



# Synthesis and equilibrium multistate of new pyrano-3-deoxyanthocyanin-type pigments in aqueous solutions



Joana L.C. Sousa<sup>a</sup>, Vânia Gomes<sup>a</sup>, Nuno Mateus<sup>a</sup>, Fernando Pina<sup>b</sup>, Victor de Freitas<sup>a</sup>, Luís Cruz<sup>a,\*</sup>

<sup>a</sup> REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal

<sup>b</sup> LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

## ARTICLE INFO

### Article history:

Received 7 June 2017

Received in revised form

23 August 2017

Accepted 28 August 2017

Available online 1 September 2017

### Keywords:

Pyrano-3-deoxyanthocyanins

Dyes

Chemical equilibria

UV–Vis spectroscopy

pK<sub>a</sub>

## ABSTRACT

Pyrano-flavylium compounds are flavylium derivatives with occurrence in processed foodstuffs such as wine and red fruit juices. In this work, the chemical equilibria of “bio-inspired” pyrano-3-deoxyanthocyanin dyes (**4–8**), presenting different substituent groups in D ring (10-methyl, 10-catechol, 10-dimethylaminophenyl, 10-carboxy) as well as in B ring (3',4'-dihydroxy, 4'-carboxy), were studied for the first time in aqueous solutions by UV–Vis spectroscopy. The presence of a methyl group at C-10 (pigment **4**) seems to stabilize the flavylium cation (AH<sup>+</sup>) shifting the deprotonation of 7-OH to a higher pK<sub>a1</sub> (pK<sub>a1</sub> = 5.0 ± 0.1). On the other hand, the quinoidal bases (A, A<sup>-</sup>) were more stabilized for the pigments which undergo the first acid-base equilibrium at C-10 substituent, as could be observed by the pK<sub>a2</sub> constants (pK<sub>a2</sub> = 8.4 ± 0.1 and pK<sub>a2</sub> = 8.1 ± 0.1, pigments **6** and **8**, respectively).

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Flavylium compounds represent a family of natural pigments present in the plant kingdom, which include anthocyanins, 3-deoxyanthocyanins and their metabolites.<sup>1–5</sup> These compounds are responsible for the coloration of many flowers and fruits (from yellow to blue) and can be found in processed beverages such as red wine. It is well known that the color of anthocyanins is greatly affected by pH. The sequence of chemical reactions was established by Brouillard *et al.*<sup>6–8</sup> using temperature and pH jumps experiments: at very acidic pH, the red flavylium cation (AH<sup>+</sup>) is the predominant species; when the pH is raised, the flavylium cation immediately undergoes proton transfer reaction, giving rise to the purple quinoidal base (A), and simultaneously, but more slowly, the flavylium cation leads to the formation of the colorless hemiketal (B) through a hydration reaction. The hemiketal further undergoes a tautomerization reaction yielding the pale yellow *cis*-chalcone (Cc) which isomerizes slowly to *trans*-chalcone (Ct) (Fig. 1).

This kind of pigments could undergo cycloaddition reactions

between C-4 and 5-OH of the flavylium cation and a double bond from other molecule such as pyruvic acid,<sup>9</sup> vinylcatechin<sup>10</sup> and vinylcatechol,<sup>11,12</sup> resulting in the formation of an additional pyran D ring. Over the last years, novel classes of pyrano-flavylium compounds such as portisins (blue pigments),<sup>13</sup> pyranoanthocyanin dimers<sup>14</sup> and pyrano-3-deoxyanthocyanins,<sup>15–17</sup> have been reported as well as important insights about their formation mechanism, physical-chemical and antioxidant properties.<sup>10,18,19</sup> Furthermore, pyranoanthocyanins have been shown to display higher color intensity and stability at a wider pH range comparatively to their anthocyanin precursors.<sup>19–21</sup>

In fact, while anthocyanins practically lose their red color between pH 1 and 5, as a result of the formation of colorless hemiketal B form (pK<sub>h</sub> 2–3), pyranoanthocyanins practically do not change their color intensity.<sup>22</sup> Equilibria-chemical network characterization of anthocyanins and several pyrano-anthocyanins are well documented in the literature. On the other hand, the kinetic, thermodynamic and photochromic features of oaklins (a family of 3-deoxyanthocyanins present in oak aged red wines) were fully studied.<sup>23</sup> Conversely, in which regards pyrano-3-deoxyanthocyanins, there is a lack of studies on their physical-chemical parameters.

The achievement of the correct chemical equilibrium

\* Corresponding author.

E-mail address: [luis.cruz@fc.up.pt](mailto:luis.cruz@fc.up.pt) (L. Cruz).

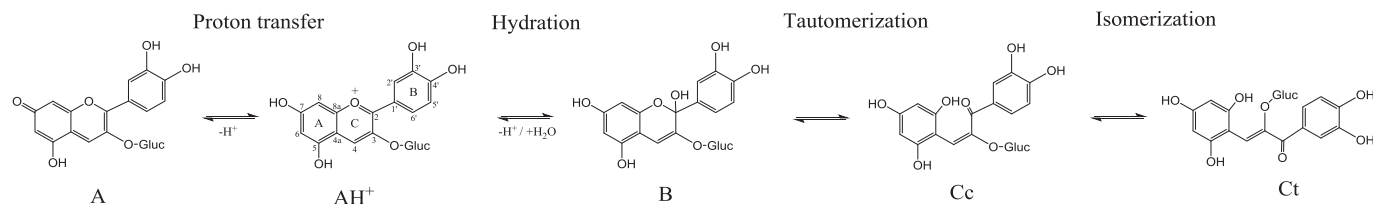


Fig. 1. Equilibrium forms of natural anthocyanins in aqueous solutions.

characterization of this kind of pigments in solution in a large pH range will allow to know the stability of their species for further potential applications such as photochromic and pH-sensors for food packaging, dyes for hair and textile, and photosensitizers for solar cells applications, among others.

