RECENT SCIENTIFIC ADVANCES ON WINE PIGMENTS

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Colour is a major organoleptic property of red wine and is of crucial commercial importance since it is the first quality attribute to be perceived by the consumer. The colour of red wine is due to the presence of a group of polyphenol compounds known as anthocyanins, which constitute a wide family of pigments present in grape skins and sometimes in the grape pulp of some “teinturiers” *Vitis vinifera* varieties. Anthocyanins have been extensively studied since the beginning of the twentieth century and the development of new analytical and structural characterization techniques (namely chromatographic methods, NMR and mass spectrometry) has pushed forward the study of these compounds over the last ten years.

These pigments are extracted from red grape skins during fermentation and post-fermentation maceration[1]. The levels of anthocyanins in young red wines are not the only factors that contribute to the colour intensity and hues. Indeed, two major factors that influence red wine colour are the wine pH and copigmentation phenomena which will determine the form of anthocyanins in the wine. It is well known that anthocyanins are present in solution as many forms in equilibrium depending on pH[2,3]: when pH increases, the red form of anthocyanins is displaced by other structures that are colourless, thereby decreasing the overall colour (Figure 1).

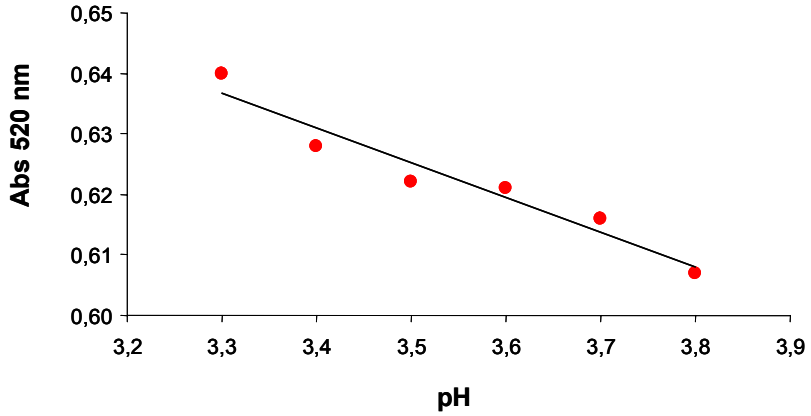


Figure 1 – Influence of pH on the colour (Abs 520 nm) of a young red table wine (c.v. Touriga Nacional, vintage 1999).

In recent studies performed in our laboratory, red wines were enriched with grape seed tannins (up to 2.0 g/L). The levels of tannins were monitored during ageing of the wines (Figure 2), as well as their red colour intensity (Figure 3).

