Anthocyanins in Fruits

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Contributor: Aistis Petruskevicius , Jonas Viskelis , Dalia Urbonaviciene , Pranas Viskelis

Different anthocyanidins determine the color of the plant and range from orange to red, blue, and purple colors. Anthocyanins have a wide range of applications in both the food and pharmaceutical industry. They have strong anti-inflammatory, antimicrobial, and antioxidative properties and research results have linked dietary enrichment with anthocyanins to a reduced risk of gastrointestinal cancers and the inhibition of neurodegenerative diseases and cognitive decline. Anthocyanins also increase the endurance and elasticity of capillaries and reduce their permeability. Additionally, they increase visual acuity and are used for some eye diseases, especially the anthocyan glycosides in bilberry. It is important to note that some anthocyanins have radioprotective effects and are used for the treatment and prophylaxis of radiation sickness.

anthocyanins antimicrobial activity antioxidant activity

1. Ericaceae

Even though the Ericaceae family has many species that grow edible fruit, not many of them accumulate large amounts of anthocyanins. For example, *Arbutus unedo* (Ericaceae) fruits are a popular research subject, known for their high accumulation of arbutin—a compound with medicinal applications, but the fruit possesses a very low anthocyanin content [1], when compared with *Vaccinium* genus species. Species of the *Vaccinium* genus are widely known to have beneficial health properties and have commonly been used as an ingredient in traditional medicine throughout Europe because of their healing properties—*Vaccinium* berries and leaves have been used to treat fever, diabetes, respiratory inflammations, common cold, and gastrointestinal disorders [2][3]. These properties are likely a result of a high polyphenolic compound, anthocyanin, and flavonoid content. Due to the accumulation of high concentrations of compounds that have relevant medicinal properties and are likely to increase in demand, it is not surprising why the species of *Vaccinium* genus are among the most researched berries in tests of plants that can be used in nutraceuticals.

European blueberries *V. myrtillus* are one of the richest natural anthocyanin sources—studies have shown that these berries contain 15 different anthocyanins, of which the most abundant are anthocyanidin- and delphinidin-based (**Table 1**). *V. corymbosum* also accumulates the same 15 anthocyanins, but in lesser quantities. According to the experiment results of Burdulis et al. [4], some blueberry *V. corymbosum* cultivars such as ‘Coville’ and ‘Northland’ accumulated slightly higher percentages of anthocyanin in the fruit skins than *V. myrtillus*—1.24% and 1.09%, respectively. Despite that, *V. myrtillus* fruit samples contained a larger percentage of anthocyanin in the fruit overall when compared with *V. corymbosum* cultivars. The results of this article and European Medicines Agency data [5] show that the most abundant anthocyanins in bilberries are delphinidin-3-*O*-galactoside (Del-3-Gal), constituting up to 14.9% of total anthocyanin, delphinidin-3-*O*-arabinoside (Del-3-Ara), up to 15.3%, delphinidin-3-*O*-glucoside (Del-3-Glu)—up to 14.0%, cyanidin-3-*O*-arabinoside Cy-3-Ara)—13.6% and cyanidin-3-*O*-glucoside (Cy-3-Glu), comprising up to 10.1% of the total anthocyanin in bilberry fruit (**Table 1**). This high concentration of anthocyanins and other polyphenols is likely a result of an adaptation to store increased amounts of defensive phytochemicals as a response to high levels of environmental stress. While it is common for anthocyanins to mostly be stored in the exocarp, in *V. myrtillus* they are accumulated throughout the fruit [4]. However, a larger percentage of anthocyanins was detected in the skins of the fruit, rather than the entire fruit.

Table 1. Anthocyanin composition of bilberry (*Vaccinium myrtillus*) [5][6].

