.250	-4.760	-5.020
Acetonitrile	E_{solution} -879.246	-1029.739	-1104.990	-954.496	-1183.609	-954.489	-1069.051	-1144.301
	$G_{\text{solution}}^{\text{therm}}$ 0.184	0.190	0.193	0.187	0.247	0.188	0.216	0.219
	G_{nes} -3.830	-3.780	-3.770	-3.820	-2.470	-3.800	-3.130	-3.120
Acetophenone	E_{solution} -879.241	-1029.734	-1104.984	-954.492	-1183.604	-954.483	-1069.046	-1144.296
	$G_{\text{solution}}^{\text{therm}}$ 0.183	0.190	0.193	0.188	0.246	0.187	0.216	0.220

---	G_{nes}	-5.360	-5.910	-6.240	-5.670	-4.430	-5.600	-4.990	-5.330
---	$G_{\text{solution}}^{\text{Evolution}}$	-879.227	-1029.718	-1104.968	-954.477	-1183.588	-954.468	-1069.031	-1144.281
Anisole	$G_{\text{solution}}^{\text{therm}}$	0.186	0.190	0.193	0.189	0.246	0.188	0.218	0.220
---	G_{nes}	-6.280	-6.580	-6.760	-6.460	-5.300	-6.400	-5.840	-6.030
---	$G_{\text{solution}}^{\text{Evolution}}$	-879.243	-1029.735	-1104.985	-954.493	-1183.605	-954.485	-1069.048	-1144.297
Benzaldehyde	$G_{\text{solution}}^{\text{therm}}$	0.183	0.190	0.193	0.188	0.246	0.187	0.216	0.220
---	G_{nes}	-6.110	-6.550	-6.820	-6.360	-5.190	-6.300	-5.730	-6.000
---	$G_{\text{solution}}^{\text{Evolution}}$	-879.244	-1029.741	-1104.993	-954.496	-1183.608	-954.489	-1069.051	-1144.302
Benzylalcohol	$G_{\text{solution}}^{\text{therm}}$	0.186	0.192	0.194	0.188	0.247	0.189	0.217	0.221
---	G_{nes}	0.670	1.840	2.480	1.300	3.750	1.210	2.470	3.110
---	$G_{\text{solution}}^{\text{Evolution}}$	-879.229	-1029.721	-1104.971	-954.480	-1183.592	-954.471	-1069.034	-1144.284
Butyl ethanoate	$G_{\text{solution}}^{\text{therm}}$	0.186	0.190	0.193	0.189	0.245	0.188	0.217	0.220
---	G_{nes}	-5.950	-6.520	-6.860	-6.280	-5.380	-6.200	-5.780	-6.120
---	$G_{\text{solution}}^{\text{Evolution}}$	-879.242	-1029.735	-1104.984	-954.492	-1183.604	-954.484	-1069.047	-1144.296
Dichloromethane	$G_{\text{solution}}^{\text{therm}}$	0.185	0.191	0.193	0.188	0.247	0.187	0.217	0.220
---	G_{nes}	-5.430	-4.880	-4.590	-5.140	-3.790	-5.160	-4.480	-4.190
---	$G_{\text{solution}}^{\text{Evolution}}$	-879.228	-1029.720	-1104.970	-954.478	-1183.591	-954.469	-1069.033	-1144.283
Diethylether	$G_{\text{solution}}^{\text{therm}}$	0.186	0.190	0.193	0.189	0.246	0.188	0.217	0.220
---	G_{nes}	-6.980	-7.560	-7.900	-7.310	-6.670	-7.240	-6.940	-7.280
---	$G_{\text{solution}}^{\text{Evolution}}$	-879.241	-1029.734	-1104.984	-954.491	-1183.604	-954.483	-1069.046	-1144.296
Dimethyl sulfoxide	$G_{\text{solution}}^{\text{therm}}$	0.184	0.190	0.193	0.188	0.246	0.188	0.215	0.219
---	G_{nes}	-2.640	-3.720	-4.340	-3.230	-1.930	-3.130	-2.490	-3.130
---	$G_{\text{solution}}^{\text{Evolution}}$	-879.249	-1029.747	-1104.999	-954.502	-1183.615	-954.495	-1069.056	-1144.308
Ethanol	$G_{\text{solution}}^{\text{therm}}$	0.187	0.192	0.195	0.189	0.246	0.190	0.217	0.220
---	G_{nes}	1.090	2.530	3.320	1.870	4.150	1.750	2.940	3.730
---	$G_{\text{solution}}^{\text{Evolution}}$	-879.232	-1029.724	-1104.974	-954.483	-1183.595	-954.474	-1069.038	-1144.287
Ethyl ethanoate	$G_{\text{solution}}^{\text{therm}}$	0.186	0.190	0.192	0.189	0.245	0.187	0.217	0.220
---	G_{nes}	-6.020	-6.600	-6.940	-6.350	-5.500	-6.280	-5.870	-6.220
---	$G_{\text{solution}}^{\text{Evolution}}$	-879.237	-1029.729	-1104.979	-954.487	-1183.599	-954.478	-1069.042	-1144.291
Ethyl methanoate	$G_{\text{solution}}^{\text{therm}}$	0.185	0.190	0.194	0.189	0.246	0.187	0.216	0.220
---	G_{nes}	-6.070	-6.550	-6.850	-6.350	-5.480	-6.280	-5.860	-6.150
---	$G_{\text{solution}}^{\text{Evolution}}$	-879.205	-1029.696	-1104.945	-954.455	-1183.567	-954.445	-1069.010	-1144.259
Hexane	$G_{\text{solution}}^{\text{therm}}$	0.187	0.191	0.195	0.191	0.248	0.189	0.219	0.221

---	G_{nes}	-7.620	-7.580	-7.580	-7.620	-7.580	-7.580	-7.620	-7.580	-7.180	-7.180
---	$G_{\text{solution}}^{\text{therm}}$	-879.240	-1029.735	-1104.986	-954.491	-1183.602	-954.484	-1069.045	-1144.295		
m-cresol	$G_{\text{solution}}^{\text{therm}}$	0.187	0.191	0.195	0.189	0.246	0.189	0.219	0.221		
---	G_{nes}	4.760	7.590	9.160	6.310	9.760	6.050	7.900	9.450		
---	$G_{\text{solution}}^{\text{therm}}$	-879.249	-1029.747	-1104.999	-954.502	-1183.615	-954.495	-1069.056	-1144.308		
Methanol	$G_{\text{solution}}^{\text{therm}}$	0.186	0.191	0.193	0.187	0.247	0.189	0.218	0.220		
---	G_{nes}	2.500	4.290	5.280	3.480	5.990	3.310	4.650	5.630		
---	$G_{\text{solution}}^{\text{therm}}$	-879.245	-1029.743	-1104.995	-954.497	-1183.610	-954.490	-1069.052	-1144.303		
Methoxyethanol	$G_{\text{solution}}^{\text{therm}}$	0.186	0.191	0.193	0.188	0.247	0.189	0.218	0.220		
---	G_{nes}	1.380	1.940	2.260	1.690	3.840	1.630	2.730	3.040		
---	$G_{\text{solution}}^{\text{therm}}$	-879.234	-1029.726	-1104.976	-954.484	-1183.597	-954.475	-1069.039	-1144.289		
Methyl ethanoate	$G_{\text{solution}}^{\text{therm}}$	0.186	0.190	0.194	0.189	0.246	0.187	0.215	0.220		
---	G_{nes}	-5.730	-6.310	-6.650	-6.060	-5.170	-5.980	-5.560	-5.890		
---	$G_{\text{solution}}^{\text{therm}}$	-879.232	-1029.724	-1104.974	-954.483	-1183.595	-954.474	-1069.038	-1144.287		
Methyl propanoate	$G_{\text{solution}}^{\text{therm}}$	0.186	0.190	0.192	0.189	0.244	0.187	0.217	0.220		
---	G_{nes}	-5.890	-6.470	-6.800	-6.220	-5.340	-6.150	-5.730	-6.070		
---	$G_{\text{solution}}^{\text{therm}}$	-879.231	-1029.723	-1104.973	-954.482	-1183.594	-954.473	-1069.036	-1144.286		
Propyl ethanoate	$G_{\text{solution}}^{\text{therm}}$	0.186	0.190	0.192	0.189	0.245	0.187	0.217	0.220		
---	G_{nes}	-6.040	-6.620	-6.960	-6.380	-5.510	-6.300	-5.890	-6.230		
---	$G_{\text{solution}}^{\text{therm}}$	-879.240	-1029.732	-1104.981	-954.490	-1183.604	-954.481	-1069.045	-1144.295		
Quinoline	$G_{\text{solution}}^{\text{therm}}$	0.185	0.190	0.193	0.188	0.246	0.187	0.216	0.220		
---	G_{nes}	-7.590	-7.680	-7.740	-7.650	-7.450	-7.620	-7.530	-7.580		
---	$G_{\text{solution}}^{\text{therm}}$	-879.235	-1029.727	-1104.977	-954.485	-1183.597	-954.476	-1069.040	-1144.289		
Tetrahydrofuran	$G_{\text{solution}}^{\text{therm}}$	0.186	0.189	0.194	0.189	0.246	0.187	0.216	0.220		
---	G_{nes}	-5.590	-6.190	-6.560	-5.940	-4.960	-5.860	-5.390	-5.750		
---	$G_{\text{solution}}^{\text{therm}}$	-879.214	-1029.705	-1104.954	-954.464	-1183.575	-954.455	-1069.019	-1144.268		
Toluene	$G_{\text{solution}}^{\text{therm}}$	0.187	0.191	0.194	0.190	0.247	0.188	0.218	0.221		
---	G_{nes}	-7.700	-7.840	-7.950	-7.800	-6.860	-7.740	-7.300	-7.400		
---	$G_{\text{solution}}^{\text{therm}}$	-879.244	-1029.743	-1104.996	-954.497	-1183.610	-954.490	-1069.051	-1144.304		
Water	$G_{\text{solution}}^{\text{therm}}$	0.185	0.190	0.193	0.188	0.246	0.188	0.218	0.219		
---	G_{nes}	7.190	8.210	8.670	7.660	10.600	7.750	9.140	9.590		

Table B.15: Gibbs free energies of solvation including thermal contributions and nonelectrostatic component (kJ mol^{-1}) of anthocyanidins in the selected solvents. ($\text{B3LYP/6-311++G(d,p)} + \text{SMD solvation model}$).

Anthocyanidins	Apigeninidin (Ap)	Cyanidin (Cy)	Delphinidin (Dp)	Luteolinidin (Lt)	Malvidin (Mv)	Pelargonidin (Pg)	Peonidin (Pn)	Petunidin (Pt)
1,2-ethanediol	-177.78	-182.67	-183.35	-179.74	-153.05	-181.13	-159.35	-159.53
1,4-dioxane	-147.41	-153.25	-154.94	-149.14	-139.48	-149.77	-141.67	-145.43
1-butanol	-229.69	-237.23	-240.27	-233.61	-222.46	-234.86	-222.61	-222.43
1-propanol	-233.96	-241.92	-245.20	-237.98	-225.56	-239.18	-227.34	-227.29
2-propanol	-241.35	-249.27	-254.97	-246.08	-230.83	-245.79	-234.09	-234.87
Acetic acid	-157.01	-153.01	-147.60	-156.03	-131.63	-156.80	-137.02	-131.23
Acetone	-252.27	-257.15	-260.73	-255.26	-243.11	-252.68	-246.75	-247.05
Acetonitrile	-255.74	-255.76	-259.24	-255.57	-241.74	-254.66	-246.21	-244.44
Acetophenone	-252.59	-250.07	-252.46	-249.20	-236.72	-248.99	-241.37	-239.52
Anisole	-211.16	-211.89	-213.47	-210.34	-201.37	-210.11	-202.00	-201.39
Benzaldehyde	-260.06	-256.22	-258.11	-255.66	-243.87	-255.63	-248.38	-245.85
Benzylalcohol	-227.04	-233.59	-238.56	-231.86	-212.77	-231.12	-217.80	-217.63
Butylacetate	-216.73	-220.40	-223.85	-217.78	-212.02	-218.10	-210.77	-210.36
Dichloromethane	-248.06	-247.07	-249.21	-247.39	-233.56	-249.44	-237.94	-235.23
Diethylether	-217.36	-220.52	-223.46	-217.83	-213.43	-217.73	-211.73	-212.16
Dimethyl sulfoxide	-235.88	-241.14	-247.16	-238.94	-225.77	-236.82	-232.23	-230.76
Ethanol	-237.19	-245.55	-249.03	-241.28	-228.71	-242.34	-230.83	-230.98
Ethyl ethanoate	-225.21	-229.43	-233.29	-226.62	-222.72	-227.44	-219.74	-219.09
Ethyl methanoate	-237.77	-240.82	-240.53	-238.52	-230.80	-238.44	-233.50	-230.34
Hexane	-155.20	-154.90	-152.24	-153.39	-144.28	-154.36	-147.90	-148.20
m-cresol	-195.57	-195.30	-190.36	-195.22	-171.29	-197.07	-176.35	-172.95
Methanol	-233.23	-240.78	-244.31	-239.38	-220.40	-238.80	-220.85	-223.53
Methoxyethanol	-226.33	-240.51	-245.60	-233.78	-216.52	-233.86	-219.65	-224.01
Methyl ethanoate	-228.18	-231.07	-232.12	-229.52	-221.61	-229.82	-227.03	-221.57
Methyl propanoate	-224.75	-228.97	-232.12	-226.16	-222.59	-227.01	-219.13	-218.43
Propyl ethanoate	-222.04	-226.02	-231.65	-223.33	-218.79	-223.93	-217.31	-215.82
Quinoline	-253.88	-254.04	-251.52	-252.55	-250.79	-253.12	-251.43	-245.59
Tetrahydrofuran	-229.84	-236.65	-234.15	-231.29	-222.56	-231.17	-226.21	-223.12
Toluene	-180.08	-180.29	-179.24	-178.85	-169.59	-179.75	-172.01	-172.65
Water	-201.96	-216.43	-223.49	-208.76	-189.37	-208.43	-190.59	-198.84

Table B.16: Electronic energies (E_{solution} (hartree)), G^{therm} (hartree) and G_{nes} (kcal/mol) represent the thermal contributions and nonelectrostatic component to the Gibbs free energy of anthocyanins in solution.

Solvent	Cyanidin-3-glucoside (Cy-3-Glc)	Delphinidin-3-glucoside (Dp-3-Glc)	Malvidin-3-glucoside (Mv-3-Glc)	Pelargonidin-3-glucoside (Pg-3-Glc)	Peonidin-3-glucoside (Pn-3-Glc)	Petunidin-3-glucoside (Pt-3-Glc)
1,2-ethanediol	E_{solution}	-1640.726	-1715.977	-1565.474	-1680.034	-1755.286
	$G^{\text{therm}}_{\text{solution}}$	0.348	0.348	0.347	0.375	0.378
	G_{nes}	16.040	16.850	14.720	16.760	17.760
1,4-dioxane	E_{solution}	-1640.677	-1715.932	-1565.427	-1679.990	-1755.241
	$G^{\text{therm}}_{\text{solution}}$	0.350	0.352	0.347	0.379	0.381
	G_{nes}	-8.450	-8.690	-7.970	-7.480	-7.830
1-butanol	E_{solution}	-1640.736	-1715.987	-1565.484	-1680.045	-1755.296
	$G^{\text{therm}}_{\text{solution}}$	0.350	0.352	0.346	0.375	0.378
	G_{nes}	3.850	4.370	3.030	4.290	4.960
1-propanol	E_{solution}	-1640.738	-1715.989	-1565.486	-1680.047	-1755.298
	$G^{\text{therm}}_{\text{solution}}$	0.349	0.351	0.346	0.375	0.377
	G_{nes}	3.610	4.120	2.790	4.020	4.700
2-propanol	E_{solution}	-1640.738	-1715.989	-1565.486	-1680.047	-1755.298
	$G^{\text{therm}}_{\text{solution}}$	0.348	0.351	0.346	0.374	0.379
	G_{nes}	1.430	1.830	0.810	1.880	2.430
Acetic acid	E_{solution}	-1640.706	-1715.955	-1565.456	-1680.016	-1755.267
	$G^{\text{therm}}_{\text{solution}}$	0.349	0.351	0.349	0.377	0.380
	G_{nes}	13.480	14.450	11.910	13.750	14.970
Acetone	E_{solution}	-1640.721	-1715.973	-1565.472	-1680.035	-1755.283
	$G^{\text{therm}}_{\text{solution}}$	0.348	0.351	0.345	0.374	0.375
	G_{nes}	-8.280	-8.320	-8.040	-7.560	-7.650
Acetonitrile	E_{solution}	-1640.723	-1715.974	-1565.473	-1680.035	-1755.284
	$G^{\text{therm}}_{\text{solution}}$	0.346	0.350	0.346	0.373	0.375
	G_{nes}	-5.310	-5.220	-5.330	-4.670	-4.590
Acetophenone	E_{solution}	-1640.716	-1715.968	-1565.467	-1680.031	-1755.278
	$G^{\text{therm}}_{\text{solution}}$	0.346	0.350	0.344	0.375	0.376

	G_{nes}	-8.700	-8.780	-7.050	-8.370	-7.800	-7.940
	$G_{\text{solution}}^{\text{E-solution}}$	-1640.698	-1715.951	-1794.569	-1565.448	-1680.011	-1755.261
Anisole	$G_{\text{solution}}^{\text{therm}}$	0.351	0.352	0.406	0.346	0.377	0.380
	G_{nes}	-9.150	-9.200	-7.780	-8.960	-8.410	-8.530
	$G_{\text{solution}}^{\text{E-solution}}$	-1640.718	-1715.969	-1794.588	-1565.469	-1680.030	-1755.280
Benzaldehyde	$G_{\text{solution}}^{\text{therm}}$	0.347	0.350	0.403	0.344	0.374	0.377
	G_{nes}	-9.420	-9.440	-7.880	-9.150	-8.540	-8.680
	$G_{\text{solution}}^{\text{E-solution}}$	-1640.731	-1715.983	-1794.598	-1565.479	-1680.040	-1755.292
Benzylalcohol	$G_{\text{solution}}^{\text{therm}}$	0.349	0.352	0.402	0.345	0.375	0.379
	G_{nes}	2.480	2.900	4.270	1.840	3.080	3.640
	$G_{\text{solution}}^{\text{E-solution}}$	-1640.702	-1715.955	-1794.573	-1565.452	-1680.015	-1755.266
Butyl ethanoate	$G_{\text{solution}}^{\text{therm}}$	0.350	0.352	0.406	0.346	0.376	0.377
	G_{nes}	-9.620	-9.760	-8.340	-9.280	-8.860	-9.080
	$G_{\text{solution}}^{\text{E-solution}}$	-1640.717	-1715.969	-1794.587	-1565.467	-1680.029	-1755.279
Dichloromethane	$G_{\text{solution}}^{\text{therm}}$	0.348	0.349	0.403	0.344	0.373	0.378
	G_{nes}	-6.130	-5.880	-5.020	-6.430	-5.740	-5.420
	$G_{\text{solution}}^{\text{E-solution}}$	-1640.701	-1715.955	-1794.572	-1565.451	-1680.014	-1755.265
Diethylether	$G_{\text{solution}}^{\text{therm}}$	0.351	0.352	0.405	0.346	0.376	0.377
	G_{nes}	-11.100	-11.220	-10.050	-10.760	-10.460	-10.660
	$G_{\text{solution}}^{\text{E-solution}}$	-1640.719	-1715.969	-1794.587	-1565.467	-1680.031	-1755.279
Dimethyl sulfoxide	$G_{\text{solution}}^{\text{therm}}$	0.348	0.350	0.403	0.345	0.374	0.376
	G_{nes}	-6.600	-6.910	-4.650	-6.070	-5.410	-5.820
	$G_{\text{solution}}^{\text{E-solution}}$	-1640.740	-1715.991	-1794.607	-1565.487	-1680.048	-1755.300
Ethanol	$G_{\text{solution}}^{\text{therm}}$	0.348	0.351	0.402	0.346	0.373	0.377
	G_{nes}	3.510	4.040	5.040	2.720	3.910	4.600
	$G_{\text{solution}}^{\text{E-solution}}$	-1640.706	-1715.959	-1794.577	-1565.456	-1680.019	-1755.269
Ethyl ethanoate	$G_{\text{solution}}^{\text{therm}}$	0.349	0.351	0.405	0.345	0.376	0.379
	G_{nes}	-9.760	-9.890	-8.520	-9.410	-9.040	-9.230
	$G_{\text{solution}}^{\text{E-solution}}$	-1640.710	-1715.963	-1794.581	-1565.460	-1680.023	-1755.273
Ethyl methanoate	$G_{\text{solution}}^{\text{therm}}$	0.347	0.350	0.404	0.344	0.375	0.379
	G_{nes}	-9.510	-9.610	-8.310	-9.220	-8.830	-8.990
	$G_{\text{solution}}^{\text{E-solution}}$	-1640.673	-1715.928	-1794.545	-1565.423	-1679.987	-1755.236
Hexane	$G_{\text{solution}}^{\text{therm}}$	0.349	0.354	0.407	0.347	0.377	0.383

	G_{nes}	-10.030	-9.920	-9.110	-10.030	-9.640	-9.530
	$G_{\text{solution}}^{\text{therm}}$	-1640.723	-1715.974	-1794.590	-1565.472	-1680.032	-1755.283
m-cresol							
	G_{nes}	11.480	12.440	13.320	9.920	11.780	13.010
	$G_{\text{solution}}^{\text{therm}}$	-1640.741	-1715.993	-1794.608	-1565.489	-1680.050	-1755.301
Methanol							
	G_{nes}	0.348	0.349	0.404	0.347	0.374	0.378
	$G_{\text{solution}}^{\text{therm}}$	6.100	7.010	7.710	5.110	6.440	7.280
	$G_{\text{solution}}^{\text{therm}}$	-1640.733	-1715.985	-1794.600	-1565.481	-1680.042	-1755.294
Methoxyethanol							
	G_{nes}	0.349	0.348	0.404	0.346	0.375	0.377
	$G_{\text{solution}}^{\text{therm}}$	1.740	2.000	3.620	1.430	2.530	2.840
	$G_{\text{solution}}^{\text{therm}}$	-1640.707	-1715.960	-1794.578	-1565.457	-1680.020	-1755.270
Methyl ethanoate							
	G_{nes}	0.349	0.351	0.405	0.345	0.374	0.378
	$G_{\text{solution}}^{\text{therm}}$	-9.320	-9.450	-8.050	-8.980	-8.590	-8.780
	$G_{\text{solution}}^{\text{therm}}$	-1640.706	-1715.959	-1794.577	-1565.455	-1680.019	-1755.269
Methyl propanoate							
	G_{nes}	0.349	0.351	0.405	0.345	0.375	0.379
	$G_{\text{solution}}^{\text{therm}}$	-9.550	-9.690	-8.290	-9.210	-8.830	-9.020
	$G_{\text{solution}}^{\text{therm}}$	-1640.705	-1715.958	-1794.575	-1565.454	-1680.018	-1755.268
Propyl ethanoate							
	G_{nes}	0.350	0.351	0.405	0.345	0.375	0.379
	$G_{\text{solution}}^{\text{therm}}$	-9.780	-9.920	-8.530	-9.430	-9.060	-9.250
	$G_{\text{solution}}^{\text{therm}}$	-1640.713	-1715.965	-1794.586	-1565.463	-1680.027	-1755.277
Quinoline							
	G_{nes}	0.347	0.350	0.404	0.343	0.376	0.378
	$G_{\text{solution}}^{\text{therm}}$	-10.510	-10.430	-10.150	-10.450	-10.370	-10.290
	$G_{\text{solution}}^{\text{therm}}$	-1640.708	-1715.961	-1794.579	-1565.458	-1680.023	-1755.271
Tetrahydrofuran							
	G_{nes}	0.348	0.351	0.405	0.345	0.376	0.379
	$G_{\text{solution}}^{\text{therm}}$	-9.200	-9.350	-7.830	-8.840	-8.460	-8.630
	$G_{\text{solution}}^{\text{therm}}$	-1640.684	-1715.938	-1794.555	-1565.433	-1679.997	-1755.248
Toluene							
	G_{nes}	0.351	0.352	0.403	0.347	0.377	0.379
	$G_{\text{solution}}^{\text{therm}}$	-10.670	-10.640	-9.590	-10.560	-10.130	-10.130
	$G_{\text{solution}}^{\text{therm}}$	-1640.737	-1715.990	-1794.604	-1565.484	-1680.048	-1755.301
Water							
	G_{nes}	0.347	0.349	0.402	0.345	0.375	0.378
	$G_{\text{solution}}^{\text{therm}}$	10.460	10.830	12.690	9.990	11.250	11.630

Table B.17: Gibbs free energies of solvation including the effect of geometrical relaxation (kJ mol^{-1}) anthocyanins and selected solvents. (B3LYP/6-311++G(d,p) + SMD solvation model).

Anthocyanins	Cyanidin-3-glucoside (Cy-3-Glc)	Delphinidin-3-glucoside (Dp-3-Glc)	Malvidin-3-glucoside (Mv-3-Glc)	Pelargonidin-3-glucoside (Pg-3-Glc)	Peonidin-3-glucoside (Pn-3-Glc)	Petunidin-3-glucoside (Pt-3-Glc)
1,2-ethanediol	-214.10	-206.21	-186.35	-210.91	-190.97	-191.06
1,4-dioxane	-182.76	-186.05	-173.91	-179.11	-168.25	-172.69
1-butanol	-285.94	-277.44	-264.94	-287.34	-271.48	-272.97
1-propanol	-293.41	-283.92	-278.89	-293.51	-278.70	-280.60
2-propanol	-304.42	-293.77	-291.99	-300.21	-289.77	-286.71
Acetic acid	-170.08	-150.46	-150.69	-168.59	-151.70	-148.84
Acetone	-304.72	-292.26	-291.14	-304.77	-298.39	-297.85
Acetonitrile	-301.20	-285.36	-285.57	-293.66	-286.97	-287.80
Acetophenone	-297.59	-284.63	-279.74	-295.55	-284.48	-283.41
Anisole	-238.92	-238.75	-229.25	-242.95	-232.30	-231.74
Benzaldehyde	-301.08	-291.26	-288.27	-302.94	-288.88	-288.01
Benzylalcohol	-281.48	-271.35	-267.92	-282.13	-265.69	-263.56
Butylacetate	-253.87	-252.34	-244.77	-255.91	-245.37	-253.03
Dichloromethane	-284.34	-276.99	-273.03	-287.03	-276.90	-270.23
Diethylether	-255.72	-255.74	-250.60	-258.49	-251.57	-257.16
Dimethyl sulfoxide	-290.39	-279.69	-273.10	-282.42	-277.51	-276.19
Ethanol	-302.36	-290.36	-286.47	-298.19	-287.42	-286.79
Ethyl ethanoate	-265.65	-262.94	-255.85	-266.57	-256.97	-257.25
Ethyl methanoate	-283.47	-275.46	-269.63	-280.55	-271.96	-267.92
Hexane	-180.15	-173.42	-168.61	-178.76	-172.43	-161.01
m-cresol	-227.02	-213.49	-200.29	-223.08	-206.41	-203.36
Methanol	-295.57	-287.09	-274.69	-287.80	-278.91	-275.75
Methoxyethanol	-292.00	-289.50	-269.74	-286.20	-273.07	-277.04
Methyl ethanoate	-269.65	-266.15	-258.45	-269.58	-263.54	-260.57
Methyl propanoate	-264.81	-261.98	-255.36	-265.62	-259.19	-256.27
Propyl ethanoate	-261.23	-259.04	-251.96	-262.65	-257.11	-253.03
Quinoline	-294.00	-284.61	-289.71	-297.00	-285.07	-285.23
Tetrahydrofuran	-273.73	-267.84	-258.38	-272.16	-265.67	-260.39
Toluene	-207.17	-208.69	-207.16	-208.64	-201.37	-205.36
Water	-270.69	-265.82	-247.68	-260.07	-250.54	-255.89

Conductor-like Screening Model for Realistic Solvent (COSMO-RS)

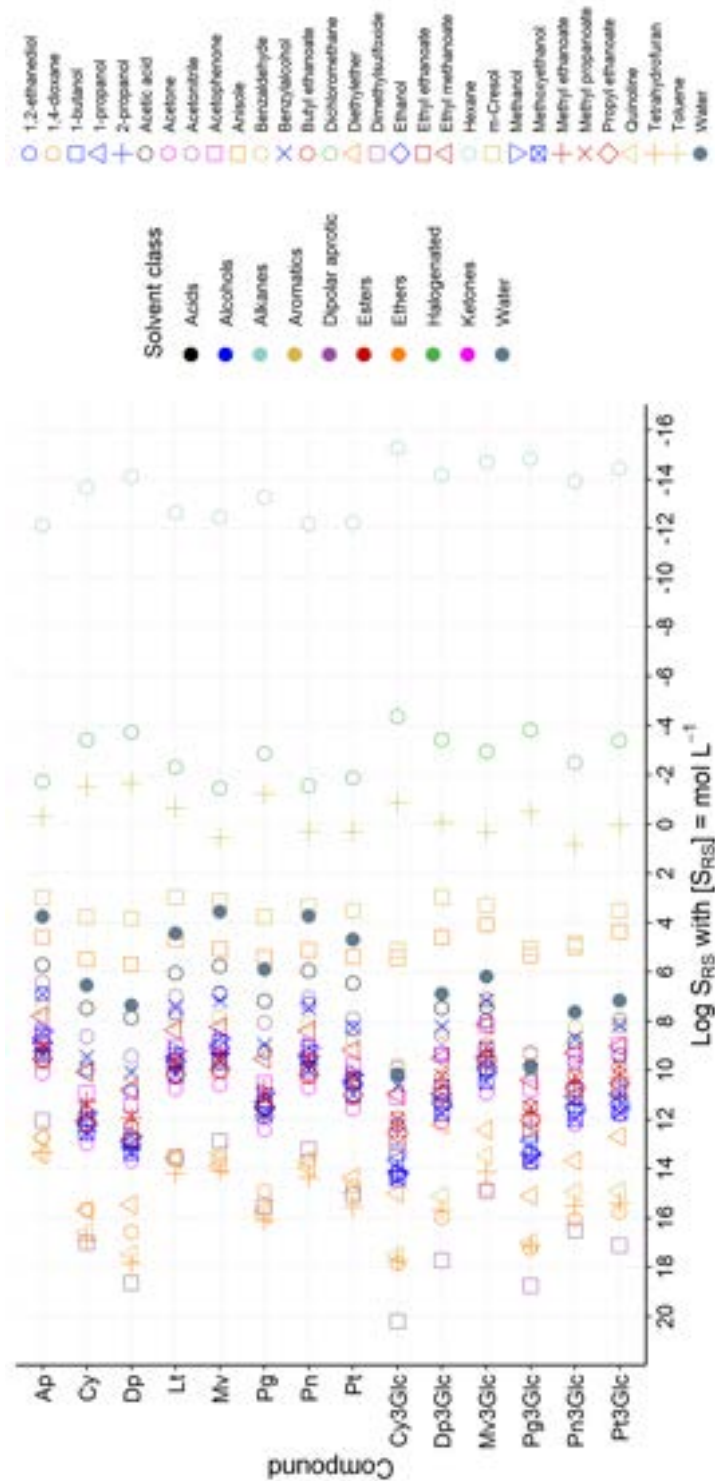


Figure B.7: Relative solubility values $\log S_{RS}$ (with $S_{RS} = \text{mol L}^{-1}$) for anthocyanidins and anthocyanins from COSMO-RS solvent screening.

Table B.18: Relative solubility values $\log S_{RS}$ (with $S_{RS} = \text{mol L}^{-1}$) for anthocyanidins from COSMO-RS solvent screening.

Anthocyanidins	Apigeninidin (Ap)	Cyanidin (Cy)	Delphinidin (Dp)	Luteolinidin (Lt)	Malvidin (Mv)	Pelargonidin (Pg)	Peonidin (Pn)	Petunidin (Pt)
1,2-ethanediol	6.899	9.977	10.864	7.666	6.883	9.240	7.308	8.321
1,4-dioxane	12.721	15.658	16.559	13.546	13.623	14.904	13.637	14.707
1-butanol	8.617	11.974	12.833	9.411	8.865	11.233	9.303	10.391
1-propanol	8.700	12.032	12.886	9.484	8.954	11.298	9.363	10.443
2-propanol	9.212	12.500	13.217	9.906	9.339	11.874	9.717	10.685
Acetic acid	5.725	7.477	7.872	6.049	5.771	7.184	5.960	6.461
Acetone	10.117	12.978	13.675	10.752	10.601	12.412	10.717	11.578
Acetonitrile	6.407	8.622	9.428	6.996	6.909	8.062	7.043	7.899
Acetophenone	8.556	10.917	11.440	9.032	8.877	10.509	9.067	9.767
Anisole	4.591	5.492	5.690	4.685	5.077	5.429	5.106	5.400
Benzaldehyde	7.451	9.644	10.271	7.948	7.850	9.186	8.046	8.780
Benzylalcohol	6.928	9.466	10.096	7.456	7.190	8.975	7.488	8.270
Butylacetate	9.292	11.752	12.306	9.852	9.614	11.262	9.832	10.580
Dichloromethane	-1.737	-3.432	-3.719	-2.310	-1.456	-2.883	-1.561	-1.865
Diethylether	13.433	15.698	15.478	13.597	13.867	15.686	13.943	14.389
Dimethyl sulfoxide	12.030	16.994	18.635	13.538	12.879	15.532	13.203	15.066
Ethanol	8.897	12.217	13.073	9.664	9.109	11.497	9.487	10.548
Ethyl ethanoate	9.586	12.181	12.866	10.223	10.020	11.599	10.185	11.045
Ethyl methanoate	7.804	10.086	10.800	8.380	8.259	9.545	8.407	9.190
Hexane	-12.118	-13.660	-14.100	-12.636	-12.456	-13.255	-12.187	-12.248
m-cresol	2.987	3.769	3.843	2.977	3.119	3.775	3.345	3.505
Methanol	8.436	11.724	12.688	9.242	8.726	10.946	9.080	10.192
Methoxyethanol	9.381	12.535	13.352	10.146	9.666	11.818	9.956	10.968
Methyl ethanoate	8.898	11.308	11.946	9.487	9.293	10.770	9.413	10.194
Methyl propanoate	9.116	11.417	11.880	9.637	9.423	10.959	9.543	10.270
Propyl ethanoate	9.550	12.125	12.775	10.174	9.962	11.560	10.162	11.001
Quinoline	12.717	16.598	17.475	13.522	13.407	15.891	13.695	14.984
Tetrahydrofuran	13.347	16.877	17.831	14.206	14.096	16.095	14.356	15.554
Toluene	-0.305	-1.537	-1.662	-0.653	0.570	-1.222	0.297	0.320
Water	3.746	6.549	7.360	4.429	3.556	5.890	3.734	4.697

Table B.19: Relative solubility values $\log S_{RS}$ (with $S_{RS} = \text{mol L}^{-1}$) for anthocyanins from COSMO-RS solvent screening.

Anthocyanins	Cyanidin-3-glucoside (Cy-3-Glc)	Delphinidin-3-glucoside (Dp-3-Glc)	Malvidin-3-glucoside (Mv-3-Glc)	Pelargonidin-3-glucoside (Pg-3-Glc)	Peonidin-3-glucoside (Pn-3-Glc)	Petunidin-3-glucoside (Pt-3-Glc)
1,2-ethanediol	12.213	9.312	7.992	11.447	9.662	9.379
1,4-dioxane	17.846	15.985	14.824	17.232	16.069	15.760
1-butanol	13.353	10.698	9.184	12.566	10.784	10.684
1-propanol	13.652	10.973	9.492	12.865	11.081	10.961
2-propanol	14.073	11.162	9.806	13.405	11.401	11.099
Acetic acid	10.182	7.469	7.421	9.853	8.865	7.942
Acetone	14.285	12.102	10.926	13.757	12.202	11.808
Acetonitrile	9.899	8.590	7.175	9.298	8.254	8.157
Acetophenone	11.115	9.360	8.195	10.738	9.412	8.974
Anisole	5.427	4.586	4.092	5.337	4.982	4.369
Benzaldehyde	9.789	8.420	7.117	9.345	8.261	7.972
Benzylalcohol	10.618	8.228	7.177	10.037	8.721	8.187
Butylacetate	11.935	10.298	9.006	11.485	10.188	9.855
Dichloromethane	-4.358	-3.424	-2.945	-3.816	-2.495	-3.382
Diethylether	15.016	12.222	12.426	15.099	13.672	12.700
Dimethyl sulfoxide	20.192	17.720	14.908	18.756	16.508	17.113
Ethanol	14.167	11.340	9.938	13.390	11.538	11.355
Ethyl ethanoate	12.931	11.284	9.909	12.386	11.080	10.841
Ethyl methanoate	10.978	9.531	8.158	10.400	9.292	9.056
Hexane	-15.257	-14.165	-14.690	-14.835	-13.910	-14.452
m-cresol	5.112	2.975	3.304	5.033	4.819	3.517
Methanol	14.226	11.475	10.121	13.435	11.668	11.548
Methoxyethanol	14.398	11.757	10.462	13.678	11.984	11.718
Methyl ethanoate	12.384	10.700	9.428	11.838	10.588	10.270
Methyl propanoate	11.980	10.228	9.102	11.514	10.250	9.831
Propyl ethanoate	12.571	10.990	9.598	12.050	10.764	10.531
Quinoline	17.547	15.110	13.491	16.992	14.955	14.905
Tetrahydrofuran	17.737	15.674	14.127	17.126	15.518	15.411
Toluene	-0.875	-0.048	0.332	-0.505	0.835	0.054
Water	10.216	6.893	6.186	9.903	7.636	7.171

Data HSPs: Binary Mixtures

Data Hansen Solubility Parameters: Acetone-Water Mixtures

Table B.20: Hansen solubility parameters for aqueous binary mixtures of acetone.

Acetone (v/v %)	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})
100	15.50	10.40	7
90	15.51	10.96	10.53
80	15.52	11.52	14.06
70	15.53	12.08	17.59
60	15.54	12.64	21.12
50	15.55	13.20	24.65
40	15.56	13.76	28.18
30	15.57	14.32	31.71
20	15.58	14.88	35.24
10	15.59	15.44	38.77
0	15.60	16.00	42.30

Table B.21: Distance R_a ($\text{MPa}^{1/2}$) between anthocyanidins or anthocyanins and aqueous binary mixtures of acetone based on Hansen solubility parameters

Anthocyanidins → Acetone v/v % ↓	Apigeninidin (Ap)	Cyanidin (Cy)	Delphinidin (Dp)	Luteolinidin (Lt)	Malvidin (Mv)	Pelargonidin (Pg)	Peonidin (Pn)	Petunidin (Pt)	Average	Std. Dev.
100	26.33	31.67	38.94	25.38	25.72	33.36	25.79	30.79	29.75	4.86
90	24.49	29.41	36.75	23.14	23.73	31.38	23.68	28.64	27.65	4.81
80	23.07	27.42	34.79	21.28	22.15	29.71	21.95	26.80	25.90	4.72
70	22.14	25.79	33.10	19.88	21.05	28.39	20.70	25.32	24.55	4.55
60	21.76	24.56	31.73	19.07	20.53	27.48	20.01	24.29	23.68	4.29
50	21.96	23.82	30.71	18.90	20.63	27.01	19.95	23.75	23.34	3.94
40	22.73	23.59	30.08	19.41	21.33	27.01	20.53	23.75	23.52	3.52
30	24.01	23.91	29.87	20.53	22.58	27.48	21.68	24.28	24.29	3.06
20	25.73	24.74	30.09	22.18	24.30	28.40	23.33	25.31	25.51	2.60
10	27.81	26.05	30.72	24.25	26.39	29.72	25.38	26.78	27.14	2.18
0	30.16	27.75	31.75	26.64	28.77	31.39	27.74	28.62	29.10	1.83
Anthocyanins → Acetone v/v % ↓	Cyanidin-3-glucoside (Cy-3-Glc)	Delphinidin-3-glucoside (Dp-3-Glc)	Malvidin-3-glucoside (Mv-3-Glc)	Pelargonidin-3-glucoside (Pg-3-Glc)	Peonidin-3-glucoside (Pn-3-Glc)	Petunidin-3-glucoside (Pt-3-Glc)	Average Std. Dev.			
100	30.71	35.33	26.48	31.42	26.68	30.12	30.12	3.29		
90	28.21	32.91	24.13	29.09	24.23	27.70	27.71	3.29		
80	25.97	30.73	22.11	27.02	22.09	25.56	25.58	3.25		
70	24.05	28.82	20.51	25.30	20.37	23.77	23.80	3.16		
60	22.54	27.25	19.45	23.98	19.16	22.40	22.46	3.01		
50	21.52	26.07	19.01	23.15	18.57	21.55	21.65	2.77		
40	21.07	25.35	19.24	22.85	18.65	21.27	21.41	2.45		
30	21.22	25.13	20.11	23.11	19.41	21.59	21.76	2.08		
20	21.96	25.41	21.54	23.91	20.77	22.48	22.68	1.70		
10	23.23	26.17	23.44	25.19	22.61	23.87	24.08	1.34		
0	24.95	27.39	25.69	26.89	24.83	25.69	25.91	1.03		

Data Hansen Solubility Parameters: Ethanol-Water Mixtures

Table B.22: Hansen solubility parameters for aqueous binary mixtures of ethanol.

Ethanol (v/v %)	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})
100	15.80	8.80	19.4
90	15.78	9.52	21.69
80	15.76	10.24	23.98
70	15.74	10.96	26.27
60	15.72	11.68	28.56
50	15.70	12.40	30.85
40	15.68	13.12	33.14
30	15.66	13.84	35.43
20	15.64	14.56	37.72
10	15.62	15.28	40.01
0	15.60	16.00	42.3

Table B.23: Distance R_a ($\text{MPa}^{1/2}$) between anthocyanidins or anthocyanins and aqueous binary mixtures of ethanol based on Hansen solubility parameters

Anthocyanidins → Ethanol v/v % ↓	Apigeninidin (Ap)	Cyanidin (Cy)	Delphinidin (Dp)	Luteolinidin (Lt)	Malvidin (Mv)	Pelargonidin (Pg)	Peonidin (Pn)	Petunidin (Pt)	Average	Std. Dev.
100	21.52	25.67	33.19	19.44	20.60	28.11	20.24	25.09	24.23	4.74
90	21.35	24.86	32.25	18.95	20.32	27.53	19.84	24.42	23.69	4.54
80	21.45	24.26	31.47	18.76	20.32	27.15	19.73	23.98	23.39	4.29
70	21.82	23.90	30.86	18.88	20.60	26.97	19.91	23.78	23.34	4.00
60	22.44	23.77	30.43	19.29	21.15	27.01	20.38	23.81	23.54	3.68
50	23.29	23.88	30.18	19.99	21.96	27.27	21.11	24.09	23.97	3.34
40	24.35	24.23	30.12	20.94	22.98	27.73	22.07	24.59	24.63	3.00
30	25.59	24.81	30.25	22.11	24.20	28.38	23.25	25.32	25.49	2.66
20	26.99	25.60	30.57	23.47	25.59	29.22	24.61	26.25	26.54	2.35
10	28.52	26.59	31.07	24.99	27.12	30.23	26.11	27.35	27.75	2.07
0	30.16	27.75	31.75	26.64	28.77	31.39	27.74	28.62	29.10	1.83
Anthocyanins → Ethanol v/v % ↓	Cyanidin-3-glucoside (Cy-3-Glc)	Delphinidin-3-glucoside (Dp-3-Glc)	Malvidin-3-glucoside (Mv-3-Glc)	Pelargonidin-3-glucoside (Pg-3-Glc)	Peonidin-3-glucoside (Pn-3-Glc)	Petunidin-3-glucoside (Pt-3-Glc)	Average Std. Dev.			
100	24.11	29.00	20.34	25.25	20.22	23.75	23.78	3.29		
90	23.10	27.93	19.66	24.38	19.44	22.85	22.89	3.16		
80	22.30	27.03	19.26	23.72	18.93	22.16	22.23	3.00		
70	21.74	26.32	19.15	23.29	18.71	21.72	21.82	2.80		
60	21.44	25.82	19.34	23.10	18.81	21.55	21.67	2.57		
50	21.40	25.53	19.82	23.16	19.20	21.64	21.79	2.31		
40	21.63	25.46	20.57	23.46	19.88	21.99	22.17	2.03		
30	22.12	25.62	21.57	24.01	20.82	22.59	22.79	1.75		
20	22.85	26.00	22.77	24.77	21.97	23.43	23.63	1.49		
10	23.80	26.60	24.16	25.74	23.32	24.47	24.68	1.24		
0	24.95	27.39	25.69	26.89	24.83	25.69	25.91	1.03		

Data Hansen Solubility Parameters: Methanol-Water Mixtures

Table B.24: Hansen solubility parameters for aqueous binary mixtures of methanol.

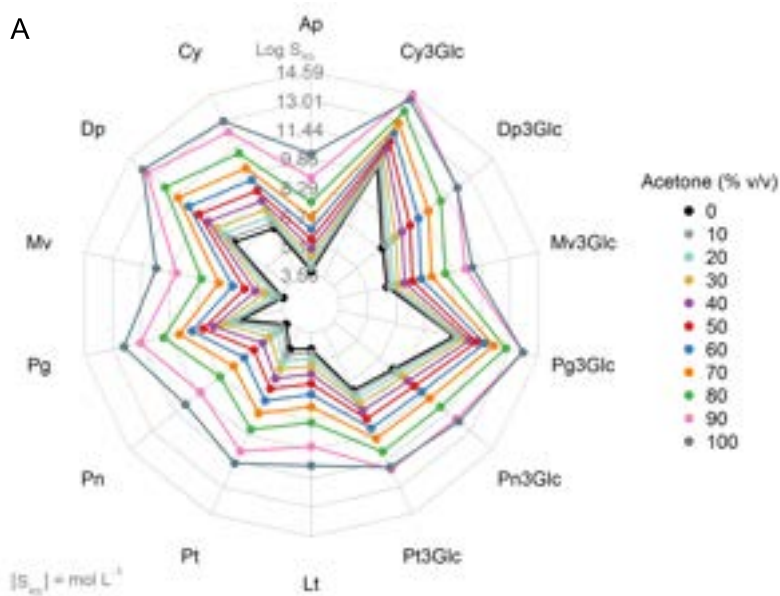
Methanol (v/v %)	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})
100	14.70	12.30	22.3
90	14.79	12.67	24.3
80	14.88	13.04	26.3
70	14.97	13.41	28.3
60	15.06	13.78	30.3
50	15.15	14.15	32.3
40	15.24	14.52	34.3
30	15.33	14.89	36.3
20	15.42	15.26	38.3
10	15.51	15.63	40.3
0	15.60	16.00	42.3

Table B.25: Distance R_a ($\text{MPa}^{1/2}$) between anthocyanidins or anthocyanins and aqueous binary mixtures of methanol based on Hansen solubility parameters

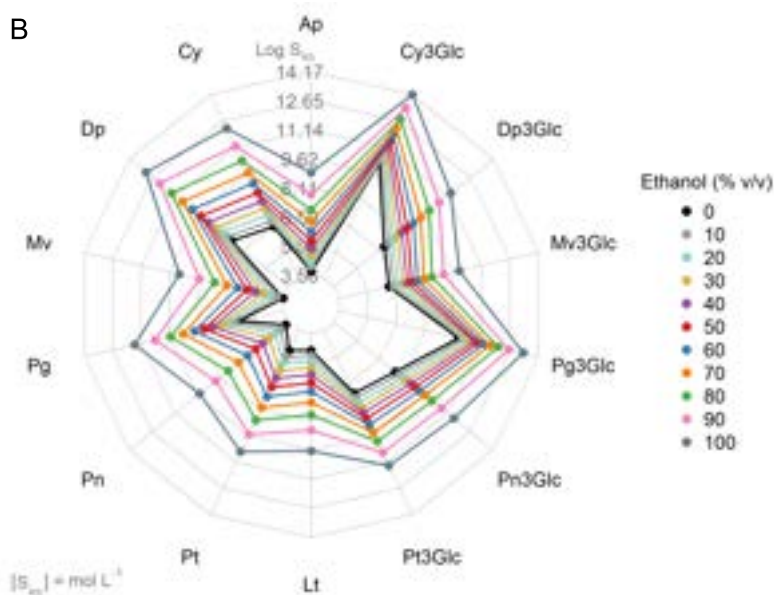
Anthocyanidins → Methanol v/v % ↓	Apigeninidin (Ap)	Cyanidin (Cy)	Delphinidin (Dp)	Luteolinidin (Lt)	Malvidin (Mv)	Pelargonidin (Pg)	Peonidin (Pn)	Petunidin (Pt)	Average	Std. Dev.
100	23.42	25.99	33.06	20.65	22.19	29.00	21.62	25.78	25.21	4.19
90	23.39	25.44	32.35	20.42	22.10	28.60	21.45	25.35	24.89	4.00
80	23.54	25.05	31.77	20.40	22.20	28.34	21.48	25.08	24.73	3.78
70	23.86	24.82	31.30	20.58	22.48	28.23	21.70	24.97	24.74	3.54
60	24.35	24.76	30.97	20.96	22.95	28.26	22.10	25.03	24.92	3.29
50	25.00	24.87	30.76	21.53	23.58	28.44	22.68	25.25	25.26	3.02
40	25.79	25.14	30.69	22.27	24.37	28.77	23.43	25.64	25.76	2.76
30	26.72	25.57	30.76	23.17	25.29	29.23	24.32	26.18	26.41	2.50
20	27.76	26.16	30.96	24.21	26.35	29.83	25.35	26.86	27.18	2.26
10	28.92	26.89	31.29	25.37	27.51	30.55	26.49	27.68	28.09	2.03
0	30.16	27.75	31.75	26.64	28.77	31.39	27.74	28.62	29.10	1.83
Anthocyanins → Methanol v/v % ↓	Cyanidin-3-glucoside (Cy-3-Glc)	Delphinidin-3-glucoside (Dp-3-Glc)	Malvidin-3-glucoside (Mv-3-Glc)	Pelargonidin-3-glucoside (Pg-3-Glc)	Peonidin-3-glucoside (Pn-3-Glc)	Petunidin-3-glucoside (Pt-3-Glc)	Average Std. Dev.			
100	23.85	28.50	20.97	25.37	20.62	23.78	23.85	2.92		
90	23.17	27.72	20.60	24.78	20.17	23.18	23.27	2.79		
80	22.65	27.07	20.42	24.35	19.92	22.75	22.86	2.63		
70	22.30	26.57	20.45	24.08	19.88	22.50	22.63	2.45		
60	22.14	26.22	20.68	23.99	20.04	22.43	22.58	2.26		
50	22.17	26.02	21.11	24.07	20.41	22.55	22.72	2.05		
40	22.38	25.98	21.72	24.32	20.98	22.85	23.04	1.83		
30	22.78	26.10	22.50	24.73	21.72	23.33	23.53	1.61		
20	23.35	26.38	23.44	25.31	22.62	23.97	24.18	1.40		
10	24.08	26.81	24.51	26.03	23.66	24.76	24.98	1.21		
0	24.95	27.39	25.69	26.89	24.83	25.69	25.91	1.03		

Data COSMO-RS: Binary Mixtures

A



B



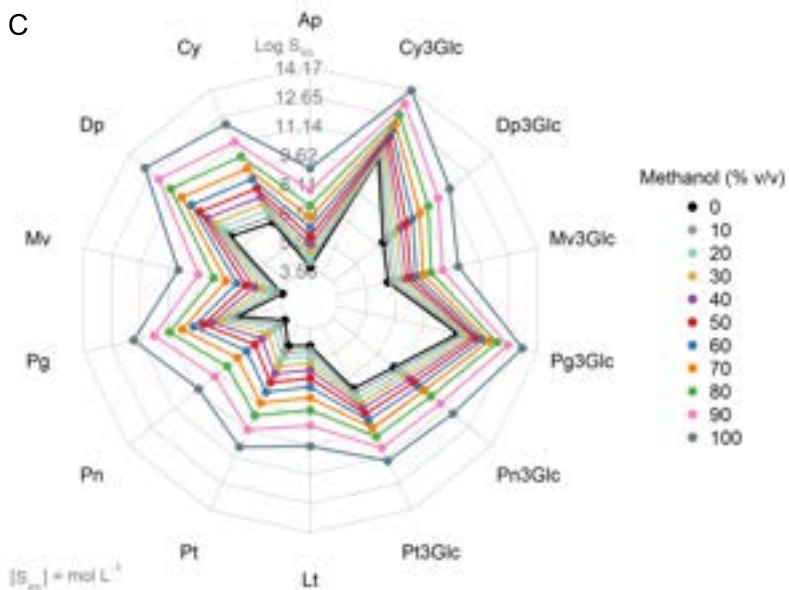


Figure B.8: Relative solubility values ($\text{Log } S_{RS}$) calculated with COSMO-RS for acetone-water (A), ethanol-water (B) and methanol-water (C) mixtures.

Data COSMO-RS: Acetone-Water Mixture

Table B.26: Relative solubility values $\log S_{RS}$ (with $S_{RS} = \text{mol L}^{-1}$) for anthocyanidins in acetone-water mixtures and pure acetone with respect to water from COSMO-RS.

Fraction acetone (% v/v)	Apigeninidin (Ap)	Cyanidin (Cy)	Delphinidin (Dp)	Luteolinidin (Lt)	Malvidin (Mv)	Pelargonidin (Pg)	Peonidin (Pn)	Petunidin (Pt)
0	3.746	6.549	7.360	4.429	3.556	5.890	3.734	4.697
10	3.957	6.846	7.688	4.663	3.835	6.164	4.031	5.021
20	4.231	7.215	8.092	4.964	4.180	6.508	4.398	5.416
30	4.576	7.662	8.579	5.337	4.599	6.928	4.840	5.891
40	4.993	8.187	9.146	5.786	5.099	7.423	5.360	6.448
50	5.482	8.784	9.787	6.306	5.686	7.990	5.959	7.085
60	6.037	9.438	10.480	6.889	6.355	8.618	6.628	7.789
70	6.674	10.156	11.225	7.547	7.120	9.316	7.377	8.567
80	7.524	11.057	12.136	8.410	8.094	10.207	8.324	9.528
90	8.823	12.328	13.375	9.699	9.475	11.493	9.662	10.843
100	10.117	12.978	13.675	10.752	10.601	12.412	10.717	11.578

Table B.27: Relative solubility values $\log S_{RS}$ (with $S_{RS} = \text{mol L}^{-1}$) for anthocyanins in acetone-water mixtures and pure acetone with respect to water from COSMO-RS.

Fraction acetone (% v/v)	Cyanidin-3-glucoside (Cy-3-Glc)	Delphinidin-3-glucoside (Dp-3-Glc)	Malvidin-3-glucoside (Mv-3-Glc)	Pelargonidin-3-glucoside (Pg-3-Glc)	Peonidin-3-glucoside (Pn-3-Glc)	Petunidin-3-glucoside (Pt-3-Glc)
0	10.216	6.893	6.186	9.903	7.636	7.171
10	10.397	7.134	6.347	10.039	7.813	7.384
20	10.634	7.437	6.555	10.226	8.038	7.653
30	10.937	7.811	6.822	10.473	8.324	7.989
40	11.313	8.267	7.162	10.788	8.679	8.402
50	11.765	8.806	7.583	11.172	9.110	8.895
60	12.280	9.416	8.084	11.615	9.610	9.457
70	12.856	10.095	8.672	12.119	10.182	10.086
80	13.586	10.943	9.440	12.781	10.920	10.871
90	14.590	12.099	10.550	13.755	11.983	11.937
100	14.285	12.102	10.926	13.757	12.202	11.808

Data COSMO-RS: Ethanol-Water Mixture

Table B.28: Relative solubility values $\log S_{RS}$ (with $S_{RS} = \text{mol L}^{-1}$) for anthocyanidins in ethanol-water mixtures and pure ethanol with respect to water from COSMO-RS.

Fraction ethanol (% v/v)	Apigeninidin (Ap)	Cyanidin (Cy)	Delphinidin (Dp)	Luteolinidin (Lt)	Malvidin (Mv)	Pelargonidin (Pg)	Peonidin (Pn)	Petunidin (Pt)
0	3.746	6.549	7.360	4.429	3.556	5.890	3.734	4.697
10	4.006	6.866	7.695	4.701	3.890	6.195	4.075	5.055
20	4.293	7.215	8.063	5.001	4.246	6.532	4.445	5.441
30	4.610	7.599	8.467	5.332	4.624	6.903	4.843	5.858
40	4.962	8.023	8.915	5.699	5.032	7.312	5.277	6.312
50	5.357	8.499	9.417	6.112	5.476	7.770	5.754	6.812
60	5.809	9.039	9.985	6.584	5.974	8.291	6.288	7.371
70	6.337	9.656	10.629	7.134	6.544	8.887	6.894	8.003
80	6.966	10.361	11.348	7.780	7.211	9.576	7.589	8.718
90	7.762	11.186	12.153	8.578	8.028	10.403	8.416	9.544
100	8.897	12.217	13.073	9.664	9.109	11.497	9.487	10.548

Table B.29: Relative solubility values $\log S_{RS}$ (with $S_{RS} = \text{mol L}^{-1}$) for anthocyanins in ethanol-water mixtures and pure ethanol with respect to water from COSMO-RS.

Fraction ethanol (% v/v)	Cyanidin-3-glucoside (Cy-3-Glc)	Delphinidin-3-glucoside (Dp-3-Glc)	Malvidin-3-glucoside (Mv-3-Glc)	Pelargonidin-3-glucoside (Pg-3-Glc)	Peonidin-3-glucoside (Pn-3-Glc)	Petunidin-3-glucoside (Pt-3-Glc)
0	10.216	6.893	6.186	9.903	7.636	7.171
10	10.447	7.171	6.430	10.101	7.887	7.440
20	10.686	7.460	6.672	10.305	8.141	7.717
30	10.935	7.763	6.915	10.516	8.398	8.003
40	11.202	8.087	7.160	10.738	8.662	8.304
50	11.497	8.445	7.419	10.981	8.943	8.631
60	11.838	8.853	7.708	11.260	9.257	9.000
70	12.248	9.333	8.055	11.598	9.628	9.434
80	12.752	9.899	8.495	12.024	10.086	9.953
90	13.387	10.573	9.094	12.594	10.693	10.591
100	14.167	11.340	9.938	13.390	11.538	11.355

Data COSMO-RS: Methanol-Water Mixture

Table B.30: Relative solubility values $\log S_{RS}$ (with $S_{RS} = \text{mol L}^{-1}$) for anthocyanidins in methanol-water mixtures and pure methanol with respect to water from COSMO-RS.

Fraction methanol (% v/v)	Apigeninidin (Ap)	Cyanidin (Cy)	Delphinidin (Dp)	Luteolinidin (Lt)	Malvidin (Mv)	Pelargonidin (Pg)	Peonidin (Pn)	Petunidin (Pt)
0	3.746	6.549	7.360	4.429	3.556	5.890	3.734	4.697
10	4.007	6.872	7.704	4.705	3.879	6.198	4.071	5.054
20	4.309	7.240	8.095	5.023	4.241	6.551	4.452	5.454
30	4.655	7.656	8.536	5.386	4.643	6.950	4.877	5.900
40	5.047	8.120	9.026	5.796	5.088	7.396	5.346	6.393
50	5.485	8.633	9.568	6.254	5.578	7.890	5.863	6.934
60	5.972	9.193	10.156	6.760	6.116	8.431	6.427	7.522
70	6.504	9.791	10.779	7.311	6.700	9.011	7.034	8.151
80	7.078	10.410	11.412	7.897	7.324	9.617	7.671	8.805
90	7.703	11.044	12.042	8.524	7.989	10.249	8.342	9.477
100	8.436	11.724	12.688	9.242	8.726	10.946	9.080	10.192

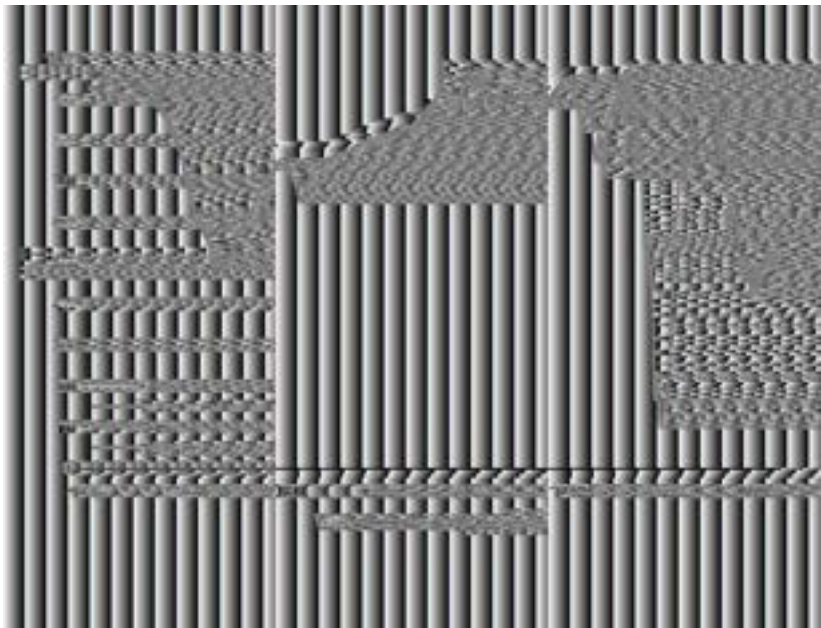
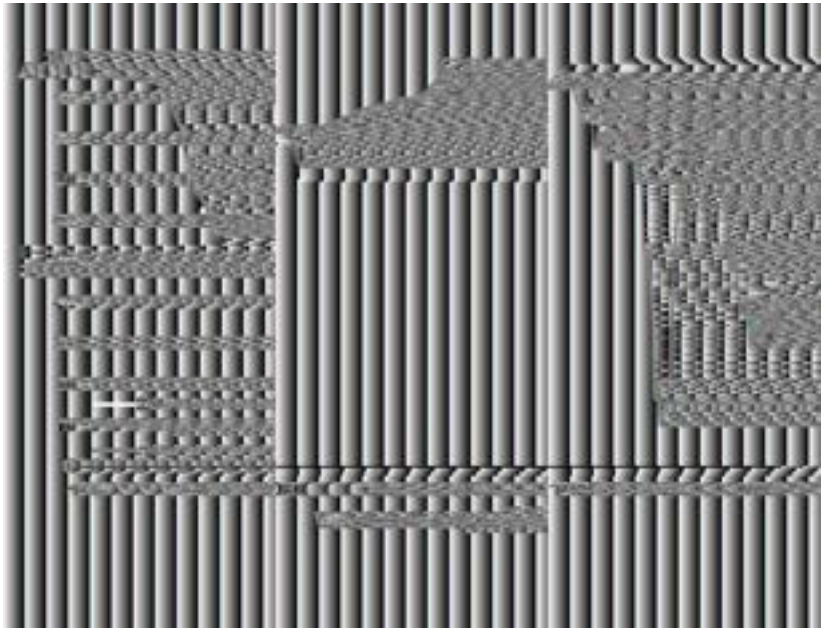
Table B.31: Relative solubility values $\log S_{RS}$ (with $S_{RS} = \text{mol L}^{-1}$) for anthocyanins in methanol-water mixtures and pure methanol with respect to water from COSMO-RS.

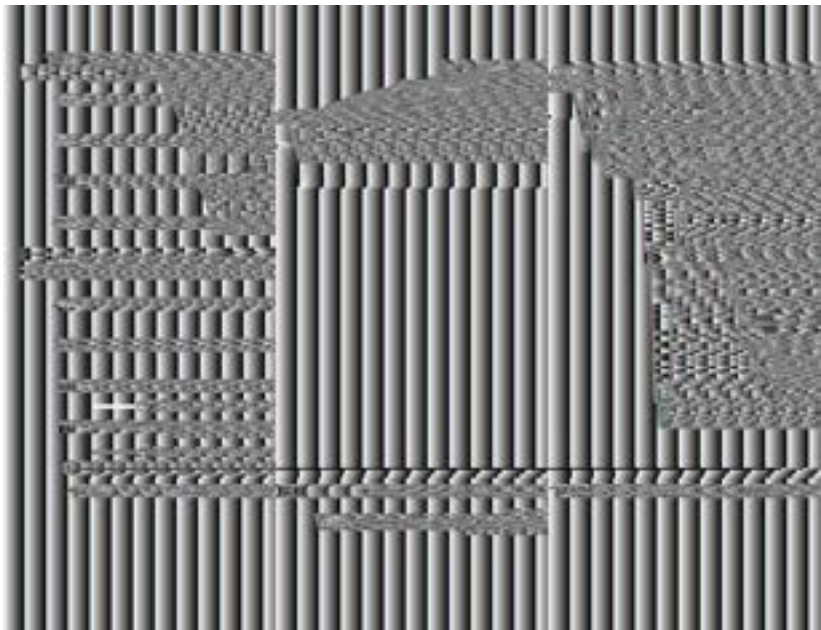
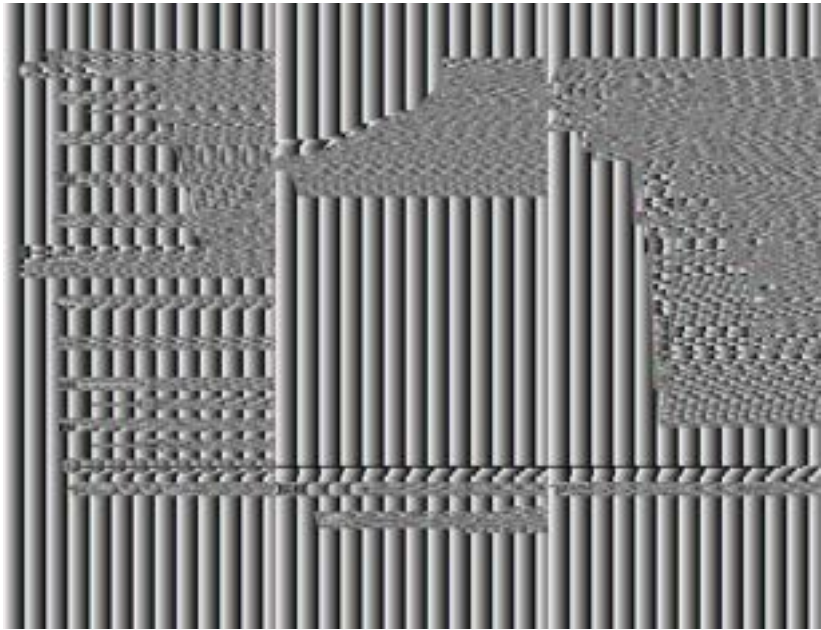
Fraction methanol (% v/v)	Cyanidin-3-glucoside (Cy-3-Glc)	Delphinidin-3-glucoside (Dp-3-Glc)	Malvidin-3-glucoside (Mv-3-Glc)	Pelargonidin-3-glucoside (Pg-3-Glc)	Peonidin-3-glucoside (Pn-3-Glc)	Petunidin-3-glucoside (Pt-3-Glc)
0	10.216	6.893	6.186	9.903	7.636	7.171
10	10.456	7.178	6.427	10.108	7.888	7.447
20	10.726	7.495	6.691	10.341	8.165	7.752
30	11.030	7.849	6.982	10.603	8.470	8.091
40	11.370	8.245	7.302	10.898	8.807	8.467
50	11.752	8.686	7.658	11.230	9.179	8.884
60	12.181	9.178	8.057	11.602	9.593	9.348
70	12.653	9.716	8.502	12.013	10.051	9.856
80	13.157	10.285	8.992	12.456	10.545	10.397
90	13.681	10.871	9.526	12.924	11.078	10.960
100	14.226	11.475	10.121	13.435	11.668	11.548

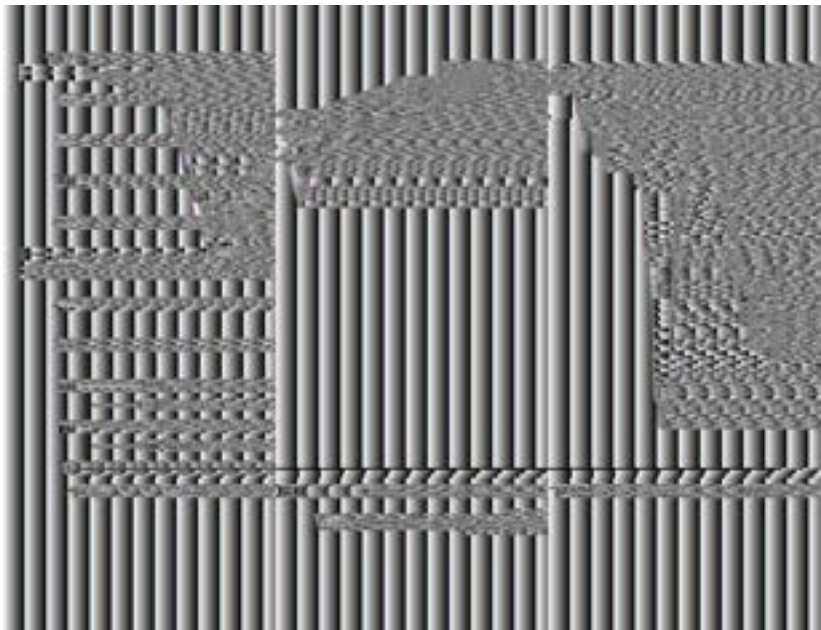
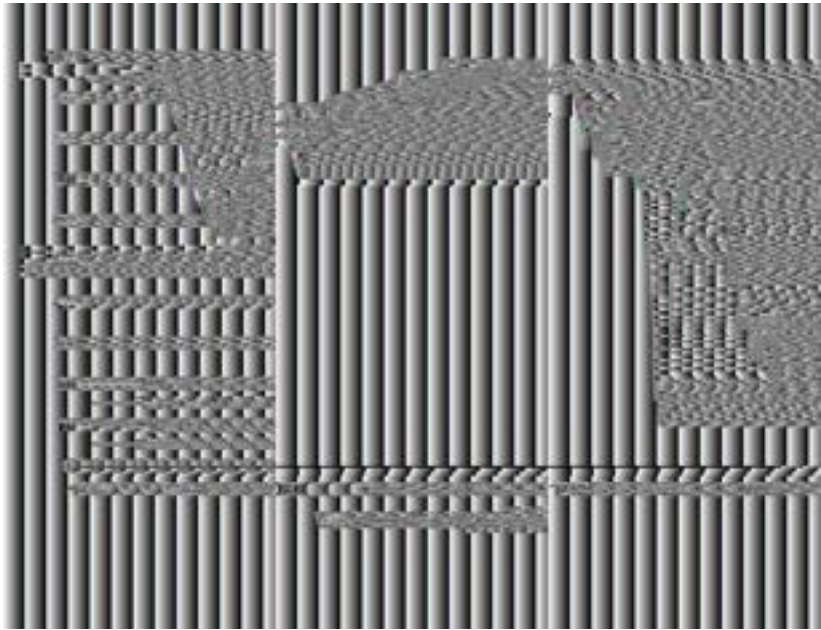


The Potential of Anthocyanins from Blueberries as a Natural Dye for Cotton: a Combined Experimental and Theoretical Study

Infrared Spectra of Premordanted, Dyed and Washed Cotton Samples







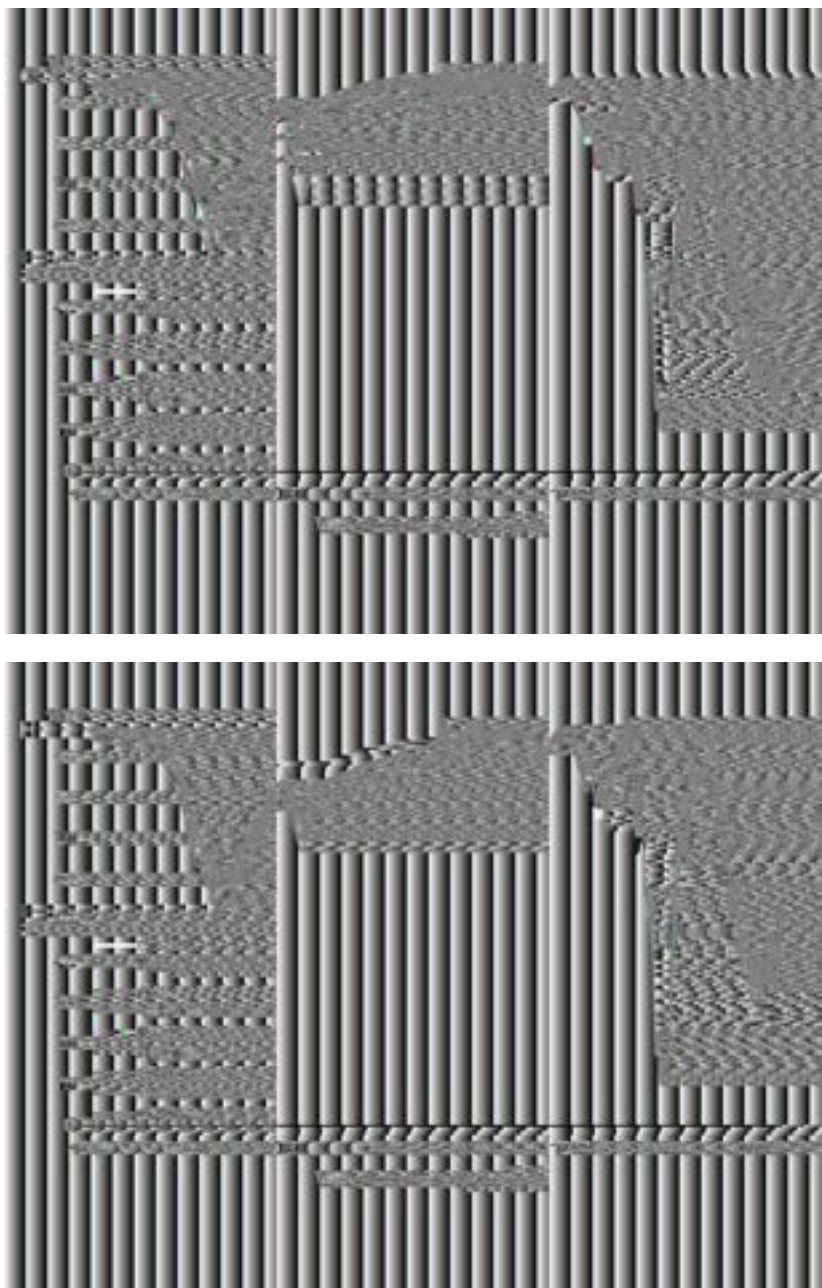
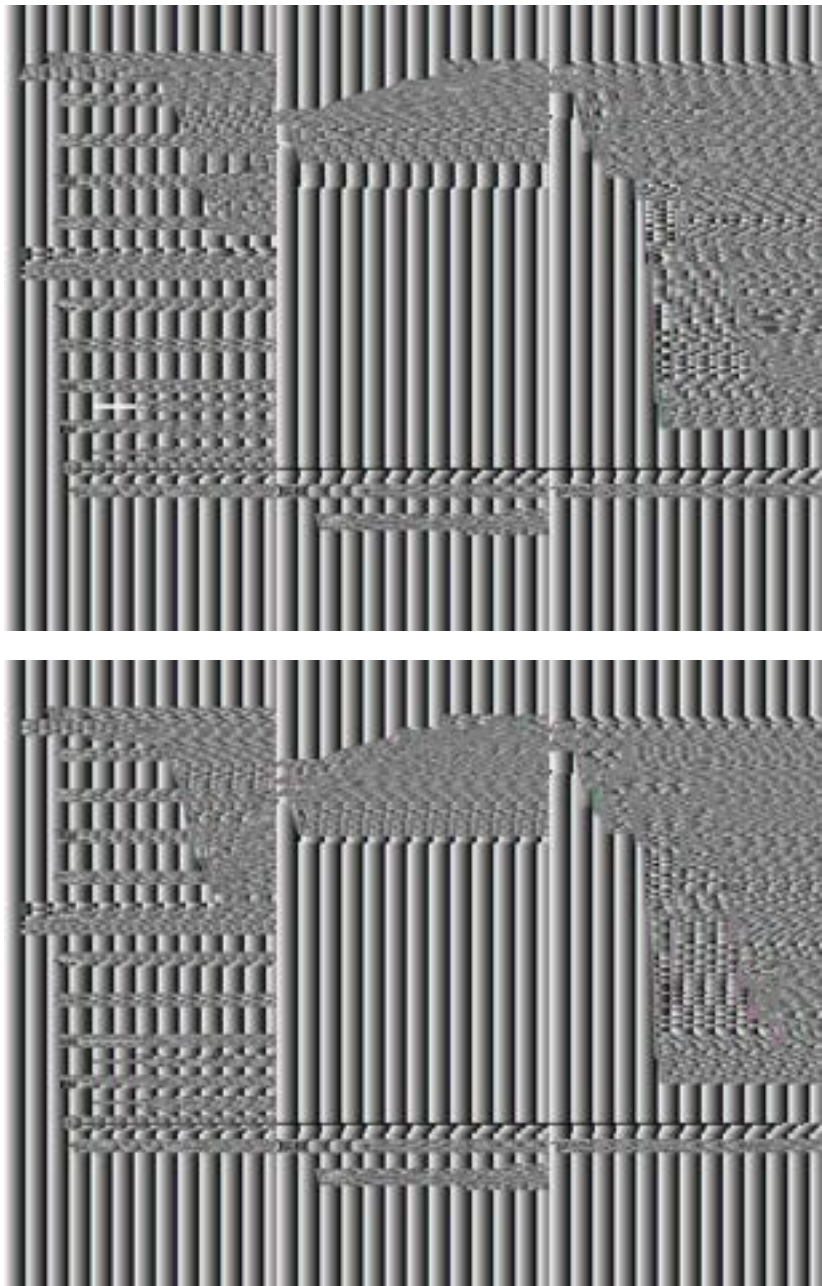
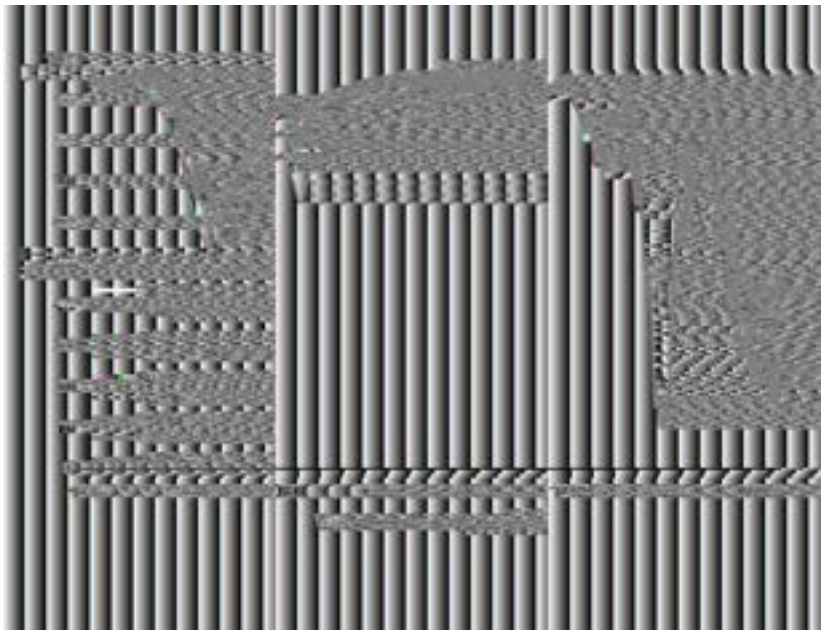
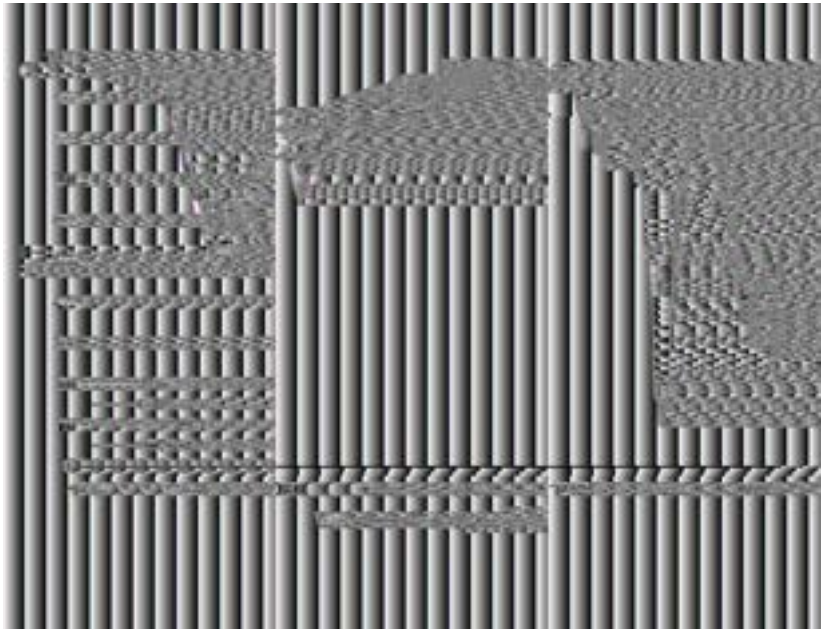


Figure C.1: The FT-IR spectra of premordanted (A-C), dyed premordanted (D-F) and washed (G: ISO105-C06 and H: ISO105-E01) cotton samples.