The influence of different substituents in C-10 and B ring of five “bio-inspired” pyrano-3-deoxyanthocyanin-type dyes (Scheme 1) in their chemical equilibria was studied by UV–Vis spectroscopy and also compared with the natural pyrano-anthocyanin analogues (with glucose moiety).

## 2. Results and discussion

### 2.1. Synthesis of the pyrano-3-deoxyanthocyanin pigments

Five different pyrano-3-deoxyanthocyanin-type pigments **4–8** were synthesized according to the conditions described in Scheme 1.

Firstly, 3-deoxyanthocyanins **3a,b** were prepared through an acidic aldol condensation between 2,4,6-trihydroxybenzaldehyde **1** and acetophenone derivatives **2a,b**.<sup>23,24</sup> The next step consisted in the cycloaddition reactions between 3-deoxyanthocyanins and cinnamic acids (or oxaloacetic acid in the case of pigments **7** and **8**). After the purification steps, the pigments were individually analyzed by LC-DAD/ESI-MS in the positive ion mode (Table 1). Full

Table 1

Mass and spectroscopic data of the synthesized pyrano-3-deoxyanthocyanins.

Pigments	$\lambda_{\max}$ (nm) <sup>a</sup>	[M] <sup>+</sup> m/z
PyLUT-10-Me <b>4</b>	460	309
PyLUT-10-Catechol <b>5</b>	496	403
PyLUT-10-N(Me) <sub>2</sub> Ph <b>6</b>	550	414
PyLUT-10-Carboxy <b>7</b>	492	339
Py-(4',10)-Dicarboxy-7-hydroxyflavylium <b>8</b>	439	351

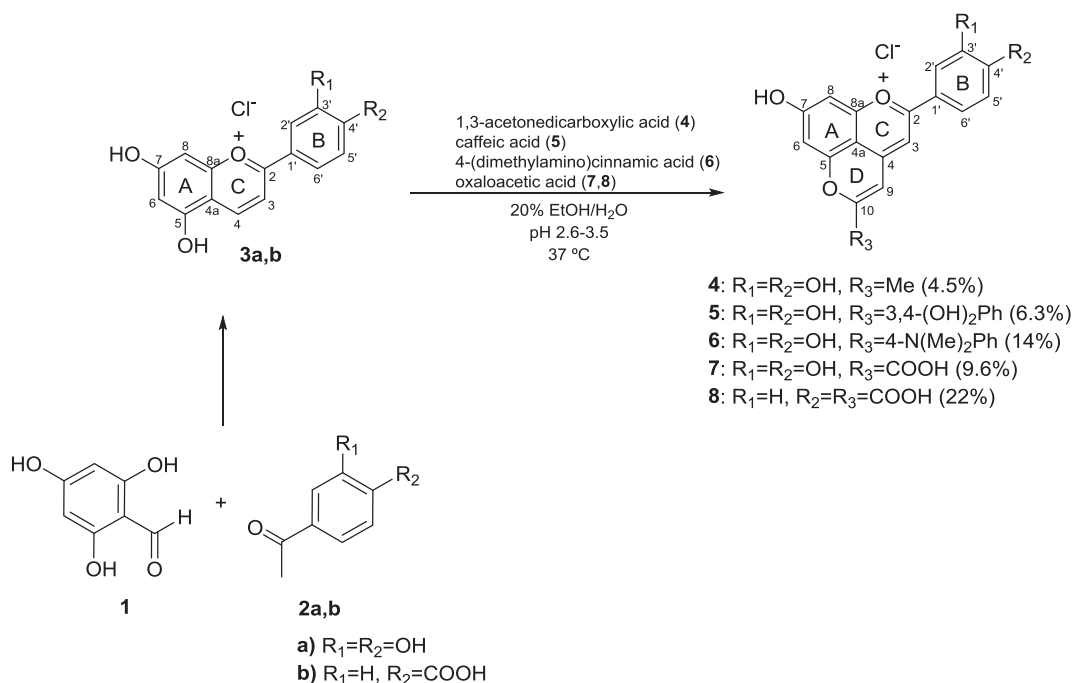
LUT: Luteolinidin.

<sup>a</sup> Recorded from the LC-DAD.

<sup>1</sup>H and <sup>13</sup>C NMR characterization confirmed the structures of the pyrano-3-deoxyanthocyanins **4–8**.

### 2.2. Thermodynamic equilibrium

In general, flavylium compounds display the same chemical equilibrium network: flavylium cation (AH<sup>+</sup>) is thermodynamically stable at very acidic pH values (pH = 1), being the dominant species of the equilibrium; when pH increases, the flavylium cation could be involved in two parallel reactions: i) acid-base reaction to form the neutral quinonoidal base (A) and ii) hydration reaction to give the colorless hemiketal (B). Proton transfer reactions take place immediately after the pH jump in a micro-seconds time scale while



Scheme 1. Synthesis strategy to obtain the pyrano-3-deoxyanthocyanin pigments **4–8**. Reagents and conditions: (**3a**) TMS-Cl (20 equiv.), AcOEt/MeOH (2:1), 0 °C, 60 min, 72%; (**3b**) AcOH/H<sub>2</sub>SO<sub>4</sub> (4:1), RT, 24 h, 59%.

Download English Version:

<https://daneshyari.com/en/article/5211887>

Download Persian Version:

<https://daneshyari.com/article/5211887>

[Daneshyari.com](https://daneshyari.com)