



Review

Previous and recent advances in pyranoanthocyanins equilibria in aqueous solution



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ABSTRACT

Pyranoanthocyanins are anthocyanin-derived compounds found in nature that present a vast palette of colours ranging from yellow to turquoise blue. Studies in aqueous solutions of these pigments by UV–Visible spectroscopy revealed their higher colour stability when compared to their anthocyanin precursors. Through Nuclear Magnetic Resonance (NMR) techniques it was possible to confirm the absence of hydration reactions in pyranoanthocyanins, contrarily to anthocyanins, which helps explaining their higher colour stability with the increase of the pH.

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1. Introduction

Pyranoanthocyanins are major polyphenolic pigments formed in red wines during their ageing and maturation [1] and are thought to contribute to the orange hues observed in those wines [2]. Their chemical formation pathway involves a cyclic addition onto carbon 4 and the hydroxyl group at the carbon 5 position of the anthocyanin, yielding a fourth ring that is responsible for the higher stability to hydration of these compounds when compared to the original anthocyanins [2–7]. Over the years, several families of pyranoanthocyanins have been described in the literature including A and B-type vitisins [3], methylpyranoanthocyanins [8–10], oxovitisins [11], acetylpyranoanthocyanins [12], pyranoanthocyanin-phenolics [4,13,14], pyranoanthocyanin-flavanols [15], A and B-type portisins [16,17], pyranoanthocyanin dimers [18] and pyranoanthocyanin-butadienyldene-phenolics [19] (Fig. 1).

In aqueous solution, anthocyanins are present in different forms in equilibrium. The anthocyanins and flavylium-like compounds equilibrium forms in aqueous solution have been vastly described in the literature [20–29]. In very acidic aqueous solution (pH < 1), these pigments are present as red flavylium cations. The increase of pH leads to a reduction of the intensity of the color due to a decrease of the concentration of the flavylium cation that is

converted into its colorless hemiketal form through nucleophilic attack of water. The hemiketal further undergoes a tautomerization reaction to give the pale yellow *cis*-chalcone (Cc), which isomerizes to *trans*-chalcone (Ct). At low acidic, neutral and basic pH values, deprotonation of the flavylium cation also occurs, giving rise to the violet/blue quinoidal forms [30] (Fig. 2).

Oppositely to anthocyanins, studies of pyranoanthocyanins equilibria in aqueous solutions are scarce in the literature [5–7,31]. Only a few papers have been published related to the physical–chemical properties of pyranoanthocyanins in aqueous solutions. The present review aims to discuss the main features of pyranoanthocyanins in aqueous solutions but also to present new data concerning the physical–chemical features of some recently described pyranoanthocyanins detected in red wines [17,18,32]. Moreover, the ionization constants will be correlated with some structural features that are important to stabilize pyranoanthocyanin in the pyranoflavylium cation form. The diverse colours presented by pyranoanthocyanins pigments and their higher colour stability, namely their colour stability at a wide pH range are important features indicating a putative application of these compounds in food products.

2. Pyranoanthocyanins in aqueous solution

Over the years, the equilibrium forms of pyranoanthocyanin pigments have been studied using NMR and UV–Visible spectroscopy [5–7,31,33]. In aqueous solutions pyranoanthocyanins have

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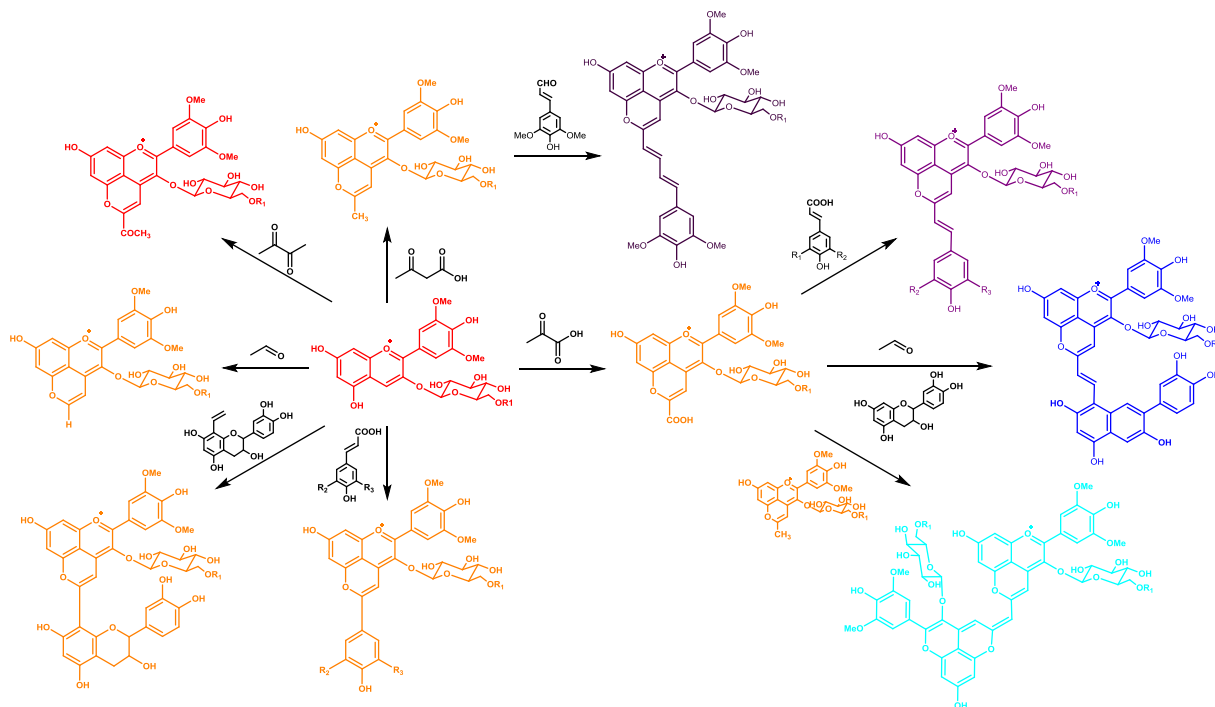