Infrared Spectra of Metamordanted and Washed Cotton Samples





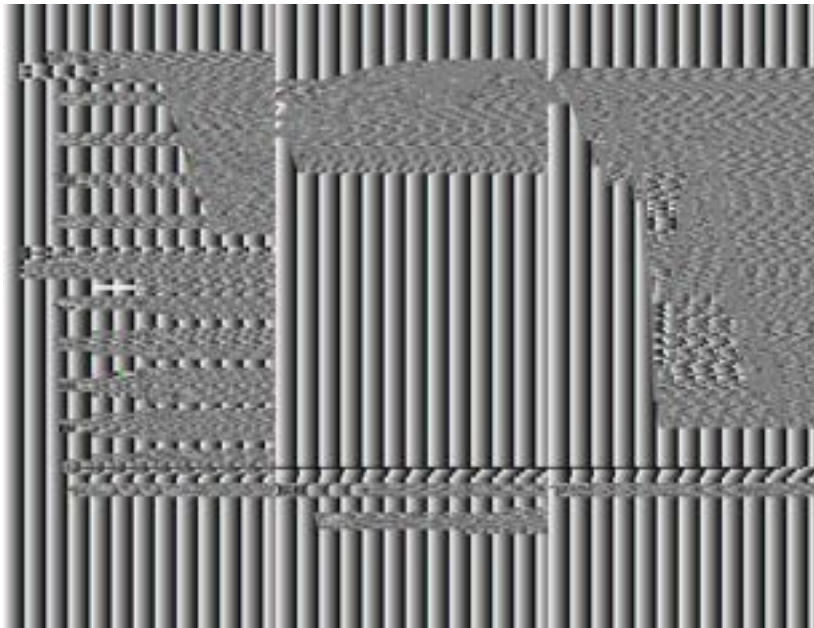


Figure C.2: The FT-IR spectra of premordanted (A-C), dyed premordanted (D-F) and washed (G: ISO105-C06 and H: ISO105-E01) cotton samples.

Degradation Factor

The dyeing experiments were accompanied with a blank dyebath, i.e., a dyeing beaker containing only the dye extract, thus without cotton fabric. Through the adsorption kinetic experiment specifically, the dye uptake, but also the degradation could be monitored over time. To include the degradation factor, the exhaustion level of the blank dyebath ($E_b\%$) was determined by means of Equations (C.1) and (C.2):

$$\text{Anthocyanin concentration} \left(\frac{\text{mg}}{\text{L}} \right) = \frac{A \cdot MW \cdot DF \cdot 1000}{\varepsilon \cdot b} \quad (\text{C.1})$$

with absorbance $A = (A_{\lambda_{\max}} - A_{700 \text{ nm}})_{\text{pH}=1.0} - (A_{\lambda_{\max}} - A_{700 \text{ nm}})_{\text{pH}=4.5}$, $\lambda_{\max}$ at 519 nm and the measurement at $\lambda = 700 \text{ nm}$ corrects for the haze within the solution,

$$E_b\% = \frac{(C_0 - C_{e,b})}{C_0} \cdot 100 \quad (\text{C.2})$$

in which, C_0 and $C_{e,b}$ define the initial and equilibrium dye concentrations (mg Mv-3-Glc equiv L^{-1}) of the blank dyebath, respectively. Thereafter, the same quantities were calculated of the dyebath containing the fabric. The only additional factor compared to the blank is the dye uptake into the fabric. Therefore, Equation (C.4) of the manuscript is applied to calculate the equilibrium adsorption capacity ($q_{e,s}$):

$$E_s\% = \frac{(C_0 - C_{e,s})}{C_0} \cdot 100 \quad (\text{C.3})$$

$$q_{e,s} = (C_0 - C_{e,s}) \cdot \frac{V_{\text{solution}}}{m_{\text{fabric}}} \quad (\text{C.4})$$

in which, C_0 and $C_{e,s}$, define the initial dyebath concentration and the equilibrium dye concentration (mg Mv-3-Glc equiv L^{-1}) of the dyebath with fabric, respectively, $q_{e,s}$ represents the amount of adsorbate per unit mass of adsorbent (mg Mv-3-Glc (g cotton) $^{-1}$), V , the volume of the dyebath (L) and m , the mass of the fabric (g). Now the amount of degradation is quantified as $E_b\%$, the effective exhaustion level, $E_{s,\text{rel}}$, and amount of dye taken up by the fabric ($q_{e,s,\text{rel}}$) can be calculated by the following equations. These relative exhaustion and dye uptake values are applied in Figures 3.2A, 3.2B and Table 3.3 of the manuscript. The importance of taking degradation into account is shown in Figure C.3.

$$E_{s,\text{rel}} = (1 - E_b\%) \cdot E_s\% \quad (\text{C.5})$$

$$q_{e,s,rel} = (1 - E_b\%) \cdot q_{e,s}\% \quad (C.6)$$

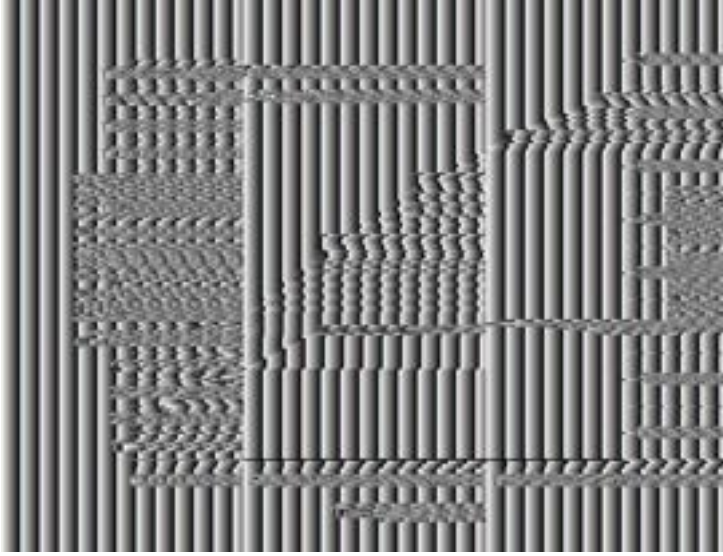


Figure C.3: The dye uptake and degradation of the dye extract as a function of time. The dye uptake corrected for degradation is given by the solid black line, the uncorrected dye uptake is represented by the dotted black line and keeps mounting over time. However, when the degradation factor is included, the corrected dye uptake hits an equilibrium, which can obviously be ascribed to the complete saturation of the fabric.

**The Colorimetric Values and Color Strength of Cotton
Samples at Different Temperatures**

Table C.1: Colorimetric values and color strength of fabrics dyed at different temperatures (uncertainties expressed as standard deviation (n = 3). Furthermore, the percentage of degradation is also described for each temperature.

T (°C)	Blank		After dyeing					After washing ISO105 C06					K/S	ΔE	Samples	
	Degr. (%)	L*	a*	b*	C*	h*	K/S	Samples	L*	a*	b*	C*				h*
30	-1.0 ± 1.8	43.2 ± 0.6	36.2 ± 0.2	0.2 ± 0.6	36.2 ± 0.2	0.8 ± 0.0	2.7 ± 0.1		79.0 ± 0.2	1.2 ± 0.1	1.5 ± 0.2	2.0 ± 0.1	51.7 ± 6.2	0.2 ± 0.0	50.1 ± 0.7	
	8.7 ± 3.1	45.9 ± 0.1	34.9 ± 0.1	-2.0 ± 0.1	34.9 ± 0.1	356.8 ± 0.1	2.1 ± 0.0		77.7 ± 0.2	1.4 ± 0.2	0.2 ± 0.3	1.5 ± 0.2	8.5 ± 8.7	0.2 ± 0.0	46.2 ± 0.3	
40	-1.3 ± 1.6	45.2 ± 0.8	34.2 ± 0.2	-2.2 ± 0.6	34.2 ± 0.1	356.4 ± 1.0	2.2 ± 0.1		77.7 ± 0.4	1.6 ± 0.1	2.2 ± 0.1	2.7 ± 0.1	53.4 ± 0.6	0.2 ± 0.0	46.2 ± 0.3	
	-3.7 ± 0.8	45.4 ± 0.9	33.7 ± 0.5	-3.0 ± 0.4	33.8 ± 0.4	354.9 ± 1.1	2.2 ± 0.2		76.7 ± 0.0	1.3 ± 0.1	0.2 ± 0.1	1.3 ± 0.1	7.4 ± 4.9	0.2 ± 0.0	45.1 ± 1.0	
70	5.6 ± 0.4	46.4 ± 0.7	31.8 ± 0.4	-3.8 ± 0.4	32.0 ± 0.3	353.2 ± 0.8	2.0 ± 0.1		74.1 ± 0.2	-0.6 ± 0.3	0.6 ± 0.5	0.9 ± 0.5	142.3 ± 17.9	0.3 ± 0.0	42.9 ± 0.3	
	34.2 ± 2.3	46.5 ± 0.2	28.2 ± 0.2	-4.5 ± 0.1	28.5 ± 0.2	350.9 ± 0.1	2.0 ± 0.0		70.8 ± 0.3	0.5 ± 0.0	0.5 ± 0.2	0.7 ± 0.1	46.0 ± 8.0	0.4 ± 0.0	37.2 ± 0.5	
90	68.9 ± 0.3	50.9 ± 0.4	21.1 ± 0.5	-2.4 ± 0.0	21.3 ± 0.5	353.5 ± 0.1	1.6 ± 0.0		67.7 ± 0.3	3.3 ± 0.1	3.9 ± 0.1	5.1 ± 0.0	49.2 ± 0.9	0.5 ± 0.0	25.3 ± 0.7	
	94.3 ± 0.1	55.6 ± 0.6	11.5 ± 0.1	7.3 ± 0.7	13.6 ± 0.3	32.3 ± 2.5	1.4 ± 0.1		64.1 ± 0.6	6.6 ± 0.1	6.9 ± 0.2	9.5 ± 0.1	46 ± 0.6	0.7 ± 0.0	9.9 ± 1.1	

Half-life Value of Blueberry Extract

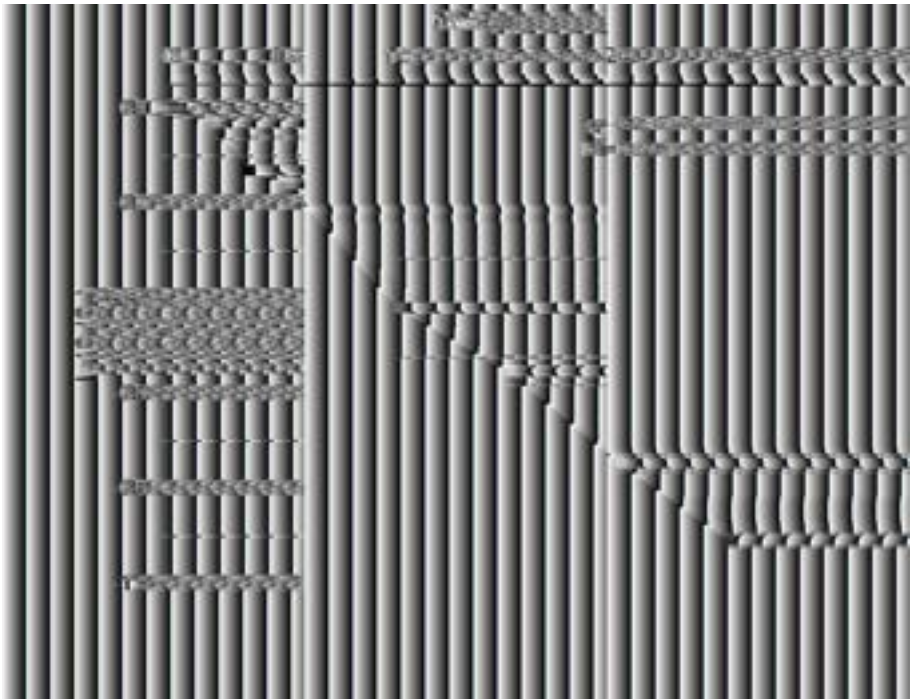


Figure C.4: The degradation of anthocyanins in the blueberry extract at pH 1.47 and 80 °C.

FT-IR on Esterification

In order to validate the effectiveness of ester bond formation, the premordanting procedure for the esterification of oxalic acid was performed as described in section 3.2.1.5, followed by an additional rinse step with grade 3 water and identical M:L ratio. Figure C.5 illustrates that the rinse step reduces the amount of ester bonds, but they still remain on the cotton fabric.

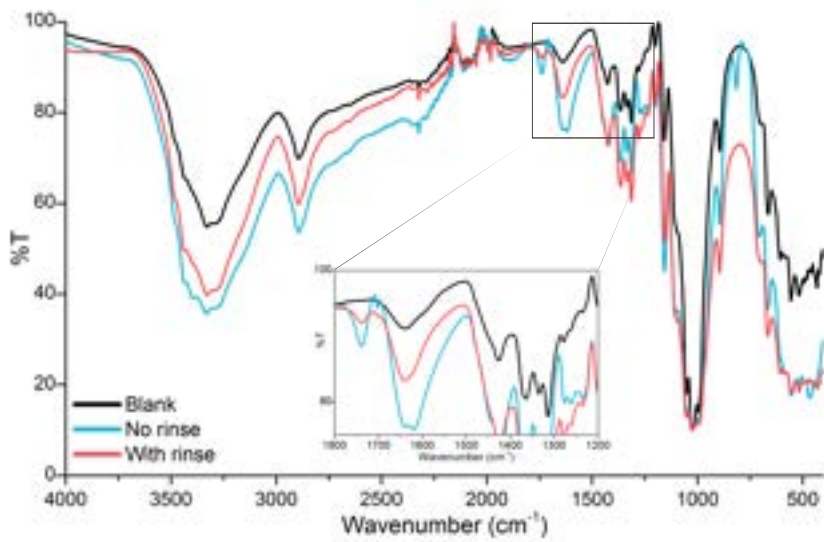


Figure C.5: The infrared spectra of blank cotton and premordanted oxalic acid with and without rinse.

UV-VIS Absorption Spectra

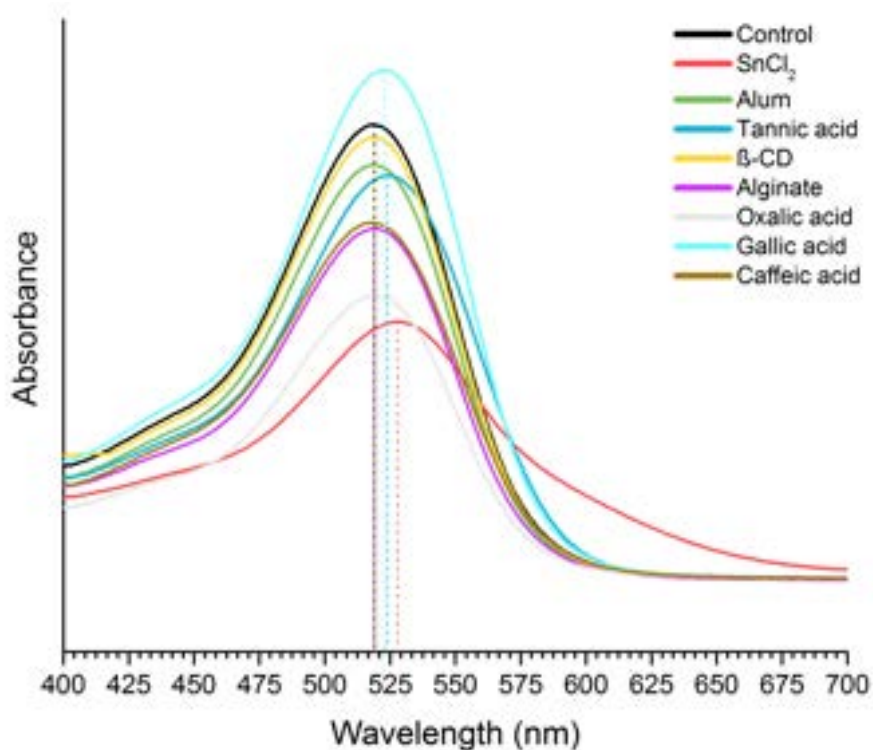


Figure C.6: A cutout from the UV-VIS absorption spectra of the dyebaths according to the metamordanting procedure (see section 3.2.1.5). The maximum absorption wavelengths (λ_{max}) are 519 nm for the control, alum, β -cyclodextrin, sodium alginate and caffeic acid dyebaths; 528 nm for the SnCl_2 dyebath; 524 nm for the tannic acid dyebath; 523 nm for the gallic acid dyebath and 521 nm for the oxalic acid dyebath.

Molecular Modeling of Dye-Mordants Interaction

Static Calculations

Geometrical Optimization

Since the natural dye is the main molecule of interest, a conformational and charge analysis of Mv-3-Glc was performed, the latter described below (Table C.2). The main noticeable observations are the B-ring, which is slightly out of AC plane with a dihedral angle $\varphi_{(O1-C2-C1'-C6')}$ of 158.1° , the methoxy group at C3'-position that has a bond angle $\theta_{(C3'-O-CH_3)}$ of 115.4° and the glucose moiety with a dihedral angle of $\varphi_{(C4-C3-O-C1'')}$ of 95.9° relative to the AC plane (Figure C.10). The hydroxyl groups within the glucose moiety were also analyzed for intramolecular hydrogen bonding [542]. Furthermore, the anionic quinoidal bases of cyanidin, delphinidin and petunidin were optimized (Figure C.7), which were applied within metal-dye coordination complexes. The dihedral angles $\varphi_{(O1-C2-C1'-C6')}$ were 171.8° , 173.3° and 168.5° , and $\varphi_{(C4-C3-O-C1'')}$ were 115.7° , 116° and 116° , respectively. There were also intramolecular H-bonds observed for delphinidin between C5'-OH and C2''-OH and between O3 and C6'-H [287]. These anionic quinoidal bases were applied for static metal complexation calculations, which is described in section 3.3.4.1.

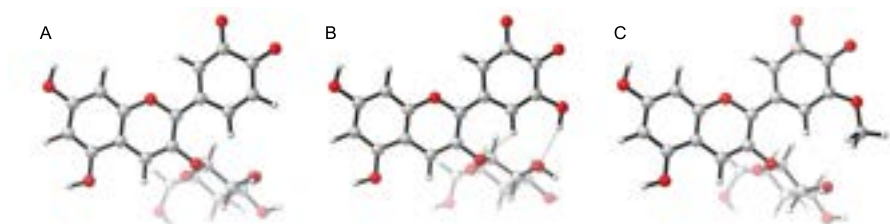


Figure C.7: The molecular structures of anthocyanins that are able to form coordination complexes with tin and aluminium: cyanidin-3-glucoside (A), delphinidin-3-glucoside (B) and petunidin-3-glucoside (C) (B3LYP/6-311++G(d,p) with PCM (water) and Grimme dispersion).

Metal-Ligand Complexes with Delphinidin-3-glucoside and Petunidin-3-glucoside

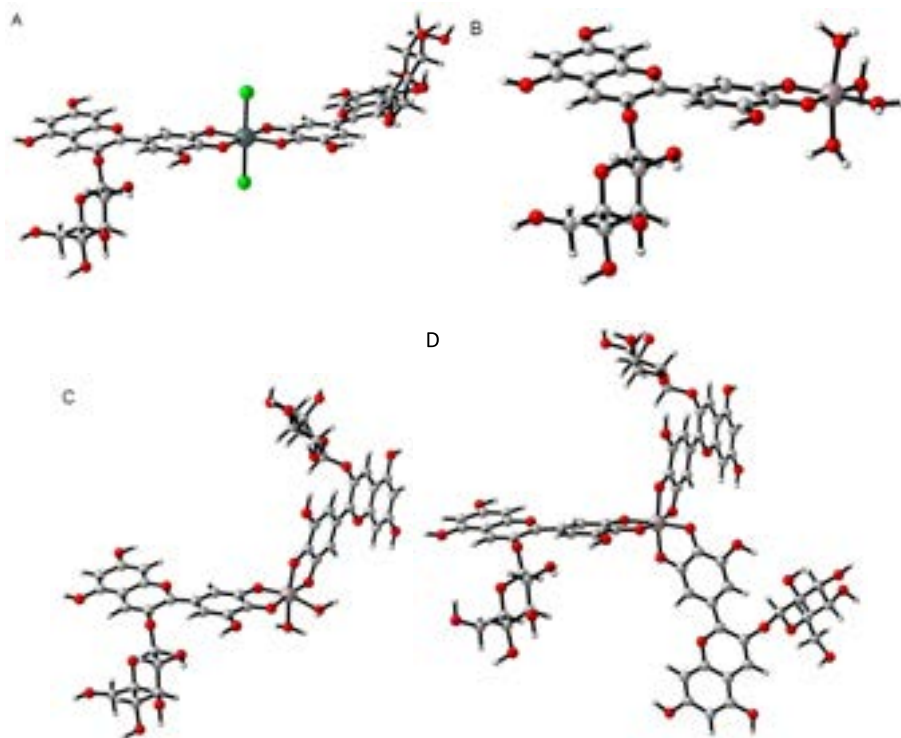


Figure C.8: The 3D illustrations of tin and aluminium coordination complexes with delphinidin-3-glucoside: $\text{Sn}(\text{Dp}-3-\text{Glc})_2\text{Cl}_2$ (A), $[\text{Al}(\text{Dp}-3-\text{Glc})(\text{H}_2\text{O})_4]_2^+$ (B), $[\text{Al}(\text{Dp}-3-\text{Glc})_2(\text{H}_2\text{O})_2]^+$ (C) and $\text{Al}(\text{Dp}-3-\text{Glc})_3$ (D) (B3LYP/DEF2TZVPP with PCM (water) and Grimme dispersion).

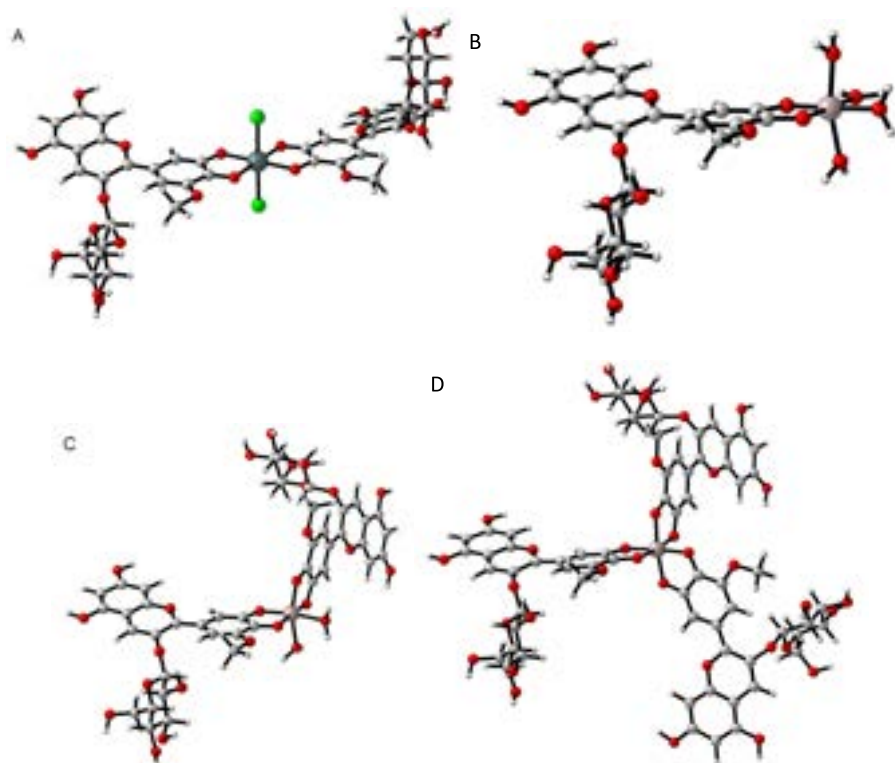


Figure C.9: The 3D illustrations of tin and aluminium coordination complexes with petunidin-3-glucoside: $\text{Sn}(\text{Pt}-3-\text{Glc})_2\text{Cl}_2$ (A), $[\text{Al}(\text{Pt}-3-\text{Glc})(\text{H}_2\text{O})_4]_2^+$ (B), $[\text{Al}(\text{Pt}-3-\text{Glc})_2(\text{H}_2\text{O})_2]^+$ (C) and $\text{Al}(\text{Pt}-3-\text{Glc})_3$ (D) (B3LYP/DEF2TZVPP with PCM (water) and Grimme dispersion).

Charge and Population Analyses of Mv-3-glc, Hydrogen Oxalate and the Flavylum Cation

This section describes the charge and population analysis of Mv-3-Glc, hydrogen oxalate and the flavylum cation without any substituents. The partial charges and atomic populations of the first two compounds are displayed in Table C.3. It shows that the partial charge of the pyrylium oxygen is less negative than the other oxygen atoms present within the dye, which indicates the delocalization of the positive charge throughout the aglycon. To eliminate the influence of substituents, partial charges and atomic populations of the flavylum cation were also generated (Table C.3), which showed similar values for the C2-O1-C9 region (Figure C.11). From the partial charges obtained, Figures C.12C and C.12D are more realistic resonance structures within the model compared to Figure C.12A. Estévez and Mosquera [284] applied the QTAIM scheme on the flavylum cation and obtained a slightly negative C2-O1-C9 region. This can be assigned to the different translation of atomic weight function, also called stockholder, within the schemes. The atomic weight function varies smoothly between 0 and 1 within Hirshfeld variants, while for QTAIM, this function equals to 1 inside the atomic basin and 0 elsewhere [320].

Table C.2: Hirshfeld I (HI) and Minimal Basis Iterative Stockholder charges (MBIS) and atomic populations of Mv-3-Glc and hydrogen oxalate (B3LYP/6-311++G(d,p) + GD3 + water (PCM)). The indices of the atoms are displayed in Figure C.6.

Mv-3-glc						Hydrogen oxalate					
		Charges		Atomic population (a.u.)				Charges		Atomic population (a.u.)	
Labels	Atom	HI	MBIS	HI	MBIS	Labels	Atom	HI	MBIS	HI	MBIS
1	C	0.57	0.57	5.43	5.43	1	C	0.69	0.63	5.31	5.37
2	C	-0.47	-0.52	6.47	6.52	2	C	0.69	0.63	5.31	5.37
3	C	0.51	0.48	5.49	5.52	3	O	-0.67	-0.65	8.67	8.65
4	C	-0.22	-0.21	6.22	6.21	4	O	-0.62	-0.60	8.62	8.60
5	C	-0.51	-0.56	6.51	6.56	5	O	-0.77	-0.77	8.77	8.77
6	C	0.43	0.45	5.57	5.55	6	O	-0.76	-0.73	8.76	8.73
7	H	0.19	0.23	0.81	0.77	7	H	0.44	0.49	0.56	0.51
8	H	0.49	0.50	0.51	0.50						
9	O	-0.60	-0.59	8.60	8.59						
10	H	0.19	0.23	0.81	0.77						
11	O	-0.62	-0.59	8.62	8.59						
12	H	0.50	0.50	0.50	0.50						
13	C	-0.03	-0.05	6.03	6.05						
14	H	0.17	0.20	0.83	0.80						
15	O	-0.18	-0.20	8.18	8.20						
16	C	0.33	0.30	5.67	5.70						
17	C	0.18	0.13	5.82	5.87						
18	O	-0.36	-0.35	8.36	8.35						
19	C	0.42	0.39	5.58	5.61						
20	C	0.09	-0.01	5.91	6.01						
21	C	0.17	0.11	5.83	5.89						
22	C	0.17	0.11	5.83	5.89						
23	H	0.09	0.12	0.91	0.88						
24	O	-0.42	-0.39	8.42	8.39						
25	C	0.14	0.08	5.86	5.92						
26	H	0.07	0.10	0.93	0.90						
27	C	0.08	0.03	5.92	5.97						
28	H	0.10	0.12	0.90	0.88						
29	H	0.09	0.10	0.91	0.90						
30	O	-0.67	-0.66	8.67	8.66						
31	H	0.44	0.46	0.56	0.54						
32	H	0.03	0.07	0.97	0.93						
33	O	-0.66	-0.63	8.66	8.63						
34	H	0.46	0.47	0.54	0.53						
35	H	0.07	0.10	0.93	0.90						
36	O	-0.68	-0.67	8.68	8.67						
37	H	0.45	0.47	0.55	0.53						
38	H	0.07	0.09	0.93	0.91						
39	O	-0.68	-0.66	8.68	8.66						
40	H	0.45	0.47	0.55	0.53						
41	C	-0.02	-0.02	6.02	6.02						
42	C	-0.28	-0.29	6.28	6.29						
43	C	-0.25	-0.26	6.25	6.26						
44	H	0.14	0.19	0.86	0.81						
45	C	0.24	0.23	5.76	5.77						
46	O	-0.32	-0.34	8.32	8.34						
47	C	-0.10	-0.12	6.10	6.12						
48	H	0.11	0.13	0.89	0.87						
49	H	0.09	0.10	0.91	0.90						
50	H	0.10	0.11	0.90	0.89						
51	C	0.24	0.17	5.76	5.83						
52	O	-0.58	-0.54	8.58	8.54						
53	H	0.46	0.48	0.54	0.52						
54	C	0.24	0.22	5.76	5.78						
55	H	0.14	0.19	0.86	0.81						
56	H	0.11	0.11	0.89	0.89						
57	O	-0.28	-0.33	8.28	8.33						
58	C	-0.11	-0.12	6.11	6.12						
59	H	0.11	0.13	0.89	0.87						
60	H	0.12	0.13	0.88	0.87						

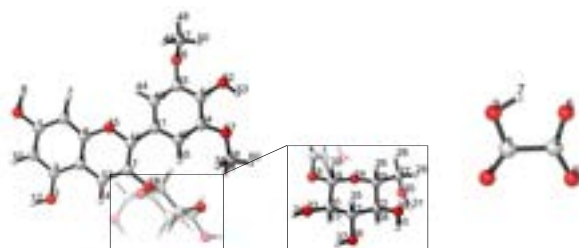


Figure C.10: The atomic labels of Mv-3-Glc (left) and hydrogen oxalate (right) for Table C.2.

Table C.3: Hirshfeld I (HI) and Minimal Basis Iterative Stockholder charges (MBIS) and atomic populations of the flavylum cation (B3LYP/6-311++G(d,p) + GD3 + water (PCM)).

Labels	Atom	Flavylum cation			
		Charges		Atomic population	
		HI	MBIS	HI	MBIS
1	C	0.00	-0.02	6.00	6.02
2	C	-0.25	-0.29	6.25	6.29
3	C	0.36	0.37	5.64	5.63
4	C	-0.06	-0.07	6.06	6.07
5	C	-0.07	-0.10	6.07	6.10
6	C	-0.10	-0.15	6.10	6.15
7	H	-0.19	-0.21	8.19	8.21
8	H	0.08	0.06	5.92	5.94
9	O	0.47	0.46	5.53	5.54
10	H	-0.09	-0.10	6.09	6.10
11	O	-0.07	-0.09	6.07	6.09
12	H	-0.10	-0.15	6.10	6.15
13	C	-0.03	-0.06	6.03	6.06
14	H	-0.06	-0.08	6.06	6.08
15	O	-0.11	-0.16	6.11	6.16
16	C	0.12	0.15	0.88	0.85
17	C	0.12	0.16	0.88	0.84
18	O	0.12	0.16	0.88	0.84
19	C	0.13	0.16	0.87	0.84
20	C	0.13	0.15	0.87	0.85
21	C	0.16	0.20	0.84	0.80
22	C	0.13	0.16	0.87	0.84
23	H	0.13	0.17	0.87	0.83
24	O	0.14	0.17	0.86	0.83
25	C	0.16	0.17	0.84	0.83
26	H	-0.30	-0.31	6.30	6.31
27	C	0.18	0.21	0.82	0.79

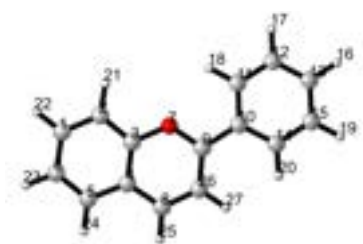


Figure C.11: The atomic labels of the flavylum cation for Table S3.

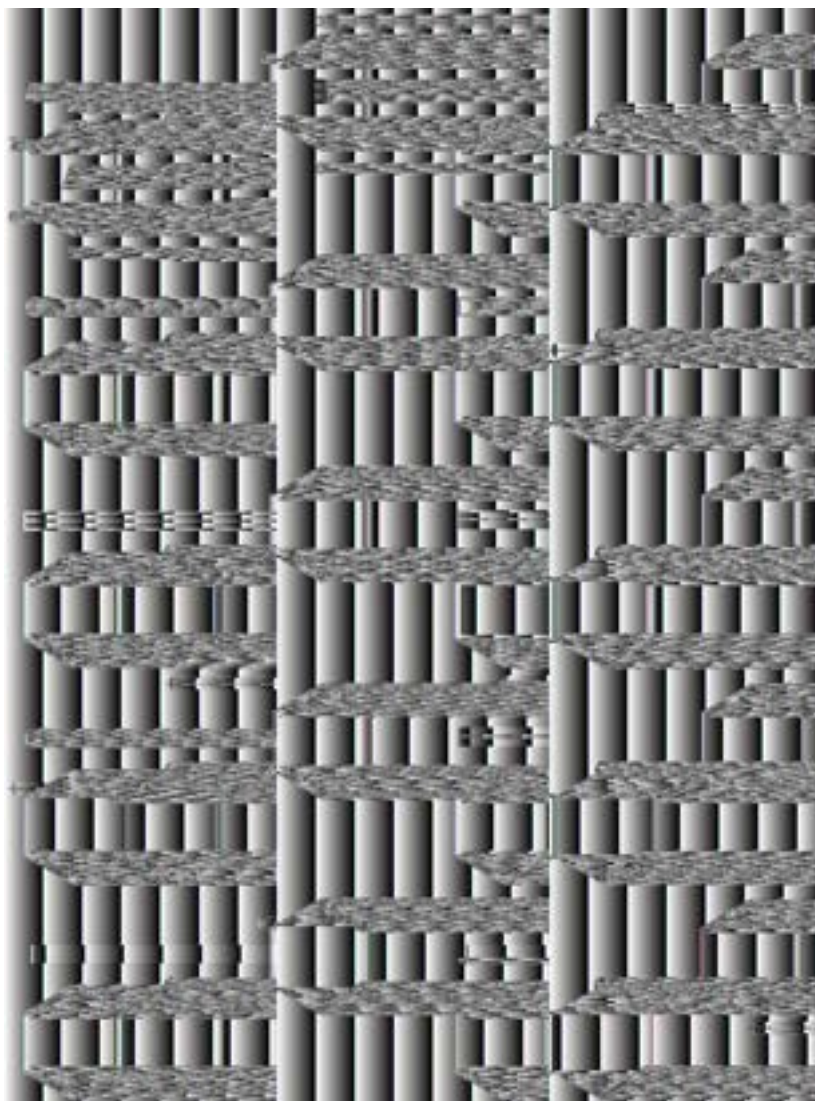


Figure C.12: The possible resonance structures of the flavylum cation.

Molecular Complexes from Static Calculations between Mv-3-glc and Hydrogen Oxalate

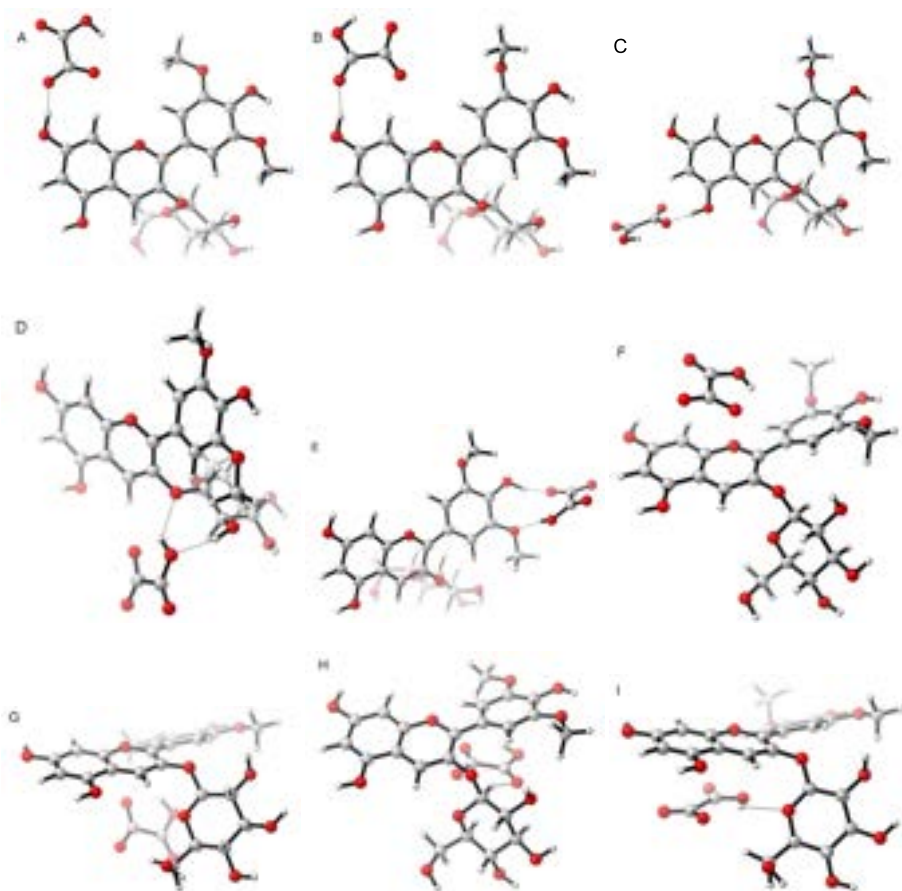


Figure C.13: The resulted conformations between Mv-3-Glc and hydrogen oxalate (B3LYP/6-311++G(d,p)) with GD3 and PCM).

Absolute Energies of the Static Calculations

Table C.4: Absolute energies of the calculated molecular structures.

Conformation	Free energies ^a (hartree)	Sum of electronic and thermal energies (hartree)	BSSE (hartree)	Figures
Static calculations				
Mv-3-Glc ^b	-1794.16458	-1794.06347		
Cy-3-glc anion ^c	-1639.63025	-1639.54093		Figure C.7A
Dp-3-glc anion ^c	-1714.88673	-1714.79501		Figure C.7B
Pt-3-glc anion ^c	-1754.17470	-1754.08007		Figure C.7C
Metal-ligand complexation ^c				
Sn(IV)Cl ₂	-1134.40382	-1134.37275		
Sn(cy-3-glc) ₂ Cl ₂	-4414.03453	-4413.86300	0.00669	Figure 3.6A
Sn(dp-3-glc) ₂ Cl ₂	-4564.54626	-4564.36969	0.00666	Figure C.8A
Sn(pt-3-glc) ₂ Cl ₂	-4643.12273	-4642.93880	0.00662	Figure C.9A
Al(H ₂ O) ₆ ³⁺	-700.89272	-700.83973	0.01199	
H ₂ O	-76.46992	-76.44944		
[Al(cy-3-glc)(H ₂ O) ₄] ₂ ⁺	-2187.69495	-2187.58412	0.01133	Figure 3.6B
[Al(dp-3-glc)(H ₂ O) ₄] ₂ ⁺	-2262.95167	-2262.83815	0.01134	Figure C.8B
[Al(pt-3-glc)(H ₂ O) ₄] ₂ ⁺	-2302.23794	-2302.12202	0.01129	Figure C.9B
[Al(cy-3-glc) ₂ (H ₂ O) ₂] ₂ ⁺	-3674.47169	-3674.30126	0.01020	Figure 3.6C
[Al(dp-3-glc) ₂ (H ₂ O) ₂] ₂ ⁺	-3824.98260	-3824.80907	0.01021	Figure C.8C
[Al(pt-3-glc) ₂ (H ₂ O) ₂] ₂ ⁺	-3903.55723	-3903.37711	0.01013	Figure C.9C
Al(cy-3-glc) ₃	-5161.22171	-5160.99527	0.00889	Figure 3.6D
Al(dp-3-glc) ₃	-5386.99288	-5386.76157	0.00876	Figure C.8D
Al(pt-3-glc) ₃	-5504.85140	-5504.61085	0.00879	Figure C.9D
Biomordant ^b				
Hydrogen oxalate	-378.02032	-377.98613		
	-2172.19316	-2172.07415	0.00148	Figure C.13A
	-2172.18535	-2172.06483	0.00127	Figure C.13B
	-2172.19006	-2172.07000	0.00161	Figure C.13C
	-2172.17872	-2172.06104	0.00262	Figure C.13D
	-2172.18134	-2172.06367	0.00219	Figure C.13E
	-2172.17932	-2172.05873	0.00333	Figure C.13F
	-2172.18172	-2172.06606	0.00399	Figure C.13G
	-2172.18331	-2172.06786	0.00419	Figure C.13H
	-2172.17986	-2172.06203	0.00406	Figure C.13I
Mv-3-Glc & hydrogen oxalate				

^a: Free energies at 298.15 K, ^b: B3LYP/6-311++G(d,p) + GD3 + PCM,

^c: B3LYP/DEF2TZVPP + GD3 + PCM

Molecular Dynamics Simulations between Tannic Acid, Dye Molecules and Solvent

Concentration Effect of the Molecular Dynamics Simulations between Tannic Acid and Multiple Mv-3-glc Molecules

The intermolecular behavior between tannic acid and Mv-3-Glc in an aqueous environment were investigated by molecular dynamics simulation. The simulation between one tannic acid and one dye molecule and its results were thoroughly described in section 3.3.4.2. In addition to that, two optional molecular dynamics simulations were performed between tannic acid and two and three Mv-3-Glc molecules. The details of the molecular dynamics simulations are displayed in Table C.5. The concentration of tannic acid and Mv-3-Glc were calculated on the basis of the properties used for the simulations, and it shows that the simulation containing one tannic acid and one dye molecule is a fair approximation of the experimental concentrations in which tannic acid is in excess compared to Mv-3-Glc. The other simulation boxes resulted in an equal or excess dye concentration relatively to tannic acid.

Table C.5: Molecular Dynamics details of the three simulation boxes containing tannic acid (TAN) and 1, 2 or 3 dye molecules (Mv-3-Glc).

	1 TAN and 1 dye	1 TAN and 2 dyes	1 TAN and 3 dyes	Experimental
Box dimensions (Å)	53 × 53 × 53	73 × 73 × 73	93 × 93 × 93	
Number of water molecules	4892	14422	31879	
Total simulation time (ns)	2294.5	344.0	169.3	
Concentration water (mol L ⁻¹)	54.58	61.58	65.84	
Concentration tannic acid (g L ⁻¹)	10.50	4.02	1.94	25
Concentration Mv-3-Glc (g L ⁻¹)	5.51	4.21	3.06	0.5

Figure C.14 illustrates the interaction behavior between tannic acid and two dyes in terms of shortest distance as a function of simulation time. Within the first nanoseconds of the simulation, tannic acid has already formed a first π - π interaction with one of the dye molecules (dye 1). At a simulation time of 125 ns, tannic acid was able to undergo a second π - π interaction with the second dye molecule (dye 2). The two dye molecules are very close to one another. In the course of the simulation, the distance of tannic acid and dye 2 has increased, while the distance between the two dyes was reduced. This indicated that two molecular geometries emerge during this simulation: one whereby tannic acid was sandwiched between two dye molecules (Figure C.14.1) and the other whereby tannic acid is positioned outside of the complex with the two dyes next to each other (Figure C.14.2). The 3D illustrations were also provided by Figure C.15. It was also noticed that the occurrence of a hydrogen bond for some functional groups of tannic acid and the A- or B-ring of the dye has been reduced by more than a factor of 2 (Figure C.16). This could be ascribed to the larger π - π complex and the higher rate of π - π overlap between the compounds in comparison to the single tannic acid and dye complex.

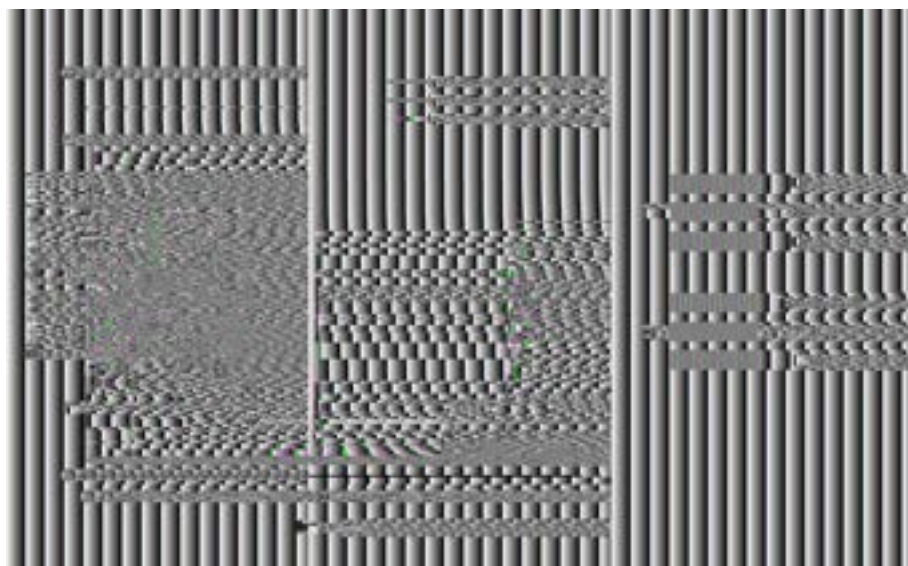


Figure C.14: The visualisation of π - π interactions between tannic acid and two dye molecules in terms of shortest distance as a function of time. The two occurring π - π stacking conformations are illustrated on the right.

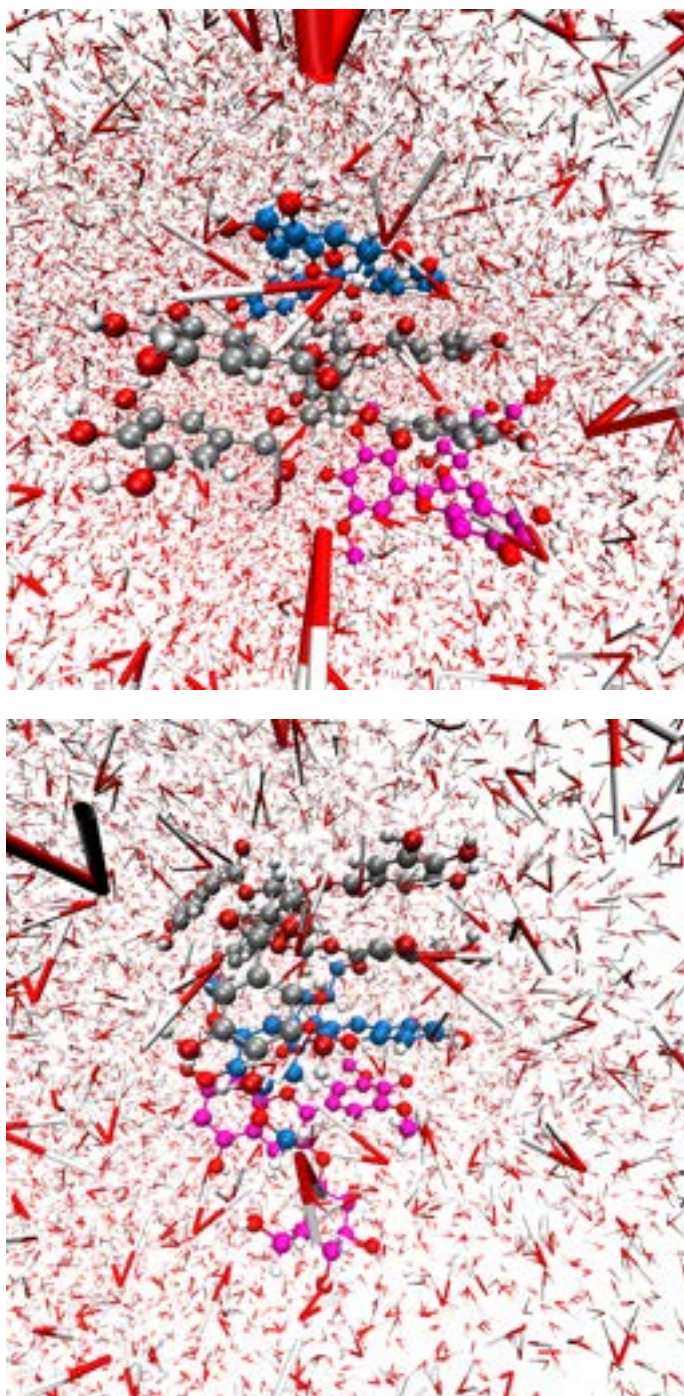


Figure C.15: The 3D illustrations of two molecular geometries observed during the molecular dynamics simulation between tannic acid (silver) and two Mv-3-Glc molecules (magenta and blue).

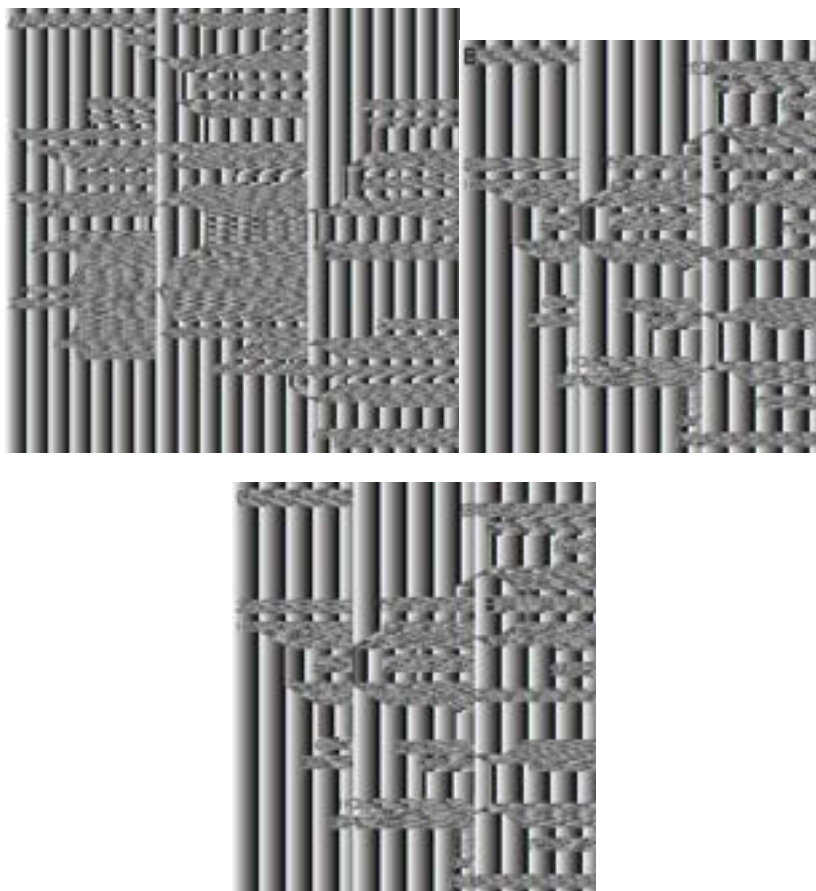


Figure C.16: The time-averaged probability that a functional group of tannic acid (A), Mv-3-Glc (dye 1, B) or Mv-3-Glc (dye 2, C) forms a hydrogen bond interaction within the molecular dynamics simulation between tannic acid and two dye molecules.

Due to tannic acid's flexibility, a simulation with three dyes was also studied. Figure C.17A illustrates the interaction pattern between tannic acid and three Mv-3-Glc molecules in terms of shortest distance as a function of simulation time. The other figure (Figure C.17B) represents the relative position between the dye molecules. The first 25 ns indicated only one π - π interaction between tannic acid and Mv-3-Glc (dye 2). Thereafter, a second (dye 3) and third dye (dye 1) molecule joined the complex (Figure C.18). However, the complexation with three dye molecules is not favorable, with the result that dye 3 has left the complex. The following stages of the simulation displayed that most of the time, tannic acid is interacting with only one or two dye molecules. The geometries of the π - π stacking complexes between tannic acid and two dye molecules are identical as described above (Figure C.19). Therefore, the probability of hydrogen bonding did not alter greatly from the simulation with two dye molecules (Figure C.20). In conclusion, these molecular dynamics simulations also demonstrate that the main intermolecular interactions between tannic acid and Mv-3-Glc are π - π interactions rather than hydrogen bonds, although the concentrations of the compounds used within these optional simulations are overestimated compared to the experimental conditions.

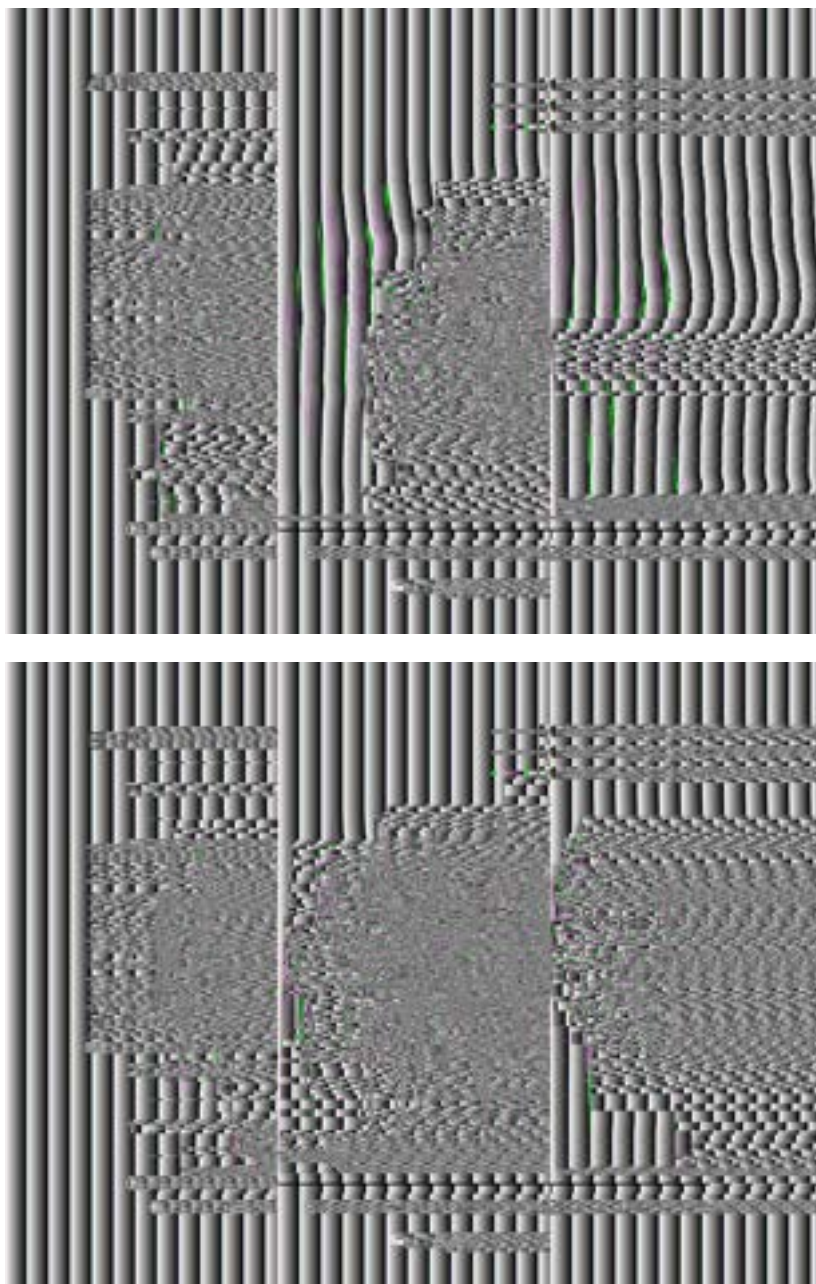


Figure C.17: The visualisation of π - π interactions between tannic acid and three dye molecules (A) and the relative position of the dyes (B) in terms of shortest distance as a function of time.

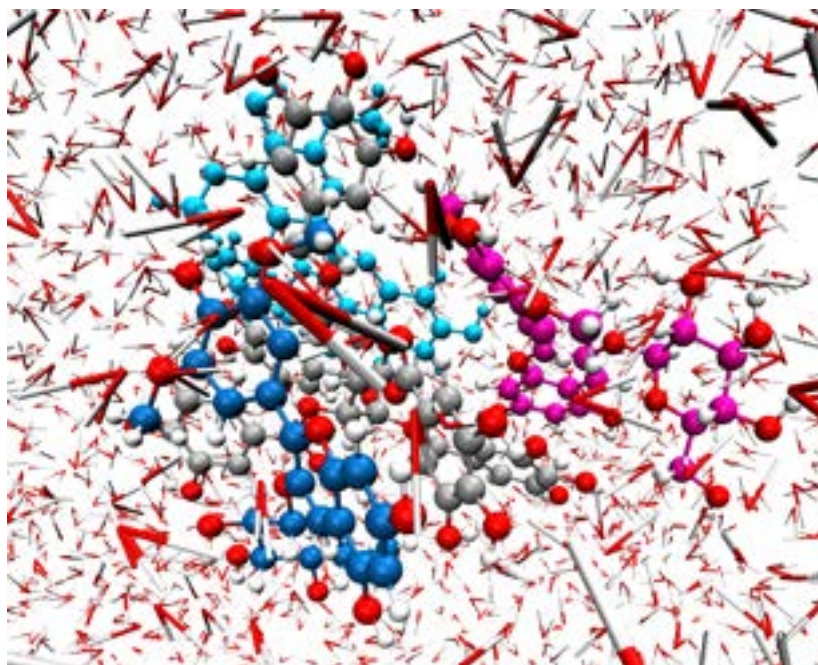


Figure C.18: A snapshot of the short-living π - π complex consisting of tannic acid (silver) and three dye molecules (magenta, blue and cyan).

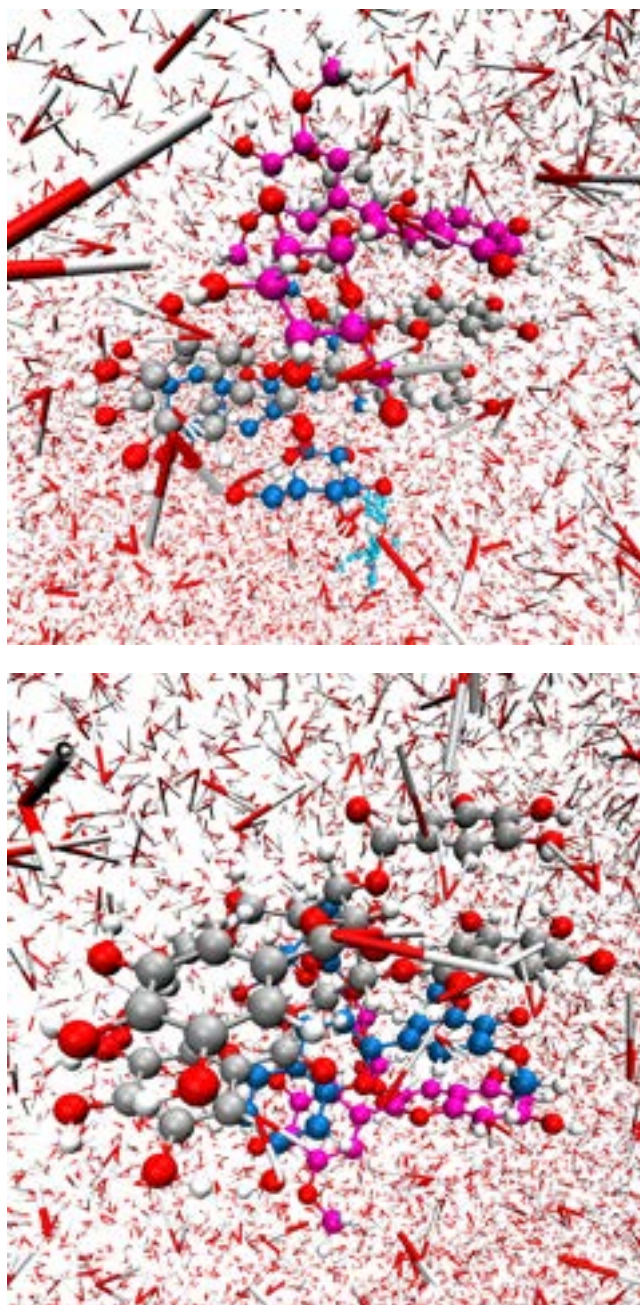


Figure C.19: The 3D illustrations of the similar π - π stacking complexes between tannic acid (silver) and two Mv-3-Glc molecules (magenta and blue), while the third dye molecule (cyan) diffused away from the complex.

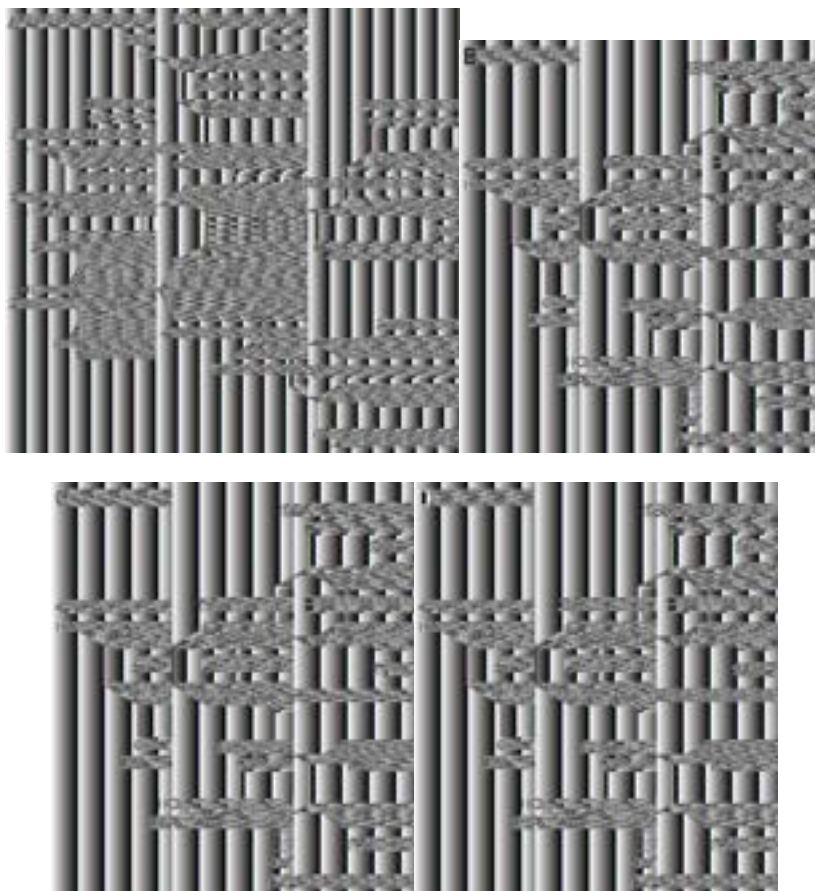
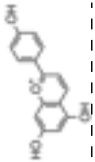
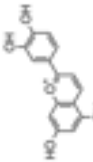
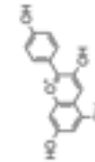
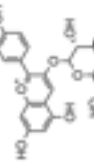
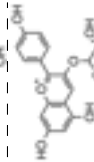
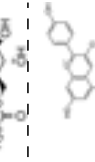


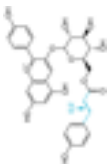
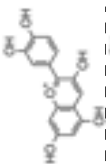
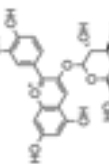
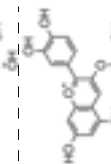
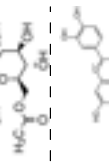
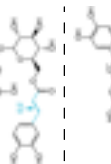
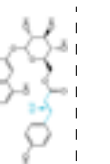
Figure C.20: The time-averaged probability that a functional group of tannic acid (A), Mv-3-Glc (dye 1, B), Mv-3-Glc (dye 2, C) or Mv-3-Glc (dye 3, D) forms a hydrogen bond interaction within the molecular dynamics simulation between tannic acid and three dye molecules.

A Comparative Study on the Photophysical Properties of Anthocyanins and Pyranoanthocyanins

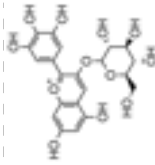
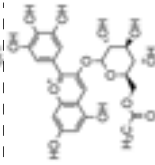
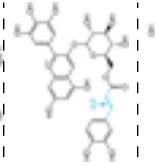
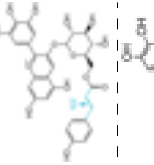
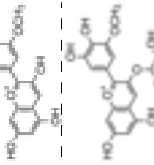
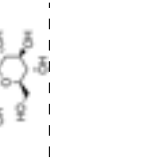
**Chemical Structures of the Studied Anthocyanin-Based
Compounds**

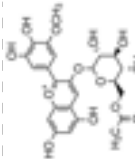
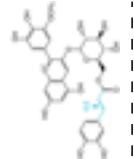
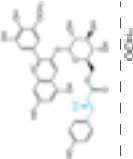
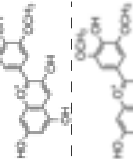
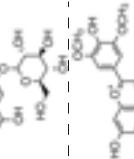
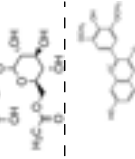
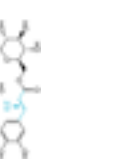
Table D.1: The chemical structures of the different anthocyanin-based compounds. The compounds are categorized by family. The substitution pattern is based on Figure 4.1.

