Wine and grape polyphenols — A chemical perspective

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ABSTRACT

Phenolic compounds constitute a diverse group of secondary metabolites which are present in both grapes and wine. The phenolic content and composition of grape processed products (wine) are greatly influenced by the technological practice to which grapes are exposed. During the handling and maturation of the grapes several chemical changes may occur with the appearance of new compounds and/or disappearance of others, and consequent modification of the characteristic ratios of the total phenolic content as well as of their qualitative and quantitative profile. The non-volatile phenolic qualitative composition of grapes and wines, the biosynthetic relationships between these compounds, and the most relevant chemical changes occurring during processing and storage will be highlighted in this review.

1. Introduction

Non-volatile phenolic compounds and derivatives are intrinsic com-ponents of grapes and related products, particularly wine. They constitute a heterogeneous family of chemical compounds with several compo-nents: phenolic acids, flavonoids, tannins, stilbenes, coumarins, lignans and phenylethanol analogs (Linskens & Jackson, 1988; Scalbert, 1993). Phenolic compounds play an important role on the sensorial characteris-tics of both grapes and wine because they are responsible for some of organoleptic properties: aroma, color, flavor, bitterness and astringency (Linskens & Jackson, 1988; Scalbert, 1993).

The knowledge of the relationship between the quality of a particu-lar wine and its phenolic composition is, at present, one of the major challenges in Enology research. Anthocyanin fingerprints of varietal wines, for instance, have been proposed as an analytical tool for authen-ticity certification (Kennedy, 2008; Kontoudakis et al., 2011). Polyphenols are also important from the taxonomical point of view. It is known that the patterns of some classes of flavonoids, such as anthocy-anins, are under strict genetic control and that their distribution varies considerably among different grape cultivars (Revilla, García-Beneytez, Cabello, Martín-Ortega, & Ryan, 2001). Moreover, the study of the inter-actions between wine polyphenols and aroma substances or proteins, at the molecular level is also a relevant topic in this field (Dufour & Bayonove, 1999; Simon et al., 2003).

Non-volatile phenolic composition of wine depends on numerous factors, such as grape variety and maturity, environmental factors in the vineyards (climate, soil, sanitary stage), and the wine-making tech-nology, as well as fermenting and aging conditions (Fang et al., 2008). Pre-fermentative practices such as addition of SO_2 and ascorbic acid before grape crushing or operations such as maceration, alcoholic fer-mentation, inoculation of different yeast strains, malolactic fermenta-tion, precipitation phenomena, oxidation or adsorption, together with β-glucosidase activity and clarification with some fining agents (used in wine clarification and filtration operations) can also influence the levels of phenolic compounds during the wine-making process (Balík et al., 2008; Kennedy, 2008; Linskens & Jackson, 1988; Saucier, 2010; Scalbert, 1993).

The study of phenolic composition of grapes and wine may allow the establishment of one or more biomarkers specific for a particular type of grapes, allowing to assess their chemical evolution during growth and maturation, and to develop new and improved methods (both qualita-tive and quantitative) for monitoring those processes. Phenolic analysis is found to fit authentication purposes, thus protecting consumers against fraud (Anastasiadi et al., 2009; Robbins, 2003).

2. Non-volatile phenolic composition of grapes and wines

There is a great chemical diversity in the non-volatile phenolic composition of grapes and wine. This is due not only to the different varieties of grapes, but also to the fact that this type of compounds exists in both the free and conjugated forms, as they may be bound to quinic acid or to one or more sugar molecules (namely glucose, galactose, sacarose and mannose) yielding mono-, di-, tri- or even tetraglycosides (Cheynier, Schneider, Salmon, & Fulcrand, 2010; Linskens & Jackson, 1988; Scalbert, 1993).

The non-volatile phenolic components of grapes and wine comprise several classes: phenolic acids, flavonoids, tannins, stilbenes, coumarins, phenylpropanol derivatives, lignans and neolignans. They have been unequivocally identified, when purification was possible, by MS and monodimensional and/or two-dimensional NMR spectroscopy (Flamini, 2003; Kosir & Kidric, 2002).

2.1. Phenolic acids

Phenolic acids are usually divided in two main groups: benzoic acids, containing seven carbon atoms (C6–C1) and cinnamic acids, comprising nine carbon atoms (C6–C3). These compounds exist predominantly as hydroxybenzoic and hydroxycinnamic acids that may occur either in their free or conjugated form.

2.1.1. Hydroxybenzoic acids

Several types of hydroxybenzoic acids (HBA) have been identified in both grapes and wine. The most abundant are *para*-hydroxybenzoic, protocatechuic, vanillic, gallic, and syringic acids (Fig. 1) (Baderschneider & Winterhalter, 2001). Gallic acid is described as the most important phenolic compound since it is the precursor of all hydrolyzable tannins and is encompassed in condensed tannins (see Section 2.3). Ethyl esters of these phenolic acids have been also identified in wine (Kallithraka, Salachaa, & Tzouroua, 2009).

2.1.2. Hydroxycinnamic acids

Hydroxycinnamic acids (HCA) are one of the most representative classes of phenolic acids found in both grapes and wine (Baderschneider & Winterhalter, 2001). *para*-Coumaric, caffeic, ferulic and sinapic acids (Fig. 1) are some of the most referenced compounds. These cinnamic acids are also associated to the wine browning process and are precursors of volatile phenolic compounds (Kallithraka et al., 2009). Cinnamic acids may display *cis* or *trans* isomeric forms, the latter being the most abundant in nature. These isomers are convertible either enzymatically or through the action of light.

Natural hydroxycinnamic acids usually appear as esters being the linkage unit quinic acid or glucose molecule. However, this type of derivatives is not present in grapes and derived products (except in

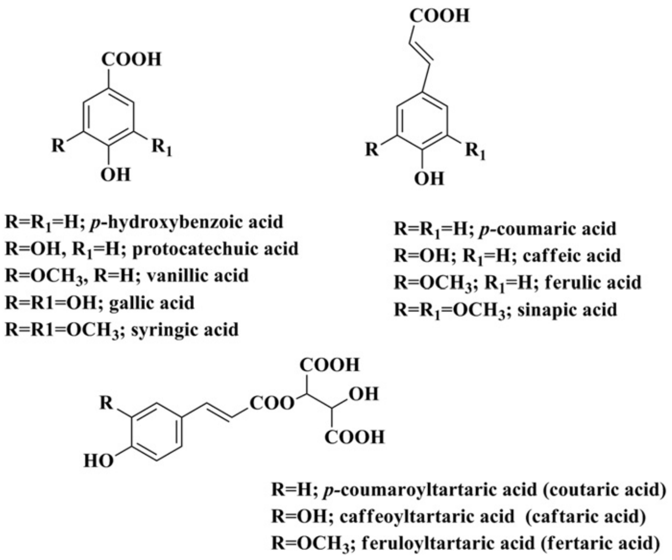


Fig. 1. Chemical structure of hydroxybenzoic, hydroxycinnamic and hydroxycinnamoyltartaric acids present in grapes and wine.

Riesling wine) being tartaric esters or diesters preferentially formed instead (hydroxycinnamoyltartaric esters, Fig. 1) (Buiarelli, Cocciolia, Merollea, Jasionowskaa, & Terracciano, 2010). The main hydroxycinnamic acids found in grapes and wines are caftaric acid (caffeoyltartaric acid), *p*-coutaric acid (coumaroyltartaric acid), and fertaric acid (feruloyltartaric acid) (Fig. 1). The presence of a double bond in the lateral side leads to the existence of two isomeric forms: *cis* and *trans*. In grape, caftaric and fertaric acids are mainly found in the *trans* form, while a negligible fraction of the *cis* form has been found for *p*-coutaric acid.

trans-Caftaric acid and *trans*-fertaric acid are mainly localized in the pulp, and during the grape pressing, they are quickly released into the juice. In contrast, the *trans* and *cis* isomers of *p*-coutaric acid are less extractable since they are mostly localized in the grape skin. These compounds are known to be partially responsible for the astringent properties of both grapes and wine.

In the case of the genus *Vitis*, for instance, it was possible to distinguish the different varieties through the degree of *p*-coumaroyl and caffeoyltartaric esters present, which are thus mentioned in the literature as taxonomic markers of both grapes and wine (Somers, Vérette, & Pocock, 1987). Although the white wines have a quite low concentration of phenolic compounds as compared to the red ones they contain, in turn, a rather high degree of hydroxycinnamoyltartaric acids (*e.g.* caftaric acid). Hydroxycinnamic acids and their tartaric esters are the main class of phenolics in white wines and the main class of nonflavonoid phenolics in red wines (Vanzo et al., 2007).

During the wine fermentation process, the partial hydrolysis of this kind of esters takes place yielding free hydroxycinnamic acids, which are then transformed into ethyl esters, namely ethyl coumarate and ethyl caffeate (Pozo-Bayón, Hernández, Martín-Álvarez, & Polo, 2003). The study of low molecular weight phenolic compounds during the aging of sparkling wines manufactured with red and white grape varieties has revealed the presence of several phenolic constituents, namely *cis*- and *trans*-caftaric, *cis*- and *trans*-fertaric, *cis*- and *trans*-caffeic, and *cis*- and *trans*-*p*-coumaric acids and their ethyl ester derivatives (Pozo-Bayón et al., 2003).

2.2. Flavonoids

Flavonoids belong to a chemical class displaying a basic structure of 15 carbon atoms comprising two aromatic rings bound through a 3 carbon chain (C6–C3–C6), which may or not be part of a third ring. This carbon skeleton is responsible for the chemical diversity of this family of compounds.