Fig. 1. Anthocyanin-derived pigments found in nature.

shown to co-exist under different equilibrium forms that are pH-dependent. NMR spectroscopy gives important information about the type of equilibrium that is occurring in aqueous solution at different pH values. In general, the peaks corresponding to proton exchange equilibrium forms are observed in the aromatic region spectrum of the ¹H NMR. No other important ¹H NMR peaks at any

pH studied corresponding to the hemiketal form described for anthocyanin compounds were observed [28,36,37] (Fig. 3). Indeed, if the hemiketal form was present, a significant displacement of about 2 ppm in the chemical shift of protons H-9 and H-10 (for vitisin B) to lower ppm values would have been observed. Santos et al. (1993) showed that the chemical shift of proton H-4 in malvin

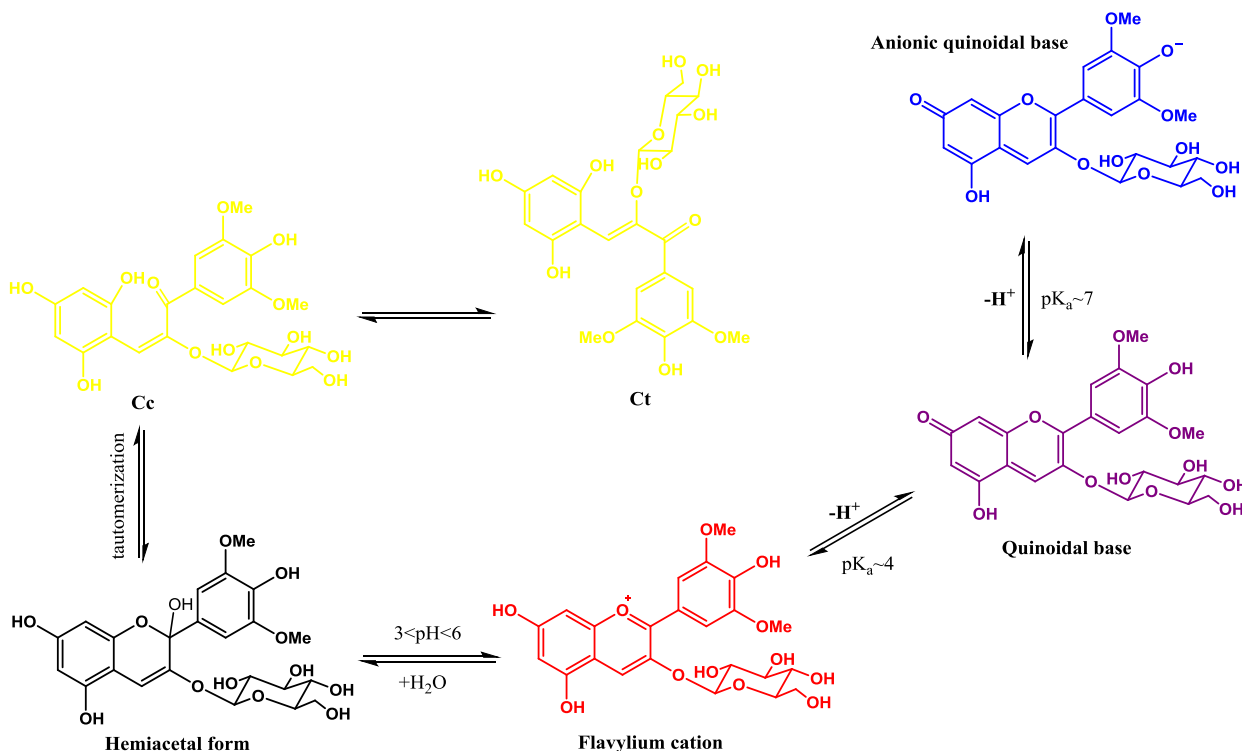


Fig. 2. Anthocyanin equilibria in aqueous solutions at different pH values.

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