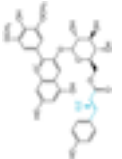
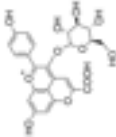
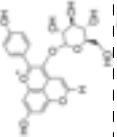
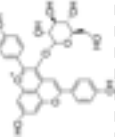
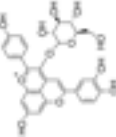
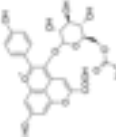
Label	Anthocyanins	Name	R ₁	R ₂	R ₃	R ₄	Chemical structure
1		Apigeninidin (Ap)	H	H	OH	H	
2		Luteolinidin (Lt)	OH	OH	OH	H	
3		Pelargonidin (Pg)	H	H	OH	H	
9		Pg-3-glucoside	H	H	OH	H	
15		Pg-acetylglucoside	H	H	OH	H	
21		Pg-3-(6-(Z)-caffeoyl)-glucoside	H	H	OH	H	

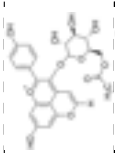
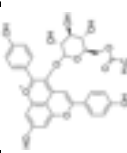
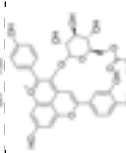
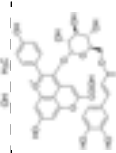
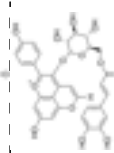
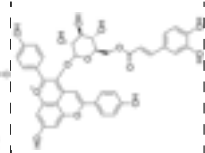
27	Pg-3-(6-(E)-caffeoyl)-glucoside	H	OH	H	OGlc-Caff	
33	Pg-3-(6-(Z)-p-coumaroyl)-glucoside	H	OH	H	OGlc-Coum	
39	Pg-3-(6-(E)-p-coumaroyl)-glucoside	H	OH	H	OGlc-Coum	
4	Cyanidin (Cy)	OH	OH	H	OH	
10	Cy-3-glucoside	OH	OH	H	OGlc	
16	Cy-3-acetyl-glucoside	OH	OH	H	OGlc-Ac	
22	Cy-3-(6-(Z)-caffeoyl)-glucoside	OH	OH	H	OGlc-Caff	
28	Cy-3-(6-(E)-caffeoyl)-glucoside	OH	OH	H	OGlc-Caff	
34	Cy-3-(6-(Z)-p-coumaroyl)-glucoside	OH	OH	H	OGlc-Coum	
40	Cy-3-(6-(E)-p-coumaroyl)-glucoside	OH	OH	H	OGlc-Coum	

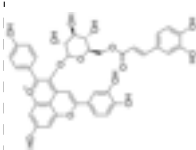
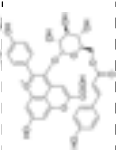
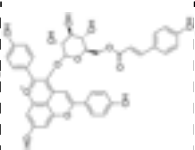
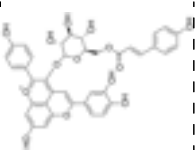
5	Peonidin (Pn)	OCH ₃	OH	H	OH	
11	Pn-3-glucoside	OCH ₃	OH	H	OGlc	
17	Pn-3-acetyl-glucoside	OCH ₃	OH	H	OGlc-Ac	
23	Pn-3-(6-(Z)-caffeoyl)-glucoside	OCH ₃	OH	H	OGlc-Caff	
29	Pn-3-(6-(E)-caffeoyl)-glucoside	OCH ₃	OH	H	OGlc-Caff	
35	Pn-3-(6-(Z)-p-coumaroyl)-glucoside	OCH ₃	OH	H	OGlc-pCoup	
41	Pn-3-(6-(E)-p-coumaroyl)-glucoside	OCH ₃	OH	H	OGlc-pCoup	
6	Delphinidin (Dp)	OH	OH	OH	OH	

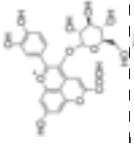
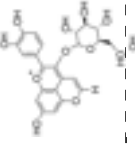
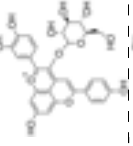
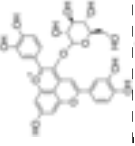
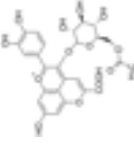
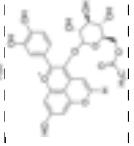
12	Dp-3-glucoside	OH	OH	OH	OH	OGlc	
18	Dp-3-acetyl-glucoside	OH	OH	OH	OH	OGlc-Ac	
24	Dp-3-(6-(Z)-caffeoyl)-glucoside	OH	OH	OH	OH	OGlc-Caff	
30	Dp-3-(6-(E)-caffeoyl)-glucoside	OH	OH	OH	OH	OGlc-Caff	
36	Dp-3-(6-(Z)-p-coumaroyl)-glucoside	OH	OH	OH	OH	OGlc-pCoup	
42	Dp-3-(6-(E)-p-coumaroyl)-glucoside	OH	OH	OH	OH	OGlc-pCoup	
7	Petunidin (Pt)	OH	OH	OH	OCH ₃	OH	
13	Pt-3-glucoside	OH	OH	OH	OCH ₃	OGlc	

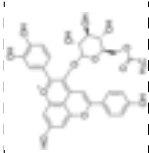
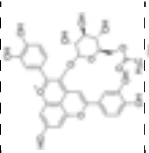
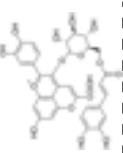
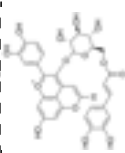
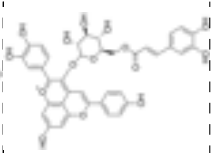
19	Pt-3-acetyl-glucoside	OH	OH	OCH ₃	OGlc-Ac	
25	Pt-3-(6-(Z)-caffeoyl)-glucoside	OH	OH	OCH ₃	OGlc-Caff	
31	Pt-3-(6-(E)-caffeoyl)-glucoside	OH	OH	OCH ₃	OGlc-Caff	
37	Pt-3-(6-(Z)-p-coumaroyl)-glucoside	OH	OH	OCH ₃	OGlc-pCoum	
43	Pt-3-(6-(E)-p-coumaroyl)-glucoside	OH	OH	OCH ₃	OGlc-pCoum	
8	Malvidin (Mv)	OCH ₃	OH	OCH ₃	OH	
14	Mv-3-glucoside	OCH ₃	OH	OCH ₃	OGlc	
20	Mv-3-acetyl-glucoside	OCH ₃	OH	OCH ₃	OGlc-Ac	
26	Mv-3-(6-(Z)-caffeoyl)-glucoside	OCH ₃	OH	OCH ₃	OGlc-Caff	

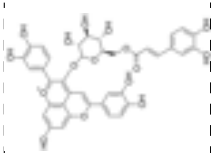
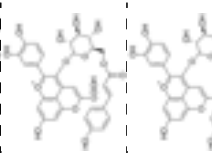
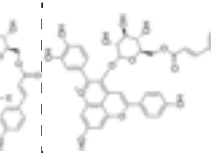
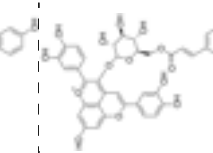
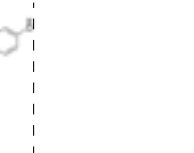
32	Mv-3-(6-(E)-caffeoyl)-glucoside	OCH ₃	OH	OCH ₃	OGlc-Caff
38	Mv-3-(6-(Z)-p-coumaroyl)-glucoside	OCH ₃	OH	OCH ₃	OGlc-pCoup
					
44	Mv-3-(6-(E)-p-coumaroyl)-glucoside	OCH ₃	OH	OCH ₃	OGlc-pCoup
Pyrananthocyanins					
	Name	R ₁	R ₂	R ₃	R ₅
45	Pg-3-Glc 10-carboxy type	H	OH	H	COOH
					
51	Pg-3-Glc 10-H type	H	OH	H	H
					
57	Pg-3-Glc-4-vinylphenol adduct	H	OH	H	Phenol
					
63	Pg-3-Glc-4-vinylcatechol adduct	H	OH	H	Catechol
					
69	Pg-3-acetyl-Glc 10-carboxy type	H	OH	H	COOH
					

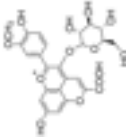
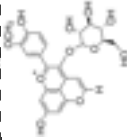
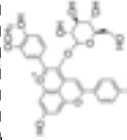
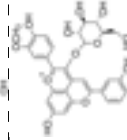
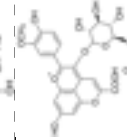
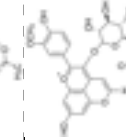
75	Pg-3-acetyl-Glc 10-H type	H	OH	H	Ac	H	
81	Pg-3-acetyl-Glc-4-vinylphenol adduct	H	OH	H	Ac	Phenol	
87	Pg-3-acetyl-Glc-4-vinylcatechol adduct	H	OH	H	Ac	Catechol	
93	Pg-(6-(E)-caffeoyl)-Glc 10-carboxy type	H	OH	H	Caff	COOH	
99	Pg-(6-(E)-caffeoyl)-Glc 10-H type	H	OH	H	Caff	H	
105	Pg-(6-(E)-caffeoyl)-Glc-4-vinylphenol adduct	H	OH	H	Caff	Phenol	

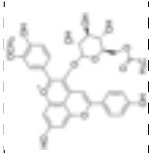
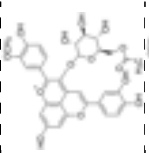
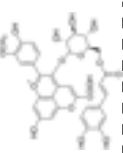
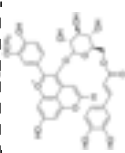
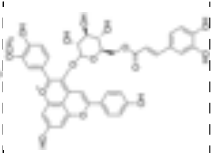
111	Pg-(6-(E)-caffeoyl)-Glc-4-vinylcatechol adduct	H	OH	H	Caff	Catechol	
117	Pg-3-(6-(E)-coum)-Glc 10-carboxy type	H	OH	H	pCoum	COOH	
123	Pg-3-(6-(E)-coum)-Glc 10-H type	H	OH	H	pCoum	H	
129	Pg-3-(6-(E)-coum)-Glc-4-vinylphenol adduct	H	OH	H	pCoum	Phenol	
135	Pg-3-(6-(E)-coum)-Glc-4-vinylcatechol adduct	H	OH	H	pCoum	Catechol	

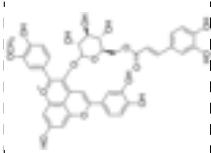
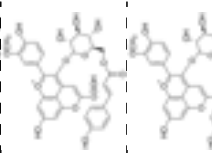
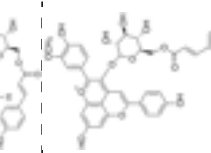
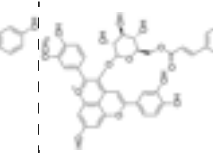
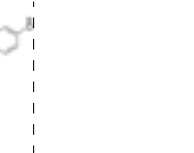
46	Cy-3-Glc 10-carboxy type	OH	OH	H	H	COOH	
52	Cy-3-Glc 10-H type	OH	OH	H	H	H	
58	Cy-3-Glc-4-vinylphenol adduct	OH	OH	H	H	Phenol	
64	Cy-3-Glc-4-vinylcatechol adduct	OH	OH	H	H	Catechol	
70	Cy-3-acetyl-Glc 10-carboxy type	OH	OH	H	Ac	COOH	
76	Cy-3-acetyl-Glc 10-H type	OH	OH	H	Ac	H	

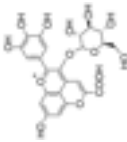
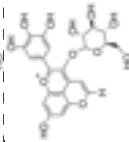
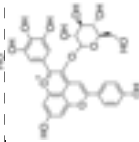
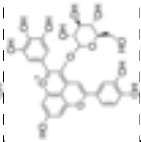
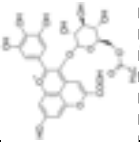
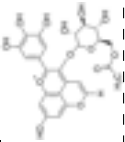
82	Cy-3-acetyl-Glc 4-vinyl/phenol adduct	OH	OH	H	Ac	Phenol	
88	Cy-3-acetyl-Glc 4-vinylcatechol adduct	OH	OH	H	Ac	Catechol	
94	Cy-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	OH	H	Caff	COOH	
100	Cy-(6-(E)-caffeoyl)-Glc 10-H type	OH	OH	H	Caff	H	
106	Cy-(6-(E)-caffeoyl)-Glc 4-vinyl/phenol adduct	OH	OH	H	Caff	Phenol	

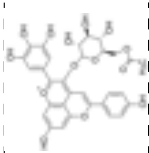
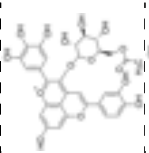
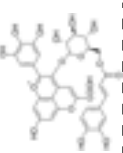
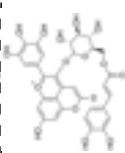
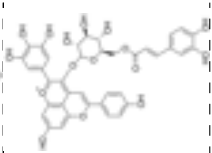
112	Cy-3-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH	OH	H	Caff	Catechol	
118	Cy-3-(6-(E)-coum)-Glc 10-carboxy type	OH	OH	H	pCoum	COOH	
124	Cy-3-(6-(E)-coum)-Glc 10-H type	OH	OH	H	pCoum	H	
130	Cy-3-(6-(E)-coum)-Glc-4-vinylphenol adduct	OH	OH	H	pCoum	Phenol	
136	Cy-3-(6-(E)-coum)-Glc-4-vinylcatechol adduct	OH	OH	H	pCoum	Catechol	

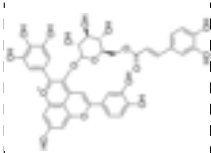
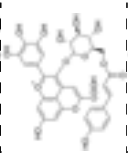
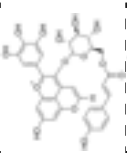
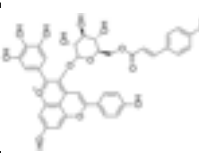
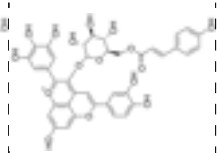
47	Pn-3-Glc 10-carboxy type	OCH ₃	OH	H	H	COOH	
53	Pn-3-Glc 10-H type	OCH ₃	OH	H	H	H	
59	Pn-3-Glc-4-vinylphenol adduct	OCH ₃	OH	H	H	Phenol	
65	Pn-3-Glc-4-vinylcatechol adduct	OCH ₃	OH	H	H	Catechol	
71	Pn-3-acetyl-Glc 10-carboxy type	OCH ₃	OH	H	Ac	COOH	
77	Pn-3-acetyl-Glc 10-H type	OCH ₃	OH	H	Ac	H	

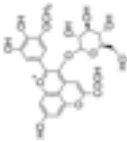
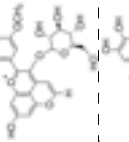
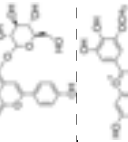
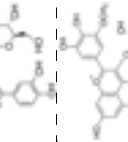
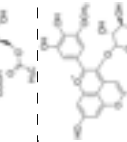
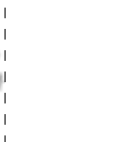
83	Pn-3-acetyl-Glc 4-vinylphenol adduct	OCH ₃	OH	H	Ac	Phenol	
89	Pn-3-acetyl-Glc 4-vinylcatechol adduct	OCH ₃	OH	H	Ac	Catechol	
95	Pn-(6-(E)-caffeoyl)-Glc 10-carboxy type	OCH ₃	OH	H	Caff	COOH	
101	Pn-(6-(E)-caffeoyl)-Glc 10-H type	OCH ₃	OH	H	Caff	H	
107	Pn-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OCH ₃	OH	H	Caff	Phenol	

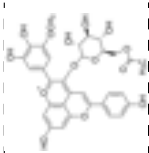
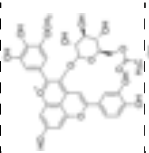
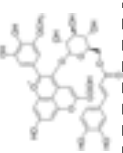
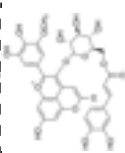
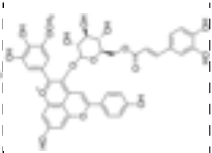
113	Pn-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OCH ₃	OH	H	Caff	Catechol	
119	Pn-3-(6-(E)-coum)-Glc 10-carboxy type	OCH ₃	OH	H	pCoum	COOH	
125	Pn-3-(6-(E)-coum)-Glc 10-H type	OCH ₃	OH	H	pCoum	H	
131	Pn-3-(6-(E)-coum)-Glc-4-vinylphenol adduct	OCH ₃	OH	H	pCoum	Phenol	
137	Pn-3-(6-(E)-coum)-Glc-4-vinylcatechol adduct	OCH ₃	OH	H	pCoum	Catechol	

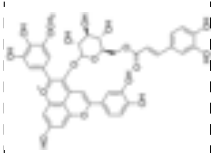
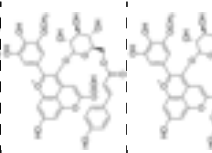
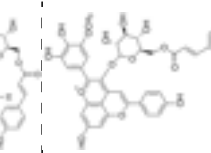
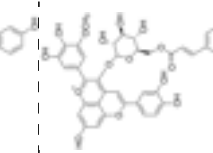
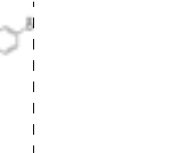
48	Dp-3-Glc 10-carboxy type	OH	OH	OH	OH	H	COOH	
54	Dp-3-Glc 10-H type	OH	OH	OH	OH	H	H	
60	Dp-3-Glc 4-vinylphenol adduct	OH	OH	OH	OH	H	Phenol	
66	Dp-3-Glc 4-vinylcatechol adduct	OH	OH	OH	OH	H	Catechol	
72	Dp-3-acetyl-Glc 10-carboxy type	OH	OH	OH	OH	Ac	COOH	
78	Dp-3-acetyl-Glc 10-H type	OH	OH	OH	OH	Ac	H	

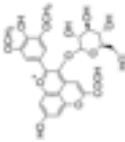
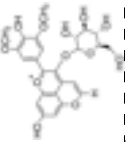
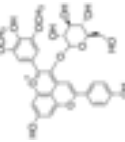
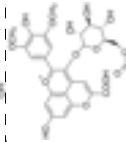
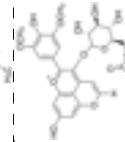
84	Dp-3-acetyl-Glc 4-vinylphenol adduct	OH	OH	OH	OH	Ac	Phenol	
90	Dp-3-acetyl-Glc 4-vinylcatechol adduct	OH	OH	OH	OH	Ac	Catechol	
96	Dp-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	OH	OH	OH	Caff	COOH	
102	Dp-(6-(E)-caffeoyl)-Glc 10-H type	OH	OH	OH	OH	Caff	H	
108	Dp-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OH	OH	OH	OH	Caff	Phenol	

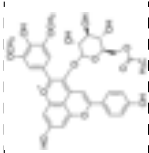
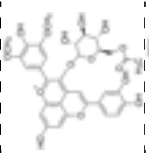
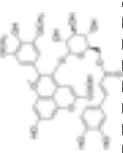
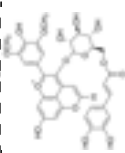
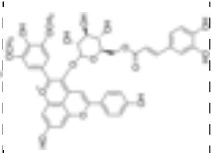
114	Dp-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH	OH	OH	Catechol	
120	Dp-3-(6-(E)-coum)-Glc 10-carboxy type	OH	OH	OH	pCoum	
126	Dp-3-(6-(E)-coum)-Glc 10-H type	OH	OH	OH	pCoum	
132	Dp-3-(6-(E)-coum)-Glc-4-vinylphenol adduct	OH	OH	OH	pCoum	
138	Dp-3-(6-(E)-coum)-Glc-4-vinylcatechol adduct	OH	OH	OH	pCoum	

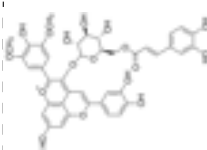
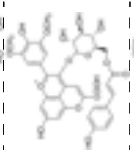
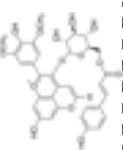
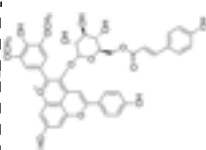
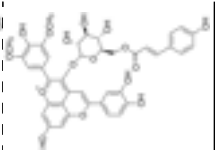
49	Pt-3-Glc 10-carboxy type	OH	OH	OCH ₃	H	COOH	
55	Pt-3-Glc 10-H type	OH	OH	OCH ₃	H	H	
61	Pt-3-Glc 4-vinylphenol adduct	OH	OH	OCH ₃	H	Phenol	
67	Pt-3-Glc 4-vinylcatechol adduct	OH	OH	OCH ₃	H	Catechol	
73	Pt-3-acetyl-Glc 10-carboxy type	OH	OH	OCH ₃	Ac	COOH	
79	Pt-3-acetyl-Glc 10-H type	OH	OH	OCH ₃	Ac	H	

85	Pt-3-acetyl-Glc 4-vinylphenol adduct	OH	OH	OCH ₃	Ac	Phenol	
91	Pt-3-acetyl-Glc 4-vinylcatechol adduct	OH	OH	OCH ₃	Ac	Catechol	
97	Pt-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	OH	OCH ₃	Caff	COOH	
103	Pt-(6-(E)-caffeoyl)-Glc 10-H type	OH	OH	OCH ₃	Caff	H	
109	Pt-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OH	OH	OCH ₃	Caff	Phenol	

115	Pt-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH	OH	OCH ₃	Caff	Catechol	
121	Pt-3-(6-(E)-coum)-Glc 10-carboxy type	OH	OH	OCH ₃	pCoum	COOH	
127	Pt-3-(6-(E)-coum)-Glc 10-H type	OH	OH	OCH ₃	pCoum	H	
133	Pt-3-(6-(E)-coum)-Glc-4-vinylphenol adduct	OH	OH	OCH ₃	pCoum	Phenol	
139	Pt-3-(6-(E)-coum)-Glc-4-vinylcatechol adduct	OH	OH	OCH ₃	pCoum	Catechol	

50	Mv-3-Glc 10-carboxy type	OCH ₃	OH	OCH ₃	H	COOH	
56	Mv-3-Glc 10-H type	OCH ₃	OH	OCH ₃	H	H	
62	Mv-3-Glc 4-vinylphenol adduct	OCH ₃	OH	OCH ₃	H	Phenol	
68	Mv-3-Glc 4-vinylcatechol adduct	OCH ₃	OH	OCH ₃	H	Catechol	
74	Mv-3-acetyl-Glc 10-carboxy type	OCH ₃	OH	OCH ₃	Ac	COOH	
80	Mv-3-acetyl-Glc 10-H type	OCH ₃	OH	OCH ₃	Ac	H	

86	Mv-3-acetyl-Glc 4-vinylphenol adduct	OCH ₃	OH	OCH ₃	Ac	Phenol	
92	Mv-3-acetyl-Glc-4-vinylcatechol adduct	OCH ₃	OH	OCH ₃	Ac	Catechol	
98	Mv-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	OH	OCH ₃	Caff	COOH	
104	Mv-(6-(E)-caffeoyl)-Glc 10-H type	OH	OH	OCH ₃	Caff	H	
110	Mv-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OH	OH	OCH ₃	Caff	Phenol	

116	Mv-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH	OH	OCH ₃	Caff	Catechol	
122	Mv-3-(6-(E)-coum)-Glc 10-carboxy type	OCH ₃	OH	OCH ₃	pCoum	COOH	
128	Mv-3-(6-(E)-coum)-Glc 10-H type	OCH ₃	OH	OCH ₃	pCoum	H	
134	Mv-3-(6-(E)-coum)-Glc 4-vinylphenol adduct	OCH ₃	OH	OCH ₃	pCoum	Phenol	
140	Mv-3-(6-(E)-coum)-Glc 4-vinylcatechol adduct	OCH ₃	OH	OCH ₃	pCoum	Catechol	

UV-Vis Spectra of Anthocyanidins and Anthocyanins

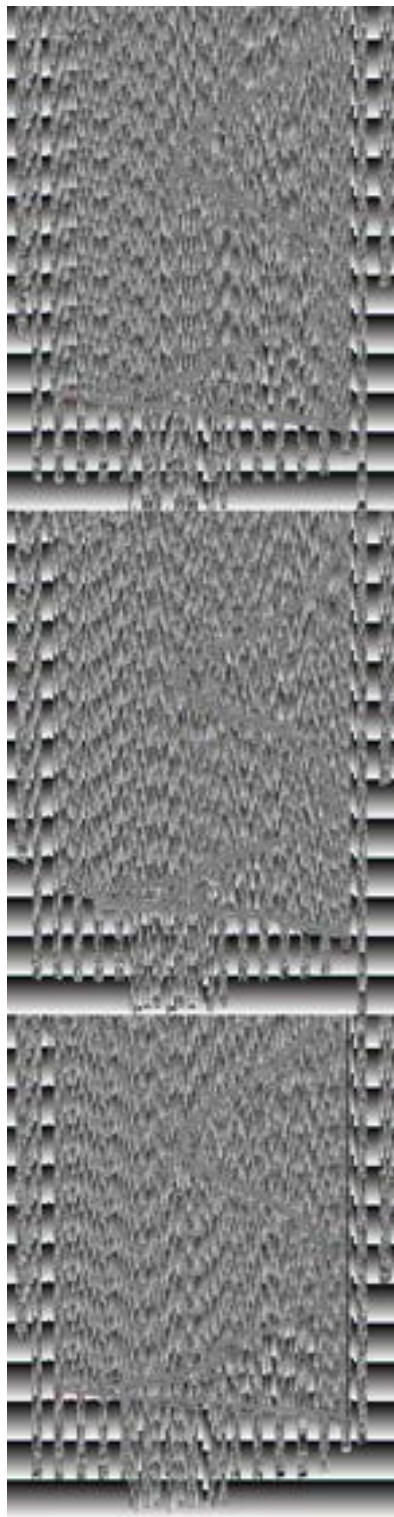


Figure D.1: Calculated UV-Vis spectra of anthocyanidins (**1-8**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.



Figure D.2: Calculated UV-Vis spectra of anthocyanins (**9-14**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

Data TD-DFT Calculations (B3LYP)

Table D.2: List of own calculated TD-DFT calculations of anthocyanins and pyrananthocyanins along with their possible substitution patterns (Figure 4.1) (B3LYP/6-311++G(d,p)). For comparison, existing TD-DFT studies and experimental literature studies are included.

Label	Anthocyanins	R ₁	R ₂	R ₃	R ₄	Own calculations		Literature Modeling		Literature Experimental	
	Name					λ_{max} , CALC (nm)	Method	λ_{max} , CALC (nm)	Method	λ_{max} , EXP (nm)	Solvent
1	Apigeninidin (Ap)	H	OH	H	H	430.84	GAS	431	B3LYP/6-31G(d) (gas)[285]	476	MeOH/HCl[543]
						463.32	PCM MeOH				
						471.29	SMD MeOH				
						464.33	PCM Water				
						472.33	SMD Water			468	KCl buffer pH=1[356]
2	Luteolinidin (Lt)	OH	OH	H	H	471.63	GAS	468	B3LYP/6-31G(d) (gas)[285]	493	MeOH/HCl[543]
						483.55	PCM MeOH				
						491.24	SMD MeOH				
						484.46	PCM Water			482	KCl buffer pH=1[356]
						490.52	SMD Water				
3	Pelargonidin (Pg)	H	OH	H	OH	468.58	GAS	470	B3LYP/6-31G(d) (gas)[285]	520	MeOH/HCl[543]
						510.27	PCM MeOH			524	MeOH/HCl[58]
						519.03	SMD MeOH				
						511.48	PCM Water	475	B3LYP/6-31+G(d) (gas)[363]	506	KCl buffer pH=1[356]
						519.77	SMD Water			505	KCl buffer pH=1[58]
9	Pg-3-glucoside	H	OH	H	OGlc	441.68	GAS	492	B3LYP/6-31+G(d) (C-PCM: water)[363]	506	MeOH/HCl[543]
						475.70	PCM MeOH			508	MeOH/HCl[58]
						480.41	SMD MeOH			503 (Rut)	TFA/H ₂ O/ACN[544]
										506 (Gen)	MeOH/HCl[543]
										508 (Rhagc)	MeOH/HCl[543]
						476.50	PCM Water			496	KCl buffer pH=1 [58]
						480.73	SMD Water			502	TFA/H ₂ O/ACN[544]
										503 (Ara)	TFA/H ₂ O/ACN[544]

15	Pg-acetyl-glucoside	H	OH	H	OGlc-Ac	480.07	SMD MeOH				500 (Gal)	TFA/H ₂ O/ACN[544]
						478.08	SMD Water				504 (OGlc-Malo)	TFA/H ₂ O/ACN[544]
21	Pg-3-(6-(Z)-caffeoyl)-glucoside	H	OH	H	OGlc-Caff	546.91	SMD MeOH				503 (OGlc-Maly)	TFA/H ₂ O/ACN[544]
						544.89	SMD Water				-	-
27	Pg-3-(6-(E)-caffeoyl)-glucoside	H	OH	H	OGlc-Caff	528.34	SMD MeOH				-	-
						523.71	SMD Water				-	-
33	Pg-3-(6-(Z)-p-coumaroyl)-glucoside	H	OH	H	OGlc-Coum	534.32	SMD MeOH				-	-
						515.24	SMD Water				-	-
39	Pg-3-(6-(E)-p-coumaroyl)-glucoside	H	OH	H	OGlc-Coum	506.39	SMD MeOH				-	-
						515.60	SMD Water				-	-
4	Cyanidin (Cy)	OH	OH	H	OH	494.21	GAS	489	B3LYP/6-31G(d) (gas)[285]		535	MeOH/HCl[543]
						522.40	PCM MeOH					
						530.33	SMD MeOH					
						523.50	PCM Water	500	B3LYP/6-31+G(d) (gas)[363]		516	KCl buffer pH=1[356]
						530.76	SMD Water					
								500	B3LYP/6-31+G(d) (C-PCM: water)[363]			
10	Cy-3-glucoside	OH	OH	H	OGlc	476.94	GAS	511	B3LYP/MIDIX+ (PCM: water, Cl ⁻ ion)[379]		512	KCl buffer pH=1[356]
						496.72	PCM MeOH	478	B3P86/6-31+G(d,p) (IEFPCM: MeOH)[387]		525	MeOH/HCl[543]
						501.37	SMD MeOH				523 (Rhagc)	MeOH/HCl[543]
											523 (Gen)	MeOH/HCl[543]
											523 (Sam)	MeOH/HCl[543]
						497.44	PCM Water	515	M06-L/6-31+G(d) (PCM: water)[379]		515	TFA/H ₂ O/ACN[544]
						501.04	SMD Water				516	FA/H ₂ O/ACN[387]
											516	TFA/H ₂ O/ACN[545]
											517	FA/H ₂ O/ACN[369]

16	Cy-3-acetyl-glucoside	OH	OH	H	OGlc-Ac	503.21	SMD MeOH	514 (Rut)	KCl buffer pH=1[356]
								515 (Rut)	TFA/H ₂ O/ACN[544]
						495.69	SMD Water	523	TFA/H ₂ O/ACN[545]
22	Cy-3-(6-(Z)-caffeoyl)-glucoside	OH	OH	H	OGlc-Caff	564.44	SMD MeOH	519	FA/H ₂ O/ACN[369]
						558.70	SMD Water	-	-
28	Cy-3-(6-(E)-caffeoyl)-glucoside	OH	OH	H	OGlc-Caff	537.40	SMD MeOH	-	-
						528.66	SMD Water	-	-
34	Cy-3-(6-(Z)-p-coumaroyl)-glucoside	OH	OH	H	OGlc-Coum	518.49	SMD MeOH	533	TFA/H ₂ O/ACN[545]
						519.19	SMD Water	-	-
40	Cy-3-(6-(E)-p-coumaroyl)-glucoside	OH	OH	H	OGlc-Coum	513.32	SMD MeOH	524	TFA/H ₂ O/ACN[545]
						520.43	SMD Water	-	-
5	Peonidin (Pn)	OCH ₃	OH	H	OH	480.29	GAS	532	MeOH/HCl[543]
						528.18	PCM MeOH	-	-
						535.36	SMD MeOH	-	-
						529.33	PCM Water	516	KCl buffer pH=1[356]
						535.73	SMD Water	-	-
								-	-
11	Pn-3-glucoside	OCH ₃	OH	H	OGlc	465.21	GAS	523	MeOH/HCl[543]
						503.84	PCM MeOH	528 (5-glc)	MeOH/HCl[543]
						509.42	SMD MeOH	517	FA/H ₂ O/ACN[387]
						504.68	PCM Water	516	TFA/H ₂ O/ACN[546]
						509.55	SMD Water	517	TFA/H ₂ O/ACN[545]
								516	FA/H ₂ O/ACN[369]
17	Pn-3-acetyl-glucoside	OCH ₃	OH	H	OGlc-Ac	503.21	SMD MeOH	522	TFA/H ₂ O/ACN[545]
						502.77	SMD Water	516	FA/H ₂ O/ACN[369]
								525 (L(+)-LA)	TFA/H ₂ O/ACN[545]

23	Pn-3-(6-(Z)-caffeoyl)-glucoside	OCH ₃ OH	H	OGlc-Caff	558.09	SMD MeOH					
29	Pn-3-(6-(E)-caffeoyl)-glucoside	OCH ₃ OH	H	OGlc-Caff	554.27	SMD Water					
35	Pn-3-(6-(Z)-p-coumaroyl)-glucoside	OCH ₃ OH	H	OGlc-pCoup	536.79	SMD MeOH				525	TFA/H ₂ O/ACN[545]
41	Pn-3-(6-(E)-p-coumaroyl)-glucoside	OCH ₃ OH	H	OGlc-pCoup	543.54	SMD Water				535	TFA/H ₂ O/ACN[545]
6	Delphinidin (Dp)	OH OH OH	OH	OH	532.43	SMD MeOH					
					529.88	SMD Water					
					517.45	SMD MeOH				526	TFA/H ₂ O/ACN[545]
					523.97	SMD Water				520	FA/H ₂ O/ACN[369]
					484.26	GAS		B3LYP/6-31G(d) (gas)[285]		546	MeOH/HCl[543]
					530.67	PCM MeOH					
					538.96	SMD MeOH					
					531.54	PCM Water					
					538.61	SMD Water					
12	Dp-3-glucoside	OH OH OH	OH	OGlc	467.92	GAS				535	MeOH/HCl[543]
					499.69	PCM MeOH				537 (Rhaglc)	MeOH/HCl[543]
					505.48	SMD MeOH				524	FA/H ₂ O/ACN[387]
					500.19	PCM Water				524	TFA/H ₂ O/ACN[545]
					504.12	SMD Water				526	TFA/H ₂ O/ACN[546]
										527	FA/H ₂ O/ACN[369]
18	Dp-3-acetyl-glucoside	OH OH OH	OH	OGlc-Ac	500.04	SMD MeOH				527	TFA/H ₂ O/ACN[545]
					499.05	SMD Water				529	FA/H ₂ O/ACN[369]
24	Dp-3-(6-(Z)-caffeoyl)-glucoside	OH OH OH	OH	OGlc-Caff	555.51	SMD MeOH				-	
					553.02	SMD Water					
30	Dp-3-(6-(E)-caffeoyl)-glucoside	OH OH OH	OH	OGlc-Caff	539.23	SMD MeOH				532	TFA/H ₂ O/ACN[545]
					549.20	SMD Water					

36	Dp-3-(6-(Z)-p-coumaroyl)-glucoside	OH	OH	OH	OGlc-pCoup	524.68	SMD MeOH	534	TFA/H ₂ O/ACN[545]
42	Dp-3-(6-(E)-p-coumaroyl)-glucoside	OH	OH	OH	OGlc-pCoup	526.99	SMD Water	531	TFA/H ₂ O/ACN[545]
7	Petunidin (Pt)	OH	OH	OH	OH	521.62	SMD MeOH	527	FA/H ₂ O/ACN[369]
						524.36	SMD Water	543	MeOH/HCl[543]
						488.75	GAS		
						536.14	PCM MeOH		
						543.15	SMD MeOH		
						537.22	PCM Water		
						543.35	SMD Water		
13	Pt-3-glucoside	OH	OH	OH	OGlc	474.08	GAS	535	MeOH/HCl[543]
						510.73	PCM MeOH	526	FA/H ₂ O/ACN[387]
						512.84	SMD MeOH	527	TFA/H ₂ O/ACN[546]
						511.66	PCM Water	525	TFA/H ₂ O/ACN[545]
						529.36	SMD Water	527	FA/H ₂ O/ACN[369]
19	Pt-3-acetyl-glucoside	OH	OH	OH	OGlc-Ac	508.00	SMD MeOH	535	MeOH/HCl[543]
						506.89	SMD Water	529	TFA/H ₂ O/ACN[545]
								530	TFA/H ₂ O/ACN[546]
								529	FA/H ₂ O/ACN[369]
25	Pt-3-(6-(Z)-caffeoyl)-glucoside	OH	OH	OH	OGlc-Caff	563.43	SMD MeOH	526 (L(+)-LA)	TFA/H ₂ O/ACN[545]
						565.47	SMD Water		
31	Pt-3-(6-(E)-caffeoyl)-glucoside	OH	OH	OH	OGlc-Caff	544.63	SMD MeOH	531	TFA/H ₂ O/ACN[545]
						534.58	SMD Water		
37	Pt-3-(6-(Z)-p-coumaroyl)-glucoside	OH	OH	OH	OGlc-pCoup	534.21	SMD MeOH	536	TFA/H ₂ O/ACN[545]
						536.19	SMD Water		
43	Pt-3-(6-(E)-p-coumaroyl)-glucoside	OH	OH	OH	OGlc-pCoup	520.42	SMD MeOH	532	TFA/H ₂ O/ACN[545]

8	Malvidin (Mv)	OCH ₃ OH	OH	519.11 497.42 546.27 552.92 548.57 552.60	SMD Water GAS PCM MeOH SMD MeOH PCM Water SMD Water	513 494 519 400 503	B3LYP/6-31G(d) (gas)[285] B3LYP/6-31+G(d) (gas)[363] B3LYP/6-31+G(d) (C-PCM: water)[363] B3P86/6-311+G(d,p) (IEFPCM: MeOH)[387]	542	MeOH/HCl[543]
14	Mv-3-glucoside	OCH ₃ OH	OGlc	490.24 525.51 525.91 526.09 522.97	GAS PCM MeOH SMD MeOH PCM Water SMD Water	497.1		535	MeOH/HCl[543]
20	Mv-3-acetyl-glucoside	OCH ₃ OH	OGlc-Ac	520.97 519.29	SMD MeOH SMD Water	494.9	B3P86/6-311+G(d,p) (IEFPCM: MeOH)[387]	527 527 527	FA/H ₂ O/ACN[387] TFA/H ₂ O/ACN[545, 546] FA/H ₂ O/ACN[369] FA/MeOH/H ₂ O[291] FA/H ₂ O/ACN[387] TFA/H ₂ O/ACN[545, 546] FA/H ₂ O/ACN[369] TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[545]
26	Mv-3-(6-(Z)-caffeoyl)-glucoside	OCH ₃ OH	OGlc-Caff	561.31 562.73	SMD MeOH SMD Water			529 530 529	-
32	Mv-(6-(E)-caffeoyl)-glucoside (E)	OCH ₃ OH	OGlc-Caff		SMD MeOH SMD Water	502.2	B3P86/6-311+G(d,p) (IEFPCM: MeOH)[387]	531 534	530 (D(-)-LA) 531 (L(+)-LA)
38	Mv-3-(6-(Z)-p-coumaroyl)-glucoside	OCH ₃ OH	OGlc-pCoup	534.32 536.79 528.03 526.88	SMD MeOH SMD Water SMD MeOH SMD Water	516	B3P86/6-311+G(d,p) (IEFPCM: MeOH)	535 532 532	FA/H ₂ O/ACN[546] FA/H ₂ O/ACN[387] TFA/H ₂ O/ACN[545]
44	Mv-3-(6-(E)-p-coumaroyl)-glucoside	OCH ₃ OH	OGlc-pCoup		SMD MeOH SMD Water				

Label	Pyrananthocyanins	Own calculations						Literature Modeling			Literature Experimental	
		R ₁	R ₂	R ₃	R _{6"}	R ₅	λ _{max} , CALC (nm)	Method	λ _{max} , CALC (nm)	Method	λ _{max} , EXP (nm)	Solvent
45	Pg-3-Glc 10-carboxy type	H	OH	H	H	COOH	525.24	SMD MeOH			-	-
51	Pg-3-Glc 10-H type	H	OH	H	H	H	525.03	SMD Water			-	-
							470.49	SMD MeOH				
57	Pg-3-Glc-4-vinylphenol adduct	H	OH	H	H	Phenol	470.61	SMD Water			-	-
							496.27	SMD MeOH				
63	Pg-3-Glc-4-vinylcatechol adduct	H	OH	H	H	Catechol	498.53	SMD Water			-	-
							511.20	SMD MeOH				
69	Pg-3-acetyl-Glc 10-carboxy type	H	OH	H	Ac	COOH	510.14	SMD Water			-	-
							482.41	SMD MeOH				
75	Pg-3-acetyl-Glc 10-H type	H	OH	H	Ac	H	486.46	SMD Water			-	-
							469.47	SMD MeOH				
81	Pg-3-acetyl-Glc-4-vinylphenol adduct	H	OH	H	Ac	Phenol	470.50	SMD Water			-	-
							488.31	SMD MeOH				
87	Pg-3-acetyl-Glc-4-vinylcatechol adduct	H	OH	H	Ac	Catechol	485.28	SMD Water			-	-
							508.59	SMD MeOH				
93	Pg-(6-(E)-caffeoyl)-Glc 10-carboxy type	H	OH	H	Caff	COOH	508.61	SMD Water			-	-
							478.03	SMD MeOH				
99	Pg-(6-(E)-caffeoyl)-Glc 10-H type	H	OH	H	Caff	H	480.72	SMD Water			-	-
							464.69	SMD MeOH				
105	Pg-(6-(E)-caffeoyl)-Glc-4-vinylphenol adduct	H	OH	H	Caff	Phenol	464.45	SMD Water			-	-
							489.83	SMD MeOH				
							482.27	SMD Water			-	-

111	Pg-(6-(E)-caffoyl)-Glc-4-vinylcatechol adduct	H	OH	H	Caff	Catechol	507.86	SMD MeOH	-	-	-
117	Pg-3-(6-(E)-coum)-Glc-10-carboxy type	H	OH	H	pCoum	COOH	504.73 509.61 509.84	SMD Water SMD MeOH SMD Water	-	-	-
123	Pg-3-(6-(E)-coum)-Glc-10-H type	H	OH	H	pCoum	H	495.33 496.28	SMD MeOH SMD Water	-	-	-
129	Pg-3-(6-(E)-coum)-Glc-4-vinylphenol adduct	H	OH	H	pCoum	Phenol	489.65 489.51	SMD MeOH SMD Water	-	-	-
135	Pg-3-(6-(E)-coum)-Glc-4-vinylcatechol adduct	H	OH	H	pCoum	Catechol	507.93 504.14	SMD MeOH SMD Water	-	-	-
46	Cy-3-Glc-10-carboxy type	OH	OH	H	H	COOH	502.62	SMD MeOH	504	FA/H ₂ O/ACN[392]	-
52	Cy-3-Glc-10-H type	OH	OH	H	H	H	504.31 491.50	SMD Water SMD MeOH	-	-	-
58	Cy-3-Glc-4-vinylphenol adduct	OH	OH	H	H	Phenol	490.71 506.33	SMD Water SMD MeOH	500	FA/H ₂ O/ACN[392]	-
64	Cy-3-Glc-4-vinylcatechol adduct	OH	OH	H	H	Catechol	506.97 513.86	SMD Water SMD MeOH	508	FA/H ₂ O/ACN[392]	-
70	Cy-3-acetyl-Glc-10-carboxy type	OH	OH	H	Ac	COOH	512.81 501.60	SMD Water SMD MeOH	-	-	-
76	Cy-3-acetyl-Glc-10-H type	OH	OH	H	Ac	H	505.09 489.75	SMD Water SMD MeOH	-	-	-
82	Cy-3-acetyl-Glc-4-vinylphenol adduct	OH	OH	H	Ac	Phenol	489.66 498.70 491.59	SMD Water SMD MeOH SMD Water	-	-	-

88	Cy-3-acetyl-Glc 4-vinylcatechol adduct	OH	OH	H	Ac	Catechol	516.77	SMD MeOH	-	-
94	Cy-6-(E)-caffeoyl-Glc 10-carboxy type	OH	OH	H	Caff	COOH	515.57 497.27	SMD Water SMD MeOH	-	-
100	Cy-6-(E)-caffeoyl-Glc 10-H type	OH	OH	H	Caff	H	499.75 484.31	SMD Water SMD MeOH	-	-
106	Cy-6-(E)-caffeoyl-Glc 4-vinylphenol adduct	OH	OH	H	Caff	Phenol	481.75 488.44	SMD Water SMD MeOH	-	-
112	Cy-6-(E)-caffeoyl-Glc 4-vinylcatechol adduct	OH	OH	H	Caff	Catechol	491.37 517.79	SMD Water SMD MeOH	-	-
118	Cy-3-(6-(E)-coum)-Glc 10-carboxy type	OH	OH	H	pCoum	COOH	510.92 512.52	SMD Water SMD MeOH	-	-
124	Cy-3-(6-(E)-coum)-Glc 10-H type	OH	OH	H	pCoum	H	513.35 501.58	SMD Water SMD MeOH	-	-
130	Cy-3-(6-(E)-coum)-Glc 4-vinylphenol adduct	OH	OH	H	pCoum	Phenol	502.84 493.51	SMD Water SMD MeOH	-	-
136	Cy-3-(6-(E)-coum)-Glc 4-vinylcatechol adduct	OH	OH	H	pCoum	Catechol	489.01 517.00	SMD Water SMD MeOH	508	FA/H ₂ O/ACN[392]
47	Pn-3-Glc 10-carboxy type	OCH ₃	OH	H	H	COOH	539	PBE0/SV(P) (Gas)[376]	-	-
53	Pn-3-Glc 10-H type	OCH ₃	OH	H	H	H	508.05 510.37	SMD MeOH SMD Water	503 505	TFA/H ₂ O/ACN[545, 546] FA/H ₂ O/ACN[392]
59	Pn-3-Glc 4-vinylphenol adduct	OCH ₃	OH	H	H	Phenol	497.33 495.65 512.62	SMD MeOH SMD Water SMD MeOH	487 500	FA/H ₂ O/ACN[392] TFA/H ₂ O/ACN[545]

65	<u>Pn-3-Glc-4-</u> vinylcatechol adduct	OCH ₃ OH	H	H	Catechol	512.93	SMD Water			499 500	FA/H ₂ O/ACN[369] FA/H ₂ O/ACN[392]
71	<u>Pn-3-acetyl-Glc</u> 10-carboxy type	OCH ₃ OH	H	Ac	COOH	511.07 515.16	SMD MeOH SMD Water			506 507	TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[392] FA/H ₂ O/ACN[392]
77	<u>Pn-3-acetyl-Glc</u> 10-H type	OCH ₃ OH	H	Ac	H	499.02	SMD MeOH			486	FA/H ₂ O/ACN[392]
83	<u>Pn-3-acetyl-Glc</u> 4-vinylphenol adduct	OCH ₃ OH	H	Ac	Phenol	499.33 504.94	SMD Water SMD MeOH			501	FA/H ₂ O/ACN[392]
89	<u>Pn-3-acetyl-Glc</u> 4-vinylcatechol adduct	OCH ₃ OH	H	Ac	Catechol	504.79 523.12	SMD Water SMD MeOH			507	FA/H ₂ O/ACN[392]
95	<u>Pn-(6-(E)-caffeoyl)-Glc</u> 10-carboxy type	OCH ₃ OH	H	Caff	COOH	520.81 503.72	SMD Water SMD MeOH			508	FA/H ₂ O/ACN[392]
101	<u>Pn-(6-(E)-caffeoyl)-Glc</u> 10-H type	OCH ₃ OH	H	Caff	H	506.04 488.39	SMD Water SMD MeOH			-	
107	<u>Pn-(6-(E)-caffeoyl)-Glc</u> 4-vinylphenol adduct	OCH ₃ OH	H	Caff	Phenol	486.19 499.51	SMD Water SMD MeOH			502	FA/H ₂ O/ACN[392]
113	<u>Pn-(6-(E)-caffeoyl)-Glc</u> 4-vinylcatechol adduct	OCH ₃ OH	H	Caff	Catechol	497.84 523.94	SMD Water SMD MeOH			508	FA/H ₂ O/ACN[392]
119	<u>Pn-3-(6-(E)-coum)-Glc</u> 10-carboxy type	OCH ₃ OH	H	pCoum	COOH	516.99 512.40	SMD Water SMD MeOH			508 513 509	TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[392] FA/H ₂ O/ACN[392]
125	<u>Pn-3-(6-(E)-coum)-Glc</u> 10-H type	OCH ₃ OH	H	pCoum	H	499.72 502.09	SMD MeOH SMD Water			485	FA/H ₂ O/ACN[392]

131	Pn-3-(6-(E)-coum)-Glc-4- vinylphenol adduct	OCH ₃ OH	H	pCoum	Phenol	499.62 496.45	SMD MeOH SMD Water	501 498 502	TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[392]
137	Pn-3-(6-(E)-coum)-Glc-4- vinylcatechol adduct	OCH ₃ OH	H	pCoum	Catechol	523.80 516.23	SMD MeOH SMD Water	508 508	TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[392]
48	Dp-3-Glc 10-carboxy type	OH OH	OH	H	COOH	506.09 507.76	SMD MeOH SMD Water	507 506 509	TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[392]
54	Dp-3-Glc 10-H type	OH OH	OH	H	H	494.85 493.20	SMD MeOH SMD Water	487	FA/H ₂ O/ACN[392]
60	Dp-3-Glc 4- vinylphenol adduct	OH OH	OH	H	Phenol	516.26 511.25	SMD MeOH SMD Water	503 504	TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[392]
66	Dp-3-Glc 4- vinylcatechol adduct	OH OH	OH	H	Catechol	521.87 520.61	SMD MeOH SMD Water	509 509	TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[392]
72	Dp-3-acetyl-Glc 10-carboxy type	OH OH	OH	Ac	COOH	505.01 506.08	SMD MeOH SMD Water	511	FA/H ₂ O/ACN[392]
78	Dp-3-acetyl-Glc 10-H type	OH OH	OH	Ac	H	492.41 491.74	SMD MeOH SMD Water	488	FA/H ₂ O/ACN[392]
84	Dp-3-acetyl-Glc 4- vinylphenol adduct	OH OH	OH	Ac	Phenol	503.36 502.02	SMD MeOH SMD Water	505	FA/H ₂ O/ACN[392]
90	Dp-3-acetyl-Glc 4- vinylcatechol adduct	OH OH	OH	Ac	Catechol	520.80 518.10	SMD MeOH SMD Water	512	FA/H ₂ O/ACN[392]
96	Dp-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH OH	OH	Caff	COOH	502.14 503.95	SMD MeOH SMD Water	-	-
102	Dp-(6-(E)-caffeoyl)-Glc 10-H type	OH OH	OH	Caff	H	491.73	SMD MeOH	-	-

108	Dp-3-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OH OH OH	Caff	Phenol	491.83	SMD Water				
					504.61	SMD MeOH			-	
114	Dp-3-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH OH OH	Caff	Catechol	505.71	SMD Water				
					519.28	SMD MeOH			-	
120	Dp-3-(6-(E)-coum)-Glc 10-carboxy type	OH OH OH	pCoum	COOH	515.91	SMD Water				
					515.72	SMD MeOH			512	FA/H ₂ O/ACN[392]
126	Dp-3-(6-(E)-coum)-Glc 10-H type	OH OH OH	pCoum	H	517.35	SMD Water				
					505.36	SMD MeOH			-	
132	Dp-3-(6-(E)-coum)-Glc-4-vinylphenol adduct	OH OH OH	pCoum	Phenol	504.09	SMD Water				
					503.27	SMD MeOH			-	
138	Dp-3-(6-(E)-coum)-Glc-4-vinylcatechol adduct	OH OH OH	pCoum	Catechol	501.42	SMD Water				
					519.28	SMD MeOH			510	FA/H ₂ O/ACN[392]
49	Pt-3-Glc 10-carboxy type	OH OH OH	H	COOH	515.67	SMD Water		PBE0/SV(P) (Gas)[376] PBE0/SV(P) (C-PCM, Water)[376]		
							547			
55	Pt-3-Glc 10-H type	OH OH OH	H	H	510.15	SMD MeOH			508	TFA/H ₂ O/ACN[545]
					511.13	SMD Water			507	TFA/H ₂ O/ACN[546]
									510	FA/H ₂ O/ACN[392]
61	Pt-3-Glc 4-vinylphenol adduct	OH OH OH	H	Phenol	500.66	SMD MeOH			492	TFA/H ₂ O/ACN[545]
					498.50	SMD Water		PBE0/SV(P) (Gas)[376] PBE0/SV(P) (C-PCM, Water)[376]	488	FA/H ₂ O/ACN[392]
							492			
					517.34	SMD MeOH			502	TFA/H ₂ O/ACN[545]
					517.50	SMD Water			503	TFA/H ₂ O/ACN[546]
67	Pt-3-Glc 4-vinylcatechol adduct	OH OH OH	H	Catechol	527.64	SMD MeOH			504	FA/H ₂ O/ACN[392]
									510	TFA/H ₂ O/ACN[545]
					526.18	SMD Water			510	FA/H ₂ O/ACN[392]

73	Pt-3-acetyl-Glc 10-carboxy type	OH	OHCH ₃	Ac	COOH	511.04	SMD MeOH		512	FA/H ₂ O/ACN[392]
79	Pt-3-acetyl-Glc 10-H type	OH	OHCH ₃	Ac	H	514.34	SMD Water		494	FA/H ₂ O/ACN[392]
85	Pt-3-acetyl-Glc 4- vinylphenol adduct	OH	OHCH ₃	Ac	Phenol	498.21	SMD MeOH		505	FA/H ₂ O/ACN[392]
91	Pt-3-acetyl-Glc 4- vinylcatechol adduct	OH	OHCH ₃	Ac	Catechol	497.41	SMD Water		511	FA/H ₂ O/ACN[392]
97	Pt-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	OHCH ₃	Caff	COOH	506.80	SMD MeOH		-	
103	Pt-(6-(E)-caffeoyl)-Glc 10-H type	OH	OHCH ₃	Caff	H	502.62	SMD Water		-	
109	Pt-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OH	OHCH ₃	Caff	Phenol	525.62	SMD MeOH		-	
115	Pt-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH	OHCH ₃	Caff	Catechol	523.99	SMD Water		-	
121	Pt-3-(6-(E)-coum)-Glc 10-carboxy type	OH	OHCH ₃	pCoum	COOH	505.92	SMD MeOH		-	
127	Pt-3-(6-(E)-coum)-Glc 10-H type	OH	OHCH ₃	pCoum	H	507.90	SMD Water		494	FA/H ₂ O/ACN[392]
133	Pt-3-(6-(E)-coum)-Glc 4- vinylphenol adduct	OH	OHCH ₃	pCoum	Phenol	491.36	SMD MeOH		504	TFA/H ₂ O/ACN[545]
139	Pt-3-(6-(E)-coum)-Glc 4- vinylcatechol adduct	OH	OHCH ₃	pCoum	Catechol	488.13	SMD Water		504	FA/H ₂ O/ACN[392]
						501.43	SMD MeOH		511	FA/H ₂ O/ACN[392]
						497.58	SMD Water			
						525.61	SMD MeOH			
						521.11	SMD Water			
						518.13	SMD MeOH			
						524.23	SMD Water			
						506.97	SMD MeOH			
						506.96	SMD Water			
						505.57	SMD MeOH			
						497.68	SMD Water			
						525.52	SMD MeOH			
						520.84	SMD Water			

50	Mv-3-Glc 10-carboxy type	CH ₃ OHCH ₃	H	COOH	524.32 527.07	SMD MeOH SMD Water	573 518	PBE0/SV(P) (Gas)[376] PBE0/SV(P) (C-PCM, Water)[376]	510 507 509 511	TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[369] FA/H ₂ O/ACN[392]
56	Mv-3-Glc 10-H type	CH ₃ OHCH ₃	H	H	515.22 512.28	SMD MeOH SMD Water	498 458	PBE0/SV(P) (Gas)[376] PBE0/SV(P) (C-PCM, Water)[376]	490 490	TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[392]
62	Mv-3-Glc 4-vinylphenol adduct	CH ₃ OHCH ₃	H	Phenol	525.97 524.98	SMD MeOH SMD Water	513 477	PBE0/SV(P) (Gas)[376] PBE0/SV(P) (C-PCM, Water)[376]	504 503 503 504	TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[369] FA/H ₂ O/ACN[392]
68	Mv-3-Glc 4-vinylcatechol adduct	CH ₃ OHCH ₃	H	Catechol	536.52 534.83	SMD MeOH SMD Water	509 471	PBE0/SV(P) (Gas)[376] PBE0/SV(P) (C-PCM, Water)[376]	510 512 511	TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[369] FA/H ₂ O/ACN[392]
74	Mv-3-acetyl-Glc 10-carboxy type	CH ₃ OHCH ₃	Ac	COOH	524.85 527.45	SMD MeOH SMD Water			514	FA/H ₂ O/ACN[392]
80	Mv-3-acetyl-Glc 10-H type	CH ₃ OHCH ₃	Ac	H	512.48	SMD MeOH			494	TFA/H ₂ O/ACN[545]
86	Mv-3-acetyl-Glc 4-vinylphenol adduct	CH ₃ OHCH ₃	Ac	Phenol	510.86 518.87	SMD Water SMD MeOH			494	FA/H ₂ O/ACN[392]
92	Mv-3-acetyl-Glc 4-vinylcatechol adduct	CH ₃ OHCH ₃	Ac	Catechol	511.91 533.98 531.16	SMD Water SMD MeOH SMD Water			505 506 513 512	TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[392] TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[392]

98	Mv-3-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	OHCH ₃	Caff	COOH	519.65	SMD MeOH		514	FA/H ₂ O/ACN[392]
104	Mv-3-(6-(E)-caffeoyl)-Glc 10-H type	OH	OHCH ₃	Caff	H	515.04	SMD Water		498	FA/H ₂ O/ACN[392]
110	Mv-3-(6-(E)-caffeoyl)-Glc 4- vinylphenol adduct	OH	OHCH ₃	Caff	Phenol	502.35	SMD MeOH		506	FA/H ₂ O/ACN[392]
116	Mv-3-(6-(E)-caffeoyl)-Glc 4- vinylcatechol adduct	OH	OHCH ₃	Caff	Catechol	505.05	SMD Water		512	FA/H ₂ O/ACN[392]
122	Mv-3-(6-(E)-coum)-Glc 10-carboxy type	OCH ₃	OHCH ₃	pCoum	COOH	510.26	SMD MeOH		514	TFA/H ₂ O/ACN[545]
128	Mv-3-(6-(E)-coum)-Glc 10-H type	OCH ₃	OHCH ₃	pCoum	H	509.33	SMD Water		516	FA/H ₂ O/ACN[369]
134	Mv-3-(6-(E)-coum)-Glc 4- vinylphenol adduct	OCH ₃	OHCH ₃	pCoum	Phenol	532.73	SMD Water		516	FA/H ₂ O/ACN[392]
140	Mv-3-(6-(E)-coum)-Glc 4- vinylcatechol adduct	OCH ₃	OHCH ₃	pCoum	Catechol	516.04	SMD MeOH		497	FA/H ₂ O/ACN[392]
						516.26	SMD Water		505	TFA/H ₂ O/ACN[545]
						512.12	SMD MeOH		506	TFA/H ₂ O/ACN[546]
						509.04	SMD Water		505	FA/H ₂ O/ACN[392]
						535.36	SMD MeOH		511	TFA/H ₂ O/ACN[545]
						527.97	SMD Water		512	TFA/H ₂ O/ACN[546]
									512	FA/H ₂ O/ACN[392]

Ara: arabinoside, Gal: galactoside, Gen: gentiobioside, LA: lactic acid, Malo: malonyl, Maly: maly, Rhaglc: rhamnoglucoside and Rut: rutinoside (chemical representations are displayed in Figures D.40 to D.42)

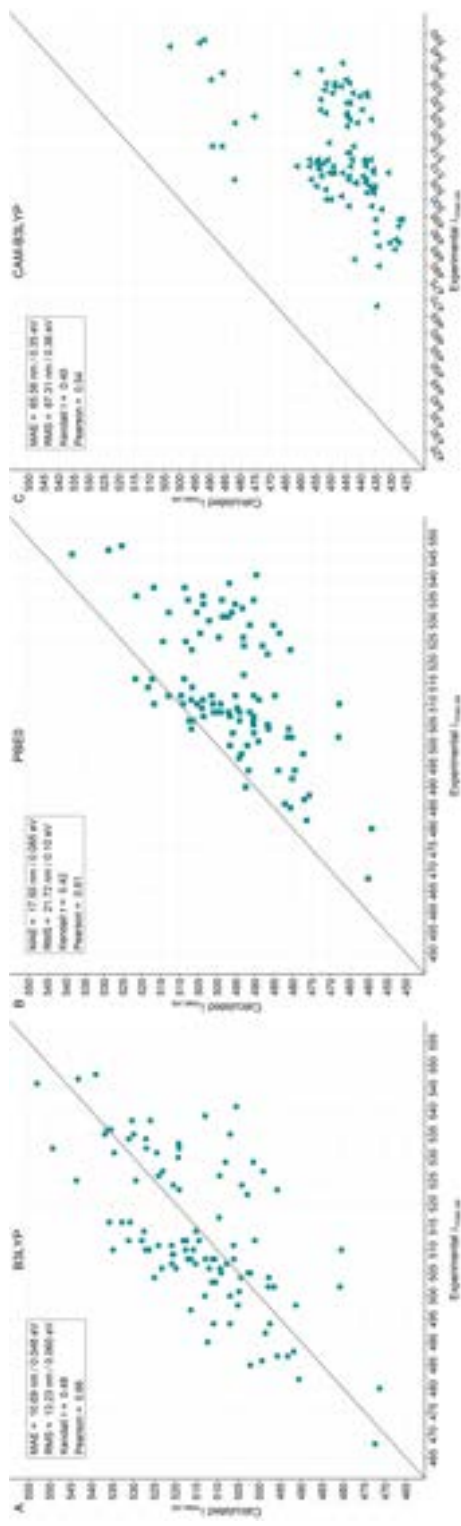


Figure D.3: Parity plots of calculated vs experimental $\lambda_{\max, \text{vis}}$ (nm) for B3LYP, PBE0 and CAM-B3LYP. The inset displays the results of mean absolute error (MAE), root-mean-square error (RMS) and Pearson correlation coefficients ($n = 101$). The normality of the datasets was evaluated with the Shapiro-Wilk test ($p = 0.05$). The highest correlation between calculated and experimental literature $\lambda_{\max, \text{vis}}$ -values and thus lowest RMS is observed in the following order: B3LYP > PBE0 > CAM-B3LYP.

Trend Analyses Anthocyanidins and Anthocyanins

Table D.3: Trend analyses on the influence of substituent patterns within anthocyanidins and anthocyanins (B3LYP/6-311++G(d,p)). Two solvation models (IEPCM and SMD) and two solvents were applied. Δ : differences are calculated in the order of first compound minus second compound, $\uparrow$: bathochromic shift and $\downarrow$: hypsochromic shift.

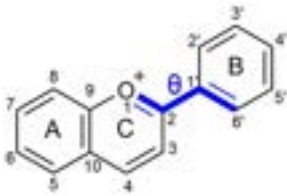
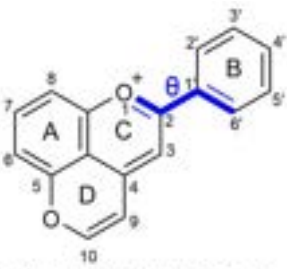
	Own calculations				Experimental literature values		
	Δ_{GAS} (nm)	$\Delta_{\text{PCM MeOH}}$ (nm)	$\Delta_{\text{SMD MeOH}}$ (nm)	$\Delta_{\text{PCM water}}$ (nm)	$\Delta_{\text{SMD water}}$ (nm)	$\Delta_{\text{exp Extrasyntes standards (nm) (MeOH/0.1\% HCl)}}$	$\Delta_{\text{exp water}}$ (nm)
Presence of hydroxyl group at C3-position: difference between anthocyanidins and 3-deoxyanthocyanidins							
Pelargonidin (3) - Apigeninidin (1)	37.74 $\uparrow$	46.95 $\uparrow$	47.74 $\uparrow$	47.15 $\uparrow$	47.44 $\uparrow$	43 $\uparrow$	38 $\uparrow$
Cyanidin (4) - Luteolinidin (2)	22.58 $\uparrow$	38.85 $\uparrow$	39.09 $\uparrow$	39.04 $\uparrow$	40.24 $\uparrow$	40 $\uparrow$	34 $\uparrow$
Additional presence of OH group at C3' next to existing C4' OH							
Luteolinidin (2) - Apigeninidin (1)	40.79 $\uparrow$	20.23 $\uparrow$	19.95 $\uparrow$	20.13 $\uparrow$	18.19 $\uparrow$	18 $\uparrow$	14 $\uparrow$
Cyanidin (4) - Pelargonidin (3)	25.63 $\uparrow$	12.13 $\uparrow$	11.30 $\uparrow$	12.02 $\uparrow$	10.99 $\uparrow$	15 $\uparrow$	10 $\uparrow$
Cy-3-Glc (10) - Pg-3-Glc (9)	35.26 $\uparrow$	21.02 $\uparrow$	20.96 $\uparrow$	20.94 $\uparrow$	20.31 $\uparrow$	19 $\uparrow$	10 $\uparrow$
Additional presence of OH group at C5' next to existing C3' and C4' OH							
Delphinidin (6) - Cyanidin (4)	9.95 $\downarrow$	8.27 $\downarrow$	8.63 $\uparrow$	8.04 $\uparrow$	7.85 $\uparrow$	10 $\uparrow$	-
Dp-3-Glc (12) - Cy-3-Glc (10)	9.02 $\downarrow$	2.97 $\uparrow$	4.11 $\uparrow$	2.75 $\uparrow$	3.08 $\uparrow$	12 $\uparrow$	12 $\uparrow$
Influence of methoxygroups on the B-ring							
Peonidin (5) - Cyanidin (4)	13.92 $\downarrow$	5.78 $\uparrow$	5.03 $\uparrow$	5.83 $\uparrow$	4.97 $\uparrow$	2 $\downarrow$	0
Petunidin (7) - Delphinidin (6)	5.24 $\uparrow$	5.47 $\uparrow$	4.19 $\uparrow$	5.68 $\uparrow$	4.74 $\uparrow$	1 $\downarrow$	-
Pn-3-Glc (11) - Cy-3-Glc (10)	11.73 $\downarrow$	7.12 $\uparrow$	8.05 $\uparrow$	7.24 $\uparrow$	8.51 $\uparrow$	3 $\downarrow$	5 $\uparrow$
Pt-3-Glc (13) - Dp-3-Glc (12)	20.82 $\downarrow$	11.04 $\uparrow$	7.36 $\uparrow$	11.47 $\uparrow$	25.24 $\uparrow$	2 $\downarrow$	1 $\uparrow$

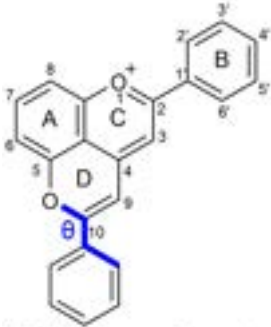
Table D.4: The influence of the glucose moiety at the C3 position on the $\lambda_{\max, \text{vis}}$ -values for anthocyanins. The calculated values are based on B3LYP/6-311++G(d,p) and SMD as solvation model. Experimental values from certified analytical standards (Extrasynthese) measured in MeOH/0.1%HCl are also included. ↓: hypsochromic shift.

Anthocyanidins	SMD MeOH			SMD Water			MeOH/0.1%HCl			SMD MeOH			SMD Water			MeOH/0.1%HCl		
	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (eV)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (eV)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (Extrasynthese) (nm)	$\lambda_{\max}$ (Extrasynthese) (eV)	Anthocyanins	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (eV)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (eV)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (Extrasynthese) (nm)	$\lambda_{\max}$ (Extrasynthese) (eV)		
Cyanidin (4)	530.33	2.3379	530.76	2.3360	538	2.3045	Cy-3-Glc (10)	501.37	2.4729	501.04	2.4745	529	2.3437					
Delphinidin (6)	538.96	2.3004	538.61	2.3019	548	2.2625	Dp-3-Glc (12)	505.48	2.4528	504.12	2.4594	541	2.2918					
Malvidin (8)	552.92	2.2423	552.6	2.2437	546	2.2708	Mv-3-Glc (14)	525.91	2.3575	522.97	2.3708	538	2.3045					
Pelargonidin (3)	519.03	2.3888	519.77	2.3854	523	2.3706	Pg-3-Glc (9)	480.41	2.5808	480.73	2.5791	510	2.4311					
Peonidin (5)	535.36	2.3159	535.73	2.3143	536	2.3131	Pt-3-Glc (11)	509.42	2.4338	509.55	2.4332	526	2.3571					
Petunidin (7)	543.15	2.2827	543.35	2.2818	547	2.2666	Pt-3-Glc (13)	512.84	2.4176	529.36	2.3422	539	2.3003					
Difference																		
SMD MeOH																		
SMD Water																		
MeOH/0.1%HCl																		
Δ (nm)																		
Δ (eV)																		
Cy-3-Glc (10) - Cyanidin (4)																		
28.96↓																		
Dp-3-Glc (12) - Delphinidin (6)																		
34.48↓																		
Mv-3-Glc (14) - Malvidin (8)																		
27.01↓																		
Pg-3-Glc (9) - Pelargonidin (3)																		
38.62↓																		
Pt-3-Glc (11) - Peonidin (5)																		
25.94↓																		
Pt-3-Glc (13) - Petunidin (7)																		
30.31↓																		
Average																		
30.72↓																		
Standard deviation																		
4.69																		

Dihedral Angles

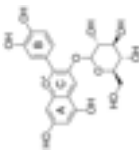
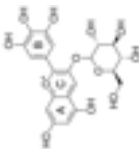
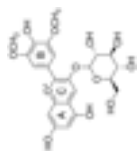
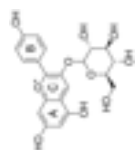
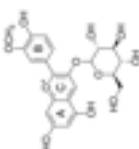
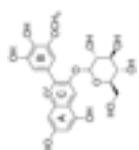
Table D.5: The average dihedral angles of the different anthocyanin and pyranoanthocyanin subclasses (B3LYP/6-311++G(d,p) with Grimme D3 dispersion corrections).

 Anthocyanin aglycone  Pyranoanthocyanin aglycone			
Compound subclass	Gas (°)	SMD MeOH (°)	SMD Water (°)
3-deoxyanthocyanidins (1-2)	0.019 ± 0.024	0.0065 ± 0.0092	0.0060 ± 0.0085
Anthocyanidins (3-8)	0.83 ± 1.99	11.92 ± 5.41	11.95 ± 6.01
Anthocyanins (9-14)	10.77 ± 3.90	24.93 ± 5.31	27.76 ± 5.91
10-carboxy types (45-50)	25.27 ± 3.01	28.04 ± 2.91	28.12 ± 2.35
10-H types (51-56)	21.55 ± 3.47	27.64 ± 3.12	27.94 ± 3.23
Vinylcatechol types (63-68)	27.16 ± 1.40	27.91 ± 2.30	27.65 ± 2.59
Vinylphenol types (57-62)	30.13 ± 1.24	29.90 ± 2.16	30.18 ± 1.95

 Vinylaryl pyranoanthocyanin aglycone			
Compound subclass	Gas (°)	SMD MeOH (°)	SMD Water (°)
Vinylcatechol types (63-68)	17.67 ± 3.52	19.65 ± 2.82	21.08 ± 2.88
Vinylphenol types (57-62)	4.55 ± 0.38	12.5 ± 4.14	6.15 ± 4.25

Molecular Orbital Compositions and Charge Transfers of Anthocyanin and Acetyl Acylated Anthocyanins

Table D.6: Molecular orbital composition of anthocyanins (9-14) and net charge transfer (e) between the most important fragments (B3LYP/6-311++G(d,p) and SMD water).

							
Fragment	Fragment contribution HOMO (%)						Average
AC rings	31.22	31.07	24.91	52.82	29.76	39.13	34.82
B-ring	67.43	67.97	74.04	45.63	68.92	59.61	63.93
Glycosyl	1.36	0.97	1.05	1.55	1.33	1.26	1.25
Fragment	Fragment contribution LUMO (%)						Average
AC rings	80.54	80.86	80.10	80.34	79.31	76.96	79.68
B-ring	18.44	18.14	18.90	18.62	19.71	22.18	19.33
Glycosyl	1.02	1.01	1.01	1.04	0.98	0.86	0.99
Net charge transfer: B-ring → AC rings							
S ₀ → S ₁	0.40012	0.40209	0.53681	0.26884	0.48160	0.28846	
S ₀ → S ₂	0.15752	0.78849	0.78844	0.03014	0.01904	0.71345	

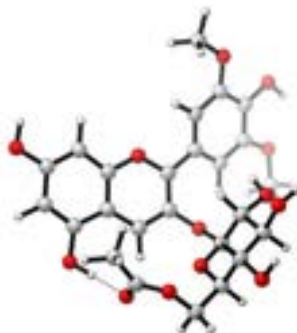
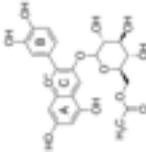
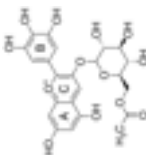
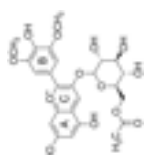
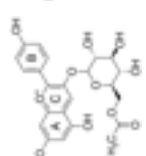
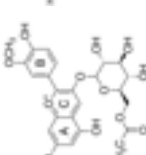
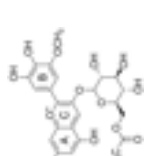


Figure D.4: A 3D representation of Mv-3-acetyl-glucoside (**20**).

Table D.7: Molecular orbital composition of acetyl acylated anthocyanins (**15-20**) and net charge transfer (*e*) between the most important fragments (B3LYP/6-311++G(d,p) and SMD water).

Fragment AC rings B-ring Glycosyl Acetyl								
	36.03	33.15	27.18	55.77	31.50	29.43	Average	
	61.78	64.92	71.08	41.03	66.24	68.91	35.41	
	2.07	1.81	1.53	2.99	1.97	1.56	62.44	
	0.12	0.12	0.09	0.22	0.10	0.10	1.97	
Fragment AC rings B-ring Glycosyl Acetyl	80.16	80.70	78.96	80.97	79.90	80.22	Average	
	18.21	17.55	19.08	17.34	18.34	18.05	80.15	
	1.17	1.24	1.21	1.19	1.23	1.23	18.07	
	0.46	0.51	0.49	0.51	0.48	0.51	1.22	
							0.50	
Net charge transfer: B-ring → AC rings								
$S_0 \rightarrow S_1$	0.32008	0.36277	0.43334	0.16087	0.38338	0.41561		
$S_0 \rightarrow S_2$	0.19522	0.78272	0.74549	0.15006	0.13364	0.71867		

Trend Analysis of Acylated Anthocyanins

Table D.8: The experimental and calculated shifts Δ (in nm) of acylated anthocyanins with respect to non-acylated anthocyanins (B3LYP/6-311++G(d,p) and SMD water). $\uparrow$: bathochromic shift and $\downarrow$: hypsochromic shift.

Experimental literature values						
Acyl group on glucose moiety	$\Delta_{Cy-3-Glc}$ (nm)	$\Delta_{Dp-3-Glc}$ (nm)	$\Delta_{Mv-3-Glc}$ (nm)	$\Delta_{Pg-3-Glc}$ (nm)	$\Delta_{Pn-3-Glc}$ (nm)	$\Delta_{Pt-3-Glc}$ (nm)
Aliphatic acids						
Acetic acid (15-20)	7 $\uparrow$	3 $\uparrow$	3 $\uparrow$	-	5 $\uparrow$	4 $\uparrow$
(Z)-Caffeic acid (21-26)	-	-	-	-	-	-
Aromatic acids						
(E)-Caffeic acid (27-32)	-	8 $\uparrow$	7 $\uparrow$	-	8 $\uparrow$	6 $\uparrow$
(Z)-p-coumaric acid (33-38)	17 $\uparrow$	10 $\uparrow$	8 $\uparrow$	-	18 $\uparrow$	11 $\uparrow$
(E)-p-coumaric acid (39-44)	8 $\uparrow$	7 $\uparrow$	5 $\uparrow$	-	9 $\uparrow$	7 $\uparrow$
Own calculations						
Acyl group on glucose moiety	$\Delta_{Cy-3-Glc}$ (nm)	$\Delta_{Dp-3-Glc}$ (nm)	$\Delta_{Mv-3-Glc}$ (nm)	$\Delta_{Pg-3-Glc}$ (nm)	$\Delta_{Pn-3-Glc}$ (nm)	$\Delta_{Pt-3-Glc}$ (nm)
Aliphatic acids						
Acetic acid (15-20)	5.35 $\downarrow$	5.07 $\downarrow$	3.68 $\downarrow$	2.65 $\downarrow$	6.78 $\downarrow$	22.47 $\downarrow$
(Z)-Caffeic acid (21-26)	57.66 $\uparrow$	48.9 $\uparrow$	39.76 $\uparrow$	64.16 $\uparrow$	44.72 $\uparrow$	36.11 $\uparrow$
Aromatic acids						
(E)-Caffeic acid (27-32)	27.62 $\uparrow$	45.08 $\uparrow$	8.13 $\uparrow$	42.98 $\uparrow$	33.99 $\uparrow$	5.22 $\uparrow$
(Z)-p-coumaric acid (33-38)	18.15 $\uparrow$	22.87 $\uparrow$	13.82 $\uparrow$	34.51 $\uparrow$	20.33 $\uparrow$	6.83 $\uparrow$
(E)-p-coumaric acid (39-44)	19.39 $\uparrow$	20.24 $\uparrow$	3.91 $\uparrow$	34.87 $\uparrow$	14.42 $\uparrow$	10.25 $\downarrow$

Rotational Barriers of Caffeoyl and Coumaroyl Acylated Anthocyanins

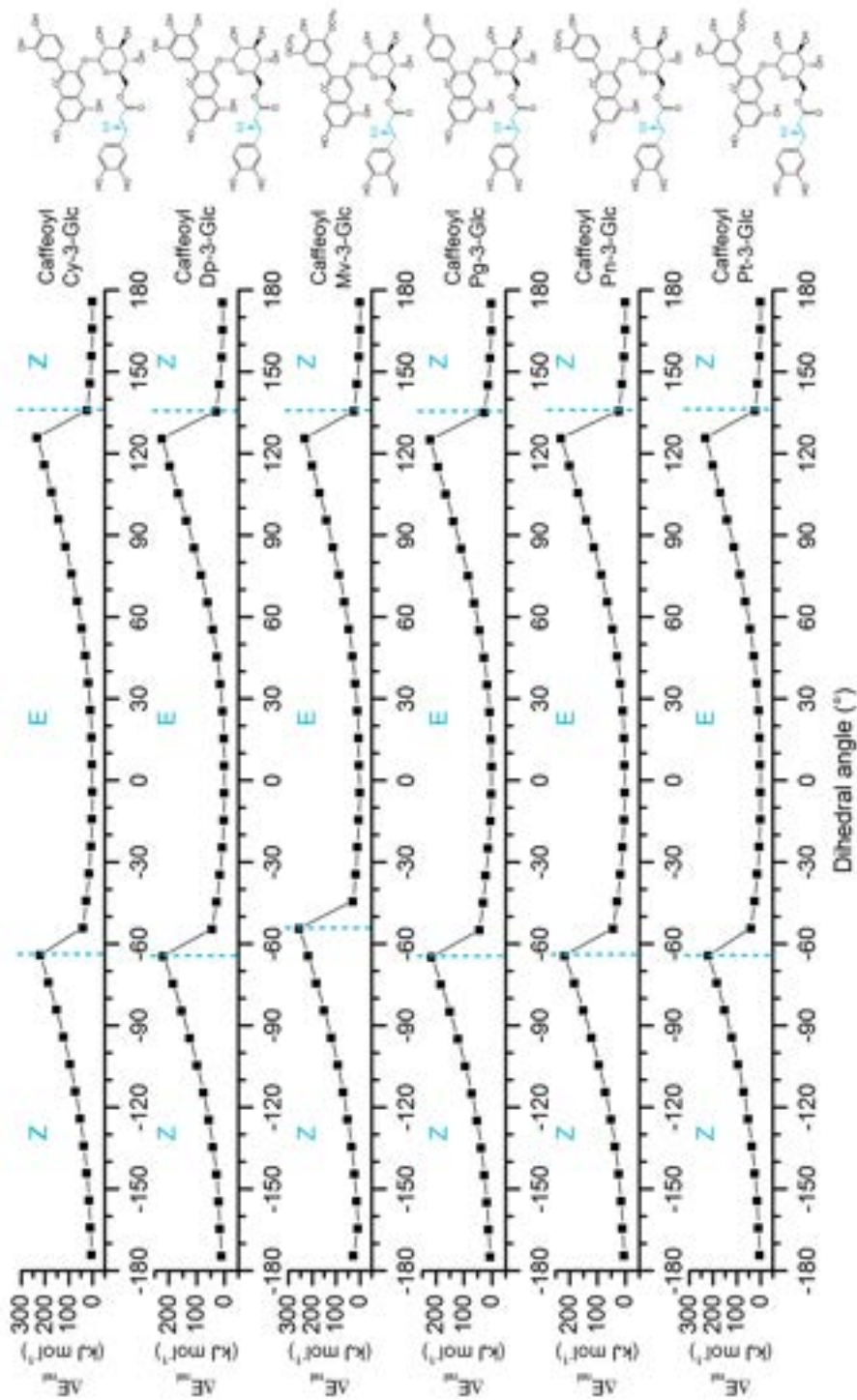


Figure D.5: Rotational barrier of (Z)- (21-26) and (E)- (27-32) caffeoyl acylated anthocyanins (B3LYP/6-311++G(d,p), GD3 and in gas phase).

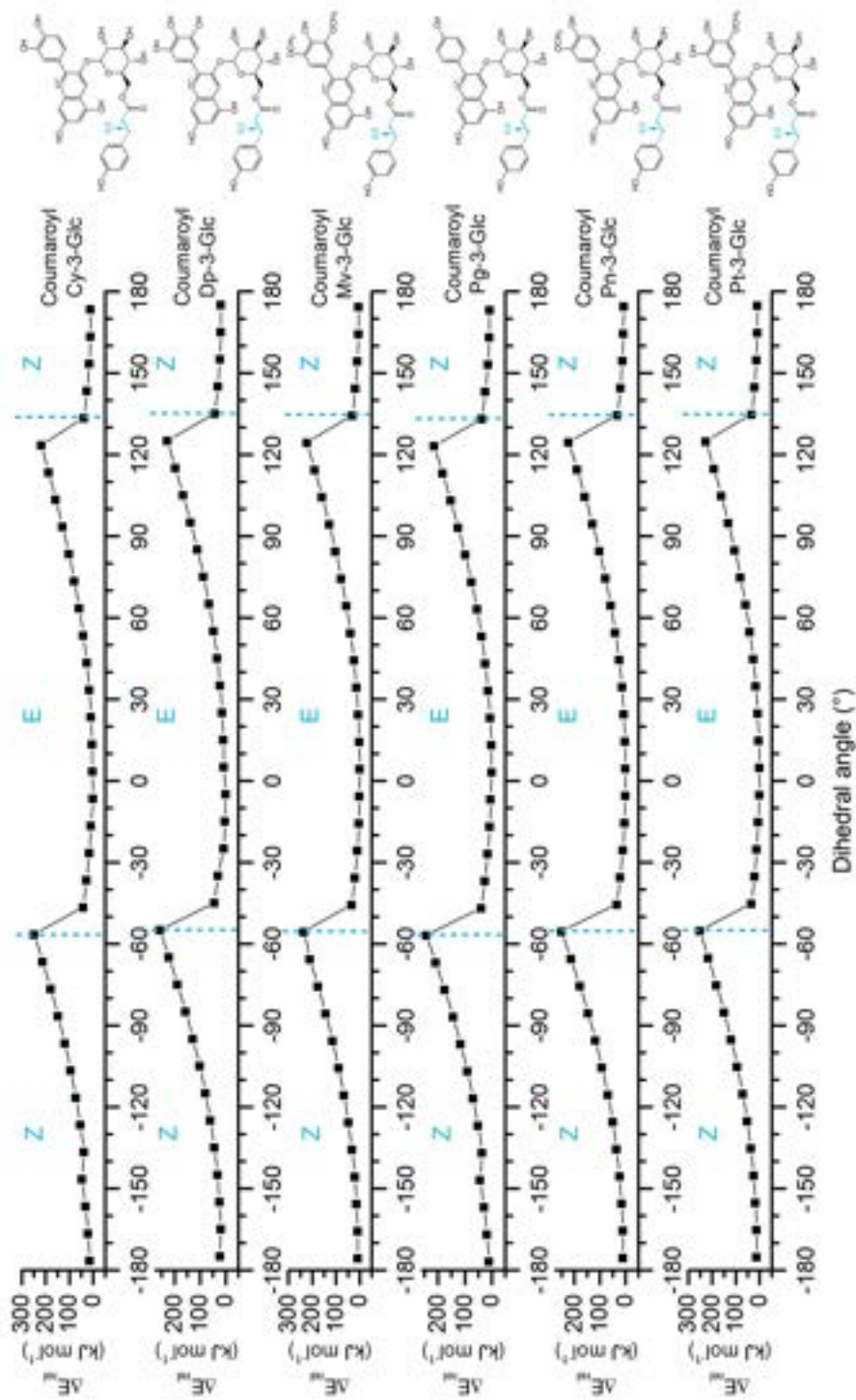


Figure D.6: Rotational barrier of (Z)- (33-38) and (E)- (39-44) coumaroyl acylated anthocyanins (B3LYP/6-311++G(d,p), GD3 and in gas phase).

Table D.9: The absolute Gibbs free energies of (Z)- and (E)-isomers of caffeoyl and coumaroyl acylated anthocyanins and the resulting energy gap between the two isomers (**21-44**) (B3LYP/6-311++G(d,p), GD3 correction and SMD as solvation model).