Flavonoids are generally grouped into several classes, which differ mainly in the oxidation degree of the central pyran ring, except in the case of chalcones (Fig. 2A). They comprise different types of compounds such as flavones, flavonols, flavanones, flavononols, flavanes, flavanols, anthocyanidins and anthocyanins, chalcones and dihydrochalcones (Fig. 2A) (Baderschneider & Winterhalter, 2001). The highest flavonol concentrations in grapes were found at flowering, followed by a decrease as the grapes increased in size. A significant level of flavonol biosynthesis was observed during berry development and the greatest increase in flavonols per berry can be observed 3–4 weeks post veraison (Mattivi, Guzzon, Vrhovsek, Stefanini, & Velasco, 2006).

Some of the flavonoids present in both grapes and wine are represented in Fig. 2B.

In nature, flavonoids can occur either in the free or conjugated form being often esterified to one or two sugar molecules through at least one hydroxyl group (*O*-glycosides, *O*-Glyc). Although the *O*-glycosylation may take place in any hydroxyl function present in the flavonoid scaffold it usually involves the OH present in the C_7 position of flavones and flavonones, in the C_3 and C_7 positions of flavonols and flavononols, or in C_3 and C_5 of anthocyanidins (Jing et al., 2008; Mattivi et al., 2006). Another type of glycosides (*C*-glycosides, *C*-Glyc) can take place in which the connection to the sugar molecule occurs directly in the flavonoid skeleton through a C – C bond. These derivatives are more resistant to hydrolysis than their *O*-analogs. The sugar associated to a particular glycoside may differ from glucose to galactose, rhamnose, xylose or arabinose. In *C*-glycosides, glucose is the more frequently found.

In the flavonoid family the chemical diversity *versus* complexity is mainly associated to the high variety of aglycons and glycosides as well as to the occurrence of condensation reactions. The latter will give rise to more complex heterogeneous systems, namely dimers or even polymers.

Attending to the high chemical diversity of flavonoids several attempts to classify them are found in the literature. Three distinct categories are usually accepted: glycosylated flavonoids, flavonoid aglycons and anthocyanidin glycosides (anthocyanins) (Zoecklein, Fugelsang, Gump, & Nury, 1995). Nonetheless, a systematic classification is assumed in the present work aiming at a more clear arrangement according to their different chemical characteristics.

2.2.1. Flavones

Flavones (Fig. 2A) are characterized by the presence of a double bond between carbons C_2 and C_3 and by the absence of a hydroxyl group in the C_3 position. These compounds are known to have an important pharmacological activity, apart from its chemotaxonomic relevance (Cieślik, Gręda, & Adamus, 2006; Macheix, Fleuriert, & Billot, 1994; Tsao, 2010).

Although flavones are widely distributed in plants, as aglycons or glycosides, they are not present in grapes in significant amounts, except for luteolin (Fig. 2B) (Fang et al., 2008).

Isoflavones are isomers of flavones, displaying the aromatic ring B in the C_3 position (Fig. 2B). Genistein is an isoflavone that has been identified in grapes and wine (Fig. 2B) (Zoecklein et al., 1995).

2.2.2. Flavanones

Flavanones (Fig. 2A), which display a saturated carbon chain between atoms C_2 and C_3, are often named dihydroflavones (by analogy with the flavones). Eriodicitol is a flavanone that has been extracted from grapes (Fig. 2B) (Cieślik et al., 2006; Macheix et al., 1994; Tsao, 2010). Naringenin and hesperetin were also found in South-Moravian wine samples (Jandera et al., 2005).

2.2.3. Flavonols

Flavonols (Fig. 2A) are characterized by the presence of a double bond between atoms C_2 and C_3, and a hydroxyl group in C_3, thus being often named 3-hydroxyflavones. Moreover, about 90% of the flavonols are hydroxylated in C_3, C_5 and C_7, thus being designated as 3,5,7-trihydroxylated derivatives (Castillo-Muñoz, Gómez-Alonso, García-Romero, & Hermosín-Gutiérrez, 2007). In grapes, glycosides from the following aglycons have been identified (Fig. 2B): quercetin (3′,4′-diOH), kaempferol (4′-OH), isorhamnetin (3′-MeO analog of quercetin), myricetin (3′,4′,5′-triOH), laricitrin (3′-MeO analog of myricetin) and syringetin (3′,5′-MeO analog of myricetin). The simultaneous presence of these aglycons was detected in different types of red wine from *Vitis vinifera* grapes (Hsu, Liang, Hung, & Kuo, 2009).

Interestingly, different sugars can be bound to the flavonols, producing glucosides, glucuronides, galactosides and diglycosides (glucosylarabinoside, glucosylgalactoside, glucosylxyloside and glucosylrhamnoside). There are several types of condensed flavonoids, the most abundant being the *O*-glucosides, the *O*-sulphates and those derivatives containing acylated sugars and aliphatic or aromatic acid groups in their structure (Jeffery, Parker, & Smith, 2008; Muñoz, Mestres, Busto, & Guasch, 2008).

In white wine, only quercetin, kaempferol and isorhamnetin have been detected. The flavonoids myricetin, laricitrin, and syringetin were missing in all white varieties, a fact that reveals that the enzyme flavonoid 3′,5′-hydroxylase is not expressed in white grape varieties (Jeffery et al., 2008; Mattivi et al., 2006). Red grape flavonol 3-*O*-glycosides comprise three different complete series, according to the nature of the sugar moiety linked to the C-3 position. The 3-*O*-

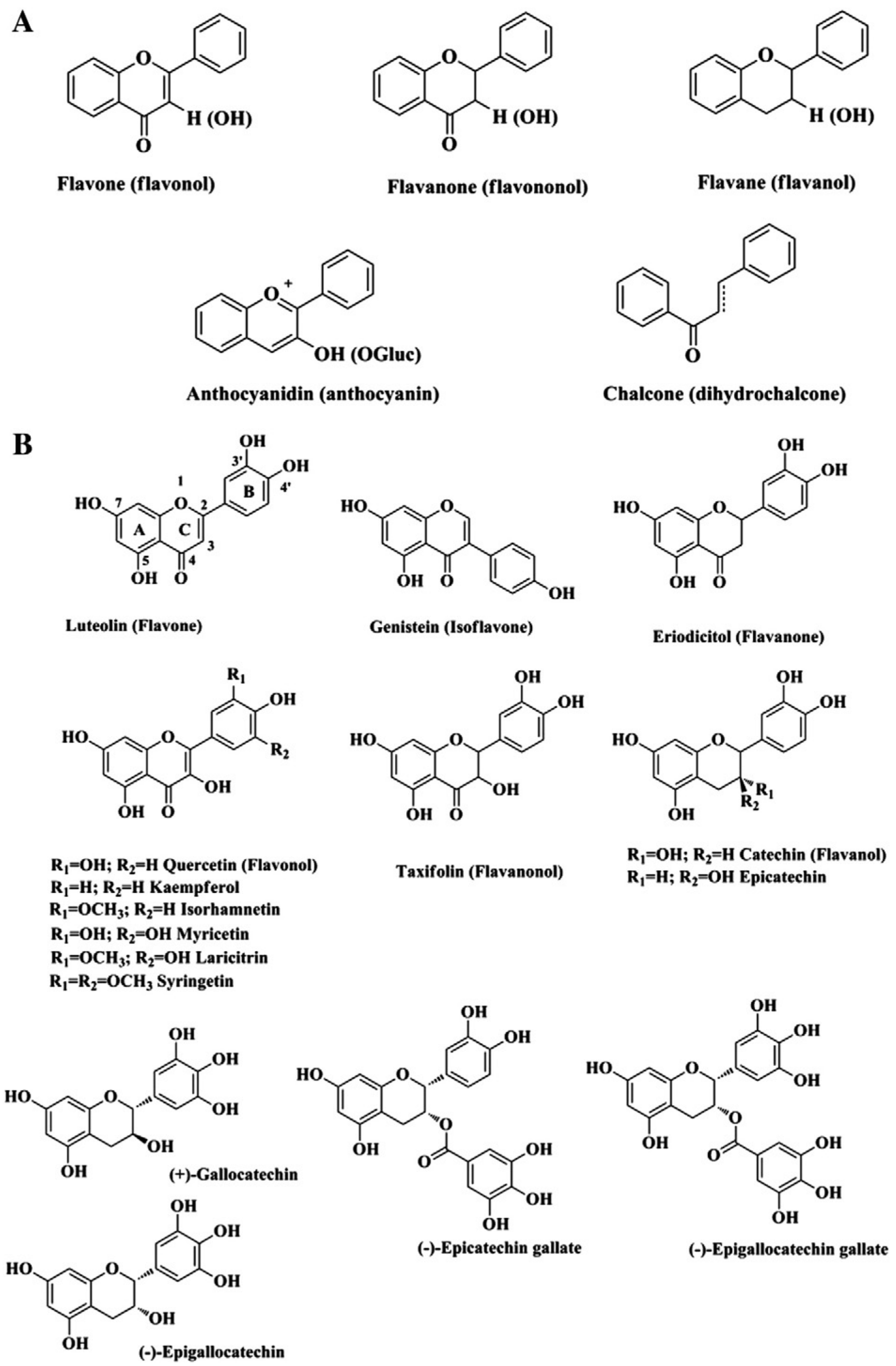


Fig. 2. A — General structure of flavonoid subgroups; B — flavonoids present in grapes and wine.

glucosides were the main derivative of the six flavonol aglycones (kaempferol, quercetin, isorhamnetin, myricetin, laricitrin, and syringetin), whereas the corresponding 3-*O*-galactoside derivatives were found to be minor compounds. The 3-*O*-glucuronides were described as the third kind of red grape flavonol derivatives and normally account as minor compounds for all of the flavonol aglycones, with the exception of quercetin 3-*O*-glucuronide, which was as abundant as quercetin 3-*O*-glucoside. The presence of quercetin 3-*O*-(6″-rhamnosyl)-glucoside (rutin) was also detected as a trace compound in the skins of Petit Verdot grapes as well as laricitrin 3-*O*-galactoside and syringetin 3-*O*-galactoside in red grapes (Castillo-Muñoz et al., 2009; Mattivi et al., 2006).

