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PERGAMON

Phytochemistry 64 (2003) 1179–1186

PHYTOCHEMISTRY

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Molecules of Interest

Why are grape/fresh wine anthocyanins so simple and why is it that red wine color lasts so long?

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Received 7 July 2003; received in revised form 30 July 2003

Abstract

Vitis vinifera red berries are characterized by anthocyanins whose chemical structures are among the simplest encountered in higher plants. On the contrary, many plants, including orchids, petunias, red cabbage, elderberries, potatoes for instance, have developed very complicated anthocyanins featuring side-chains at the available positions of the aglycone skeleton. Such pigments were shown to possess bio-physico-chemical properties not to be seen with the grape common anthocyanins. Among beverages (water, tea, beer, wine, coffee, juices, milk), red wine is the only one whose organoleptic properties improve with time and this is called ageing. The grape/fresh red wine pigments, after a few months, disappear from the wine giving birth to new pigments resulting from the wine spontaneous chemistry allowing it to remain red for many years. What are the wine pigments and why are they so stable is the purpose of this mini-review. The structural simplicity of grape anthocyanins and the long lasting colour of red wine is another French paradox; we call it French paradox II.

Keywords: *Vitis vinifera*; European grapevine; Red wine ageing; Anthocyanins; Tannins; Red wine pigments; Flower anthocyanins; Phloroglucinol moiety; French paradox II

1. Introduction

One of the authors (RB) was lucky enough to witness, as a young adult, the treasure discovered by one of his uncles, of Burgundy red wine bottles which have been hidden underneath a coal heap in a Parisian cellar, probably a little before invasion of the French capital. The 'discovery' took place at the beginning of the seventies and the bottles dated back to the mid-twenties to the mid-thirties. There was a great emotion among the 'inventors', but no one was surprised by the fact that, among the two dozens of Pinot Noir prestigious wines (La Romanée-Conti and Pommard, for instance), all have largely retained their original red colour, even if over the four coal-storage decades, loss and change of colour have probably occurred.

The aim of this mini-review is to unravel the mystery of red wine colour, that is to say the formation of red wine pigments. We came to an early conclusion which is to focus the attention on two points, which surely will not be addressed elsewhere at the moment. These two points are:

(i) To compare *vinifera* grape anthocyanins with those of *Pharbitis nil* (morning glory), *Matthiola incana* violet flowers, *Bletilla striata*, *Phalaenopsis* and *Dendrobium Laeliocattleya* (orchids), *Senecio cruentus*, *Petunia integrifolia*, *Triteleia bridgesii* and *Petunia hybrida* cultivar "Festival". It will be emphasized that the anthocyanins produced by flowers are usually characterized by highly sophisticated chemical structures featuring interesting color stabilization and variation mechanisms, which are not to be encountered with the grape so simple anthocyanins. Amazingly, the famous Pinot Noir cépage synthesizes anthocyanins which are the simplest found among higher plants. The paradox is that the Pinot Noir vine is at the origin of the world's best red wines. This assumption will not be shared by everybody; it is the authors' personal view and experience.

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doi:10.1016/S0031-9422(03)00518-1

(ii) In an essentially aqueous medium like red wine, simple anthocyanins are not believed to remain stable for a long time. Therefore, for a red wine to keep red over years, its native anthocyanins *must* evolve towards, new visible light absorbing, chemical chromophores. In our 1997 review (Brouillard et al., 1997), we pointed out the crucial role played by the flavylium 5-OH in the formation of red wine pigment analogs. Indeed, the xanthylium chromophore was not obtained without a phloroglucinol A-ring and the acetaldehyde promoted anthocyanin and (+)-catechin dimer also needs this fundamental anthocyanin moiety. Recently, during the course of our synthetic experiments, once more we demonstrated the importance of that structural feature, in the preparation of a few pyranoanthocyanins (Roehri-Stoeckel et al., 2001). The consequence is that this is probably the first definite scientific fact (need of a 5-OH) demonstrating the superiority of the European grapevine (*Vitis vinifera*) to produce red wines with the highest organoleptic quality.

