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#### Review

# Classification of fruits based on anthocyanin types and relevance to their health effects



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#### ABSTRACT

Anthocyanins are a group of water-soluble pigments that confer the blue, purple, and red color to many fruits. Anthocyanin-rich fruits can be divided into three groups based on the types of aglycones of their anthocyanins: pelargonidin group, cyanidin/peonidin group, and multiple anthocyanidins group. Some fruits contain a major anthocyanin type and can serve as useful research tools. Cyanidin glycosides and peonidin glycosides can be metabolically converted to each other by methylation and demethylation. Both cyanidin and peonidin glycosides can be metabolized to protocatechuic acid and vanillic acid. Pelargonidin-3-glucoside is metabolized to 4-hydroxybenoic acid. On the other hand, phenolic acid metabolites of delphinidin, malvidin, and petunidin glycosides are unstable and can be further fragmented into smaller molecules. A literature review indicates berries with higher cyanidin content, such as black raspberries, chokeberries, and bilberries are more likely to produce an antiinflammatory effect. This observation seems to be consistent with the hypothesis that one or more stable phenolic acid metabolites contribute to the antiinflammatory effects of anthocyanin-rich fruits. More studies are needed before we can conclude that fruits rich in cyanidin, peonidin, or pelargonidin glycosides have better antiinflammatory effects. Additionally, fruit polyphenols other than anthocyanins could contribute to their antiinflammatory effects. Furthermore, blueberries could exert their health effects with other mechanisms such as improving intestinal microbiota composition. In summary, this classification system can facilitate our understanding of the absorption and metabolic processes of anthocyanins and the health effects of different fruits.

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#### Introduction

Anthocyanins are a group of water-soluble pigments that confer the blue, purple, and red color to many fruits and vegetables (Fig. 1). The health benefits of anthocyanins have been the subject of intensive research in the past 20 y. The type and concentration of anthocyanins differ widely among different fruits and vegetables [1,2]. As a result, intake levels of anthocyanins varies widely by region, season, and among individuals with different social, cultural, and educational backgrounds [3–5].

High intakes of anthocyanins can be achieved with regular consumption of fruits, such as blueberries, blackberries, raspberries, strawberries, red grapes, and saskatoon berries. Population-based investigations revealed an association between anthocyanins and reduced incidences of cardiovascular disease, diabetes mellitus, and cancer [6–8]. Likewise, food intervention studies showed improved clinical and biomedical indexes following intakes of fruits rich in anthocyanins by volunteers with various health conditions [9].

Despite the accumulating evidence supporting their health effects, anthocyanin plasma concentrations were found to be low [10,11]. In human studies, <0.1% of intact anthocyanins are excreted in urine. The literature suggests that the apparent low bioavailabilities of some anthocyanins are due to their extensive presystemic metabolism, rather than their poor absorption from the gastrointestinal lumen [12]. It is suggested that phenolic acid metabolites may contribute to the health benefits of anthocyanins as some of these metabolites exhibit antioxidant, antiinflammatory, and other beneficial properties [13].

A comprehensive literature review was conducted on the relative contents of specific anthocyanins in fruits. The anthocyanin-rich fruits were then classified into groups based on

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the types of anthocyanins. This classification system can be used to reanalyze existing data and guide future studies on the health benefits of anthocyanin-rich fruits.

#### Methods

The US Department of Agriculture Database for the Flavonoid Content of Selected Foods (release 3.1, 2014) and other relevant publications were used as initial source of information to select fruits rich in anthocyanins [1]. Anthocyanin contents were ranked (Table 1). When data were insufficient or missing for certain fruits, literature searches were conducted.

A search strategy was developed in the Web of Science Core Collection (Thomson Reuters) using EndNote (Philadelphia, PA, USA). This search was limited to anthocyanin content directly measured by high-performance liquid chromatography (HPLC) methods and did not include the colorimetric "total anthocyanin assays" [119]. The following keyword combination was used to search the "Title/Keywords/Abstract" section: "anthocyanin" or "anthocyanins" or "cyanidin" or "malvidin" or "peonidin" or "delphinidin" or "petunidin" or "pelargonidin." The search results were narrowed with EndNote set at "search retrieved references" using the search combination: "HPLC" or "HPLC-MS/MS" or "MS/MS" or "chromatograph" or "chromatography" or "mass spectrometer" or "mass spectrometry." This anthocyanin content pool of references consisted of 3530 references. The search was conducted on December 10. 2014.