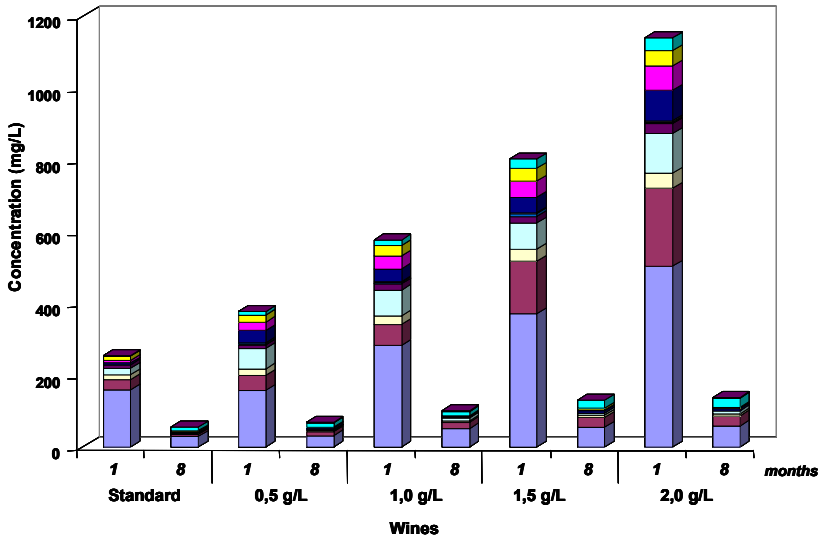


Figure 2 – Wine tannin composition after 1 and 8 months ageing

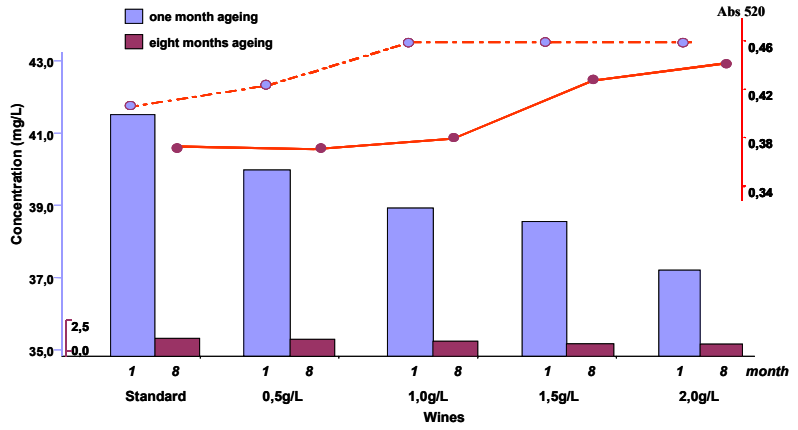


Figure 3 – Anthocyanin concentration and red colour of the wines after 1 and 8 months of ageing.

All the wines tested were found to display red colour intensification immediately after addition of the tannins (due to copigmentation phenomena), and an increase of 15 % after eight months of ageing when compared with the original wine after the same period of ageing. Copigmentation – which is defined as a physical-chemical interaction between wine pigments and colourless phenolic compounds also present in the wine (*e. g.* condensed tannins) – is an important factor that influences red wine colour. Copigmentation is often thought to be the first step in the formation of new anthocyanin-derived pigments, thus playing a crucial role in the evolution of wine colour (Figure 4).[4]

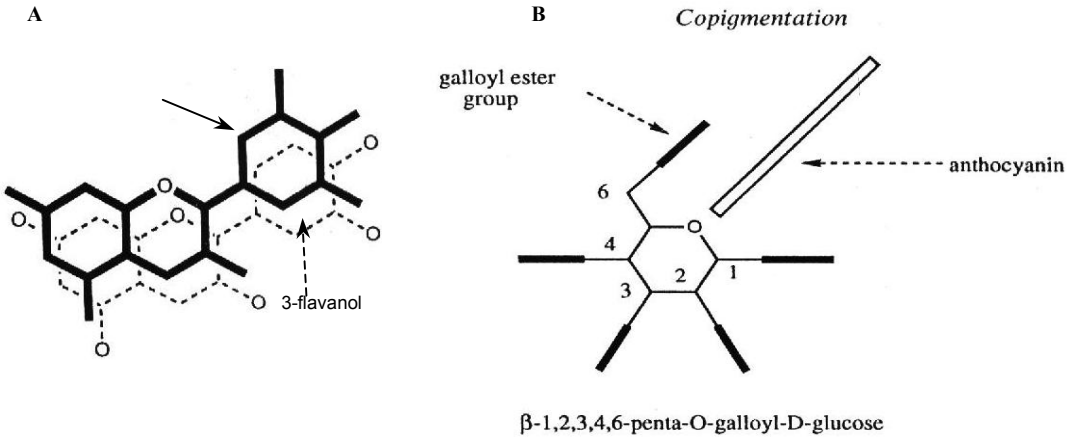
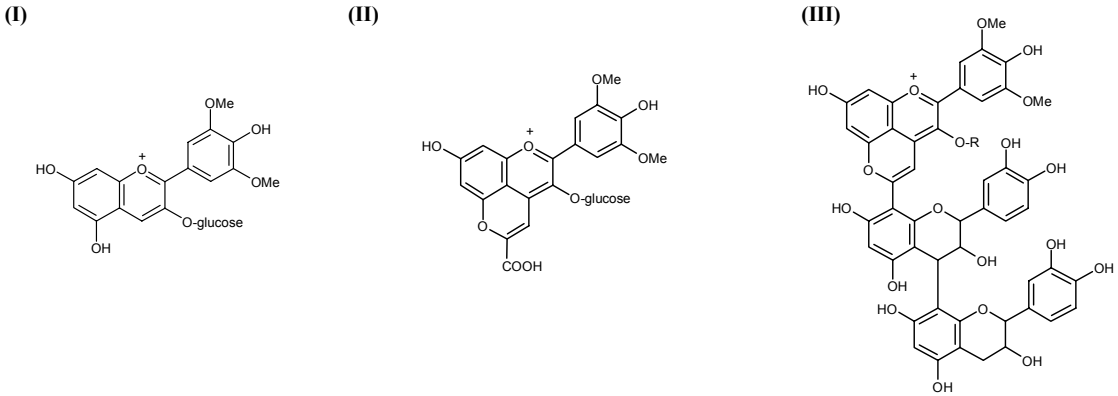


