



Anthocyanins and derivatives are more than flavylium cations



Fernando Pina^{a,*}, Joana Oliveira^b, Victor de Freitas^{b,*}

^a REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Monte de Caparica, Portugal

^b Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal

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ABSTRACT

Anthocyanins are much more than flavylium cation. At least four other species in moderately acidic solutions are formed constituting a pH reversible network of chemical reactions. The study of this network is an indispensable tool to rationalize the colour as well as the reactivity of these molecules. The network of anthocyanins was revisited and the one of related compounds, such as vitisins, described in detail. The colour given by anthocyanins is function of their concentration due to self-aggregation as well as by the possibility of co-pigmentation with other wine components. These phenomena can only be fully understood if the thermodynamic and kinetics of anthocyanins and related compounds are known. In aged red wines, vitisins nicely illustrate the evolution of anthocyanins. These compounds result from the chemical reaction of anthocyanins with other wine components and are very resistant to the hydration lacking the colourless hemiketals formation. This indicates that less colorant is necessary to confer colour to the wine and also explains the colour change from the red-violet in young wines to the red-orange observed in aged wines.

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1. Introduction

Anthocyanins are commonly associated to the respective flavylium cation that has a red colour. However, in vitro, flavylium cation is stable only at very acidic pH values ($\text{pH} \leq 1$) that is very rare in natural environments. At moderately acid pH values, as those found in wines (3.5–4.0), other species are present in solution. For example, in vitro the red colour of flavylium cation at $\text{pH}=1$ turns immediately purple/blue if the pH is increased to 4, but the blue colour fades in several minutes.

An overview of the anthocyanins literature confirms that many authors are not acquainted with the details of the physical chemistry of anthocyanins, probably they don't feel that it is necessary to invest time in one subject that at a first glance seems to be very complex and of uncertain interest. We would like to stress the importance of this knowledge and get some clues to the questions: which forms of anthocyanin other than flavylium cation are present in red wines? Is the flavylium cation the only possible reaction route for the evolution of anthocyanins in wine?

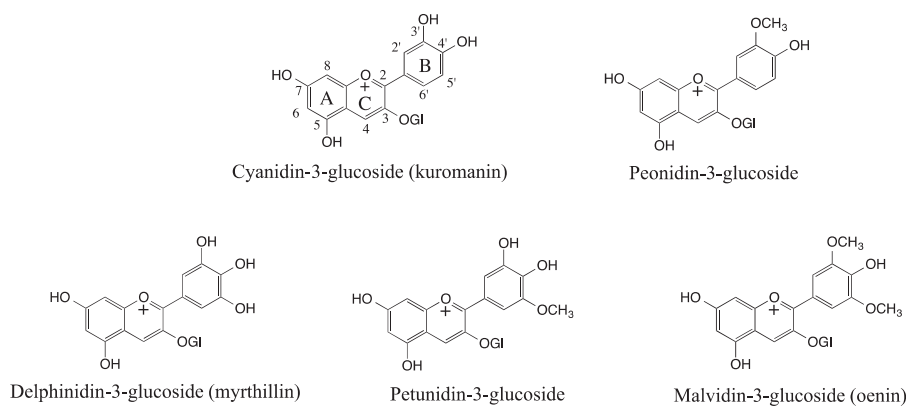
During wine ageing the intense red-violet colour starts to change giving origin to wines with more orange hues.^{1,2} These colour changes are due to the reaction of anthocyanins with other wine components leading to the formation of anthocyanin-derived

pigments with a colour different from red. In the first stages of wine maturation, it was reported that anthocyanins react with flavan-3-ols, directly or mediated by aldehydes.^{3–10} These products are thought to contribute to the red/purple colour intensification observed in young red wines during maturation.^{9,10} Anthocyanins can also react with phenolic acids¹¹ and small molecules derived from the yeast metabolism during fermentation such as pyruvic acid,¹² acetaldehyde,¹³ acetoacetic acid,¹⁴ diacetyl,¹⁵ vinylphenol,¹⁶ vinylguaiacol¹⁷ vinylcatechol¹⁸ and vinylcatechin.¹⁹ Those reactions lead to the formation of orange pyranoanthocyanin compounds. The formation of these compounds are pointed as being responsible for the red-orange hues observed in the first stages of the wine ageing process. In fact, anthocyanin-pyruvic acid adducts were described in the literature as being the main pigments detected by HPLC in Port wines with only two years of ageing.²⁰ A few years ago, it was identified in young Port wines two new classes of pyranoanthocyanin compounds with unusual blue and turquoise colours at acidic pH values, named as portisins^{21,22}, and pyranoanthocyanin dimer pigments,²³ respectively.

2. The network of chemical reactions of flavylium-derived compounds

As mentioned above, anthocyanins are generally identified by their flavylium forms. Scheme 1 presents the flavylium structure of the five most common anthocyanins-3-glucoside present in wines.