Caffeoyl acylated	SMD MeOH			SMD Water		
	Sum of electronic and thermal energies (hartree)		ΔG_{Z-E} (kJ/mol)	Sum of electronic and thermal energies (hartree)		ΔG_{Z-E} (kJ/mol)
Compound (Z E)	Z	E		Z	E	
Cy-3-Glc (22 28)	-2212.7209	-2212.7246	9.56	-2212.7194	-2212.7204	2.53
Dp-3-Glc (24 30)	-2287.9716	-2287.9744	7.42	-2287.9685	-2287.9699	3.78
Mv-3-Glc (26 32)	-2366.5347	-2366.5378	8.24	-2366.5307	-2366.5310	0.83
Pg-3-Glc (21 27)	-2137.4484	-2137.4525	10.70	-2137.4652	-2137.4691	10.19
Pr-3-Glc (23 29)	-2252.0049	-2252.0076	7.19	-2252.0015	-2252.0012	-0.90
Pt-3-Glc (25 31)	-2327.2513	-2327.2583	18.37	-2327.2270	-2327.2308	9.94
Average			10.25			4.40
Standard deviation			4.19			4.67
Coumaroyl acylated	SMD MeOH			SMD Water		
	Sum of electronic and thermal energies (hartree)		ΔG_{Z-E} (kJ/mol)	Sum of electronic and thermal energies (hartree)		ΔG_{Z-E} (kJ/mol)
Compound (Z E)	Z	E		Z	E	
Cy-3-Glc (34 40)	-2137.4692	-2137.4733	10.83	-2137.4646	-2137.4691	11.66
Dp-3-Glc (36 42)	-2212.7190	-2212.7225	9.18	-2212.7151	-2212.7190	10.42
Mv-3-Glc (38 44)	-2291.2832	-2291.2860	7.44	-2291.2778	-2291.2807	7.61
Pg-3-Glc (33 39)	-2062.2184	-2062.2228	11.54	-2062.2120	-2062.2175	14.37
Pr-3-Glc (35 41)	-2176.7538	-2176.7588	12.95	-2176.7472	-2176.7516	11.64
Pt-3-Glc (37 43)	-2252.0022	-2252.0062	10.41	-2251.9979	-2252.0021	11.04
Average			10.41			11.12
Standard deviation			1.90			2.19

UV-Vis Spectra of Caffeoyl and Coumaroyl Acylated Anthocyanins



Figure D.7: Calculated UV-Vis spectra of (Z)-caffeoyl acylated anthocyanins (21-26) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

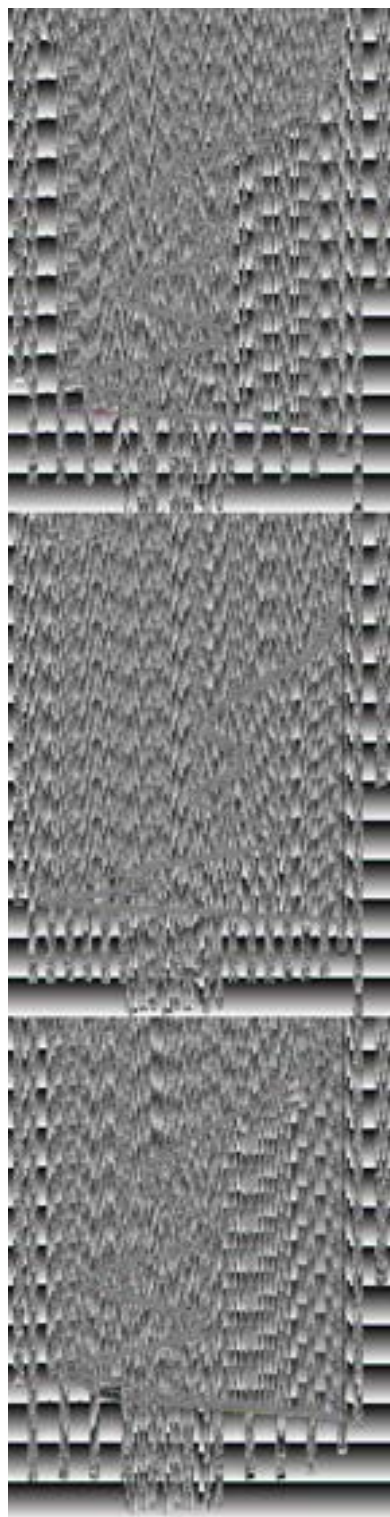


Figure D.8: Calculated UV-Vis spectra of (E)-caffeoyl acylated anthocyanins (27-32) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.



Figure D.9: Calculated UV-Vis spectra of (Z)-coumaroyl acylated anthocyanins (**33-38**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.



Figure D.10: Calculated UV-Vis spectra of (E)-coumaroyl acylated anthocyanins (**39-44**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

Excitation Energies and Oscillator Strengths

Table D.10: Excitation energies (eV) and oscillator strengths for the first 50 vertical excitation energies of cyanidin and malvidin anthocyanin- and pyranoanthocyanin based compounds (B3LYP/6-311++G** and SMD water). For other compounds only the first two excitation energies are given as they are responsible for $\lambda_{\text{max,vis}}$. Compound labels are according to Table D.1.

Anthocyanins											
Compound (1)		Compound (4)		Compound (8)		Compound (9)		Compound (10)		Compound (14)	
E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f
2.625	0.991	2.336	0.9096	2.2437	0.9747	2.5791	0.8786	2.4745	0.8144	2.3708	0.8466
3.0424	0.1621	2.8556	0.0674	2.7352	0.0118	3.0076	0.1269	2.8981	0.0034	2.7449	0.008
Compound (2)		3.1346	0.108	2.834	0.0575	Compound (11)		3.1938	0.1656	2.8986	0.0006
2.5276	0.9924	3.8197	0.0938	3.5735	0.1187	2.4332	0.8505	3.6734	0.0568	3.625	0.2322
2.9888	0.0357	4.3785	0.2499	4.2565	0.1801	2.9024	0.0022	3.829	0.0908	3.6937	0.0064
Compound (3)		4.5734	0.0841	4.4803	0.1682	Compound (12)		4.1757	0.0007	4.1546	0.1822
2.3854	0.8835	4.7042	0.2706	4.6636	0.2533	2.4594	0.8565	4.2946	0.1781	4.1807	0.0037
2.9683	0.2132	4.8881	0.1711	4.6955	0.1026	2.7333	0.0127	4.362	0.0002	4.3592	0.0002
Compound (5)		5.0544	0.0931	4.995	0.2732	Compound (13)		4.5129	0.0008	4.4665	0.0383
2.3143	0.9243	5.2402	0.3497	5.0507	0.0334	2.3422	0.9175	4.5927	0.4728	4.5116	0.0061
2.8473	0.042	5.3079	0.0137	5.1629	0.0014	2.7238	0.0221	4.633	0.011	4.5588	0.4551
Compound (6)		5.4349	0.0483	5.2213	0.2229			4.7711	0.0025	4.637	0.0028
2.3019	0.9179	5.4542	0.0061	5.3211	0.0007			4.8452	0.0469	4.7379	0.0619
2.7303	0.0137	5.5165	0.2473	5.4655	0.1153			5.0433	0.3265	4.813	0.0897
Compound (7)		5.6302	0.0248	5.4883	0.0008			5.0704	0.0365	5.0881	0.0962
2.2818	0.9225	5.6392	0.0499	5.5207	0.0007			5.2752	0.2029	5.1931	0.0968
2.7214	0.0144	5.6637	0.0016	5.5737	0.1			5.3976	0.0031	5.2608	0.0483
		5.6907	0.0136	5.6079	0.2874			5.4107	0.016	5.2662	0.0453
		5.8135	0.0737	5.66	0.3239			5.4393	0.0054	5.3969	0.0013
		5.8619	0.0073	5.6618	0.0441			5.4869	0.0108	5.4245	0.0665
		5.9069	0.5592	5.6914	0.0006			5.5842	0.0645	5.4586	0.0428
		5.9212	0.0137	5.6974	0.02			5.6464	0.0522	5.504	0.0092
		5.9848	0.3142	5.7389	0.0001			5.6708	0.006	5.5622	0.0434
		6.0002	0.2329	5.845	0.0001			5.7203	0.1503	5.5829	0.2965
		6.0329	0.0073	5.8573	0.0274			5.7923	0.055	5.6483	0.0142
		6.0394	0.0009	5.8785	0.0001			5.8148	0.0709	5.6747	0.0206
		6.091	0.0229	5.9089	0.0099			5.9013	0.0626	5.682	0.4213
		6.1756	0.0024	5.9212	0.5508			5.9201	0.4494	5.6873	0.0193
		6.223	0.0077	5.9466	0.0236			5.9434	0.0658	5.7418	0.0509
		6.2781	0.0022	5.982	0.0016			5.9537	0.0823	5.7775	0.011
		6.3047	0.0003	6.0391	0.0069			5.9667	0.0201	5.8214	0.0242
		6.3165	0.0078	6.0894	0.0129			5.9794	0.113	5.8381	0.0474
		6.3329	0.0043	6.0936	0.0005			5.9921	0.3066	5.8829	0.2683
		6.3551	0.1139	6.0969	0.0068			6.0355	0.0033	5.8972	0.0167
		6.4343	0.0338	6.1413	0.3927			6.057	0.0006	5.9135	0.2075
		6.4477	0.0087	6.1435	0.0483			6.0867	0.0013	5.9219	0.0025
		6.5033	0.0109	6.1955	0.0007			6.0943	0.0037	5.9642	0.0053
		6.5117	0.012	6.2387	0.0004			6.1136	0.062	5.9773	0.0065
		6.5568	0.0018	6.2568	0.1787			6.1179	0.0096	5.9832	0.0951
		6.5759	0.0001	6.2883	0.0145			6.1895	0.0141	6.0045	0.1613
		6.5899	0.0394	6.3027	0.0015			6.2174	0.0022	6.0107	0.0178
		6.5981	0.0011	6.3463	0.0001			6.2307	0.0029	6.0359	0.1277
		6.6272	0.1507	6.3532	0.0544			6.2351	0.0012	6.0495	0.0524
		6.6788	0.0014	6.3713	0.0021			6.311	0.0211	6.0715	0.0178
		6.7142	0.001	6.4639	0.0034			6.3231	0.065	6.0745	0.0047
		6.7416	0.002	6.4691	0.0532			6.3423	0.003	6.1014	0.043
		6.7799	0.0035	6.4877	0.0023			6.3433	0.0055	6.1712	0.0031
		6.8229	0.0539	6.5054	0.0005			6.3712	0.0742	6.2185	0.0498
		6.85	0.0124	6.5384	0.0001			6.3834	0.0286	6.2292	0.0104
		6.8871	0.0066	6.5796	0.0001			6.3956	0.0053	6.2399	0.1731

Compound (15)		Compound (16)		Compound (20)		Compound (21)		Compound (22)		Compound (26)	
E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f
2.5934	0.8065	2.5013	0.804	2.3876	0.8578	2.2754	0.0348	2.2192	0.0214	2.2033	0.0126
2.9904	0.1647	2.8676	0.0249	2.8088	0.0092	2.5518	0.7278	2.5039	0.7067	2.4021	0.7798
Compound (17)		3.1885	0.1384	2.858	0.0083	Compound (23)		2.7818	0.0852	2.7677	0.0219
2.466	0.818	3.6686	0.0185	3.5586	0.1143	2.2369	0.0397	2.9943	0.0081	2.8252	0.0091
2.8717	0.008	3.8003	0.1295	3.6899	0.1037	2.446	0.7078	3.2322	0.1241	3.0103	0.0028
Compound (18)		4.2676	0.0029	4.1514	0.208	Compound (24)		3.7115	0.0204	3.5873	0.1186
2.4844	0.8232	4.3086	0.2084	4.2686	0.0029	2.242	0.0372	3.8009	0.1268	3.7324	0.0842
2.8226	0.0113	4.4263	0.0003	4.4171	0.0005	2.4587	0.7782	3.8175	0.3663	3.8079	0.3652
Compound (19)		4.5301	0.4443	4.4897	0.1659	Compound (25)		3.9752	0.0464	3.9674	0.0815
2.446	0.8252	4.5452	0.0262	4.5062	0.328	2.1926	0.0141	4.0908	0.0035	4.0918	0.0042
2.809	0.0148	4.5815	0.0053	4.5169	0.0181	2.4444	0.7453	4.2471	0.0623	4.1502	0.0752
		4.8179	0.0445	4.5878	0.0181			4.2977	0.0005	4.2508	0.1136
		4.8478	0.0066	4.7714	0.0972			4.3549	0.056	4.2956	0.0015
		4.998	0.1924	4.8361	0.0174			4.3979	0.2155	4.3743	0.1283
		5.0244	0.1283	5.0604	0.0737			4.4844	0.0261	4.4776	0.1745
		5.1242	0.0238	5.0716	0.0301			4.5009	0.2629	4.4941	0.1414
		5.2584	0.2193	5.1849	0.1819			4.5628	0.003	4.5414	0.0242
		5.3647	0.0217	5.2046	0.09			4.6422	0.0128	4.5659	0.0006
		5.3762	0.0033	5.2242	0.0172			4.7038	0.0085	4.6212	0.0134
		5.4221	0.0096	5.2452	0.0067			4.7191	0.0646	4.7102	0.0211
		5.4331	0.0095	5.3559	0.0059			4.8005	0.0303	4.718	0.0613
		5.5069	0.0775	5.4357	0.056			4.8687	0.1041	4.7411	0.0039
		5.5644	0.1144	5.5152	0.0234			4.9086	0.0238	4.8015	0.0238
		5.6354	0.0178	5.5449	0.0461			4.9195	0.1085	4.8219	0.1743
		5.7116	0.0065	5.5711	0.0458			5.0046	0.08	4.9174	0.0092
		5.7313	0.0044	5.6131	0.3015			5.0164	0.2165	4.9507	0.18
		5.7579	0.0254	5.6318	0.1377			5.0356	0.053	5.0048	0.1556
		5.7792	0.0797	5.6689	0.2692			5.0548	0.1299	5.0782	0.0427
		5.821	0.012	5.6894	0.0038			5.0772	0.0299	5.1384	0.0147
		5.8846	0.5969	5.7085	0.019			5.1815	0.0364	5.155	0.177
		5.9129	0.4772	5.7899	0.0301			5.2299	0.0189	5.1892	0.0026
		5.9436	0.0196	5.7997	0.0087			5.2381	0.1525	5.209	0.0234
		5.9656	0.0044	5.8069	0.0362			5.3635	0.0177	5.2123	0.0238
		5.985	0.0157	5.8132	0.0294			5.3686	0.0016	5.2523	0.0323
		6.0128	0.0116	5.8211	0.0232			5.375	0.0051	5.3005	0.0089
		6.0138	0.0023	5.8633	0.3783			5.3975	0.0169	5.3051	0.0192
		6.043	0.0111	5.8873	0.0015			5.4083	0.094	5.3398	0.0011
		6.0796	0.0152	5.9065	0.0234			5.4137	0.0413	5.3475	0.01
		6.0934	0.0067	5.9163	0.0085			5.448	0.0271	5.3882	0.0055
		6.1197	0.0039	5.9479	0.0148			5.4778	0.0252	5.4175	0.0242
		6.1216	0.0009	5.952	0.0161			5.4969	0.013	5.4385	0.2018
		6.1426	0.0122	5.9577	0.0154			5.5162	0.0286	5.4702	0.0348
		6.1547	0.0128	5.9971	0.143			5.5336	0.0025	5.4927	0.0104
		6.1776	0.0043	6.02	0.177			5.5496	0.0091	5.5021	0.0155
		6.1943	0.0101	6.0514	0.0487			5.554	0.0102	5.5263	0.0353
		6.2422	0.0043	6.0768	0.0108			5.5877	0.0648	5.5399	0.0103
		6.2526	0.0015	6.0827	0.0223			5.6191	0.0601	5.5629	0.0058
		6.2565	0.0049	6.0873	0.0886			5.6453	0.1672	5.5826	0.0799
		6.2749	0.0588	6.0948	0.0072			5.6719	0.1691	5.5908	0.0311
		6.2962	0.1042	6.104	0.0034			5.682	0.0908	5.6112	0.2205

Compound (27)		Compound (28)		Compound (32)		Compound (33)		Compound (34)		Compound (38)	
E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f
2.3674	0.0091	2.3452	0.0096	2.3345	0.0472	2.4063	0.0308	2.388	0.1036	2.3097	0.0412
2.5906	0.8093	2.5112	0.764	2.3785	0.7589	2.5285	0.7889	2.4558	0.7284	2.3997	0.782
Compound (29)		2.9047	0.0035	2.8021	0.0095	Compound (35)		2.8255	0.0309	2.8175	0.0119
2.281	0.0259	3.1338	0.0252	2.891	0.0002	2.3398	0.0076	3.1222	0.0831	2.8554	0.0054
2.4316	0.7013	3.2507	0.1106	3.1447	0.0095	2.44	0.7491	3.3765	0.0596	3.2416	0.0264
Compound (30)		3.3371	0.8184	3.3302	0.8153	Compound (36)		3.744	0.5069	3.6111	0.0597
2.2576	0.0208	3.6236	0.0111	3.5583	0.0217	2.3527	0.0031	3.786	0.0043	3.7472	0.1092
2.4638	0.7508	3.7171	0.0167	3.5614	0.0519	2.4518	0.8229	3.8484	0.1146	3.846	0.4912
Compound (31)		3.8168	0.1495	3.6961	0.1766	Compound (37)		4.0291	0.0347	4.0577	0.0607
2.3193	0.0169	4.0344	0.1733	4.0045	0.0867	2.3123	0.0067	4.117	0.0326	4.0847	0.036
2.4339	0.757	4.0519	0.003	4.0349	0.0539	2.4454	0.7853	4.1669	0.002	4.1539	0.0065
		4.0822	0.0151	4.0375	0.0487			4.2428	0.0039	4.23	0.1708
		4.2447	0.0065	4.1185	0.0028			4.2876	0.1584	4.267	0.002
		4.3128	0.035	4.1616	0.2163			4.3793	0.0797	4.4659	0.0942
		4.3266	0.1689	4.2485	0.0044			4.427	0.0133	4.4838	0.1951
		4.4178	0.0007	4.3054	0.0014			4.5121	0.2028	4.5086	0.0271
		4.4607	0.0091	4.4069	0.0009			4.5459	0.1171	4.5415	0.0002
		4.4938	0.0043	4.4763	0.0048			4.591	0.0832	4.5648	0.0807
		4.5725	0.0963	4.5089	0.0342			4.652	0.004	4.5973	0.0767
		4.5915	0.3641	4.5445	0.3076			4.7822	0.0853	4.6835	0.0164
		4.7634	0.0004	4.5584	0.1598			4.8253	0.0038	4.7056	0.002
		4.8069	0.0432	4.6047	0.0011			4.846	0.0264	4.8018	0.1059
		4.8164	0.0215	4.745	0.0106			4.944	0.0191	4.8714	0.116
		4.8332	0.1179	4.7871	0.0875			4.974	0.1719	4.9007	0.0051
		4.8676	0.0431	4.7957	0.0466			5.0417	0.094	4.9498	0.0397
		4.8943	0.0483	4.8269	0.0172			5.0624	0.1267	4.9873	0.0301
		4.9183	0.1606	4.8452	0.1327			5.0835	0.0025	5.0579	0.1193
		4.9571	0.0435	4.9196	0.2046			5.1689	0.0274	5.1235	0.0107
		5.0312	0.2634	4.9556	0.0108			5.1783	0.0952	5.1443	0.1091
		5.0594	0.0073	5.0206	0.0062			5.229	0.1237	5.1657	0.1424
		5.0639	0.0121	5.0405	0.1068			5.2685	0.0161	5.2019	0.011
		5.0656	0.0179	5.1577	0.1756			5.2873	0.0152	5.219	0.0179
		5.1953	0.0051	5.1908	0.0032			5.3069	0.156	5.2285	0.1069
		5.2325	0.1693	5.2269	0.0035			5.3502	0.0029	5.3249	0.0245
		5.2973	0.0051	5.2447	0.0572			5.3538	0.0005	5.3434	0.0122
		5.3425	0.0266	5.2821	0.0118			5.3562	0.0289	5.386	0.0326
		5.359	0.0725	5.287	0.0015			5.4177	0.1501	5.4083	0.0123
		5.362	0.02	5.3478	0.0067			5.4345	0.0047	5.413	0.049
		5.4163	0.0353	5.3521	0.0354			5.5101	0.0212	5.427	0.0515
		5.4425	0.0047	5.3639	0.0058			5.5142	0.0108	5.4374	0.0476
		5.4539	0.0113	5.3999	0.0141			5.5335	0.01	5.4504	0.0167
		5.4914	0.0248	5.419	0.0919			5.5509	0.0102	5.4728	0.01
		5.5088	0.0579	5.4391	0.0006			5.5653	0.0031	5.497	0.1078
		5.5116	0.0034	5.4816	0.0052			5.5951	0.0362	5.5155	0.1137
		5.578	0.0049	5.5072	0.0017			5.5986	0.0388	5.5446	0.0042
		5.5962	0.0204	5.5381	0.0295			5.654	0.0005	5.5609	0.0309
		5.6335	0.1199	5.5708	0.0544			5.6691	0.0024	5.5926	0.0051
		5.6715	0.0132	5.5767	0.019			5.676	0.0114	5.6037	0.0943
		5.6863	0.0009	5.591	0.2713			5.6784	0.0821	5.6374	0.0053
		5.7023	0.141	5.6492	0.3022			5.7003	0.0719	5.6502	0.0251

Compound (39)		Compound (40)		Compound (44)	
E (eV)	f	E (eV)	f	E (eV)	f
2.4047	0.2151	2.3823	0.2737	2.3532	0.6592
2.6654	0.5816	2.579	0.4848	2.5188	0.1702
Compound (41)		2.896	0.0051	2.8148	0.0098
2.3662	0.4518	3.2231	0.145	2.9047	0.0014
2.559	0.2986	3.4412	0.879	3.4517	0.8616
Compound (42)		3.5401	0.0066	3.5389	0.1059
2.3645	0.322	3.6199	0.001	3.6473	0.0066
2.5629	0.4712	3.7728	0.0068	3.6561	0.1132
Compound (43)		3.7989	0.2436	3.691	0.1798
2.3884	0.4884	4.0603	0.0229	4.0474	0.0229
2.5298	0.3281	4.1226	0.0923	4.1062	0.152
		4.2058	0.0082	4.1847	0.0026
		4.3426	0.0658	4.2121	0.0765
		4.3782	0.05	4.2625	0.0025
		4.406	0.0098	4.3936	0.0047
		4.4083	0.0152	4.4023	0.0037
		4.4848	0.0254	4.43	0.0004
		4.5734	0.0273	4.5082	0.0295
		4.6	0.4254	4.5209	0.0033
		4.7167	0.0029	4.5584	0.3685
		4.7237	0.0035	4.5902	0.0888
		4.7949	0.0538	4.6196	0.0194
		4.8282	0.0198	4.7679	0.0393
		4.8421	0.1086	4.8189	0.0709
		4.9191	0.0022	4.8546	0.1114
		4.9933	0.1726	4.8605	0.0046
		5.0306	0.242	4.9787	0.0198
		5.0716	0.0395	5.0104	0.2307
		5.1176	0.0084	5.0782	0.0202
		5.1293	0.0079	5.0919	0.015
		5.1495	0.0103	5.1666	0.1892
		5.2243	0.1153	5.1881	0.0474
		5.2763	0.0259	5.2151	0.0036
		5.3107	0.1047	5.2656	0.0028
		5.3268	0.0333	5.3007	0.0141
		5.3871	0.0292	5.3355	0.0154
		5.4051	0.0059	5.3502	0.0099
		5.4077	0.0193	5.3576	0.0059
		5.4341	0.0137	5.4064	0.0078
		5.4591	0.1222	5.4191	0.0707
		5.4663	0.0071	5.4715	0.1242
		5.498	0.1063	5.5016	0.0807
		5.5176	0.0023	5.5234	0.0184
		5.5431	0.0005	5.5466	0.3453
		5.5467	0.0122	5.5728	0.0034
		5.5865	0.0306	5.5914	0.0054
		5.6605	0.0116	5.5961	0.0402
		5.6679	0.0284	5.6149	0.063
		5.7062	0.0034	5.6793	0.0064
		5.7146	0.001	5.6855	0.0021

Pyranoanthocyanins											
Compound (45)		Compound (46)		Compound (50)		Compound (51)		Compound (52)		Compound (56)	
E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f
2.5627	0.8872	2.4585	0.8061	2.3523	0.775	2.6346	0.925	2.5266	0.8222	2.4202	0.8275
3.0021	0.0934	2.9345	0.0682	2.8046	0.0041	3.1186	0.0913	3.0493	0.0656	2.8273	0.0057
Compound (47)		3.172	0.09	2.8713	0.0658	Compound (53)		3.2499	0.1018	3.0459	0.0621
2.4293	0.7301	3.3081	0.0003	3.3023	0.1693	2.5014	0.7572	3.603	0.2115	3.4631	0.1776
2.8883	0.0788	3.5065	0.2624	3.4067	0.0339	2.9941	0.0763	3.7399	0.0181	3.736	0.0128
Compound (48)		3.6543	0.0019	3.463	0.0006	Compound (54)		4.2065	0.175	4.0855	0.2503
2.4418	0.8689	3.7072	0.0202	3.7094	0.0006	2.5139	0.896	4.2176	0.0028	4.2022	0.001
2.7685	0.0082	3.9364	0.0131	3.9172	0.0129	2.8401	0.0114	4.4194	0.0011	4.3278	0.1264
Compound (49)		4.0312	0.0029	3.9698	0.2979	Compound (55)		4.5071	0.0106	4.4299	0.0037
2.4257	0.7755	4.0823	0.2417	4.0161	0.0189	2.4871	0.8236	4.5514	0.0417	4.4339	0.004
2.8087	0.0054	4.333	0.0064	4.2035	0.2009	2.8205	0.0121	4.5964	0.0091	4.4405	0.0476
		4.3748	0.0555	4.3395	0.0031			4.658	0.2413	4.5763	0.0027
		4.4691	0.0773	4.3614	0.0142			4.7242	0.0004	4.6516	0.3363
		4.5302	0.0006	4.3722	0.0446			4.8154	0.188	4.7347	0.0005
		4.5751	0.2816	4.4415	0.0048			4.8924	0.056	4.8341	0.1501
		4.6606	0.0037	4.5003	0.361			4.9538	0.0754	4.9532	0.0312
		4.6815	0.104	4.6711	0.049			5.0427	0.4749	4.9647	0.0008
		4.8149	0.1181	4.8092	0.0014			5.2541	0.042	5.0888	0.172
		4.8561	0.0472	4.905	0.0052			5.3116	0.0643	5.1507	0.0245
		4.8853	0.0006	4.9107	0.0002			5.3446	0.0359	5.173	0.2901
		4.9475	0.3395	4.9317	0.2732			5.3616	0.5853	5.2012	0.0731
		5.1527	0.0403	4.9934	0.0424			5.4008	0.0012	5.2408	0.1171
		5.2284	0.0332	5.0555	0.0443			5.5276	0.055	5.3849	0.0221
		5.2475	0.0063	5.0667	0.0358			5.5919	0.0059	5.4436	0.2501
		5.2658	0.5497	5.1388	0.0754			5.6329	0.0445	5.451	0.0116
		5.301	0.0054	5.151	0.2193			5.6403	0.0919	5.5429	0.0532
		5.3406	0.0408	5.2021	0.003			5.7055	0.002	5.5831	0.5203
		5.4651	0.0506	5.3194	0.0073			5.7601	0.0016	5.6005	0.1299
		5.4966	0.0001	5.3415	0.3006			5.7959	0.006	5.6356	0.0138
		5.5318	0.0146	5.4635	0.0009			5.8206	0.3244	5.7014	0.119
		5.5468	0.0189	5.4847	0.0251			5.8767	0.0146	5.7445	0.0053
		5.5916	0.1499	5.5093	0.1228			5.8961	0.0079	5.7732	0.0254
		5.6214	0.0485	5.5377	0.0329			5.9151	0.0823	5.7854	0.0114
		5.6336	0.0114	5.5438	0.1556			5.9353	0.0067	5.7899	0.0057
		5.6732	0.0845	5.5767	0.0961			5.9761	0.0159	5.812	0.1407
		5.7371	0.0372	5.5838	0.0229			5.9876	0.1019	5.8519	0.0049
		5.7481	0.1872	5.6006	0.2484			6.0212	0.001	5.894	0.0096
		5.7616	0.0015	5.6465	0.1145			6.0286	0.0053	5.9052	0.0162
		5.812	0.0103	5.6724	0.0023			6.0433	0.0522	5.9119	0.0304
		5.8333	0.0582	5.6835	0.0337			6.0743	0.0051	5.9176	0.0191
		5.8398	0.0016	5.7165	0.0227			6.0906	0.0391	5.9525	0.1681
		5.8737	0.029	5.7438	0.0389			6.0967	0.0076	5.9782	0.0708
		5.9141	0.0121	5.7576	0.0056			6.1501	0.0223	5.9907	0.0265
		5.9311	0.1401	5.7708	0.0221			6.1764	0.0445	6.0174	0.0322
		5.9476	0.0273	5.8103	0.1697			6.1923	0.1621	6.0347	0.0058
		5.96	0.0098	5.8415	0.0759			6.1973	0.0032	6.0389	0.0205
		5.975	0.0317	5.864	0.0551			6.2049	0.0926	6.0719	0.004
		6.0077	0.0613	5.8829	0.0374			6.2426	0.0422	6.0923	0.052
		6.0111	0.0811	5.8884	0.0156			6.2752	0.0012	6.1165	0.006
		6.0287	0.0248	5.8987	0.0063			6.3097	0.0093	6.132	0.0604

Compound (57)		Compound (58)		Compound (62)		Compound (63)		Compound (64)		Compound (68)	
E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f
2.487	1.3716	2.4456	1.3015	2.3617	1.2348	2.4304	1.2866	2.4177	1.2864	2.3182	1.2956
2.8555	0.3373	2.7802	0.2884	2.7468	0.3893	2.7327	0.2135	2.6951	0.1905	2.6255	0.2183
Compound (59)		3.0551	0.0949	2.9045	0.0304	Compound (65)		2.9897	0.006	2.8977	0.011
2.4172	1.2586	3.3469	0.1777	3.0727	0.0768	2.3696	1.278	3.2183	0.1892	2.9786	0.0271
2.7745	0.3806	3.6794	0.0007	3.56	0.1009	2.6524	0.1899	3.3959	0.1424	3.2463	0.1648
Compound (60)		3.7709	0.016	3.7745	0.0098	Compound (66)		3.6997	0.0039	3.5886	0.0614
2.4251	1.3173	3.8368	0.006	3.7937	0.0328	2.3815	1.2967	3.852	0.0058	3.8337	0.0151
2.7787	0.3274	3.9998	0.0416	3.8943	0.052	2.6647	0.1991	3.9736	0.0014	3.8827	0.0138
Compound (61)		4.1608	0.0009	4.1626	0.0292	Compound (67)		4.0987	0.4832	4.0445	0.4776
2.3958	1.2928	4.2038	0.3875	4.1722	0.3257	2.3563	1.3093	4.3471	0.0025	4.2717	0.0059
2.7613	0.3358	4.3784	0.0241	4.3205	0.0146	2.6479	0.199	4.3636	0.0003	4.3505	0.0073
		4.4659	0.0025	4.336	0.0184			4.4019	0.0931	4.3601	0.0148
		4.4722	0.1385	4.4344	0.0165			4.5023	0.0089	4.4095	0.1366
		4.6047	0.0097	4.4922	0.2348			4.5656	0.0025	4.4227	0.0225
		4.6427	0.0061	4.5133	0.0124			4.5877	0.015	4.6028	0.0023
		4.7007	0.1246	4.6381	0.0021			4.6268	0.0097	4.6227	0.0223
		4.742	0.1245	4.6975	0.288			4.6771	0.1114	4.6277	0.038
		4.7751	0.0139	4.7255	0.0227			4.7717	0.0507	4.6368	0.1616
		4.8393	0.0386	4.7574	0.0145			4.7988	0.0038	4.7443	0.0009
		4.883	0.1105	4.8481	0.0185			4.8498	0.262	4.7832	0.2039
		4.9629	0.4949	4.8522	0.0364			4.9234	0.1673	4.8699	0.0085
		5.03	0.0805	4.9175	0.0695			4.9629	0.0687	4.8924	0.03
		5.0793	0.0013	5.0582	0.2119			5.0631	0.3835	4.9396	0.1123
		5.1494	0.01	5.0645	0.0329			5.1031	0.0034	5.0774	0.2113
		5.1841	0.0439	5.097	0.0257			5.1542	0.0465	5.0939	0.0341
		5.2213	0.0337	5.108	0.0221			5.2051	0.0056	5.1225	0.0225
		5.2867	0.0021	5.1562	0.1468			5.2141	0.2167	5.1413	0.1737
		5.2989	0.0232	5.2214	0.0371			5.2788	0.008	5.1697	0.0062
		5.3453	0.2109	5.2384	0.0075			5.2813	0.0113	5.1894	0.1252
		5.3784	0.0818	5.3141	0.0068			5.3385	0.0089	5.2574	0.0488
		5.4246	0.1387	5.335	0.3706			5.3521	0.0276	5.2907	0.1304
		5.48	0.0019	5.4067	0.0111			5.3725	0.0036	5.3055	0.0436
		5.5259	0.128	5.4316	0.1099			5.4311	0.1174	5.3329	0.005
		5.5446	0.0314	5.4825	0.0437			5.4644	0.0328	5.4272	0.004
		5.5585	0.0226	5.4889	0.3519			5.5391	0.0657	5.4877	0.0931
		5.5888	0.2055	5.5471	0.1364			5.5532	0.0593	5.5128	0.4224
		5.5925	0.0002	5.5596	0.0012			5.5934	0.1069	5.5273	0.0993
		5.6065	0.0041	5.5738	0.0065			5.6074	0.228	5.5429	0.1338
		5.6474	0.0145	5.5747	0.0102			5.6519	0.2486	5.545	0.0023
		5.673	0.2294	5.5864	0.0798			5.6656	0.0183	5.584	0.0267
		5.6993	0.0527	5.5929	0.0337			5.675	0.0896	5.5991	0.1434
		5.7477	0.0071	5.6569	0.0525			5.7136	0.0045	5.6216	0.0717
		5.7578	0.0961	5.6732	0.0046			5.7301	0.0085	5.6548	0.0238
		5.7835	0.0098	5.6913	0.0522			5.7436	0.0732	5.6827	0.0215
		5.801	0.0436	5.7083	0.0167			5.7807	0.0055	5.6853	0.0377
		5.812	0.0202	5.7186	0.015			5.7952	0.0082	5.695	0.0168
		5.8679	0.0041	5.7455	0.0259			5.8133	0.1371	5.7171	0.0392
		5.8748	0.0146	5.7645	0.0029			5.8335	0.005	5.7576	0.0084
		5.8866	0.0633	5.7944	0.0776			5.86	0.0085	5.7701	0.0317
		5.9027	0.0048	5.7982	0.0212			5.8913	0.2817	5.7816	0.011

Compound (69)		Compound (70)		Compound (74)		Compound (75)		Compound (76)		Compound (80)	
E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f
2.5487	0.8744	2.4547	0.7793	2.3506	0.7951	2.6352	0.9116	2.5321	0.8045	2.427	0.8254
3.0053	0.1052	2.9361	0.0667	2.7894	0.0031	3.1167	0.0993	3.0478	0.0632	2.8525	0.0052
Compound (71)		3.1925	0.0959	2.9239	0.0659	Compound (77)		3.2667	0.104	3.0388	0.0576
2.4067	0.8065	3.3062	0.0004	3.3078	0.015	2.483	0.824	3.6089	0.2047	3.4625	0.1727
2.9347	0.0663	3.5164	0.2509	3.3671	0.18	3.0448	0.0607	3.8488	0.0142	3.8374	0.006
Compound (72)		3.6535	0.0018	3.6601	0.0002	Compound (78)		4.2034	0.1699	4.0899	0.2413
2.4499	0.8599	3.7565	0.012	3.7525	0.0054	2.5213	0.8618	4.2708	0.0024	4.2554	0.0167
2.7999	0.0085	3.9402	0.0146	3.9372	0.077	2.8664	0.0112	4.3142	0.0006	4.3081	0.011
Compound (73)		4.0777	0.2296	3.9658	0.2242	Compound (79)		4.4974	0.0069	4.3583	0.0941
2.4105	0.7988	4.1644	0.0007	4.1546	0.0659	2.4926	0.8102	4.5456	0.0485	4.4242	0.0118
2.7754	0.0055	4.2187	0.0052	4.209	0.0493	2.843	0.008	4.5657	0.0006	4.4526	0.044
		4.3629	0.0466	4.2573	0.0808			4.6413	0.2171	4.5638	0.0011
		4.4602	0.0652	4.3413	0.0053			4.6926	0.044	4.6381	0.3103
		4.4857	0.0062	4.3548	0.0406			4.8093	0.1852	4.6784	0.0312
		4.5657	0.2673	4.4863	0.0032			4.8814	0.0458	4.8178	0.1507
		4.6031	0.0432	4.5481	0.3639			4.9902	0.0468	4.9732	0.0003
		4.6813	0.092	4.5904	0.0167			5.0402	0.4686	4.992	0.0081
		4.8158	0.0947	4.6788	0.0652			5.1499	0.0255	5.0811	0.1739
		4.8831	0.0002	4.8582	0.0025			5.2514	0.0426	5.1389	0.0141
		4.9023	0.0102	4.8839	0.0073			5.2935	0.0996	5.1553	0.1135
		4.9355	0.3685	4.909	0.0018			5.3377	0.0239	5.1702	0.2171
		5.065	0.0283	4.9639	0.2389			5.3536	0.565	5.196	0.0972
		5.1549	0.0568	5.046	0.0553			5.4928	0.0029	5.2567	0.09
		5.2041	0.0761	5.0809	0.1105			5.4949	0.0013	5.3783	0.0043
		5.2458	0.0373	5.1351	0.099			5.5788	0.0067	5.4185	0.2298
		5.259	0.4681	5.1395	0.0905			5.6054	0.0595	5.4864	0.0349
		5.3293	0.0343	5.1865	0.0595			5.6757	0.0352	5.4908	0.0366
		5.3546	0.0059	5.2493	0.0019			5.6935	0.0055	5.5878	0.4256
		5.4656	0.0504	5.3338	0.1211			5.733	0.0022	5.5915	0.1712
		5.4899	0.0021	5.358	0.1517			5.7768	0.3595	5.6249	0.0189
		5.4955	0.0001	5.3774	0.0049			5.8638	0.0239	5.6822	0.0964
		5.5191	0.0216	5.477	0.1021			5.8871	0.0101	5.7603	0.0627
		5.5414	0.0097	5.494	0.0003			5.8958	0.0841	5.7625	0.0181
		5.5896	0.157	5.5414	0.3876			5.9184	0.0135	5.8047	0.0592
		5.6891	0.0309	5.5529	0.1809			5.9241	0.0467	5.8096	0.1447
		5.6934	0.2802	5.586	0.0458			5.9468	0.027	5.8198	0.0124
		5.7328	0.0005	5.5923	0.0099			5.9594	0.0118	5.8743	0.0096
		5.7585	0.0301	5.6216	0.0108			5.9669	0.0276	5.8757	0.0657
		5.7671	0.0048	5.6461	0.1031			5.9836	0.0348	5.8977	0.0052
		5.7917	0.0438	5.7148	0.0491			5.9913	0.0194	5.918	0.0389
		5.8172	0.0504	5.7406	0.1005			6.0308	0.0061	5.9253	0.0338
		5.8272	0.0314	5.7543	0.0299			6.053	0.0113	5.9343	0.0231
		5.842	0.0002	5.7605	0.0083			6.0585	0.0115	5.9496	0.0134
		5.8602	0.0132	5.7892	0.0422			6.0603	0.0295	5.9518	0.0124
		5.9002	0.118	5.7995	0.0052			6.1363	0.019	5.9632	0.0013
		5.9242	0.0118	5.8212	0.0105			6.1366	0.0256	5.9782	0.0163
		5.9525	0.0078	5.8269	0.0401			6.1624	0.0201	5.9816	0.0447
		5.9612	0.0258	5.8396	0.0121			6.1785	0.0769	6.0067	0.0393
		5.9687	0.0133	5.8507	0.0254			6.1831	0.162	6.0233	0.0589
		5.9856	0.0609	5.8798	0.0086			6.1947	0.0283	6.036	0.0061

Compound (81)		Compound (82)		Compound (86)		Compound (87)		Compound (88)		Compound (92)	
E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f
2.5549	1.2791	2.5221	1.2072	2.422	1.1821	2.4377	1.2963	2.4048	1.2788	2.3342	1.2912
2.9127	0.3184	2.8227	0.2949	2.761	0.3676	2.7302	0.2049	2.6748	0.1878	2.6239	0.1982
Compound (83)		3.1138	0.0715	2.9913	0.0096	Compound (89)		2.98	0.0329	2.876	0.0111
2.4561	1.2476	3.4036	0.161	3.1146	0.089	2.3806	1.2868	3.1951	0.1109	2.9777	0.0289
2.7827	0.3219	3.6671	0.007	3.5976	0.1085	2.6556	0.1897	3.368	0.1871	3.2473	0.1718
Compound (84)		3.7881	0.0276	3.7266	0.0397	Compound (90)		3.707	0.0036	3.5844	0.0645
2.4697	1.2509	3.8301	0.0092	3.8207	0.0119	2.393	1.2972	3.775	0.0154	3.7549	0.0226
2.8116	0.3407	4.0677	0.0049	3.9327	0.0381	2.6638	0.1827	3.9599	0.0168	3.8831	0.0103
Compound (85)		4.236	0.3468	4.154	0.3762	Compound (91)		4.0861	0.4287	4.0298	0.4858
2.4668	1.2363	4.2842	0.0222	4.3049	0.0111	2.3661	1.3125	4.2831	0.0006	4.2601	0.0033
2.7887	0.3119	4.3909	0.0328	4.3232	0.0006	2.6416	0.1785	4.3675	0.0026	4.3094	0.0047
		4.4184	0.0006	4.3674	0.0272			4.4035	0.1339	4.3248	0.0074
		4.5145	0.1929	4.4289	0.0004			4.5285	0.0028	4.3993	0.1396
		4.5843	0.0024	4.4827	0.1489			4.5694	0.0528	4.4367	0.0417
		4.6743	0.0265	4.5125	0.04			4.6018	0.0284	4.534	0.0038
		4.708	0.0913	4.5804	0.0162			4.6684	0.107	4.6174	0.1713
		4.7399	0.1967	4.672	0.3203			4.7605	0.0678	4.6209	0.0375
		4.8243	0.0399	4.7491	0.0485			4.8313	0.2745	4.7771	0.2209
		4.8706	0.0392	4.8495	0.0583			4.854	0.0014	4.8469	0.0011
		4.953	0.0927	4.8709	0.0051			4.8875	0.0936	4.8491	0.0002
		4.9747	0.3548	4.923	0.0975			4.9618	0.15	4.9004	0.0461
		5.02	0.0159	4.9588	0.022			5.0095	0.0034	4.9269	0.095
		5.0504	0.0396	4.9895	0.0084			5.0621	0.011	4.9806	0.0104
		5.113	0.001	5.057	0.08			5.0668	0.1131	5.037	0.0043
		5.1464	0.0436	5.0692	0.0959			5.1425	0.0166	5.0572	0.1664
		5.1952	0.1962	5.1163	0.116			5.1682	0.0103	5.1032	0.0264
		5.22	0.0138	5.123	0.0885			5.1847	0.034	5.1275	0.1022
		5.2655	0.0643	5.1467	0.034			5.198	0.3897	5.1602	0.0419
		5.2961	0.0119	5.1531	0.0112			5.2174	0.0037	5.1731	0.0798
		5.3366	0.0036	5.227	0.0542			5.2968	0.0272	5.1853	0.0916
		5.386	0.212	5.3147	0.0041			5.3243	0.0236	5.2022	0.0062
		5.4054	0.1303	5.3382	0.2276			5.3371	0.0973	5.2274	0.0463
		5.4181	0.1312	5.3622	0.0046			5.3549	0.0007	5.2794	0.1695
		5.5082	0.0465	5.3978	0.1409			5.4202	0.2978	5.3342	0.0021
		5.5235	0.0743	5.4314	0.007			5.4323	0.0036	5.3632	0.0108
		5.5533	0.0012	5.4747	0.1687			5.4526	0.015	5.4294	0.0415
		5.5648	0.0349	5.5012	0.141			5.4712	0.023	5.4398	0.0161
		5.5705	0.0049	5.5323	0.2471			5.5017	0.024	5.481	0.1034
		5.6001	0.1239	5.5526	0.0459			5.5335	0.0008	5.5009	0.4082
		5.6383	0.0305	5.5902	0.0443			5.6033	0.0847	5.5387	0.2574
		5.6858	0.0071	5.6199	0.014			5.6168	0.0848	5.5475	0.0173
		5.6985	0.0635	5.6238	0.0338			5.6604	0.0447	5.5622	0.0067
		5.7133	0.0035	5.6488	0.0086			5.6702	0.0892	5.5814	0.0036
		5.7307	0.0008	5.6517	0.0561			5.6864	0.0072	5.6142	0.0159
		5.7471	0.0167	5.6603	0.0107			5.7086	0.0097	5.6282	0.1044
		5.798	0.0104	5.6786	0.0202			5.715	0.0388	5.6312	0.0588
		5.8012	0.0049	5.696	0.0282			5.7323	0.0439	5.6836	0.001
		5.8052	0.0084	5.7083	0.003			5.7384	0.2051	5.6918	0.0033
		5.8139	0.0234	5.7289	0.0076			5.7497	0.0229	5.6997	0.0087
		5.8334	0.0397	5.73	0.0014			5.7886	0.0042	5.7153	0.15

Compound (93)		Compound (94)		Compound (98)		Compound (99)		Compound (100)		Compound (104)	
E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f
2.3091	0.0172	2.2995	0.0267	2.2568	0.2641	2.3672	0.0914	2.3529	0.139	2.3981	0.3586
2.5792	0.8431	2.4809	0.7382	2.4073	0.5389	2.6695	0.7969	2.5736	0.65	2.4549	0.4738
Compound (95)		2.9146	0.061	2.7924	0.0026	Compound (101)		3.0056	0.0425	2.8565	0.0048
2.307	0.0396	3.1674	0.0427	2.8875	0.0469	2.3618	0.1567	3.2726	0.1014	3.007	0.0358
2.4501	0.6499	3.1967	0.0474	3.2408	0.0262	2.5501	0.5933	3.3258	0.0225	3.2565	0.0735
Compound (96)		3.2973	0.0059	3.3176	0.0125	Compound (102)		3.3674	0.7185	3.3975	0.7655
2.2798	0.0219	3.4081	0.801	3.365	0.6921	2.3857	0.0186	3.6279	0.1656	3.498	0.136
2.4603	0.8234	3.5045	0.2586	3.3999	0.1352	2.5209	0.8063	3.7652	0.062	3.5298	0.0353
Compound (97)		3.646	0.003	3.6521	0.0756	Compound (103)		3.8569	0.0153	3.8361	0.0057
2.2937	0.0382	3.7895	0.018	3.6684	0.0004	2.3546	0.1951	3.9663	0.0383	3.9972	0.0459
2.4411	0.7116	3.8033	0.0042	3.7639	0.008	2.54	0.6203	4.0575	0.1684	4.0256	0.0341
		3.897	0.0101	3.844	0.083			4.2308	0.0431	4.0468	0.0201
		3.9099	0.0153	3.9467	0.0205			4.2421	0.1384	4.1114	0.213
		4.1019	0.1576	4.0082	0.2132			4.2635	0.0732	4.1617	0.1218
		4.1153	0.242	4.0172	0.1067			4.2839	0.0014	4.2201	0.0198
		4.1848	0.0578	4.1481	0.1222			4.3102	0.0024	4.3232	0.0028
		4.2133	0.0176	4.1548	0.0129			4.4068	0.0017	4.3668	0.007
		4.2276	0.003	4.1806	0.0394			4.4596	0.0456	4.382	0.0847
		4.2724	0.0007	4.2113	0.0032			4.5257	0.0097	4.4123	0.0048
		4.3175	0.0013	4.2262	0.1136			4.5692	0.0447	4.4552	0.0055
		4.3778	0.0597	4.2603	0.0373			4.5762	0.0198	4.4754	0.0417
		4.4786	0.0245	4.3493	0.0357			4.6357	0.2786	4.485	0.0134
		4.4834	0.0689	4.3713	0.0094			4.7074	0.0356	4.5629	0.0082
		4.4954	0.0088	4.3878	0.0582			4.7688	0.1485	4.6243	0.3058
		4.5864	0.2899	4.4887	0.0049			4.7829	0.007	4.6664	0.0124
		4.6372	0.0003	4.5073	0.0265			4.8149	0.2255	4.8078	0.0049
		4.6643	0.0021	4.5288	0.422			4.8505	0.0273	4.8286	0.1425
		4.6786	0.0781	4.6126	0.0082			4.876	0.0833	4.863	0.196
		4.7772	0.0213	4.6786	0.1122			4.9338	0.0873	4.8997	0.3442
		4.7985	0.0142	4.7556	0.2425			4.9585	0.0778	4.9538	0.0042
		4.8098	0.0434	4.8146	0.0028			4.9919	0.0197	4.959	0.0027
		4.8302	0.0679	4.817	0.0305			5.0583	0.0287	5.0129	0.0004
		4.8779	0.3849	4.8392	0.0083			5.0624	0.3639	5.0629	0.0112
		4.8879	0.0179	4.8742	0.0036			5.0785	0.0097	5.0991	0.0226
		4.8985	0.0168	4.8954	0.01			5.1397	0.0224	5.1174	0.0223
		4.9169	0.0266	4.9047	0.0011			5.151	0.0209	5.1398	0.0552
		4.9586	0.2955	4.9493	0.0526			5.1779	0.0309	5.1475	0.18
		5.0146	0.0032	5.0052	0.1799			5.27	0.0764	5.1579	0.0178
		5.0179	0.0205	5.0326	0.0245			5.2921	0.0639	5.1758	0.0302
		5.0515	0.0041	5.0516	0.003			5.3267	0.0448	5.2002	0.1441
		5.092	0.0305	5.0672	0.0496			5.3707	0.24	5.2371	0.1452
		5.0974	0.0008	5.0775	0.0073			5.3986	0.2309	5.274	0.0909
		5.1433	0.0003	5.126	0.1267			5.4613	0.0914	5.3685	0.0569
		5.1677	0.0298	5.1335	0.0764			5.4651	0.0294	5.4207	0.0014
		5.1899	0.006	5.161	0.0934			5.5008	0.0197	5.4399	0.0325
		5.2453	0.0684	5.1768	0.0561			5.5231	0.0045	5.4563	0.0692
		5.2543	0.0088	5.1857	0.0001			5.5331	0.0122	5.464	0.0795
		5.2744	0.4678	5.2557	0.0065			5.573	0.0001	5.5065	0.0612
		5.334	0.0675	5.2612	0.0007			5.6012	0.0044	5.5159	0.0312
		5.3952	0.0094	5.3212	0.0235			5.6237	0.0959	5.5225	0.0014

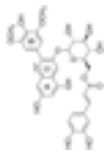
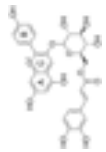
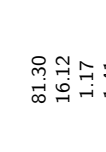
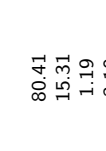
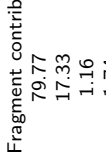
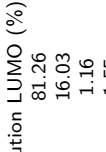
Compound (105)		Compound (106)		Compound (110)		Compound (111)		Compound (112)		Compound (116)	
E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f
2.4794	0.0126	2.464	0.0423	2.4342	1.0386	2.4565	1.2805	2.4267	1.2548	2.3484	1.2733
2.5709	1.1884	2.5232	1.1184	2.5031	0.0087	2.7051	0.0027	2.6925	0.0646	2.6434	0.2296
Compound (107)		2.8179	0.2971	2.7752	0.4139	Compound (113)		2.7008	0.1406	2.6938	0.0029
2.4706	0.0049	3.0471	0.0703	2.9736	0.0028	2.3982	1.2673	2.9959	0.0217	2.9073	0.0114
2.4904	1.0857	3.3661	0.023	3.0527	0.0874	2.6762	0.2066	3.2209	0.1226	2.99	0.0168
Compound (108)		3.3904	0.774	3.3956	0.2195	Compound (114)		3.2831	0.8661	3.2658	0.2132
2.4517	1.1566	3.3967	0.1784	3.4003	0.6144	2.4032	1.3004	3.3811	0.1737	3.2848	0.8191
2.478	0.0811	3.6278	0.0046	3.5128	0.0046	2.6766	0.1119	3.5237	0.0005	3.4834	0.0008
Compound (109)		3.6939	0.0054	3.5984	0.1134	Compound (115)		3.5585	0.0001	3.5559	0.0004
2.4584	0.01	3.788	0.0338	3.7446	0.0341	2.3792	1.307	3.7178	0.0029	3.5969	0.0714
2.4917	1.0768	3.8325	0.0081	3.8201	0.0001	2.6594	0.1938	3.7924	0.0006	3.686	0.0004
		3.8631	0.0039	3.8405	0.0122			3.7935	0.0105	3.7724	0.0142
		3.9432	0.0224	3.9584	0.035			4.0012	0.2462	3.9068	0.0148
		4.0108	0.0539	3.9875	0.0693			4.0039	0.0236	4.0023	0.2526
		4.1047	0.009	3.9952	0.05			4.1381	0.4074	4.0634	0.4722
		4.2056	0.0898	4.0498	0.0038			4.1564	0.0009	4.0972	0.0001
		4.2687	0.2296	4.2148	0.0927			4.1586	0.0149	4.14	0.0033
		4.2852	0.0885	4.224	0.29			4.3386	0.0007	4.1487	0.0003
		4.3105	0.042	4.2889	0.0358			4.3603	0.0001	4.2919	0.0042
		4.4172	0.0058	4.3257	0.0017			4.3958	0.0027	4.3495	0.0019
		4.4265	0.0446	4.3661	0.0254			4.4396	0.141	4.3592	0.0078
		4.469	0.0046	4.4196	0.0401			4.4854	0.0004	4.3905	0.0009
		4.483	0.0072	4.4287	0.0096			4.5838	0.0306	4.4184	0.1485
		4.5081	0.2035	4.4792	0.002			4.5886	0.0005	4.4405	0.0347
		4.6067	0.0074	4.5037	0.217			4.6116	0.044	4.4849	0.0021
		4.6514	0.0304	4.5646	0.0139			4.6383	0.0001	4.6314	0.0319
		4.7146	0.1144	4.5954	0.0019			4.6959	0.0004	4.6345	0.0258
		4.7396	0.0594	4.625	0.0065			4.6972	0.0048	4.6465	0.1615
		4.757	0.0017	4.6903	0.2885			4.7003	0.1213	4.6882	0.0026
		4.8112	0.0124	4.7566	0.0239			4.7623	0.0012	4.692	0
		4.8171	0.0991	4.7897	0.0081			4.7807	0.058	4.7611	0.0002
		4.8288	0.0156	4.8191	0.0315			4.8488	0.2305	4.773	0.0018
		4.8422	0.0053	4.8297	0.1002			4.8585	0.0668	4.7982	0.2011
		4.8553	0.025	4.8398	0.116			4.8771	0.2866	4.864	0.1527
		4.8567	0.0163	4.8441	0.0452			4.8993	0.0158	4.872	0.0003
		4.8745	0.1094	4.8691	0.0832			4.9158	0.1407	4.8831	0.2137
		4.8844	0.2704	4.8745	0.0074			4.9479	0.0137	4.9142	0.0383
		4.912	0.0241	4.8812	0.0471			4.9816	0.1457	4.9266	0.0071
		4.9856	0.3808	4.9306	0.0788			5.0025	0.0122	4.9535	0.0966
		4.9941	0.0105	4.9652	0.0774			5.0221	0.0003	4.9796	0.0136
		5.0209	0.007	5.0232	0.0345			5.0956	0.1506	5.0033	0.0005
		5.0488	0.0111	5.0454	0.001			5.1796	0.0001	5.0962	0.2476
		5.076	0.0352	5.075	0.0265			5.1814	0.0003	5.1314	0.0614
		5.0929	0.0008	5.0877	0.0685			5.196	0.0291	5.1538	0.1068
		5.1147	0.0038	5.096	0.0854			5.2077	0.0979	5.1779	0.0016
		5.1431	0.112	5.1001	0.0369			5.2212	0.2661	5.1806	0.0001
		5.1996	0.1076	5.103	0.0216			5.2394	0.0008	5.1989	0.0902
		5.2169	0.0705	5.1147	0.1187			5.2552	0.0135	5.2219	0.0016
		5.2254	0.0065	5.1898	0.0126			5.301	0.026	5.2262	0.0045
		5.2726	0.0485	5.1938	0.0383			5.3216	0.0144	5.2692	0.1524

Compound (117)		Compound (118)		Compound (122)		Compound (123)		Compound (124)		Compound (128)	
E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f
2.4318	0.0529	2.4152	0.1519	2.3273	0.5933	2.4982	0.1934	2.4657	0.3676	2.4016	0.6416
2.5829	0.8133	2.4916	0.6127	2.4637	0.2091	2.6758	0.7066	2.5961	0.43	2.5545	0.1788
Compound (119)		2.9139	0.0621	2.7953	0.004	Compound (125)		3.0373	0.0451	2.8572	0.006
2.3824	0.3463	3.1796	0.0878	2.9167	0.0448	2.4694	0.4633	3.2885	0.109	3.0259	0.042
2.4928	0.4055	3.2954	0.0062	3.3145	0.0193	2.5859	0.3021	3.5235	0.8339	3.46	0.1577
Compound (120)		3.5029	0.2006	3.3756	0.1659	Compound (126)		3.5606	0.2365	3.5111	0.8134
2.3965	0.1911	3.5477	1.0598	3.5013	0.802	2.4596	0.3216	3.788	0.0513	3.6811	0.1548
2.4728	0.66	3.619	0.0098	3.6636	0.0016	2.5714	0.5344	3.7987	0.0415	3.7648	0.0135
Compound (121)		3.6598	0.0165	3.6705	0.142	Compound (127)		3.8549	0.0153	3.8535	0.0105
2.3651	0.4073	3.7886	0.0192	3.6839	0.0195	2.4456	0.4857	4.0919	0.0747	4.0581	0.1575
2.4828	0.3959	3.8271	0.0117	3.7666	0.0106	2.5746	0.336	4.1929	0.0206	4.1365	0.0104
		3.9121	0.0138	3.9315	0.1722			4.2483	0.1215	4.1665	0.108
		4.0199	0.0357	3.9514	0.0375			4.3018	0.0028	4.1868	0.009
		4.1242	0.2216	4.0515	0.0906			4.3336	0.0022	4.2912	0.0214
		4.1576	0.0099	4.1073	0.0167			4.3617	0.033	4.3244	0.0328
		4.2297	0.0046	4.1737	0.022			4.4277	0.0375	4.3501	0.0267
		4.3037	0.0041	4.1797	0.1221			4.4376	0.0073	4.3668	0.0488
		4.3384	0.009	4.2287	0.0129			4.5201	0.0104	4.4304	0.036
		4.3645	0.0156	4.2553	0.0307			4.5329	0.0451	4.4673	0.0083
		4.3793	0.049	4.3032	0.0316			4.5717	0.0223	4.4753	0.0197
		4.4543	0.0009	4.3781	0.024			4.5786	0.0351	4.4776	0.0483
		4.48	0.0153	4.3862	0.029			4.6513	0.2428	4.5671	0.0028
		4.485	0.0815	4.4062	0.0454			4.7058	0.0353	4.5767	0.0919
		4.5259	0.0252	4.4157	0.0343			4.7895	0.1674	4.6491	0.3278
		4.5879	0.2814	4.489	0.0026			4.826	0.0833	4.6949	0.0194
		4.6573	0.0002	4.55	0.3448			4.8699	0.0208	4.829	0.1793
		4.6643	0.002	4.5647	0.1634			4.8903	0.1191	4.8655	0.0437
		4.6812	0.092	4.614	0.0087			4.9326	0.1771	4.9037	0.2261
		4.8127	0.0278	4.7077	0.0905			4.9899	0.0176	4.9728	0.0042
		4.8171	0.0705	4.8209	0.0063			5.033	0.2987	4.9904	0.0028
		4.8418	0.0231	4.8467	0.095			5.0877	0.0128	5.0239	0.0161
		4.8867	0.0251	4.8594	0.087			5.1226	0.1041	5.0753	0.0099
		4.8986	0.0222	4.8778	0.0211			5.1484	0.0165	5.1204	0.2731
		4.9424	0.4896	4.8958	0.0042			5.181	0.2474	5.1342	0.1152
		4.9551	0.0867	4.9045	0.0018			5.2243	0.0129	5.1515	0.0456
		5.014	0.0226	4.9555	0.0169			5.3097	0.0483	5.1794	0.0176
		5.0361	0.0038	5.0108	0.2018			5.3204	0.0411	5.1965	0.1306
		5.0604	0.0545	5.062	0.089			5.3333	0.1358	5.2567	0.0105
		5.0735	0.003	5.0688	0.0258			5.3944	0.0002	5.3004	0.0791
		5.1189	0.004	5.1093	0.1212			5.4095	0.0288	5.3513	0.0138
		5.1637	0.028	5.1325	0.0797			5.4213	0.2378	5.371	0.0049
		5.2072	0.0088	5.1629	0.0758			5.482	0.139	5.4019	0.1404
		5.2342	0.0346	5.1728	0.0173			5.5146	0.0068	5.4563	0.0521
		5.2551	0.3678	5.1904	0.0001			5.5193	0.0224	5.4756	0.2547
		5.2597	0.0033	5.2394	0.043			5.5292	0.0066	5.5068	0.0109
		5.2892	0.1029	5.249	0.0156			5.5333	0.0118	5.5224	0.0759
		5.3284	0.0007	5.2601	0.003			5.6386	0.0606	5.526	0.1171
		5.3404	0.0967	5.2653	0.0062			5.6449	0.0003	5.5566	0.0493
		5.3948	0.0041	5.3494	0.1353			5.666	0.0236	5.5707	0.0196
		5.4537	0.0019	5.3647	0.0091			5.6911	0.0069	5.5791	0.0011

Compound (129)		Compound (130)		Compound (134)		Compound (135)		Compound (136)		Compound (140)	
E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f
2.5328	1.2816	2.5354	1.1160	2.4356	1.0480	2.4593	1.2828	2.4283	1.2520	2.3483	1.2748
2.6134	0.0400	2.5659	0.0491	2.5956	0.0738	2.7607	0.2226	2.6999	0.2070	2.6440	0.2319
Compound (131)		2.8466	0.2562	2.7858	0.3353	Compound (137)		2.8461	0.0002	2.8425	0.0003
2.4974	1.1098	3.1085	0.1011	2.9780	0.0031	2.4017	1.2569	2.9984	0.0221	2.9076	0.0115
2.6198	0.0386	3.3998	0.1497	3.1009	0.1179	2.6761	0.2096	3.2225	0.1175	2.9908	0.0171
Compound (132)		3.5165	0.9438	3.5212	0.7469	Compound (138)		3.3825	0.1899	3.2662	0.1686
2.4727	1.1985	3.6673	0.0205	3.5559	0.2587	2.4043	1.2966	3.4410	1.1201	3.4408	1.1206
2.5858	0.0616	3.7044	0.0073	3.5950	0.1169	2.6798	0.1971	3.5481	0.0036	3.5054	0.0135
Compound (133)		3.7800	0.0239	3.7391	0.0270	Compound (139)		3.7168	0.0031	3.5967	0.0700
2.4912	1.0831	3.7882	0.0021	3.8122	0.0035	2.3804	1.3064	3.7922	0.0106	3.7073	0.0003
2.5687	0.0774	3.8394	0.0115	3.8410	0.0159	2.6609	0.2000	3.8173	0.0002	3.7702	0.0144
		3.9161	0.0164	3.8502	0.0054			4.0043	0.0000	3.9056	0.0147
		4.0467	0.0615	3.9925	0.0683			4.0058	0.0188	3.9999	0.0000
		4.1172	0.0070	4.0688	0.0400			4.1415	0.4202	4.0627	0.4770
		4.1541	0.0268	4.0865	0.0029			4.1807	0.0005	4.1178	0.0001
		4.2913	0.2090	4.1288	0.0132			4.3089	0.0005	4.1704	0.0003
		4.3258	0.0594	4.2356	0.2662			4.3392	0.0006	4.2860	0.0025
		4.3394	0.0615	4.3102	0.0233			4.3634	0.0088	4.2922	0.0026
		4.4271	0.0478	4.3613	0.0350			4.3841	0.0002	4.3486	0.0018
		4.4759	0.0036	4.3893	0.0041			4.3962	0.0029	4.3581	0.0077
		4.4837	0.0106	4.4219	0.0354			4.4416	0.1394	4.3631	0.0088
		4.4999	0.0010	4.4666	0.0127			4.4871	0.0004	4.4111	0.0151
		4.5056	0.0011	4.4824	0.0040			4.5851	0.0311	4.4185	0.1338
		4.5590	0.1718	4.4862	0.0007			4.6106	0.0179	4.4398	0.0353
		4.6148	0.0057	4.5436	0.1554			4.6143	0.0273	4.4840	0.0019
		4.6528	0.0360	4.5878	0.0131			4.7006	0.1221	4.6325	0.0256
		4.7318	0.1788	4.6190	0.0066			4.7194	0.0018	4.6432	0.1922
		4.7704	0.1152	4.6237	0.0095			4.7510	0.0005	4.7091	0.0010
		4.7863	0.0070	4.7024	0.3520			4.7809	0.0586	4.7457	0.0001
		4.8236	0.0101	4.7762	0.0037			4.7889	0.0008	4.7841	0.0061
		4.8293	0.0243	4.8141	0.0186			4.7970	0.0004	4.7921	0.0007
		4.8656	0.0105	4.8325	0.0019			4.8496	0.2263	4.7933	0.0029
		4.8727	0.0657	4.8666	0.0792			4.8781	0.0025	4.7979	0.1940
		4.8794	0.0011	4.8732	0.0014			4.9167	0.1594	4.8722	0.0003
		4.9293	0.0194	4.8799	0.0025			4.9188	0.0115	4.8853	0.0042
		4.9327	0.1403	4.8977	0.0112			4.9261	0.2441	4.9137	0.0383
		4.9577	0.1339	4.9119	0.0369			4.9438	0.0138	4.9229	0.0033
		5.0077	0.4115	4.9393	0.3094			4.9810	0.1510	4.9262	0.2712
		5.0627	0.0136	5.0294	0.0650			5.0018	0.0127	4.9530	0.0971
		5.0690	0.0126	5.0503	0.0020			5.0957	0.1510	4.9798	0.0135
		5.0851	0.0238	5.0697	0.0160			5.1951	0.0256	5.0953	0.2472
		5.1225	0.0055	5.0890	0.0054			5.2021	0.0006	5.1314	0.0547
		5.1276	0.0046	5.0933	0.0662			5.2082	0.0851	5.1384	0.0017
		5.1516	0.0072	5.1081	0.0170			5.2206	0.2766	5.1539	0.1130
		5.2047	0.2286	5.1143	0.1625			5.2535	0.0151	5.1776	0.0020
		5.2229	0.0154	5.1186	0.1290			5.3237	0.0061	5.1985	0.0906
		5.2380	0.0043	5.1636	0.0087			5.3299	0.0043	5.2225	0.0054
		5.2555	0.0004	5.2112	0.0275			5.3310	0.0027	5.2689	0.1967
		5.2771	0.0666	5.2431	0.0339			5.3328	0.0056	5.2887	0.0346
		5.3006	0.0230	5.2713	0.0021			5.3425	0.1227	5.3224	0.0036

Molecular Orbital Analysis of (E)-Caffeoyl Anthocyanins

Table D.11: Molecular orbital composition of (E)-caffeoyl acylated anthocyanins (**27-32**) and net charge transfer (e) between the most important fragments (B3LYP/6-311++G(d,p) and SMD water).

Fragment					Fragment contribution HOMO (%)			Average			
	AC rings	B-ring	Glycosyl	Caffeoyl	0.50	1.41	0.65		0.52	1.72	0.66
					0.07	0.01	0.27	0.04	0.13	0.09	0.11
					1.60	1.46	1.63	1.61	1.53	1.63	1.57
					97.83	97.13	97.44	97.83	96.56	97.62	97.31
Fragment					Fragment contribution LUMO (%)			Average			
	AC rings	B-ring	Glycosyl	Caffeoyl	81.30	80.41	79.77		81.26	79.75	80.81
					16.12	15.31	17.33	16.03	16.13	16.07	16.17
					1.17	1.19	1.16	1.16	1.15	1.14	1.16
					1.41	3.10	1.74	1.55	2.92	1.98	2.26
Net charge transfer: B-ring → AC rings											
$S_0 \rightarrow S_1$	0.00005	-0.00146	0.02796	0.14517	-0.00112	0.00004					
$S_0 \rightarrow S_2$	0.46285	0.45561	0.50324	0.26250	0.48526	0.50110					
Net charge transfer: Caffeoyl → AC rings											
$S_0 \rightarrow S_1$	0.80541	0.79201	0.74766	0.80569	0.77609	0.79482					
$S_0 \rightarrow S_2$	0.00925	0.01059	0.04922	0.02239	0.01113	0.00844					

Trend Analysis of Pyranoanthocyanins

Table D.12: Trend analysis of pyranoanthocyanins with respect to anthocyanins from literature values and own calculated UV-Vis data (B3LYP/6-311++G(d,p) with SMD as implicit solvation model and water as solvent). All wavelength shifts of pyranoanthocyanins Δ_1 , Δ_2 , Δ_3 and Δ_4 are relatively to the respective anthocyanins ($\downarrow$: hypsochromic and $\uparrow$: bathochromic shift).

Literature									
Anthocyanin (9-14)	10-carboxy types (45-50)		10-H types (51-56)		Vinylcatechol adduct (63-68)		Vinylphenol adduct (57-62)		
	$\lambda_{\text{max, EXP}}$ (nm)	$\lambda_{\text{max, EXP}}$ (nm)	Δ_1 (nm)	$\lambda_{\text{max, EXP}}$ (nm)	Δ_2 (nm)	$\lambda_{\text{max, EXP}}$ (nm)	Δ_3	$\lambda_{\text{max, EXP}}$ (nm)	Δ_4 (nm)
Cy-3-Glc	512[356]	504[392]	8 $\downarrow$	-	-	508[392]	4 $\downarrow$	500[392]	12 $\downarrow$
Dp-3-Glc	524[387, 545]	507[545]	17 $\downarrow$	-	-	509[545]	15 $\downarrow$	503[545]	21 $\downarrow$
Mv-3-Glc	527[387]	510[545]	17 $\downarrow$	490	37 $\downarrow$	510[545]	17 $\downarrow$	504[545]	23 $\downarrow$
Pg-3-Glc	496[58]	-	-	-	-	-	-	-	-
Pn-3-Glc	517[387, 545]	503[545, 546]	14 $\downarrow$	-	-	506[545]	11 $\downarrow$	500[545]	17 $\downarrow$
Pt-3-Glc	525[545]	508[545]	17 $\downarrow$	492	33 $\downarrow$	510[545]	15 $\downarrow$	502[545]	23 $\downarrow$
Anthocyanin (9-14)	10-carboxy types (45-50)		10-H types (51-56)		Vinylcatechol adduct (63-68)		Vinylphenol adduct (57-62)		
	$\lambda_{\text{max, CALC}}$ (nm)	$\lambda_{\text{max, CALC}}$ (nm)	Δ_1 (nm)	$\lambda_{\text{max, CALC}}$ (nm)	Δ_2 (nm)	$\lambda_{\text{max, CALC}}$ (nm)	Δ_3	$\lambda_{\text{max, CALC}}$ (nm)	Δ_4 (nm)
Cy-3-Glc	501.04	504.31	3.27 $\uparrow$	490.71	10.33 $\downarrow$	512.81	11.77 $\uparrow$	506.97	5.93 $\uparrow$
Dp-3-Glc	504.12	507.76	3.64 $\uparrow$	493.20	10.92 $\downarrow$	520.61	16.49 $\uparrow$	511.25	7.13 $\uparrow$
Mv-3-Glc	522.97	527.07	4.10 $\uparrow$	512.28	10.69 $\downarrow$	534.83	11.86 $\uparrow$	524.98	2.01 $\uparrow$
Pg-3-Glc	480.73	483.80	3.07 $\uparrow$	470.61	10.12 $\downarrow$	510.14	29.41 $\uparrow$	498.53	17.8 $\uparrow$
Pn-3-Glc	509.55	510.37	0.82 $\uparrow$	495.65	13.90 $\downarrow$	523.22	13.67 $\uparrow$	512.93	3.38 $\uparrow$
Pt-3-Glc	529.36	511.13	18.23 $\downarrow$	498.50	30.86 $\downarrow$	526.18	3.18 $\downarrow$	517.50	11.86 $\downarrow$

Rotational Barriers of Pyranoanthocyanins

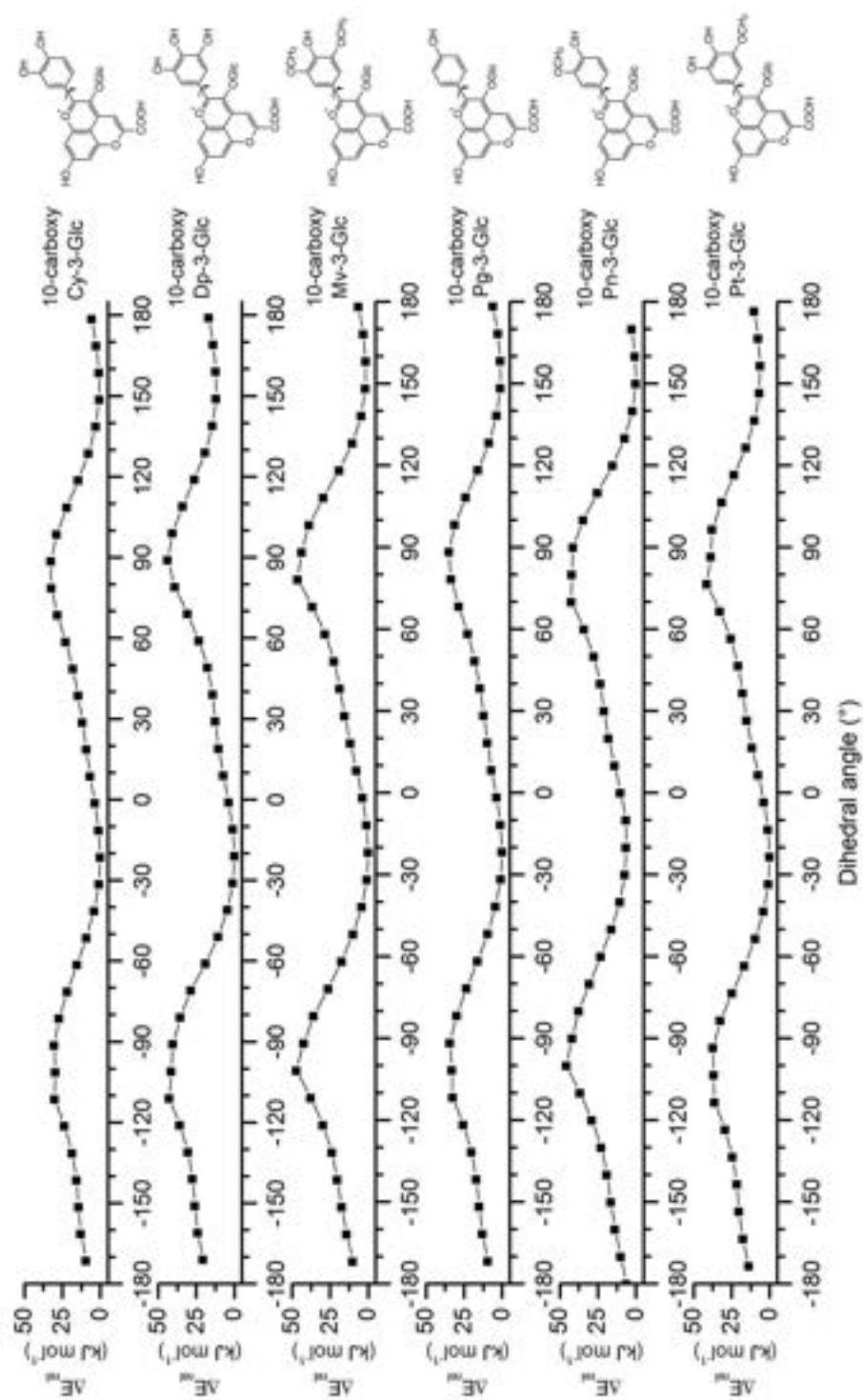


Figure D.11: The B-ring rotational barrier of 10-carboxy pyranoanthocyanins (**45-50**) (B3LYP/6-311++G(d,p), GD3 and in gas phase).

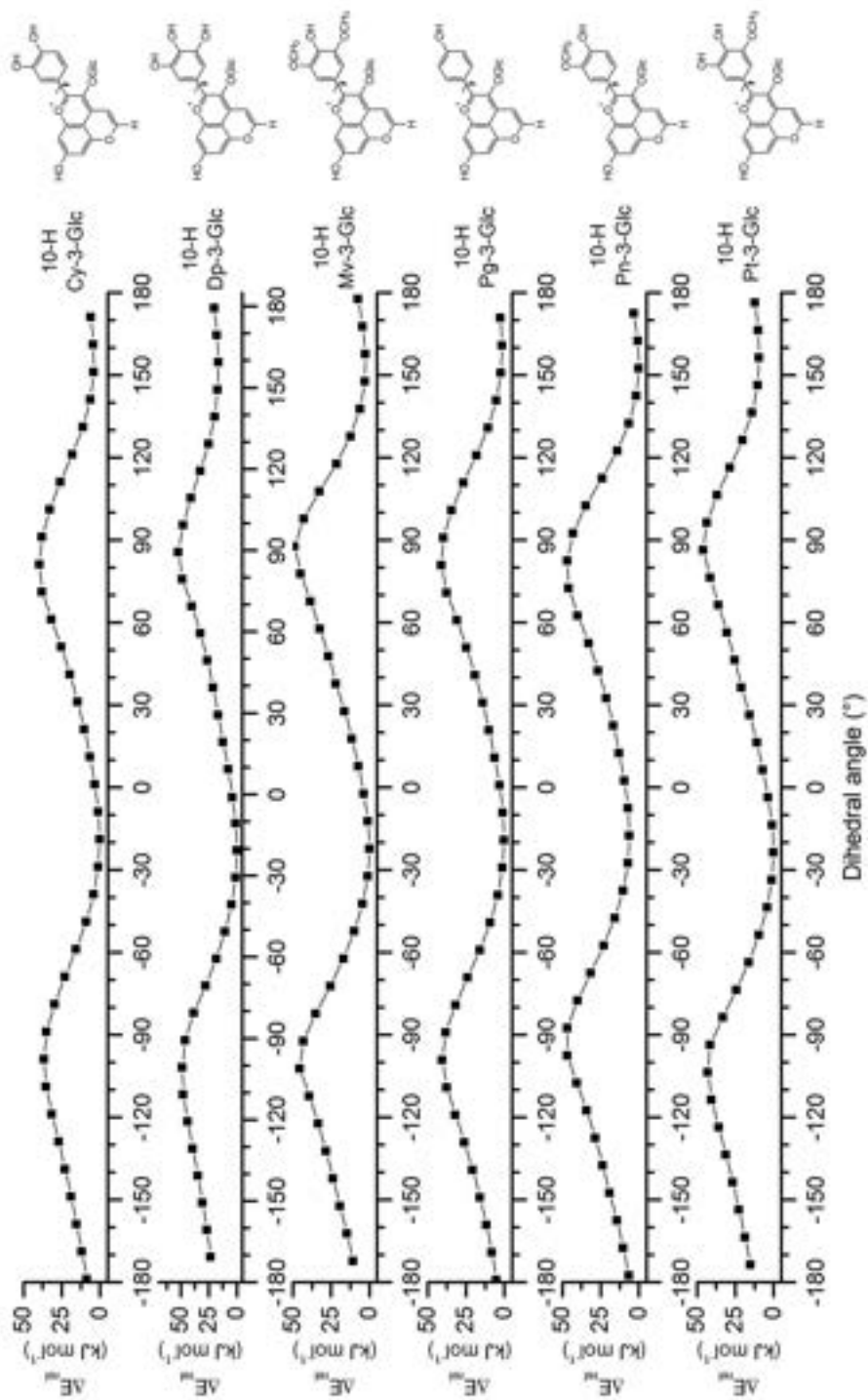


Figure D.12: The B-ring rotational barrier of 10-H pyranoanthocyanins (51-56) (B3LYP/6-311++G(d,p), GD3 and in gas phase).