2.2.4. Flavononols

Flavononols (Fig. 2A) are characterized by the absence of a double bond in the heterocyclic ring, and by the presence of a hydroxyl

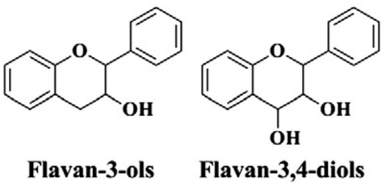


Fig. 3. Chemical structure of flavan-3-ols and flavan-3,4-diols.

group in the C_3 position, being also named 3-hydroxyflavonones or dihydroflavonols. Taxifolin (Fig. 2B), astilbin and dihydromyricetin 3-*O*-rhamnoside are elements of this category often reported in the literature (Zoecklein et al., 1995). The optic isomerism is present in this type of compounds due to the presence of asymmetric carbon atoms.

2.2.5. Flavanes

Flavanes (Fig. 2A) are flavonoids which display a saturated carbon chain between C_2 and C_3, and no carbonyl group in C_4 (Linskens & Jackson, 1988; Scalbert, 1993). The flavane nucleus forms the common basic structure for many hundreds of different molecules, namely of flavanols (Section 2.2.6).

2.2.6. Flavanols

Flavanols (Fig. 2A) are benzopyrans that have a saturated carbon chain between C_2 and C_3, a hydroxyl function in C_3, and no carbonyl group in C_4. Both flavan-3-ols and flavan-3,4-diols (Fig. 3) can be found in nature, the latter being often present in wood and tree bark, but rarely found in fruits. Flavan-3,4-diols are also often referred to as leucoanthocyanidins.

The most abundant flavan-3-ols in nature are catechin and its enantiomer epicatechin (Fig. 2B). These compounds are present in the skin and seeds of grapes as well as in wine. In white wines produced under special conditions, avoiding a prolonged contact with the skin of the grapes, catechin was determined to be the most abundant flavonoid, being largely responsible for the characteristic taste of the wine (Lunte, Blankenship, & Read, 1988). Some catechin derivatives, namely gallocatechin, epigallocatechin, epicatechin gallate and epigallocatechin gallate (Fig. 4), have been identified in grapes and wine (Decendit et al., 2002; Mattivi, Vrhovsek, Masuero, & Trainotti, 2009).

2.2.7. Chalcones and dihydrochalcones

Chalcones are flavonoids with two aromatic rings linked by a carbonylic α,β-insaturated system (Fig. 2A). Dihydrochalcones are obtained from chalcones through a reduction process (Moreno-Arribas & Polo, 2008). Chalcone derivatives are important intermediates and are precursor for a vast range of flavonoid derivatives found either in grapes or wine (Sections 4.3 and 5.2).

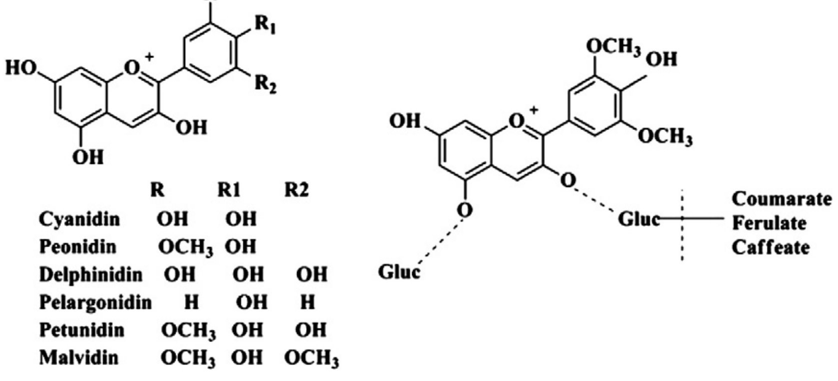
2.2.8. Anthocyanic pigments

Over the last years several families of anthocyanin derivatives have been reported in grapes, wine and wine-like solutions. Anthocyanic pigments (anthocyanidins and anthocyanins, Fig. 4) have a structure based on the flavylium cation (2-phenylbenzopyrylium). Chemically, anthocyanins are anthocyanidin glycosides being the corresponding aglycons (anthocyanidins) obtained by hydrolysis.

Anthocyanic pigments are responsible for the color of grapes and wine, a characteristic that is determined by their chemical structure, namely their degree of hydroxylation, methylation and/or glucosilation (He et al., 2010). In red grapes and wine, six anthocyanidins have been identified: cyanidin (orange red), peonidin (red), delphinidin (bluish red), pelargonidin (orange), petunidin and malvidin (bluish red) (Fig. 4) (He et al., 2010; Koponen, Happonen, Mattila, & Törrönen, 2007). The latter is considered to be the most representative compound in *V. vinifera* grapes (Castillo-Muñoz et al., 2010).

Anthocyanidins are usually found in nature in their glucosylated form, *e.g.* 3-monoglucosides, 3,5- and 3,7-diglucosides (Koponen et al., 2007). However, galactose, rhamnose, arabinose, rutinose (rhamnosylglucose), sophorose (glucosylglucose), and sambubiose (xylosylglucose) have also been described as common sugar moieties. The 3-*O*-monoglucosides of the six anthocyanidins previously referred have already been identified in grapes, as well as some mono-, di- and tri-saccharine derivatives (Castillo-Muñoz et al., 2010; He et al., 2010; Koponen et al., 2007). Anthocyanidins are also found as (acyl)glycosides, and free aglycones rarely occur in fresh plant material. In fact in some anthocyanins, the sugar molecule may be bound to para-coumaric, caffeic or ferulic acids, yielding numerous cinnamoyl derivatives which have been detected in grapes (Fig. 4). Acylated anthocyanins in the *Vitis* variety have been described to enclose chemotaxonomic interest (Koponen et al., 2007).

The anthocyanins are only found in the skin of the grape, while the flavonoids occur both in the skin and in the seeds. The amount of anthocyanins and flavonoids extracted upon vinification depends on the duration of the process and on the conditions under which it takes place, such as the temperature or the extent of disruption of the grapes (Zoecklein et al., 1995). In the grape vines (*V. vinifera* L.) anthocyanins accumulate in the leaves during senescence and are responsible for the coloration of the grape skin in red and rose cultivars. In some cases, these pigments are also predominant in the grape pulp. The anthocyanidin composition of grapes is considered to be affected by several factors, as the origin and type of the grape vine, the degree of maturity, and the weather conditions, especially the light intensity and the temperature (Ferrandino & Guidoni, 2010). The profiles of anthocyanins for each grape variety are relatively stable, while absolute concentrations can vary widely between different vintages due to environmental and agronomical factors (Gil-Muñoz, Fernández-Fernández, Vila-López, & Martinez-Cutillas, 2010). The anthocyanin profile was proposed as a chemotaxonomic parameter for the classification of red *V. vinifera* varieties.



	R	R1	R2
Cyanidin	OH	OH	
Peonidin	OCH_3	OH	
Delphinidin	OH	OH	OH
Pelargonidin	H	OH	H
Petunidin	OCH_3	OH	OH
Malvidin	OCH_3	OH	OCH_3

Fig. 4. Anthocyanidins and anthocyanins frequently present in grapes and wine.

Among the new pigments detected thus far, pyranoanthocyanins gained increasing attention because of the large number of compounds detected in wines and their unusual spectroscopic properties.

The copigmentation of anthocyanins and its contribution to the color of red wine are an interesting topic of research that has been the subject of a review (Boulton, 2001). Copigmentation studies are of critical importance for the understanding of the relationship between the grape composition and the color of the wine.

2.3. Tannins

Tannins are polyphenolic compounds displaying astringent properties, which were found to be able to cause protein precipitation. They are usually divided into two classes: the hydrolyzable and the non-hydrolyzable or condensed tannins (Linskens & Jackson, 1988; Scalbert, 1993). The natural tannins present in grapes and wine are predominantly of the condensed type.

In young wines, tannins occur mainly in the form of dimers or trimers. However the concentration of these oligomeric species decreases with aging due to oxidation and precipitation processes (Cheynier et al., 2006).

2.3.1. Hydrolyzable tannins

Hydrolyzable tannins are complex polyphenols that can be degraded through pH changes as well as by enzymatic or non-enzymatic hydrolysis into smaller fragments, mainly sugars and phenolic acids.

The basic unit of hydrolyzable tannins of polyester type is gallic and hexahydroxydiphenic acids (Figs. 1 and 5), and its derivatives (*e.g.* ellagic acid). These acids are usually esterified with D-glucose yielding 500 to 2800 molecular weight species. These hydrolyzable tannin classes of polyphenols have been named gallotannins (which hydrolyze in gallic acid) or ellagitannins (which hydrolyze in ellagic acid) (Figs. 1 and 5). They can contain one or more hexahydroxydiphenic acid moieties esterified to a polyol, usually glucose. Hydrolysis of ellagitannins, with acids or bases, yields hexahydroxydiphenic acid that spontaneously lactonizes to ellagic acid (Koponen et al., 2007).