Red wine ageing is more and more an important subject in oenology (chemistry and biochemistry) and many researchers are now analyzing novel wine pigment structures (Rivas-Gonzalo et al., 1995; Santos-Buelga et al., 1995; Escribano-Bailon et al., 1996, 2001; Bakker and Timberlake, 1997; Bakker et al., 1997; Fulcrand et al., 1997, 1998; Francia-Aricha et al., 1997; Revilla et al., 1999; Romero and Bakker, 1999, 2000; Es-Safi et al., 1999a,b; Mateus et al., 2001, 2002a,b; Mateus and de Freitas, 2001; Vivar-Quintana et al., 2002; Atanasova et al., 2002; Rémy-Tanneau et al., 2003; Hakansson et al., 2003).

Grosso modo three main strategies are now developed:

(i) One concerns red wine model solutions, where carefully selected reagents are left to interact for hours, days if not weeks and months. Pigment yields are generally poor and by-products numerous.

(ii) The second approach deals directly with the red wines and it is aimed at isolating and purifying pigments initially not present in the corresponding grape juices or musts. Due to the large diversity of red grape cultivars and the varied vinification techniques, there is no limit to the number of investigations that can be undertaken that way.

(iii) The third approach is to chemically synthesize red wine pigments or analogs starting from selected organic precursors (Fulcrand et al., 1998; Es-Safi et al., 1999b; Lu and Foo, 2001; Roehri-Stoeckel et al., 2001; Atanasova et al., 2002; Hakansson et al., 2003). In that case, fairly pure pigments and large amounts (Roehri-Stoeckel et al., 2001) may be obtained. In all cases, powerful separation and structure elucidation techniques are used. These are essentially HPLC, mass and NMR spectroscopies (^{1}H, ^{13}C), with their multiple facets.

2. How anthocyanins have established chemical communication in the plant kingdom

Anthocyanins of *V. vinifera* grapes are essentially 3-monoglucosides of the five aglycones malvidin, peonidin, petunidin, cyanidin and delphinidin. Attached to the glucosyl group, one may found sometimes acetyl and cinnamoyl residues (Ribéreau-Gayon, 1982; Mazza and Miniati, 1993). Strikingly, Pinot Noir does not possess acylated anthocyanins. So, in the wine ageing investigations, malvidin-3-glucoside or oenin (commercially available) is almost always present with the starting chemicals used to produce red wine novel pigments (Fig. 1). Other *Vitis* species always contain significant amounts of 3,5-diglucosides (acylated or not) even if 3-monoglucosides are still existing (Ribéreau-Gayon, 1982). Therefore, the anthocyanin structural emerging characteristics which makes the difference between *Vitis* species in general is that all *vinifera* anthocyanins do possess a free 5-OH in the A-ring. We will see further how important is the existence of that group for the development of red wine pigments during maturation and ageing phases. We must add that structurally simple anthocyanins does not mean at all *unreactive* anthocyanins. On the contrary, taken out from well-organized grape skin vacuoles, those simple anthocyanins are much more exposed to damaging chemical and biochemical degradation reactions than are the more sophisticated, and probably better protected, flower anthocyanins (see orchids, for instance).

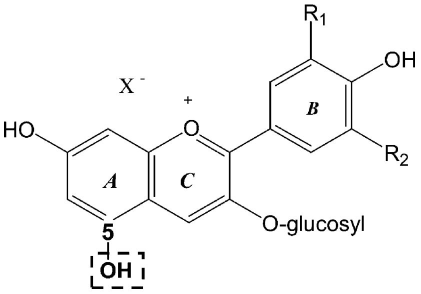

Fig. 1. Pinot Noir anthocyanins (R_1, R_2 are H, OH or OCH_3) are among the simplest encountered in the plant kingdom. One should note that a free 5-OH is a permanent structural feature common to all *vinifera* anthocyanins.