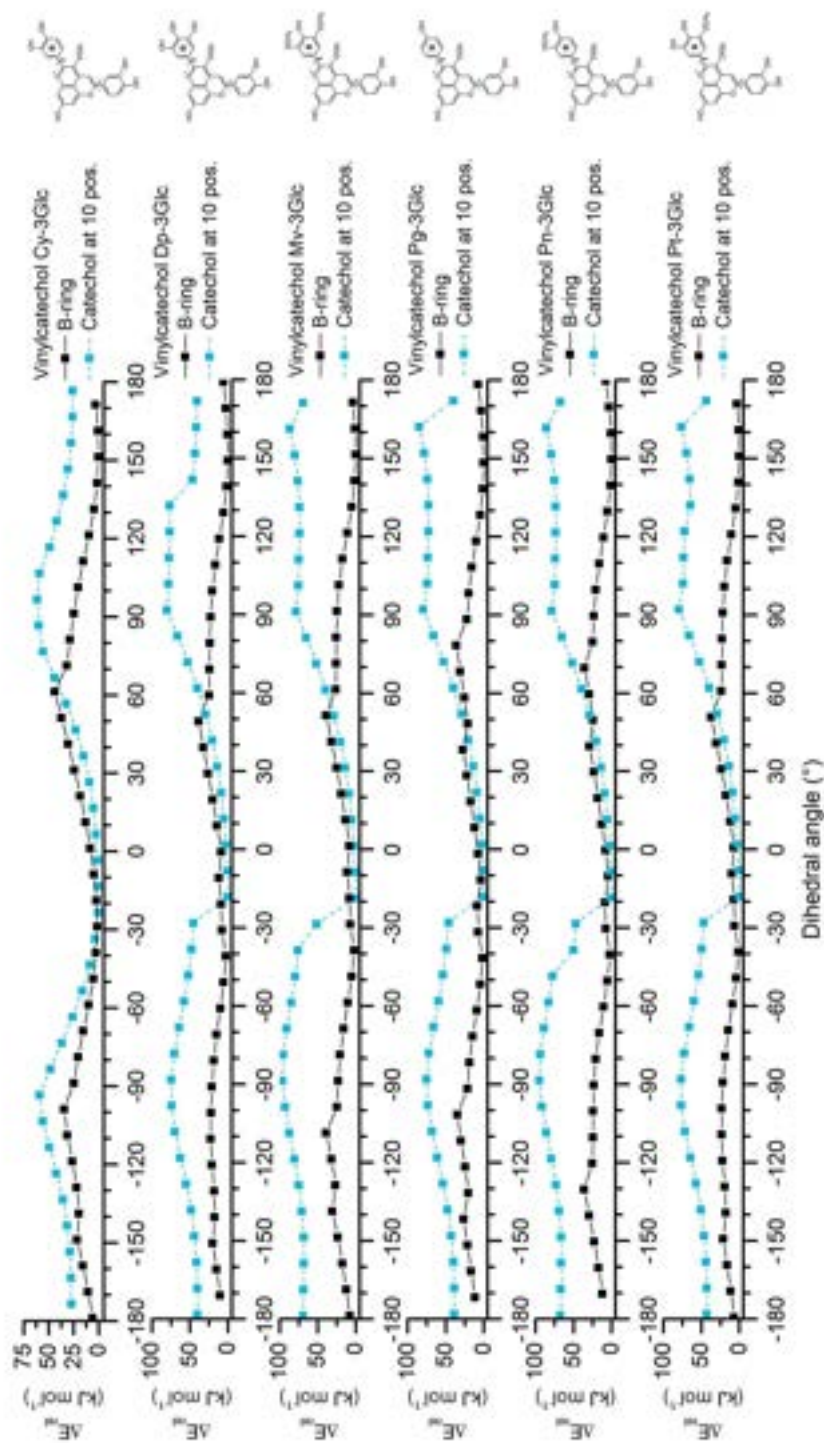


Figure D.13: The B-ring and 10-catechol moiety rotational barriers of vinylcatechol pyranoanthocyanins (**63-68**) (B3LYP/6-311++G(d,p), GD3 and in gas phase).

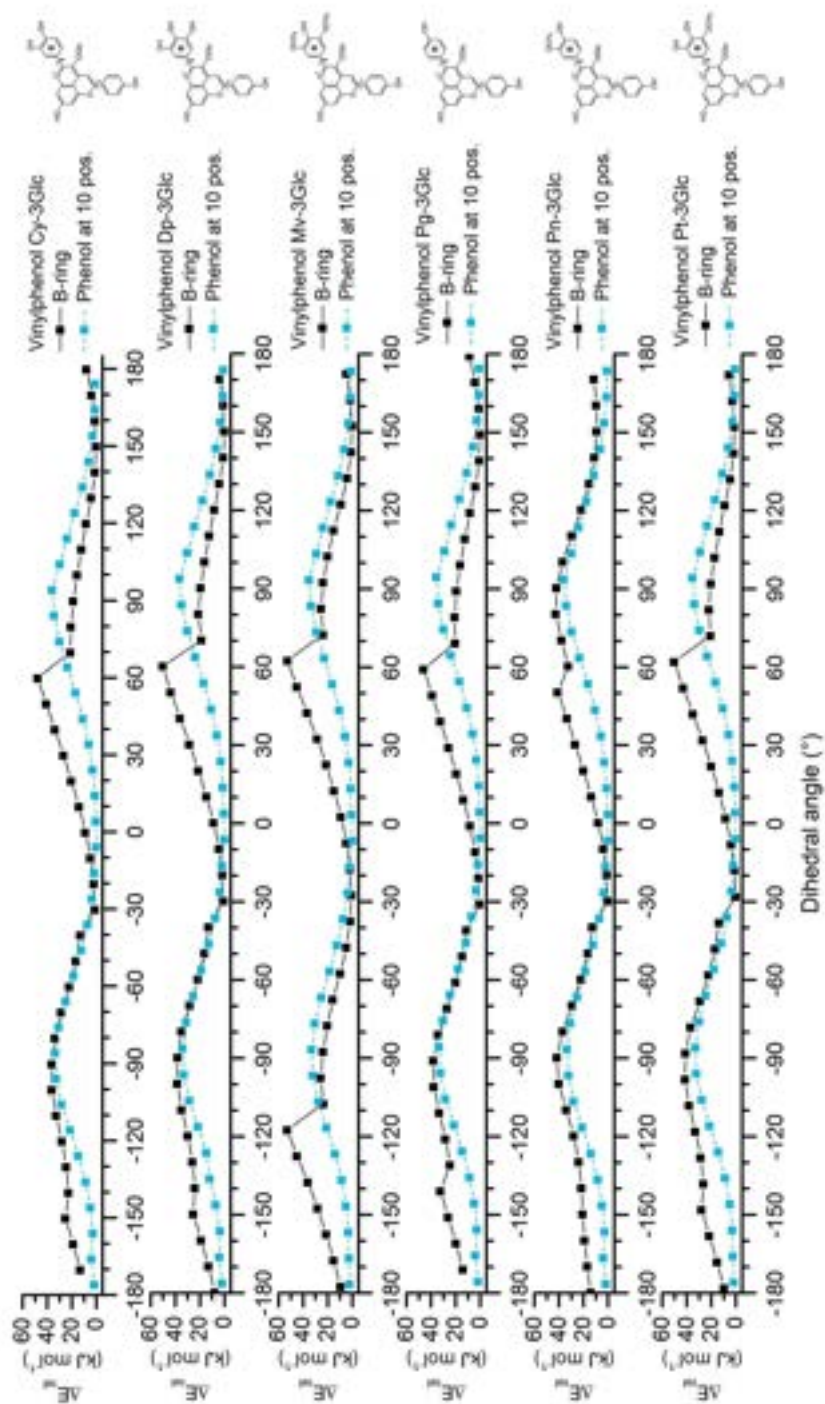


Figure D.14: The B-ring and 10-phenol moiety rotational barriers of vinylphenol pyranoanthocyanins (**57-62**) (B3LYP/6-311++G(d,p), GD3 and in gas phase).

UV-Vis Spectra of 10-carboxy and 10-H Pyranoanthocyanins



Figure D.15: Calculated UV-Vis spectra of 10-carboxy pyrananthocyanins (**45-50**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.



Figure D.16: Calculated UV-Vis spectra of 10-H pyranoanthocyanins (**51-56**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

Molecular Orbital Analysis of Pyranoanthocyanins

Table D.13: Molecular orbital composition of 10-carboxy pyranoanthocyanins (**45-50**) and net charge transfer (e) between the most important fragments (B3LYP/6-311++G(d,p) and SMD water).

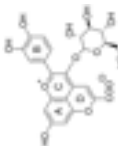
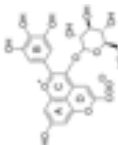
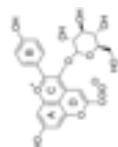
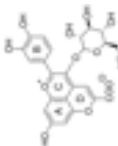
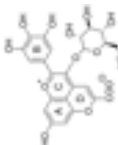
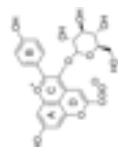
Fragment					Fragment contribution HOMO (%)			Average		
					30.03	30.66	23.29	47.76	26.29	30.32
					67.96	67.23	75.20	49.47	72.04	67.72
					1.40	1.46	1.19	2.11	1.31	1.47
					0.42	0.42	0.32	0.66	0.37	0.42
Fragment					Fragment contribution LUMO (%)			Average		
					79.25	78.82	79.88	79.55	80.43	79.63
					13.36	13.74	12.71	12.95	12.21	12.92
					10.73	0.81	0.68	0.86	0.70	0.77
					6.55	6.44	6.74	6.64	6.67	6.62
Net charge transfer: B-ring → ACD rings									0.53923	0.75220
Net charge transfer: 10-COO- → ACD rings									-0.01370	-0.00159
Net charge transfer: S ₀ → S ₁										
Net charge transfer: S ₀ → S ₂										
Net charge transfer: S ₀ → S ₁										
Net charge transfer: S ₀ → S ₂										

Table D.14: Molecular orbital composition of 10-H pyranoanthocyanins (**51-56**) and net charge transfer (e) between the most important fragments (B3LYP/6-311++G(d,p) and SMD water).

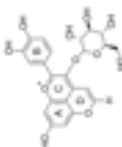
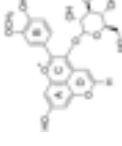
							
Fragment	29.77	30.72	23.19	47.00	24.07	25.64	Average
ACD rings	68.01	67.38	75.20	50.13	74.34	72.64	30.06
B-ring	2.14	1.81	1.54	2.75	1.53	1.65	67.95
Glycosyl	0.08	0.09	0.07	0.12	0.06	0.07	1.90
10-H							0.08
Fragment							Average
ACD rings	82.35	81.67	82.32	82.52	83.09	82.94	82.48
B-ring	15.53	16.33	15.52	15.35	14.73	14.93	15.40
Glycosyl	0.91	0.81	0.95	0.91	0.95	0.90	0.91
10-H	1.21	1.19	1.21	1.22	1.23	1.23	1.22
Fragment contribution LUMO (%)							
Net charge transfer: B-ring → ACD rings							
S ₀ → S ₁	0.51694	0.50074	0.58481	0.34926	0.58457	0.56387	
S ₀ → S ₂	0.09589	0.80641	0.81030	-0.00619	0.16405	0.80335	
Net charge transfer: 10-H → ACD rings							
S ₀ → S ₁	-0.00131	-0.00131	-0.00100	-0.00215	-0.00108	-0.00113	
S ₀ → S ₂	-0.00325	-0.00008	-0.00009	-0.00384	-0.00303	-0.00015	

Table D.15: Molecular orbital composition of vinylcatechol pyranoanthocyanins (**63-68**) and net charge transfer (e) between the most important fragments (B3LYP/6-311++G(d,p) and SMD water).

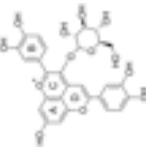
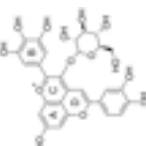
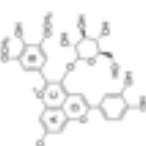
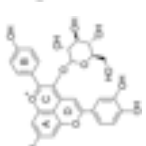
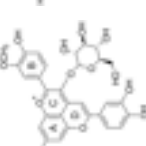
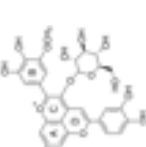
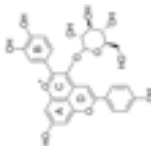
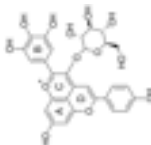
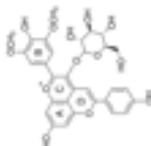
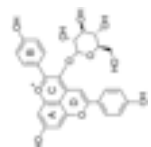
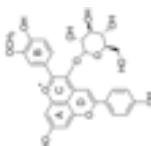
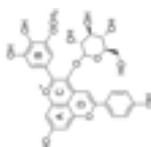
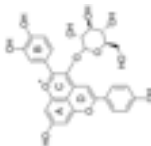
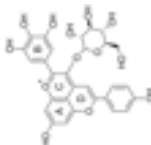
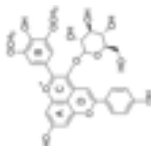
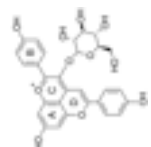
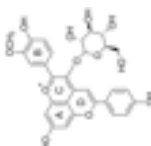
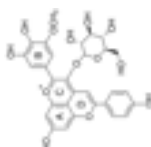
							
Fragment	31.32	30.06	27.19	31.93	30.07	29.48	Average
ACD rings	31.19	32.17	54.20	13.55	41.50	42.30	30.01
B-ring	1.39	1.25	1.30	1.13	1.37	1.33	35.82
Glycosyl	36.11	36.54	17.32	53.39	27.06	26.90	1.29
10-catechol							32.89
Fragment contribution HOMO (%)							
Fragment	73.30	73.60	72.83	74.01	73.49	73.23	Average
ACD rings	10.96	13.27	13.23	11.60	12.69	12.59	73.41
B-ring	0.58	0.56	0.56	0.55	0.53	0.57	12.39
Glycosyl	15.16	13.63	13.38	13.84	13.29	13.61	0.56
10-catechol							13.82
Fragment contribution LUMO (%)							
Net charge transfer: B-ring → ACD rings							
S ₀ → S ₁	0.19581	0.19915	0.35272	0.06375	0.26851	0.27297	
S ₀ → S ₂	0.23781	0.21883	0.09943	0.16857	0.17012	0.15584	
Net charge transfer: 10-catechol → ACD rings							
S ₀ → S ₁	0.21874	0.22929	0.08989	0.34318	0.16074	0.15777	
S ₀ → S ₂	0.25502	0.28248	0.40542	0.15710	0.34614	0.34829	

Table D.16: Molecular orbital composition of vinylphenol pyranoanthocyanins (**57-62**) and net charge transfer (e) between the most important fragments (B3LYP/6-311++G(d,p) and SMD water).

Fragment							Fragment contribution HOMO (%)		Average			
							36.43	35.51	27.26	47.27	32.14	35.20
							45.51	47.59	62.79	24.25	54.59	47.97
							1.84	1.83	1.58	2.12	1.72	1.83
							16.23	15.07	8.36	26.37	11.56	15.00
Fragment							Fragment contribution LUMO (%)		Average			
							72.80	72.38	72.32	72.57	72.39	72.50
							11.10	11.05	11.63	10.64	11.90	11.21
							0.58	0.57	0.57	0.59	0.56	0.58
							15.52	16.00	15.49	16.21	15.15	15.71
Net charge transfer: B-ring → ACD rings												
$S_0 \rightarrow S_1$	0.28785	0.30085	0.35507	0.13015	0.34313	0.34751						
$S_0 \rightarrow S_2$	0.16344	0.12746	0.13883	0.12239	0.11620	0.09835						
Net charge transfer: 10-phenol → ACD rings												
$S_0 \rightarrow S_1$	0.06347	0.05432	0.06108	0.11976	0.04007	0.03659						
$S_0 \rightarrow S_2$	0.19929	0.20515	0.20956	0.14539	0.22076	0.22467						

UV-Vis Spectra of Vinylcatechol and Vinylphenol Pyranoanthocyanins

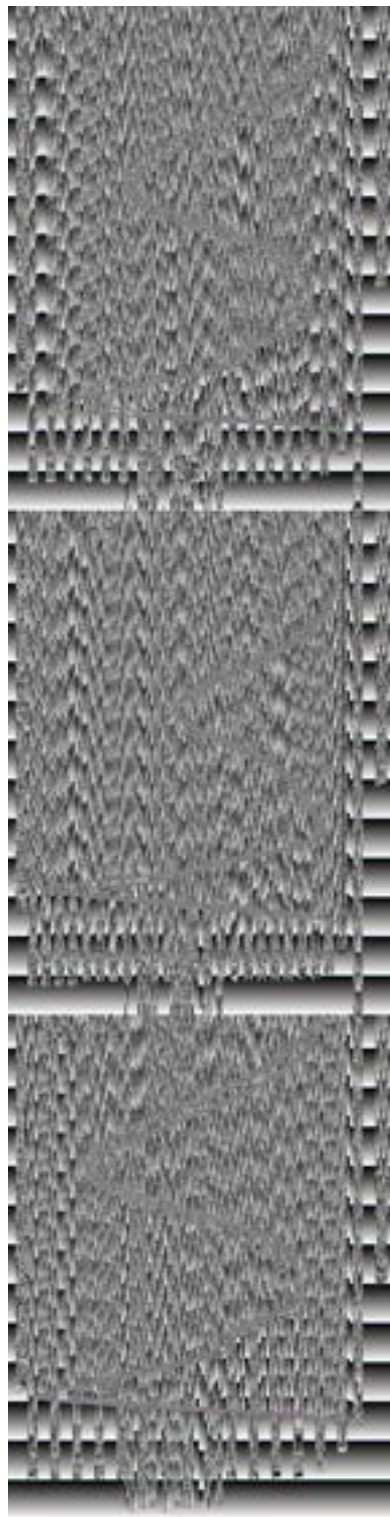


Figure D.17: Calculated UV-Vis spectra of vinylcatechol pyranoanthocyanins (**63-68**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

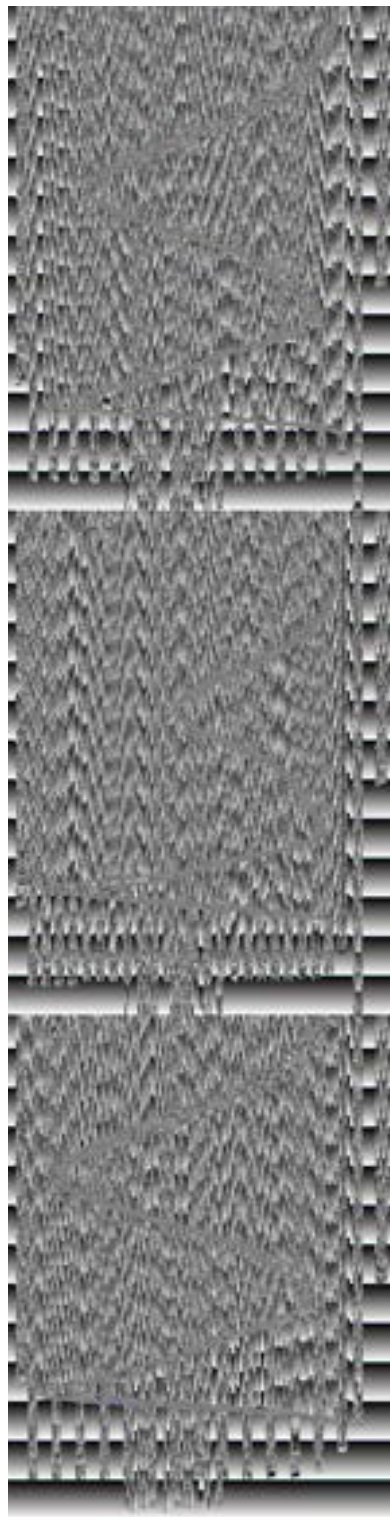


Figure D.18: Calculated UV-Vis spectra of vinylphenol pyranocanthocyanins (57-62) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

Trend analyses of acylated pyranoanthocyanins

Table D.19: Trend analysis acylated pyranoanthocyanins relatively to pyranoanthocyanins: own calculated values (B3LYP/6-311++G(d,p) and SMD water)

Calculated values pyranoanthocyanins	10-carboxy (45-50)		10-H (51-56)		Vinylcatechol (63-68)		Vinylphenol (57-62)	
	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)
Cy-3-Glc	504.31	2.46	490.71	2.53	512.81	2.53	506.97	2.49
Dp-3-Glc	507.76	2.44	493.20	2.51	520.61	2.51	511.25	2.46
Mv-3-Glc	527.07	2.35	512.28	2.42	534.83	2.42	524.98	2.39
Pg-3-Glc	483.80	2.66	470.61	2.63	510.14	2.63	498.53	2.54
Pn-3-Glc	510.37	2.43	495.65	2.50	523.22	2.50	512.93	2.45
Pt-3-Glc	511.13	2.43	498.50	2.49	526.18	2.49	517.50	2.45

Table D.20: The respective calculated shifts between acylated pyranoanthocyanins with respect to pyranoanthocyanins (B3LYP/6-311++G(d,p) and SMD water, ↓: hypsochromic and ↑: bathochromic shift). Δ are differences between the acylated pyranoanthocyanins with respect to non-acylated pyranoanthocyanins.

Acetyl acylated pyranoacy vs pyranoacy	10-carboxy (69-74)		10-H (75-80)		Vinylcatechol (87-92)		Vinylphenol (81-86)		Caff acylated pyranoacy vs pyranoacy		10-carboxy (93-98)		10-H (99-104)		Vinylcatechol (111-116)		Vinylphenol (105-110)		Cumm acylated pyranoacy vs pyranoacy		10-carboxy (117-122)		10-H (123-128)		Vinylcatechol (135-140)		Vinylphenol (129-134)	
	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)
Cy-3-Glc	0.78↑	1.05↓	2.76↑	15.38↓	1.68↓	9.23↓	13.07↓	13.25↓	8.14↓	14.88↓	2.19↓	1.09↓	3.68↑	2.41↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓	3.67↓	2.51↓
Dp-3-Glc	1.68↓	1.46↓	2.51↓	9.23↓	13.07↓	13.25↓	8.14↓	14.88↓	2.19↓	1.09↓	3.68↑	2.41↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓	3.67↓	2.51↓	1.46↓	1.68↓
Mv-3-Glc	0.38↑	1.42↓	3.67↓	13.07↓	13.25↓	8.14↓	14.88↓	2.19↓	1.09↓	3.68↑	2.41↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑
Pg-3-Glc	2.66↑	0.11↓	3.68↑	13.25↓	8.14↓	14.88↓	2.19↓	1.09↓	3.68↑	2.41↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓
Pn-3-Glc	4.79↑	3.68↑	2.41↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓	3.67↓
Pt-3-Glc	3.21↑	1.09↓	3.68↑	13.25↓	8.14↓	14.88↓	2.19↓	1.09↓	3.68↑	2.41↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓	3.67↓	2.51↓	1.46↓	1.68↓	0.38↑	1.42↓

Table D.21: Trend analysis acylated pyranoanthocyanins relatively to acylated anthocyanins: experimental literature values

Experimental literature, acylated anthocyanins	Acetyl (15-20)			(E)-caffeoyl (27-32)			(Z)-coumaroyl (33-38)			(E)-coumaroyl (39-44)		
	λ_{max} (nm)	Solvent	λ_{max} (eV)	λ_{max} (nm)	Solvent	λ_{max} (eV)	λ_{max} (nm)	Solvent	λ_{max} (eV)	λ_{max} (nm)	Solvent	λ_{max} (eV)
Cy-3-Glc	523	TFA/H ₂ O/ACN	2.37	-	-	-	533	TFA/H ₂ O/ACN	2.33	524	TFA/H ₂ O/ACN	2.37
Dp-3-Glc	527	TFA/H ₂ O/ACN	2.35	532	TFA/H ₂ O/ACN	2.33	534	TFA/H ₂ O/ACN	2.32	531	TFA/H ₂ O/ACN	2.33
Mv-3-Glc	530	TFA/H ₂ O/ACN	2.34	534	TFA/H ₂ O/ACN	2.32	535	TFA/H ₂ O/ACN	2.32	532	TFA/H ₂ O/ACN	2.33
Pg-3-Glc	-	-	-	-	-	-	-	-	-	-	-	-
Pn-3-Glc	522	TFA/H ₂ O/ACN	2.38	525	TFA/H ₂ O/ACN	2.36	535	TFA/H ₂ O/ACN	2.32	526	TFA/H ₂ O/ACN	2.36
Pt-3-Glc	535	MeOH/HCl	2.32	531	TFA/H ₂ O/ACN	2.33	536	TFA/H ₂ O/ACN	2.31	532	TFA/H ₂ O/ACN	2.33

Table D.22: The respective experimental shifts between acylated pyranoanthocyanins with respect to acylated anthocyanins (↓: hypsochromic and ↑: bathochromic shift). Δ are differences between the acylated pyranoanthocyanins with respect to acylated anthocyanins.

Acetyl acylated pyranoacy vs acetyl acylated ACYn	10-carboxy (69-74)	10-H (75-80)	Vinylcatechol (87-92)	Vinylphenol (81-86)	Caff			10-H (99-104)	Vinylcatechol (111-116)	Vinylphenol (105-110)	Coum acylated pyranoacy vs Coum acylated ACY			10-carboxy (117-122)	10-H (123-128)	Vinylcatechol (135-140)	Vinylphenol (129-134)
					acylated Caff	acylated ACY	Δ (nm)				acylated Caff	acylated ACY	Δ (nm)				
Cy-3-Glc	-	-	-	-	Cy-3-Glc	-	-	-	-	-	Cy-3-Glc	-	-	-	-	25↓	-
Dp-3-Glc	16↓	30↓	15↓	22↓	Dp-3-Glc	-	-	-	-	-	Dp-3-Glc	-	-	22↓	-	24↓	-
Mv-3-Glc	16↓	36↓	18↓	24↓	Mv-3-Glc	20↓	36↓	22↓	28↓	-	Mv-3-Glc	19↓	38↓	19↓	38↓	23↓	30↓
Pg-3-Glc	-	-	-	-	Pg-3-Glc	-	-	-	-	-	Pg-3-Glc	-	-	-	-	-	-
Pn-3-Glc	15↓	36↓	15↓	21↓	Pn-3-Glc	17↓	-	17↓	-	23↓	Pn-3-Glc	26↓	50↓	26↓	50↓	27↓	33↓
Pt-3-Glc	23↓	41↓	24↓	30↓	Pt-3-Glc	-	-	-	-	-	Pt-3-Glc	-	42↓	-	42↓	25↓	32↓

Table D.23: Trend analysis acylated pyranoanthocyanins relatively to acylated anthocyanins: own calculated values (B3LYP/6-311++G(d,p) SMD water)

Calculated values acylated anthocyanins	Acetyl (15-20)		(E)-caffeoyl (27-32)		(E)-coumaroyl (39-44)	
	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)
Cy-3-Glc	495.69	2.50	528.66	2.35	520.43	2.38
Dp-3-Glc	499.05	2.48	549.20	2.26	524.36	2.36
Mv-3-Glc	519.29	2.39	531.10	2.33	526.88	2.35
Pg-3-Glc	478.08	2.59	523.71	2.37	515.60	2.40
Pn-3-Glc	502.77	2.47	543.54	2.28	523.97	2.37
Pt-3-Glc	506.89	2.45	534.58	2.32	519.11	2.39

Table D.24: The respective calculated shifts between acylated pyranoanthocyanins with respect to acylated anthocyanins (B3LYP/6-311++G(d,p) and SMD water, ↓: hypsochromic and ↑: bathochromic shift).

Acetyl acylated pyrano vs acetyl acylated ACYn	10-carboxy (69-74)		10-H (75-80)		Vinylcatechol (87-92)		Vinylphenol (81-86)		Caff acylated pyrano vs Caff acylated ACY		10-carboxy (93-98)		10-H (99-104)		Vinylcatechol (111-116)		Vinylphenol (105-110)		10-carboxy (117-122)		10-H (123-128)		Vinylcatechol (135-140)		Vinylphenol (129-134)		
	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	Δ (nm)	
Cy-3-Glc	9.4↑	6.03↓	19.88↑	4.10↓	19.05↑	19.88↑	28.91↓	46.91↓	57.37↓	33.29↓	17.74↓	37.29↓	43.49↓	7.08↓	17.59↓	20.27↓	17.59↓	9.84↓	31.42↓								
Dp-3-Glc	7.03↑	7.31↓	19.05↑	2.97↑	8.43↓	11.87↑	45.25↓	57.37↓	26.05↓	3.16↓	33.29↓	43.49↓	21.77↓	7.01↓	20.27↓	10.62↓	8.69↓	22.94↓									
Mv-3-Glc	8.16↑	8.43↓	11.87↑	7.38↓	30.53↑	11.87↑	16.06↓	26.05↓	3.16↓	21.77↓	3.16↓	21.77↓	43.49↓	5.85↑	10.62↓	19.32↓	1.09↑	17.84↓									
Pg-3-Glc	8.38↑	7.58↓	30.53↑	7.20↑	18.04↑	3.44↓	42.99↓	59.26↓	18.98↓	41.44↓	18.98↓	41.44↓	41.44↓	5.76↓	19.32↓	11.46↓	11.46↓	26.09↓									
Pn-3-Glc	12.39↑	7.45↑	9.48↓	2.02↑	17.10↑	4.27↓	37.50↓	57.35↓	26.55↓	45.70↓	26.55↓	45.70↓	45.70↓	3.56↓	21.88↓	7.74↓	7.74↓	27.52↓									
Pt-3-Glc	7.45↑	9.48↓	17.10↑	4.27↓	17.10↑	4.27↓	26.68↓	46.45↓	57.35↓	13.47↓	13.47↓	37.00↓	37.00↓	5.12↑	12.15↓	12.15↓	1.73↑	21.43↓									

Molecular Orbital Composition of Caffeoyl Acylated Vinylcatechol and Vinylphenol Pyranoanthocyanins

Table D.25: Molecular orbital composition of caffeoyl acylated vinylcatechol pyranoanthocyanins (**111-116**) and net charge transfer (e) between the most important fragments (B3LYP/6-311++G(d,p) and SMD water).

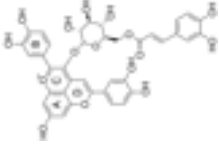
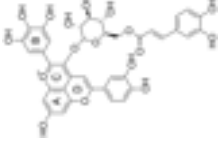
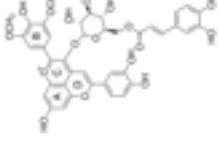
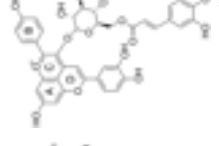
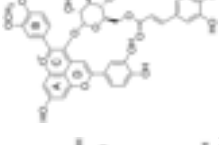
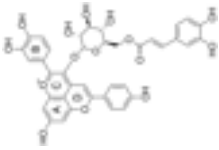
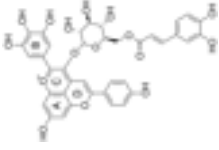
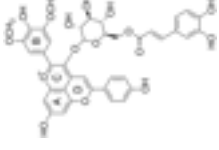
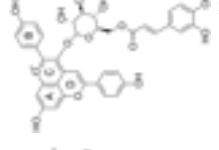
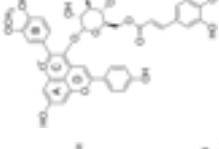
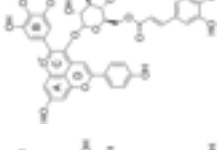
							
Fragment	0.09	0.20	25.55	0.10	0.54	3.21	Average
ACD rings	0.04	0.14	55.49	0.02	0.59	4.36	4.95
B-ring	1.68	1.68	1.21	1.67	1.66	1.62	10.11
Glycosyl	0.39	0.59	17.24	0.45	1.01	3.97	1.59
10-catechol	97.80	97.39	0.40	97.75	96.20	86.85	3.94
Caffeoyl							79.40
Fragment							Average
ACD rings	74.42	73.86	73.33	74.26	73.96	73.41	73.87
B-ring	11.04	11.69	12.14	10.97	11.34	12.24	11.57
Glycosyl	0.54	0.54	0.39	0.54	0.55	0.53	0.52
10-catechol	14.00	13.89	13.98	14.21	14.14	13.81	14.00
Caffeoyl	0.01	0.01	0.02	0.01	0.01	0.02	0.01
Net charge transfer: B-ring → ACD rings							
S ₀ → S ₁	0.16863	0.20005	0.36722	0.05533	0.26836	0.27692	
S ₀ → S ₂	0.06941	0.10134	0.11034	0.00007	0.17421	0.13555	
Net charge transfer: 10-catechol → ACD rings							
S ₀ → S ₁	0.26959	0.22771	0.08998	0.35342	0.17844	0.16226	
S ₀ → S ₂	0.08929	0.17621	0.38673	0.00290	0.32688	0.34744	
Net charge transfer: caffeoyl → ACD rings							
S ₀ → S ₁	0.00262	0.00535	0.00277	0.00315	0.00029	0.00033	
S ₀ → S ₂	0.51575	0.32623	0.01079	0.72757	0.02658	0.01513	

Table D.26: Molecular orbital composition of caffeoyl acylated vinylphenol pyranoanthocyanins (**105-110**) and net charge transfer (e) between the most important fragments (B3LYP/6-311++G(d,p) and SMD water).

							
Fragment	2.663	2.5	3.275	3.005	2.824	2.733	Average
ACD rings	0.053	0.246	4.122	0.053	0.077	0.059	2.8
B-ring	1.296	1.312	1.282	1.311	1.321	1.314	0.8
Glycosyl	1.155	1.511	2.126	0.929	0.849	0.869	1.3
10-phenol	94.833	94.446	89.196	94.915	94.927	95.026	1.2
Caffeoyl							93.9
Fragment	74.026	72.585	74.354	75.022	74.384	74.594	Average
ACD rings	8.103	10.238	9.09	8.403	8.672	8.479	74.2
B-ring	0.73	0.972	0.684	0.74	0.754	0.757	8.8
Glycosyl	15.949	15.621	15.05	14.651	14.766	14.708	0.8
10-phenol	1.191	0.932	0.822	1.701	1.395	1.463	15.1
Caffeoyl							1.3
$S_0 \rightarrow S_1$	-0.00151	0.28377	0.38338	-0.00179	-0.00156	-0.00162	
$S_0 \rightarrow S_2$	0.26412	0.03709	0.01229	0.12561	0.30707	0.31410	
$S_0 \rightarrow S_1$	0.00512	0.05217	0.06192	0.00342	0.00296	0.00325	
$S_0 \rightarrow S_2$	0.08020	-0.00719	-0.00030	0.13667	0.08370	0.08625	
$S_0 \rightarrow S_1$	0.70399	0.06033	0.00797	0.72293	0.72039	0.71881	
$S_0 \rightarrow S_2$	0.00150	0.64060	0.71995	0.00083	-0.00195	-0.00156	

Net charge transfer: B-ring $\rightarrow$ ACD rings

Net charge transfer: 10-phenol $\rightarrow$ ACD rings

Net charge transfer: caffeoyl $\rightarrow$ ACD rings

Data TD-DFT calculations (PBE0)

Table D.27: List of own calculated TD-DFT calculations of anthocyanins and pyranoanthocyanins along with their possible substitution patterns (Figure 4.1) (PBE0/6-311++G(d,p)). For comparison, existing TD-DFT studies and experimental literature studies are included.

Label	Anthocyanins	Own calculations				Literature Modeling			Literature Experimental			
	Name	R ₁	R ₂	R ₃	R ₄	λ _{max} , CALC (nm)	Method	λ _{max} , CALC (nm)	Method	λ _{max} , EXP (nm)	Solvent	
1	Apigeninidin (Ap)	H	OH	H	H	459.03	SMD MeOH	431	B3LYP/6-31G(d) (gas)[285]	476	MeOH/HCl[543]	
						460.00	SMD Water			468	KCl buffer pH=1[356]	
		OH	OH	H	H	477.21	SMD MeOH	468	B3LYP/6-31G(d) (gas)[285]	493	MeOH/HCl[543]	
2	Luteolinidin (Lt)					476.28	SMD Water			482	KCl buffer pH=1[356]	
		H	OH	H	OH	506.74	SMD MeOH	470	B3LYP/6-31G(d) (gas)[285]	520	MeOH/HCl[543]	
3	Pelargonidin (Pg)					507.40	SMD Water	475	B3LYP/6-31+G(d) (gas)[363]	524	MeOH/HCl[58]	
								492	B3LYP/6-31+G(d) (C-PCM; water)	506	KCl buffer pH=1[356]	
		H	OH	H	OGlc	467.66 467.86	SMD MeOH SMD Water			505 506	KCl buffer pH=1[58] MeOH/HCl[543]	
9	Pg-3-glucoside									508	MeOH/HCl[58]	
										503 (Rut) 506 (Gen) 508 (Rhaglc)	TFA/H ₂ O/ACN[544] MeOH/HCl[543] MeOH/HCl[543]	
										496 502 503 (Ara) 500 (Gal)	KCl buffer pH=1 [58] TFA/H ₂ O/ACN[544] TFA/H ₂ O/ACN[544] TFA/H ₂ O/ACN[544]	
15	Pg-acetyl-glucoside									504 (OGlc-Malo)	TFA/H ₂ O/ACN[544]	
		H	OH	H	OGlc-Ac	467.30 465.14	SMD MeOH SMD Water			503 (OGlc-Maly)	TFA/H ₂ O/ACN[544]	
21	Pg-3-(6-(Z)-caffeoyl)-glucoside											
		H	OH	H	OGlc-Caff	513.31 511.22	SMD MeOH SMD Water					

34	Cy-3-(6-(Z)-p-coumaroyl)-glucoside	OH	OH	H	OGlc-Coum	490.97	SMD Water					533	TFA/H ₂ O/ACN[545]	
40	Cy-3-(6-(E)-p-coumaroyl)-glucoside	OH	OH	H	OGlc-Coum	493.30	SMD Water					524	TFA/H ₂ O/ACN[545]	
5	Peonidin (Pn)	OCH ₃ OH	H	OH	OH	492.88	SMD Water			B3LYP/6-31G(d) (gas)[285]		532	MeOH/HCl[543]	
						521.40	SMD MeOH		476	B3LYP/6-31+G(d) (gas)[363]		516	KCl buffer pH=1[356]	
						521.65	SMD Water		500	B3LYP/6-31+G(d) (C-PCM: water)[363]				
11	Pn-3-glucoside	OCH ₃ OH	H	OGlc	OGlc	493.08	SMD MeOH		482.8	B3P86/6-311+G** (IEFPCM: MeOH)[387]		523	MeOH/HCl[543]	
17	Pn-3-acetyl-glucoside	OCH ₃ OH	H	OGlc-Ac	OGlc-Ac	487.05	SMD MeOH					528 (5-glc)	MeOH/HCl[543]	
						486.66	SMD Water					517	FA/H ₂ O/ACN[387]	
23	Pn-3-(6-(Z)-caffeoyl)-glucoside	OCH ₃ OH	H	OGlc-Caff	OGlc-Caff	523.67	SMD MeOH					516	TFA/H ₂ O/ACN[546]	
						520.11	SMD Water					517	TFA/H ₂ O/ACN[545]	
29	Pn-3-(6-(E)-caffeoyl)-glucoside	OCH ₃ OH	H	OGlc-Caff	OGlc-Caff	500.92	SMD MeOH					516	FA/H ₂ O/ACN[369]	
						508.31	SMD Water					522	TFA/H ₂ O/ACN[545]	
35	Pn-3-(6-(Z)-p-coumaroyl)-glucoside	OCH ₃ OH	H	OGlc-pCoum	OGlc-pCoum	501.66	SMD MeOH					516	FA/H ₂ O/ACN[369]	
						498.71	SMD Water					525 (L(+)-LA)	TFA/H ₂ O/ACN[545]	
41	Pn-3-(6-(E)-p-coumaroyl)-glucoside	OCH ₃ OH	H	OGlc-pCoum	OGlc-pCoum	494.48	SMD MeOH					535	TFA/H ₂ O/ACN[545]	
						499.56	SMD Water					526	TFA/H ₂ O/ACN[545]	
6	Delphinidin (Dp)	OH	OH	OH	OH	525.28	SMD MeOH		490	B3LYP/6-31G(d) (gas)[285]		520	FA/H ₂ O/ACN[369]	
												546	MeOH/HCl[543]	

12	Dp-3-glucoside	OH	OH	OH	OGlc	524.91	SMD Water	514	B3LYP/6-31+G(d) (gas)[363]	535	MeOH/HCl[543]	
								505	B3LYP/6-31+G(d) (C-PCM: water)[363]	537 (Rhaglc)	MeOH/HCl[543]	
						489.62	SMD MeOH	482.8	B3P86/6-311+G(d,p) (IEFPCM: MeOH)[387]	524	FA/H ₂ O/ACN[387]	
						488.00	SMD Water			526	TFA/H ₂ O/ACN[545]	
18	Dp-3-acetyl-glucoside	OH	OH	OH	OGlc-Ac	484.32	SMD MeOH			527	TFA/H ₂ O/ACN[546]	
						483.48	SMD Water				FA/H ₂ O/ACN[369]	
24	Dp-3-(6-(Z)-caffeoyl)-glucoside	OH	OH	OH	OGlc-Caff	521.28	SMD MeOH			529	TFA/H ₂ O/ACN[369]	
						518.91	SMD Water			-	-	
30	Dp-3-(6-(E)-caffeoyl)-glucoside	OH	OH	OH	OGlc-Caff	505.39	SMD MeOH			532	TFA/H ₂ O/ACN[545]	
						512.83	SMD Water					
36	Dp-3-(6-(Z)-p-coumaroyl)-glucoside	OH	OH	OH	OGlc-pCoun	493.89	SMD MeOH			534	TFA/H ₂ O/ACN[545]	
						495.21	SMD Water					
42	Dp-3-(6-(E)-p-coumaroyl)-glucoside	OH	OH	OH	OGlc-pCoun	497.63	SMD MeOH			531	TFA/H ₂ O/ACN[545]	
						497.10	SMD Water			527	FA/H ₂ O/ACN[369]	
7	Petunidin (Pt)	OH	OH	OH	OH	528.75	SMD MeOH	502	B3LYP/6-31G(d) (gas)[285]	543	MeOH/HCl[543]	
						528.92	SMD Water					
13	Pt-3-glucoside	OH	OH	OH	OGlc	496.79	SMD MeOH	483.4	B3P86/6-311+G(d,p) (IEFPCM: MeOH)[387]	535	MeOH/HCl[543]	
						514.36	SMD Water			526	FA/H ₂ O/ACN[387]	
										527	TFA/H ₂ O/ACN[546]	
										525	TFA/H ₂ O/ACN[545]	
										527	FA/H ₂ O/ACN[369]	
19	Pt-3-acetyl-glucoside	OH	OH	OH	OGlc-Ac	491.35	SMD MeOH			535	MeOH/HCl[543]	
						490.32	SMD Water			529	TFA/H ₂ O/ACN[545]	

25	Pt-3-(6-(Z)-caffeoyl)-glucoside	OH	OHCH ₃	OGlc-Caff	528.23	SMD MeOH	530 529 526 (L(+)-LA)	TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[369] TFA/H ₂ O/ACN[545]
31	Pt-3-(6-(E)-caffeoyl)-glucoside	OH	OHCH ₃	OGlc-Caff	530.05	SMD Water	531	TFA/H ₂ O/ACN[545]
37	Pt-3-(6-(Z)-p-coumaroyl)-glucoside	OH	OHCH ₃	OGlc-pCoup	508.41	SMD MeOH	536	TFA/H ₂ O/ACN[545]
43	Pt-3-(6-(E)-p-coumaroyl)-glucoside	OH	OHCH ₃	OGlc-pCoup	498.52	SMD Water	532	TFA/H ₂ O/ACN[545]
8	Malvidin (Mv)	OCH ₃	OHCH ₃	OH	501.86	SMD MeOH	542	MeOH/HCl[543]
14	Mv-3-glucoside	OCH ₃	OHCH ₃	OGlc	503.74	SMD Water	527	FA/H ₂ O/ACN[387]
20	Mv-3-acetyl-glucoside	OCH ₃	OHCH ₃	OGlc-Ac	496.92	SMD MeOH	529	FA/H ₂ O/ACN[387]
26	Mv-3-(6-(Z)-caffeoyl)-glucoside	OCH ₃	OHCH ₃	OGlc-Caff	496.09	SMD Water	529	TFA/H ₂ O/ACN[545, 546]
32	Mv-3-(6-(E)-caffeoyl)-glucoside	OCH ₃	OHCH ₃	OGlc-Caff	538.45	SMD MeOH	531 (L(+)-LA)	TFA/H ₂ O/ACN[545]
					513	SMD MeOH	531 (L(+)-LA)	TFA/H ₂ O/ACN[545]
					538.05	SMD Water	535	MeOH/HCl[543]
					494 519	SMD Water	527	FA/H ₂ O/ACN[387]
					400 503	SMD Water	527	FA/H ₂ O/ACN[387]
					497.1	SMD MeOH	527	FA/H ₂ O/ACN[387]
					504.50	SMD Water	527	FA/H ₂ O/ACN[387]
					503.90	SMD MeOH	529	FA/H ₂ O/ACN[387]
					502.13	SMD Water	529	TFA/H ₂ O/ACN[545, 546]
					526.79	SMD MeOH	530	FA/H ₂ O/ACN[387]
					527.87	SMD Water	531	FA/H ₂ O/ACN[387]
					502.2	SMD Water	531	FA/H ₂ O/ACN[387]

Label	Pyrananthocyanins	Own calculations					Literature Modeling			Literature Experimental		
		R ₁	R ₂	R ₃	R _{6''}	R ₅	λ _{max, CALC} (nm)	Method	λ _{max, CALC} (nm)	Method	λ _{max, EXP} (nm)	Solvent
38	Mv-3-(6-(Z)-p-coumaroyl)-glucoside	H	OH	H	H	COOH	467.45	SMD MeOH				
							469.50	SMD Water				
		OCH ₃	OH	OCH ₃	OGlc-pCoup	H	457.04	SMD MeOH	B3P86/6-311+G(d,p) (IEFPCM: MeOH)[387]	516	TFA/H ₂ O/ACN[546]	
44	Mv-3-(6-(E)-p-coumaroyl)-glucoside	H	OH	H	OGlc-pCoup	Phenol	457.19	SMD Water				
							482.84	SMD MeOH				
							485.23	SMD Water				
63	Pg-3-Glc-4-vinylcatechol adduct	H	OH	H	H	Catechol	495.38	SMD MeOH				
							494.60	SMD Water				
		H	OH	H	Ac	COOH	468.58	SMD MeOH				
69	Pg-3-acetyl-Glc-10-carboxy type	H	OH	H	Ac	COOH	472.33	SMD Water				
							456.43	SMD MeOH				
		H	OH	H	Ac	H	457.41	SMD Water				
75	Pg-3-acetyl-Glc-10-H type	H	OH	H	Ac	Phenol	474.88	SMD MeOH				
							472.09	SMD Water				
		H	OH	H	Ac	Catechol	492.91	SMD MeOH				
81	Pg-3-acetyl-Glc-4-vinylphenol adduct	H	OH	H	Ac		493.06	SMD Water				
		H	OH	H	Ac							
87	Pg-3-acetyl-Glc-4-vinylcatechol adduct	H	OH	H	Ac							
		H	OH	H	Ac							

93	Pg-(6-(E)-caFFEoyl)-Glc 10-carboxy type	H	OH	H	Caff	COOH	500.75	SMD MeOH	-	-
99	Pg-(6-(E)-caFFEoyl)-Glc 10-H type	H	OH	H	Caff	H	499.71 488.56	SMD Water SMD MeOH	-	-
105	Pg-(6-(E)-caFFEoyl)-Glc-4- vinylphenol adduct	H	OH	H	Caff	Phenol	489.83 476.58	SMD Water SMD MeOH	-	-
111	Pg-(6-(E)-caFFEoyl)-Glc-4- vinylcatechol adduct	H	OH	H	Caff	Catechol	470.66 491.88	SMD Water SMD MeOH	-	-
117	Pg-3-(6-(E)-coum)-Glc 10-carboxy type	H	OH	H	pCoum	COOH	489.33 476.10	SMD Water SMD MeOH	-	-
123	Pg-3-(6-(E)-coum)-Glc 10-H type	H	OH	H	pCoum	H	476.92 466.64	SMD Water SMD MeOH	-	-
129	Pg-3-(6-(E)-coum)-Glc-4- vinylphenol adduct	H	OH	H	pCoum	Phenol	468.85 491.81	SMD Water SMD MeOH	-	-
135	Pg-3-(6-(E)-coum)-Glc-4- vinylcatechol adduct	H	OH	H	pCoum	Catechol	488.85 476.26 476.20	SMD Water SMD MeOH SMD Water	-	-
46	Cy-3-Glc 10-carboxy type	OH	OH	H	H	COOH	484.73	SMD MeOH	504	FA/H ₂ O/ACN[392]
52	Cy-3-Glc 10-H type	OH	OH	H	H	H	486.38 474.34	SMD Water SMD MeOH	-	-
58	Cy-3-Glc 4- vinylphenol adduct	OH	OH	H	H	Phenol	473.83 491.11	SMD Water SMD MeOH	500	FA/H ₂ O/ACN[392]
64	Cy-3-Glc 4- vinylcatechol adduct	OH	OH	H	H	Catechol	496.97 497.80	SMD Water SMD MeOH	508	FA/H ₂ O/ACN[392]

70	Cy-3-acetyl-Glc 10-carboxy type	OH	OH	H	Ac	COOH	484.08	SMD MeOH	-	-
76	Cy-3-acetyl-Glc 10-H type	OH	OH	H	Ac	H	487.38 473.14	SMD Water SMD MeOH	-	-
82	Cy-3-acetyl-Glc 4- vinylphenol adduct	OH	OH	H	Ac	Phenol	473.15 483.12	SMD Water SMD MeOH	-	-
88	Cy-3-acetyl-Glc 4- vinylcatechol adduct	OH	OH	H	Ac	Catechol	476.97 493.82	SMD Water SMD MeOH	-	-
94	Cy-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	OH	H	Caff	COOH	499.01 502.66	SMD Water SMD MeOH	-	-
100	Cy-(6-(E)-caffeoyl)-Glc 10-H type	OH	OH	H	Caff	H	502.04 493.98	SMD Water SMD MeOH	-	-
106	Cy-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OH	OH	H	Caff	Phenol	494.17 475.45	SMD Water SMD MeOH	-	-
112	Cy-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH	OH	H	Caff	Catechol	477.66 500.64	SMD Water SMD MeOH	-	-
118	Cy-3-(6-(E)-coum)-Glc 10-carboxy type	OH	OH	H	pCoum	COOH	494.43 482.74	SMD Water SMD MeOH	-	-
124	Cy-3-(6-(E)-coum)-Glc 10-H type	OH	OH	H	pCoum	H	484.94 477.19	SMD Water SMD MeOH	-	-
130	Cy-3-(6-(E)-coum)-Glc 4- vinylphenol adduct	OH	OH	H	pCoum	Phenol	478.64 475.86	SMD Water SMD MeOH	-	-
136	Cy-3-(6-(E)-coum)-Glc 4- vinylcatechol adduct	OH	OH	H	pCoum	Catechol	474.24 499.74	SMD Water SMD MeOH	508	FA/H ₂ O/ACN[392]
							494.09	SMD Water		

47	Pn-3-Glc 10-carboxy type	OCH ₃ OH	H	COOH	488.04	SMD MeOH	539	PBE0/SV(P) (Gas)[376]	503	TFA/H ₂ O/ACN[545, 546]
					490.26	SMD Water	506	PBE0/SV(P) (C-PCM, Water)[376]	505	FA/H ₂ O/ACN[392]
53	Pn-3-Glc 10-H type	OCH ₃ OH	H	H	478.43	SMD MeOH			487	FA/H ₂ O/ACN[392]
					476.95	SMD Water				
59	Pn-3-Glc 4-vinylphenol adduct	OCH ₃ OH	H	Phenol	482.84	SMD MeOH			500	TFA/H ₂ O/ACN[545]
					496.60	SMD Water			499	FA/H ₂ O/ACN[369]
									500	FA/H ₂ O/ACN[392]
65	Pn-3-Glc 4-vinylcatechol adduct	OCH ₃ OH	H	Catechol	507.87	SMD MeOH			506	TFA/H ₂ O/ACN[545]
					506.32	SMD Water			507	TFA/H ₂ O/ACN[546]
71	Pn-3-acetyl-Glc 10-carboxy type	OCH ₃ OH	H	COOH	492.84	SMD MeOH			506	FA/H ₂ O/ACN[392]
			Ac		496.58	SMD Water			507	FA/H ₂ O/ACN[392]
77	Pn-3-acetyl-Glc 10-H type	OCH ₃ OH	H	H	481.73	SMD MeOH			486	FA/H ₂ O/ACN[392]
			Ac		482.05	SMD Water				
83	Pn-3-acetyl-Glc 4-vinylphenol adduct	OCH ₃ OH	H	Phenol	488.03	SMD MeOH			501	FA/H ₂ O/ACN[392]
			Ac		489.08	SMD Water				
89	Pn-3-acetyl-Glc 4-vinylcatechol adduct	OCH ₃ OH	H	Catechol	505.49	SMD MeOH			507	FA/H ₂ O/ACN[392]
			Ac		503.62	SMD Water				
95	Pn-(6-(E)-caffeoyl)-Glc 10-carboxy type	OCH ₃ OH	H	COOH	502.02	SMD MeOH			508	FA/H ₂ O/ACN[392]
			Caff		500.91	SMD Water				
101	Pn-(6-(E)-caffeoyl)-Glc 10-H type	OCH ₃ OH	H	H	492.34	SMD MeOH			-	
			Caff		493.02	SMD Water				
107	Pn-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OCH ₃ OH	H	Phenol	483.41	SMD MeOH			502	FA/H ₂ O/ACN[392]
			Caff		481.34	SMD Water				

113	Pn-(6-(E)-caffoyl)-Glc 4-vinylcatechol adduct	OCH ₃ OH	H	Caff	Catechol	506.09	SMD MeOH			508	FA/H ₂ O/ACN[392]
119	Pn-3-(6-(E)-coum)-Glc 10-carboxy type	OCH ₃ OH	H	pCoum	COOH	499.85 486.56 494.69	SMD Water SMD MeOH SMD Water			508 513 509 485	TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[392] FA/H ₂ O/ACN[392]
125	Pn-3-(6-(E)-coum)-Glc 10-H type	OCH ₃ OH	H	pCoum	H	479.36	SMD MeOH				
131	Pn-3-(6-(E)-coum)-Glc-4- vinylphenol adduct	OCH ₃ OH	H	pCoum	Phenol	480.59 483.21 480.22	SMD Water SMD MeOH SMD Water			501 498 502	TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[392]
137	Pn-3-(6-(E)-coum)-Glc-4- vinylcatechol adduct	OCH ₃ OH	H	pCoum	Catechol	505.95	SMD MeOH			508	TFA/H ₂ O/ACN[546]
48	Dp-3-Glc 10-carboxy type	OH OH OH	OH	H	COOH	499.00 488.60 490.25	SMD Water SMD MeOH SMD Water			508 507 506 509 487	FA/H ₂ O/ACN[392] TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[392] FA/H ₂ O/ACN[392]
54	Dp-3-Glc 10-H type	OH OH OH	OH	H	H	478.42	SMD MeOH				
60	Dp-3-Glc 4- vinylphenol adduct	OH OH OH	OH	H	Phenol	476.97 500.67	SMD Water SMD MeOH			503 504	TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[392]
66	Dp-3-Glc 4- vinylcatechol adduct	OH OH OH	OH	H	Catechol	495.85 504.97	SMD Water SMD MeOH			509	TFA/H ₂ O/ACN[545]
72	Dp-3-acetyl-Glc 10-carboxy type	OH OH OH	OH	Ac	COOH	504.00 487.56	SMD Water SMD MeOH			509 511	FA/H ₂ O/ACN[392] FA/H ₂ O/ACN[392]
78	Dp-3-acetyl-Glc 10-H type	OH OH OH	OH	Ac	H	488.95 476.12 475.63	SMD Water SMD MeOH SMD Water			488	FA/H ₂ O/ACN[392]

84	Dp-3-acetyl-Glc 4-vinylphenol adduct	OH OH OH	Ac	Phenol	487.63	SMD MeOH	505	FA/H ₂ O/ACN[392]
90	Dp-3-acetyl-Glc 4-vinylcatechol adduct	OH OH OH	Ac	Catechol	486.61 503.80	SMD Water SMD MeOH	512	FA/H ₂ O/ACN[392]
96	Dp-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH OH OH	Caff	COOH	501.44 508.83	SMD Water SMD MeOH	-	
102	Dp-(6-(E)-caffeoyl)-Glc 10-H type	OH OH OH	Caff	H	506.63 493.34	SMD Water SMD MeOH	-	
108	Dp-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OH OH OH	Caff	Phenol	485.87 485.43	SMD Water SMD MeOH	-	
114	Dp-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH OH OH	Caff	Catechol	489.90 501.93	SMD Water SMD MeOH	-	
120	Dp-3-(6-(E)-coum)-Glc 10-carboxy type	OH OH OH	pCoum	COOH	499.34 487.01	SMD Water SMD MeOH	512	FA/H ₂ O/ACN[392]
126	Dp-3-(6-(E)-coum)-Glc 10-H type	OH OH OH	pCoum	H	490.30 481.70	SMD Water SMD MeOH	-	
132	Dp-3-(6-(E)-coum)-Glc-4-vinylphenol adduct	OH OH OH	pCoum	Phenol	481.12 487.42	SMD Water SMD MeOH	-	
138	Dp-3-(6-(E)-coum)-Glc-4-vinylcatechol adduct	OH OH OH	pCoum	Catechol	485.93 501.86	SMD Water SMD MeOH	510	FA/H ₂ O/ACN[392]
49	Pt-3-Glc 10-carboxy type	OH OH OCH ₃	H	COOH	490.06 490.28 491.37	SMD Water SMD MeOH SMD Water	547 503	PBE0/SV(P) (Gas)[376] PBE0/SV(P) (C-PCM, Water)[376]
							508 507 510	TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[392]

55	Pt-3-Glc 10-H type	OH	OHCH ₃	H	H	481.99	SMD MeOH			492	TFA/H ₂ O/ACN[545]
						480.09	SMD Water			488	FA/H ₂ O/ACN[392]
61	Pt-3-Glc 4-vinylphenol adduct	OH	OHCH ₃	H	Phenol					492	PBE0/SV(P) (Gas)[376]
										467	PBE0/SV(P) (C-PCM, Water)[376]
						500.81	SMD MeOH			502	TFA/H ₂ O/ACN[545]
						501.14	SMD Water			503	TFA/H ₂ O/ACN[546]
										504	FA/H ₂ O/ACN[392]
67	Pt-3-Glc 4-vinylcatechol adduct	OH	OHCH ₃	H	Catechol	510.28	SMD MeOH			510	TFA/H ₂ O/ACN[545]
						509.08	SMD Water			510	FA/H ₂ O/ACN[392]
						492.12	SMD MeOH			512	FA/H ₂ O/ACN[392]
73	Pt-3-acetyl-Glc 10-carboxy type	OH	OHCH ₃	Ac	COOH	495.19	SMD Water				
						480.12	SMD MeOH			494	FA/H ₂ O/ACN[392]
79	Pt-3-acetyl-Glc 10-H type	OH	OHCH ₃	Ac	H	479.46	SMD Water				
						489.81	SMD MeOH			505	FA/H ₂ O/ACN[392]
85	Pt-3-acetyl-Glc 4-vinylphenol adduct	OH	OHCH ₃	Ac	Phenol	486.64	SMD Water				
						508.16	SMD MeOH			511	FA/H ₂ O/ACN[392]
91	Pt-3-acetyl-Glc 4-vinylcatechol adduct	OH	OHCH ₃	Ac	Catechol	506.89	SMD Water				
						504.72	SMD MeOH			-	
97	Pt-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	OHCH ₃	Caff	COOH	503.82	SMD Water				
						495.93	SMD MeOH			-	
103	Pt-(6-(E)-caffeoyl)-Glc 10-H type	OH	OHCH ₃	Caff	H	495.19	SMD Water				
						484.86	SMD MeOH			-	
109	Pt-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OH	OHCH ₃	Caff	Phenol	480.92	SMD Water				
						507.98	SMD MeOH			-	
115	Pt-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH	OHCH ₃	Caff	Catechol	504.03	SMD Water				

121	Pt-3-(6-(E)-coum)-Glc 10-carboxy type	OH	OHCH ₃	pCoum	COOH	493.51	SMD MeOH		-	
127	Pt-3-(6-(E)-coum)-Glc 10-H type	OH	OHCH ₃	pCoum	H	498.82	SMD Water		494	FA/H ₂ O/ACN[392]
133	Pt-3-(6-(E)-coum)-Glc-4- vinylphenol adduct	OH	OHCH ₃	pCoum	Phenol	483.74	SMD MeOH			
139	Pt-3-(6-(E)-coum)-Glc-4- vinylcatechol adduct	OH	OHCH ₃	pCoum	Catechol	483.78	SMD Water			
50	Mv-3-Glc 10-carboxy type	OCH ₃	OHCH ₃	H	COOH	489.53	SMD MeOH		504	TFA/H ₂ O/ACN[545]
56	Mv-3-Glc 10-H type	OCH ₃	OHCH ₃	H	H	481.05	SMD Water		504	FA/H ₂ O/ACN[392]
62	Mv-3-Glc 4- vinylphenol adduct	OCH ₃	OHCH ₃	H	Phenol	507.81	SMD MeOH		511	FA/H ₂ O/ACN[392]
68	Mv-3-Glc 4- vinylcatechol adduct	OCH ₃	OHCH ₃	H	Catechol	503.77	SMD Water			
								PBE0/SV(P) (Gas)		
								PBE0/SV(P) (C-PCM, Water)		
									510	TFA/H ₂ O/ACN[545]
									507	TFA/H ₂ O/ACN[546]
									509	FA/H ₂ O/ACN[369]
									511	FA/H ₂ O/ACN[392]
									490	TFA/H ₂ O/ACN[545]
									490	FA/H ₂ O/ACN[392]
									504	TFA/H ₂ O/ACN[545]
									503	TFA/H ₂ O/ACN[546]
									503	FA/H ₂ O/ACN[369]
									504	FA/H ₂ O/ACN[392]
									510	TFA/H ₂ O/ACN[545]
									512	FA/H ₂ O/ACN[369]
									511	FA/H ₂ O/ACN[392]

74	Mv-3-acetyl-Glc 10-carboxy type	OCH ₃ OH	Ac	COOH	504.25	SMD MeOH	514	FA/H ₂ O/ACN[392]
80	Mv-3-acetyl-Glc 10-H type	OCH ₃ OH	Ac	H	506.57 493.29	SMD Water SMD MeOH	494	TFA/H ₂ O/ACN[545]
86	Mv-3-acetyl-Glc 4- vinylphenol adduct	OCH ₃ OH	Ac	Phenol	491.68 500.05	SMD Water SMD MeOH	494 505	FA/H ₂ O/ACN[392] TFA/H ₂ O/ACN[545]
92	Mv-3-acetyl-Glc 4- vinylcatechol adduct	OCH ₃ OH	Ac	Catechol	494.06 515.12	SMD Water SMD MeOH	506 513	FA/H ₂ O/ACN[392] TFA/H ₂ O/ACN[545]
98	Mv-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	Caff	COOH	512.87 505.42	SMD Water SMD MeOH	512 514	FA/H ₂ O/ACN[392] FA/H ₂ O/ACN[392]
104	Mv-(6-(E)-caffeoyl)-Glc 10-H type	OH	Caff	H	518.29 500.38	SMD Water SMD MeOH	498	FA/H ₂ O/ACN[392]
110	Mv-(6-(E)-caffeoyl)-Glc 4- vinylphenol adduct	OH	Caff	Phenol	493.55 491.31	SMD Water SMD MeOH	506	FA/H ₂ O/ACN[392]
116	Mv-(6-(E)-caffeoyl)-Glc 4- vinylcatechol adduct	OH	Caff	Catechol	490.47 516.49	SMD Water SMD MeOH	512	FA/H ₂ O/ACN[392]
122	Mv-3-(6-(E)-coum)-Glc 10-carboxy type	OCH ₃ OH	pCoum	COOH	509.55 504.15	SMD Water SMD MeOH	514 516	TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[369] FA/H ₂ O/ACN[392]
128	Mv-3-(6-(E)-coum)-Glc 10-H type	OCH ₃ OH	pCoum	H	494.17 494.14	SMD MeOH SMD Water	497	FA/H ₂ O/ACN[392]
134	Mv-3-(6-(E)-coum)-Glc 4- vinylphenol adduct	OCH ₃ OH	pCoum	Phenol	493.03 490.35	SMD MeOH SMD Water	505 506	TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546]
140	Mv-3-(6-(E)-coum)-Glc 4- vinylcatechol adduct	OCH ₃ OH	pCoum	Catechol	516.37	SMD MeOH	505 511	FA/H ₂ O/ACN[392] TFA/H ₂ O/ACN[545]

Data TD-DFT calculations (CAM-B3LYP)

Table D.28: List of own calculated TD-DFT calculations of anthocyanins and pyrananthocyanins along with their possible substitution patterns (Figure 4.1) (CAM-B3LYP/6-311++G(d,p)). For comparison, existing TD-DFT studies and experimental literature studies are included.