Aging in oak barrels is known to promote the extraction of low molecular weight phenolic compounds, mainly from ellagitannins, into wine. Ellagic acid and myricetin, for instance, are probably the major phenolic compounds present in muscadine grapes (*Vitis rotundifolia*) (Pastrana-Bonilla, Akoh, Dsellappan, & Krewer, 2003). Ellagic acid, in particular, is regarded as a characteristic compound formed upon by barrique wine aging, thus being proposed as a marker of maturity for this type of wines (Matějíček, Mikeš, Klejdus, Štěrbová, & Kubáň, 2005).

2.3.2. Condensed tannins

Condensed tannins or proanthocyanidins are polymeric compounds that give rise to anthocyanidins (Koponen et al., 2007; Linskens & Jackson, 1988; Silva, Rigaud, Cheynier, Cheminat, & Moutounet, 1991). They are found in residual amounts in the solid components of grapes (*e.g.* skin, seeds) as well as in the pulp. Proanthocyanidin quantity, structure and degree of polymerization depend on their particular localization in the grape tissues. These compounds are transferred into the must during wine-making operations (such as crushing, maceration, and fermentation) (Koponen et al., 2007; Linskens & Jackson, 1988; Silva et al., 1991).

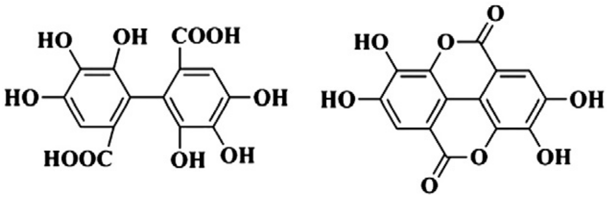


Fig. 5. Chemical structure of hexahydroxyphenic acid and its derivative ellagic acid.

Proanthocyanidins generally occur as oligomers and polymers of flavan-3-ols (Figs. 3 and 6). The flavan-3,4-diols, also named leucoanthocyanins, are the precursors of flavan-3-ols, and are thus indirectly involved in proanthocyanidin production (Koponen et al., 2007; Zoecklein et al., 1995). Partial galloylation of the flavanol 3-hydroxyl group as well as combinations of α or β C_4–C_6 or C_4–C_8 linkages originate a wide range of structurally different oligomers (Gu et al., 2003). The proportion of the polymer units and the average number of proanthocyanidins has been already determined using LC–MS/MS and thiolytic degradation (Gu et al., 2003).

The identified proanthocyanidins in *V. vinifera* grapes are mainly oligomers and polymers of (+)-catechin and (−)-epicatechin linked through C_4-C_8 bonds. These monomeric units may also be stabilized by C_4-C_6 or C_4-C_8 bonds (Fig. 6) (He, Pan, Shi, & Duan, 2008; Zhao, Duan, & Wang, 2010). The procyanidins and prodelphinidins, which hydrolyze to cyanidin and delphinidin, respectively, are known to be the most abundant condensed tannins in grapes and wine (Fig. 6) (He et al., 2008; Hellström, Törrönen, & Mattila, 2009; Zhao et al., 2010).

The relationship between monomeric, oligomeric and flavan-3-ol composition has been thoroughly established in grapes and wines. Oligomers with a maximum degree of polymerization of 16 have been identified in *V. vinifera*. Grape seed tannins are polymers of flavan-3-ols (catechin and epicatechin) and (−)-epigallocatechin monomers linked by and/or C_4-C_6 bonds (B type) and grape skin tannins contain (−)-epigallocatechin and trace amounts of (+)-gallocatechin and (−)-epigallocatechin gallate (He et al., 2008; Hellström et al., 2009; Zhao et al., 2010).

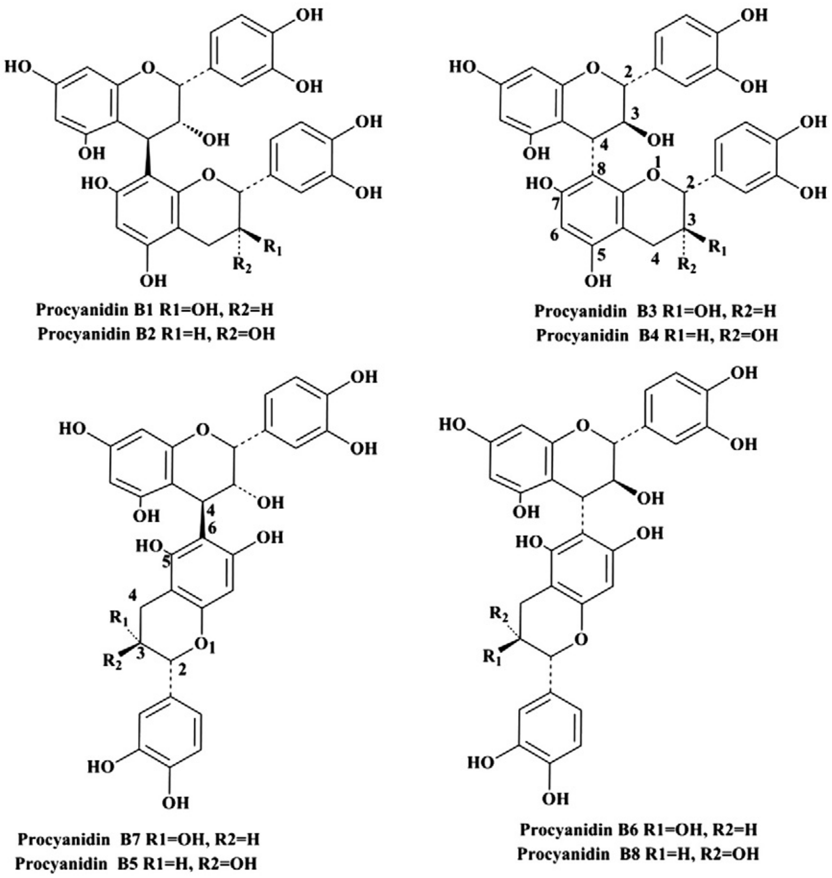
The identification and study of the physical–chemical properties of proanthocyanidins constitute a relevant subject of research in Enology, since these compounds are mainly responsible for the sensory characteristics of wine (color, taste, astringency and bitterness). In fact, proanthocyanidins play an important role in the wine aging process due to their oxidation, condensation and polymerization capabilities.

2.4. Stilbenes

Stilbenes are phenolic compounds comprising two aromatic rings linked by an ethene bridge. Resveratrol (3,5,4′-trihydroxystilbene, Fig. 7) is the stilbene most referenced as present in grapes and wine. Apart from wine, it has been identified in vine leaf and in the skin of the grapes, and its concentration is known to decrease significantly upon grape maturation. Resveratrol is considered by some authors to be a phytoalexin, *i.e.* a toxin produced in the grapes due to fungic infection (*e.g.* by *Botrytis cinerea Pers* or *Plasmopora viticola*), or a product produced from abiotic stress (through UV radiation, heavy metal catalysis, *etc.*). Its biosynthesis is mediated by an enzyme, stilbene-synthase, which combines one molecule of hydroxycinnamoyl-CoA and three molecules of malonyl-CoA (Lima et al., 1999; Moreno-Labanda et al., 2004; Pezet et al., 2003; Püssa, Floren, Kuldkepp, & Raal, 2006). This enzyme has also been detected in grapes.

Once resveratrol is present in the skin of the grapes, the wine processing methods determine its concentration in the final product depending on the particular enologic technique used. Thus, those wines resulting from longer maturation periods contain a higher content of resveratrol, the concentration of this compound being also higher in red wines as compared to white wines (Lima et al., 1999; Moreno-Labanda et al., 2004; Pezet et al., 2003; Püssa et al., 2006). A high percentage of *cis*-resveratrol is present in wine although this isomer is found to be only in traces in grapes.

Fig. 7 comprises stilbenes that have recently been identified in both grapes and wine: piceid, piceatannol glucoside (usually named astringin), pterostilbene, pallidol, parthenocissin and ameurensin G (Jiang, He, Jiang, Sun, & Pan, 2010). Oligomeric forms of the oxidation products of resveratrol–viniferins (*e.g.* ε-viniferin, Fig. 7) were also identified in


Procyanidin B1 R1=OH, R2=H
Procyanidin B2 R1=H, R2=OH

Procyanidin B3 R1=OH, R2=H
Procyanidin B4 R1=H, R2=OH

Procyanidin B7 R1=OH, R2=H
Procyanidin B5 R1=H, R2=OH

Procyanidin B6 R1=OH, R2=H
Procyanidin B8 R1=H, R2=OH

Fig. 6. Procyanidins present in grapes and wine.

grapevine leaves and wine by-products (Jiang et al., 2010; Lima et al., 1999; Moreno-Labanda et al., 2004; Pezet et al., 2003; Püssa et al., 2006; Vitrac et al., 2005).

The presence of stilbenes in wine has lately turned into a hot topic of research, aiming at the correlation of their profiles with winemaking procedures and with the different grape wine varieties.

2.5. Coumarins

Coumarins are lactones obtained by cyclisation of the *cis*-2-hydroxycinnamic acid and its derivatives, which is formed through isomerization and hydroxylation of the structural analog *trans*-2-hydroxycinnamic acid.

The high number of natural compounds based on benzo-α-pyrone has urged a classification according to their chemical structure (Borges, Roleira, Milhazes, Santana, & Uriarte, 2005). Attending to the fact that the most abundant coumarins found in grapes and wines are the simple coumarins, these are the only ones to be focused. In general, natural simple coumarins are characterized by a great diversity differing mainly in the oxygenation degree of their benzopyrane moiety. The hydroxylation in C_7 is the most common.

