Chapter 9C
Non-flavonoid Phenolic Compounds

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Contents

The non-flavonoid phenolic constituents in wine are divided into hydroxybenzoic acids and hydroxycinnamic acids, volatile phenols, stilbenes and miscellaneous compounds (e.g. lignans and coumarins). Although non-colored, the non-flavonoid constituents are known to enhance and stabilize the color of red wines by intra- and intermolecular reactions. They furthermore contribute to wine flavor (volatile phenolic acids) and some of them (e.g. resveratrol) exhibit potent biological activities.

## 9C.1 Phenolic Acids

9C.1.1 Hydroxybenzoic Acids (HBA)

Being derived from benzoic acid, hydroxybenzoic acids are characterized by a C6-C1 skeleton (Fig. 9C.1). The most common derivatives found in wine are gallic acid, gentisic acid, *p*-hydroxybenzoic acid, protocatechuic acid, syringic acid, salicylic acid, and vanillic acid. In wine the different hydroxybenzoic acids can be mainly found in their free form (Drawert et al. 1974; Fernandéz de Simon et al. 1992; Garcia-Viguera and Bridle 1995; Güntert et al. 1986; Monagas et al. 2005a,b; Peña-Neira et al. 2000; Pozo-Bayón et al. 2003; Salagoïty-Auguste and Bertrand 1984;

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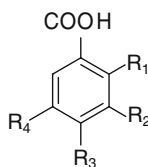
Hydroxybenzoic acids	R_1	R_2	R_3	R_4	MW
Gallic acid	H	OH	OH	OH	170
Gentisic acid	OH	H	H	OH	154
p-Hydroxybenzoic acid	H	H	OH	H	138
Protocatechuic acid	H	OH	OH	H	154
Salicylic acid	OH	H	H	H	138
Syringic acid	H	OCH_3	OH	OCH_3	198
Vanillic acid	H	OCH_3	OH	H	168

Fig. 9C.1 Structures of hydroxybenzoic acids in wine

Vanhoenacker et al. 2001). Gallic acid is one of the HBA with the highest concentrations in wine. It not only originates from the grape itself but is also formed by hydrolysis of hydrolyzable and condensed tannins, i.e. the gallic acid esters of flavan-3-ols.

The levels of HBA in wine show great variability depending on grape variety and growing conditions. Pozo-Bayón et al. (2003) reported values between 0.3 and 1.3 mg/L for gallic acid in Spanish sparkling wines from white and red grapes, respectively. For protocatechuic acid the values were between 0.5 and 0.93 mg/L, while the concentrations for p-hydroxycinnamic acid were in the range of 0–0.22 mg/L. Peña-Neira et al. (2000) detected concentrations of gallic acid in wine from La Rioja with up to 2.29 mg/L while Sladkovský et al. (2004) reported concentrations of 4.8 mg/L in tawny port. In a study that evaluated the effect of certain yeast strains during malolactic fermentation on non-flavonoid polyphenols in red wine from La Rioja (Hernández et al. 2007) the authors report a gallic acid concentration of up to 41.6 mg/L. However, in comparison to the group of hydroxycinnamic acids, the overall concentration of HBAs in wine is relatively low.

Among the derivates of HBAs, further compounds have been identified. Güntert et al. (1986) identified ethyl esters of vanillic acid and p-hydroxybenzoic acid, and methyl esters of vanillic acid and protocatechuic acid. Ethyl esters of protocatechuic acid and vanillic acid, as well as the glucose ester of vanillic acid, were isolated from a German Riesling wine (Baderschneider and Winterhalter 2001). Analytically, HBA are mostly determined as trimethylsilane derivatives by using

gas chromatographic analysis. A good overview on analytical methods as well as mass spectrometric data is given by Monagas et al. (2005b).

9C.1.2 Hydroxycinnamic Acids (HCA)

Hydroxycinnamic acids possess a C6-C3 skeleton and formally belong to the group of phenylpropanoids. The different compounds present in wine are mainly derived from the hydroxycinnamic acids caffeic acid, *p*-coumaric acid, ferulic acid, and sinapic acid (Fig. 9C.2). These derivatives can be present in *cis*- and *trans*-configured forms, while the *trans* forms are more stable and therefore more prevalent. In wine HCA are present in low amounts in their free form, while the depside forms, i.e. esters of l-(+)-tartaric acid, are predominant. The ubiquitous chlorogenic acids, esters of HCA and quinic acid, cannot be found in wine but are replaced by the tartaric acid esters instead (Ong and Nagel 1978; Singleton et al. 1978; Somers et al. 1987).