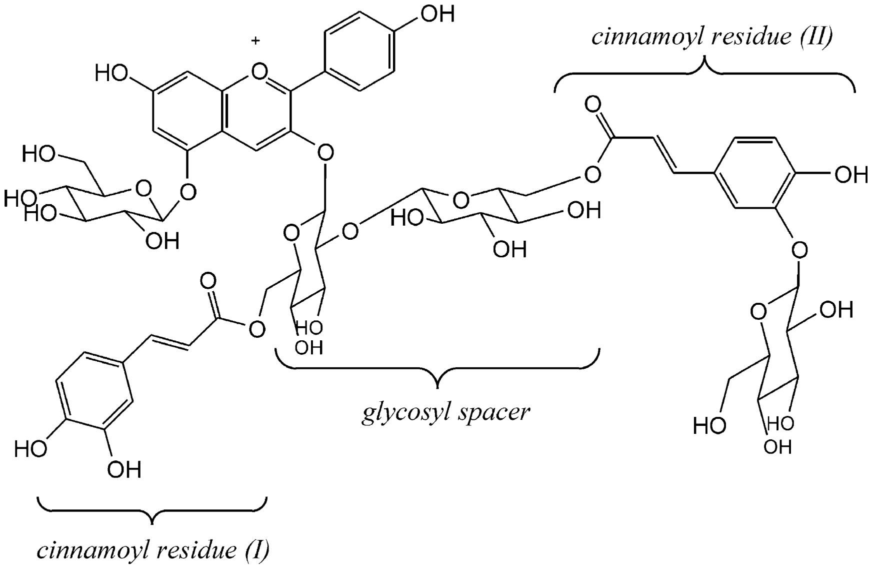

Fig. 2. One of the morning glory (*Pharbitis nil*) flower anthocyanins or 3-*O*-(2-*O*-(6-*O*-(*trans*-3-*O*-(β-D-glucopyranosyl)caffeyl)-β-D-glucopyranosyl)-6-*O*-(*trans*-caffeyl)-β-D-glucopyranosyl)-5-*O*-β-D-glucopyranosyl pelargonidin. Approximatively 94% of the pigment chromophore is protected against hydration (Dangles et al., 1993).