The chemical characteristics of simple coumarins are dependent upon their biosynthetic precursors: the *para*-coumaric acid yields umbeliferone, the caffeic acid yields esculetin and the ferulic acid yields scopoletin (Fig. 8) (Moreno-Arribas & Polo, 2008). The *O*-methylation and *O*-glucosylation enzymatic reactions, in turn, are referenced as being classic biosynthetic steps characteristic of this group of compounds (Moreno-Arribas & Polo, 2008).

2.6. Phenylethanol derivatives

Phenylethanol derivatives present in wine have eight carbon atoms (C_6–C_2) and mainly comprise 3,4-dihydroxyphenylethanol (hydroxytyrosol) and 4-hydroxyphenylethanol (tyrosol) (Fig. 8) (Moreno-Arribas & Polo, 2008). These superior alcohols are formed during the fermentation process, by microbial transformation of amino acids. Tyrosol, for instance, is a phenolic alcohol produced from tyrosine, due to the action of a particular set of yeasts (Fig. 8) (Moreno-Arribas & Polo, 2008). The amount of tyrosol in wine was found to be independent of its type or age (Di Stefano, 1999).

2.7. Lignans and neolignans

Lignans are dimers (with two C_6–C_3 units) resulting from the tail-to-tail linkage of two coniferyl or sinapyl alcohol units. Neolignans are related dimers formed by head-to-tail condensation reactions. Isolariciresinol, secoisolariciresinol, lariciresinol, and cedrusin and its glucosides are examples of this kind of compounds (Fig. 8) (Marinosa, Tatea, & Williams, 1992; Nurmi et al., 2003).

3. Biosynthesis of phenolic compounds

The preferential presence of phenolic compounds in grapes and wine is often pointed out in the literature. In general, they are found in vacuoles and cell walls as well as in seeds. Benzoic and cinnamic acids, flavonoids, stilbenes and anthocyanins have been detected in the skin of the grape. In pulp, the flavonoids and benzoic phenolic acids are predominant (Rapisarda, Carollo, Fallico, Tomaselli, & Maccarone, 1998). As the

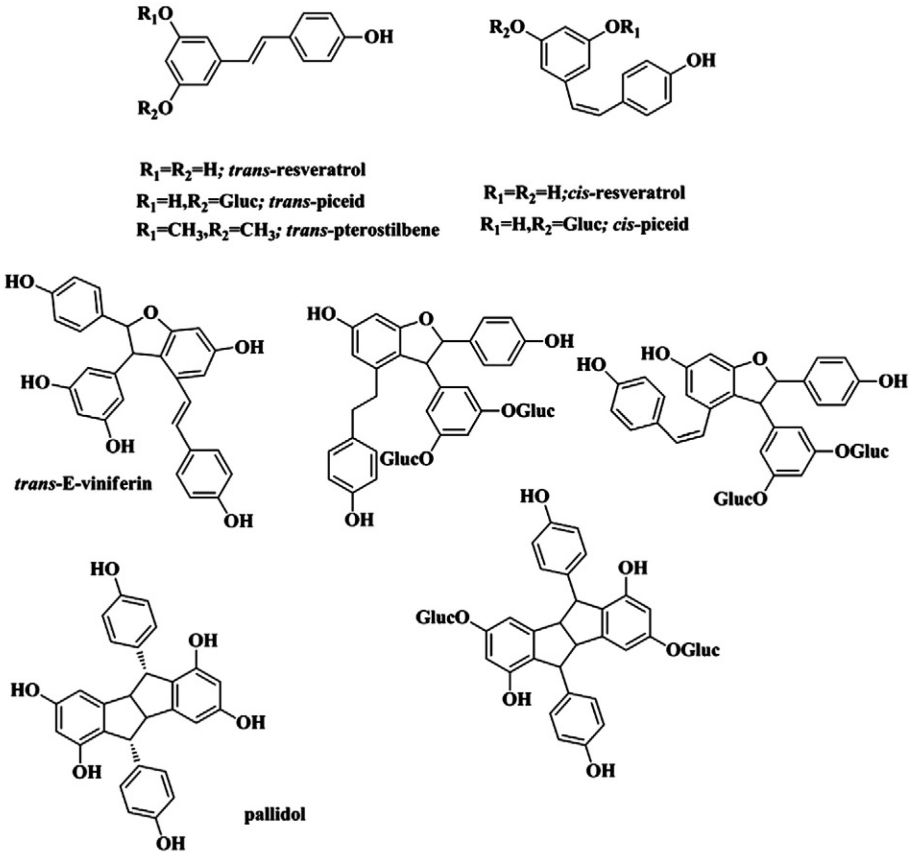


Fig. 7. Stilbenes and their derivatives present in grapes and wine.

reason for this distribution is mainly biosynthetic it is consensual to consider that the knowledge of biosynthetic pathways can help to characterize the phenolic profile of the grapes and envisage the different phenolic compounds detected in wine.

According to the biosynthetic pathway natural compounds can be gathered in two major metabolite categories: primary and secondary metabolites. Among the latter, the phenolic derivatives are by far the most important, both regarding enological issues and human health. Cinnamic acids are presently considered as being the biosynthetic precursors of the different classes of non-volatile phenolic compound found in grapes and wine (Fig. 9). Different enzymatic reactions, such as hydroxylation, conjugation and hydrolysis are responsible for the great chemical diversity.

Cinnamic acids are biosynthesized from phenylalanine through the shikimate pathway: the amino acid is converted into *trans*-cinnamic acid by an enzymatic ammonia elimination step (Moreno-Arribas & Polo, 2008). Other cinnamic acids are formed from *trans*-cinnamic acid through hydroxylation and *O*-methylation processes. However, the aromatization of the dehydroshikimic acid may also occur during biosynthesis yielding gallic acid and its derivatives. The mixed shikimate/

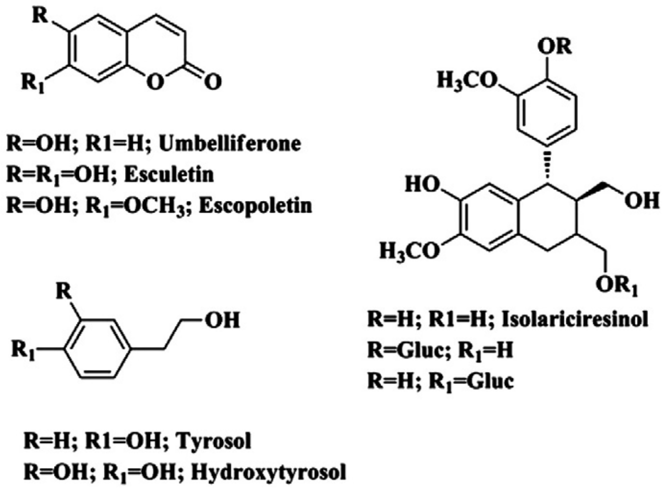


Fig. 8. Chemical structures of coumarins, phenylethanol derivatives and lignans.

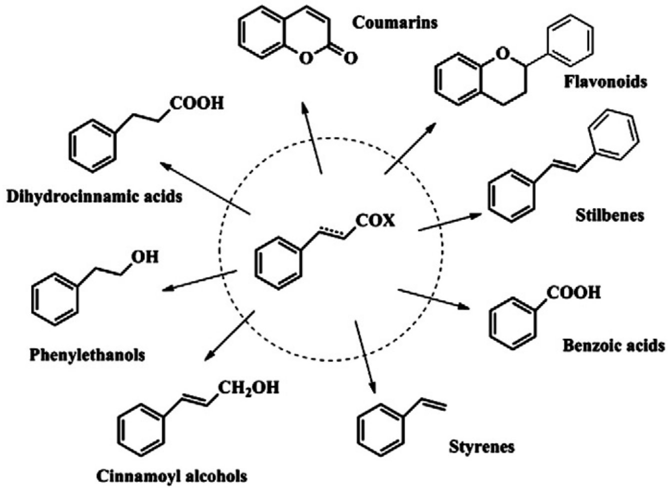


Fig. 9. Biosynthetic relationships between phenolic compounds.

acetate synthetic pathway, involving phenylpropanoids and acetate moieties, is the proposed one for the flavonoid family. In this process, the aromatic ring A is formed through condensation of three acetate units yielded by malonyl-CoA, while ring B and atoms 2, 3 and 4 of ring C are from the phenylpropanoid precursor (Figs. 2A and 9) (Moreno-Arribas & Polo, 2008).

All the phenolic compounds described in this work display a clear biosynthetic relationship that determines its presence in grapes and derived products as well as its preferential occurrence (Fig. 9). Thus, this biosynthetic correlation greatly contributes to an easy prediction and characterization of this type of compounds in both grapes and wine. Furthermore, the relative variations and the presence or absence of the different classes of phenolic compounds during grape maturation are in accordance with the biosynthetic and metabolic pathways.

4. Factors influencing phenolic content and composition of wine

Wine phenolic composition depends on the grapes used to make the wine and on the vinification conditions although a wide range of variables such as cultivar, viticulture practices and vinification techniques can also affect their phenolic composition. The growing season, variety, environmental and climatic conditions, plant disease, soil type, geographic locations and even maturity seem to influence the concentration of phenolic compounds within grapes (Cejudo-Bastante, Pérez-Coello, & Hermosín-Gutiérrez, 2011; Gómez-Plaza, Gil-Muñoz, López-Roca, & Martínez, 2000; Macheix et al., 1994; Mulero, Pardo, & Zafrilla, 2009; Orduña, 2010).

