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Formation of new stable pigments from condensation reaction between malvidin 3-glucoside and (−)-epicatechin mediated by acetaldehyde: Effect of tartaric acid concentration

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Abstract

The objective of this work was to study the effect of tartaric acid concentration on the condensation reaction between malvidin 3-glucoside (Mv-glc) and flavanols mediated by acetaldehyde in the model solution. The model wine solutions were prepared by 12% ethanol in water (v/v) with two different L-tartaric acid concentrations (5 g/l and 25 g/l, respectively) and at two different pH values (3.2 and 1.7, respectively). Four new pigments were detected in model wine solutions containing Mv-glc, (−)-epicatechin and acetaldehyde. By reverse-phase HPLC-DAD, ESI-MS and MS^n fragmentation analysis, the four new pigments were tentatively identified as four isomers of hydroxyethyl malvidin-3-glucoside-ethyl-flavanol. The decrease in the concentration of Mv-glc and (−)-epicatechin and the increase in the concentration of the new identified pigments were more pronounced at higher tartaric acid concentration. At pH 1.7, although the two well-recognized ethyl-linked Mv-glc-flavanol isomers were quantitatively the major pigmented products in the reaction solution throughout the assay period, they appeared less stable than the four new pigments. At pH 3.2, the rate of formation of ethyl-linked Mv-glc-flavanol pigments was much slower than at pH 1.7, whereas the four new pigments were quantitatively the predominant pigmented products at the latter stage of the reaction.

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1. Introduction

It is well known that the reaction of anthocyanins and flavanols is one of the most important reactions during ageing and storage of red wine. The newly formed pigments are more stable than their anthocyanins precursors, and present distinct sensory properties. Two major ways of anthocyanins and flavanols reactions have been reported: direct reaction and indirect reaction (Timberlake & Bridle, 1976). Both of these two types of reactions have been intensively studied during the last years (Cheynier, 2002; Dueñas, Fulcrand & Cheynier, 2006; Es-Safi, Cheynier & Moutounet, 2000; Fulcrand, Atanasova, Salas & Cheynier, 2004, chap. 6; Pissarra, Mateus, Rivas-Gonzalo, Santos-Buelga & De Freitas, 2003; Rivas-Gonzalo, Bravo-Haro & Santos-Buelga, 1995; Salas, Fulcrand, Meudec & Cheynier, 2003).

For direct reaction between anthocyanins and flavanols, two mechanisms have been proposed. One is the formation of anthocyanin–flavanol (A^+–T) adduct, and another one is the formation of flavanol–anthocyanin (T–A^+) adduct. The mechanisms of formation of T–A^+ adduct and A^+–T adduct are presented in Fig. 1.

In the formation of A^+–T adduct, anthocyanin is in the flavylium form and acts as an electrophile. Nucleophilic addition of the flavanol onto the flavylium cation produces the colourless flavene, which can be either oxidized to the red flavylium, or proceed to a colourless cyclic condensation product.

In the formation of T–A^+ adduct, procyanidins release the intermediate carbocation by acid-catalyzed cleavage of their interflavanic bond, which acts as an electrophile,