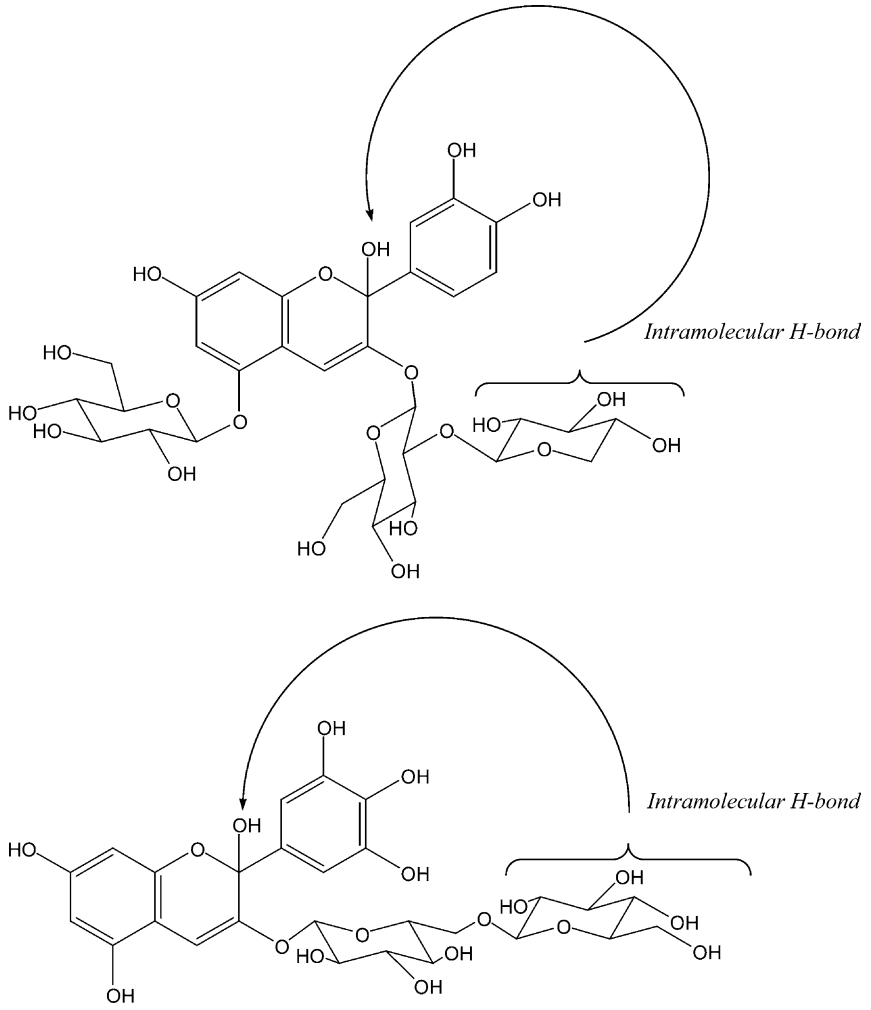

Fig. 3. Two anthocyanins of the disaccharide subgroup. It has been demonstrated that a H- bond could be established between the hemiacetalic OH and one of the terminal sugar free hydroxyl groups.

Copigmentation or copigment effect is divided into intermolecular copigmentation and intramolecular copigmentation (Brouillard and Dangles, 1993; Boulton, 2001). The intramolecular copigment effect is more efficient in the protection against water nucleophilic addition leading to color loss, than is the intermolecular effect. Full color stabilization, accompanied by some color variation, is best achieved when the anthocyanin bears more than one aromatic acyl residue of the cinnamoyl acid family. A nice example provided by a structurally homogeneous series of anthocyanins extracted from morning glory (*Pharbitis nil*) flowers is given. Such polyacylated anthocyanins with glycosyl spacers (Fig. 2) have been essentially uncovered over the past decade (Terahara et al., 1996).

At vacuolar pH values, the hydrophobic Π–Π stacking provides at the same time color stabilization and variation (hyperchromic and bathochromic shifts). The sandwich configuration is the more favorable to keep the flavylium chromophore away from water molecules, nevertheless partially satisfying the electronic demand of both 2 and 4 electrophilic sites. Even the more complex *Vitis* anthocyanins possess at most, only one cinnamoyl ester residue and such structures are scarce compared to the unsubstituted 3-glucosides (*V. vinifera*) and 3,5-diglucosides (*Vitis riparia*, for instance). However, it has been demonstrated that intermolecular copigmentation occurs with red grape anthocyanins and, since copigments are frequently found in grapes and yeasts, the copigment effect has become a major field of research in oenology nowadays (Boulton, 2001; Lambert, 2002).

In other cases, it was observed a very large value for the hydration thermodynamic constant, much larger than that of malvidin 3-glucoside and even larger than the one of malvidin 3,5-diglucoside (Figueiredo et al., 1996a,b). Anthocyanins of that type are to be found among 3-disaccharides (Fig. 3). Their distinguishing structural feature is their ability of preferential stabilization of the hemiacetal colorless form by formation of intramolecular hydrogen bond between the hemiacetalic OH and one of the free hydroxyl groups of the terminal sugar.

Another intramolecular H-bond, between the malonyl moiety of the 5-glucosyl and the 7-OH in the A-ring, has been highlighted (Figueiredo et al., 1996b). Such anthocyanins have a fairly acidic 7-OH group and they feature a cooperative mechanism using intramolecular copigmentation and intramolecular H-bonding. In this case, proton transfer (acidity) constants are larger than the corresponding hydration constants which is quite unusual (Fig. 4). Among *Vitis* anthocyanins malonyl substituents are unknown, and this very efficient color protecting cooperative mechanism therefore cannot exist with grape/fresh wine color producing pigments.