Anthocyanin	Amount, Percent of Total Anthocyanins (%)
Dephinidin-3-*O*-glucoside	13.7–14.0
Cyanidin-3-*O*-galactoside	9.0–9.2
Cyanidin-3-O-glucoside	8.5–10.1
Cyanidin-3-*O*-arabinoside	7.7–13.6
Petunidin-3-*O*-glucoside	6.0–8.8
Peonidin-3-*O*-galactoside	0.6–1.1
Peonidin-3-*O*-arabinoside	0.5–1.0
Malvidin-3-*O*-glucoside	7.9–8.4
Delphinidin-3-*O*-galactoside	14.3–14.9
Delphinidin-3-*O*-arabinoside	12.1–15.3
Petunidin-3-*O*-galactoside	2.1–4.0
Petunidin-3-*O*-arabinoside	1.3–2.6
Peonidin-3-*O*-glucoside	0.1–3.7
Malvidin-3-*O*-galactoside	2.5–3.1
Malvidin-3-*O*-arabinoside	1.5–2.4

2. Caprifoliaceae

Much like berries from *Vaccinium* genus, berries from the Caprifoliaceae family have historically been utilized as an ingredient of traditional medicinal remedies because of their properties. Commonly known as elderberries, *Sambucus* sp. are rich sugars, organic acids, and polyphenols—anthocyanins [7]. Because of this polyphenolic compound accumulation, they also show antioxidant activity, anti-inflammatory, and immune-stimulating properties [8]. Berries from the Caprifoliaceae family do not contain as many anthocyanins when compared with *Vaccinium* sp. berries; however, the anthocyanin composition that is accumulated differs considerably in comparison.

Caprifoliaceae family plants synthesize anthocyanins that are not found in previously mentioned *Vaccinium* species. Most abundantly accumulated anthocyanins in *Sambucus nigra*, *S. caerulea*, and *S. ebulus* were ones that are cyanidin-based (**Table 1**). In research conducted by Wu and others [9] anthocyanins were extracted by using a methanol/water/acid extraction system because it was found that the use of acetone, a reagent that is commonly used in anthocyanin extraction, may cause anthocyanin conversions to pyranoanthocyanins. In total, seven anthocyanins were found in *S. nigra*. Four of them were the most abundant and commonly found in this species—cyanidin-*O*-3-sambubiosil-5-*O*-glucoside, cyanidin-3,5-*O*-diglucoside, cyanidin-3-*O*-sambubioside, and cyanidin-3-*O*-glucoside. The other three anthocyanins were cyanidin-3-*O*-rutinoside, pelargonidin-3-*O*-glucoside, and pelargonidin-3-*O*-sambubioside. According to the researchers, it was the first time pelargonidin-based anthocyanins were detected in *S. nigra* at the time. Oancea and other researchers confirmed it and identified pelargonidin anthocyanins in *S. nigra* and found that pelargonidin and delphinidin-based anthocyanins were among the major anthocyanins in the fruit [10]. However most other authors listed cyanidin anthocyanins as the most found major anthocyanins in this species [7][9][11]. However, interspecies hybrids of *Sambucus* genus might have a different anthocyanin profile entirely, containing anthocyanins that are not found in a non-hybrid specimen, for example cyanidin-xylosyl-dihexoside [12].

Lonicera caerulea is another species of anthocyanin-accumulating berries that has potential to become an efficient ingredient for super foods. These berries accumulate large amounts of secondary metabolites—among them tannins, saponins, phenolics, ascorbic acid, and other compounds that have many health benefits [12][13]. Anthocyanins are the predominant compounds and constitute from 38 up to 91% of total identified phenolic compounds. The total amount of identified anthocyanins varies widely within cultivars. The highest average amounts are found in Amphora (401 mg/100 g FW), Indigo Gem, Nimfa, Tundra, Leningradskij Velikan, and the lowest—in the fruits of Tola, Wojtek, and Iga varieties—3.83, 13.58, and 44,92 mg/100 g FW, respectively [14]. In the experiment conducted by Senica and others [15] anthocyanins were extracted from *Lonicera caerulea* using ultrasound-assisted methanolic extraction. It was found that the main anthocyanin in *L. caerulea* was cyanidin-3-*O*-glucoside (56.93 mg/100 g FW) (**Table 2**). In the analysis conducted by Khattab and others [16] it was found that there can be a considerable variation in Cy-3-Glu accumulation depending on the cultivar—*Indigo gem* cultivar accumulated up to 649 mg/100 g of Cy-3-glu while *Berry blue* only accumulated 342 mg/100 g FW. Peonidin-based anthocyanins were also among the major anthocyanins, while others were only found in small quantities—0.15–16.39 mg/100 g FW [14]. These findings are in line with other researchers' work—cyanidin-3-*O*-glucoside is a major anthocyanin while the most abundant minor anthocyanins are rutinosides [14][17] (**Table 3**).