Among the hydroxycinnamic acids, caftaric acid predominates (up to 50% of total hydroxycinnamic acids). Other important substances are the tartaric esters of *p*-coumaric acid and ferulic acid, and the *trans-p*-coumaric glucoside (Somers et al. 1987). The concentration levels of hydroxycinnamic acid derivatives in wine depend on many factors like grape variety, growing conditions, climate, etc. It is
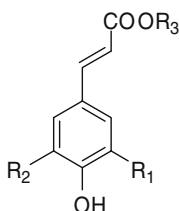
Hydroxycinnamic acids	R_1	R_2	R_3	MW
Caffeic acid	OH	H	H	180
Caftaric acid	OH	H	Tartaric acid	312
p-Coumaric acid	H	H	H	164
p-Coutaric acid	H	H	Tartaric acid	296
Ferulic acid	OCH_3	H	H	194
Fertaric acid	OCH_3	H	Tartaric acid	326
Sinapic acid	OCH_3	OCH_3	H	224

Fig. 9C.2 Structures of hydroxycinnamic acids in wine

therefore not surprising to find great differences in the concentrations published for different wines. In general, concentrations around 100 mg/L are described. For *p*-coutaric and fertaric acid the values are around 55 mg/L and 16 mg/L, respectively (Andres-Lacueva et al. 1996; Baldi et al. 1993; Boursiquot et al. 1986; Cheynier et al. 1989; Herrick and Nagel 1985; Herrmann 1989; Lao et al. 1996; Lee and Jaworski 1989; Okamura and Watanabe 1981; Ricardo-da-Silva et al. 1993; Singleton et al. 1978; Singleton et al. 1986). While in juices and young wines the content of free hydroxycinnamic acids is very low, an increase can be observed during storage. The tartaric esters are hydrolyzed and give rise to free forms of HCAs (Andres-Lacueva et al. 1996; Betés-Saura et al. 1996; Somers et al. 1987; Würdig and Woller 1989).

Betés-Saura et al. (1996) reported a loss of 27% of hydroxycinnamates during vinification in white wines from Penedès (46.76 mg/L in juices vs 34.07 mg/L in wine). With a share of around 73% of total phenolics, hydroxycinnamates were the most important group of phenolics in these white wines. Among them *trans*-caftaric acid was the major phenol with values between 10 and 13 mg/L. Okamura and Watanabe (1981) gave an overview of the concentrations of caftaric, coutaric, caffeic, and coumaric acid in commercial white wines. Average values were 23.0, 5.0, 0.9, and 0.7 mg/L for Semillon wines (Bordeaux), 29.0, 10.0, 1.7, and 0.9 mg/L in Chardonnay (California), 112.0, 53.0, 3.1, and 2.1 mg/L for Koshu wine (Japan), and 51.0, 13.0, 4.1, and 2.9 mg/L for Riesling wine (Germany).

There are also reports of numerous derivatives of HCAs occurring during aging. Apart from tartaric esters, ethyl esters of caffeic acid and coumaric acid, as well as ethyl esters and diethyl esters of caftaric acid were detected and characterized (Baderschneider and Winterhalter 2001; Somers et al. 1987). Also described were the 4-*O*-glucosides of ferulic acid and coumaric acid, the glucosides of caffeic acid, coumaric acid, ferulic acid, and sinapic acid (Baderschneider and Winterhalter 2001; Cooper and Marshall 2001; Monagas et al. 2005a). Cheynier et al. (1986) demonstrated that the reaction product of caftaric acid and glutathione, 2-*S*-glutathionylcaftaric acid, is the major phenolic product formed by enzymatic oxidation. This colorless product that is also called "grape reaction product (GRP)" is considered as a measure to estimate the oxidation and browning potential of grape musts. High GPR levels were reported to correlate with a lower sensitivity to browning reactions (Rigaud et al. 1991).

Additionally, hydroxycinnamates are important constituents of acylated anthocyanins. In red wine, the 6-*O*-coumaroylglucosides and caffeoylglucosides are common constituents (Mazza and Miniati 1993). In the authenticity control of red wine the relation of acetylated and coumaroylated anthocyanins can be used for the assessment of the grape variety (Holbach et al. 2001; Otteneder et al. 2002).
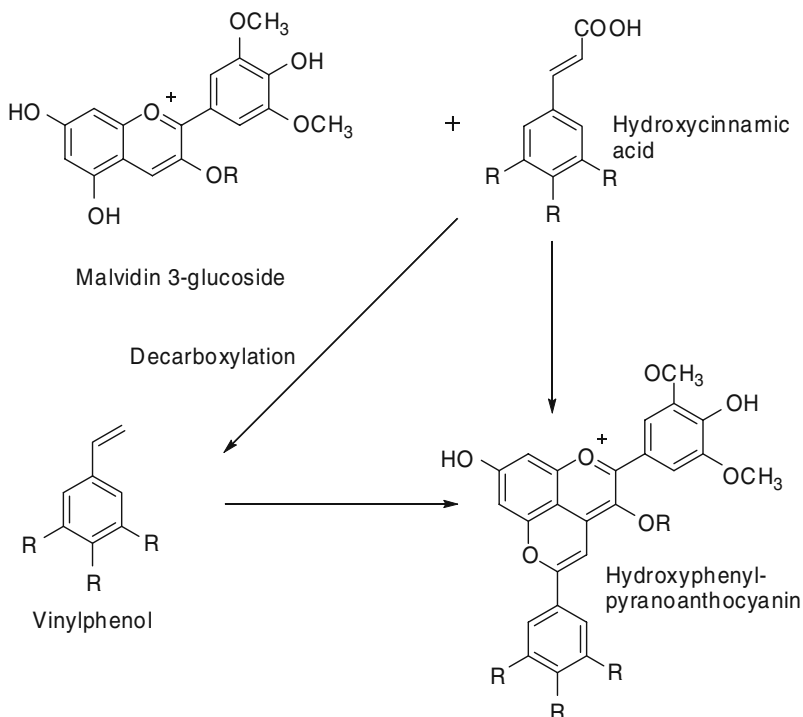
9C.1.2.1 Reactions of Hydroxycinnamic Acids with Anthocyanins