Further investigations of sophisticated anthocyanins (Fig. 5), this time extracted from *Petunia integrifolia* and *Triteleia bridgesii*, demonstrated that isomerisation from a *trans*- to a *cis*-caffeoyl moiety produces, at the same time, color intensification and resistance to pyrilium ring hydration (George et al., 2001). Cinnamoyl substituent *cis* isomers are not frequent among anthocyanins. They are formed under the effect of UV-A

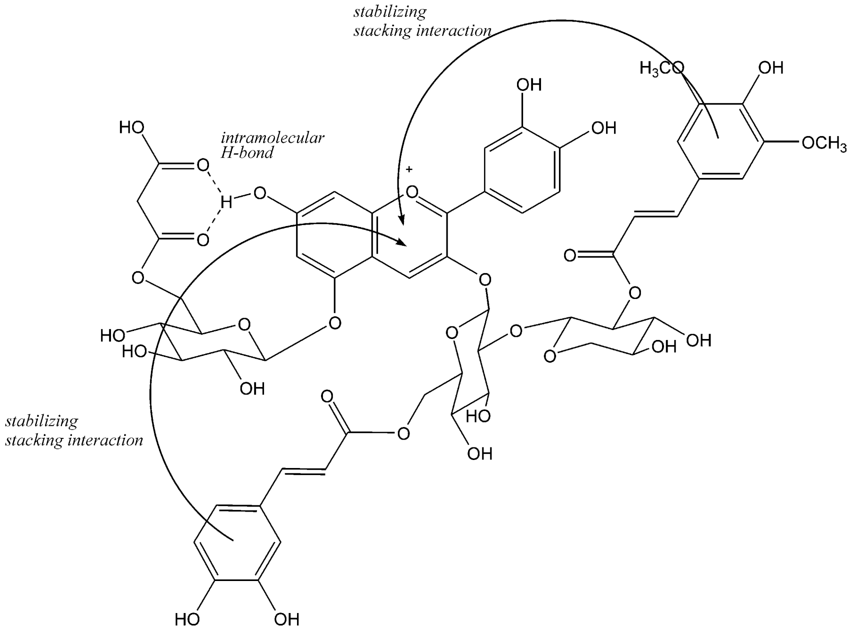

Fig. 4. One of the several *Matthiola incana* anthocyanins characterized by a proton transfer constant larger than the hydration constant ($pK_a = 1.96$ and $pK_h = 2.84$). The malonyl residue establishes a H-bond with the 7-OH, while the cinnamoyl esters stack on both sides of the pyrilium ring. The first effect increases the 7-OH acidity and the second effect partially protects the chromophore central ring from hydration.