Figure 4 – Copigmentation phenomenon between anthocyanins and 3-flavanols (A), and galloyl groups of β-1,2,3,4,5,6-pentagalloylglucose (B).[5]

During storage and ageing, the red-purple colour of young red wines changes towards more brick orange-like hues. In general, the evolution of red wine colour during ageing is a result of several reactions comprising oxidation-reduction, complexation with carbohydrates, proteins or metals and chemical reactions with other compounds such as polyphenols (especially flavanols). Some of these reactions lead to the progressive displacement of anthocyanins (I) by more stable pigments with different colour features.[6,7] These red wine pigments were first thought to result mainly from condensation reactions between anthocyanins and flavanols either directly or mediated by acetaldehyde (VI).[8]

Although acetaldehyde is the major aldehyde present in red wine, mostly arising from ethanol oxidation, recent studies in our laboratory have shown that other aldehydes present in red wines may also lead to the formation of anthocyanin-derived pigments and induce colour changes in the wine.[9,10] Furthermore, reactions between anthocyanins and other smaller compounds such as pyruvic acid[11,12] or vinylphenol[13] have recently been demonstrated yielding new families of anthocyanin-derived pigments (Figure 5), namely pyranoanthocyanins and xanthylium derivatives with spectroscopic features that may contribute to a more orange-red colour.

More recently, a new class of wine pigments displaying unusual chromatic features, namely bluish hues at wine pH, were discovered in our laboratory and named as portisins (IV) (as they were first found in Port wines).[14]