Table 2. Specific anthocyanin contents found in the fruits of the Caprifoliaceae family.

Anthocyanin	*S. nigra* (mg/100 g FW)	*S. caerulea* (mg/100 g FW)	*S. ebulus* (mg/100 g FW)	*L. caerulea* (mg/100 g FW)
Cyanidin-3-*O*-galactoside	0.32 [11]			0.05–0.83 [14]
Cyanidin-3-*O*-glucoside	376.2 [7] 449 [11]; 739.8 [9]	2.85 [11]	0.49 [11]	33.97–56.93 [15] 342–649 [16] 3.3–230 [14]

Anthocyanin	*S. nigra* (mg/100 g FW)	*S. caerulea* (mg/100 g FW)	*S. ebulus* (mg/100 g FW)	*L. caerulea* (mg/100 g FW)
Cyanidin-3,5-*O*-diglucoside	5.46 [9] 5.91 [11]; 14.34 [7]			1.39–2.38 [15] 15–31 [16] 0.4–17.6 [14]
Cyanidin-3-*O*-sambubioside	344.44 [11] 438.8 [7] 545.9 [9]	63.43 [11]	6.56 [11]	
Cyanidin-3-*O*-sambubiosil-5-*O*-glucoside	30.77 [7] 42.19 [11] 82.6 [9]			
Cyanidin-pentoside-hexoside	1.08 [11]	78.99 [11]	345.82 [11]	
Cyanidin-3-*O*-rutinoside	9.36 [11]			5.66–10.21 [15] 10.0–37.0 [16] 0.21–10.04 [14]
Pelargonidin-3-*O*-glucoside	1.80 [9]			2.30–5.90 [15] 5–12 [16]
Pelargonidin-dihexoside				0.82–6.29 [15]
Peonidin-3,5-*O*-dihexoside				13.88–18.94 [15] [14][15][16][18]
[illegible]				6.55–14.53 [15] 25.0 [16]

Anthocyanin	Amount, Percent of Total Anthocyanins (%)
Cyanidin-3-*O*-glucoside	71–89
Cyanidin-3-*O*-rutinoside	7–23
Cyanidin-3,5-*O*-diglucoside	2.2–0.4
Peonidin-3-*O*-glucoside	>0.5
Pelargonidin-3-*O*-rutinoside	>0.1

3. Grossulariaceae

The Grossulariaceae family only consists of a single genus—*Ribes* [19]. In Europe the most widely grown species from this genus are blackcurrant (*Ribes nigrum*) and redcurrant (*Ribes rubrum*) and are among the most grown berries in the region [20]. Currants, both red and black, are commonly used to make jams, syrups, and juices. In the United States of America, the cultivation of blackcurrants used to be banned until around 1980 due to fears of spreading fungal pathogen *Cronartium ribicola* which caused financial losses to lumber industry sector. Since then, new cultivars were selected that do not spread this pathogen and as such the restrictions were lifted, granting more opportunities to research the species more widely [21]. Black currants especially are very rich in anthocyanins as indicated by their saturated dark color [22]. *Ribes rubrum*, however, accumulates different anthocyanins in comparison (**Table 4**), and lesser quantities of said anthocyanins which can also be determined by the difference in the color. The total anthocyanins content of *Ribes rubrum* in the study in [23] was 63 mg/100 g FW, much higher than that reported by the authors of [11][17][24]. Significant differences in total anthocyanin content can be attributed to the variety of wild red currants. The major anthocyanins in *Ribes nigrum* are both rutinosides with different anthocyanidins—cyanidin-3-*O*-rutinoside and delphinidin-3-*O*-rutinoside, accumulated up to 138.81 mg/100 g FW and 311.42 mg/100 g FW, respectively. A similar anthocyanin composition can be found in other researchers' work as well [25]. However, in red currant *R. rubrum* delphinidin-based anthocyanin delphinidin-3-O-sambubioside is only a minor anthocyanin and all major anthocyanins are cyanidin-based, the most abundant being cyanidin-3-*O*-xylosylrutinoside and cyanidin-3-sambubioside, neither of which were detected in *R. nigrum.* Other researchers have also detected cyanidin-3-*O*-xylosylrutinoside as a major anthocyanin in *R. rubrum*; this anthocyanin was not present in *R. nigrum* or any other analyzed fruit in that research, including blueberries, bilberries, and cranberries [26].