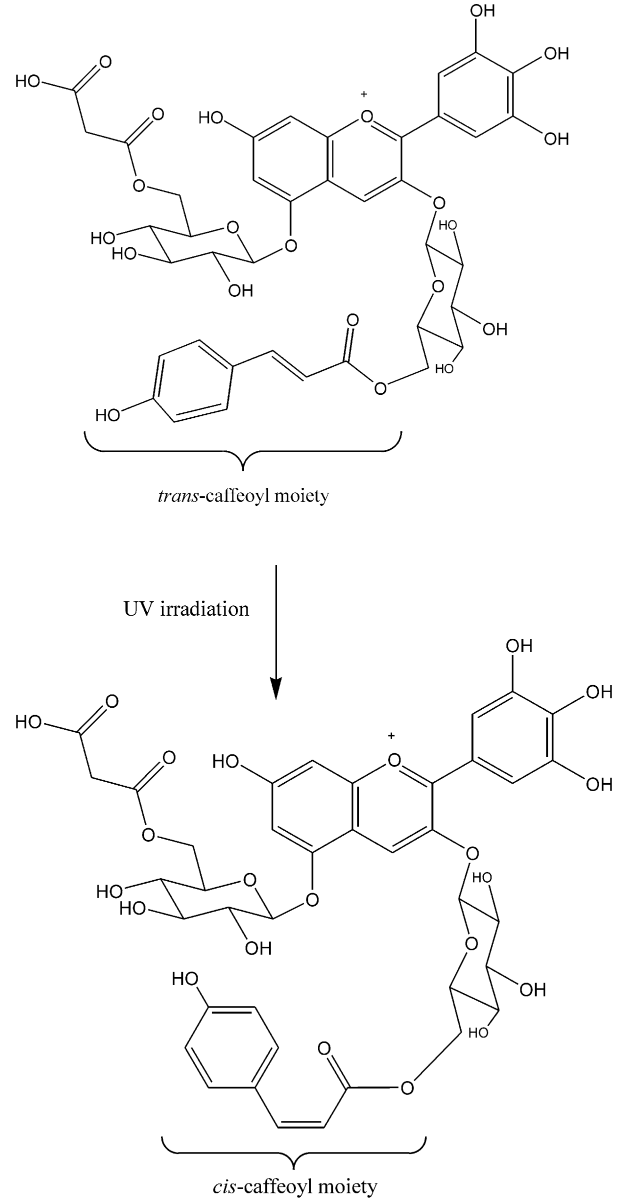

Fig. 5. One couple of anthocyanin *trans* and *cis* stereoisomers (George et al., 2001).

light starting from the corresponding usually stable *trans* isomers. *Vitis* anthocyanins bearing a cinnamoyl moiety have always been identified in the *trans* (or *E*) form.

An ultimate example is taken from the popular petunia flowers. Thirty-five genes are known to affect flower color in petunia. Reports on anthocyanin structures in that plant provide an impressive list which follows: the 3-glucosides of the six common aglycones; the 3-rutinosides of delphinidin, cyanidin, petunidin and pelargonidin; the 3-sophorosides of cyanidin and peonidin; the 3-gentiobioside and the 3,7-diglucoside of cyanidin; the 3-rutinoside-5-glucosides and the 3-(*E* or *Z*)-*p*-coumaroylrutinoside-5-glucosides of cyanidin, peonidin, petunidin, delphinidin and malvidin; the 3-caffeoylrutinoside-5-glucosides of malvidin, petunidin and peonidin; the 3-glucosyl-*p*-coumaroylrutinoside-5-glucosides of malvidin, petunidin and delphinidin; the 3-glucosylcaffeoylrutinoside-5-glucosides of malvidin and petunidin (Ando et al., 1999; Gonzalez et al., 2001). The 3-caffeoylglucosylcaffeoylrutinoside-5-glucosides of malvidin and petunidin, the 3-caffeoylglucosyl-*p*-coumaroylrutinoside-5-glucosides of malvidin, petunidin and delphinidin and the 3-caffeoylglucosyl-*p*-coumaroylrutinoside of malvidin, all being diacylated anthocyanins, have been recently elucidated (Ando et al., 1999; Tatsuzawa et al., 2000). Petunia flowers possess a remarkable diversity of sugar substituents not to be encountered with *Vitis* pigments. Sugars are good spacers maintaining chemical communication between the different parts of the molecule. Looking at the large numbers of published results on petunia anthocyanins, it seemed almost impossible to uncover novel structures. This was nevertheless the case and one of the two new structures extracted from the cultivated *Petunia hybrida* cv 'Festival' (violet flowers) is shown in Fig. 6 (Gonzalez et al., 2001). Remarkably, that malvidin derivative is characterized by a 3-side-chain featuring alternating glucosyl, rhamnosyl, coumaroyl, glucosyl and feruloyl groups which can wrap the malvidin chromophore.

The petunia case is particularly interesting since the many genes coding for the synthesis of anthocyanins could be introduced in *vinifera* cells, thus opening the way for a vine to produce new pigments with different and more stable colors. This is one of the reasons to compare pigments present in flowers and fruits to those of the *Vitis* genus.

3. The phloroglucinol A-ring with its 5-OH characteristic structural feature, or the so simple *vinifera* red grape anthocyanin monoglucosides need nothing more for entering in the ageing phase

We have already seen that for a young red wine to remain red over the years, its anthocyanins have to combine with tannins for instance, to generate genuine wine pigments which are not grape pigments, even if the precursors have to be found in the grape skins and seeds or in the yeasts. Over the past 5 years, a lot of works have revealed the existence of such wine pigments. A few of these works are quoted here. A pioneer work was published by Fulcrand and collaborators (1996) quickly followed by an impressive series of publications from the same group in Montpellier, France (Fulcrand et al., 1998; Es-Safi et al., 1999a,b; Rémy-Tanneau et al., 2003; Atanasova et al., 2002; Atanasova, 2003). Vitisins, as they were called, were found in red wines by a group with a strong experience in the field of wine chemistry and wine ageing (Bakker and Timberlake, 1997; Bakker et al., 1997; Romero and Bakker, 1999). A malvidin 3-