Label	Anthocyanins	Own calculations				Literature Modeling		Literature Experimental			
		R ₁	R ₂	R ₃	R ₄	λ _{max} , CALC (nm)	Method	λ _{max} , CALC (nm)	Method	λ _{max} , EXP (nm)	Solvent
1	Apigeninidin (Ap)	H	OH	H	H	433.83	SMD MeOH	431	B3LYP/6-31G(d) (gas)[285]	476	MeOH/HCl[543]
						434.54	SMD Water			468	KCl buffer pH=1 [356]
2	Luteolinidin (Lt)	OH	OH	H	H	433.83	SMD MeOH	468	B3LYP/6-31G(d) (gas)[285]	493	MeOH/HCl[543]
						441.97	SMD Water			482	KCl buffer pH=1 [356]
3	Pelargonidin (Pg)	H	OH	H	OH	481.59	SMD MeOH	470	B3LYP/6-31G(d) (gas)[285]	520	MeOH/HCl[543]
						481.73	SMD Water	475	B3LYP/6-31+G(d) (gas)[363]	524	MeOH/HCl[58]
								492	B3LYP/6-31+G(d) (C-PCM: water)[363]	506	KCl buffer pH=1 [356]
9	Pg-3-glucoside	H	OH	H	OGlc	438.18	SMD MeOH			505	KCl buffer pH=1 [58]
						437.8	SMD Water			506	MeOH/HCl[543]
										508	MeOH/HCl[58]
										503 (Rut)	TFA/H ₂ O/ACN[544]
										506 (Gen)	MeOH/HCl[543]
										508 (Rhaglc)	MeOH/HCl[543]
										496	KCl buffer pH=1 [58]
										502	TFA/H ₂ O/ACN[544]
										503 (Ara)	TFA/H ₂ O/ACN[544]
										500 (Gal)	TFA/H ₂ O/ACN[544]
15	Pg-acetyl-glucoside	H	OH	H	OGlc-Ac	437.52	SMD MeOH			504 (OGlc-Malo)	TFA/H ₂ O/ACN[544]
21	Pg-3-(6-(Z)-caffeoyl)-glucoside					433.70	SMD Water			503 (OGlc-Maly)	TFA/H ₂ O/ACN[544]
		H	OH	H	OGlc-Caff	441.41	SMD MeOH				

6	Delphinidin (Dp)	OH	OH	OH	OH	444.40	SMD Water	490	B3LYP/6-31G(d) (gas)[285] B3LYP/6-31+G(d) (gas)[363] B3LYP/6-31+G(d) (C-PCM: water)[363] B3P86/6-311+G(d,p) (IEFPCM: MeOH)[387]	520	FA/H ₂ O/ACN[369] MeOH/HCl[543]
12	Dp-3-glucoside	OH	OH	OH	OGlc	445.88	SMD MeOH	482.8		535	MeOH/HCl[543] MeOH/HCl[543] FA/H ₂ O/ACN[387] TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[369] TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[369]
18	Dp-3-acetyl-glucoside	OH	OH	OH	OGlc-Ac	440.05	SMD MeOH			537 (Rhg(c)) 524 524 526 527	
24	Dp-3-(6-(Z)-caffeoyl)-glucoside	OH	OH	OH	OGlc-Caff	446.39	SMD MeOH			529	
30	Dp-3-(6-(E)-caffeoyl)-glucoside	OH	OH	OH	OGlc-Caff	442.75	SMD MeOH			532	TFA/H ₂ O/ACN[545]
36	Dp-3-(6-(Z)-p-coumaroyl)-glucoside	OH	OH	OH	OGlc-pCoup	448.86	SMD MeOH			534	TFA/H ₂ O/ACN[545]
42	Dp-3-(6-(E)-p-coumaroyl)-glucoside	OH	OH	OH	OGlc-pCoup	442.74	SMD MeOH			531	TFA/H ₂ O/ACN[545]
7	Petunidin (Pt)	OH	OH	OH	OH	493.28	SMD MeOH	502	B3LYP/6-31G(d) (gas)[285]	543	MeOH/HCl[543]
13	Pt-3-glucoside	OH	OH	OH	OGlc	452.97	SMD MeOH	483.4	B3P86/6-311+G(d,p) (IEFPCM: MeOH)[387]	535	MeOH/HCl[543] FA/H ₂ O/ACN[387] TFA/H ₂ O/ACN[546]

19	Pt-3-acetyl-glucoside	OH	OHCH ₃	OGlc-Ac	444.48 443.50	SMD MeOH SMD Water	525 527 535 529 530 529	TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[369] MeOH/HCl[543] TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[369] TFA/H ₂ O/ACN[545]
25	Pt-3-(6-(Z)-caffeoyl)-glucoside	OH	OHCH ₃	OGlc-Caff	447.04	SMD MeOH	526 (L(+)-LA)	-
31	Pt-3-(6-(E)-caffeoyl)-glucoside	OH	OHCH ₃	OGlc-Caff	443.50 441.55 440.14	SMD Water SMD MeOH SMD Water	531	TFA/H ₂ O/ACN[545]
37	Pt-3-(6-(Z)-p-coumaroyl)-glucoside	OH	OHCH ₃	OGlc-pCoum	446.24	SMD MeOH	536	TFA/H ₂ O/ACN[545]
43	Pt-3-(6-(E)-p-coumaroyl)-glucoside	OH	OHCH ₃	OGlc-pCoum	444.70 443.24 442.41	SMD Water SMD MeOH SMD Water	532	TFA/H ₂ O/ACN[545]
8	Malvidin (Mv)	OCH ₃	OHCH ₃	OH	503.03 502.13	SMD MeOH SMD Water	542	MeOH/HCl[543]
14	Mv-3-glucoside	OCH ₃	OHCH ₃	OGlc	460.93 453.15	SMD MeOH SMD Water	535 527 527	MeOH/HCl[543] FA/H ₂ O/ACN[387] TFA/H ₂ O/ACN[545, 546] FA/H ₂ O/ACN[369]
20	Mv-3-acetyl-glucoside	OCH ₃	OHCH ₃	OGlc-Ac	455.42 453.05	SMD MeOH SMD Water	529 530 529 530 (D(-)-LA)	FA/MeOH/H ₂ O[291] FA/H ₂ O/ACN[387] TFA/H ₂ O/ACN[545, 546] FA/H ₂ O/ACN[369] TFA/H ₂ O/ACN[545]

Label	Pyrananthocyanins	Own calculations					Literature Modeling			Literature Experimental		
		R ₁	R ₂	R ₃	R ₆ ^o	R ₅	λ _{max} CALC (nm)	Method	λ _{max} CALC (nm)	Method	λ _{max} EXP (nm)	Solvent
26	Mv-3-(6-(Z)-cafeoyl)-glucoside	OCH ₃ OH	OH	OCH ₃	OGlc-Caff	450.88	SMD MeOH			531 (LC(+)-LA)	TFA/H ₂ O/ACN[545]	-
32	Mv-6-(E)-cafeoyl)-glucoside " (E)	OCH ₃ OH	OH	OCH ₃	OGlc-Caff	447.51	SMD Water		B3P86/6-311+G(d,p) (IEFPCM: MeOH)[387]	531	FA/H ₂ O/ACN[387]	-
38	Mv-3-(6-(Z)-p-coumaroyl)-glucoside	OCH ₃ OH	OH	OCH ₃	OGlc-pCoup	450.53	SMD MeOH			534	TFA/H ₂ O/ACN[545]	-
44	Mv-3-(6-(E)-p-coumaroyl)-glucoside	OCH ₃ OH	OH	OCH ₃	OGlc-pCoup	448.41	SMD Water		B3P86/6-311+G(d,p) (IEFPCM: MeOH)[387]	535	TFA/H ₂ O/ACN[546]	-
						452.41	SMD MeOH	516		532	FA/H ₂ O/ACN[387]	-
						451.23	SMD Water			532	TFA/H ₂ O/ACN[545]	-
						451.14	SMD MeOH					
						449.23	SMD Water					
Label	Pyrananthocyanins	Own calculations					Literature Modeling			Literature Experimental		
		R ₁	R ₂	R ₃	R ₆ ^o	R ₅	λ _{max} CALC (nm)	Method	λ _{max} CALC (nm)	Method	λ _{max} EXP (nm)	Solvent
45	Pg-3-Glc 10-carboxy type	H	OH	H	H	COOH	430.69	SMD MeOH			-	-
51	Pg-3-Glc 10-H type	H	OH	H	H	H	432.21	SMD Water			-	-
57	Pg-3-Glc-4-vinylphenol adduct	H	OH	H	H	Phenol	423.43	SMD MeOH			-	-
							423.59	SMD Water			-	-
							445.48	SMD MeOH			-	-
63	Pg-3-Glc-4-vinylcatechol adduct	H	OH	H	H	Catechol	448.59	SMD Water			-	-
							450.76	SMD MeOH			-	-
69	Pg-3-acetyl-Glc 10-carboxy type	H	OH	H	Ac	COOH	450.71	SMD Water			-	-
							431.96	SMD MeOH			-	-
75	Pg-3-acetyl-Glc 10-H type	H	OH	H	Ac	H	434.75	SMD Water			-	-
							423.25	SMD MeOH			-	-
							424.02	SMD Water			-	-

81	Pg-3-acetyl-Glc-4-vinylphenol adduct	H	OH	H	Ac	Phenol	436.81	SMD MeOH	-	-
87	Pg-3-acetyl-Glc-4-vinylcatechol adduct	H	OH	H	Ac	Catechol	435.12 448.51	SMD Water SMD MeOH	-	-
93	Pg-(6-(E)-caffeoyl)-Glc-10-carboxy type	H	OH	H	Caff	COOH	448.85 427.78	SMD Water SMD MeOH	-	-
99	Pg-(6-(E)-caffeoyl)-Glc-10-H type	H	OH	H	Caff	H	429.23 421.77	SMD Water SMD MeOH	-	-
105	Pg-(6-(E)-caffeoyl)-Glc-4-vinylphenol adduct	H	OH	H	Caff	Phenol	423.68 438.71	SMD Water SMD MeOH	-	-
111	Pg-(6-(E)-caffeoyl)-Glc-4-vinylcatechol adduct	H	OH	H	Caff	Catechol	431.61 446.94	SMD Water SMD MeOH	-	-
117	Pg-3-(6-(E)-coum)-Glc-10-carboxy type	H	OH	H	pCoum	COOH	445.70 427.80	SMD Water SMD MeOH	-	-
123	Pg-3-(6-(E)-coum)-Glc-10-H type	H	OH	H	pCoum	H	429.39 421.25	SMD Water SMD MeOH	-	-
129	Pg-3-(6-(E)-coum)-Glc-4-vinylphenol adduct	H	OH	H	pCoum	Phenol	422.97 438.35	SMD Water SMD MeOH	-	-
135	Pg-3-(6-(E)-coum)-Glc-4-vinylcatechol adduct	H	OH	H	pCoum	Catechol	438.44 446.57	SMD Water SMD MeOH	-	-
46	Cy-3-Glc 10-carboxy type	OH	OH	H	H	COOH	445.45 435.23	SMD Water SMD MeOH	504	FA/H ₂ O/ACN[392]
52	Cy-3-Glc 10-H type	OH	OH	H	H	H	436.76 427.52 427.86	SMD Water SMD MeOH SMD Water	-	-

58	Cy-3-Glc-4-vinylphenol adduct	OH	OH	H	H	Phenol	448.08	SMD MeOH		500	FA/H ₂ O/ACN[392]
64	Cy-3-Glc-4-vinylcatechol adduct	OH	OH	H	H	Catechol	449.63	SMD Water		508	FA/H ₂ O/ACN[392]
70	Cy-3-acetyl-Glc 10-carboxy type	OH	OH	H	Ac	COOH	450.44	SMD MeOH		-	
76	Cy-3-acetyl-Glc 10-H type	OH	OH	H	Ac	H	450.18	SMD Water		-	
82	Cy-3-acetyl-Glc 4-vinylphenol adduct	OH	OH	H	Ac	Phenol	434.48	SMD MeOH		-	
88	Cy-3-acetyl-Glc 4-vinylcatechol adduct	OH	OH	H	Ac	Catechol	437.12	SMD Water		-	
94	Cy-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	OH	H	Caff	COOH	426.91	SMD MeOH		-	
100	Cy-(6-(E)-caffeoyl)-Glc 10-H type	OH	OH	H	Caff	H	427.24	SMD Water		-	
106	Cy-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OH	OH	H	Caff	Phenol	438.67	SMD MeOH		-	
112	Cy-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH	OH	H	Caff	Catechol	436.93	SMD Water		-	
118	Cy-3-(6-(E)-coum)-Glc 10-carboxy type	OH	OH	H	pCoum	COOH	449.73	SMD MeOH		-	
124	Cy-3-(6-(E)-coum)-Glc 10-H type	OH	OH	H	pCoum	H	450.13	SMD Water		-	

130	Cy-3-(6-(E)-coum)-Glc-4-vinylphenol adduct	OH	OH	H	pCoup	Phenol	434.52	SMD MeOH			-	
136	Cy-3-(6-(E)-coum)-Glc-4-vinylcatechol adduct	OH	OH	H	pCoup	Catechol	433.14	SMD Water			508	FA/H ₂ O/ACN[392]
47	Pn-3-Glc 10-carboxy type	OCH ₃ OH		H	H	COOH	443.94	SMD MeOH				
							445.88	SMD Water				
53	Pn-3-Glc 10-H type	OCH ₃ OH		H	H	H	433.96	SMD MeOH	539	PBE0/SV(P) (Gas)[376]	503	TFA/H ₂ O/ACN[545, 546]
							435.85	SMD Water	506	PBE0/SV(P) (C-PCM, Water)[376]	505	FA/H ₂ O/ACN[392]
59	Pn-3-Glc-4-vinylphenol adduct	OCH ₃ OH		H	H	Phenol	427.86	SMD MeOH			487	FA/H ₂ O/ACN[392]
							427.11	SMD Water				
65	Pn-3-Glc-4-vinylcatechol adduct	OCH ₃ OH		H	H	Phenol	452.28	SMD MeOH			500	TFA/H ₂ O/ACN[545]
							451.28	SMD Water			499	FA/H ₂ O/ACN[369]
											500	FA/H ₂ O/ACN[392]
71	Pn-3-acetyl-Glc 10-carboxy type	OCH ₃ OH		H	Ac	COOH	457.25	SMD MeOH			506	TFA/H ₂ O/ACN[545]
							456.23	SMD Water			507	TFA/H ₂ O/ACN[546]
77	Pn-3-acetyl-Glc 10-H type	OCH ₃ OH		H	Ac	H	441.06	SMD MeOH			506	FA/H ₂ O/ACN[392]
							443.75	SMD Water			507	FA/H ₂ O/ACN[392]
							433.55	SMD MeOH			486	FA/H ₂ O/ACN[392]
83	Pn-3-acetyl-Glc 4-vinylphenol adduct	OCH ₃ OH		H	Ac	Phenol	433.86	SMD Water				
							440.20	SMD MeOH			501	FA/H ₂ O/ACN[392]
89	Pn-3-acetyl-Glc 4-vinylcatechol adduct	OCH ₃ OH		H	Ac	Catechol	446.25	SMD Water			507	FA/H ₂ O/ACN[392]
							453.33	SMD MeOH				
95	Pn-(6-(E)-caffoyl)-Glc 10-carboxy type	OCH ₃ OH		H	Caff	COOH	452.82	SMD Water			508	FA/H ₂ O/ACN[392]
							429.80	SMD MeOH				

101	Pn-(6-(E)-caffeoyl)-Glc 10-H type	OCH ₃ OH	H	Caff	H	430.70	SMD Water					
						425.71	SMD MeOH					
107	Pn-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OCH ₃ OH	H	Caff	Phenol	425.95	SMD Water					
						439.07	SMD MeOH					FA/H ₂ O/ACN[392]
113	Pn-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OCH ₃ OH	H	Caff	Catechol	435.65	SMD Water					
						453.32	SMD MeOH					FA/H ₂ O/ACN[392]
119	Pn-3-(6-(E)-coum)-Glc 10-carboxy type	OCH ₃ OH	H	pCoum	COOH	449.69	SMD Water					
						430.03	SMD MeOH					TFA/H ₂ O/ACN[545]
						435.61	SMD Water					TFA/H ₂ O/ACN[546]
125	Pn-3-(6-(E)-coum)-Glc 10-H type	OCH ₃ OH	H	pCoum	H	428.64	SMD MeOH					FA/H ₂ O/ACN[392]
						428.54	SMD Water					
131	Pn-3-(6-(E)-coum)-Glc-4 vinylphenol adduct	OCH ₃ OH	H	pCoum	Phenol	438.41	SMD MeOH					TFA/H ₂ O/ACN[545]
						435.46	SMD Water					TFA/H ₂ O/ACN[546]
137	Pn-3-(6-(E)-coum)-Glc-4 vinylcatechol adduct	OCH ₃ OH	H	pCoum	Catechol	453.14	SMD MeOH					FA/H ₂ O/ACN[392]
						448.59	SMD Water					TFA/H ₂ O/ACN[546]
48	Dp-3-Glc 10-carboxy type	OH OH	OH	H	COOH	437.40	SMD MeOH					FA/H ₂ O/ACN[392]
						439.08	SMD Water					TFA/H ₂ O/ACN[545]
54	Dp-3-Glc 10-H type	OH OH	OH	H	H	430.85	SMD MeOH					TFA/H ₂ O/ACN[546]
						430.25	SMD Water					FA/H ₂ O/ACN[392]
60	Dp-3-Glc 4- vinylphenol adduct	OH OH	OH	H	Phenol	456.95	SMD MeOH					FA/H ₂ O/ACN[392]
						451.47	SMD Water					TFA/H ₂ O/ACN[545]
66	Dp-3-Glc 4- vinylcatechol adduct	OH OH	OH	H	Catechol	453.66	SMD MeOH					FA/H ₂ O/ACN[392]
						453.59	SMD Water					

72	Dp-3-acetyl-Glc 10-carboxy type	OH OH OH	Ac	COOH	435.71	SMD MeOH	511	FA/H ₂ O/ACN[392]
78	Dp-3-acetyl-Glc 10-H type	OH OH OH	Ac	H	438.06 428.05	SMD Water SMD MeOH	488	FA/H ₂ O/ACN[392]
84	Dp-3-acetyl-Glc 4- vinylphenol adduct	OH OH OH	Ac	Phenol	428.23 441.55	SMD Water SMD MeOH	505	FA/H ₂ O/ACN[392]
90	Dp-3-acetyl-Glc 4- vinylcatechol adduct	OH OH OH	Ac	Catechol	441.70 451.80	SMD Water SMD MeOH	512	FA/H ₂ O/ACN[392]
96	Dp-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH OH OH	Caff	COOH	450.78 435.70	SMD Water SMD MeOH	-	
102	Dp-(6-(E)-caffeoyl)-Glc 10-H type	OH OH OH	Caff	H	436.47 427.71	SMD Water SMD MeOH	-	
108	Dp-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OH OH OH	Caff	Phenol	428.34 438.69	SMD Water SMD MeOH	-	
114	Dp-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH OH OH	Caff	Catechol	444.12 449.28	SMD Water SMD MeOH	-	
120	Dp-3-(6-(E)-coum)-Glc 10-carboxy type	OH OH OH	pCoum	COOH	449.31 432.00	SMD Water SMD MeOH	512	FA/H ₂ O/ACN[392]
126	Dp-3-(6-(E)-coum)-Glc 10-H type	OH OH OH	pCoum	H	436.51 427.47	SMD Water SMD MeOH	-	
132	Dp-3-(6-(E)-coum)-Glc-4- vinylphenol adduct	OH OH OH	pCoum	Phenol	428.80 441.24	SMD Water SMD MeOH	-	
138	Dp-3-(6-(E)-coum)-Glc-4- vinylcatechol adduct	OH OH OH	pCoum	Catechol	440.05 449.05 448.91	SMD Water SMD MeOH SMD Water	510	FA/H ₂ O/ACN[392]

49	Pt-3-Glc 10-carboxy type	OH	OHCH ₃	H	COOH				547	PBE0/SV(P) (Gas)[376] PBE0/SV(P) (C-PCM, Water)[376]	508 507 510 492 488	TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[392] TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[392]
55	Pt-3-Glc 10-H type	OH	OHCH ₃	H	H		433.59 435.64	SMD MeOH SMD Water	503			
61	Pt-3-Glc 4-vinylphenol adduct	OH	OHCH ₃	H	Phenol		428.11 427.29	SMD MeOH SMD Water	492	PBE0/SV(P) (Gas)[376] PBE0/SV(P) (C-PCM, Water)[376]	502 503 504 510 510 512	TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[392] TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[392] FA/H ₂ O/ACN[392]
67	Pt-3-Glc 4-vinylcatechol adduct	OH	OHCH ₃	H	Catechol		452.28 453.44	SMD MeOH SMD Water	467			
73	Pt-3-acetyl-Glc 10-carboxy type	OH	OHCH ₃	Ac	COOH		456.83 436.17	SMD Water SMD MeOH				
79	Pt-3-acetyl-Glc 10-H type	OH	OHCH ₃	Ac	H		438.53 427.06	SMD Water SMD MeOH			494	FA/H ₂ O/ACN[392]
85	Pt-3-acetyl-Glc 4-vinylphenol adduct	OH	OHCH ₃	Ac	Phenol		427.02 441.02	SMD Water SMD MeOH			505	FA/H ₂ O/ACN[392]
91	Pt-3-acetyl-Glc 4-vinylcatechol adduct	OH	OHCH ₃	Ac	Catechol		441.70 454.55	SMD Water SMD MeOH			511	FA/H ₂ O/ACN[392]
97	Pt-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	OHCH ₃	Caff	COOH		454.51 429.58	SMD Water SMD MeOH			-	
103	Pt-(6-(E)-caffeoyl)-Glc 10-H type	OH	OHCH ₃	Caff	H		430.56 426.44	SMD Water SMD MeOH			-	
							426.75	SMD Water				

109	Pt-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OH	OHCH ₃	Caff	Phenol	438.80	SMD MeOH	-	-	-
115	Pt-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH	OHCH ₃	Caff	Catechol	434.45 454.14	SMD Water SMD MeOH	-	-	-
121	Pt-3-(6-(E)-coum)-Glc 10-carboxy type	OH	OHCH ₃	pCoum	COOH	452.23 434.02	SMD Water SMD MeOH	-	-	-
127	Pt-3-(6-(E)-coum)-Glc 10-H type	OH	OHCH ₃	pCoum	H	436.07 425.88	SMD Water SMD MeOH	494	FA/H ₂ O/ACN[392]	-
133	Pt-3-(6-(E)-coum)-Glc-4- vinylphenol adduct	OH	OHCH ₃	pCoum	Phenol	426.12 444.61	SMD Water SMD MeOH	504	TFA/H ₂ O/ACN[545]	-
139	Pt-3-(6-(E)-coum)-Glc-4- vinylcatechol adduct	OH	OHCH ₃	pCoum	Catechol	435.07 453.81	SMD Water SMD MeOH	504 511	FA/H ₂ O/ACN[392] FA/H ₂ O/ACN[392]	-
50	Mv-3-Glc 10-carboxy type	OCH ₃	OHCH ₃	H	COOH	451.98	SMD Water	-	-	-
56	Mv-3-Glc 10-H type	OCH ₃	OHCH ₃	H	H	439.31 443.21	SMD MeOH SMD Water	510 507 509 511	TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[369] FA/H ₂ O/ACN[392]	-
62	Mv-3-Glc 4- vinylphenol adduct	OCH ₃	OHCH ₃	H	Phenol	436.93 434.82	SMD MeOH SMD Water	490 490	TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[392]	-
						453.28 454.52	SMD MeOH SMD Water	504 503 503 504	TFA/H ₂ O/ACN[545] TFA/H ₂ O/ACN[546] FA/H ₂ O/ACN[369] FA/H ₂ O/ACN[392]	-

68	Mv-3-Glc 4- vinylcatechol adduct	OCH ₃ OH	OCH ₃	H	Catechol	461.37 460.95	SMD MeOH SMD Water	509 471	PBE0/SV(P) (Gas)[376] PBE0/SV(P) (C-PCM, Water)[376]	510 512 511 514	TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[369] FA/H ₂ O/ACN[392] FA/H ₂ O/ACN[392]
74	Mv-3-acetyl-Glc 10-carboxy type	OCH ₃ OH	OCH ₃	Ac	COOH	442.64 444.20	SMD MeOH SMD Water				
80	Mv-3-acetyl-Glc 10-H type	OCH ₃ OH	OCH ₃	Ac	H	436.29 434.95	SMD MeOH SMD Water			494 494	TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[392]
86	Mv-3-acetyl-Glc 4- vinylphenol adduct	OCH ₃ OH	OCH ₃	Ac	Phenol	445.39 443.84	SMD MeOH SMD Water			505 506	TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[392]
92	Mv-3-acetyl-Glc 4- vinylcatechol adduct	OCH ₃ OH	OCH ₃	Ac	Catechol	457.17 456.78	SMD MeOH SMD Water			513 512	TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[392]
98	Mv-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	OH	Caff	COOH	435.62 443.57	SMD MeOH SMD Water			514	FA/H ₂ O/ACN[392]
104	Mv-(6-(E)-caffeoyl)-Glc 10-H type	OH	OH	Caff	H	433.29 436.28	SMD MeOH SMD Water			498	FA/H ₂ O/ACN[392]
110	Mv-(6-(E)-caffeoyl)-Glc 4- vinylphenol adduct	OH	OH	Caff	Phenol	438.05 437.92	SMD MeOH SMD Water			506	FA/H ₂ O/ACN[392]
116	Mv-(6-(E)-caffeoyl)-Glc 4- vinylcatechol adduct	OH	OH	Caff	Catechol	458.41 453.91	SMD MeOH SMD Water			512	FA/H ₂ O/ACN[392]
122	Mv-3-(6-(E)-c-oum)-Glc 10-carboxy type	OCH ₃ OH	OCH ₃	pC-oum	COOH	439.45 436.07	SMD MeOH SMD Water			514 516 516	TFA/H ₂ O/ACN[545] FA/H ₂ O/ACN[369] FA/H ₂ O/ACN[392]
128	Mv-3-(6-(E)-c-oum)-Glc 10-H type	OCH ₃ OH	OCH ₃	pC-oum	H	432.92 426.12	SMD MeOH SMD Water			497	FA/H ₂ O/ACN[392]

134	Mv-3-(6-(E)-coum)-Glc 4-vinylphenol adduct	OCH ₃ OH	pCoum	Phenol	440.22	SMD MeOH			505	TFA/H ₂ O/ACN[545]
					435.07	SMD Water			506	TFA/H ₂ O/ACN[546]
									505	FA/H ₂ O/ACN[392]
140	Mv-3-(6-(E)-coum)-Glc 4-vinylcatechol adduct	OCH ₃ OH	pCoum	Catechol	458.12	SMD MeOH			511	TFA/H ₂ O/ACN[545]
					451.98	SMD Water			512	TFA/H ₂ O/ACN[546]
									512	FA/H ₂ O/ACN[392]

Ara: arabinoside, Gal: galactoside, Gen: gentiobioside, LA: lactic acid, Malo: malonyl, Maly: malyl, Rhagl: rhamnoglucoside and Rut: rutinoside (chemical representations are displayed in Figures D.40 to D.42)

Calculations of the MAE for each anthocyanin subclass and functional

Table D.29: An overview of the anthocyanidins involved for calculating the MAE of the different functionals (6-311++G(d,p) basis set and SMD as solvation model). Δ indicates the difference between the calculated value for that particular functional and the experimental literature value.

Anthocyanidins		B3LYP		PBE0		CAM-B3LYP		Experimental		B3LYP		PBE0		CAM-B3LYP	
	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (nm)	λ_{max} (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)
SMD Water															
Apigeninidin (1)	472.33	2.625	460	2.6953	434.54	2.8533	468.00	356	2.6492	4.33	-0.0242	-8	0.0461	-33.46	0.2041
Cyanidin (4)	530.76	2.336	517.21	2.3972	485.83	2.552	516.00	356	2.4028	14.76	-0.0668	1.21	-0.0056	-30.17	0.1492
Luteolinidin (2)	490.52	2.5276	476.28	2.6032	441.97	2.8052	482.00	356	2.5723	8.52	-0.0447	-5.72	0.0309	-40.03	0.2329
Pelargonidin (3)	519.77	2.3854	507.4	2.4435	481.73	2.5737	506.00	356	2.4503	13.77	-0.0649	1.4	-0.0068	-24.27	0.1234
Peonidin (5)	535.73	2.3143	521.65	2.3768	489.04	2.5352	516.00	356	2.4028	19.73	-0.0885	5.65	-0.026	-26.96	0.1324
MAE =										12.22	0.0578	4.4	0.0231	30.98	0.1684
Anthocyanidins															
	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (nm)	λ_{max} (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)
SMD MeOH															
Apigeninidin (1)	471.29	2.6308	459.03	2.701	433.83	2.8579	480.00	547	2.583	-8.71	0.0478	-20.97	0.118	-46.17	0.2749
Cyanidin (4)	530.33	2.3379	516.78	2.3991	485.68	2.5528	538.00	547	2.3045	-7.67	0.0334	-21.22	0.0946	-52.32	0.2483
Delphinidin (6)	538.96	2.3004	525.28	2.3604	491.75	2.5213	548.00	547	2.2625	-9.04	0.0379	-22.72	0.0979	-56.25	0.2588
Luteolinidin (2)	491.24	2.5239	477.21	2.5981	443.8	2.7937	498.00	547	2.4896	-6.76	0.0343	-20.79	0.1085	-54.2	0.3041
Malvidin (8)	552.92	2.2423	538.45	2.3026	503.03	2.4648	546.00	547	2.2708	6.92	-0.0285	-7.55	0.0318	-42.97	0.194
Pelargonidin (3)	519.03	2.3888	506.74	2.4467	481.59	2.5745	523.00	547	2.3706	-3.97	0.0182	-16.26	0.0761	-41.41	0.2039
Peonidin (5)	535.36	2.3159	521.4	2.3779	489.42	2.5333	536.00	547	2.3131	-0.64	0.0028	-14.6	0.0648	-46.58	0.2202
Petunidin (7)	543.15	2.2827	528.75	2.3449	493.28	2.5135	547.00	547	2.2666	-3.85	0.0161	-18.25	0.0783	-53.72	0.2469
MAE =										5.94	0.0274	17.8	0.0837	49.2	0.2439

Table D.30: An overview of the anthocyanins involved for calculating the MAE of the different functionals (6-311++G(d,p) basis set and SMD as solvation model). Δ indicates the difference between the calculated value for that particular functional and the experimental literature value.

Anthocyanins	B3LYP		PBE0		CAM-B3LYP		Experimental		B3LYP		PBE0		CAM-B3LYP	
	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)
Anthocyanins														
SMD Water														
Cyanidin 3-glucoside (10)	501.04	2.4745	484.7	2.558	442.71	2.8006	512.00[356]	2.4216	-10.96	0.0529	-27.3	0.1364	-69.29	0.379
Delphinidin 3-glucoside (12)	504.12	2.4594	488	2.5407	443.45	2.7959	524.00[545]	2.3661	-19.88	0.0933	-36	0.1746	-80.55	0.4298
Malvidin 3-glucoside (14)	522.97	2.3708	504.5	2.4576	453.15	2.736	527.00[545]	2.3526	-4.03	0.0182	-22.5	0.105	-73.85	0.3834
Pelargonidin 3-glucoside (9)	480.73	2.5791	467.86	2.6501	437.8	2.832	502.00[544]	2.4698	-21.27	0.1093	-34.14	0.1803	-64.2	0.3622
Peonidin 3-glucoside (11)	509.55	2.4332	492.93	2.5152	450.37	2.753	517.00[545]	2.3981	-7.45	0.0351	-24.07	0.1171	-66.63	0.3549
Petunidin 3-glucoside (13)	529.36	2.3422	514.36	2.4104	475.1	2.6097	525.00[545]	2.3616	4.36	-0.0194	-10.64	0.0488	-49.9	0.2481
MAE =									11.33	0.0547	25.78	0.127	67.4	0.3596
Anthocyanins														
SMD MeOH														
Cyanidin 3-glucoside (10)	501.37	2.4729	485.1	2.5558	443.36	2.7965	529.00[547]	2.3437	-27.63	0.1292	-43.9	0.2121	-85.64	0.4528
Delphinidin 3-glucoside (12)	505.48	2.4528	489.62	2.5322	445.88	2.7807	541.00[547]	2.2918	-35.52	0.161	-34.38	0.2404	-95.12	0.4889
Malvidin 3-glucoside (14)	525.91	2.3575	508.62	2.4377	460.93	2.6898	538.00[547]	2.3045	-12.09	0.053	-18.38	0.1332	-77.07	0.3853
Pelargonidin 3-glucoside (9)	480.41	2.5808	467.66	2.6512	438.18	2.8295	510.00[547]	2.4311	-29.59	0.1497	-34.34	0.2201	-71.82	0.3984
Peonidin 3-glucoside (11)	509.42	2.4338	493.08	2.5145	451.39	2.7467	526.00[547]	2.3571	-16.58	0.0767	-23.92	0.1574	-74.61	0.3896
Petunidin 3-glucoside (13)	512.84	2.4176	496.79	2.4957	452.97	2.7371	539.00[547]	2.3003	-26.16	0.1173	-28.21	0.1954	-86.03	0.4368
MAE =									24.6	0.1145	30.52	0.1931	81.72	0.4253

(Z)-coumaroyl acylated ($S_0 \rightarrow S_1$)														
	B3LYP		PBE0		CAM-B3LYP		Experimental		B3LYP		PBE0		CAM-B3LYP	
	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)
SMD Water														
(Z)-coumaroyl acylated Cy-3-Glc (34)	519.19	2.388	493.3	2.5133	451.85	2.7439	533.00[545]	2.3262	-13.81	0.0618	-39.7	0.1871	-81.15	0.4177
(Z)-coumaroyl acylated Dp-3-Glc (36)	526.99	2.3527	495.21	2.5037	446.37	2.7776	534.00[545]	2.3218	-7.01	0.0309	-38.79	0.1819	-87.63	0.4558
(Z)-coumaroyl acylated Mv-3-Glc (38)	536.79	2.3097	507.74	2.4419	451.23	2.7477	535.00[546]	2.3175	1.79	-0.0078	-27.26	0.1244	-83.77	0.4302
(Z)-coumaroyl acylated Pr-3-Glc (35)	529.88	2.3398	498.71	2.4861	448.39	2.7651	535.00[545]	2.3175	-5.12	0.0223	-36.29	0.1686	-86.61	0.4476
(Z)-coumaroyl acylated Pt-3-Glc (37)	536.19	2.3123	503.74	2.4613	444.7	2.788	536.00[545]	2.3131	0.19	-0.0008	-32.26	0.1482	-91.3	0.4749
								MAE =	5.58	0.0247	34.86	0.1621	86.09	0.4453
(E)-coumaroyl acylated ($S_0 \rightarrow S_1$)														
	B3LYP		PBE0		CAM-B3LYP		Experimental		B3LYP		PBE0		CAM-B3LYP	
	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)
SMD Water														
(E)-coumaroyl acylated Cy-3-Glc (40)	520.43	2.3823	492.88	2.5155	436.38	2.8412	524.00[545]	2.3661	-3.57	0.0162	-31.12	0.1494	-87.62	0.4751
(E)-coumaroyl acylated Dp-3-Glc (42)	524.36	2.3645	497.1	2.4941	437.59	2.8334	531.00[545]	2.3349	-6.64	0.0296	-33.9	0.1592	-93.41	0.4985
(E)-coumaroyl acylated Mv-3-Glc (44)	526.88	2.3532	505.44	2.453	449.23	2.76	532.00[545]	2.3305	-5.12	0.0227	-26.56	0.1225	-82.77	0.4295
(E)-coumaroyl acylated Pr-3-Glc (41)	523.97	2.3662	499.56	2.4819	444.4	2.7899	526.00[545]	2.3571	-2.03	0.0091	-26.44	0.1248	-81.6	0.4328
(E)-coumaroyl acylated Pt-3-Glc (43)	519.11	2.3884	496.09	2.4992	442.41	2.8025	532.00[545]	2.3305	-12.89	0.0579	-35.91	0.1687	-89.59	0.472
								MAE =	6.05	0.0271	30.79	0.1449	87.00	0.4616

Table D.32: An overview of the acylated anthocyanins ($S_0 \rightarrow S_2$) involved for calculating the MAE of the different functionals (6-311++G(d,p) basis set and SMD as solvation model). Δ indicates the difference between the calculated value for that particular functional and the experimental literature value.

(E)-caffeoyl acylated ($S_0 \rightarrow S_2$)	B3LYP		PBE0		Experimental		B3LYP		PBE0	
	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (eV)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (eV)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)
SMD Water										
(E)-caffeoyl acylated Dp-3-Glc (30)	503.23	2.4638	486.08	2.5507	532.00[545]	2.3305	-28.77	0.1333	-45.92	0.2202
(E)-caffeoyl acylated Mv-3-Glc (32)	521.27	2.3785	493.19	2.5139	534.00[545]	2.3218	-12.73	0.0567	-40.81	0.1921
(E)-caffeoyl acylated Pn-3-Glc (29)	509.9	2.4316	491.07	2.5248	525.00[545]	2.3616	-15.1	0.07	-33.93	0.1632
(E)-caffeoyl acylated Pt-3-Glc (31)	509.41	2.4339	490.3	2.5287	531.00[545]	2.3349	-21.59	0.099	-40.7	0.1938
					MAE =		19.55	0.0897	40.34	0.1923
(Z)-coumaroyl acylated ($S_0 \rightarrow S_2$)	B3LYP		PBE0		Experimental		B3LYP		PBE0	
	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (eV)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (eV)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)
SMD Water										
(Z)-coumaroyl acylated Cy-3-Glc (34)	504.86	2.4558	482.33	2.5705	533.00[545]	2.3262	-28.14	0.1296	-50.67	0.2443
(Z)-coumaroyl acylated Dp-3-Glc (36)	505.68	2.4518	488.86	2.5362	534.00[545]	2.3218	-28.32	0.13	-45.14	0.2144
(Z)-coumaroyl acylated Mv-3-Glc (38)	516.67	2.3997	495.5	2.5022	535.00[546]	2.3175	-18.33	0.0822	-39.5	0.1847
(Z)-coumaroyl acylated Pn-3-Glc (35)	508.12	2.44	489.96	2.5305	535.00[545]	2.3175	-26.88	0.1225	-45.04	0.213
(Z)-coumaroyl acylated Pt-3-Glc (37)	507	2.4454	489.42	2.5333	536.00[545]	2.3131	-29	0.1323	-46.58	0.2202
					MAE =		26.13	0.1193	45.39	0.2153
(E)-coumaroyl acylated ($S_0 \rightarrow S_2$)	B3LYP		PBE0		Experimental		B3LYP		PBE0	
	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (eV)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (eV)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)
SMD Water										
(E)-coumaroyl acylated Cy-3-Glc (40)	480.74	2.579	457.33	2.711	524.00[545]	2.3661	-43.26	0.2129	-66.67	0.3449
(E)-coumaroyl acylated Dp-3-Glc (42)	483.77	2.5629	459.6	2.6976	531.00[545]	2.3349	-47.23	0.228	-71.4	0.3627
(E)-coumaroyl acylated Mv-3-Glc (44)	492.23	2.5188	461.56	2.6862	532.00[545]	2.3305	-39.77	0.1883	-70.44	0.3557
(E)-coumaroyl acylated Pn-3-Glc (41)	484.51	2.559	457.6	2.7095	526.00[545]	2.3571	-41.49	0.2019	-68.4	0.3524
(E)-coumaroyl acylated Pt-3-Glc (43)	490.09	2.5298	461.57	2.6861	532.00[545]	2.3305	-41.91	0.1993	-70.43	0.3556
					MAE =		42.73	0.2061	69.47	0.3542

Table D.33: An overview of the pyranoanthocyanins involved for calculating the MAE of the different functionals (6-311++G(d,p) basis set and SMD as solvation model). Δ indicates the difference between the calculated value for that particular functional and the experimental literature value.

10-carboxy types		B3LYP		PBE0		CAM-B3LYP		Experimental		B3LYP		PBE0		CAM-B3LYP	
SMD Water		λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)
10-carboxy Cy-3-Glc	(46)	504.31	2.4585	486.38	2.5491	436.76	2.8387	504.00[392]	2.46	0.31	-0.0015	-17.62	0.0891	-67.24	0.3787
10-carboxy Dp-3-Glc	(54)	507.76	2.4418	490.25	2.529	439.08	2.8237	507.00[545]	2.4454	0.76	-0.0036	-16.75	0.0836	-67.92	0.3783
10-carboxy Mv-3-Glc	(50)	527.07	2.3523	505.31	2.4536	443.21	2.7974	510.00[545]	2.4311	17.07	-0.0788	-4.69	0.0225	-66.79	0.3663
10-carboxy Pn-3-Glc	(47)	510.37	2.4293	490.26	2.5289	435.85	2.8446	503.00[545]	2.4649	7.37	-0.0356	-12.74	0.064	-67.15	0.3797
10-carboxy Pt-3-Glc	(49)	511.13	2.4257	491.37	2.5232	435.64	2.846	508.00[545]	2.4406	3.13	-0.0149	-16.63	0.0826	-72.36	0.4054
								MAE =		5.73		0.0269		68.29	
								Experimental		B3LYP		PBE0		CAM-B3LYP	
10-H types		B3LYP		PBE0		CAM-B3LYP		Experimental		B3LYP		PBE0		CAM-B3LYP	
SMD Water		λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)
10-H Dp-3-Glc	(54)	493.2	2.5139	476.97	2.5994	430.25	2.8816	487.00[392]	2.5459	6.2	-0.032	-10.03	0.0535	-56.75	0.3357
10-H Mv-3-Glc	(56)	512.28	2.4202	492.44	2.5178	434.82	2.8514	490.00[545]	2.5303	22.28	-0.1101	2.44	-0.0125	-55.18	0.3211
10-H Pn-3-Glc	(53)	495.65	2.5014	476.95	2.5995	427.11	2.9029	487.00[392]	2.5459	8.65	-0.0445	-10.05	0.0536	-59.89	0.357
10-H Pt-3-Glc	(55)	498.5	2.4871	480.09	2.5825	427.29	2.9016	492.00[545]	2.52	6.5	-0.0329	-11.91	0.0625	-64.71	0.3816
								MAE =		10.91		0.0549		59.13	
								Experimental		B3LYP		PBE0		CAM-B3LYP	
Vinylphenol adduct		B3LYP		PBE0		CAM-B3LYP		Experimental		B3LYP		PBE0		CAM-B3LYP	
SMD Water		λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)
Vinylphenol Cy-3-Glc	(58)	506.97	2.4456	491.98	2.5201	449.63	2.7575	500.00[392]	2.4797	6.97	-0.0341	-8.02	0.0404	-50.37	0.2778
Vinylphenol Dp-3-Glc	(60)	511.25	2.4251	495.85	2.5004	451.47	2.7462	503.00[545]	2.4649	8.25	-0.0398	-7.15	0.0355	-51.53	0.2813
Vinylphenol Mv-3-Glc	(62)	524.98	2.3617	506.84	2.4462	454.52	2.7278	504.00[545]	2.46	20.98	-0.0983	2.84	-0.0138	-49.48	0.2678
Vinylphenol Pn-3-Glc	(59)	512.93	2.4172	496.6	2.4967	451.28	2.7474	500.00[545]	2.4797	12.93	-0.0625	-3.4	0.017	-48.72	0.2677
Vinylphenol Pt-3-Glc	(61)	517.5	2.3958	501.14	2.474	453.44	2.7343	504.00[545]	2.46	13.5	-0.0642	-2.86	0.014	-50.56	0.2446
								MAE =		12.53		0.0598		50.13	
								Experimental		B3LYP		PBE0		CAM-B3LYP	
Vinylcatechol adduct		B3LYP		PBE0		CAM-B3LYP		Experimental		B3LYP		PBE0		CAM-B3LYP	
SMD Water		λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)
Vinylcatechol Cy-3-Glc	(64)	512.81	2.4177	496.97	2.4948	450.18	2.7541	508.00[392]	2.4406	4.81	-0.0229	-11.03	0.0542	-57.82	0.3135
Vinylcatechol Dp-3-Glc	(66)	520.61	2.3815	504	2.46	453.59	2.7334	509.00[545]	2.4358	11.61	-0.0543	-5	0.0242	-55.41	0.2976
Vinylcatechol Mv-3-Glc	(68)	534.83	2.3182	516.71	2.3995	460.95	2.6898	510.00[545]	2.4311	24.83	-0.1129	6.71	-0.0316	-49.05	0.2587
Vinylcatechol Pn-3-Glc	(65)	523.22	2.3696	506.32	2.4487	456.23	2.7176	506.00[545]	2.4503	17.22	-0.0807	0.32	-0.0016	-49.77	0.2673
Vinylcatechol Pt-3-Glc	(67)	526.18	2.3563	509.08	2.4354	456.83	2.714	510.00[545]	2.4311	16.18	-0.0748	-0.92	0.0043	-53.17	0.2829
								MAE =		14.93		0.0691		53.04	
								Experimental		B3LYP		PBE0		CAM-B3LYP	

Table D.34: An overview of the acetyl acylated pyrananthocyanins involved for calculating the MAE of the different functionals (6-311++G(d,p) basis set and SMD as solvation model). Δ indicates the difference between the calculated value for that particular functional and the experimental literature value.

Acetyl acylated pyrananthocyanins	B3LYP		PBE0		CAM-B3LYP		Experimental		B3LYP		PBE0		CAM-B3LYP	
	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)
SMD Water														
Acetyl acylated 10-carboxy Dp-3-Glc (72)	506.08	2.4499	488.95	2.5357	438.06	2.8303	511.00[392]	2.4263	-4.92	0.0236	-22.05	0.1094	-72.94	0.404
Acetyl acylated 10-carboxy Mv-3-Glc (74)	527.45	2.3506	506.57	2.4475	444.2	2.7912	514.00[392]	2.4121	13.45	-0.0615	-7.43	0.0354	-69.8	0.3791
Acetyl acylated 10-carboxy Pn-3-Glc (71)	515.16	2.4067	496.58	2.4967	443.75	2.794	507.00[392]	2.4454	8.16	-0.0387	-10.42	0.0513	-63.25	0.3486
Acetyl acylated 10-carboxy Pt-3-Glc (73)	514.34	2.4105	495.19	2.5038	438.53	2.8273	512.00[392]	2.4216	2.34	-0.0111	-16.81	0.0822	-73.47	0.4057
Acetyl acylated 10-H Dp-3-Glc (78)	491.74	2.5213	475.63	2.6068	428.23	2.8953	488.00[392]	2.5407	3.74	-0.0194	-12.37	0.0661	-59.77	0.3546
Acetyl acylated 10-H Mv-3-Glc (80)	510.86	2.427	491.68	2.5217	434.95	2.8505	494.00[392]	2.5098	16.86	-0.0828	-2.32	0.0119	-59.05	0.3407
Acetyl acylated 10-H Pn-3-Glc (77)	499.33	2.483	482.05	2.572	433.86	2.8577	486.00[392]	2.5511	13.33	-0.0681	-3.95	0.0209	-52.14	0.3066
Acetyl acylated 10-H Pt-3-Glc (79)	497.41	2.4926	479.46	2.5859	427.02	2.9035	494.00[392]	2.5098	3.41	-0.0172	-14.54	0.0761	-66.98	0.3937
Acetyl acylated vinylphenol Dp-3-Glc (84)	502.02	2.4697	486.61	2.5479	441.7	2.807	505.00[392]	2.4551	-2.98	0.0146	-18.39	0.0928	-63.3	0.3519
Acetyl acylated vinylphenol Mv-3-Glc (86)	511.91	2.422	494.06	2.5095	443.84	2.7935	506.00[392]	2.4503	5.91	-0.0283	-11.94	0.0592	-62.16	0.3432
Acetyl acylated vinylphenol Pn-3-Glc (83)	504.79	2.4561	489.08	2.5351	446.25	2.7784	501.00[392]	2.4747	3.79	-0.0186	-11.92	0.0604	-54.75	0.3037
Acetyl acylated vinylphenol Pt-3-Glc (85)	502.62	2.4668	486.64	2.5478	441.26	2.8098	505.00[392]	2.4551	-2.38	0.0117	-18.36	0.0927	-63.74	0.3547
Acetyl acylated catechol Dp-3-Glc (90)	518.1	2.393	501.44	2.4726	450.78	2.7504	512.00[392]	2.4216	6.1	-0.0286	-10.56	-0.051	-61.22	0.3288
Acetyl acylated catechol Mv-3-Glc (92)	531.16	2.3342	512.87	2.4174	456.78	2.7143	512.00[392]	2.4216	19.16	-0.0874	0.87	0.0042	-55.22	0.2927
Acetyl acylated catechol Pn-3-Glc (89)	520.81	2.3806	503.62	2.4619	452.82	2.7381	507.00[392]	2.4454	13.81	-0.0648	-3.38	-0.0165	-54.18	0.2927
Acetyl acylated catechol Pt-3-Glc (91)	523.99	2.3661	506.89	2.446	454.51	2.7279	511.00[392]	2.4263	12.99	-0.0602	-4.11	-0.0197	-56.49	0.3016
								MAE =	8.33	0.0398	10.59	0.0531	61.78	0.3439

Table D.35: An overview of the caffeoyl acylated pyrananthocyanins involved for calculating the MAE of the different functionals (6-311++G(d,p) basis set and SMD as solvation model). Δ indicates the difference between the calculated value for that particular functional and the experimental literature value.

Caffeoyl acylated pyrananthocyanins	B3LYP		PBE0		CAM-B3LYP		Experimental		B3LYP		PBE0		CAM-B3LYP	
	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)
SMD Water														
Caffeoyl acylated 10-carboxy Mv-3-Glc (98)	515.04	2.4073	518.29	2.3922	443.57	2.7951	514.00[392]	2.4121	1.04	-0.0048	4.29	0.1281	-70.43	0.383
Caffeoyl acylated 10-carboxy Pn-3-Glc (95)	506.04	2.4501	500.91	2.4752	430.7	2.8787	508.00[392]	2.4406	-1.96	0.0095	-7.09	0.1148	-77.3	0.4381
Caffeoyl acylated 10-H Mv-3-Glc (104)	505.05	2.4549	493.55	2.5121	436.28	2.8418	498.00[392]	2.4896	7.05	-0.0347	-4.45	0.1182	-61.72	0.3522
Caffeoyl acylated vinylphenol Mv-3-Glc (110)	509.33	2.4342	490.47	2.5279	437.92	2.8312	506.00[392]	2.4503	3.33	0.0528	-15.53	0.0776	-68.08	0.3809
Caffeoyl acylated vinylphenol Pn-3-Glc (107)	497.84	2.4904	481.34	2.5758	435.65	2.846	502.00[392]	2.4698	-4.16	0.0206	-20.66	0.106	-66.35	0.3762
Caffeoyl acylated vinylcatechol Mv-3-Glc (116)	527.94	2.3484	509.55	2.4332	453.91	2.7314	512.00[392]	2.4216	15.94	-0.0732	-2.45	0.0116	-58.09	0.3098
Caffeoyl acylated vinylcatechol Pn-3-Glc (113)	516.99	2.3982	499.85	2.4804	449.69	2.7571	508.00[392]	2.4406	8.99	-0.0424	-8.15	0.0398	-58.31	0.3165
								MAE =	6.07	0.034	8.95	0.0851	65.75	0.3652

Table D.36: An overview of the coumaroyl acylated pyrananthocyanins involved for calculating the MAE of the different functionals (6-311++G(d,p) basis set and SMD as solvation model). Δ indicates the difference between the calculated value for that particular functional and the experimental literature value.

Coumaroyl acylated pyrananthocyanins		B3LYP		PBE0		CAM-B3LYP		Experimental		B3LYP		PBE0		CAM-B3LYP	
SMD Water		λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	λ_{max} (nm)	λ_{max} (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)	Δ (nm)	Δ (eV)
Coumaroyl acylated 10-carboxy Dp-3-Glc (120)		517.35	2.3965	490.3	2.5287	436.51	2.8404	512.00[392]	2.4216	5.35	-0.0251	-21.7	0.1071	-75.49	0.4188
Coumaroyl acylated 10-carboxy Mv-3-Glc (122)		532.73	2.3273	508.8	2.4368	442.21	2.8037	516.00[392]	2.4028	16.73	-0.0755	-7.2	0.034	-73.79	0.4009
Coumaroyl acylated 10-carboxy Pt-3-Glc (119)		520.41	2.3824	494.69	2.5063	435.61	2.8462	509.00[392]	2.4358	11.41	-0.0534	-14.31	0.0705	-73.39	0.4104
Coumaroyl acylated 10-H Mv-3-Glc (128)		516.26	2.4016	494.14	2.5091	432.94	2.8638	497.00[392]	2.4947	19.26	-0.0931	-2.86	0.0144	-64.06	0.3691
Coumaroyl acylated 10-H Pt-3-Glc (125)		502.09	2.4694	480.59	2.5798	428.54	2.8932	485.00[392]	2.5564	17.09	-0.087	-4.41	0.0234	-56.46	0.3368
Coumaroyl acylated 10-H Pt-3-Glc (127)		506.96	2.4456	483.78	2.5628	426.12	2.9096	494.00[392]	2.5098	12.96	-0.0642	-10.22	0.053	-67.88	0.3998
Coumaroyl acylated vinylphenol Mv-3-Glc (134)		509.04	2.4356	490.35	2.5285	438.26	2.829	505.00[392]	2.4551	4.04	-0.0195	-14.65	0.0734	-66.74	0.3739
Coumaroyl acylated vinylphenol Pt-3-Glc (131)		496.45	2.4974	480.22	2.5818	435.46	2.8472	502.00[392]	2.4698	-5.55	0.0276	-21.78	0.112	-66.54	0.3774
Coumaroyl acylated vinylphenol Pt-3-Glc (133)		497.68	2.4912	481.05	2.5774	435.07	2.8497	504.00[392]	2.446	-6.32	0.0312	-22.95	0.1174	-68.93	0.3897
Coumaroyl acylated vinylcatechol Cy-3-Glc (136)		510.59	2.4283	494.09	2.5094	445.88	2.7806	508.00[392]	2.4406	2.59	-0.0123	-13.91	0.0688	-62.12	0.34
Coumaroyl acylated vinylcatechol Dp-3-Glc (138)		515.67	2.4043	499.06	2.4844	448.91	2.7619	510.00[392]	2.4311	5.67	-0.0268	-10.94	0.0533	-61.09	0.3308
Coumaroyl acylated vinylcatechol Mv-3-Glc (140)		527.97	2.3483	509.59	2.433	453.96	2.7311	512.00[392]	2.4216	15.97	-0.0733	-2.41	0.0114	-58.04	0.3095
Coumaroyl acylated vinylcatechol Pt-3-Glc (137)		516.23	2.4017	499	2.4847	448.59	2.7639	508.00[392]	2.4406	8.23	-0.0389	-9	0.0441	-59.41	0.3233
Coumaroyl acylated vinylcatechol Pt-3-Glc (139)		520.84	2.3804	503.77	2.4611	451.98	2.7431	511.00[392]	2.4263	9.84	-0.0459	-7.23	0.0348	-59.02	0.3168
MAE =										10.07	0.0481	11.68	0.0584	65.21	0.3641

Molecular Absorption Coefficients of the Studied Anthocyanin-Based Compounds

Table D.37: The molecular absorption coefficients of the studied anthocyanin-based compounds (B3LYP/6 311++G(d,p) with SMD solvation model and methanol (MeOH) and water as solvents.

Label	Anthocyanins Name	R ¹	R ²	R ³	R ⁴	SMD solvent	Molecular absorption coefficient (ε)
1	Apigeninidin (Ap)	H	OH	H	H	MeOH	41922
2	Luteolinidin (Lt)	OH	OH	H	H	Water	42367
						MeOH	40782
3	Pelargonidin (Pg)	H	OH	H	OH	Water	40683
						MeOH	36511
9	Pg-3-glucoside	H	OH	H	OGlc	Water	36807
15	Pg-acetylglucoside	H	OH	H	OGlc-Ac	MeOH	37018
						Water	37204
21	Pg-3-(6-(Z)-caffeoyl)-glucoside	H	OH	H	OGlc-Caff	MeOH	36707
27	Pg-3-(6-(E)-caffeoyl)-glucoside	H	OH	H	OGlc-Caff	Water	35161
33	Pg-3-(6-(Z)-p-coumaroyl)-glucoside	H	OH	H	OGlc-Coum	MeOH	34761
39	Pg-3-(6-(E)-p-coumaroyl)-glucoside	H	OH	H	OGlc-Coum	Water	34693
4	Cyanidin (Cy)	OH	OH	H	OH	MeOH	35095
						Water	35424
10	Cy-3-glucoside	OH	OH	H	OGlc	MeOH	35098
10	Cy-3-glucoside	OH	OH	H	OGlc	Water	35705
						MeOH	33914
10	Cy-3-glucoside	OH	OH	H	OGlc	Water	32689
						MeOH	37074
10	Cy-3-glucoside	OH	OH	H	OGlc	Water	37421
						MeOH	32974
10	Cy-3-glucoside	OH	OH	H	OGlc	Water	33294
						MeOH	33294

16	Cy-3-acetyl-l-glucoside	OH	OH	H	OGlc-Ac	MeOH	33193
						Water	33303
22	Cy-3-(6-(Z)-caffeoyl)-glucoside	OH	OH	H	OGlc-Caff	MeOH	30705
						Water	31530
28	Cy-3-(6-(E)-caffeoyl)-glucoside	OH	OH	H	OGlc-Caff	MeOH	31529
						Water	32037
34	Cy-3-(6-(Z)-p-coumaroyl)-glucoside	OH	OH	H	OGlc-Coum	MeOH	33570
						Water	34332
40	Cy-3-(6-(E)-p-coumaroyl)-glucoside	OH	OH	H	OGlc-Coum	MeOH	29716
						Water	29176
5	Peonidin (Pn)	OCH ₃	OH	H	OH	MeOH	37567
						Water	37773
11	Pn-3-glucoside	OCH ₃	OH	H	OGlc	MeOH	34595
						Water	34620
17	Pn-3-acetyl-l-glucoside	OCH ₃	OH	H	OGlc-Ac	MeOH	32774
						Water	33425
23	Pn-3-(6-(Z)-caffeoyl)-glucoside	OCH ₃	OH	H	OGlc-Caff	MeOH	30120
						Water	30669
29	Pn-3-(6-(E)-caffeoyl)-glucoside	OCH ₃	OH	H	OGlc-Caff	MeOH	30467
						Water	29821
35	Pn-3-(6-(Z)-p-coumaroyl)-glucoside	OCH ₃	OH	H	OGlc-pCoum	MeOH	30468
						Water	30885
41	Pn-3-(6-(E)-p-coumaroyl)-glucoside	OCH ₃	OH	H	OGlc-pCoum	MeOH	28934
						Water	28006
6	Delphinidin (Dp)	OH	OH	OH	OH	MeOH	37770
						Water	37970
12	Dp-3-glucoside	OH	OH	OH	OGlc	MeOH	35412
						Water	35176

18	Dp-3-acetyl-l-glucoside	OH	OH	OH	OH	OGlc-Ac	MeOH	33358
							Water	34004
24	Dp-3-(6-(Z)-caffeoyl)-glucoside	OH	OH	OH	OH	OGlc-Caff	MeOH	33934
							Water	34259
30	Dp-3-(6-(E)-caffeoyl)-glucoside	OH	OH	OH	OH	OGlc-Caff	MeOH	33991
							Water	31833
36	Dp-3-(6-(Z)-p-coumaroyl)-glucoside	OH	OH	OH	OH	OGlc-pCoup	MeOH	33628
							Water	34171
42	Dp-3-(6-(E)-p-coumaroyl)-glucoside	OH	OH	OH	OH	OGlc-pCoup	MeOH	30966
							Water	29944
7	Petunidin (Pt)	OH	OH	OCH ₃		OH	MeOH	37801
							Water	38026
13	Pt-3-glucoside	OH	OH	OCH ₃		OGlc	MeOH	36439
							Water	38026
19	Pt-3-acetyl-l-glucoside	OH	OH	OCH ₃		OGlc-Ac	MeOH	33473
							Water	33968
25	Pt-3-(6-(Z)-caffeoyl)-glucoside	OH	OH	OCH ₃		OGlc-Caff	MeOH	32644
							Water	31830
31	Pt-3-(6-(E)-caffeoyl)-glucoside	OH	OH	OCH ₃		OGlc-Caff	MeOH	31982
							Water	31940
37	Pt-3-(6-(Z)-p-coumaroyl)-glucoside	OH	OH	OCH ₃		OGlc-pCoup	MeOH	32607
							Water	32800
43	Pt-3-(6-(E)-p-coumaroyl)-glucoside	OH	OH	OCH ₃		OGlc-pCoup	MeOH	31601
							Water	31919
8	Malvidin (Mv)	OCH ₃	OH	OCH ₃		OH	MeOH	39658
							Water	39841
14	Mv-3-glucoside	OCH ₃	OH	OCH ₃		OGlc	MeOH	36187
							Water	34428

20	Mv-3-acetyl-glucoside	OCH ₃	OH	OCH ₃	OGlc-Ac	MeOH	34777
						Water	34951
26	Mv-3-(6-(Z)-caffeoyl)-glucoside	OCH ₃	OH	OCH ₃	OGlc-Caff	MeOH	32769
						Water	32495
32	Mv-3-(6-(E)-caffeoyl)-glucoside	OCH ₃	OH	OCH ₃	OGlc-Caff	MeOH	32850
						Water	32874
38	Mv-3-(6-p-(Z)-coumaroyl)-glucoside	OCH ₃	OH	OCH ₃	OGlc-pCoup	MeOH	32992
						Water	33493
44	Mv-3-(6-p-(E)-coumaroyl)-glucoside	OCH ₃	OH	OCH ₃	OGlc-pCoup	MeOH	32594
						Water	32686

Pyrananthocyanins

	Name	R ¹	R ²	R ³	R ^{6''}	R ⁵	
45	Pg-3-Glc 10-carboxy type	H	OH	H	H	COOH	36709
							37137
51	Pg-3-Glc 10-H type	H	OH	H	H	H	37841
							38356
57	Pg-3-Glc-4-vinylphenol adduct	H	OH	H	H	Phenol	60666
							61717
63	Pg-3-Glc-4-vinylcatechol adduct	H	OH	H	H	Catechol	56658
							50105
69	Pg-3-acetyl-Glc 10-carboxy type	H	OH	H	Ac	COOH	36288
							36609
75	Pg-3-acetyl-Glc 10-H type	H	OH	H	Ac	H	37346
							37898
81	Pg-3-acetyl-Glc-4-vinylphenol adduct	H	OH	H	Ac	Phenol	58772
							57917
87	Pg-3-acetyl-Glc-4-vinylcatechol adduct	H	OH	H	Ac	Catechol	58467

93	Pg-(6-(E)-caffeoyl)-Glc 10-carboxy type	H	OH	H	Caff	COOH	Water	57942
							MeOH	36348
99	Pg-(6-(E)-caffeoyl)-Glc 10-H type	H	OH	H	Caff	H	Water	36408
							MeOH	37003
105	Pg-(6-(E)-caffeoyl)-Glc-4-vinylphenol adduct	H	OH	H	Caff	Phenol	Water	37235
							MeOH	58505
							Water	55955
111	Pg-(6-(E)-caffeoyl)-Glc-4-vinylcatechol adduct	H	OH	H	Caff	Catechol	MeOH	58140
							Water	58016
117	Pg-3-(6-(E)-coum)-Glc 10-carboxy type	H	OH	H	pCoum	COOH	MeOH	36336
							Water	36318
123	Pg-3-(6-(E)-coum)-Glc 10-H type	H	OH	H	pCoum	H	MeOH	36341
							Water	36692
129	Pg-3-(6-(E)-coum)-Glc-4-vinylphenol adduct	H	OH	H	pCoum	Phenol	MeOH	58982
							Water	58882
135	Pg-3-(6-(E)-coum)-Glc-4-vinylcatechol adduct	H	OH	H	pCoum	Catechol	MeOH	57516
							Water	57600
46	Cy-3-Glc 10-carboxy type	OH	OH	H	H	COOH	MeOH	32908
							Water	33473
52	Cy-3-Glc 10-H type	OH	OH	H	H	H	MeOH	33013
							Water	33959
58	Cy-3-Glc-4-vinylphenol adduct	OH	OH	H	H	Phenol	MeOH	57822
							Water	59023
64	Cy-3-Glc-4-vinylcatechol adduct	OH	OH	H	H	Catechol	MeOH	56509
							Water	55161
70	Cy-3-acetyl-Glc 10-carboxy type	OH	OH	H	Ac	COOH	MeOH	31713
							Water	32327
76	Cy-3-acetyl-Glc 10-H type	OH	OH	H	Ac	H	MeOH	32580

82	Cy-3-acetyl-Glc 4-vinylphenol adduct	OH	OH	H	Ac	Phenol	Water	33230
							MeOH	55471
88	Cy-3-acetyl-Glc 4-vinylcatechol adduct	OH	OH	H	Ac	Catechol	Water	56040
							MeOH	56484
94	Cy-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	OH	H	Caff	COOH	Water	56885
							MeOH	31504
100	Cy-(6-(E)-caffeoyl)-Glc 10-H type	OH	OH	H	Caff	H	Water	31887
							MeOH	31476
							Water	31806
106	Cy-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OH	OH	H	Caff	Phenol	MeOH	53654
							Water	54779
112	Cy-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH	OH	H	Caff	Catechol	MeOH	56637
							Water	56696
118	Cy-3-(6-(E)-coum)-Glc 10-carboxy type	OH	OH	H	pCoum	COOH	MeOH	31492
							Water	31814
124	Cy-3-(6-(E)-coum)-Glc 10-H type	OH	OH	H	pCoum	H	MeOH	31508
							Water	31713
130	Cy-3-(6-(E)-coum)-Glc-4-vinylphenol adduct	OH	OH	H	pCoum	Phenol	MeOH	54458
							Water	53498
136	Cy-3-(6-(E)-coum)-Glc-4-vinylcatechol adduct	OH	OH	H	pCoum	Catechol	MeOH	55873
							Water	56308
47	Pn-3-Glc 10-carboxy type	OCH ₃	OH	H	H	COOH	MeOH	30190
							Water	30658
53	Pn-3-Glc 10-H type	OCH ₃	OH	H	H	H	MeOH	30925
							Water	31562
59	Pn-3-Glc-4-vinylphenol adduct	OCH ₃	OH	H	H	Phenol	MeOH	56806
							Water	58213
65	Pn-3-Glc-4-vinylcatechol adduct	OCH ₃	OH	H	H	Catechol	MeOH	56873

71	Pn-3-acetyl-Glc 10-carboxy type	OCH ₃	OH	H	Ac	COOH	Water	53347
							MeOH	32930
77	Pn-3-acetyl-Glc 10-H type	OCH ₃	OH	H	Ac	H	Water	33200
							MeOH	33326
							Water	33798
83	Pn-3-acetyl-Glc 4-vinylphenol adduct	OCH ₃	OH	H	Ac	Phenol	MeOH	54101
							Water	57467
89	Pn-3-acetyl-Glc 4-vinylcatechol adduct	OCH ₃	OH	H	Ac	Catechol	MeOH	56622
							Water	57105
95	Pn-(6-(E)-caffeoyl)-Glc 10-carboxy type	OCH ₃	OH	H	Caff	COOH	MeOH	29264
							Water	29099
101	Pn-(6-(E)-caffeoyl)-Glc 10-H type	OCH ₃	OH	H	Caff	H	MeOH	29972
							Water	30487
107	Pn-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OCH ₃	OH	H	Caff	Phenol	MeOH	53642
							Water	52180
113	Pn-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OCH ₃	OH	H	Caff	Catechol	MeOH	56549
							Water	57123
119	Pn-3-(6-(E)-coum)-Glc 10-carboxy type	OCH ₃	OH	H	pCoum	COOH	MeOH	29029
							Water	30483
125	Pn-3-(6-(E)-coum)-Glc 10-H type	OCH ₃	OH	H	pCoum	H	MeOH	30700
							Water	30614
131	Pn-3-(6-(E)-coum)-Glc 4-vinylphenol adduct	OCH ₃	OH	H	pCoum	Phenol	MeOH	53704
							Water	53556
137	Pn-3-(6-(E)-coum)-Glc 4-vinylcatechol adduct	OCH ₃	OH	H	pCoum	Catechol	MeOH	56380
							Water	56391
48	Dp-3-Glc 10-carboxy type	OH	OH	OH	H	COOH	MeOH	35379
54	Dp-3-Glc 10-H type	OH	OH	OH	H	H	Water	35969
							MeOH	36355

60	Dp-3-Glc 4-vinylphenol adduct	OH	OH	OH	H	Phenol	Water	36946
							MeOH	60476
66	Dp-3-Glc 4-vinylcatechol adduct	OH	OH	OH	H	Catechol	Water	59023
							MeOH	57054
72	Dp-3-acetyl-Glc 10-carboxy type	OH	OH	OH	Ac	COOH	Water	54971
							MeOH	33547
78	Dp-3-acetyl-Glc 10-H type	OH	OH	OH	Ac	H	Water	35623
							MeOH	34917
84	Dp-3-acetyl-Glc 4-vinylphenol adduct	OH	OH	OH	Ac	Phenol	Water	35575
							MeOH	56658
90	Dp-3-acetyl-Glc 4-vinylcatechol adduct	OH	OH	OH	Ac	Catechol	Water	57612
							MeOH	57797
96	Dp-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	OH	OH	Caff	COOH	Water	57548
							MeOH	35373
102	Dp-(6-(E)-caffeoyl)-Glc 10-H type	OH	OH	OH	Caff	H	Water	35113
							MeOH	33652
108	Dp-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OH	OH	OH	Caff	Phenol	Water	34346
							MeOH	55064
114	Dp-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH	OH	OH	Caff	Catechol	Water	57090
							MeOH	56978
120	Dp-3-(6-(E)-coum)-Glc 10-carboxy type	OH	OH	OH	pCoum	COOH	Water	58248
							MeOH	33956
126	Dp-3-(6-(E)-coum)-Glc 10-H type	OH	OH	OH	pCoum	H	Water	31989
							MeOH	33162
132	Dp-3-(6-(E)-coum)-Glc 4-vinylphenol adduct	OH	OH	OH	pCoum	Phenol	Water	34703
							MeOH	55846
138	Dp-3-(6-(E)-coum)-Glc 4-vinylcatechol adduct	OH	OH	OH	pCoum	Catechol	Water	56558
							MeOH	56649

49	Pt-3-Glc 10-carboxy type	OH	OH	OCH ₃	H	COOH	Water MeOH	57837 32350
55	Pt-3-Glc 10-H type	OH	OH	OCH ₃	H	H	Water MeOH	32217 33330
61	Pt-3-Glc 4-vinylphenol adduct	OH	OH	OCH ₃	H	Phenol	Water MeOH	33938 57944
67	Pt-3-Glc 4-vinylcatechol adduct	OH	OH	OCH ₃	H	Catechol	Water MeOH	58833 57399
73	Pt-3-acetyl-Glc 10-carboxy type	OH	OH	OCH ₃	Ac	COOH	Water MeOH	55135 32497
79	Pt-3-acetyl-Glc 10-H type	OH	OH	OCH ₃	Ac	H	Water MeOH	32950 32744
85	Pt-3-acetyl-Glc 4-vinylphenol adduct	OH	OH	OCH ₃	Ac	Phenol	Water MeOH	33309 54803
91	Pt-3-acetyl-Glc 4-vinylcatechol adduct	OH	OH	OCH ₃	Ac	Catechol	Water MeOH	57177 57779
97	Pt-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	OH	OCH ₃	Caff	COOH	Water MeOH	58029 26543
103	Pt-(6-(E)-caffeoyl)-Glc 10-H type	OH	OH	OCH ₃	Caff	H	Water MeOH	31141 32015
109	Pt-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OH	OH	OCH ₃	Caff	Phenol	Water MeOH	32469 53915
115	Pt-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH	OH	OCH ₃	Caff	Catechol	Water MeOH	52376 57623
121	Pt-3-(6-(E)-coum)-Glc 10-carboxy type	OH	OH	OCH ₃	pCoum	COOH	Water MeOH	58293 32371
127	Pt-3-(6-(E)-coum)-Glc 10-H type	OH	OH	OCH ₃	pCoum	H	Water MeOH	31530 31816

133	Pt-3-(6-(E)-coum)-Glc-4-vinylphenol adduct	OH	OH	OCH ₃	pCoum	Phenol	Water	32351
							MeOH	57808
139	Pt-3-(6-(E)-coum)-Glc-4-vinylcatechol adduct	OH	OH	OCH ₃	pCoum	Catechol	Water	53317
							MeOH	57434
50	Mv-3-Glc 10-carboxy type	OCH ₃	OH	OCH ₃	H	COOH	Water	58177
							MeOH	30797
56	Mv-3-Glc 10-H type	OCH ₃	OH	OCH ₃	H	H	Water	31959
							MeOH	33473
62	Mv-3-Glc 4-vinylphenol adduct	OCH ₃	OH	OCH ₃	H	Phenol	Water	33822
							MeOH	55025
68	Mv-3-Glc 4-vinylcatechol adduct	OCH ₃	OH	OCH ₃	H	Catechol	Water	56676
							MeOH	56918
74	Mv-3-acetyl-Glc 10-carboxy type	OCH ₃	OH	OCH ₃	Ac	COOH	Water	56321
							MeOH	32345
80	Mv-3-acetyl-Glc 10-H type	OCH ₃	OH	OCH ₃	Ac	H	Water	32592
							MeOH	33460
86	Mv-3-acetyl-Glc 4-vinylphenol adduct	OCH ₃	OH	OCH ₃	Ac	Phenol	Water	33733
							MeOH	52959
92	Mv-3-acetyl-Glc-4-vinylcatechol adduct	OCH ₃	OH	OCH ₃	Ac	Catechol	Water	55441
							MeOH	56344
98	Mv-(6-(E)-caffeoyl)-Glc 10-carboxy type	OH	OH	OCH ₃	Caff	COOH	Water	57245
							MeOH	30754
104	Mv-(6-(E)-caffeoyl)-Glc 10-H type	OH	OH	OCH ₃	Caff	H	Water	31761
							MeOH	31631
110	Mv-(6-(E)-caffeoyl)-Glc 4-vinylphenol adduct	OH	OH	OCH ₃	Caff	Phenol	Water	33901
							MeOH	50174
116	Mv-(6-(E)-caffeoyl)-Glc 4-vinylcatechol adduct	OH	OH	OCH ₃	Caff	Catechol	Water	50883
							MeOH	56565

122	Mv-3-(6-(E)-coum)-Glc 10-carboxy type	OCH ₃	OH	OCH ₃	pCoum	COOH	Water	57348
							MeOH	31500
							Water	31824
128	Mv-3-(6-(E)-coum)-Glc 10-H type	OCH ₃	OH	OCH ₃	pCoum	H	MeOH	31997
							Water	32458
134	Mv-3-(6-(E)-coum)-Glc 4-vinylphenol adduct	OCH ₃	OH	OCH ₃	pCoum	Phenol	MeOH	50893
							Water	51530
140	Mv-3-(6-(E)-coum)-Glc-4-vinylcatechol adduct	OCH ₃	OH	OCH ₃	pCoum	Catechol	MeOH	56381
							Water	57275

Efficiency Parameters of Anthocyanin-Based Compounds for DSSC

Table D.38: The Gibbs free energy change for electron injection ΔG_{inj} , estimated open circuit voltage (eV_{oc}), regeneration efficiency (ΔG_{reg}) and light harvesting efficiency (LHE) for anthocyanin-related compounds, based on B3LYP/6-311++G(d,p) orbital energies with SMD methanol (MeOH) and water.

Compound (label Figure D.3)	SMD MeOH				SMD Water			
Anthocyanidins	ΔG_{inject} (eV)	eV_{oc} (eV)	LHE	ΔG_{reg} (eV)	ΔG_{inject} (eV)	eV_{oc} (eV)	LHE	ΔG_{reg} (eV)
Ap (1)	-0.111	0.740	0.895	-1.720	-0.145	0.780	0.898	-1.680
Cy (4)	-0.118	0.670	0.875	-1.420	-0.146	0.710	0.877	-1.390
Dp (6)	-0.110	0.650	0.878	-1.390	-0.142	0.690	0.879	-1.360
Lt (2)	-0.154	0.720	0.899	-1.570	-0.188	0.770	0.898	-1.540
Mv (8)	-0.162	0.670	0.893	-1.280	-0.184	0.710	0.894	-1.260
Pg (3)	-0.109	0.690	0.867	-1.480	-0.145	0.730	0.869	-1.440
Pn (5)	-0.146	0.690	0.880	-1.370	-0.174	0.730	0.881	-1.340
Pt (7)	-0.133	0.660	0.879	-1.350	-0.152	0.700	0.880	-1.330
Anthocyanins								
Cy-3-Glc (10)	-0.103	0.690	0.844	-1.570	-0.125	0.720	0.847	-1.550
Dp-3-Glc (12)	-0.103	0.670	0.863	-1.550	-0.119	0.700	0.861	-1.540
Mv-3-Glc (14)	-0.158	0.680	0.871	-1.400	-0.171	0.720	0.858	-1.400
Pg-3-Glc (9)	-0.071	0.700	0.866	-1.710	-0.099	0.740	0.868	-1.680
Pn-3-Glc (11)	-0.134	0.700	0.859	-1.500	-0.153	0.740	0.859	-1.480
Pt-3-Glc (13)	-0.138	0.680	0.870	-1.480	-0.112	0.670	0.879	-1.430
Acylated anthocyanins								
Acetyl acylated Cy-3-Glc (16)	-0.144	0.720	0.845	-1.520	-0.121	0.720	0.843	-1.580
Acetyl acylated Dp-3-Glc (18)	-0.090	0.660	0.844	-1.590	-0.114	0.700	0.850	-1.570
Acetyl acylated Mv-3-Glc (20)	-0.140	0.680	0.860	-1.440	-0.168	0.720	0.861	-1.420
Acetyl acylated Pg-3-Glc (15)	-0.103	0.730	0.863	-1.680	-0.093	0.740	0.844	-1.700
Acetyl acylated Pn-3-Glc (17)	-0.114	0.690	0.842	-1.550	-0.146	0.730	0.848	-1.520
Acetyl acylated Pt-3-Glc (19)	-0.121	0.680	0.846	-1.520	-0.146	0.720	0.850	-1.500
(Z)-caffeoyl acylated Cy-3-Glc (22)	-0.107	0.740	0.040	-1.290	-0.139	0.770	0.048	-1.280
(Z)-caffeoyl acylated Dp-3-Glc (24)	-0.132	0.760	0.085	-1.300	-0.162	0.790	0.082	-1.280
(Z)-caffeoyl acylated Mv-3-Glc (26)	-0.109	0.740	0.047	-1.300	-0.143	0.770	0.029	-1.260
(Z)-caffeoyl acylated Pg-3-Glc (21)	-0.177	0.810	0.031	-1.290	-0.195	0.820	0.077	-1.280
(Z)-caffeoyl acylated Pn-3-Glc (23)	-0.122	0.750	0.077	-1.300	-0.157	0.780	0.087	-1.280
(Z)-caffeoyl acylated Pt-3-Glc (25)	-0.101	0.730	0.071	-1.300	-0.143	0.780	0.032	-1.250
(E)-caffeoyl acylated Cy-3-Glc (28)	-0.197	0.680	0.039	-1.310	-0.225	0.710	0.022	-1.320
(E)-caffeoyl acylated Dp-3-Glc (30)	-0.199	0.720	0.139	-1.300	-0.158	0.710	0.047	-1.300
(E)-caffeoyl acylated Mv-3-Glc (32)	-0.183	0.680	0.184	-1.310	-0.215	0.710	0.103	-1.320
(E)-caffeoyl acylated Pg-3-Glc (27)	-0.207	0.700	0.019	-1.340	-0.247	0.740	0.021	-1.320
(E)-caffeoyl acylated Pn-3-Glc (29)	-0.200	0.690	0.079	-1.310	-0.191	0.730	0.058	-1.290
(E)-caffeoyl acylated Pt-3-Glc (31)	-0.177	0.680	0.096	-1.300	-0.199	0.710	0.038	-1.320
(Z)-coumaroyl acylated Cy-3-Glc (34)	-0.151	0.740	0.303	-1.440	-0.188	0.770	0.212	-1.400
(Z)-coumaroyl acylated Dp-3-Glc (36)	-0.123	0.740	0.007	-1.440	-0.153	0.770	0.007	-1.400
(Z)-coumaroyl acylated Mv-3-Glc (38)	-0.110	0.720	0.125	-1.410	-0.130	0.750	0.091	-1.380
(Z)-coumaroyl acylated Pg-3-Glc (33)	-0.167	0.750	0.091	-1.440	-0.206	0.790	0.068	-1.400
(Z)-coumaroyl acylated Pn-3-Glc (35)	-0.099	0.720	0.034	-1.430	-0.140	0.760	0.017	-1.400
(Z)-coumaroyl acylated Pt-3-Glc (37)	-0.091	0.710	0.011	-1.430	-0.122	0.740	0.015	-1.390
(E)-coumaroyl acylated Cy-3-Glc (40)	-0.165	0.690	0.466	-1.450	-0.192	0.730	0.468	-1.390
(E)-coumaroyl acylated Dp-3-Glc (42)	-0.177	0.720	0.640	-1.400	-0.175	0.720	0.524	-1.390
(E)-coumaroyl acylated Mv-3-Glc (44)	-0.158	0.690	0.781	-1.390	-0.193	0.730	0.781	-1.360

(E)-coumaroyl acylated Pg-3-Glc (39)	-0.188	0.710	0.344	-1.460	-0.215	0.750	0.391	-1.390
(E)-coumaroyl acylated Pn-3-Glc (41)	-0.166	0.700	0.660	-1.430	-0.196	0.740	0.647	-1.370
(E)-coumaroyl acylated Pt-3-Glc (43)	-0.162	0.690	0.660	-1.420	-0.188	0.720	0.675	-1.400
Pyranoanthocyanins								
10-carboxy Cy-3-Glc (46)	-0.227	0.780	0.838	-1.440	-0.209	0.770	0.844	-1.450
10-carboxy Dp-3-Glc (48)	-0.230	0.760	0.860	-1.420	-0.202	0.750	0.865	-1.440
10-carboxy Mv-3-Glc (50)	-0.225	0.740	0.820	-1.340	-0.202	0.720	0.832	-1.350
10-carboxy Pg-3-Glc (45)	-0.195	0.790	0.867	-1.580	-0.173	0.780	0.870	-1.590
10-carboxy Pn-3-Glc (47)	-0.250	0.790	0.808	-1.390	-0.229	0.780	0.814	-1.400
10-carboxy Pt-3-Glc (49)	-0.260	0.790	0.833	-1.370	-0.186	0.720	0.832	-1.440
10-H Cy-3-Glc (52)	-0.233	0.790	0.841	-1.490	-0.257	0.830	0.849	-1.470
10-H Dp-3-Glc (54)	-0.226	0.770	0.869	-1.480	-0.254	0.810	0.873	-1.460
10-H Mv-3-Glc (56)	-0.276	0.790	0.849	-1.330	-0.300	0.830	0.851	-1.320
10-H Pg-3-Glc (51)	-0.195	0.800	0.878	-1.640	-0.225	0.840	0.881	-1.610
10-H Pn-3-Glc (53)	-0.253	0.800	0.819	-1.440	-0.281	0.840	0.825	-1.420
10-H Pt-3-Glc (55)	-0.256	0.790	0.845	-1.420	-0.277	0.830	0.850	-1.410
Vinylcatechol Cy-3-Glc (64)	-0.233	0.800	0.947	-1.380	-0.258	0.840	0.948	-1.360
Vinylcatechol Dp-3-Glc (66)	-0.226	0.790	0.948	-1.350	-0.252	0.820	0.949	-1.330
Vinylcatechol Mv-3-Glc (68)	-0.261	0.800	0.948	-1.250	-0.278	0.830	0.949	-1.240
Vinylcatechol Pg-3-Glc (63)	-0.245	0.810	0.946	-1.380	-0.260	0.850	0.948	-1.370
Vinylcatechol Pn-3-Glc (65)	-0.242	0.800	0.949	-1.320	-0.270	0.840	0.947	-1.300
Vinylcatechol Pt-3-Glc (67)	-0.240	0.790	0.950	-1.310	-0.266	0.820	0.951	-1.290
Vinylphenol Cy-3-Glc (58)	-0.229	0.800	0.947	-1.420	-0.246	0.830	0.950	-1.400
Vinylphenol Dp-3-Glc (60)	-0.242	0.810	0.955	-1.360	-0.245	0.820	0.952	-1.380
Vinylphenol Mv-3-Glc (62)	-0.267	0.800	0.938	-1.290	-0.282	0.830	0.942	-1.280
Vinylphenol Pg-3-Glc (57)	-0.208	0.810	0.955	-1.490	-0.237	0.840	0.957	-1.450
Vinylphenol Pn-3-Glc (59)	-0.239	0.810	0.941	-1.380	-0.267	0.840	0.945	-1.350
Vinylphenol Pt-3-Glc (61)	-0.237	0.790	0.947	-1.360	-0.266	0.830	0.949	-1.330
Acylated Pyranoanthocyanins								
Acetyl acylated 10-carboxy Cy-3-Glc (70)	-0.252	0.800	0.827	-1.420	-0.225	0.780	0.834	-1.430
Acetyl acylated 10-carboxy Dp-3-Glc (72)	-0.245	0.780	0.845	-1.410	-0.220	0.760	0.862	-1.430
Acetyl acylated 10-carboxy Mv-3-Glc (74)	-0.292	0.810	0.837	-1.270	-0.261	0.780	0.840	-1.290
Acetyl acylated 10-carboxy Pg-3-Glc (69)	-0.220	0.810	0.863	-1.550	-0.189	0.790	0.866	-1.560
Acetyl acylated 10-carboxy Pn-3-Glc (71)	-0.276	0.810	0.841	-1.350	-0.247	0.790	0.844	-1.360
Acetyl acylated 10-carboxy Pt-3-Glc (73)	-0.266	0.800	0.837	-1.360	-0.231	0.770	0.841	-1.380
Acetyl acylated 10-H Cy-3-Glc (76)	-0.252	0.810	0.837	-1.480	-0.272	0.840	0.843	-1.460
Acetyl acylated 10-H Dp-3-Glc (78)	-0.248	0.800	0.858	-1.470	-0.271	0.830	0.863	-1.450
Acetyl acylated 10-H Mv-3-Glc (80)	-0.289	0.820	0.848	-1.330	-0.307	0.850	0.851	-1.320
Acetyl acylated 10-H Pg-3-Glc (75)	-0.221	0.830	0.874	-1.620	-0.245	0.860	0.877	-1.590
Acetyl acylated 10-H Pn-3-Glc (77)	-0.275	0.820	0.846	-1.410	-0.293	0.850	0.850	-1.390
Acetyl acylated 10-H Pt-3-Glc (79)	-0.269	0.810	0.841	-1.420	-0.293	0.840	0.845	-1.400
Acetyl acylated vinylcatechol Cy-3-Glc (88)	-0.269	0.830	0.946	-1.330	-0.265	0.840	0.947	-1.340
Acetyl acylated vinylcatechol Dp-3-Glc (90)	-0.261	0.820	0.951	-1.320	-0.253	0.830	0.950	-1.340
Acetyl acylated vinylcatechol Mv-3-Glc (92)	-0.292	0.830	0.946	-1.230	-0.284	0.840	0.949	-1.250
Acetyl acylated vinylcatechol Pg-3-Glc (87)	-0.268	0.840	0.951	-1.370	-0.268	0.850	0.949	-1.370
Acetyl acylated vinylcatechol Pn-3-Glc (89)	-0.280	0.840	0.947	-1.290	-0.271	0.850	0.948	-1.310
Acetyl acylated vinylcatechol Pt-3-Glc (91)	-0.269	0.830	0.951	-1.290	-0.266	0.830	0.951	-1.300
Acetyl acylated vinylphenol Cy-3-Glc (82)	-0.316	0.890	0.936	-1.370	-0.302	0.900	0.938	-1.420
Acetyl acylated vinylphenol Dp-3-Glc (84)	-0.303	0.880	0.941	-1.360	-0.320	0.900	0.944	-1.350
Acetyl acylated vinylphenol Mv-3-Glc (86)	-0.350	0.890	0.927	-1.240	-0.332	0.890	0.934	-1.290
Acetyl acylated vinylphenol Pg-3-Glc (81)	-0.289	0.900	0.950	-1.450	-0.295	0.910	0.947	-1.460
Acetyl acylated vinylphenol Pn-3-Glc (83)	-0.325	0.900	0.930	-1.330	-0.296	0.880	0.943	-1.360
Acetyl acylated vinylphenol Pt-3-Glc (85)	-0.326	0.890	0.933	-1.320	-0.317	0.890	0.942	-1.350
Caffeoyl acylated 10-carboxy Cy-3-Glc (94)	-0.315	0.810	0.060	-1.180	-0.290	0.790	0.060	-1.210
Caffeoyl acylated 10-carboxy Dp-3-Glc (96)	-0.298	0.790	0.034	-1.170	-0.270	0.780	0.049	-1.210
Caffeoyl acylated 10-carboxy Mv-3-Glc (98)	-0.316	0.820	0.182	-1.180	-0.297	0.800	0.456	-1.160

Caffeoyl acylated 10-carboxy Pg-3-Glc (93)	-0.323	0.820	0.042	-1.180	-0.299	0.800	0.039	-1.210
Caffeoyl acylated 10-carboxy Pn-3-Glc (95)	-0.320	0.820	0.081	-1.180	-0.297	0.800	0.087	-1.210
Caffeoyl acylated 10-carboxy Pt-3-Glc (97)	-0.308	0.810	0.079	-1.180	-0.284	0.790	0.084	-1.210
Caffeoyl acylated 10-H Cy-3-Glc (100)	-0.338	0.820	0.210	-1.210	-0.363	0.860	0.274	-1.190
Caffeoyl acylated 10-H Dp-3-Glc (102)	-0.289	0.800	0.070	-1.260	-0.326	0.840	0.042	-1.260
Caffeoyl acylated 10-H Mv-3-Glc (104)	-0.332	0.830	0.467	-1.210	-0.338	0.860	0.562	-1.260
Caffeoyl acylated 10-H Pg-3-Glc (99)	-0.348	0.830	0.130	-1.220	-0.377	0.870	0.190	-1.190
Caffeoyl acylated 10-H Pn-3-Glc (101)	-0.351	0.840	0.259	-1.210	-0.372	0.870	0.303	-1.190
Caffeoyl acylated 10-H Pt-3-Glc (103)	-0.335	0.820	0.283	-1.210	-0.355	0.850	0.362	-1.200
Caffeoyl acylated vinylcatechol Cy-3-Glc (112)	-0.285	0.830	0.946	-1.310	-0.317	0.840	0.944	-1.310
Caffeoyl acylated vinylcatechol Dp-3-Glc (114)	-0.278	0.820	0.948	-1.310	-0.293	0.820	0.950	-1.310
Caffeoyl acylated vinylcatechol Mv-3-Glc (116)	-0.296	0.830	0.946	-1.220	-0.278	0.830	0.947	-1.270
Caffeoyl acylated vinylcatechol Pg-3-Glc (111)	-0.331	0.850	0.949	-1.310	-0.347	0.850	0.948	-1.310
Caffeoyl acylated vinylcatechol Pn-3-Glc (113)	-0.276	0.840	0.946	-1.290	-0.288	0.840	0.946	-1.310
Caffeoyl acylated vinylcatechol Pt-3-Glc (115)	-0.269	0.830	0.950	-1.290	-0.269	0.830	0.951	-1.310
Caffeoyl acylated vinylphenol Cy-3-Glc (106)	-0.409	0.880	0.029	-1.240	-0.414	0.900	0.093	-1.250
Caffeoyl acylated vinylphenol Dp-3-Glc (108)	-0.407	0.890	0.066	-1.250	-0.402	0.910	0.930	-1.250
Caffeoyl acylated vinylphenol Mv-3-Glc (110)	-0.350	0.880	0.908	-1.280	-0.374	0.910	0.909	-1.260
Caffeoyl acylated vinylphenol Pg-3-Glc (105)	-0.427	0.900	0.081	-1.260	-0.429	0.920	0.029	-1.250
Caffeoyl acylated vinylphenol Pn-3-Glc (107)	-0.403	0.880	0.018	-1.240	-0.421	0.920	0.011	-1.250
Caffeoyl acylated vinylphenol Pt-3-Glc (109)	-0.397	0.870	0.042	-1.240	-0.418	0.910	0.023	-1.240
Coumaroyl acylated 10-carboxy Cy-3-Glc (118)	-0.289	0.810	0.239	-1.330	-0.265	0.790	0.295	-1.350
Coumaroyl acylated 10-carboxy Dp-3-Glc (120)	-0.274	0.800	0.299	-1.330	-0.257	0.780	0.356	-1.340
Coumaroyl acylated 10-carboxy Mv-3-Glc (122)	-0.301	0.820	0.756	-1.250	-0.277	0.800	0.745	-1.250
Coumaroyl acylated 10-carboxy Pg-3-Glc (117)	-0.303	0.820	0.089	-1.330	-0.282	0.800	0.115	-1.350
Coumaroyl acylated 10-carboxy Pn-3-Glc (119)	-0.290	0.820	0.493	-1.330	-0.282	0.810	0.549	-1.300
Coumaroyl acylated 10-carboxy Pt-3-Glc (121)	-0.303	0.820	0.593	-1.290	-0.265	0.790	0.609	-1.300
Coumaroyl acylated 10-H Cy-3-Glc (124)	-0.302	0.830	0.540	-1.370	-0.326	0.860	0.571	-1.340
Coumaroyl acylated 10-H Dp-3-Glc (126)	-0.263	0.810	0.504	-1.390	-0.290	0.840	0.523	-1.370
Coumaroyl acylated 10-H Mv-3-Glc (128)	-0.303	0.830	0.780	-1.300	-0.322	0.860	0.772	-1.280
Coumaroyl acylated 10-H Pg-3-Glc (123)	-0.323	0.840	0.275	-1.380	-0.348	0.870	0.359	-1.350
Coumaroyl acylated 10-H Pn-3-Glc (125)	-0.291	0.840	0.715	-1.390	-0.309	0.870	0.656	-1.360
Coumaroyl acylated 10-H Pt-3-Glc (127)	-0.296	0.820	0.664	-1.350	-0.316	0.850	0.673	-1.330
Coumaroyl acylated vinylcatechol Cy-3-Glc (136)	-0.268	0.840	0.945	-1.330	-0.258	0.840	0.944	-1.370
Coumaroyl acylated vinylcatechol Dp-3-Glc (138)	-0.268	0.820	0.947	-1.320	-0.254	0.820	0.949	-1.350
Coumaroyl acylated vinylcatechol Mv-3-Glc (140)	-0.296	0.830	0.946	-1.220	-0.278	0.830	0.947	-1.270
Coumaroyl acylated vinylcatechol Pg-3-Glc (135)	-0.271	0.850	0.947	-1.370	-0.259	0.850	0.948	-1.400
Coumaroyl acylated vinylcatechol Pn-3-Glc (137)	-0.277	0.840	0.946	-1.290	-0.272	0.850	0.945	-1.330
Coumaroyl acylated vinylcatechol Pt-3-Glc (139)	-0.279	0.830	0.950	-1.280	-0.260	0.830	0.951	-1.320
Coumaroyl acylated vinylphenol Cy-3-Glc (130)	-0.362	0.870	0.658	-1.350	-0.375	0.920	0.923	-1.360
Coumaroyl acylated vinylphenol Dp-3-Glc (132)	-0.314	0.890	0.935	-1.350	-0.333	0.920	0.937	-1.340
Coumaroyl acylated vinylphenol Mv-3-Glc (134)	-0.331	0.880	0.910	-1.290	-0.356	0.910	0.910	-1.280
Coumaroyl acylated vinylphenol Pg-3-Glc (129)	-0.332	0.900	0.948	-1.400	-0.353	0.930	0.948	-1.380
Coumaroyl acylated vinylphenol Pn-3-Glc (131)	-0.312	0.880	0.925	-1.370	-0.337	0.920	0.922	-1.360
Coumaroyl acylated vinylphenol Pt-3-Glc (139)	-0.272	0.840	0.942	-1.380	-0.341	0.910	0.917	-1.350

Additional UV-Vis Spectra

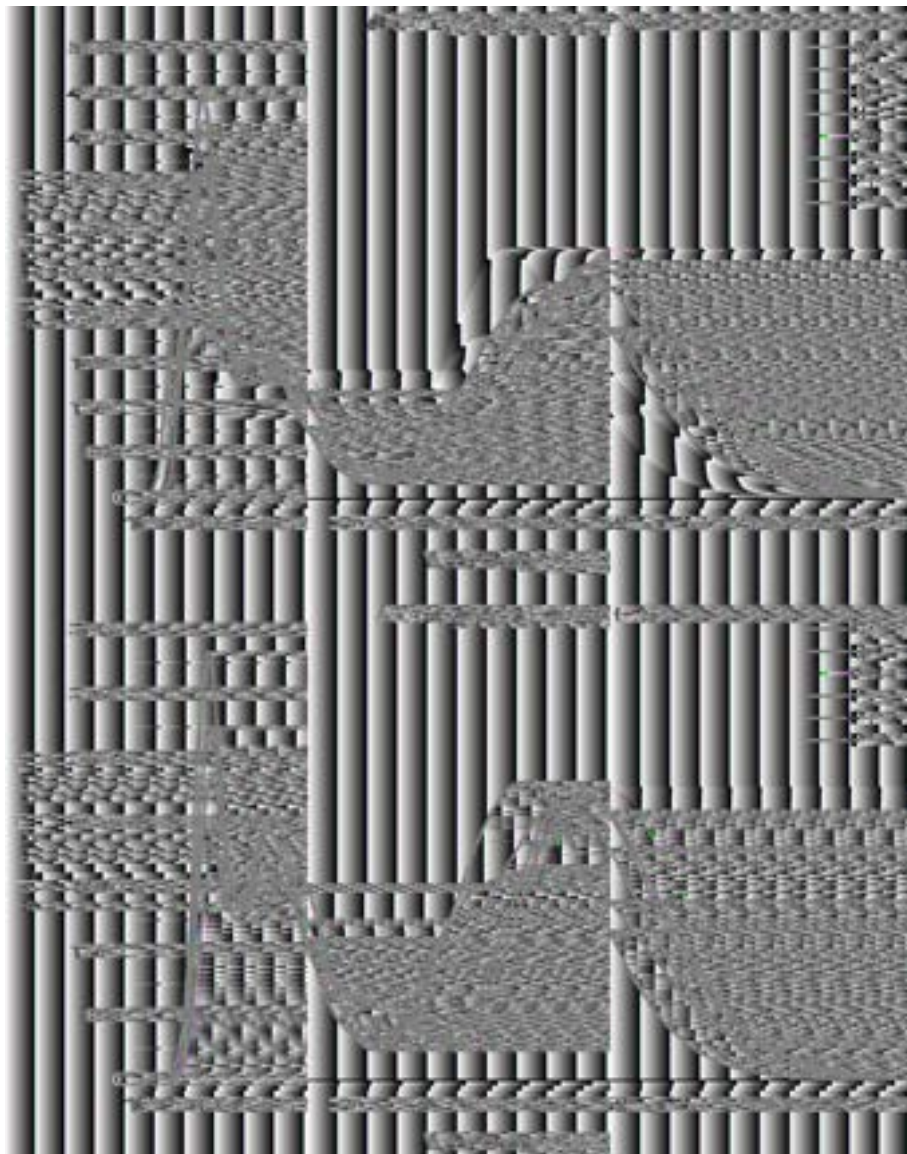


Figure D.19: Calculated UV-Vis spectra of anthocyanidins (1-8) and anthocyanins (9-14) in the gas phase (B3LYP/6-311++G(d,p)).