The qualitative changes that occur in the phenolic composition of wine, as compared to the composition of the corresponding grapes, are mainly due to the production of new phenolic derivatives, as tyrosol, flavenes and free phenolic acids (*para*-hydroxybenzoic, gallic, *para*-coumaric, caffeic, *etc.*). The hydroxycinnamic acid derivatives are a good example: one-third does not suffer any changes during processing and storage, the other third is oxidized and binds to sulfhydryl-containing molecules and the last one is modified by protein complexation reactions (Cieślik et al., 2006; Macheix et al., 1994; Tsao, 2010). The environment in which both the must and the wine are processed may also contribute to the generation of new phenolic compounds. Simple volatile or non-volatile phenols, flavonoids and hydrolyzable tannins may be extracted progressively from the barrel wood, thus modifying the wine composition as well as its organoleptic characteristics (Cieślik et al., 2006; Macheix et al., 1994; Tsao, 2010).

4.1. The effect of raw matter

Phenolic compounds represent, after carbohydrates and fruit acids, the third most abundant constituents in grapes and wines.

Grape phenolics are mainly distributed in the skin, stem, leaf and seed of grape (Makris, Boskou, Andrikopoulos, & Kefalas, 2008; Revilla, Alonso, & Kovac, 1997; Shi, Yu, Pohorly, & Kakuda, 2003). The total phenolic content of grape skins varied with cultivar, soil composition, climate, geographic origin, and cultivation practices or exposure to diseases, such as fungal infections (Bruno & Sparapano, 2007). In fact, the content of phenolics in grapes is clearly affected by four agroecological factors: the cultivar, the year of production (*i.e.*, the climatic condition from year to year), the site of production (the effect of geographic origin of grapes, soil chemistry, and fertilization), and the degree of maturation (Hernandez-Jimenez, Gomez-Plaza, Martinez-Cutillas, & Kennedy, 2009; Revilla et al., 1997).

Many studies have focused on defining the effects of growing conditions on grape and wine phenolic composition and of the impact of light and temperature conditions around the fruit on berry flavonoid composition (Ristic, Bindon, Francis, Herderich, & Iland, 2010). The results showed that the concentration and composition of flavonoid compounds were determined by combined complex effects of solar radiation and temperature. While moderate bunch exposure and berry temperature were favorable for anthocyanin accumulation, skin tannin enhancement was noted in berries from bunches exposed to sunlight or from low vigor vines compared with berries from shaded bunches or dense canopies (Ristic et al., 2010). At the same time, seed tannin concentration was the least susceptible to changes in light/temperature conditions (Ristic et al., 2010). Regarding tannins, some authors claim that these changes may only be due to the increase of the grape dimensions. In fact, maturation is associated to polymerization of phenols, which leads to a marked decrease of astringency (Kennedy, Hayasaka, Vidal, Waters, & Jones, 2001; Zoecklein et al., 1995).

It may then be concluded that both the qualitative and quantitative changes in the phenolic composition of grapes are associated to its stage of development, as well as to environmental factors such as light and temperature. These variations are the cause, or maybe a consequence, of physiological responses on certain biological systems.

4.2. The effect of technological procedures

The main degradation processes of phenolic compounds take place in the first steps of vinification and continue during storage (Gómez-Plaza & Cano-López, 2011). However the processing operations, such as ionic exchange, filtration, centrifugation and cold stabilization may also modify significantly the composition and consequently the color of the wine (mainly in red wine) (Gambuti, Strollo, Ugliano, Lecce, & Moio, 2004; Netzel et al., 2003).

The methods of vinification and applied technological procedures (maceration, fermentation, clarification, aging, *etc.*) can significantly modify both the concentration and composition of phenolic compounds and, therefore, also the color intensity and hue of red wines (Balík et al., 2008). Wine clarification decreases the content of extractive and volatile compounds and very often also represents a significant interference into the content of polyphenols. The range of changes and mainly losses of individual phenolic compounds is dependent on the type of the clarifying agent and chemical structure of phenols (Balík et al., 2008).

Several processes are employed for extracting phenolic compounds from grapes and wine that can alter, either qualitatively or quantitatively, the phenolic content of the final processed product (Netzel et al., 2003). A prolonged wine fermentation is usually responsible for a higher tannin content yielding wines with a complex chemical composition that is reflected in a stronger taste and body. Moreover, a vigorous crashing or pressing of the grapes, which is used for the extraction of tannins and anthocyanins, leads to bitter and highly astringent wines. In this particular case, the enzymatic oxidation of the phenols is increased, which may lead to a noticeable browning of the must and to distinct changes in the organoleptic characteristics of the resulting wine.

Other factors may also affect the characteristics of the wine such as temperature, ethanol content, and process of must homogenization or addition of specific chemicals (*e.g.* bisulphite). The overall process is responsible for including in the human diet some phenols present in the skin and seeds of the grapes once they are solubilized during the wine-making process (Di Stefano, 1999).

4.3. The effect of wine aging process

The phenolic composition of the wine is known to change either qualitatively or quantitatively, along the wine aging process, which is mainly associated to the presence of hydroxycinnamic esters, anthocyanidins and tannins. These changes are reflected in the color and astringency degree of the final product and the nature of the anthocyanins present is determined by the type of wine and by its storage conditions. The relative anthocyanin content is known to decrease upon aging although this chemical modification, that does not follow a linear function relative to time, is accompanied by a very clear change in color (He et al., 2012; Saucier, 2010; Wrolstad, Durst, & Lee, 2005). This characteristic is often used as a quality standard for aged wines: a new wine contains a significant amount of anthocyanin conjugated species (as compared to the free forms). The storage temperature is one of the main factors responsible for anthocyanin loss: thermal and enzymatic treatments under anaerobic conditions move the anthocyanin equilibria toward the chalcone forms. For instance 2,4,6-trihydroxybenzaldehyde and syringic acid can be formed from maldivin 3-*O*-glucoside (Saucier, 2010).

5. Chemical modification of phenolic composition of wines

The phenolic composition of wines is closely related to the quality of the processed product, namely to their organoleptic characteristics, such as color, astringency and aroma (Kennedy, 2008). The phenolic profile in finished wines depends on both viticulture (grape growing) and viniculture (winemaking) practices. Numerous chemical changes involving phenolic derivatives take place upon winemaking and aging producing a huge variety of colorless products and pigments.

The stability of the phenolic compounds present in the final product (wine) is thus rather different from the one *in situ* (non-harvested grapes), and depends on factors such as the environmental conditions, such as light intensity, oxygen and metal ion content (Benítez, Castro, & Barroso, 2003; Castellari, Matricardi, Arfelli, Galassi, & Amati, 2000; Clarck, Prenzler, & Scollary, 2003). Actually, several chemical changes, which already begin in the grapes (namely during storage), reach completion only after the processing period (both fermentation and aging) (Macheix et al., 1994; Remy-Tanneau, Guernevé, Meudec, & Cheynier, 2003). In general, the chemical composition of the final product is much more complex than the one of the raw material, due to the formation of a variety of new compounds.

In summary, one can say that changes in polyphenolic composition are mainly due to the participation of grape phenolics in haze formation and in numerous copigmentation, cycloaddition, polymerization and oxidation reactions. These enzymatic and non-enzymatic reactions start just after grape crushing and continue throughout fermentation and aging, contributing to important changes in wine sensory properties and to the obtention of a great diversity of new phenolic structures (Guadalupe & Ayestarán, 2008; Pérez-Magariño & González-San José, 2004; Sun & Spranger, 2005).

The present review aims to present a number of the major non-enzymatic chemical degradation reactions occurring in wine since the enzymatic degradation processes occurring in winemaking have been recently reviewed in literature (Karbowiak et al., 2009; Li, Guo, & Wang, 2008).

5.1. Flavonoid degradation

Flavan-3-ols and flavan-3,4-diols are considered to be the most vulnerable flavonoids, in a context of non-enzymatic degradation processes (Fernández-Zurbano, Ferreira, Escudero, & Cacho, 1998; Li et al., 2008). During fermentation this kind of compounds (*e.g.* catechins) can undergo partial cleavage into lower molecular weight phenolic units. The process is mainly due to the increase of temperature (Fig. 10).

Flavonoids are also responsible for changes in the color of the processed product. In fact, this kind of compounds can react with aldehydes present in the medium (*e.g.* vanillin) yielding colored compounds (Fig. 11). In order to evaluate the contribution of yeasts to color changes in fermented drinks, such as white wine, the condensation reaction between catechin and acetaldehyde was deeply studied. It was concluded that the yeasts retain the oligomers produced in the reaction, although they have no inhibitory effect on the condensation reaction (Lopez-Toledano, Villaño-Valencia, Mayen, Merida, & Medina, 2004). Thus, this type of reaction can contribute to the color change observed in white wine after bottling.

5.2. Anthocyanin and anthocyanidin degradation

The color of both anthocyanins and anthocyanidins is affected by several parameters such as temperature and pH, the presence of transition metal ions, type of solvent, structural characteristics, and copigmentation (He et al., 2012). Among these, pH is considered to be the most important factor.

Kinetic, thermodynamic and spectroscopic studies have evidenced the presence of four anthocyanin species in equilibrium (for aqueous solutions, at 25 °C): the quinonoidal base (species A, blue), the flavylium cation (AH^+, red), the pseudocarbinol base (species B, colorless) and the chalcone (species C, colorless) (Fig. 12). For most anthocyanins the thermodynamically favored species, at low pH values, is the flavylium cation (Figueiredo et al., 1996; Saucier, 2010). As pH increases the concentration of this ion decreases giving rise to other compounds, the concentration of which depends mainly on the nature of the flavylium substituents. Until a final equilibrium is reached several color changes are observed: at pH *ca.* 1 the solution is red due to the presence of the flavylium cation (AH^+); as the pH is raised to about 4 an intense blue color appears, associated to the formation of the quinonoidal base A, through a fast proton transfer reaction. Identification of the anthocyanin derived compounds A, AH^+, B and C constitutes an emerging subject of research. The pH stability of several anthocyanins has recently been reported (Nielsen, Haren, Magnussen, Dragsted, & Rasmussen, 2003). In Fig. 13 the degradation reaction proposed for malvidin, which yields less complex colorless phenolic compounds, is presented (Ducruet, 1998).