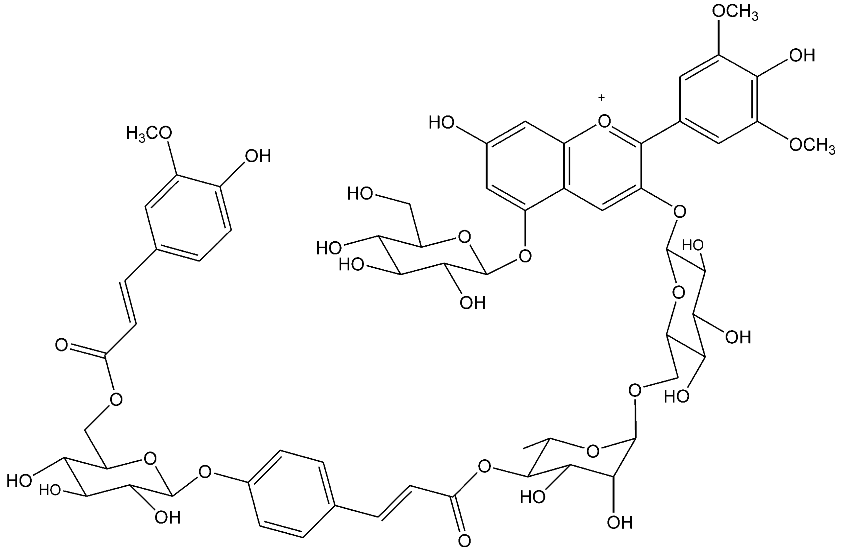

Fig. 6. *Petunia hybrida* cv ‘Festival’ new anthocyanin (Gonzalez et al., 2001).

glucoside pyruvic acid adduct could be detected in Port wines (Mateus and de Freitas, 2001; Mateus et al., 2001; 2002a,b). The acetaldehyde condensation product between catechin and malvidin 3-glucoside was studied as a function of the medium acidity (Escribano-Bailon et al., 2001).

In 1997, we stressed the fact that a phloroglucinol A-ring is a key element in the formation of red wine new pigments (Brouillard et al., 1997). We used 3-*O*-methylated synthetic, non natural, flavylium salts. From the comparison of the products obtained from two different flavylium salts, one with a phloroglucinol A-ring, the other with a resorcinol A-ring, we concluded that for genuine wine pigments, like xanthylium salts and acetaldehyde bridged anthocyanin–tannin structures to be formed, a phloroglucinol