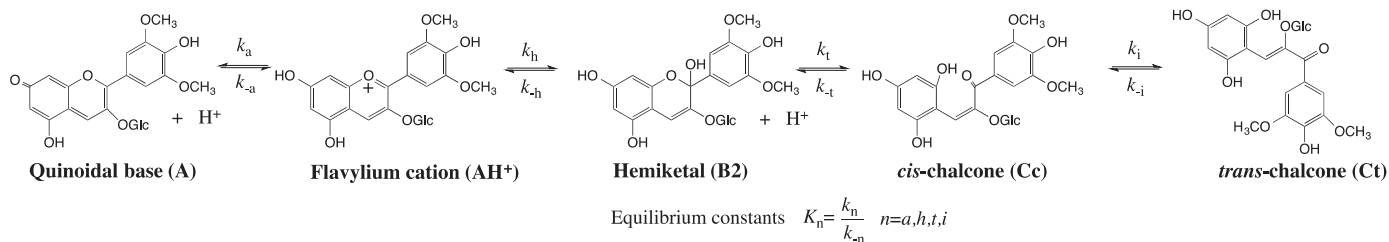
* Corresponding authors. Tel.: +351 220402558; fax: +351 220402658; e-mail addresses: fjp@fct.unl.pt (F. Pina), vfreitas@fc.up.pt (V. de Freitas).



Scheme 1. Flavylium forms of the five most common anthocyanidin-3-glucosides in grapes and wines.

The description of the thermodynamics and kinetics of the chemical reactions taking place at higher pH values directly or indirectly from flavylium cation was firmly established after the work of Brouillard and co-workers.^{24,25} The flavylium cation can deprotonated to give the quinoidal base, or hydrate to lead the hemiketal. This last species gives the *cis*-chalcone upon tautomerization (ring opening), and finally *trans*-chalcone is formed from isomerization of the *cis* analogue, see [Scheme 2](#).

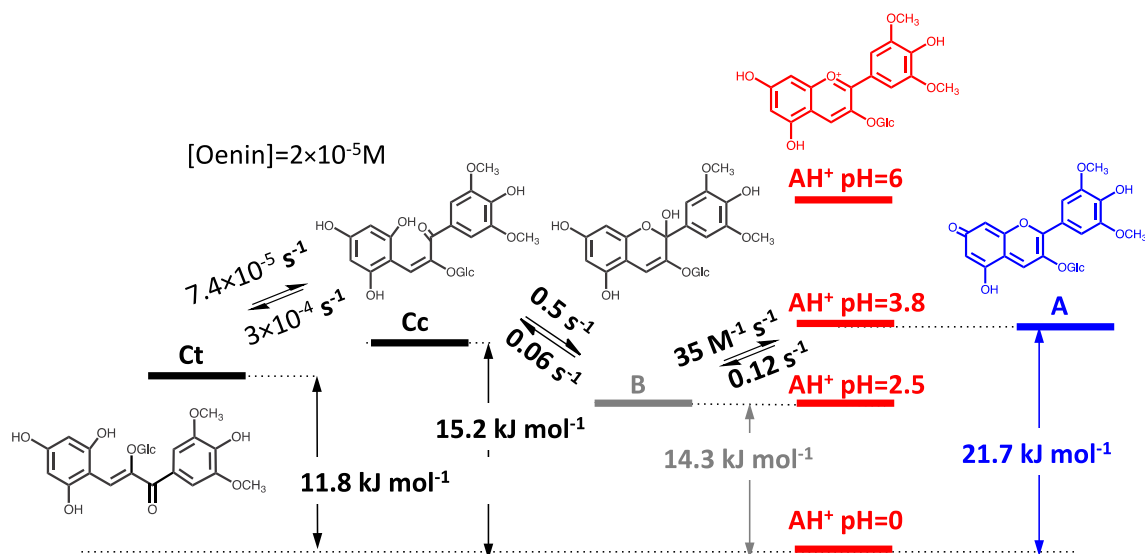
[Scheme 3](#) is very useful to understand the details of the oenin network of chemical reactions and can be applied for the other anthocyanins and flavylium derivatives in general. At very low pH values the red flavylium cation is the most stable specie of the network. Raising the pH to, for example, pH=3.8, equal quantities of the red **AH⁺** and the blue **A** are formed during the mixing time of the solutions, because the acid-base reaction is by far the fastest of the network. The colour of the solution is purple (a mixture of red



Scheme 2. Sequence of chemical species originated directly or indirectly from flavylium cation for oenin.

A very convenient way to visualize the network of chemical reactions of anthocyanins is the use of a diagram as the one reported in [Scheme 3](#) for oenin.

and blue). On the other hand raising the pH to 2.5 gives only 4.8% of quinoidal base. Alternatively, in a direct pH jump to pH=6, **A** is formed in 99.3%. These are the first visual impacts when solutions



Scheme 3. Energy-level diagram for malvidin-3-glucoside (Oenin), according to the procedure reported elsewhere.²⁶

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