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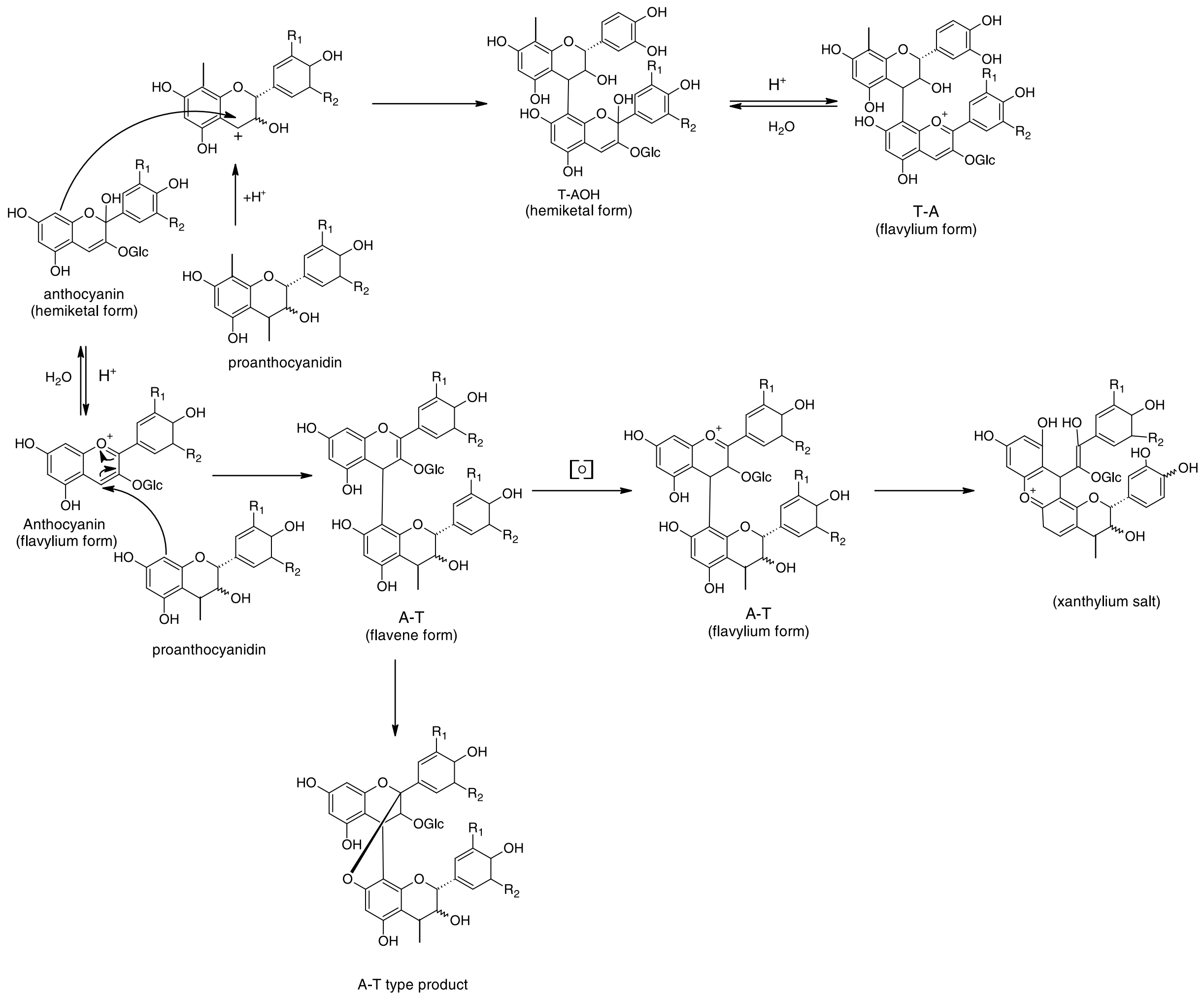

Fig. 1. Hypothetical mechanisms of direct reaction between anthocyanins and flavanols in wine (Cheynier, 2002).

while the anthocyanin, in its hemiketal form, acts as a nucleophile. The produced colourless dimer in the hemiketal form will further dehydrate to the red flavylium form.

For indirect reaction between anthocyanins and flavanols mediated by acetaldehyde, the reaction begins with nucleophilic addition of the flavanol on protonated acetaldehyde. The product thus formed loses a water molecule to give a new carbocation intermediate which, proceeds nucleophilic addition by anthocyanins in the hemiketal form, to produce ethyl linked T–A adducts. The nucleophilic addition may also occur by another flavanol, to ethyl-linked T–T adduct. Moreover, cycloaddition of anthocyanins with acetaldehyde can also occur, producing orange pigment. Fig. 2 presents the hypothetical mechanisms of indirect reaction between anthocyanins and flavanols mediated by acetaldehyde.

It has been well documented that the ratio of anthocyanin to flavanol, pH and temperature, oxygen availability and other co-factors like metal ions can affect anthocyanin–flavanol interactions (Dueñas et al., 2006; Es-Safi, Fulcrand, Cheynier & Moutounet, 1999; Guerra, 1997; Remy, Fulcrand, Labarbe, Cheynier & Moutounet, 2000; Salas et al., 2003). However, it was not clear if the different tartaric acid concentration can also affect such reactions. The motive that we verified the effect of tartaric acid concentration on this reaction is because some red wines, such as one of the characteristic wines in Portugal – "Vinho Verde" wines – often contain very high amounts of tartaric acid.

2. Materials and methods

2.1. Chemicals

Mv-glc was isolated from Pinot Noir grape skins as described previously (Sun, Santos, Leandro, De Freitas, & Spranger, 2007). (−)-Epicatechin was purchased from Fluka A. G. (Buchs, Switzerland). Acetaldehyde (analytical grade) was obtained from Merck (Darmstadt, Germany). All organic solvents were of HPLC grade.

2.2. Preparation of model solution

Model solution used for the reaction was prepared as described previously (Sun et al., 2007). Furthermore, 12%

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