Usually *O*-glycosylation can stabilize anthocyanins that in turn can be stored in vacuole without hydrolysis by the action of anthocyanase. However, anthocyanins are readily hydrolyzed to their corresponding anthocyanidins and sugars when the grape cells are broken or infected. In fact, anthocyanins or anthocyanidins possessing *ortho*-diphenol structures can easily suffer degradation by enzymatic and non-enzymatic oxidation reactions (He et al., 2012; Saucier, 2010; Wrolstad et al., 2005). In the autoxidation of *ortho*-diphenol function the formation of the corresponding *ortho*-quinone and hydrogen peroxide takes place as by-products, which can catalyze the further oxidation processes of other phenolic compounds to form dimeric *ortho*-diphenols (He et al., 2010).

The gradual disappearance of anthocyanins during wine aging is also attributed to condensation reactions. Anthocyanins may undergo condensation with flavonoids (mainly with flavanols, through position C_4), either directly or *via* an intermediate (*e.g.* an acetaldehyde) yielding both dimeric and polymeric species (Atanasova, Poncet-Legrand,

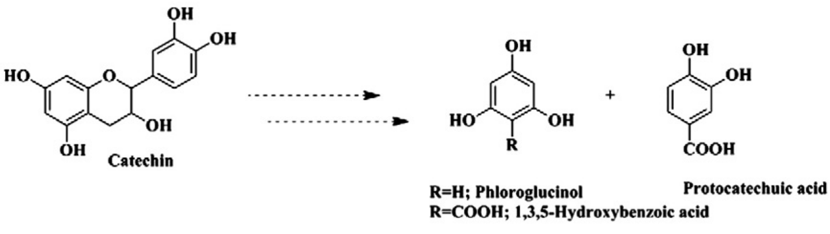


Fig. 10. Catechin degradation products.

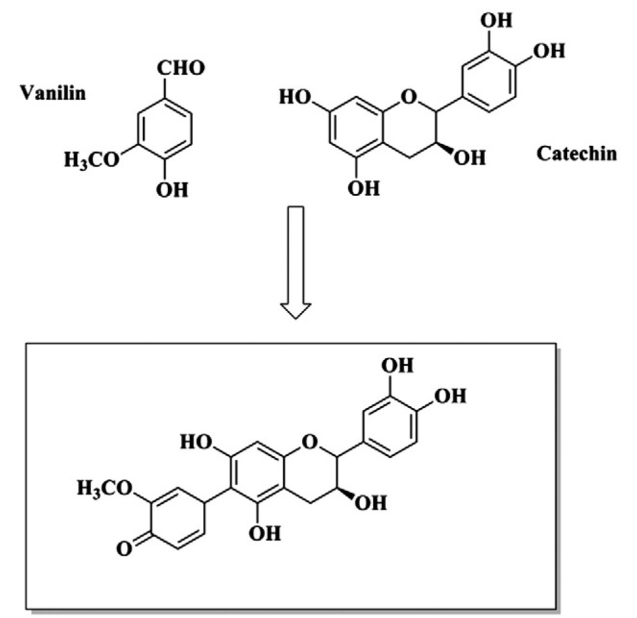


Fig. 11. Reaction of vanillin with catechin and formation of the corresponding colored product.

Meudec, Mazauric, & Cheynier, 2004; Guadalupe & Ayestarán, 2008; Mateus, Oliveira, Haettich-Motta, & Freitas, 2004; Mateus, Silva, Vercuteren, & Freitas, 2001; Remy-Tanneau et al., 2003; Salas et al., 2004).

The condensation reaction that occurs between C_3-glucosylated malvidin and catechin are represented in Fig. 14A. The resulting flavene can undergo further oxidation reactions giving rise to red quinonoid-type compounds. In addition, acetaldehyde condensation reactions and cycloaddition processes have been described to occur between anthocyanins and flavonols or procyanidins, generating for instance pyranoanthocyanins, a subclass of compounds thoroughly identified by NMR (Atanasova, Fulcrand, Cheynier, & Moutounet, 2002; Atanasova, Fulcrand, Guernevé, Cheynier, & Moutounet, 2002; Lee, Swinny, & Jones, 2004; Mateus et al., 2001; Nave, Teixeira, Mateus, & Freitas, 2010).

Up to this date, the catechin–acetaldehyde condensation dimers have been identified through spectroscopic methods and molecular modeling in mimetic models (Saucier, Guerra, Pianet, Laguerre, & Glories, 1997). The Vitisin A content of wines and its contribution to the color of aged red wines were the subject of a recent study (Schwarz, Quast, Baer, Winterhalter, & Vitisin, 2003; Wang, Race, & Shrikhande, 2003).

The reactions of anthocyanins and/or flavanols with compounds such as pyruvic acid, vinylphenols, vinylcatechol, vinylguaiacol, acetone or glyoxylic acid (a product of tartaric acid oxidation) have also been characterized, and new classes of pigments (*e.g.* pyranoanthocyanins and xanthylium derivatives) were identified (see Fig. 14B) (Atanasova, Fulcrand, Cheynier, & Moutounet, 2002; Clarck et al., 2003; Fulcrand, Benabdeljalil, Rigaud, Cheynier, & Moutounet, 1998; Lopez-Toledano et al., 2004; Remy-Tanneau et al., 2003; Saucier, 2010). These pigments were proposed to be a reaction product between anthocyanins and vinyl–flavonol adducts that were derived either from the cleavage of ethyl-linked flavonoid oligomers or from the dehydration of the flavonol–ethanol adduct formed after reaction with acetaldehyde (Atanasova, Fulcrand, Cheynier, & Moutounet, 2002; Lee et al., 2004; Lopez-Toledano et al., 2004; Mateus et al., 2001).

Several pyranoanthocyanins and anthocyanin–vinylphenol adducts bearing different flavan-3-ol substituents as well as their acetyl and coumaroyl glucosides were identified in wines by NMR spectroscopy and MS (Atanasova, Fulcrand, Cheynier, & Moutounet, 2002; Håkansson, Pardon, Hayasaka, Sa, & Herderich, 2003; Remy-Tanneau et al., 2003). Wang et al. (2003) verified that the main anthocyanins present in grape extract are malvidin 3-*O*-glucoside and malvidin 3-*O*-acetylglucoside. However in maturated wine these anthocyanins are transformed into anthocyanin–vinyl derivatives, ethyl bridged anthocyanin–flavanol and anthocyanin–flavanol adducts: malvidin 3-*O*-glucoside-piruvate, malvidin 3-*O*-acetylglucoside-piruvate, malvidin 3-*O*-coumaroylglucoside-piruvate, malvidin 3-*O*-glucoside-4-

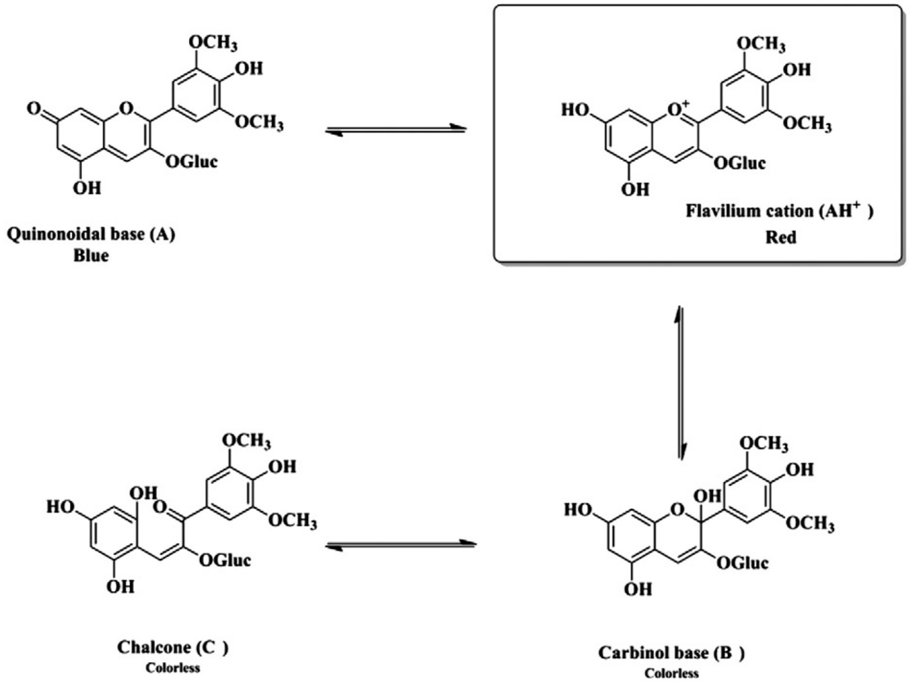


Fig. 12. Chemical species present in aqueous solution associated to C_3-glucosylated malvidin.