Table 4. Specific anthocyanin contents found in fruits from Grossulariaceae family.

Anthocyanin	*Ribes nigrum* (mg/100 g FW)	*Ribes rubrum* (mg/100 g FW)
Delphinidin-3-*O*-glucoside	39.64 [22] 37.2 [6] 44.33 [27] 52.88 [28] 113.21 [9]	
Delphinidin-3-*O*-rutinoside	91.6 [29] 109.93 [27]; 157.58 [28] 194.17 [22] 311.42 [9]	
Cyanidin-3-*O*-glucoside	8.52 [27] 16.5 [6] 16.68 [22] 28.56 [9] 39.42 [28]	0.16 [9] 2.52 [30]
Cyanidin-3-*O*-rutinoside	20.78 [27] 89.0 [6] 133.71 [22] 138.83 [9] 138.81 [28]	1.61 [9] 3.68 [30]
Cyanidin-3-*O*-sambubioside		3.39 [9]
Delphinidin-3-*O*-sambubioside		0.10 [9]
Cyanidin-3-*O*-sophoroside		0.11 [9]
Cyanidin-3-*O*-glucosylrutinoside		0.49 [9]
Cyanidin-3-*O*-xylosylrutinoside		6.93 [9]
Petunidin-3-*O*-rutinoside	0.1 [6] 4.15 [9] 5.67 [28]	
Petunidin-3-*O*-glucoside	3.97 [28] T [9]	
Pelargonidin-3-*O*-rutinoside	1.20 [28] 2.22 [9]	
Peonidin-3-*O*-glucoside	2.64 [28] T [9]	

4. Rosaceae

Anthocyanin	***Ribes nigrum* (mg/100 g FW)** [31]	***Ribes rubrum* (mg/100 g FW)**
Peonidin-3-*O*-rutinoside	1.2 [6] 2.94 [28] 0.77 [9]	

T—trace.

nutritional …hysical— …gestion of blackberry metabolites in rodents reduced brain neurodegenerative processes and injections of *Prunus avium* extracts had positive results in reducing learning impairments and memory deficits in mice [32][33]. These effects are in line with other high anthocyanin concentration-accumulating fruit health impacts. One of the fruits in this family—*Aronia melanocarpa*, which originates from North America but is widely spread in Europe nowadays—is one of the richest fruits in polyphenolic compounds and most of these accumulated compounds are anthocyanins [34]. *Aronia melanocarpa* accumulates lower amounts of cyanidin-3-*O*-glucoside when compared with *Rubus fruticosus* and *Rubus idaeus* but is rich in cyanidin-3-*O*-galactoside, and cyanidin-3-arabinoside which are not commonly found in fruits of other species from *Rosaceae* family (**Table 5**). Blackberry (*Rubus fruticosus*) also contains high levels of anthocyanins—especially cyanidin-3-*O*-glucoside (111.3–122.54 mg/100 g FW), which makes up around 89% of the total anthocyanin content in the fruit (**Table 6**). This anthocyanin has been detected in comparable concentrations in *V. myrtillus*. The other major anthocyanin in blackberry is cyanidin-3-*O*-sophoroside and some researchers have also found cyanidin-3-*O*-rutinoside, neither of which is present in *V. myrtillus*. Major anthocyanins in red raspberry (*Rubus idaeus*) are mostly cyanidin- or pelargonidin-based. The main anthocyanin in *R. idaeus* is cyanidin-3-*O*-sophoroside, which was found in concentrations up to 63.86 mg/100 g FW. Red raspberry accumulates less anthocyanins than blackberry overall, which is also indicated by the reduced color saturation of the fruit. Sweet cherry (*Prunus avium*) accumulates only a small amount of anthocyanins, the major one being peonidin-3-*O*-rutinoside, only making up 16.2 mg of 100 g of fresh fruit weight. However, sour cherry *(Prunus cerasus*), while not accumulating large amounts of most anthocyanins—concentrations reaching up to 13 or 16 mg/100 g of FW— was found in some cases to accumulate substantial amounts of cyanidin-3-*O*-glucosylrutinsoide —up to 235.1 mg/100 g FW during the analysis conducted in Italy. The only other major anthocyanin in *Prunus cerasus* that was found in the analyzed research was peonidin-3-*O*-rutinoside, which was noted in concentrations reaching up to 68.1 mg/100 g FW.