Figure D.20: Calculated UV-Vis spectra of acetyl acylated anthocyanins (**15-20**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

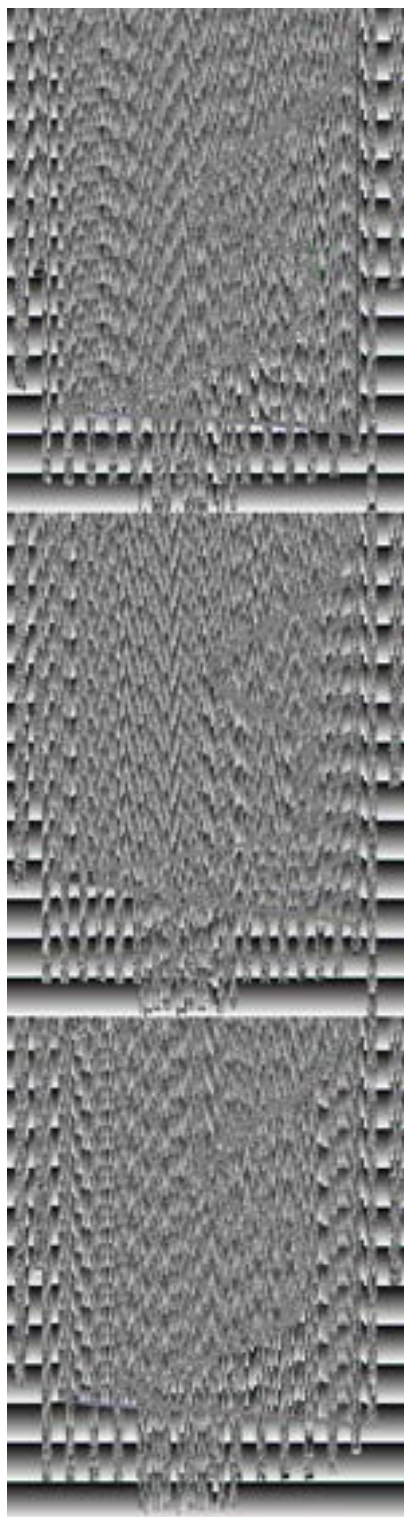


Figure D.21: Calculated UV-Vis spectra of acetyl acylated 10-carboxy pyranocanthocyanins (**69-74**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

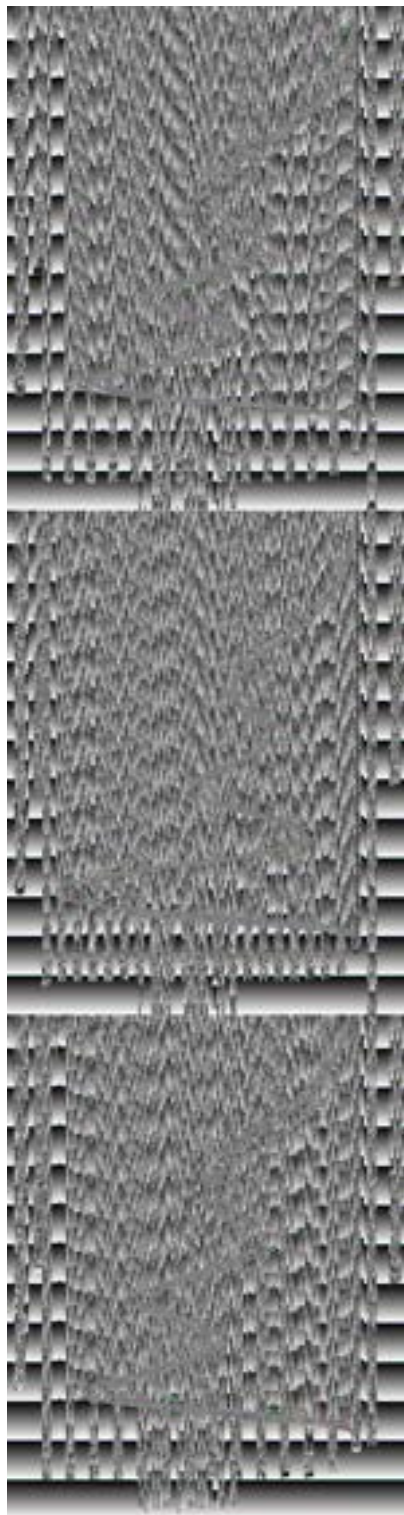


Figure D.22: Calculated UV-Vis spectra of caffeoyl acylated 10-carboxy pyranoanthocyanins (**93-98**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

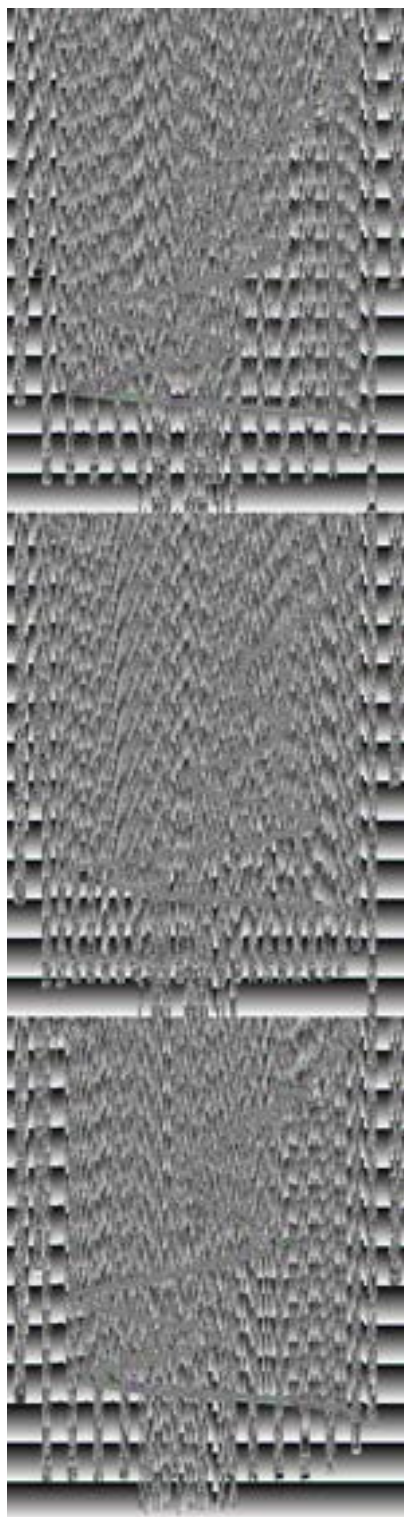


Figure D.23: Calculated UV-Vis spectra of coumaroyl acylated 10-carboxy pyranoanthocyanins (117-122) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.



Figure D.24: Calculated UV-Vis spectra of acetyl acylated 10-H pyranoanthocyanins (**75-80**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

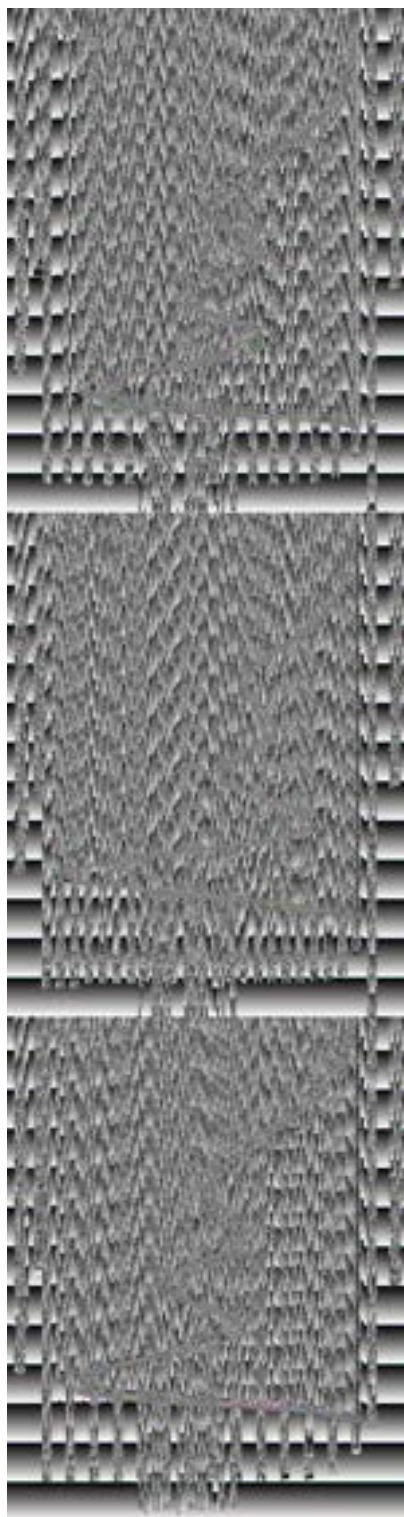


Figure D.25: Calculated UV-Vis spectra of caffeoyl acylated 10-H pyranoanthocyanins (**99-104**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

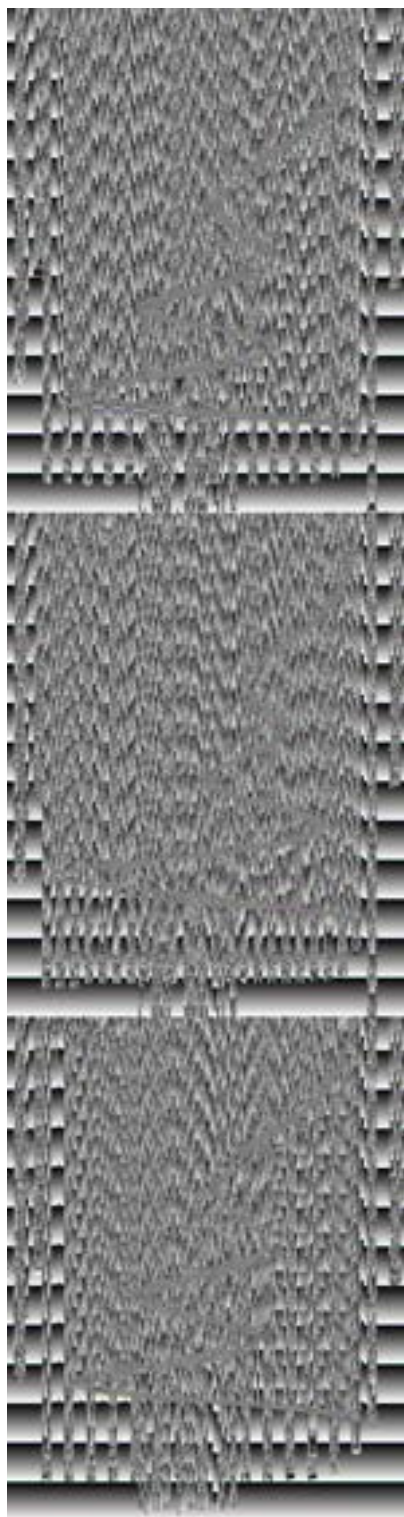


Figure D.26: Calculated UV-Vis spectra of coumaroyl acylated 10-H pyranoanthocyanins (**123-128**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

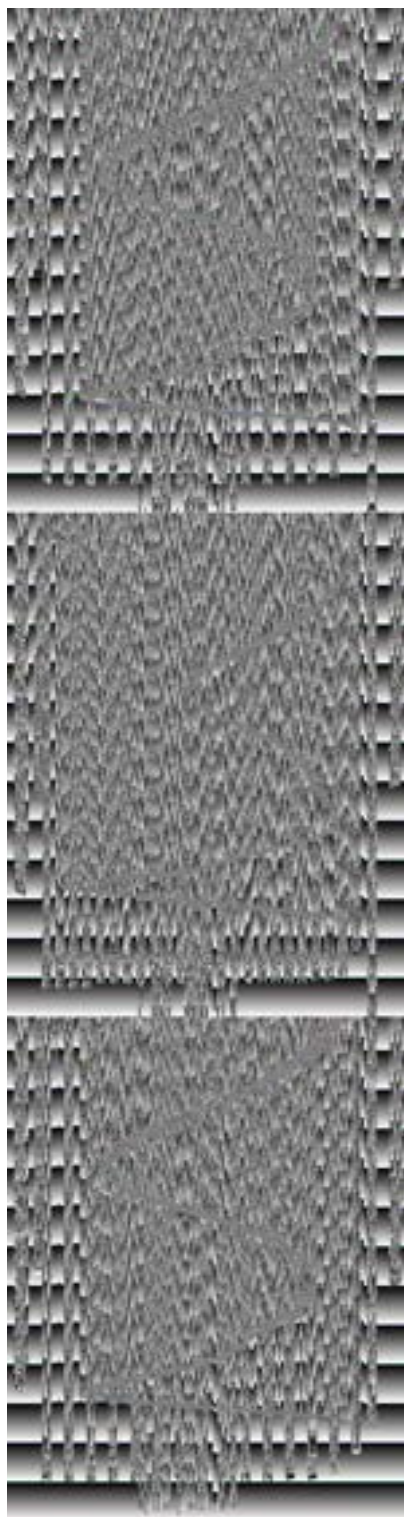


Figure D.27: Calculated UV-Vis spectra of acylated vinylcatechol pyranoanthocyanins (**87-92**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

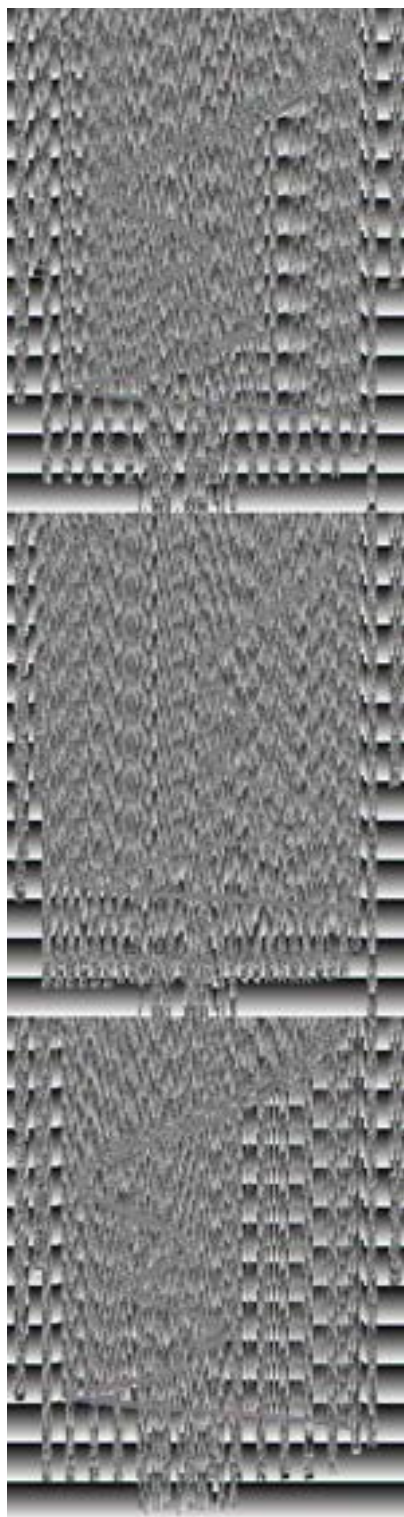


Figure D.28: Calculated UV-Vis spectra of caffeeoyl acylated vinylcatechol pyranoanthocyanins (**111-116**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

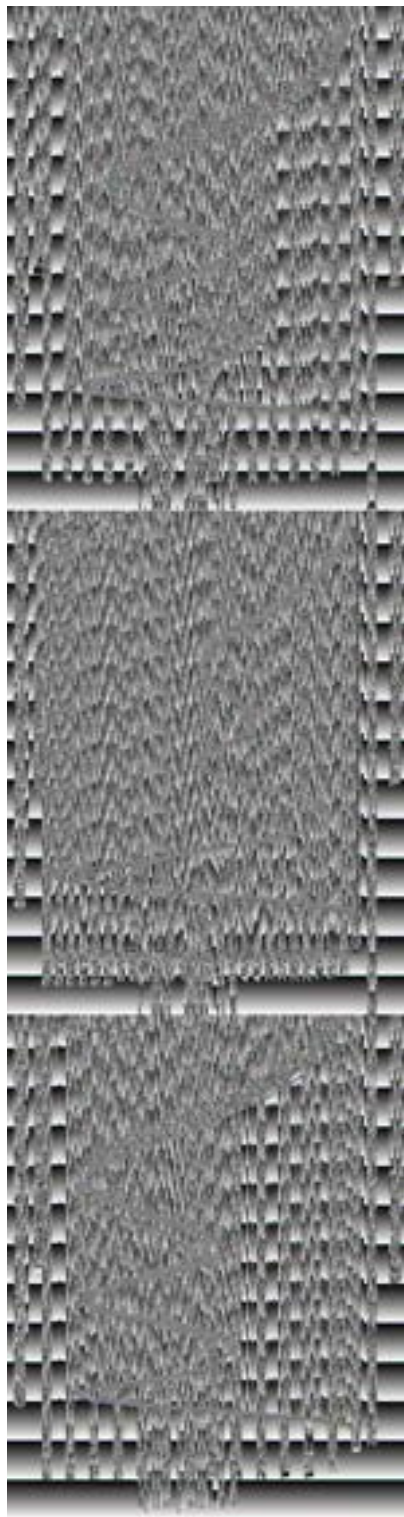


Figure D.29: Calculated UV-Vis spectra of coumaroyl acylated vinylcatechol pyranoanthocyanins (**135-140**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

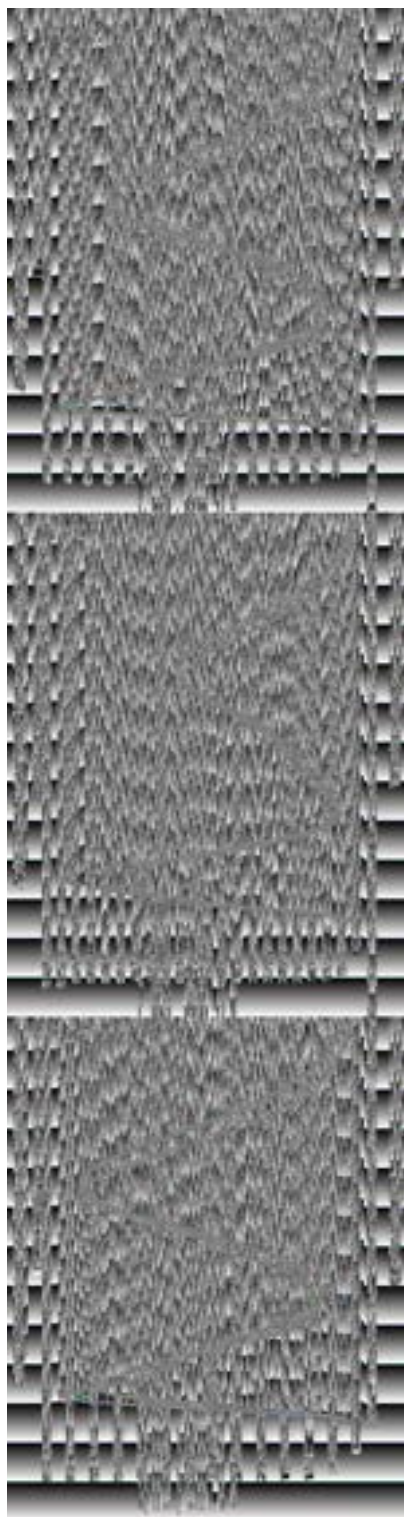


Figure D.30: Calculated UV-Vis spectra of acetyl acylated vinylphenol pyranoanthocyanins (**81-86**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

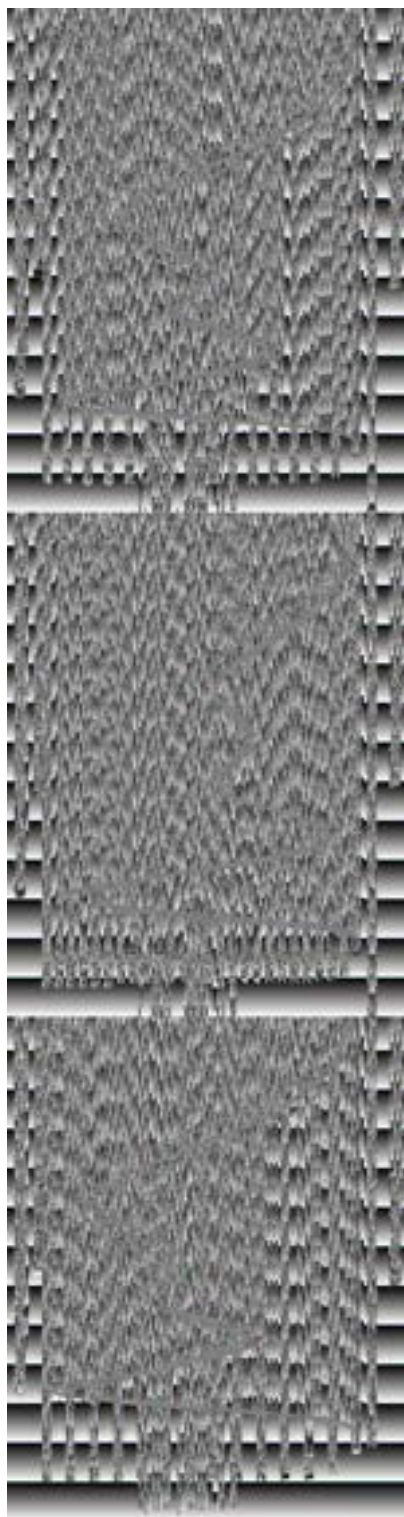


Figure D.31: Calculated UV-Vis spectra of caffeoyl acylated vinylphenol pyranoanthocyanins (**105-110**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.



Figure D.32: Calculated UV-Vis spectra of coumaroyl acylated vinylphenol pyranoanthocyanins (**129-134**) with B3LYP, CAM-B3LYP and PBE0 (6-311++G(d,p) basis set) with SMD solvation model and water as solvent.

Orbital Energies

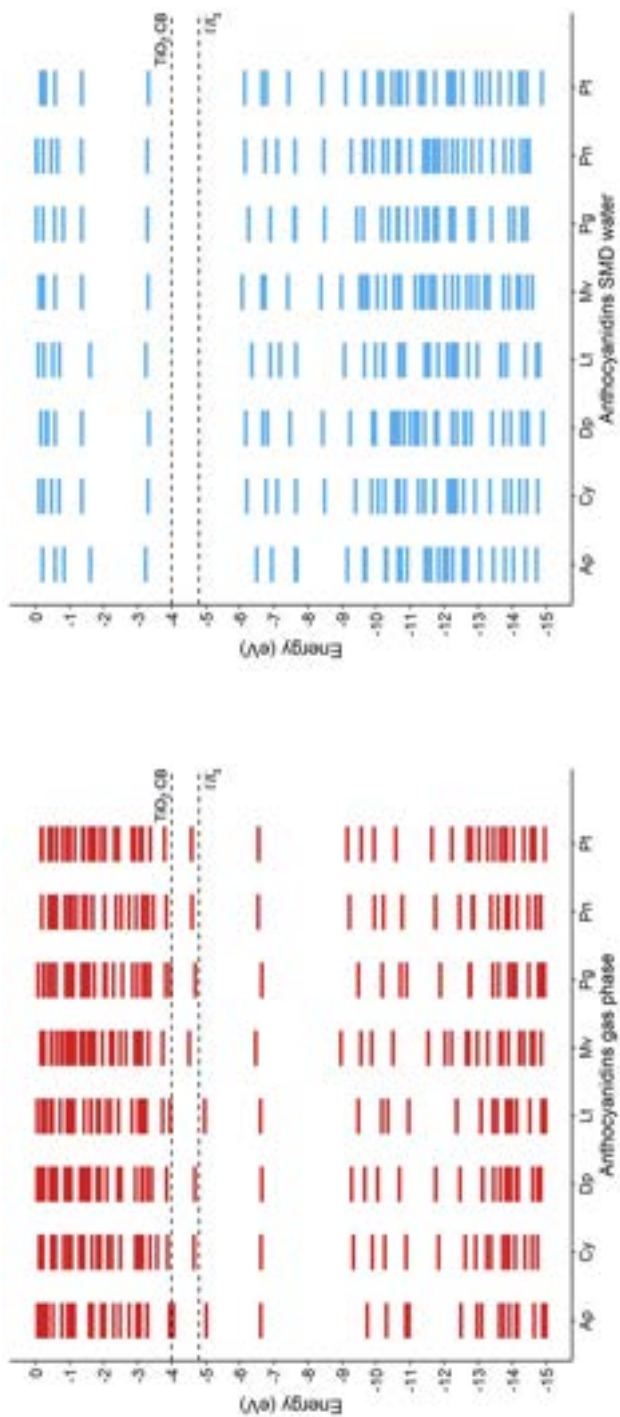


Figure D.33: Computed energy levels of anthocyanidins (1-8) in the gas phase and with SMD water model (B3LYP/6-311++G(d,p)). The dotted lines represent the energy levels of TiO₂ conduction band and the iodide/triiodide redox potential.

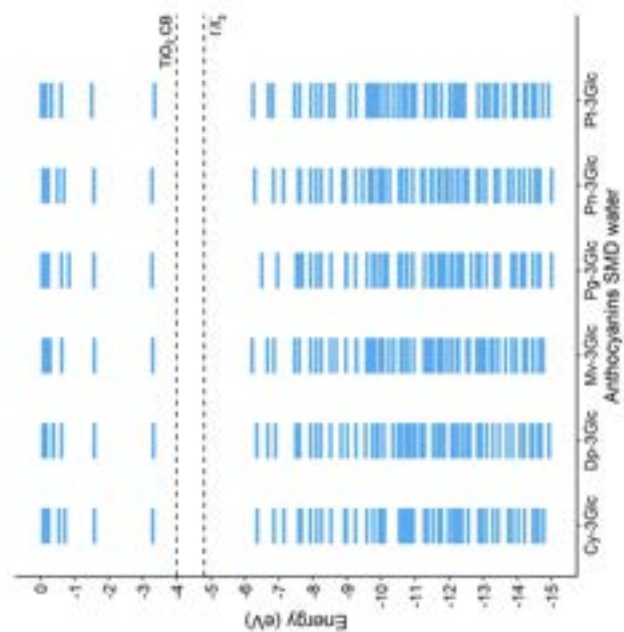


Figure D.34: Computed energy levels of anthocyanins (**9-14**) (B3LYP/6-311++G(d,p) with SMD water). The dotted lines represent the energy levels of TiO₂ conduction band and the iodide/triiodide redox potential.

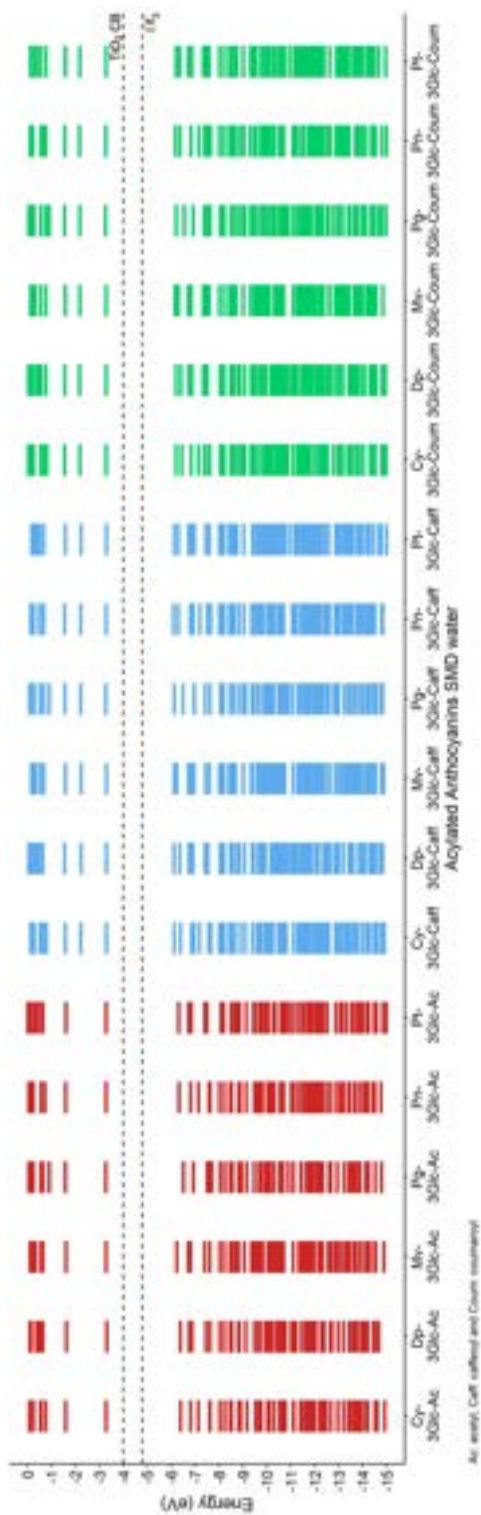


Figure D.35: Computed energy levels of acylated anthocyanins (Ac: **15-20**, Caff: **27-32** and Coum: **39-44**) (B3LYP/6-311++G(d,p) with SMD water). The dotted lines represent the energy levels of TiO₂ conduction band and the iodide/triiodide redox potential.



Figure D.37: Computed energy levels of acylated 10-carboxy pyrananthocyanins (Ac: **69-74**, Caff: **93-98** and Coum: **117-122**) (B3LYP/6-311++G(d,p) with SMD water). The dotted lines represent the energy levels of TiO₂ conduction band and the iodide/triiodide redox potential.

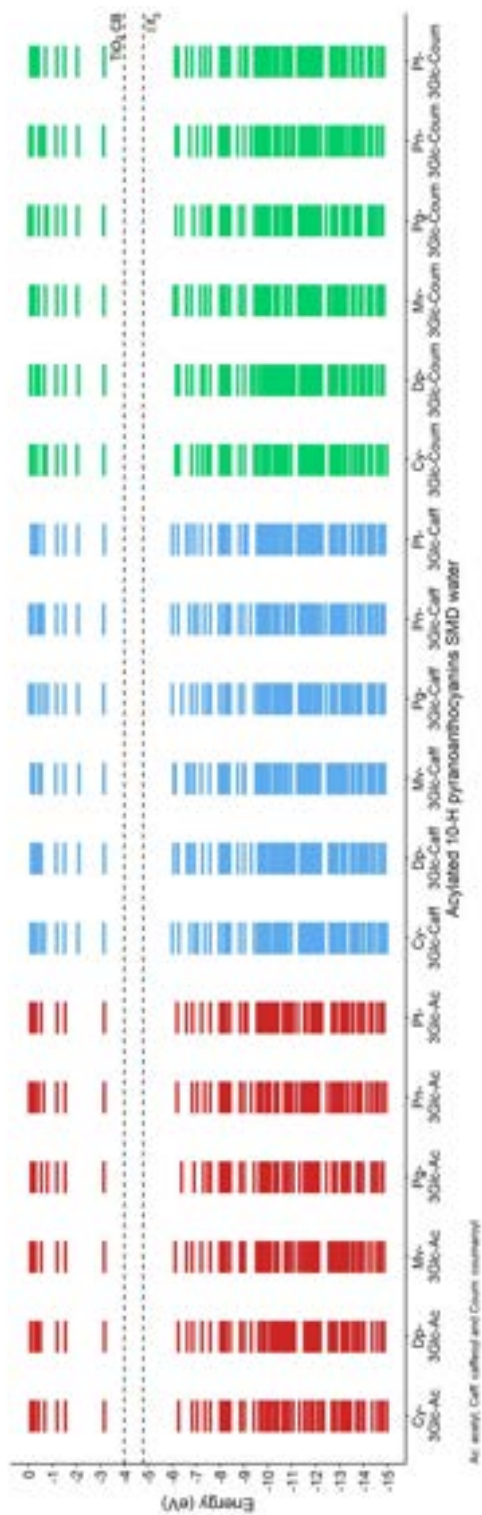


Figure D.38: Computed energy levels of acylated 10-H pyrananthocyanins (Ac: **75-80**, Caff: **99-104** and Coum: **123-128**) (B3LYP/6-311++G(d,p) with SMD water). The dotted lines represent the energy levels of TiO₂ conduction band and the iodide/triiodide redox potential.

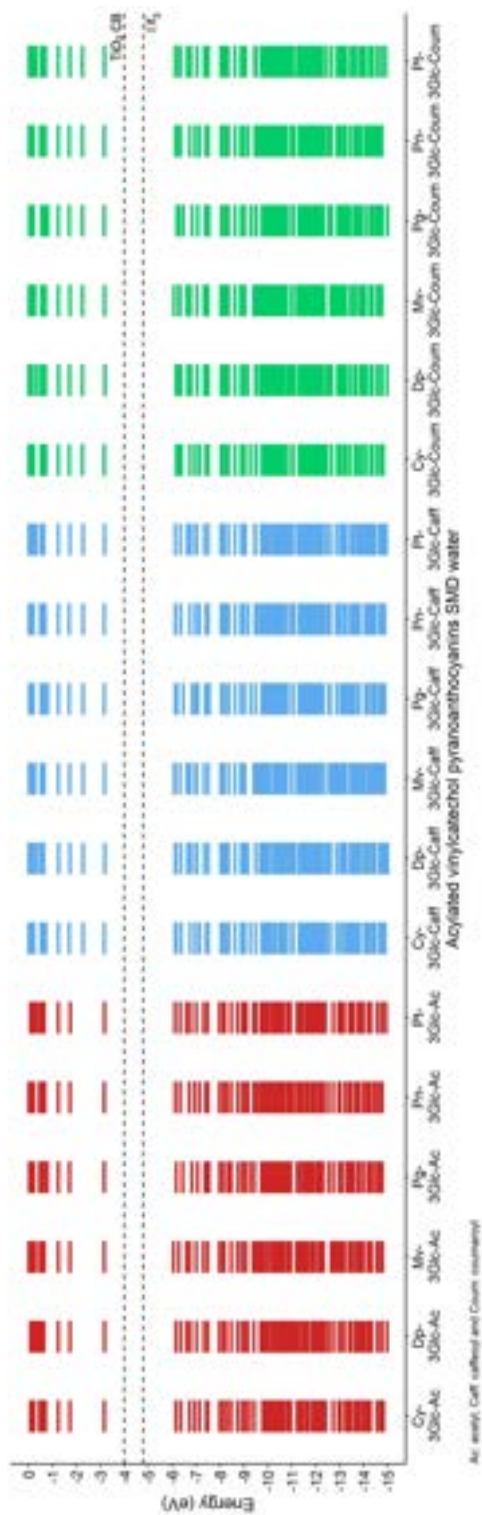


Figure D.39: Computed energy levels of acylated vinylcatechol pyrananthocyanins (Ac: **87-92**, Caff: **111-116** and Coum: **135-140**) (B3LYP/6-311++G(d,p) with SMD water). The dotted lines represent the energy levels of TiO₂ conduction band and the iodide/triiodide redox potential.

Chemical Moieties

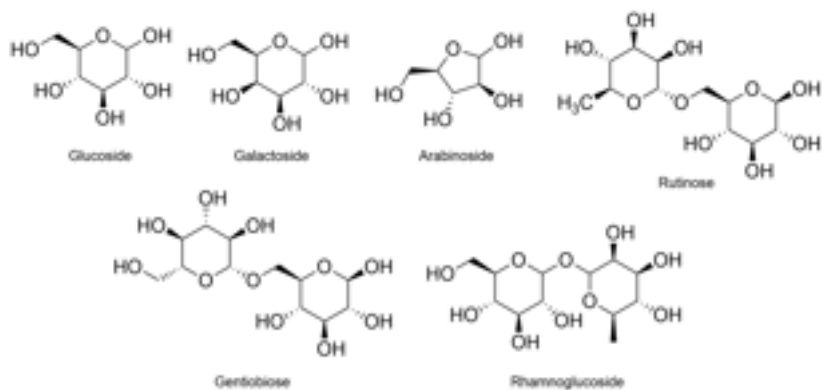


Figure D.40: Different sugar moieties detected with anthocyanins

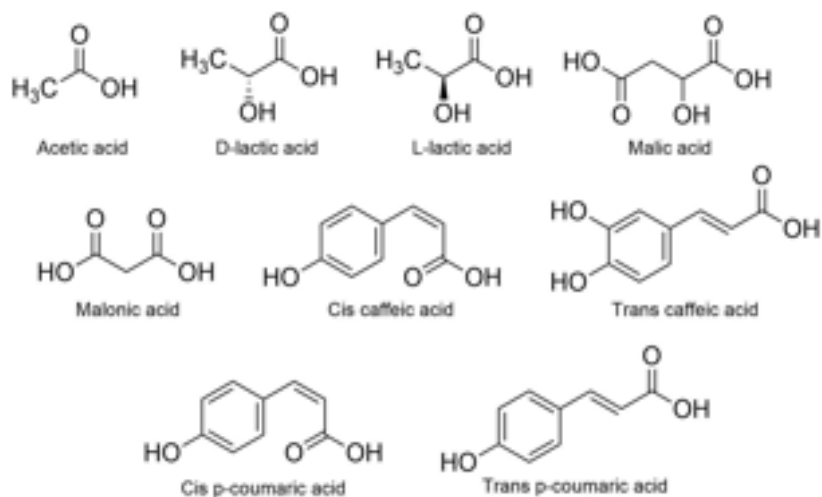
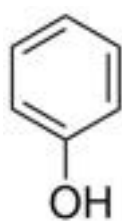
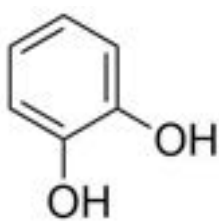


Figure D.41: Different aliphatic and aromatic (phenolic) acids that acylate the sugar moiety



Phenol

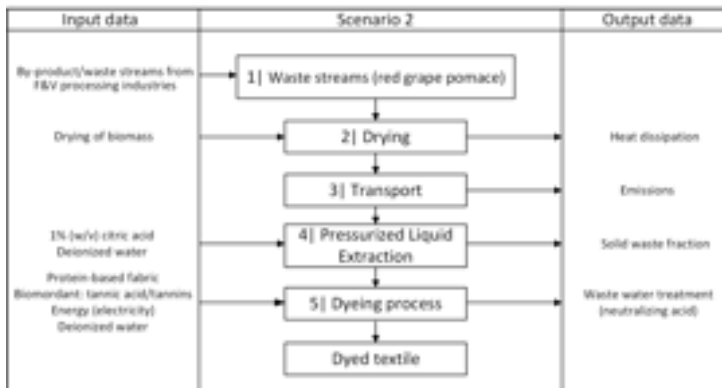
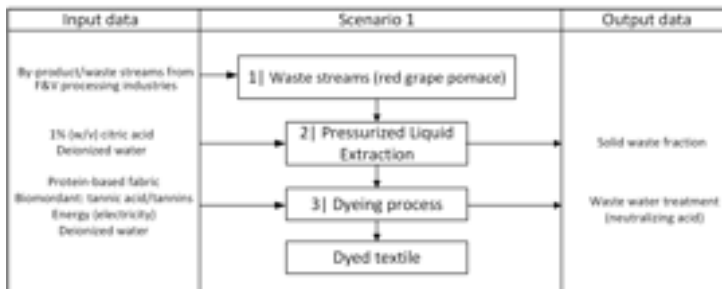


Catechol

Figure D.42: Different substituents encountered on pyranoanthocyanins

LCA of the Production of Naturally-Dyed Fabrics from Agro-Food Residues

The Different Explorative Scenarios for the LCA Analysis in Detail



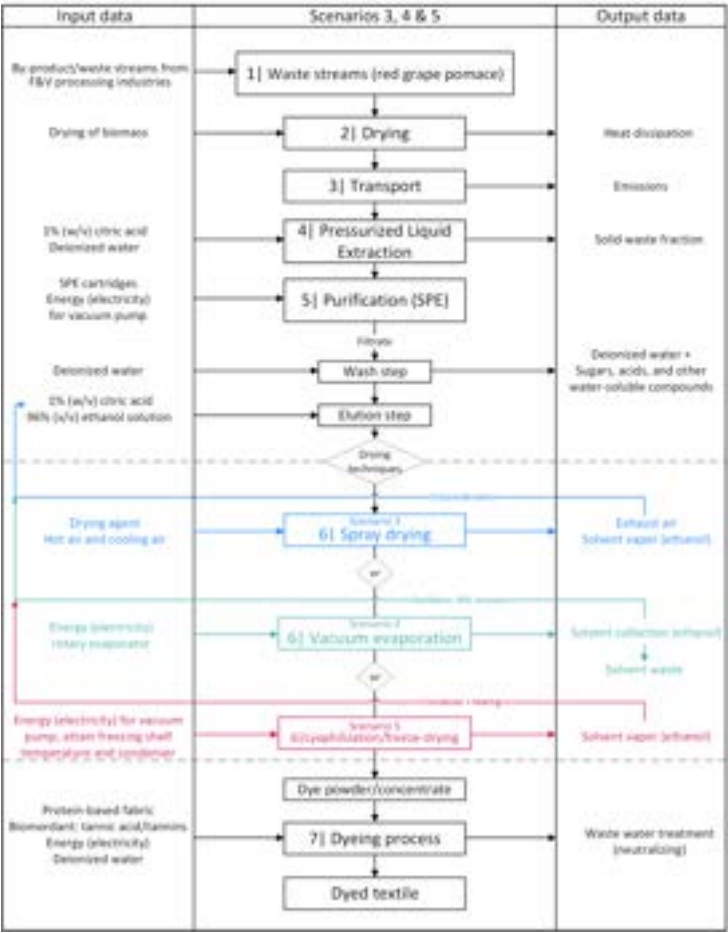
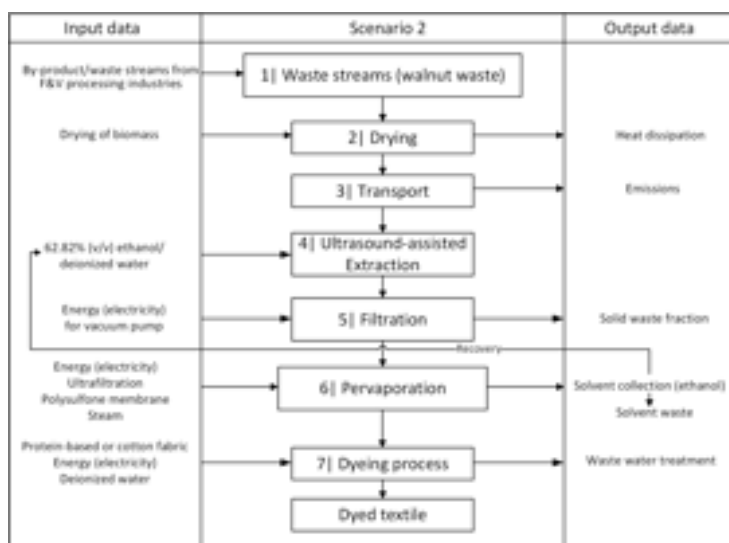
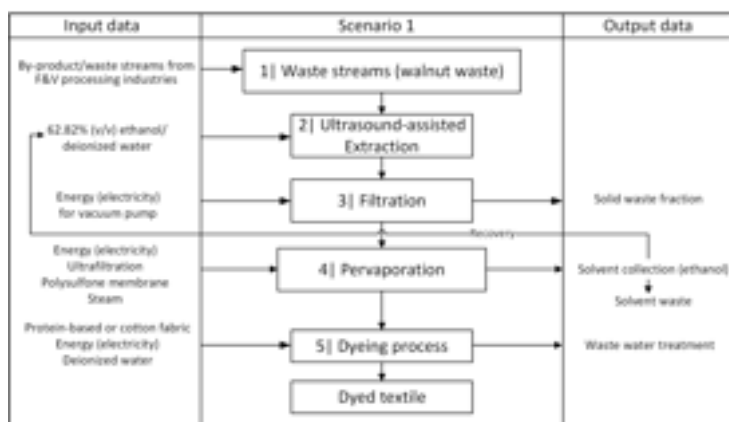


Figure E.1: The different explorative scenarios for the LCA analysis of the extraction and dyeing with anthocyanins.



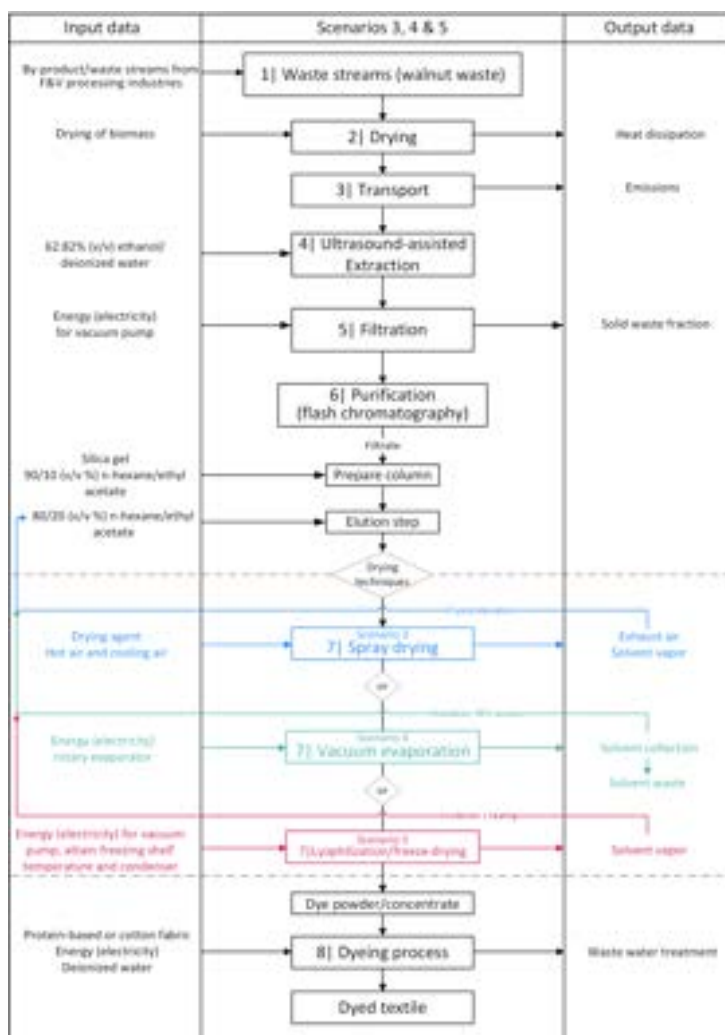
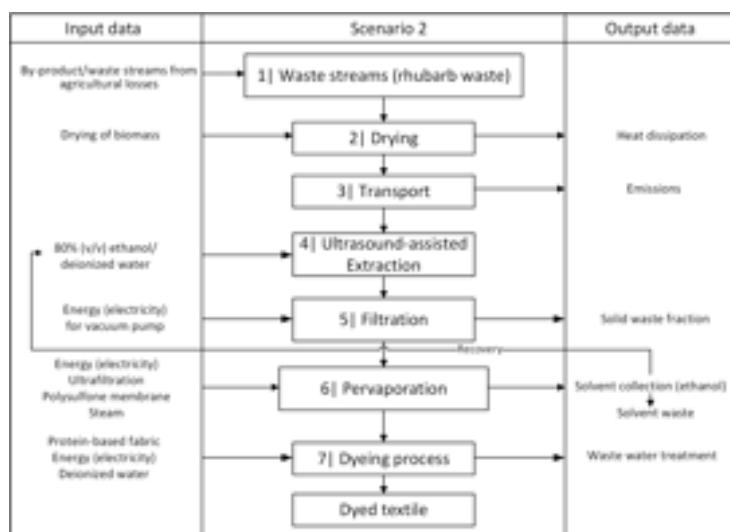
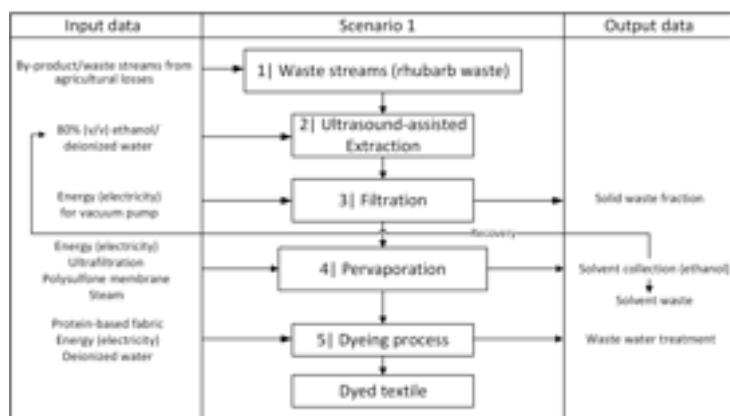


Figure E.2: The different explorative scenarios for the LCA analysis of the extraction and dyeing with naphthoquinones.



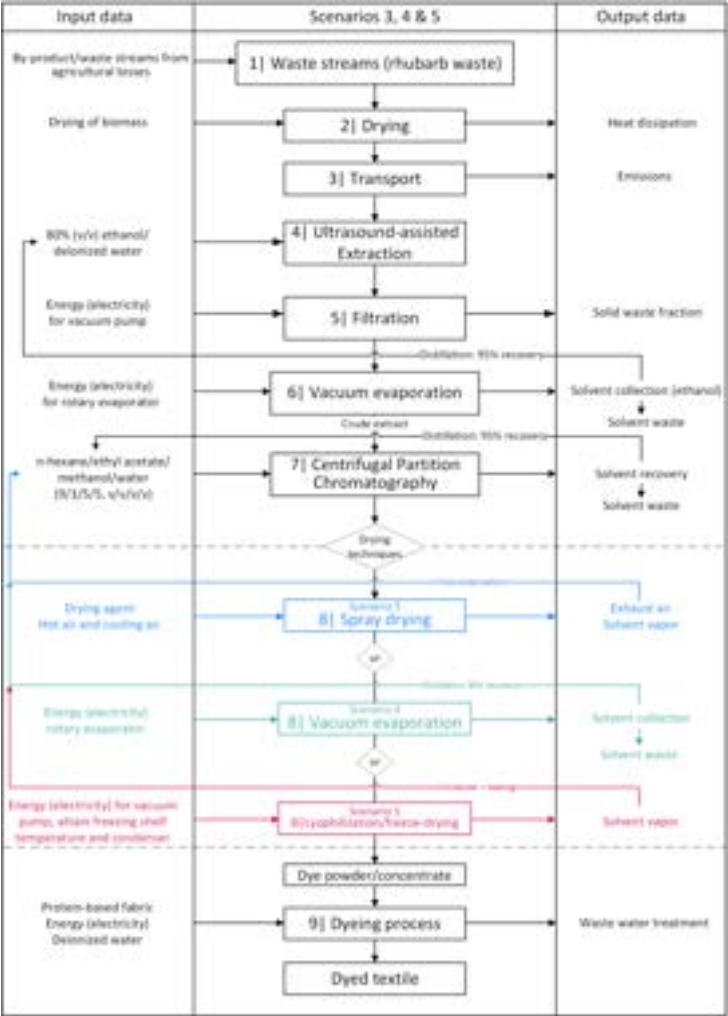
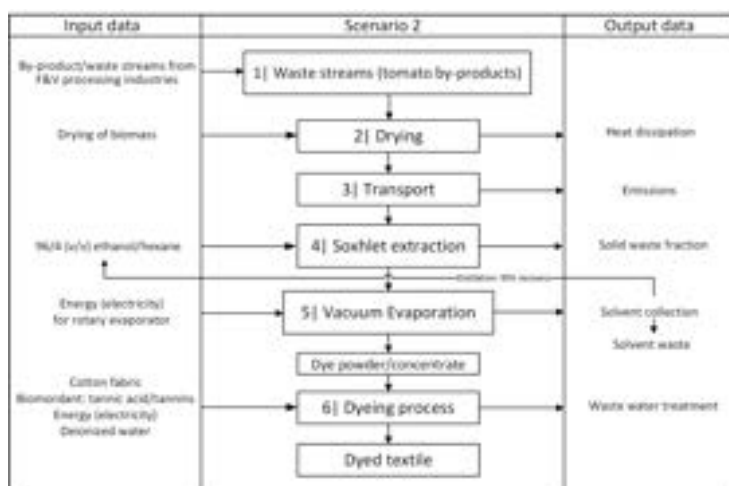
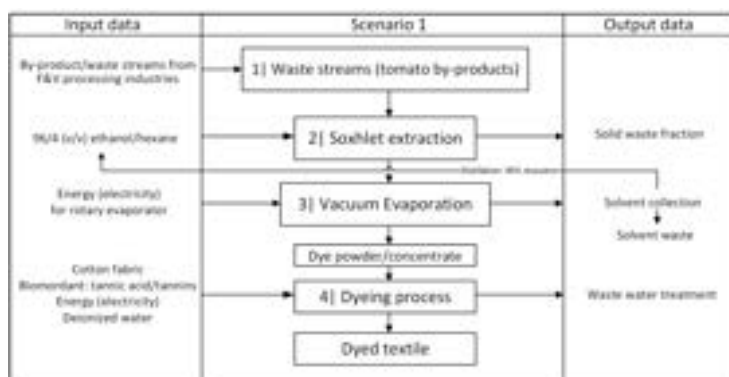


Figure E.3: The different explorative scenarios for the LCA analysis of the extraction and dyeing with anthraquinones.



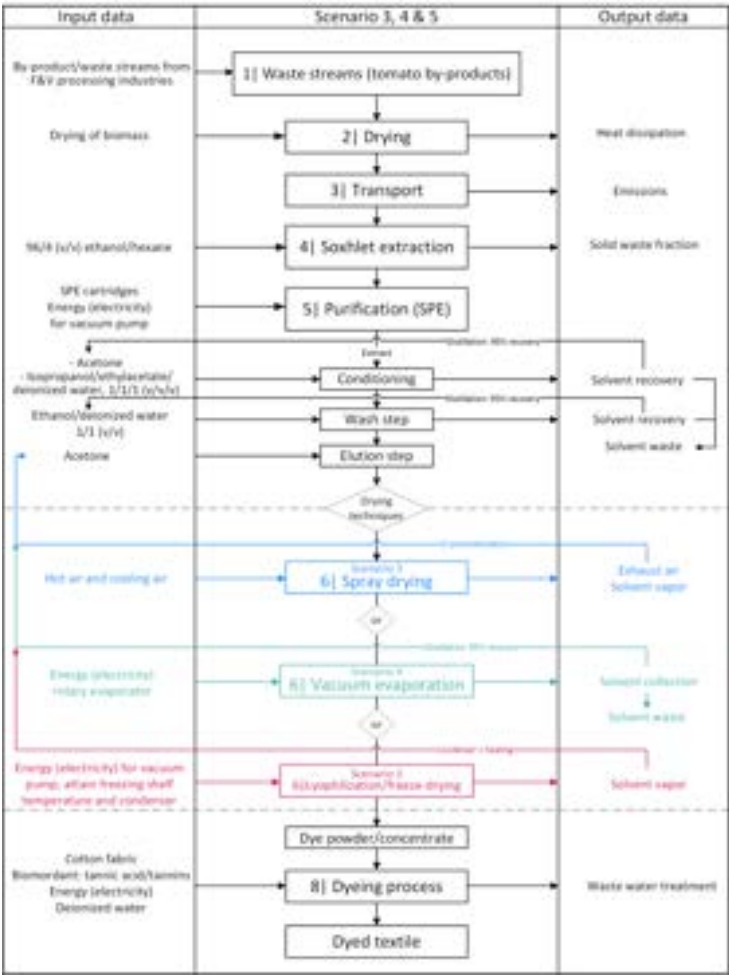


Figure E.4: The different explorative scenarios for the LCA analysis of the extraction and dyeing with carotenoids.

Data - LCA of the Extraction and Dyeing 1 m² Cotton with Anthocyanins

Table E.1: The amount of consumables used in the calculation of the life cycle assessment of dyeing 1 m² cotton with anthocyanins.

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Anthocyanin content in by-product	g/kg FW by-product			20.5			[74]
Amount of dye required for 1 m ² cotton at 12.5% owf	g			23.75			
Amount of by-product (wet)	kg	1.16	1.16	1.28	1.28	1.37	
Density grape pomace	kg/m ³	-		1330			[548]
Moisture content initial - Moisture content after drying	%	-		81.7 - 4.5			[549]
Mass of by-product after drying	kg	-	0.26	0.29	0.29	0.31	
Transport food processing industry - extraction site	km	-		114.75			[550]
Extraction material:liquid ratio	kg:L		1:3				[409]
Extraction solvent:							
Deionized water	L	3.48	0.79	0.87	0.87	0.94	
1% (w/v %) citric acid	kg	0.035	0.0079	0.0087	0.0087	0.0094	
Purification SPE Amberlite XAD 7 sorbent	kg	-	-	0.15	0.14	0.15	[409]
Electricity for SPE	kWh	-	-	0.30	0.30	0.32	[551]
Reusability SPE cartridge	times	-	-		100		[552]
Wash step: deionized water	L	-	-	4.04	4.03	4.33	
Elution step: acidified 96 (v/v %) ethanol/water mixture							
96 (v/v %) ethanol	L	-	-	0.25	0.25	0.27	
4 (v/v %) deionized water	L	-	-	0.010	0.010	0.011	
1% (w/v %) citric acid	kg	-	-	0.0026	0.0026	0.0028	
Solvent recovery EtOH	%	-	-		95		
Compound recovery SPE	%	-	-		90		
Spray drying	kWh	-	-	0.13	-	-	[553]
Cryocondensation: energy consumption	kWh	-	-	0.000016	-	-	[554]
Cryocondensation: liquid N ₂	kg	-	-	0.000013	-	-	[554]
Drying agent (maltodextrin)	kg	-	-	0.055	-	0.055	[555]
Recovery spray drying	%			99.8			[556]
Rotary evaporator	kWh	-	-	-	0.051	-	
Solvent recovery EtOH (95%)	kWh	-	-		0.0075	-	
Freeze-drying	kWh	-	-	-	-	0.74	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density cotton	g/m ²			190			
Dyeing	kWh			0.25			[558]
Biomordant: tannic acid/tannins at 50% owf	kg			0.095			
Dyed cotton fabric	m ²			1			
Waste water treatment	L	3.48	0.79	13.54	13.54	13.85	

Table E.2: The collected data for the life cycle assessment of dyeing 1 m² cotton with anthocyanins

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Anthocyanin content in by-product	g/kg FW by-product			20.5			[74]
Amount of dye required for 1 m ² cotton at 12.5% owf	g			23.75			
Amount of by-product (wet)	kg	1.16	1.16	1.28	1.28	1.37	
Drying biomass	Ecpts	-	0.049	0.054	0.054	0.058	
Density grape pomace	kg/m ³	-		1330			[548]
Moisture content initial - Moisture content after drying	%	-	81.7 - 4.5				[549]
Transport food processing industry - extraction site	Ecpts	-	0.00054	0.00060	0.00060	0.00064	[550]
Extraction material:liquid ratio	kg:L			1:3			[409]
Extraction energy consumption	Ecpts	0.0048	0.0011	0.0012	0.0012	0.0013	[559]
Extraction solvent:							
Deionized water	Ecpts	0.00055	0.00013	0.00014	0.00014	0.00015	
1% (w/v %) citric acid	Ecpts	0.00065	0.00015	0.00016	0.00016	0.00018	
Purification SPE Amberlite XAD 7 sorbent	Ecpts	-	-	0.00028	0.00028	0.00030	[409]
Electricity for SPE	Ecpts	-	-	0.0070	0.0070	0.0075	[551]
Reusability SPE cartridge	Times	-	-		100		[552]
Wash step: deionized water	Ecpts	-	-	0.00063	0.00063	0.00068	
Elution step: acidified 96/4 (v/v %) ethanol/water mixture							
96 (v/v %) ethanol	Ecpts	-	-	0.0011	0.0011	0.0012	
4 (v/v %) deionized water	Ecpts	-	-	0.0000016	0.0000016	0.0000018	
1% (w/v %) citric acid	Ecpts	-	-	0.000048	0.000048	0.000052	
Solvent recovery EtOH	%	-	-		95		
Compound recovery SPE	%	-	-		90		
Spray drying	Ecpts	-	-	0.0031	-	-	[553]
Cryocondensation: energy consumption	Ecpts	-	-	0.00000037	-	-	[554]
Cryocondensation: liquid N ₂	Ecpts	-	-	0.00000074	-	-	[554]
Drying agent (maltodextrin)	Ecpts	-	-	0.018	-	0.018	[555]
Recovery spray drying	%	-	-	99.8			[556]
Rotary evaporator	Ecpts	-	-	-	0.0012	-	
Solvent recovery EtOH (95%)	Ecpts	-	-	-	0.00017	-	
Freeze-drying	Ecpts	-	-	-	-	0.017	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density cotton	g/m ²			190			
Dyeing	Ecpts			0.0057			[558]
Biomordant: tannic acid/tannins at 50% owf	Ecpts			0.030			
Dyed cotton fabric	m ²			1			
Waste water treatment	Ecpts	0.000094	0.000021	0.00037	0.00037	0.00037	
Total	Ecpts	0.042	0.087	0.12	0.10	0.14	

Data - LCA of the Extraction and Dyeing 1 m² Wool with Anthocyanins

Table E.3: The amount of consumables used in the calculation of the life cycle assessment of dyeing 1 m² wool with anthocyanins.

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Anthocyanin content in by-product	g/kg FW by-product			20.5			[74]
Amount of dye required for 1 m ² wool at 12.5% owf	g			15.63			
Amount of by-product (wet)	kg	0.76	0.76	0.84	0.84	0.90	
Density grape pomace	kg/m ³	-		1330			[548]
Moisture content initial - Moisture content after drying	%	-		81.7 - 4.5			[549]
Mass of by-product after drying	kg	-	0.17	0.19	0.19	0.21	
Transport food processing industry - extraction site	km	-		114.75			[550]
Extraction material:liquid ratio	kg:L			1:3			[409]
Extraction solvent:							
Deionized water	L	2.29	0.52	0.58	0.57	0.62	
1% (w/v %) citric acid	kg	0.023	0.0052	0.0058	0.0057	0.0062	
Purification SPE Amberlite XAD 7 sorbent	kg	-	-	0.10	0.095	0.10	[409]
Electricity for SPE	kWh	-	-	0.20	0.20	0.21	[551]
Reusability SPE cartridge	Times	-	-		100		[552]
Wash step: deionized water	L	-	-	2.66	2.65	2.85	
Elution step: acidified 96 (v/v %) ethanol/water mixture							
96 (v/v %) ethanol	L	-	-	0.16	0.16	0.18	
4 (v/v %) deionized water	L	-	-	0.0068	0.0068	0.0073	
1% (w/v %) citric acid	kg	-	-	0.0017	0.0017	0.0018	
Solvent recovery EtOH	%	-	-		95		
Compound recovery SPE	%	-	-		90		
Spray drying	kWh	-	-	0.087	-	-	[553]
Cryocondensation: energy consumption	kWh	-	-	0.000011	-	-	[554]
Cryocondensation: liquid N ₂	kg	-	-	0.000013	-	-	[554]
Drying agent (maltodextrin)	kg	-	-	0.036	-	0.036	[555]
Recovery spray drying	%			99.8			[556]
Rotary evaporator	kWh	-	-	-	0.034	-	
Solvent recovery EtOH (95%)	kWh	-	-	-	0.0049	-	
Freeze-drying	kWh	-	-	-	-	0.49	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density wool	g/m ²			125			
Dyeing	kWh			0.25			[558]
Biomordant: tannic acid/tannins at 50% owf	kg			0.063			
Dyed wool fabric	m ²			1			
Waste water treatment	L	2.29	0.52	8.91	8.91	9.11	

Table E.4: The collected data for the life cycle assessment of dyeing 1 m² wool with anthocyanins.

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Anthocyanin content in by-product	g/kg FW by-product			20.5			[74]
Amount of dye required for 1 m ² wool at 12.5% owf	g			15.63			
Amount of by-product (wet)	kg	0.76	0.76	0.84	0.84	0.90	
Drying biomass	Ecpts	-	0.032	0.036	0.036	0.038	
Density grape pomace	kg/m ³	-		1330			[548]
Moisture content initial - Moisture content after drying	%	-		81.7 - 4.5			[549]
Transport food processing industry - extraction site	Ecpts	-	0.00036	0.00040	0.00039	0.00042	[550]
Extraction material:liquid ratio	kg:L			1:3			[409]
Extraction energy consumption	Ecpts	0.0032	0.00072	0.00079	0.00079	0.00085	[559]
Extraction solvent:							
Deionized water	Ecpts	0.00036	0.000082	0.000090	0.000090	0.000097	
1% (w/v %) citric acid	Ecpts	0.00043	0.00010	0.00011	0.00011	0.00012	
Purification SPE Amberlite XAD 7 sorbent	Ecpts	-	-	0.00018	0.00018	0.00019	[409]
Electricity for SPE	Ecpts	-	-	0.0046	0.0046	0.0049	[551]
Reusability SPE cartridge	Times	-	-		100		[552]
Wash step: deionized water	Ecpts	-	-	0.00042	0.00042	0.00045	
Elution step: acidified 96/4 (v/v %) ethanol/water mixture							
96 (v/v %) ethanol	Ecpts	-	-	0.00075	0.00075	0.00080	
4 (v/v %) deionized water	Ecpts	-	-	0.0000011	0.0000011	0.0000012	
1% (w/v %) citric acid	Ecpts	-	-	0.000032	0.000032	0.000034	
Solvent recovery EtOH	%	-	-		95		
Compound recovery SPE	%	-	-		90		
Spray drying	Ecpts	-	-	0.0020	-	-	[553]
Cryocondensation: energy consumption	Ecpts	-	-	0.00000024	-	-	[554]
Cryocondensation: liquid N ₂	Ecpts	-	-	0.00000074	-	-	[554]
Drying agent (maltodextrin)	Ecpts	-	-	0.012	-	0.012	[555]
Recovery spray drying	%			99.8			[556]
Rotary evaporator	Ecpts	-	-	-	0.00078	-	
Solvent recovery EtOH (95%)	Ecpts	-	-	-	0.00011	-	
Freeze-drying	Ecpts	-	-	-	-	0.011	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density wool	g/m ²			125			
Dyeing	Ecpts			0.0057			[558]
Biomordant: tannic acid/tannins at 50% owf	Ecpts			0.020			
Dyed wool fabric	m ²			1			
Waste water treatment	Ecpts	0.000062	0.000014	0.00024	0.00024	0.00025	
Total	Ecpts	0.030	0.059	0.082	0.070	0.095	

Data - LCA of the Extraction and Dyeing 1 m² Cotton with Naphthoquinones

Table E.5: The amount of consumables used in the calculation of the life cycle assessment of dyeing 1 m² cotton with naphthoquinones.