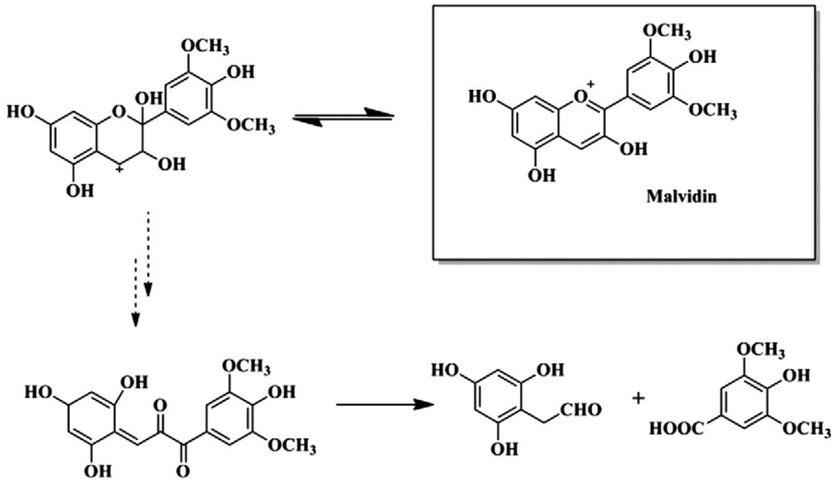


Fig. 13. Degradation reactions proposed for malvidin.

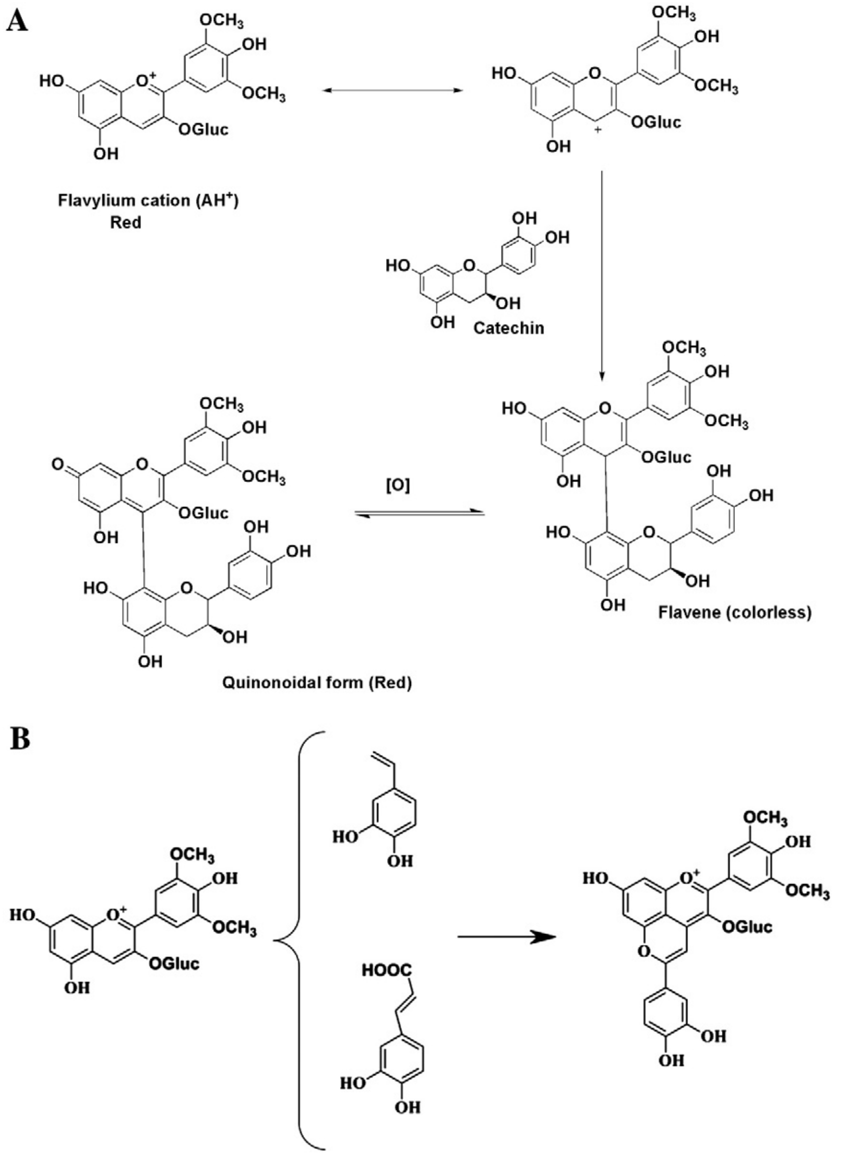


Fig. 14. Formation of a flavene (A) and an anthocyanin–vinylphenol adduct (B), through degradation reactions of malvidin 3-glucoside.

vinylphenol, malvidin 3-*O*-acetylglucoside-4-vinylphenol and malvidin 3-*O*-coumaroylglucoside-4-vinylphenol (Wang et al., 2003). A colorless anthocyanin-flavan-3-ol dimer, containing both carbon–carbon and ether interflavonoid linkages, was also characterized by NMR and MS spectrometry in a model system (Remy-Tanneau et al., 2003). Blue anthocyanin-derived pigments were isolated from red wines, their structure consisting of a pyranoanthocyanin moiety linked to a flavanol by a vinyl bridge (Mateus et al., 2001). The formation of these particular pigments was found to arise from the reaction between anthocyanin–pyruvic acid and vinyl–flavonol adducts (Mateus et al., 2001). This new family of bluish vinylpyranoanthocyanins, named portisins was recently reviewed (Mateus et al., 2004) and the majority of the compounds belonging to this family have already been completely characterized.

Up to now, some of these compounds have been considered to result from the reaction between anthocyanins and the products generated during fermentation by enzymatic decarboxylation of cinnamic acids. Yet, Schwarz, Wabnitz, and Winterhalter (2003) demonstrated that they could be formed by a novel reaction that could occur between anthocyanins and intact hydroxycinnamic acids, such as coumaric, ferulic, caffeic and sinapic acids. Decarboxylation, dehydration and oxidation of the pyran moieties are considered to be the final steps of this reaction (Fig. 14B).

Although initially related to grape composition, wine procyanidins were found to evolve during wine aging (Dufour & Bayonove, 1999). The disappearance of anthocyanins is known to occur simultaneously with the formation of more stable oligomeric pigments (Dufour & Bayonove, 1999). The anthocyanin condensation products are less sensitive to pH than their anthocyanin precursors, and do not suffer discoloration (Remy-Tanneau et al., 2003). In fact, these pigments show a remarkable stability and resistance to several wine-making processes, such as sulfite bleaching (Atanasova, Fulcrand, Cheynier, & Moutounet, 2002; Mateus et al., 2001). Oxygenated wines displayed characteristic color changes, along with a significant increase in the concentration of pyranoanthocyanins and related pigments (Atanasova, Fulcrand, Cheynier, & Moutounet, 2002; Gómez-Plaza & Cano-López, 2011; Kilmartin, 2010).

In summary, one can say that a diversity of products can be obtained from condensation reactions between anthocyanins and tannins, namely tannin–tannin and tannin–anthocyanin mixed polymers. Actually, some have been already investigated but others are still an interesting topic of research (Atanasova, Fulcrand, Cheynier, & Moutounet, 2002; Atanasova, Fulcrand, Guernevé, Cheynier, & Moutounet, 2002; Mateus, Silva, Rivas-Gonzalo, Santos-Buelga, & Freitas, 2003; Mateus et al., 2001; Remy-Tanneau et al., 2003).

5.3. Sulfur anhydride mediated degradation

Sulfur dioxide (SO_2) is an antioxidant that interferes with many of the key oxidation reactions: for example, it reacts with hydrogen peroxide (H_2O_2) and acetaldehyde, which are often required for condensation reactions, and also binds directly with anthocyanins, inhibiting the production of polymeric pigments (Berké, Chèze, Vercauteren, & Deffieux, 1998). Moreover, while the direct interaction of oxygen and bisulphate is very unlikely to occur to any significant degree in wine, because of the radical-scavenging activity of polyphenols, SO_2 also has the ability to reduce oxidized polyphenols back to their reduced forms (Danilewicz, 2007).

Sulfur dioxide (SO_2) reacts with anthocyanins giving rise to new compounds through an irreversible addition in C_4 (Berké et al., 1998; Ducruet, 1998). Thus, adding SO_2 to the wine must (during the extraction process) leads to an increase of the flavan-3-ols content with the consequent enhancement of both color and bitterness of the wine (Zoecklein et al., 1995).

Sulfonation of tannins has also been shown to occur in experiments involving much higher concentrations of bisulphite than normally used in winemaking or at elevated temperature and pH. However, the formation of such adducts of a lower molecular weight may still occur more slowly under regular wine conditions (Foo, McGraw, & Hemingway, 1983; Vidal, Cartalade, Souquet, Fulcrand, & Cheynier, 2002).

6. Concluding remarks

In the last decades, the study of the phenolic composition of both grapes and wine has become a topic of enthusiastic research. Since taxonomically related plants produce related phenolic compounds, the knowledge of the chemical composition of the different types of grapes is believed to be of utmost importance, since a database that would allow an easy and reliable chemical identification of wines could thus be obtained. Actually, the phenolic composition of wines, responsible for its organoleptic properties, and containing information on the main wine characteristics, can be used as a fingerprint for their differentiation, according to the geographical origin, vine variety and vintage.

The choice of specific wine-making practices aimed at the improvement of wine quality is related to the knowledge of intrinsic physico-chemical characteristics of the grape cultivar employed in the vinification as well as to the evaluation of the influence of different practices on the final composition of wine. Because of the increasing demand for high quality wines, extensive studies on the factors influencing the chemical composition and biological effects of wine are required. The chemical processes described along this work may cause either a decrease in the quality of the wines, namely regarding its color and nutritional value, or an improvement in what taste is concerned. The knowledge of these chemical reactions will hopefully allow, in the near future, achieving a better quality control of the final products.

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