Further searches were conducted within the anthocyanin content reference pool for information on specific fruits: Acerola: "malpighia emarginata" or "acerola" or "barbados cherry" or "west Indian cherry"; Arctic bramble berries: "rubus arcticus" or "arctic bramble" or "arctic raspberry"; Açaí berries: "acai" or "açaí" or "euterpe oleracea"; Black raspberries: "rubus occidentalis" or "black raspberry" or "black raspberries" or "thimbleberry" or "thimbleberries" or "black caps"; Blood orange: "citrus sinensis" or "blood orange" or "tarocco" or "sanguinello" or "moro"; Blueberries: "vaccinium" or "blueberry" or "blueberries"; Bilberries: "vaccinium" or "biberry" or "bilberries"; Capulin: "Prunus salicifolia" or "capulin" or "capuli" or "tropic cherry" or "mexican cherry" or "cereza"; Eggplant: "solanum melongena" or "eggplant" or "aubergine"; Vitis vinifera grape: "vitis vinifera" or "grape" or "grapes"; Grape, not vitis vinifera: "grape" or "grapes" not "vitis vinifera"; Hybrid grape: "vitis vinifera" or "grape" or "grapes" and "hybrid"; Honeyberries: "lonicera caerulea" or "haskap" or "honeysuckle" or "honeyberry"; Lingonberries: "vaccinium vitis-idaea" or "lingonberry" or "lingonberries" or "cowberry" or "cowberries"; Maqui: "aristotelia chilensis" or "maqui" or "chilean wineberry"; Red currant: "ribes rubrum" or "red currant" or "red currants" or "redcurrant" or "red currants"; Saskatoon berry; "amelanchier alnifolia" or "saskatoon berry" or "saskatoon berries" or "saskatoon" or "serviceberry" or "serviceberries" or "juneberry" or "juneberries" or "shadbush"; Sour cherry: "prunus cerasus" or "sour cherry" or "sour cherries" or "tart cherry" or "tart cherries" or "dwarf cherry" or "dwarf cherries."

Name	R <sub>1</sub>	$R_2$
Pelargonidin (Pg)	Н	Н
Cyanidin (Cy)	ОН	Н
Delphinidin (De)	ОН	ОН
Peonidin (Pn)	OCH <sub>3</sub>	Н
Petunidin (Pt)	ОН	OCH <sub>3</sub>
Malvidin (Ma)	OCH <sub>3</sub>	OCH <sub>3</sub>

Fig. 1. Structures of common anthocyanidins.

Where the search strategy described above did not yield enough references on the topic, the following search combinations were used to search for references directly in the Web of Sciences Core Collection: Blackthorns: "prunus spinosa" or "blackthorn" or "blackthorns" and "anthocyanins"; Chokecherries: "prunus virginiana" or "chokecherry" or "chokecherries" or "bitterberry" or "chokecherries" and "anthocyanins"; Crowberry" or "crowberry" or "crowberries" and "anthocyanins"; Mulberries: "morus" or "mulberries"; Jambul: "syzgium cumini" or "jambolão" or "jambul" or "jamun" or "jambolag" and "anthocyanins."

In addition to these databases, the bibliographies of retrieved articles were also reviewed to obtain additional citations. Titles and abstracts of the references were scanned and full papers that were likely to contain comprehensive information on the anthocyanin contents of the fruits were obtained. Because some anthocyanins are not stable during storage [120], only fresh fruit and freshly squeezed juice were considered for anthocyanin content. Fruits are considered only if their total anthocyanin contents were >20 mg/100 g fruit. The rank order of anthocyanin contents was evaluated for each fruit. If different rank orders were found in different papers, the anthocyanins are listed and separated by commas in Table 1. When too many references were found, only recent references on the common fruit varieties are cited.

#### Results and discussion

A comprehensive literature search was conducted and resulted in the compilation of the major anthocyanins found in different fruits (Table 1). Fruits can be divided into groups based on the types of anthocyanin aglycones (Fig. 1), that is, the pelargonidin group, cyanidin/peonidin group, and multiple anthocyanins group.

Some fruits contain one predominant anthocyanin (indicated by >> in Table 1) and are important for research on the absorption and health benefits of anthocyanin-rich fruits. These include strawberries (pelargonidin-3-glucoside), honeyberries (cyanidin-3-glucoside [Cy-3-glc]), sweet cherries (cyanidin-3-rutinoside), and lingonberries (cyanidin-3-galactoside). For example, strawberries were studied for the absorption, metabolism, and excretion of pelargonidin-3-glucoside, the dominant anthocyanin in this fruit [121]. The North America commercial eggplant peel contains predominantly delphinidin-3-rutinoside and could also be a useful research tool [122–124]. In addition to fruits with one predominant anthocyanin, some fruits of the cyanidin/peonidin and multiple anthocyanins groups contain one or more major anthocyanin that is also indicated by > in Table 1.

The cyanidin/peonidin group contains the largest number of fruit varieties. Cyanidin glycosides and peonidin glycosides can be metabolically converted to each other by methylation and demethylation [10]. Both are also metabolized to protocatechuic acid (PCA) and vanillic acid. Therefore, peonidin containing fruits, such as cranberries and blackberries, are also classified into the cyanidin/peonidin group.

The multiple anthocyanidins group contains a variety of anthocyanin types and includes some of the most common fruits such as blueberries and grapes. The grapes of the *Vitis vinifera* variety include common wine grapes such as cabernet sauvignon and merlot. These grapes contain mainly anthocyanidin monoglycosides with a malvidin-3-glucoside content higher than those of other anthocyanins. Wine grape varieties other than *V. vinifera* contain mainly anthocyanidin diglucosides. Hybrid cultivars of *V. vinifera* contain both anthocyanidin monoglycosides and diglycosides [107].

Phenolic acid metabolites are suggested to contribute to the beneficial effects of anthocyanins. For example, PCA, a metabolite of cyanidin/peonidin glycosides, was suggested to possess antioxidative and antiinflammatory properties [13,125]. If the phenolic acid metabolites are indeed responsible for the systemic beneficial effects of anthocyanins, then these effects could be different among anthocyanins depending on the

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