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Stabilisation of Anthocyanins from *Aronia melanocarpa* as a Sustainable Source of Natural Colorants

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Black chokeberry (*Aronia melanocarpa*) contains anthocyanins in high concentration and has a relatively simple anthocyanin profile compared to other anthocyanin-containing berries, which makes it an attractive source for studies on chemical reactivity [1]. Anthocyanins display different colours over various ranges of pH, however their instability towards light, heat, oxygen, pH, and hydrolysis limits their application as natural colorants. In keeping with our interest in use of anthocyanins in consumer products [2,3], we have investigated a range of fundamental chemical transformations to potentially enhance their stability and lipophilicity, to facilitate more widespread potential for use, whilst also providing a greater understanding of the fundamental chemical reactivity of anthocyanin derivatives.

We chose waste *A. melanocarpa* skins generated as a by-product following pressing of the berries for the production of *Aronia* fruit juice, as it is readily available and has significant potential as a sustainable and renewable resource. The skins were extracted, and anthocyanins isolated, characterised [4], and various approaches to chemical modification were investigated to improve stability. Methods have been developed to enable variation of the anionic counterion (X, Figure 1) to form salts of acids weaker than HCl, specifically formate, trifluoroacetate, acetate and octanoate. In general, these new salts showed enhanced stability relative to more conventional chloride salts. During these studies it also proved possible to isolate and characterise the cyanidin hemiketal derivatives (**1**), in a remarkably pure form as a 61:39 ratio of epimers at the hemiketal centre.

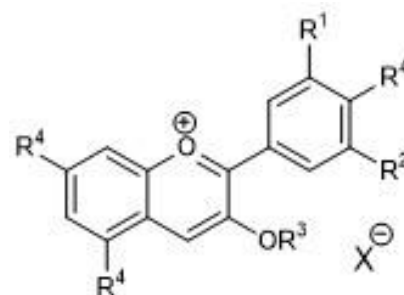


Figure 1. The general structure of anthocyanins, R¹, R² = H, OH, or OCH₃; R³ = glycosyl or H; and R⁴ = OH or O-glycosyl.

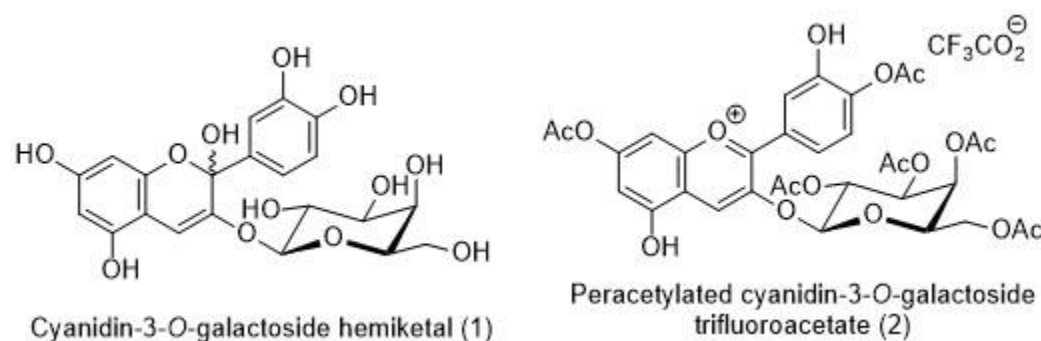


Figure 2. Examples of anthocyanin structures prepared and studied.

A second approach to formation of more stable and/or lipophilic anthocyanins was by chemical acylation of the sugar moiety to different degrees. A wide range of peracylated anthocyanins were prepared (e.g. Figure 2, **(2)**) and characterised as their trifluoroacetate salts. Unsurprisingly, sugar hydroxyl groups were acylated preferentially with the primary alcohol group reacting first. The remaining secondary alcohol groups then reacted in a reasonably selective manner, and finally, the phenolic positions could be acylated. A limited range of butanoyl and octanoyl derivatives were also prepared. LogP and UV-Vis of all the new anthocyanins was measured. A selected group of mono and di-esterified anthocyanin derivatives were studied further. DPPH antioxidant capacity was measured, and whilst there was a decrease in activity, this was modest. Finally thermal stability of mono and di-esterified anthocyanins was measured in n-octanol at 25, 40 and 60 °C, with notably longer half-lives for dibutanoate and diacetate esters of cyanidin-3-O-galactoside trifluoroacetate compared to the parent anthocyanin.

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