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Quinone content in by-product	g/kg FW by-product			23			[417]
Amount of dye required for 1 m ² cotton at 12.5% owf	g			23.75			
Amount of by-product (wet)	kg	1.03	1.03	1.06	1.06	1.15	
Density walnut by-products	kg/m ³			875			[560]
Moisture content initial - Moisture content after drying	%	-		87.7 - 8.0			[419]
Mass of by-product after drying	kg	-	0.21	0.22	0.22	0.23	
Transport food processing industry - extraction site	km	-		114.75			[550]
Extraction material:liquid ratio	kg:L			1:5			[423]
Extraction solvent:							
62.82 v/v% ethanol	L	3.24	0.66	0.68	0.68	0.73	
37.18 v/v% deionized water	L	1.92	0.39	0.40	0.40	0.43	
Microfiltration	kWh	0.010	0.0021	0.0021	0.0021	0.0023	[561]
Pervaporation							
Ultrafiltration	kWh	0.016	0.0033	-	-	-	[561]
Polysulfone membrane	kg	0.35	0.35	-	-	-	[438, 562, 563]
Pumps	kWh	0.23	0.047	-	-	-	[564]
Steam at 1.8 bars	kg	0.42	0.085	-	-	-	[565]
Cooling water	L	0.064	0.013	-	-	-	[565]
Silica gel	kg	-	-	1.70	1.70	1.84	[425]
Electricity for flash chromatography	kWh	-	-	0.17	0.17	0.19	[551]
Reusability of column	times	-	-	100			[552]
Column solvent: 90 v/v % n-hexane/ethyl acetate mixture							
90 v/v % n-hexane	L	-	-	1.53	1.53	1.65	
10 v/v % ethyl acetate	L	-	-	0.17	0.17	0.18	
Elution step: 80 v/v % n-hexane/ethyl acetate mixture							
80 v/v % n-hexane	L	-	-	0.16	0.16	0.18	
20 v/v % ethyl acetate	L	-	-	0.041	0.041	0.044	
Solvent recovery	%	-	-	95			
Compound recovery	%	-	-	98			[566]
Spray drying	kWh	-	-	0.045	-	-	[553]
Cryocondensation: energy consumption	kWh	-	-	0.000014	-	-	[554]
Cryocondensation: liquid N ₂	kg	-	-	0.000013	-	-	[554]
Drying agent (maltodextrin)	kg	-	-	0.055	-	0.055	[555]
Recovery spray drying	%	-	-	99.8	-	-	[556]
Rotary evaporator	kWh	-	-	-	0.015	-	
Solvent recovery (95%)	kWh	-	-	-	0.0040	-	
Freeze-drying	kWh	-	-	-	-	0.59	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density cotton	g/m ²			190			
Dyeing	kWh			0.25			[558]
Dyed cotton fabric	m ²			1			
Waste water treatment	L	1.89	0.38	9.90	9.90	9.93	

Table E.6: The collected data for the life cycle assessment of dyeing 1 m² cotton with naphthoquinones.

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Quinone content in by-product	g/kg FW by-product			23			[417]
Amount of dye required for 1 m ² cotton at 12.5% owf	g			23.75			
Amount of by-product (wet)	kg	1.03	1.03	1.06	1.06	1.15	
Drying biomass	Ecpts	-	0.067	0.069	0.069	0.074	
Density walnut by-products	kg/m ³			875			[560]
Moisture content initial - Moisture content after drying	%	-			87.7 - 8.0		[419]
Transport food processing industry - extraction site	Ecpts	-	0.00043	0.00045	0.00045	0.00048	[550]
Extraction material:liquid ratio	kg:L			1:5			[423]
Extraction energy consumption	Ecpts	0.0043	0.00087	0.00089	0.00089	0.00096	
Extraction solvent:							
62.82 v/v% ethanol	Ecpts	0.015	0.0030	0.0031	0.0031	0.0033	
37.18 v/v% deionized water	Ecpts	0.00030	0.000061	0.000063	0.000063	0.000068	
Microfiltration	Ecpts	0.00024	0.000048	0.000049	0.000049	0.000053	[561]
Pervaporation							
Ultrafiltration	Ecpts	0.00037	0.000075	-	-	-	[561]
Polysulfone membrane (per 1000 L permeate)	Ecpts	0.00039	0.00039	-	-	-	[438, 562, 563]
Pumps	Ecpts	0.0053	0.0011	-	-	-	[564]
Steam at 1.8 bars	Ecpts	0.0085	0.0017	-	-	-	[565]
Cooling water	Ecpts	0.0000020	0.00000041	-	-	-	[565]
Silica gel	Ecpts	-	-	0.0033	0.0033	0.0035	[425]
Electricity for flash chromatography	Ecpts	-	-	0.0040	0.0040	0.0043	[551]
Reusability of column	Times	-	-		100		[552]
Column solvent: 90 v/v % n-hexane/ethyl acetate mixture							
90 v/v % n-hexane	Ecpts	-	-	0.0037	0.0037	0.0039	
10 v/v % ethyl acetate	Ecpts	-	-	0.0026	0.0026	0.0028	
Elution step: 80 v/v % n-hexane/ethyl acetate mixture							
80 v/v % n-hexane	Ecpts	-	-	0.00039	0.00039	0.00042	
20 v/v % ethyl acetate	Ecpts	-	-	0.00063	0.00063	0.00068	
Solvent recovery	%	-	-		95		
Compound recovery	%	-	-		98		[566]
Spray drying	Ecpts	-	-	0.0010	-	-	[553]
Cryocondensation: energy consumption	Ecpts	-	-	0.00000032	-	-	[554]
Cryocondensation: liquid N ₂	Ecpts	-	-	0.00000074	-	-	[554]
Drying agent (maltodextrin)	Ecpts	-	-	0.018	-	0.018	[555]
Recovery spray drying	%	-	-	99.8	-	-	[556]
Rotary evaporator	Ecpts	-	-	-	0.00034	-	
Solvent recovery (95%)	Ecpts	-	-	-	0.000092	-	
Freeze-drying	Ecpts	-	-	-	-	0.014	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density cotton	g/m ²			190			
Dyeing	Ecpts			0.0057			[558]
Dyed cotton fabric	m ²			1			
Waste water treatment	Ecpts	0.000051	0.000010	0.00027	0.00027	0.00027	
Total	Ecpts	0.040	0.080	0.11	0.094	0.13	

Data - LCA of the Extraction and Dyeing 1 m² Wool with Naphthoquinones

Table E.7: The amount of consumables used in the calculation of the life cycle assessment of dyeing 1 m² wool with naphthoquinones.

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Quinone content in by-product	g/kg FW by-product			23			[417]
Amount of dye required for 1 m ² wool at 12.5% owf	g			15.63			
Amount of by-product (wet)	kg	0.68	0.68	0.70	0.70	0.76	
Density walnut by-products	kg/m ³			875			[560]
Moisture content initial - Moisture content after drying	%	-		87.7 - 8.0			[419]
Mass of by-product after drying	kg	-	0.14	0.14	0.14	0.15	
Transport food processing industry - extraction site	km	-		114.75			[550]
Extraction material:liquid ratio	kg:L			1:5			[423]
Extraction solvent:							
62.82 v/v% ethanol	L	2.13	0.43	0.45	0.45	0.48	
37.18 v/v% deionized water	L	1.26	0.26	0.26	0.26	0.29	
Microfiltration	kWh	0.0067	0.0014	0.0014	0.0014	0.0015	[561]
Pervaporation							
Ultrafiltration	kWh	0.011	0.0021	-	-	-	[561]
Polysulfone membrane	kg	0.35	0.35	-	-	-	[438, 562, 563]
Pumps	kWh	0.15	0.031	-	-	-	[564]
Steam at 1.8 bars	kg	0.27	0.056	-	-	-	[565]
Cooling water	L	0.042	0.0086	-	-	-	[565]
Silica gel	kg	-	-	1.12	1.12	1.21	[425]
Electricity for flash chromatography	kWh	-	-	0.11	0.11	0.12	[551]
Reusability of column	Times	-	-		100		[552]
Column solvent: 90 v/v % n-hexane/ethyl acetate mixture							
90 v/v % n-hexane	L	-	-	1.01	1.01	1.09	
10 v/v % ethyl acetate	L	-	-	0.11	0.11	0.12	
Elution step: 80 v/v % n-hexane/ethyl acetate mixture							
80 v/v % n-hexane	L	-	-	0.11	0.11	0.12	
20 v/v % ethyl acetate	L	-	-	0.027	0.027	0.029	
Solvent recovery	%	-	-		95		
Compound recovery	%	-	-		98		[566]
Spray drying	kWh	-	-	0.029	-	-	[553]
Cryocondensation: energy consumption	kWh	-	-	0.0000091	-	-	[554]
Cryocondensation: liquid N ₂	kg	-	-	0.000013	-	-	[554]
Drying agent (maltodextrin)	kg	-	-	0.037	-	0.036	[555]
Recovery spray drying	%	-	-	99.8	-	-	[556]
Rotary evaporator	kWh	-	-	-	0.010-		
Solvent recovery (95%)	kWh	-	-	-	0.0026-		
Freeze-drying	kWh	-	-	-	-	0.39	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density wool	g/m ²			125			
Dyeing	kWh			0.25			[558]
Dyed wool fabric	m ²			1			
Waste water treatment	L	1.24	0.25	6.51	6.51	6.54	

Table E.8: The collected data for the life cycle assessment of dyeing 1 m² wool with naphthoquinones.

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Quinone content in by-product	g/kg FW by-product			23			[417]
Amount of dye required for 1 m ² wool at 12.5% owf	g			15.63			
Amount of by-product (wet)	kg	0.68	0.68	0.70	0.70	0.76	
Drying biomass	Ecpts	-	0.044	0.045	0.045	0.049	
Density walnut by-products	kg/m ³			875			[560]
Moisture content initial - Moisture content after drying	%	-		87.7 - 8.0			[419]
Transport food processing industry - extraction site	Ecpts	-	0.00028	0.00029	0.00029	0.00032	[550]
Extraction material:liquid ratio	kg:L			1:5			[423]
Extraction energy consumption	Ecpts	0.0028	0.00057	0.00059	0.00059	0.00063	
Extraction solvent:							
62.82 v/v% ethanol	Ecpts	0.0097	0.0020	0.0020	0.0020	0.0022	
37.18 v/v% deionized water	Ecpts	0.00020	0.000040	0.000041	0.000041	0.000045	
Microfiltration	Ecpts	0.00016	0.000032	0.000033	0.000033	0.000035	[561]
Pervaporation							
Ultrafiltration	Ecpts	0.00024	0.000049	-	-	-	[561]
Polysulfone membrane (per 1000 L permeate)	Ecpts	0.00039	0.00039	-	-	-	[438, 562, 563]
Pumps	Ecpts	0.0035	0.00071	-	-	-	[564]
Steam at 1.8 bars	Ecpts	0.0056	0.0011	-	-	-	[565]
Cooling water	Ecpts	0.0000013	0.00000027	-	-	-	[565]
Silica gel	Ecpts	-	-	0.0021	0.0021	0.0023	[425]
Electricity for flash chromatography	Ecpts	-	-	0.0026	0.0026	0.0029	[551]
Reusability of column	Times	-	-		100		[552]
Column solvent: 90 v/v % n-hexane/ethyl acetate mixture							
90 v/v % n-hexane	Ecpts	-	-	0.0024	0.0024	0.0026	
10 v/v % ethyl acetate	Ecpts	-	-	0.0017	0.0017	0.0019	
Elution step: 80 v/v % n-hexane/ethyl acetate mixture							
80 v/v % n-hexane	Ecpts	-	-	0.00026	0.00026	0.00028	
20 v/v % ethyl acetate	Ecpts	-	-	0.00041	0.00041	0.00044	
Solvent recovery	%	-	-		95		
Compound recovery	%	-	-		98		[566]
Spray drying	Ecpts	-	-	0.00068	-	-	[553]
Cryocondensation: energy consumption	Ecpts	-	-	0.00000021	-	-	[554]
Cryocondensation: liquid N ₂	Ecpts	-	-	0.00000074	-	-	[554]
Drying agent (maltodextrin)	Ecpts	-	-	0.012	-	0.012	[555]
Recovery spray drying	%	-	-	99.8	-	-	[556]
Rotary evaporator	Ecpts	-	-	-	0.00022	-	
Solvent recovery (95%)	Ecpts	-	-	-	0.000060	-	
Freeze-drying	Ecpts	-	-	-	-	0.0090	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density wool	g/m ²			125			
Dyeing	Ecpts			0.0057			[558]
Dyed wool fabric	m ²			1			
Waste water treatment	Ecpts	0.000034	0.0000068	0.00018	0.00018	0.00018	
Total	Ecpts	0.028	0.055	0.076	0.064	0.089	

Data - LCA of the Extraction and Dyeing 1 m² Cotton with Anthraquinones

Table E.9: The amount of consumables used in the calculation of the life cycle assessment of dyeing 1 m² cotton with anthraquinones.

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Anthraquinone content in by-product	g/kg FW by-product			4.53			[95]
Amount of dye required for 1 m ² cotton at 2% owf	g			3.8			
Amount of by-product (wet)	kg	0.84	0.84	0.87	0.87	0.93	
Density rhubarb by-products	kg/m ³			545			[567]
Moisture content initial - Moisture content after drying	%	-		75 - 8.0			
Mass of by-product after drying	kg	-	0.28	0.29	0.29	0.31	
Transport food processing industry - extraction site	km	-			114.75		[550]
Extraction material:liquid ratio	kg:L			1:5			[423, 424]
Extraction solvent:							
80 v/v% ethanol	L	3.36	1.11	1.14	1.14	1.23	
20 v/v% deionized water	L	0.84	0.28	0.29	0.29	0.31	
Microfiltration	kWh	0.0083	0.0027	0.0028	0.0028	0.0031	[561]
Pervaporation							
Ultrafiltration	kWh	0.017	0.0055	-	-	-	[561]
Polysulfone membrane	kg	0.35	0.35	-	-	-	[438, 562, 563]
Pumps	kWh	0.24	0.079	-	-	-	[564]
Steam at 1.8 bars	kg	0.43	0.14	-	-	-	[565]
Cooling water	L	0.066	0.022	-	-	-	[565]
Rotary evaporator before purification	kWh	-	-	0.38	0.38	0.41	
Solvent recovery (95%)	kWh	-	-	0.036	0.036	0.038	
Centrifugal Partition Chromatography (CPC)							
Crude extract	kg	-	-	0.26	0.26	0.28	[60, 568]
Column stat. phase: n-hexane	L	-	-	14.54	14.54	15.70	[569]
Column stat. phase: ethyl acetate	L	-	-	1.62	1.62	1.74	
Sample preparation: n-hexane	L	-	-	1.16	1.16	1.26	
Sample preparation: ethyl acetate	L	-	-	0.13	0.13	0.14	
Sample preparation: methanol	L	-	-	0.65	0.65	0.70	
Sample preparation: water	L	-	-	0.65	0.65	0.70	
Elution: n-hexane	L	-	-	4.88	4.88	5.27	
Elution: ethyl acetate	L	-	-	0.54	0.54	0.59	
Elution: methanol	L	-	-	2.71	2.71	2.93	
Elution: water	L	-	-	2.71	2.71	2.93	
Energy consumption CPC	kWh	-	-	0.35	0.35	0.35	[570]
Solvent recovery (95%)	kWh	-	-	0.071	0.071	0.076	
Compound recovery	%	-	-		98		
Spray drying	kWh	-	-	0.79	-	-	[553]
Cryocondensation: energy consumption	kWh	-	-	0.00041	-	-	[554]
Cryocondensation: liquid N ₂	kg	-	-	0.000013	-	-	[554]
Drying agent (maltodextrin)	kg	-	-	0.0089	-	0.0089	[555]
Recovery spray drying	%	-	-	99.8	-	-	[556]
Rotary evaporator after CPC purification	kWh	-	-	-	8.34	-	
Solvent recovery (95%)	kWh	-	-	-	0.16	-	
Freeze-drying	kWh	-	-	-	-	17.56	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density cotton	g/m ²			190			
Dyeing	kWh			0.25			[558]
Dyed cotton fabric	m ²			1			
Waste water treatment	L	0.83	0.27	12.86	12.86	13.13	

Table E.10: The collected data for the life cycle assessment of dyeing 1 m² cotton with anthraquinones.

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Anthraquinone content in by-product	g/kg FW by-product			4.53			[95]
Amount of dye required for 1 m ² cotton at 2% owf	g			3.8			
Amount of by-product (wet)	kg	0.84	0.84	0.87	0.87	0.93	
Drying biomass	Ecpts	-	0.087	0.090	0.090	0.097	
Density rhubarb by-products	kg/m ³			545			[560]
Moisture content initial - Moisture content after drying	%	-		75 - 8.0			
Transport food processing industry - extraction site	Ecpts	-	0.00057	0.00059	0.00059	0.00064	[550]
Extraction material:liquid ratio	kg:L			1:5			[423, 424]
Extraction energy consumption	Ecpts	0.0035	0.0011	0.0012	0.0012	0.0013	
Extraction solvent:							
80 v/v% ethanol	Ecpts	0.015	0.0051	0.0052	0.0052	0.005630	
20 v/v% deionized water	Ecpts	0.00013	0.000044	0.000045	0.000045	0.000048	
Microfiltration	Ecpts	0.00019	0.000063	0.000065	0.000065	0.000071	[561]
Pervaporation							
Ultrafiltration	Ecpts	0.00038	0.00013	-	-	-	[561]
Polysulfone membrane (per 1000 L permeate)	Ecpts	0.00039	0.00039	-	-	-	[438, 562, 563]
Pumps	Ecpts	0.0055	0.0018	-	-	-	[564]
Steam at 1.8 bars	Ecpts	0.0087	0.0029	-	-	-	[565]
Cooling water	Ecpts	0.0000021	0.00000069	-	-	-	[565]
Rotary evaporator before purification	Ecpts	-	-	0.0087	0.0087	0.0094	
Solvent recovery (95%)	Ecpts	-	-	0.00082	0.00082	0.00089	
Centrifugal Partition Chromatography (CPC)							[60, 568]
Crude extract	kg	-	-	0.26	0.26	0.28	[569]
Column stat. phase: n-hexane	Ecpts	-	-	0.035	0.035	0.038	
Column stat. phase: ethyl acetate	Ecpts	-	-	0.025	0.025	0.027	
Sample preparation: n-hexane	Ecpts	-	-	0.0028	0.0028	0.0030	
Sample preparation: ethyl acetate	Ecpts	-	-	0.0020	0.0020	0.0021	
Sample preparation: methanol	Ecpts	-	-	0.0030	0.0030	0.0032	
Sample preparation: water	Ecpts	-	-	0.00010	0.00010	0.00011	
Elution: n-hexane	Ecpts	-	-	0.012	0.012	0.013	
Elution: ethyl acetate	Ecpts	-	-	0.0083	0.0083	0.0090	
Elution: methanol	Ecpts	-	-	0.012	0.012	0.013	
Elution: water	Ecpts	-	-	0.00043	0.00043	0.00046	
Energy consumption CPC	Ecpts	-	-	0.0080	0.0080	0.0080	[570]
Solvent recovery	Ecpts	-	-	0.0016	0.0018	0.0018	
Compound recovery	%	-	-		98		
Spray drying	Ecpts	-	-	0.018	-	-	[553]
Cryocondensation: energy consumption	Ecpts	-	-	0.0000096	-	-	[554]
Cryocondensation: liquid N ₂	Ecpts	-	-	0.00000074	-	-	[554]
Drying agent (maltodextrin)	Ecpts	-	-	0.0028	-	0.0028	[555]
Recovery spray drying	%	-	-	99.8	-	-	[556]
Rotary evaporator after CPC purification	Ecpts	-	-	-	0.19	-	
Solvent recovery (95%)	Ecpts	-	-	-	0.0038	-	
Freeze-drying	Ecpts	-	-	-	-	0.41	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density cotton	g/m ²			190			
Dyeing	Ecpts			0.0057			[558]
Dyed cotton fabric	m ²			1			
Waste water treatment	Ecpts	0.000022	0.0000074	0.00035	0.00035	0.00035	
Total	Ecpts	0.040	0.11	0.24	0.42	0.65	

Data - LCA of the Extraction and Dyeing 1 m² Wool with Anthraquinones

Table E.11: The amount of consumables used in the calculation of the life cycle assessment of dyeing 1 m² wool with anthraquinones.

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Anthraquinone content in by-product	g/kg FW by-product			4.53			[95]
Amount of dye required for 1 m ² wool at 2% owf	g			2.5			
Amount of by-product (wet)	kg	0.55	0.55	0.57	0.57	0.61	
Density rhubarb by-products	kg/m ³			545			[567]
Moisture content initial - Moisture content after drying	%	-		75 - 8.0			
Mass of by-product after drying	kg	-	0.18	0.19	0.19	0.31	
Transport food processing industry - extraction site	km	-			114.75		[550]
Extraction material:liquid ratio	kg:L			1:5			[423, 424]
Extraction solvent:							
80 v/v% ethanol	L	2.21	0.73	0.75	0.75	0.81	
20 v/v% deionized water	L	0.55	0.18	0.19	0.19	0.20	
Microfiltration	kWh	0.0055	0.0018	0.0019	0.0019	0.0020	[561]
Pervaporation							
Ultrafiltration	kWh	0.011	0.0036	-	-	-	[561]
Polysulfone membrane	kg	0.35	0.35	-	-	-	[438, 562, 563]
Pumps	kWh	0.16	0.052	-	-	-	[564]
Steam at 1.8 bars	kg	0.28	0.094	-	-	-	[565]
Cooling water	L	0.044	0.014	-	-	-	[565]
Rotary evaporator before purification	kWh	-	-	0.25	0.25	0.27	
Solvent recovery (95%)	kWh	-	-	0.023	0.023	0.025	
Centrifugal Partition Chromatography (CPC)							[60, 568]
Crude extract	kg	-	-	0.17	0.17	0.18	[569]
Column stat. phase: n-hexane	L	-	-	9.56	9.56	10.33	
Column stat. phase: ethyl acetate	L	-	-	1.06	1.06	1.15	
Sample preparation: n-hexane	L	-	-	0.77	0.77	0.83	
Sample preparation: ethyl acetate	L	-	-	0.085	0.085	0.092	
Sample preparation: methanol	L	-	-	0.43	0.43	0.46	
Sample preparation: water	L	-	-	0.43	0.43	0.46	
Elution: n-hexane	L	-	-	3.21	3.21	3.47	
Elution: ethyl acetate	L	-	-	0.36	0.36	0.39	
Elution: methanol	L	-	-	1.79	1.79	1.93	
Elution: water	L	-	-	1.79	1.79	1.93	
Energy consumption CPC	kWh	-	-	0.35	0.35	0.35	[570]
Solvent recovery (95%)	kWh	-	-	0.047	0.047	0.050	
Compound recovery	%	-	-		98		
Spray drying	kWh	-	-	0.52	-	-	[553]
Cryocondensation: energy consumption	kWh	-	-	0.00027	-	-	[554]
Cryocondensation: liquid N ₂	kg	-	-	0.000013	-	-	[554]
Drying agent (maltodextrin)	kg	-	-	0.0058	-	0.0058	[555]
Recovery spray drying	%	-	-	99.8	-	-	[556]
Rotary evaporator after CPC purification	kWh	-	-	-	3.61	-	
Solvent recovery (95%)	kWh	-	-	-	0.15	-	
Freeze-drying	kWh	-	-	-	-	11.55	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density cotton	g/m ²			125			
Dyeing	kWh			0.25			[558]
Dyed wool fabric	m ²			1			
Waste water treatment	L	0.54	0.18	8.46	8.46	8.64	

Table E.12: The collected data for the life cycle assessment of dyeing 1 m² wool with anthraquinones.

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Anthraquinone content in by-product	g/kg FW by-product			4.53			[95]
Amount of dye required for 1 m ² wool at 2% owf	g			2.5			
Amount of by-product (wet)	kg	0.55	0.55	0.57	0.57	0.61	
Drying biomass	Ecpts	-	0.057	0.059	0.059	0.064	
Density rhubarb by-products	kg/m ³			545			[560]
Moisture content initial - Moisture content after drying	%	-		75 - 8.0			
Transport food processing industry - extraction site	Ecpts	-	0.00038	0.00039	0.00039	0.00042	[550]
Extraction material:liquid ratio	kg:L			1:5			[423, 424]
Extraction energy consumption	Ecpts	0.0023	0.00075	0.00078	0.00078	0.00084	
Extraction solvent:							
80 v/v% ethanol	Ecpts	0.010	0.0033	0.0034	0.0034	0.0037	
20 v/v% deionized water	Ecpts	0.000087	0.000029	0.000029	0.000029	0.000032	
Microfiltration	Ecpts	0.00013	0.000042	0.000043	0.000043	0.000046	[561]
Pervaporation							
Ultrafiltration	Ecpts	0.00025	0.000083	-	-	-	[561]
Polysulfone membrane (per 1000 L permeate)	Ecpts	0.00039	0.00039	-	-	-	[438, 562, 563]
Pumps	Ecpts	0.0036	0.0012	-	-	-	[564]
Steam at 1.8 bars	Ecpts	0.0057	0.0019	-	-	-	[565]
Cooling water	Ecpts	0.0000014	0.00000045	-	-	-	[565]
Rotary evaporator before purification	Ecpts	-	-	0.0057	0.0057	0.0062	
Solvent recovery (95%)	Ecpts	-	-	0.00054	0.00054	0.00058	
Centrifugal Partition Chromatography (CPC)							[60, 568]
Crude extract	kg	-	-	0.17	0.17	0.18	[569]
Column stat. phase: n-hexane	Ecpts	-	-	0.023	0.023	0.025	
Column stat. phase: ethyl acetate	Ecpts	-	-	0.016	0.016	0.018	
Sample preparation: n-hexane	Ecpts	-	-	0.0018	0.0018	0.0020	
Sample preparation: ethyl acetate	Ecpts	-	-	0.0013	0.0013	0.0014	
Sample preparation: methanol	Ecpts	-	-	0.0019	0.0019	0.0021	
Sample preparation: water	Ecpts	-	-	0.000067	0.000067	0.000072	
Elution: n-hexane	Ecpts	-	-	0.0077	0.0077	0.0083	
Elution: ethyl acetate	Ecpts	-	-	0.0055	0.0055	0.0059	
Elution: methanol	Ecpts	-	-	0.0082	0.0082	0.0088	
Elution: water	Ecpts	-	-	0.00028	0.00028	0.00030	
Energy consumption CPC	Ecpts	-	-	0.0080	0.0080	0.0080	[570]
Solvent recovery	Ecpts	-	-	0.0011	0.0011	0.0012	
Compound recovery	%	-	-		98		
Spray drying	Ecpts	-	-	0.012	-	-	[553]
Cryocondensation: energy consumption	Ecpts	-	-	0.0000063	-	-	[554]
Cryocondensation: liquid N ₂	Ecpts	-	-	0.00000074	-	-	[554]
Drying agent (maltodextrin)	Ecpts	-	-	0.0019	-	0.0019	[555]
Recovery spray drying	%	-	-	99.8	-	-	[556]
Rotary evaporator after CPC purification	Ecpts	-	-	-	0.084	-	
Solvent recovery (95%)	Ecpts	-	-	-	0.0035	-	
Freeze-drying	Ecpts	-	-	-	-	0.27	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density wool	g/m ²			125			
Dyeing	Ecpts			0.0057			[558]
Dyed wool fabric	m ²			1			
Waste water treatment	Ecpts	0.000015	0.0000048	0.00023	0.00023	0.00023	
Total	Ecpts	0.028	0.071	0.17	0.24	0.43	

Data - LCA of the extraction and dyeing 1 m² cotton with carotenoids

Table E.13: The amount of consumables used in the calculation of the life cycle assessment of dyeing 1 m² cotton with carotenoids.

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Carotenoid content in by-product	g/kg FW by-product			103.78			[99]
Amount of dye required for 1 m ² cotton at 12.5% owf	g			23.75			
Amount of by-product (wet)	kg	0.23	0.23	0.25	0.25	0.25	
Density tomato by-products	kg/m ³			399			[571]
Moisture content initial - Moisture content after drying	%	-		84 - 10.7			[99, 572]
Mass of by-product after drying	kg	-	0.061	0.067	0.067	0.067	
Transport food processing industry - extraction site	km	-		114.75			[550]
Extraction material:liquid ratio	kg:L			1:20			[432]
Extraction solvent:							
96 v/v% ethanol	L	4.39	1.17	1.28	1.28	1.28	
4 v/v% hexane	L	0.18	0.049	0.054	0.053	0.053	
SEP PAK C18 cartridge	kg	-	-	0.028	0.028	0.028	[433]
Electricity for SPE	kWh	-	-	0.40	0.40	0.40	[551]
Reusability of SPE cartridge	Times	-	-		100		[552]
Conditioning: acetone	L	-	-	0.83	0.83	0.83	
Conditioning: isopropanol/ethyl acetate/deionized water, 1/1/1, v/v/v							
Isopropanol	L	-	-	0.28	0.28	0.28	
Ethyl acetate	L	-	-	0.28	0.28	0.28	
Deionized water	L	-	-	0.28	0.28	0.28	
Wash step: ethanol/deionized water. 1/1. v/v							
Ethanol	L	-	-	1.10	1.10	1.10	
Deionized water	L	-	-	1.10	1.10	1.10	
Recovery solvents (95%) (conditioning/wash)	kWh	-	-	0.085	0.085	0.086	
Elutant: acetone	L	-	-	1.66	1.65	1.65	
Compound recovery	%	-	-		90.7		[433]
Spray drying	kWh	-	-	0.51	-	-	[553]
Cryocondensation: energy consumption	kWh	-	-	0.00011	-	-	[554]
Cryocondensation: liquid N ₂	kg	-	-	0.000013	-	-	[554]
Drying agent (maltodextrin)	kg	-	-	0.055	-	0.055	[555]
Recovery spray drying	%	-	-	99.8	-	-	[556]
Rotary evaporator	kWh	0.84	0.23	-	0.19	-	
Solvent recovery (95%)	kWh	0.78	0.21	-	0.031	-	
Freeze-drying	kWh	-	-	-	-	4.41	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density cotton	g/m ²			190			
Dyeing	kWh			0.25			[558]
Biomordant: tannic acid/tannins at 50% owf	kg			0.095			
Dyed cotton fabric	m ²			1			
Waste water treatment	L	9.5	9.5	10.88	10.88	10.88	

Table E.14: The collected data for the life cycle assessment of dyeing 1 m² cotton with carotenoids.

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Carotenoid content in by-product	g/kg FW by-product			103.78			[99]
Amount of dye required for 1 m ² cotton at 12.5% owf	g			23.75			
Amount of by-product (wet)	kg	0.23	0.23	0.25	0.25	0.25	
Drying biomass	Ecpts	-	0.032	0.035	0.035	0.035	
Density tomato by-products	kg/m ³			399			[571]
Moisture content initial - Moisture content after drying	%	-		84 - 10.7			[99, 572]
Transport food processing industry - extraction site	Ecpts	-	0.00013	0.00014	0.00014	0.00014	[550]
Extraction material:liquid ratio	kg:L			1:20			[432]
Extraction energy consumption	Ecpts	0.00095	0.00025	0.00028	0.00028	0.00028	
Extraction solvent:							
96 v/v% ethanol	Ecpts	0.020	0.0054	0.0059	0.0059	0.0059	
4 v/v% hexane	Ecpts	0.00044	0.00012	0.00013	0.00013	0.00013	
SEP PAK C18 cartridge	Ecpts	-	-	0.000053	0.000053	0.000053	[433]
Electricity for SPE	Ecpts	-	-	0.0092	0.0092	0.0092	[551]
Reusability of SPE cartridge	times	-	-		100		[552]
Conditioning: acetone	Ecpts	-	-	0.032	0.032	0.033	
Conditioning: isopropanol/ethyl acetate/deionized water, 1/1/1, v/v/v							
Isopropanol	Ecpts	-	-	0.0027	0.0027	0.0027	
Ethyl acetate	Ecpts	-	-	0.0042	0.0042	0.0043	
Deionized water	Ecpts	-	-	0.000043	0.000043	0.000044	
Wash step: ethanol/deionized water, 1/1, v/v							
Ethanol	Ecpts	-	-	0.0064	0.0064	0.0064	
Deionized water	Ecpts	-	-	0.00017	0.00017	0.00017	
Recovery solvents (conditioning/wash)	Ecpts	-	-	0.0020	0.0020	0.0020	
Elutant: acetone	Ecpts	-	-	0.017	0.017	0.018	
Compound recovery	%	-	-		90.7		[433]
Spray drying	Ecpts	-	-	0.012	-	-	[553]
Cryocondensation: energy consumption	Ecpts	-	-	0.0000026	-	-	[554]
Cryocondensation: liquid N ₂	Ecpts	-	-	0.00000074	-	-	[554]
Drying agent (maltodextrin)	Ecpts	-	-	0.018	-	0.018	[555]
Recovery spray drying	%	-	-	99.8	-	-	[556]
Rotary evaporator	Ecpts	0.019	0.0052	-	0.0043	-	
Solvent recovery (95%)	Ecpts	0.018	0.0048	-	0.00071	-	
Freeze-drying	Ecpts	-	-	-	-	0.10	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density cotton	g/m ²			190			
Dyeing	Ecpts			0.0057			[558]
Biomordant: tannic acid/tannins at 50% owf	Ecpts			0.030			
Dyed cotton fabric	m ²			1			
Waste water treatment	Ecpts	0.00026	0.00026	0.00029	0.00029	0.00029	
Total	Ecpts	0.095	0.084	0.18	0.16	0.27	

Data - LCA of the Extraction and Dyeing 1 m² Wool with Carotenoids

Table E.15: The amount of consumables used in the calculation of the life cycle assessment of dyeing 1 m² wool with carotenoids.

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Carotenoid content in by-product	g/kg FW by-product			103.78			[99]
Amount of dye required for 1 m ² cotton at 12.5% owf	g			15.63			
Amount of by-product (wet)	kg	0.15	0.15	0.16	0.16	0.16	
Density tomato by-products	kg/m ³			399			[571]
Moisture content initial - Moisture content after drying	%	-		84 - 10.7			[99, 572]
Mass of by-product after drying	kg	-	0.040	0.044	0.044	0.044	
Transport food processing industry - extraction site	km	-		114.75			[550]
Extraction material:liquid ratio	kg:L			1:20			[432]
Extraction solvent:							
96 v/v% ethanol	L	0.12	0.032	0.035	0.035	0.035	
4 v/v% hexane	L	2.89	0.77	0.85	0.84	0.84	
SEP PAK C18 cartridge	kg	-	-	0.018	0.018	0.018	[433]
Electricity for SPE	kWh	-	-	0.26	0.26	0.26	[551]
Reusability of SPE cartridge	Times	-	-		100		[552]
Conditioning: acetone	L	-	-	0.54	0.54	0.55	
Conditioning: isopropanol/ethyl acetate/deionized water, 1/1/1, v/v/v							
Isopropanol	L	-	-	0.18	0.18	0.18	
Ethyl acetate	L	-	-	0.18	0.18	0.18	
Deionized water	L	-	-	0.18	0.18	0.18	
Wash step: ethanol/deionized water. 1/1. v/v							
Ethanol	L	-	-	0.73	0.73	0.73	
Deionized water	L	-	-	0.73	0.73	0.73	
Recovery solvents (95%) (conditioning/wash)	kWh	-	-	0.022	0.022	0.022	
Elutant: acetone	L	-	-	1.09	1.09	1.09	
Compound recovery	%	-	-		90.7		[433]
Spray drying	kWh	-	-	0.34	-	-	[553]
Cryocondensation: energy consumption	kWh	-	-	0.000073	-	-	[554]
Cryocondensation: liquid N ₂	kg	-	-	0.000013	-	-	[554]
Drying agent (maltodextrin)	kg	-	-	0.036	-	0.036	[555]
Recovery spray drying	%	-	-	99.8	-	-	[556]
Rotary evaporator	kWh	0.55	0.15	-	0.12	-	
Solvent recovery (95%)	kWh	0.51	0.14	-	0.020	-	
Freeze-drying	kWh	-	-	-	-	2.90	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density wool	g/m ²			125			
Dyeing	kWh			0.25			[558]
Biomordant: tannic acid/tannins at 50% owf	kg			0.063			
Dyed wool fabric	m ²			1			
Waste water treatment	L	6.25	6.25	7.16	7.16	7.16	

Table E.16: The collected data for the life cycle assessment of dyeing 1 m² wool with carotenoids.

Material	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	References
Carotenoid content in by-product	g/kg FW by-product			103.78			[99]
Amount of dye required for 1 m ² cotton at 12.5% owf	g			15.63			
Amount of by-product (wet)	kg	0.15	0.15	0.16	0.16	0.16	
Drying biomass	Ecpts	-	0.021	0.023	0.023	0.023	
Density tomato by-products	kg/m ³			399			[571]
Moisture content initial - Moisture content after drying	%	-		84 - 10.7			[99, 572]
Transport food processing industry - extraction site	Ecpts	-	0.000083	0.000091	0.000091	0.000091	[550]
Extraction material:liquid ratio	kg:L			1:20			[432]
Extraction energy consumption	Ecpts	0.00062	0.00017	0.00018	0.00018	0.00018	
Extraction solvent:							
96 v/v% ethanol	Ecpts	0.013	0.0035	0.0039	0.0039	0.0039	
4 v/v% hexane	Ecpts	0.00029	0.000077	0.000084	0.000084	0.000084	
SEP PAK C18 cartridge	Ecpts	-	-	0.000035	0.000035	0.000035	[433]
Electricity for SPE	Ecpts	-	-	0.0061	0.0061	0.0061	[551]
Reusability of SPE cartridge	Times	-	-	100			[552]
Conditioning: acetone	Ecpts	-	-	0.021	0.021	0.022	
Conditioning: isopropanol/ethyl acetate/deionized water, 1/1/1, v/v/v							
Isopropanol	Ecpts	-	-	0.0018	0.0018	0.0018	
Ethyl acetate	Ecpts	-	-	0.0028	0.0028	0.0028	
Deionized water	Ecpts	-	-	0.000029	0.000028	0.000028	
Wash step: ethanol/deionized water, 1/1, v/v							
Ethanol	Ecpts	-	-	0.0042	0.0042	0.0042	
Deionized water	Ecpts	-	-	0.00011	0.00011	0.00011	
Recovery solvents (conditioning/wash)	Ecpts	-	-	0.0013	0.0013	0.0013	
Elutant: acetone	Ecpts	-	-	0.012	0.011	0.012	
Compound recovery	%	-	-		90.7		[433]
Spray drying	Ecpts	-	-	0.0078	-	-	[553]
Cryocondensation: energy consumption	Ecpts	-	-	0.0000017	-	-	[554]
Cryocondensation: liquid N ₂	Ecpts	-	-	0.00000074	-	-	[554]
Drying agent (maltodextrin)	Ecpts	-	-	0.012	-	0.012	[555]
Recovery spray drying	%	-	-	99.8	-	-	[556]
Rotary evaporator	Ecpts	0.013	0.0034	-	0.0028	-	
Solvent recovery (95%)	Ecpts	0.012	0.0032	-	0.00046	-	
Freeze-drying	Ecpts	-	-	-	-	0.067	[557]
Recovery freeze-drying	%	-	-	-	-	91.8	[556]
Density wool	g/m ²			125			
Dyeing	Ecpts			0.0057			[558]
Biomordant: tannic acid/tannins at 50% owf	Ecpts			0.020			
Dyed wool fabric	m ²			1			
Waste water treatment	Ecpts	0.00017	0.00017	0.00019	0.00019	0.00019	
Total	Ecpts	0.064	0.057	0.12	0.11	0.18	

Results LCA for 1 m² Naturally Dyed Cotton and Wool

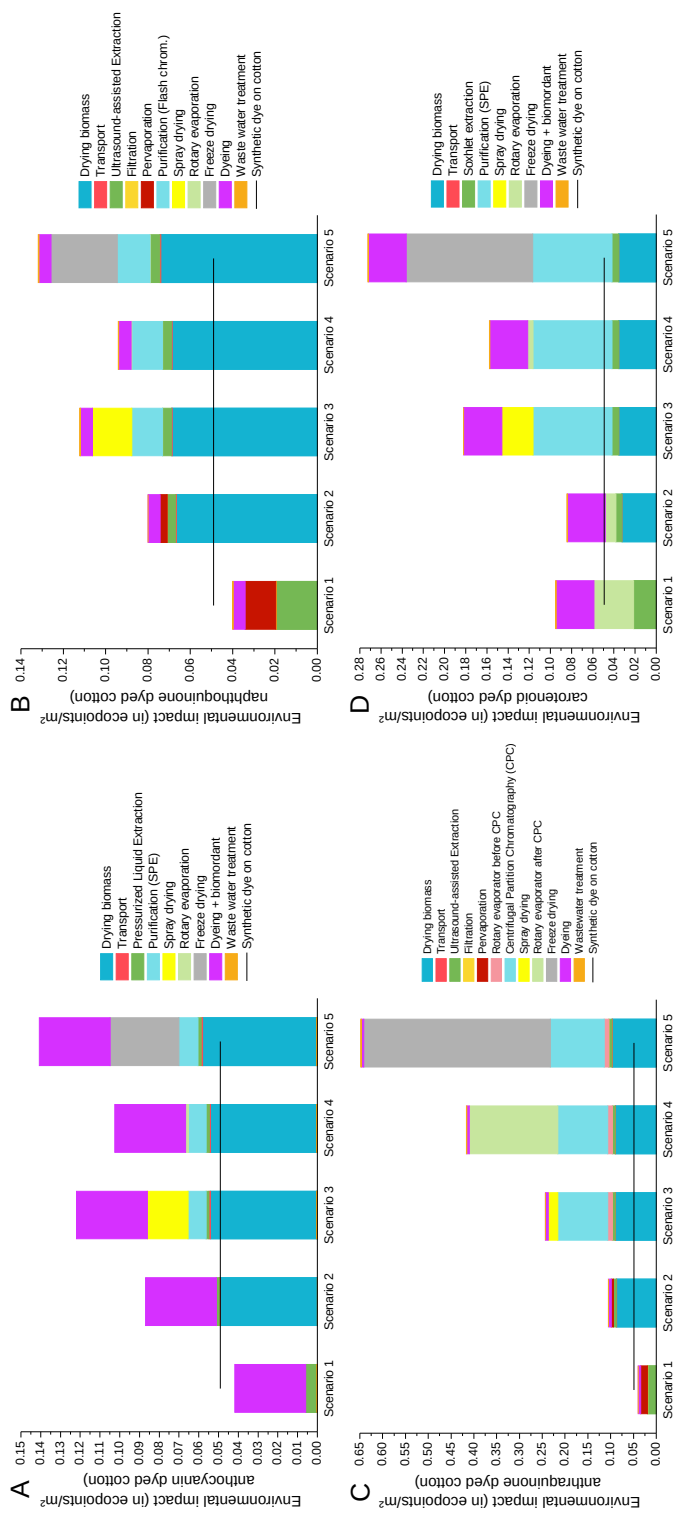


Figure E.5: The environmental impact of dyeing one m² cotton with anthocyanins (A), naphthoquinones (B), anthraquinones (C) or carotenoids (D). The horizontal bar represents the synthetic dye reference.

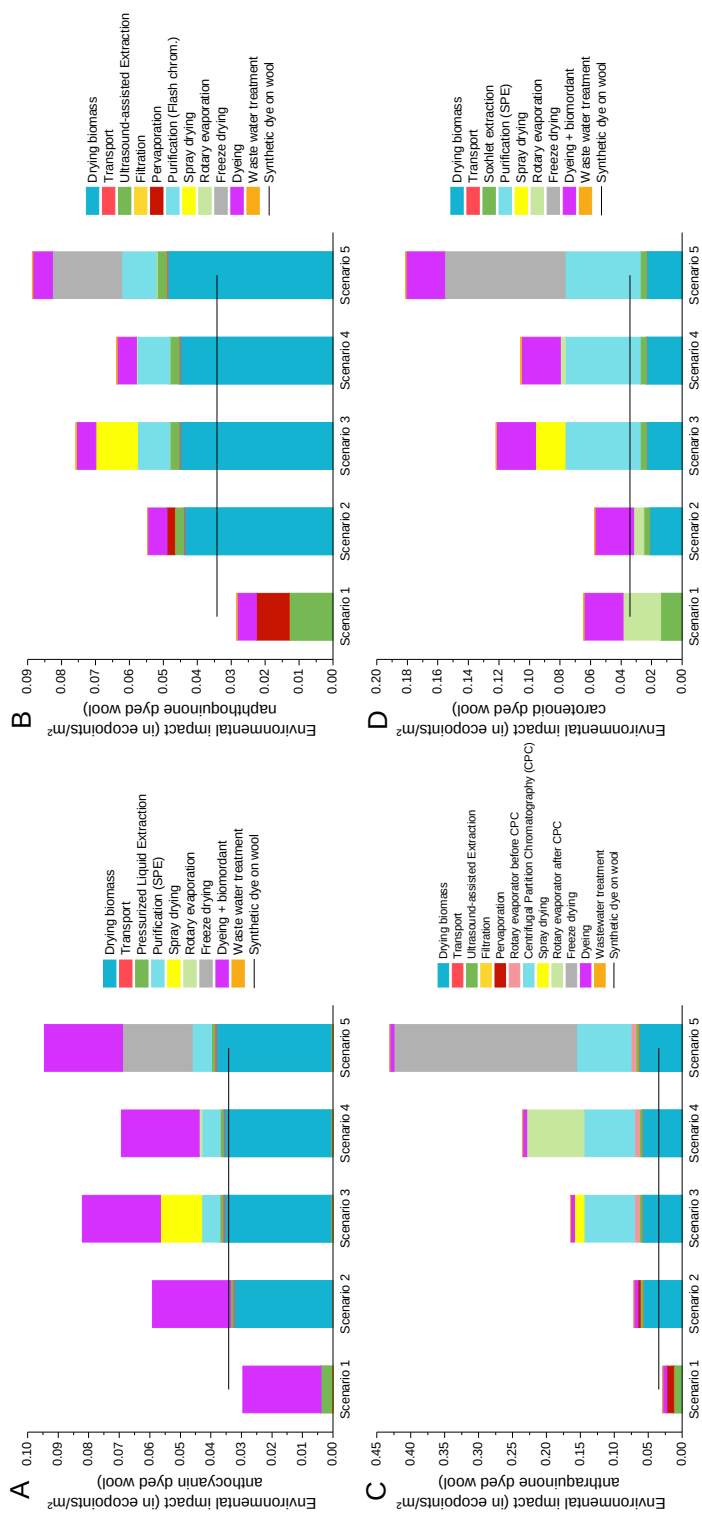


Figure E.6: The environmental impact of dyeing one m² wool with anthocyanins (A), naphthoquinones (B), anthraquinones (C) or carotenoids (D). The horizontal bar represents the synthetic dye reference.

Sensitivity Analyses for Dyeing 1 m² Cotton

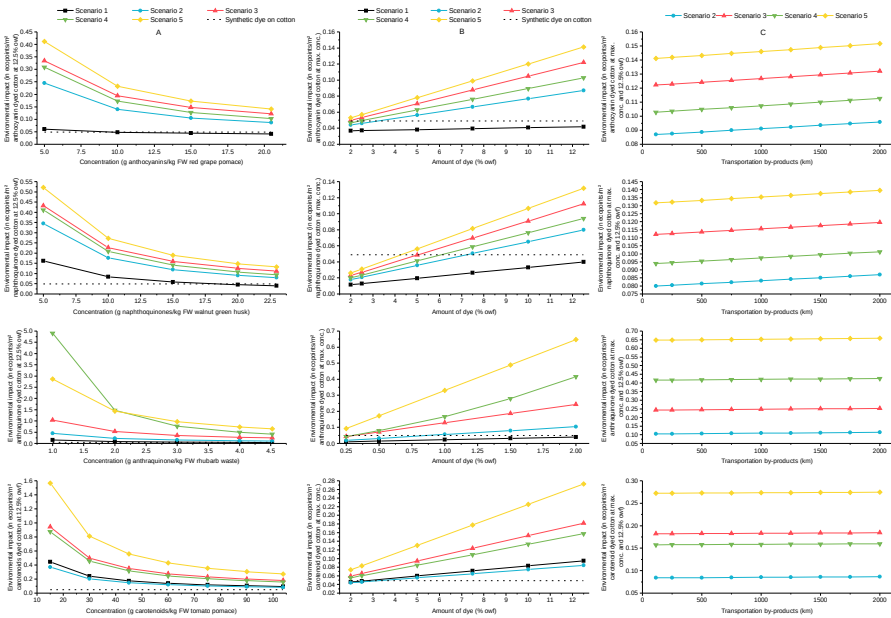


Figure E.7: The environmental impact for dyeing 1 m² naturally dyed cotton as a function of the extraction yield (A), the required dye amount for 1 m² cotton (B) and the transportation of the by-products between the site of sidestream generation to extraction/dyeing site (C). From top to bottom: anthocyanins, naphthoquinones, anthraquinones and carotenoids.

Table E.17: The environmental impact of 1 m² naturally dyed cotton for each scenario with a varying extraction yield applied at a 12.5% owf.

Anthocyanins					
Conc. (g dye/kg FW red grape pomace applied at 12.5% owf)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
5	0.0607	0.2450	0.3342	0.3092	0.4115
10	0.0483	0.1404	0.1939	0.1727	0.2326
15	0.0441	0.1056	0.1472	0.1271	0.1729
20.47	0.0419	0.0869	0.1222	0.1028	0.1411
Naphthoquinones					
Conc. (g dye/kg FW walnut green husk applied at 12.5% owf)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
5	0.1617	0.3457	0.4314	0.4110	0.5212
10	0.0839	0.1759	0.2274	0.2085	0.2724
15	0.0580	0.1193	0.1595	0.1410	0.1894
20	0.0450	0.0910	0.1255	0.1072	0.1480
23	0.0399	0.0799	0.1122	0.0940	0.1317
Anthraquinones					
Conc. (g dye/kg FW rhubarb waste applied at 12.5% owf)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
1	0.1590	0.4522	1.0408	4.9067	2.8705
2	0.0826	0.2292	0.5288	1.4736	1.4436
3	0.0571	0.1548	0.3581	0.7679	0.9680
4	0.0443	0.1176	0.2728	0.4973	0.7302
4.525	0.0399	0.1047	0.2431	0.4159	0.6474
Carotenoids					
Conc. (g dye/kg FW tomato pomace applied at 12.5% owf)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
15	0.4436	0.3694	0.9424	0.8758	1.5670
30	0.2398	0.2028	0.4980	0.4559	0.8103
45	0.1719	0.1472	0.3499	0.3160	0.5581
60	0.1379	0.1194	0.2758	0.2460	0.4320
75	0.1176	0.1027	0.2314	0.2040	0.3563
90	0.1040	0.0916	0.2018	0.1760	0.3059
103.78	0.0950	0.0843	0.1821	0.1575	0.2724

Table E.18: The environmental impact of 1 m² naturally dyed cotton for each scenario with a varying dye amount for dyeing at maximal extraction content.

Anthocyanins						
Dye amount (% owf)	Dye amount (g)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
2	3.8	0.0368	0.0440	0.0499	0.0468	0.0529
2.5	4.75	0.0370	0.0460	0.0533	0.0494	0.0571
5	9.5	0.0383	0.0563	0.0705	0.0628	0.0781
7.5	14.25	0.0395	0.0665	0.0877	0.0761	0.0991
10	19	0.0407	0.0767	0.1050	0.0895	0.1201
12.5	23.75	0.0419	0.0869	0.1222	0.1028	0.1411
Naphthoquinones						
Dye amount (% owf)	Dye amount (g)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
2	3.8	0.0115	0.0179	0.0230	0.0201	0.0261
2.5	4.75	0.0129	0.0209	0.0272	0.0236	0.0311
5	9.5	0.0196	0.0356	0.0485	0.0412	0.0563
7.5	14.25	0.0264	0.0504	0.0697	0.0588	0.0814
10	19	0.0332	0.0652	0.0909	0.0764	0.1066
12.5	23.75	0.0399	0.0799	0.1122	0.0940	0.1317
Anthraquinones						
Dye amount (% owf)	Dye amount (g)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
0.25	0.475	0.0103	0.0184	0.0426	0.0435	0.0932
0.50	0.95	0.0146	0.0308	0.0713	0.0787	0.1724
1	1.9	0.0230	0.0554	0.1285	0.1670	0.3307
1.50	2.85	0.0315	0.0800	0.1858	0.2794	0.4891
2	3.8	0.0399	0.1047	0.2431	0.4159	0.6474
Carotenoids						
Dye amount (% owf)	Dye amount (g)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
2	3.8	0.0455	0.0438	0.0594	0.0555	0.0739
2.5	4.75	0.0479	0.0457	0.0653	0.0604	0.0833
5	9.5	0.0596	0.0554	0.0945	0.0846	0.1306
7.5	14.25	0.0714	0.0650	0.1237	0.1089	0.1779
10	19	0.0832	0.0746	0.1529	0.1332	0.2251
12.5	23.75	0.0950	0.0843	0.1821	0.1575	0.2724

Table E.19: The environmental impact of 1 m² naturally dyed cotton for each scenario with a varying transportation distance between processing industry unit and biorefinery.

Anthocyanins				
Transportation (km)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
114.75	0.0869	0.1222	0.1028	0.1411
250	0.0876	0.1229	0.1035	0.1418
500	0.0888	0.1242	0.1048	0.1432
750	0.0899	0.1255	0.1061	0.1446
1000	0.0911	0.1268	0.1074	0.1460
1250	0.0923	0.1281	0.1087	0.1474
1500	0.0935	0.1294	0.1100	0.1488
1750	0.0947	0.1307	0.1113	0.1502
2000	0.0959	0.1320	0.1127	0.1516
Naphthoquinones				
Transportation (km)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
114.75	0.0799	0.1122	0.0940	0.1317
250	0.0804	0.1127	0.0945	0.1323
500	0.0814	0.1137	0.0955	0.1333
750	0.0823	0.1147	0.0965	0.1344
1000	0.0833	0.1156	0.0975	0.1354
1250	0.0842	0.1166	0.0984	0.1365
1500	0.0851	0.1176	0.0994	0.1375
1750	0.0861	0.1185	0.1004	0.1386
2000	0.0870	0.1195	0.1013	0.1396
Anthraquinones				
Transportation (km)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
114.75	0.1047	0.2431	0.4159	0.6474
250	0.1054	0.2438	0.4166	0.6482
500	0.1066	0.2451	0.4179	0.6496
750	0.1078	0.2463	0.4192	0.6510
1000	0.1091	0.2476	0.4205	0.6523
1250	0.1103	0.2489	0.4218	0.6537
1500	0.1116	0.2502	0.4230	0.6551
1750	0.1128	0.2515	0.4243	0.6565
2000	0.1141	0.2527	0.4256	0.6579
Carotenoids				
Transportation (km)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
114.75	0.0843	0.1821	0.1575	0.2724
250	0.0844	0.1823	0.1576	0.2725
500	0.0844	0.1826	0.1579	0.2728
750	0.0850	0.1829	0.1582	0.2731
1000	0.0852	0.1832	0.1585	0.2734
1250	0.0855	0.1835	0.1588	0.2737
1500	0.0858	0.1838	0.1591	0.2740
1750	0.0861	0.1841	0.1594	0.2743
2000	0.0863	0.1844	0.1597	0.2746

Sensitivity Analyses for Dyeing 1 m² Wool

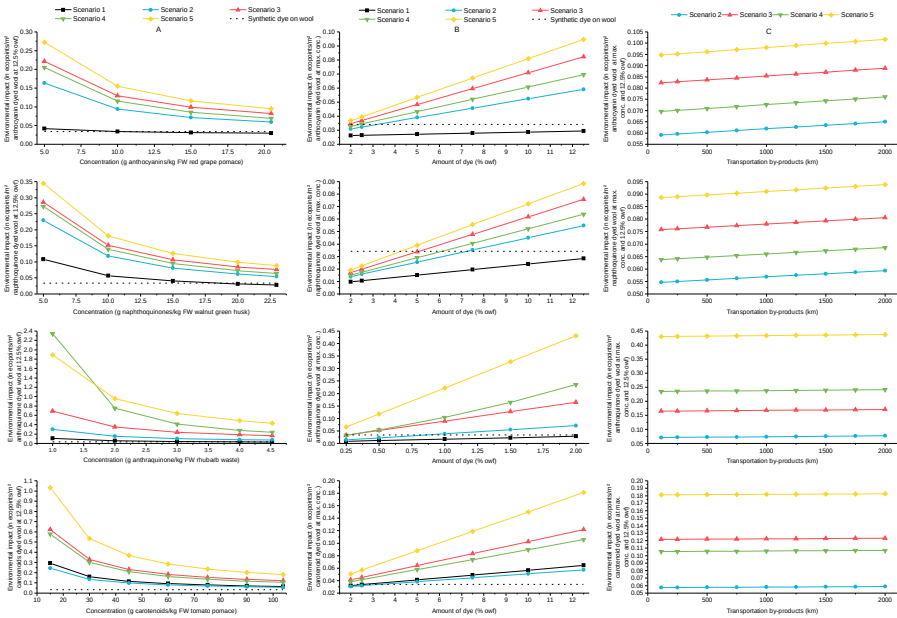


Figure E.8: The environmental impact for dyeing 1 m² naturally dyed wool as a function of the extraction yield (A), the required dye amount for 1 m² wool (B) and the transportation of the by-products between the site of sidestream generation to extraction/dyeing site (C). From top to bottom: anthocyanins, naphthoquinones, anthraquinones and carotenoids.

Table E.20: The environmental impact of 1 m² naturally dyed wool for each scenario with a varying extraction yield applied at a 12.5% owf.

Anthocyanins					
Conc. (g dye/kg FW red grape pomace applied at 12.5% owf)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
5	0.0419	0.1632	0.2218	0.2054	0.2727
10	0.0337	0.0943	0.1295	0.1155	0.1550
15	0.0310	0.0714	0.0988	0.0856	0.1157
20.47	0.0295	0.0591	0.0823	0.0696	0.0948
Naphthoquinones					
Conc. (g dye/kg FW walnut green husk applied at 12.5% owf)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
5	0.1085	0.2295	0.2857	0.2723	0.3449
10	0.0573	0.1178	0.1516	0.1391	0.1812
15	0.0402	0.0806	0.1069	0.0947	0.1266
20	0.0317	0.0620	0.0845	0.0725	0.0993
23	0.0284	0.0547	0.0758	0.0638	0.0886
Anthraquinones					
Conc. (g dye/kg FW rhubarb waste applied at 12.5% owf)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
1	0.1067	0.2996	0.6894	2.3444	1.8932
2	0.0564	0.1528	0.3526	0.7522	0.9545
3	0.0396	0.1039	0.2403	0.4113	0.6416
4	0.0313	0.0795	0.1842	0.2765	0.4851
4.525	0.0283	0.0710	0.1646	0.2351	0.4306
Carotenoids					
Conc. (g dye/kg FW tomato pomace applied at 12.5% owf)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
15	0.2938	0.2450	0.6220	0.5782	1.0329
30	0.1597	0.1353	0.3296	0.3019	0.5351
45	0.1151	0.0988	0.2322	0.2098	0.3691
60	0.0927	0.0805	0.1834	0.1638	0.2862
75	0.0793	0.0696	0.1542	0.1362	0.2364
90	0.0704	0.0622	0.1347	0.1178	0.2032
103.78	0.0644	0.0574	0.1218	0.1055	0.1812

Table E.21: The environmental impact of 1 m² naturally dyed wool for each scenario with a varying dye amount for dyeing at maximal extraction content.

Anthocyanins						
Dye amount (% owf)	Dye amount (g)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
2	2.5	0.0262	0.0309	0.0348	0.0327	0.0367
2.5	3.125	0.0263	0.0322	0.0370	0.0345	0.0395
5	6.25	0.0271	0.0390	0.0483	0.0432	0.0533
7.5	9.375	0.0279	0.0457	0.0597	0.0520	0.0671
10	12.5	0.0287	0.0524	0.0710	0.0608	0.0809
12.5	15.625	0.0295	0.0591	0.0823	0.0696	0.0948
Naphthoquinones						
Dye amount (% owf)	Dye amount (g)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
2	2.5	0.0097	0.0139	0.0171	0.0152	0.0191
2.5	3.125	0.0106	0.0158	0.0199	0.0175	0.0224
5	6.25	0.0150	0.0255	0.0338	0.0291	0.0390
7.5	9.375	0.0195	0.0352	0.0478	0.0406	0.0555
10	12.5	0.0239	0.0450	0.0618	0.0522	0.0721
12.5	15.625	0.0284	0.0547	0.0758	0.0638	0.0886
Anthraquinones						
Dye amount (% owf)	Dye amount (g)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
0.25	0.3125	0.0089	0.0142	0.0327	0.0328	0.0660
0.50	0.625	0.0117	0.0223	0.0516	0.0539	0.1181
1	1.25	0.0172	0.0385	0.0893	0.1039	0.2223
1.50	1.875	0.0228	0.0547	0.1269	0.1643	0.3265
2	2.5	0.0283	0.0710	0.1646	0.2351	0.4306
Carotenoids						
Dye amount (% owf)	Dye amount (g)	Scenario 1 (Ecopts)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
2	2.5	0.0319	0.0308	0.0411	0.0385	0.0506
2.5	3.125	0.0334	0.0320	0.0449	0.0417	0.0568
5	6.25	0.0412	0.0384	0.0641	0.0576	0.0879
7.5	9.375	0.0489	0.0447	0.0833	0.0736	0.1190
10	12.5	0.0567	0.0511	0.1025	0.0896	0.1501
12.5	15.625	0.0644	0.0574	0.1218	0.1055	0.1812

Table E.22: The environmental impact of 1 m² naturally dyed wool for each scenario with a varying transportation distance between processing industry unit and biorefinery.

Anthocyanins				
Transportation (km)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
114.75	0.0591	0.0823	0.0696	0.0948
250	0.0596	0.0828	0.0701	0.0953
500	0.0604	0.0837	0.0709	0.0962
750	0.0611	0.0845	0.0718	0.0971
1000	0.0619	0.0854	0.0726	0.0980
1250	0.0627	0.0862	0.0735	0.0989
1500	0.0635	0.0871	0.0743	0.0999
1750	0.0643	0.0880	0.0752	0.1008
2000	0.0650	0.0888	0.0761	0.1017
Naphthoquinones				
Transportation (km)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
114.75	0.0547	0.0758	0.0638	0.0886
250	0.0550	0.0761	0.0642	0.0890
500	0.0556	0.0767	0.0648	0.0897
750	0.0562	0.0774	0.0654	0.0904
1000	0.0569	0.0780	0.0661	0.0911
1250	0.0575	0.0787	0.0667	0.0917
1500	0.0581	0.0793	0.0673	0.0924
1750	0.0587	0.0799	0.0680	0.0931
2000	0.0593	0.0806	0.0686	0.0938
Anthraquinones				
Transportation (km)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
114.75	0.0710	0.1646	0.2351	0.4306
250	0.0714	0.1651	0.2356	0.4311
500	0.0722	0.1659	0.2364	0.4320
750	0.0730	0.1668	0.2372	0.4330
1000	0.0739	0.1676	0.2381	0.4339
1250	0.0747	0.1684	0.2389	0.4348
1500	0.0755	0.1693	0.2398	0.4357
1750	0.0763	0.1701	0.2406	0.4366
2000	0.0771	0.1710	0.2415	0.4375
Carotenoids				
Transportation (km)	Scenario 2 (Ecopts)	Scenario 3 (Ecopts)	Scenario 4 (Ecopts)	Scenario 5 (Ecopts)
114.75	0.0574	0.1218	0.1055	0.1812
250	0.0575	0.1219	0.1057	0.1813
500	0.0577	0.1221	0.1058	0.1815
750	0.0578	0.1223	0.1060	0.1817
1000	0.0580	0.1225	0.1062	0.1819
1250	0.0582	0.1227	0.1064	0.1821
1500	0.0584	0.1229	0.1066	0.1822
1750	0.0586	0.1231	0.1068	0.1824
2000	0.0588	0.1233	0.1070	0.1826

Table E.23: The influence of the concentration of natural anthraquinone extracted and the amount of dye (% owf) on the environmental impact (ecopts) of dyeing 1 m² of wool (scenario 2).

Concentration extracted from rhubarb waste (g/ kg FW) ↓ Amount of dye* (% owf) →	0.25	0.50	1.00	1.50	2.00
0.5	0.079	0.153	0.300	0.446	0.593
0.625	0.065	0.123	0.241	0.358	0.476
0.75	0.055	0.104	0.202	0.300	0.397
1	0.043	0.079	0.153	0.226	0.300
1.25	0.035	0.065	0.123	0.182	0.241
1.5	0.031	0.055	0.104	0.153	0.202
1.75	0.027	0.048	0.090	0.132	0.174
2	0.024	0.043	0.079	0.116	0.153
2.5	0.021	0.035	0.065	0.094	0.123
3	0.018	0.031	0.055	0.079	0.104
3.5	0.017	0.027	0.048	0.069	0.090
4	0.015	0.024	0.043	0.061	0.079
4.525	0.014	0.022	0.039	0.055	0.071

* : density wool: 125 g/m²

Table E.24: The influence of the concentration of natural anthraquinone extracted and the transportation of the by-products on the environmental impact (ecopts) of dyeing 1 m² of wool (scenario 2).

Concentration extracted from rhubarb waste (g/ kg FW) ↓ Transportation (km) →	114.75	250	500	750	1000	1250	1500	1750	2000
0.5	0.593	0.597	0.604	0.612	0.619	0.627	0.634	0.641	0.649
0.625	0.476	0.479	0.485	0.491	0.497	0.503	0.508	0.514	0.520
0.75	0.397	0.400	0.405	0.410	0.415	0.420	0.425	0.430	0.435
1	0.300	0.302	0.305	0.309	0.313	0.316	0.320	0.324	0.328
1.25	0.241	0.242	0.245	0.248	0.251	0.254	0.257	0.260	0.263
1.5	0.202	0.203	0.206	0.208	0.210	0.213	0.215	0.218	0.220
1.75	0.174	0.175	0.177	0.179	0.181	0.183	0.186	0.188	0.190
2	0.153	0.154	0.156	0.158	0.159	0.161	0.163	0.165	0.167
2.5	0.123	0.124	0.126	0.127	0.129	0.130	0.132	0.133	0.135
3	0.104	0.105	0.106	0.107	0.108	0.110	0.111	0.112	0.113
3.5	0.090	0.091	0.092	0.093	0.094	0.095	0.096	0.097	0.098
4	0.079	0.080	0.081	0.082	0.083	0.084	0.085	0.086	0.086
4.525	0.071	0.071	0.072	0.073	0.074	0.075	0.075	0.076	0.077

European Production of Woven Fabrics

Table E.25: European production values of various woven fabrics in square meters (m²) [416].

PRCCODE		Value (m ²)
13201230	Woven fabrics of carded wool or carded fine animal hair	50 491 045
13201260	Woven fabrics of combed wool or combed fine animal hair; woven fabrics of coarse animal hair	150 596 082
13201330	Woven fabrics of flax, containing ≥ 85 % by weight of flax	19 932 349
13201360	Woven fabrics of flax, containing < 85 % by weight of flax	10 512 622
13201400	Woven fabrics of jute or of other textile bast fibres (excluding flax, true hemp, ramie)	7 999 324
13201900	Woven fabrics of true hemp, ramie or other vegetable textile fibres (excluding flax, jute, other textile bast fibres); paper yarn	250 991
13202014	Woven fabrics of cotton, not of yarns of different colors, weighing ≤ 200 g/m ² , for clothing	157 386 185
13202017	Woven fabrics of cotton, not of yarns of different colors, weighing ≤ 200 g/m ² , for household linen or home furnishing textiles	160 000 000
13202019	Woven fabrics of cotton, not of yarns of different colors, weighing ≤ 200 g/m ² , for technical or industrial uses (excluding gauze, medical gauze)	60 000 000
13202031	Woven fabrics of cotton of yarns of different colors, weighing ≤ 200 g/m ² , for shirts and blouses	67 660 973
13202042	Woven fabrics of cotton, not of yarns of different colors, weighing > 200 g/m ² , for clothing	108 898 622
13202044	Woven fabrics of cotton, not of yarns of different colors, weighing > 200 g/m ² , for household linen or home furnishing textiles	120 000 000
13202049	Woven fabrics of cotton, not of yarns of different colors, weighing > 200 g/m ² , for technical or industrial uses	97 035 435
13202072	Woven fabrics of cotton of yarns of different colors, for other clothing	32 933 881
13202074	Woven fabrics of cotton of yarns of different colors, for household linen or home furnishing textiles	76 370 411
13202079	Woven fabrics of cotton of yarns of different colors, for technical or industrial uses	23 816 357
132020Z1	Cotton fabrics, ≤ 200 g/m ² (excluding gauze and colored yarns)	427 065 967
132020Z2	Cotton fabrics, > 200 g/m ² (excluding colored yarns)	330 155 155
132020Z3	Woven fabrics of cotton of yarns of different colors (excluding denim)	200 781 602
13203150	Woven fabrics of synthetic filament yarns (excluding those obtained from high tenacity yarn or strip and the like)	583 264 815
13203170	Woven fabrics of artificial filament yarns (excluding those obtained from high tenacity yarn)	102 228 416
13203210	Woven fabrics of synthetic staple fibres, containing 85 % or more by weight of synthetic staple fibres	473 558 504
13203220	Woven fabrics of synthetic staple fibres, containing less than 85 % by weight of such fibres, mixed mainly or solely with cotton (excluding fabrics of yarns of different colors)	128 260 417
13203230	Woven fabrics of synthetic staple fibres, containing less than 85 % by weight of such fibres, mixed mainly or solely with cotton, of yarns of different colors	119 871 206
13203240	Woven fabrics of synthetic staple fibres mixed mainly or solely with carded wool or fine animal hair	6 054 968
13203250	Woven fabrics of synthetic staple fibres mixed mainly or solely with combed wool or fine animal hair	22 000 000
13203290	Woven fabrics of synthetic staple fibres mixed other than with wool, fine animal hair or cotton	49 883 028
13203330	Woven fabrics of artificial staple fibres, not of yarns of different colors	139 201 609
13204200	Terry towelling and similar woven terry fabrics of cotton	41 657 539
13204300	Terry towelling and similar woven terry fabrics (excluding of cotton)	180 000
	Total	3 768 047 503

Data - LCA of Dyeing 1 m² Wool or Cotton with a Synthetic Dye

Table E.26: The data inventory for dyeing 1 m² wool or cotton with the synthetic anthraquinone dye as reference.

Material	Unit	Value
Dyeing wool		
Density wool	g/m ²	125
Synthetic anthraquinone dye 2% owf	g	2.5
Synthetic anthraquinone dye 2% owf	Ecopts	0.0075
Dyeing	kWh	0.25
Dyeing	Ecopts	0.0057
Biomordant: tannic acid/tannins at 50% owf	kg	0.063
Biomordant: tannic acid/tannins at 50% owf	Ecopts	0.020
Water used for dyeing (liquor ratio (M:L) 1:50)	L	6.25
Water used for dyeing (liquor ratio (M:L) 1:50)	Ecopts	0.0010
Waste water treatment	Ecopts	0.00017
Total	Ecopts	0.034
Dyeing cotton		
Density cotton	g/m ²	190
Synthetic anthraquinone dye 2% owf	g	3.8
Synthetic anthraquinone dye 2% owf	Ecopts	0.012
Dyeing	kWh	0.25
Dyeing	Ecopts	0.0057
Biomordant: tannic acid/tannins at 50% owf	kg	0.095
Biomordant: tannic acid/tannins at 50% owf	Ecopts	0.030
Water used for dyeing (liquor ratio (M:L) 1:50)	L	9.5
Water used for dyeing (liquor ratio (M:L) 1:50)	Ecopts	0.0015
Waste water treatment	Ecopts	0.00026
Total	Ecopts	0.049

Data from Ecoinvent Database

Table E.27: The data derived from the ecoinvent version 3.1 database for the LCA calculations ([435]).

Material	Unit	Value
Drying of grass	Ecopts/L	0.0564
Transport, freight, lorry 16-32 metric ton, EURO5	Ecopts/t km	0.0178
Water production, deionized, from tap water, at user	Ecopts/kg	0.000157
Methanol production	Ecopts/kg	0.116
Ethanol production, without water, in 99.7% solution state	Ecopts/kg	0.116
Soybean meal and crude oil production, mechanical extraction	Ecopts/kg	0.00413
Polysulfone production, for membrane filtration production	Ecopts/kg	1.129
Steam production, in chemical industry, alloc. default, U:	Ecopts/kg	0.0203
Acetone production, liquid	Ecopts/kg	0.269
Ethyl acetate production	Ecopts/kg	0.340
Citric acid production	Ecopts/kg	0.0186
Hexane production	Ecopts/kg	0.0729
Isopropanol production	Ecopts/kg	0.246
Activated silica production	Ecopts/kg	0.191
Electricity, high voltage, production mix	Ecopts/kWh	0.0231
Chemical production, organic	Ecopts/kg	0.317
Liquid N ₂	Ecopts/kg	0.0587
Synthetic anthraquinone	Ecopts/kg	3.02
Treatment of wastewater, average, capacity 1.1 ¹⁰ L/year	Ecopts/m ³	0.0270

Additional Data: Thermodynamic Properties

Table E.28: The data derived from the ecoinvent version 3.1 database for the LCA calculations ([435]).

Property	Unit	Solvent						
		Acetone	Ethanol	Ethyl acetate	Hexane	Isopropanol	Methanol	Water
Specific heat capacity	kJ/kg K	2.14	2.57	1.937	2.26	2.68	2.53	4.18
Density	kg/L	0.7846	0.789	0.902	0.655	0.785	0.792	0.997
Boiling point	K	329.15	351.15	350.25	341.85	355.65	337.85	373.15
Latent heat of vaporization	MJ/kg	0.518	0.846	0.367	0.365	0.664	1.109	2.256

Curriculum vitae

Personalia

Name: Phan Kim

Date and place of birth: 31/01/1991, Kortrijk

Nationality: Belgian

Telephone: 0032479281988

E-mail: Kim.Phan@Ugent.be, phankimtrong@msn.com

Education

03/2017 – 2021: PhD candidate in Bioscience Engineering: Chemistry and Bioprocess Technology

Doctoral dissertation: 'Non-food Applications of Anthocyanins Extracted from Agro-Food Residues: a Combined Experimental and Theoretical Study'

Promoters: prof. dr. ir. Steven De Meester, prof. dr. ir. Veronique Van Speybroeck, prof. dr. ir. Katleen Raes and prof. dr. ir. Karen De Clerck

2012 – 09/2016: Master of Science in Chemistry (GIT) (Major analysis and characterization), Faculty of Sciences, Ghent University - Campus De Sterre

Master thesis: 'Trace element analysis of blood via tandem ICP-mass spectrometry after volumetric absorptive microsampling'

Promoters: prof. dr. Frank Vanhaecke, dr. Lieve Balcaen

09/2009 – 2015: Bachelor of Science in Chemistry (GIT), Faculty of Sciences, Ghent University - Campus De Sterre

List of peer-reviewed scientific publications

Phan, K., Van Den Broeck, E., Van Speybroeck, V., De Clerck, K., Raes, K., and De Meester, S. (2020). The Potential of Anthocyanins from Blueberries as a Natural Dye for Cotton: A Combined Experimental and Theoretical Study. *Dyes and Pigments*, 176, 108180.

Phan, K., De Meester, S., Raes, K., De Clerck, K., and Van Speybroeck, V. (2021). A Comparative Study on the Photophysical Properties of Anthocyanins and Pyranoanthocyanins. *Chemistry-A European Journal*, 27, 5956 - 5971.

Phan, K., Raes, K., Van Speybroeck, V., Roosen, M., De Clerck, K., and De Meester, S. Non-Food Applications of Natural Dyes Extracted from Agro-Food Residues: a Critical Review. *Journal of Cleaner Production*, 301, 126920.

Phan, K., Raes, K., De Clerck, K., Van Speybroeck, V., and De Meester, S. An in silico Study on the Solvent Dependency of Anthocyanin Extraction Profiles. *To be submitted*

Dulo, B., Phan, K., Githaiga, J., Raes, K., De Meester, S. Natural quinone dyes: a review on structure, extraction techniques, analysis and application potential. *Waste and Biomass Valorization*

Other peer-reviewed scientific publications in international journals

Bolea-Fernandez, E., Phan, K., Balcaen, L., Resano, M., and Vanhaecke, F. (2016). Determination of ultra-trace amounts of prosthesis-related metals in whole blood using volumetric absorptive micro-sampling and tandem ICP–Mass spectrometry. *Analytica chimica acta*, 941, 1-9.

Conference proceedings

Phan, K., Van Speybroeck, V., Raes, K., and De Meester. The valorization of natural colorants from waste streams and subsequent application on fibers. (2018, May 30th- June 1st). *14th International conference on Renewable Resources and Biorefineries (RRB-14)*.

Phan, K., Van Den Broeck, E., Van Speybroeck, V., De Clerck, K., Raes, K., and De Meester, S. (2019, June 11th-13th) Exploring the potential of anthocyanins as a natural dye for non-food applications. *23rd Green Chemistry & Engineering conference (GCE) ; 9th International conference on Green and Sustainable Chemistry (GSC)*.

Teaching activities

Supervision of Maxime Claeys. Master thesis student during 1 academic year (2017-2018). De Studie naar de Affiniteit van Anthocyaninen als Natuurlijke Kleurstoffen Op Textielvezels.

Supervision of Tom Schuurmans. Master thesis student during 1 academic year (2018-2019). Het Potentieel van Enzymatisch Verven van Katoen met Anthocyaninen.

Guidance of Maud Verstringe. Master thesis student during 1 academic year (2018-2019). The Vanishing Act of Colours, Designing Opportunities for a Natural Dye Derived from Blueberries.

Supervision of Clara Matthijs. Master thesis student during 1 academic year (2020-2021). Natural Dyes from Food Waste Applied in Printing Inks for Biodegradable Packaging: Quinones from Henna and Cashew Nuts as a Natural Dye.

Supervision of Pauline Matthijs. Master thesis student during 1 academic year (2020-2021). Natural Dyes from Food Waste Applied in Printing Inks for Biodegradable Packaging: Anthocyanins from Blueberries as a Natural Dye.