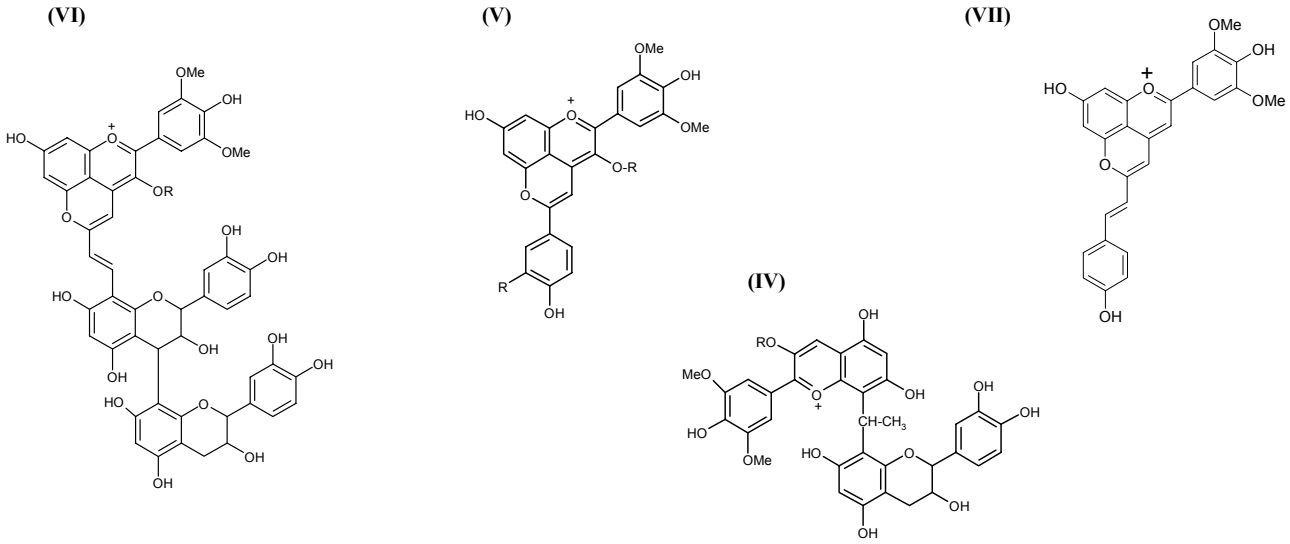


Figure 5 – Examples of different families of anthocyanic pigments occurring in red wine: anthocyanins (I), pyruvic acid adduct (II)[11,12], pyranoanthocyanin-flavanol (III)[15,16], portisin (IV)[14], pyranoanthocyanin-fenol (V)[17,18], anthocyanin-ethyl-flavanol (VI)[19], vinylpyranoanthocyanin-fenol (VII).[20]

The detection of these new wine pigments is extremely dependent on the analytical approach, which is mostly based on HPLC. For instance, anthocyanin-pyruvic acid adducts are the major wine pigments detected by HPLC after two years of ageing (Figure 6).[21] Nevertheless, other polymeric pigments that are not detected by HPLC methods still need to be assayed and quantified. Although the amounts of all these new anthocyanin-derived pigments in the wine are not easily ascertained yet, they should altogether contribute to the changes of the colour of red wine during ageing.

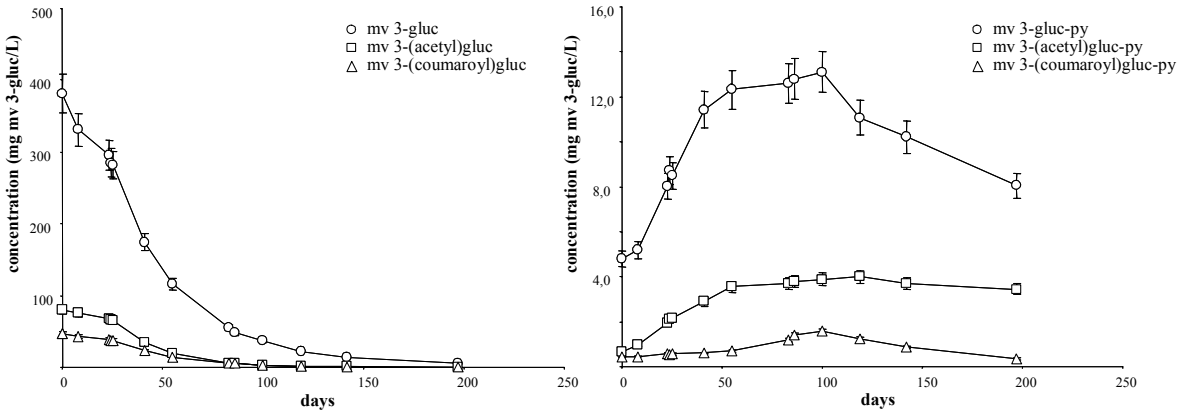


Figure 6 – Evolution of the level of malvidin 3-glucoside, malvidin 3-(acetyl)glucoside and malvidin 3-(coumaroyl)glucoside, and their pyruvic acid derivatives in a monovarietal Port wine, during 38 months stored in oak barrels. [21]

The mysteries of red wine pigments have attracted the interest of many researchers in recent years. Nevertheless, the formation mechanisms of anthocyanin-derived pigments remain a matter of interest and constitute a stimulating challenge for the wine chemists. A better understanding of all

the factors affecting red wine colour will certainly help oenologists to perform better practices, especially during wine ageing, aiming to improve the wine final quality.

There are several future perspectives in this field regarding the study and application of wine pigments:

a) The determination of calibration curves will allow the quantification of different classes of wine pigments in several types of red wines;
b) The contribution of newly-formed anthocyanin-derived pigments to the overall wine colour could be assessed after the isolation and full characterization of each pigment in terms of its chromatic features
c) Technological applications include the improvement of winemaking practices will be aimed in order to achieve the better wine chromatic features
d) The putative use of wine pigments as age-markers or authenticity markers would bring many benefits for the wine industry.

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Acknowledgments

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