Table 5. Specific anthocyanin contents found in the fruits of Caprifoliaceae family.

Anthocyanin	***Rubus idaeus* (mg/100 g FW)**	***Rubus fruticosus* (mg/100 g FW)**	***Prunus avium* (mg/100 g FW)**	***Prunus cerasus* (mg/100 g FW)**	***Aronia melanocarpa* (mg/100 g FW)**
Pelargonidin-3-*O*-sophoroside	8.77 [35]				
Cyanidin-3-*O*-rutinoside	10.53 [35] 4.1 [36]	4.66 [37] 31.9 [38]	13.5 [39] 52 [40] 64.16 [41] 66.81 [42]	4.9 [43] 7.3 [44] 17.11 [41]	
Cyanidin-3-2-glucosylrutinoside	11.9 [36]	19.3 [38]			

Anthocyanin	*Rubus idaeus* (mg/100 g FW)	*Rubus fruticosus* (mg/100 g FW)	*Prunus avium* (mg/100 g FW)	*Prunus cerasus* (mg/100 g FW)	*Aronia melanocarpa* (mg/100 g FW)
Pelargonidin-3-*O*-glucoside	4.23 [35]		N.D. [41]		
Cyanidin-3-*O*-glucoside	11.5 [36] 25.12 [35] 43.61 [45]	111.3 [38] 122.54 [37]	2.3 [39] 5.26 [41] 8.02 [40] 8.85 [42]	2.91 [41] 4.5 [46] 5.3 [44]	1.69 [47] 5.62 [48] 37.6 [9]
Delphinidin-3-*O*-glucoside	2.88 [35]				
Pelargonidin-3-*O*-rutinoside			0.4 [40] 1.08 [39] 1.48 [41] 3.40 [42]	N.D. [41]	
Peonidin-3-*O*-rutinoside			0.9 [40] 2.89 [42] 3.84 [41] 16.2 [39]	2.47 [41] 68.1 [44]	
Cyanidin-3-*O*-galactoside					100.68 [48] 125.63 [47] 989.7 [9]
Cyanidin-3-*O*-glucosylrutinsoide			N.D. [41]	16.5 [43] 43.82 [41] 235.1 [44]	
Cyanidin-3-*O*-arabinoside		0.41 [37]			46.58 [48] 142.43 [47] 399.3 [9]
Cyanidin-3-*O*-xyloside		6.37 [37]			4.69 [47] 5.14 [48] 51.5 [9]
Malvidin-3-*O*-glucoside	3.64 [35]				
Cyanidin-3-*O*-xylosyl-6-rutinoside		3.6 [38]			
Cyanidin-3-*O*-glucorutinoside	11.58 [35]				
Cyanidin-3-*O*-sambubioside		1.8 [38]			[37][38][49]

Anthocyanin	Amount, Percent of Total Anthocyanins (%)
Cyanidin-3-*O*-glucoside	90.72
Cyanidin-3-*O*-xyloside	3.44
Cyanidin-3-*O*-malonylglucoside	2.97

Anthocyanin	Amount, Percent of Total Anthocyanins (%)
Cyanidin-3-*O*-dioxalylglucoside	2.04
Cyanidin-3-*O*-sambubioside	0.84

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