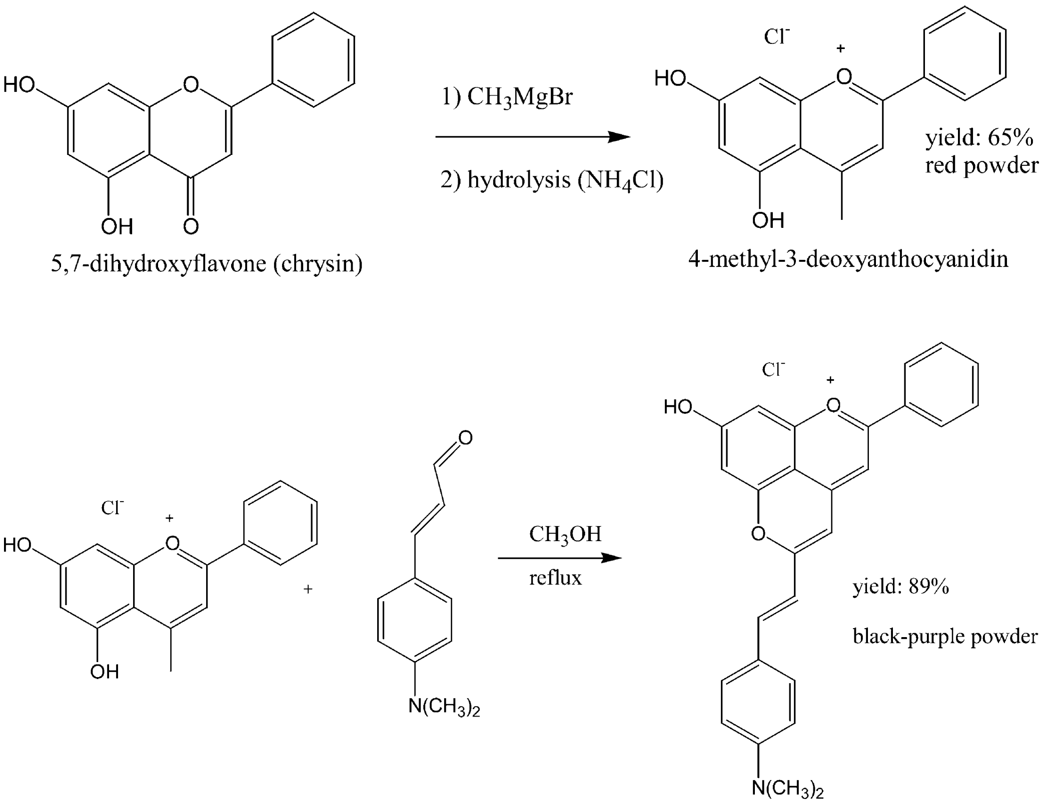

Fig. 7. A synthetic, non natural, vitisin analog: mechanistic scheme (Roehri-Stoeckel et al., 2001).

ring was absolutely necessary (Escribano-Bailon et al., 1996).

Two years ago, we demonstrated by means of chemical synthesis the importance of the presence of the 5-OH to reach another type of pigments outcoming from the red wine ageing chemistry (Roehri-Stoeckel et al., 2001). We were not the first to prepare such pigments, but we were the first to synthesize them in good yields with cheap starting chemicals, not to be found in the grapes, nor in the yeasts. The synthetic scheme is briefly described in Fig. 7.

Very recently, anthocyanidin 3-monoglucosides have been demonstrated to prevent linoleic acid peroxidation (Rossetto et al., 2002). In this work, (+)-catechin, one of the monomeric tannins, was shown to regenerate the oxidized anthocyanin free radical and the sum of malvidin 3-monoglucoside and (+)-catechin antioxidant individual activities was less than the activity observed when both molecules were present, leading the authors to conclude to the existence of a synergistic effect between malvidin 3-glucoside and (+)-catechin. This is an interesting observation, since in red wine pigments anthocyanin monomer and tannin monomer are often bound together.

Five years ago (Brouillard et al., 1997), we pointed out that the French paradox first version has probably much more to do with red wine pigments than with grape native pigments and tannins. Indeed, no molecular explanation has been given until now to the French paradox first version. Therefore, it is of the utmost importance to understand if grape/fresh wine molecular species are responsible for the beneficial effects brought to human health or if these benefits come from the only recently discovered red wine genuine pigments. Our interpretation opens the way to a deepening of the first version of the French paradox and we call this the French paradox step II.

4. Concluding remarks

Three research 'tracks' may be followed:

(i) Elucidate more red wine genuine pigments and have them tested for their in vitro and in vivo biological activities. Interesting pigments to human health should then be synthesized.
(ii) Genetic engineering applied to the vine plant would allow new genes coding for new red grape pigments, nowadays mostly found in flowers like petunias, orchids, to be introduced.
(iii) The ageing phase of red wine has no equivalent among other human beverages like tea, beer, coffee, fruit juice or milk, for instance. However, an exception could be made concerning green tea, where the native flavanols are chemically transformed in the oxidative fermentation process, leading to black tea. Both black and green teas possess tannins 'good to your health'. Finally, one may think of having some of the red wine genuine pigments added to these beverages to see whether or not this could preserve their initial organoleptic characteristics.

Acknowledgements

We are greatly indebted to Dr. Richard Thwaites (CRC for Bioproducts, Australia) for his comments and encouragement.

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