Hydroxycinnamic acids take part in numerous reactions that occur during wine-making and wine aging. They are important compounds in oxidation processes

of wine. During storage oxygen reacts over a coupled oxidation with vicinal di- and trihydroxyphenols, like caffeic acid, to produce the corresponding chinones (Singleton 1987; Wildenradt and Singleton 1974) The subsequent reactions result in the oxidation of ethanol to acetaldehyde, which has been shown to take part in condensation reactions between the wine polyphenols, such as anthocyanins and flavan-3-ols (Dallas et al. 1996a, b; Es-Safi et al. 1999; Fulcrand et al. 1996b; Rivas-Gonzalo et al. 1995; Santos-Buelga et al. 1995) forming a great variety of new, partly ethyl-linked, pigments (Dallas et al. 1996a, b; Es-Safi et al. 1999; Fulcrand et al. 1996b; Rivas-Gonzalo et al. 1995; Santos-Buelga et al. 1995; Timberlake and Bridle 1976). The oxidation of hydroxycinnamates also contributes to the browning of white wines during aging (Cheynier et al. 1990; Cilliers and Singleton 1990). The browning effect seemed to correlate with the oxidation of caffeic acid although it was shown that the effect of catechin was far greater than that of hydroxycinnamic acids (Okamura and Watanabe 1981).

The color of red wine is also strongly influenced by the presence of hydroxycinnamic acids. They play an important role in the phenomenon of copigmentation which describes the color intensification of anthocyanin solutions by the presence of other phenolic compounds (Baranac et al. 1996; Darias-Martín et al. 2002; Dimitric Markovic et al. 2000, 2005; Miniati et al. 1992). The intensification and the observed bathochromic shift of color are due to two main mechanisms, the intermolecular and the intramolecular copigmentation. Intermolecular copigmentation describes the stabilization of flavylium cations of anthocyanins by copigments over π-complexes between different molecules. Intramolecular copigmentation can occur for example in the case of anthocyanins acylated with hydroxycinnamic acids (sandwich type) (Figueiredo et al. 1999). A summary of copigmentation effects in red wine is given by Boulton (2001).

Another important reaction of hydroxycinnamic acids with anthocyanins is the formation of pyranoanthocyanins (Rentzsch et al. 2007b). These pigments are formed by direct reaction of hydroxycinnamic acids and their corresponding vinylphenols with anthocyanins present in red wine (Fig. 9C.3) (Fulcrand et al. 1996a; Hayasaka and Asenstorfer 2002; Håkansson et al. 2003; Sarni-Manchado et al. 1996; Schwarz et al. 2003). While in young wines the reaction of the vinylphenols is predominating, due to an enzymatic decarboxylation of coumaric and ferulic acid, during storage the share of direct reaction products of caffeic acid becomes more important (Rentzsch et al. 2007a; Schwarz et al. 2004). It was shown that caffeic and sinapic acid are not decarboxylated to their vinylphenols by yeast activity (Chatonnet et al. 1993); instead the formation of pyranoanthocyanis takes place over the direct reaction of caffeic acid, sinapic acid and anthocyanins. Schwarz et al. (2003) described the pathway of formation of hydroxyphenyl-pyranoanthocyanins over direct reaction with hydroxycinnamates. The stabilization of an intermediated carbenium ion structure by electron donating substituents on the aromatic ring of hydroxycinnamic acids is essential for the formation of these new pigments. Among the hydroxycinnamic acids, sinapic acid showed the fasted reaction followed by caffeic acid and ferulic acid. Coumaric acid exhibited the slowest reactivity. However, due to the high concentration of coumaric acid and caffeic acid in red wine, the

Fig. 9C.3 Reactions of hydroxycinnamic acids and their corresponding vinylphenols hydroxyphenyl-pyranoanthocyanins

hydroxyphenyl-pyranoanthocyanins resulting from these precursors are predominant. An overview on pyranoanthocyanins is given by Rentzsch et al. (2007b).

9C.2 Volatile Phenols

The volatile phenols possess the lowest concentration among the phenolic compounds in wine. However, due to their odor activity they have a great influence on the sensory characteristics of wine. Two sources for volatile phenols can be distinguished. One is the enzymatic formation from precursors present in wine and the other origin is due to migration from wood during barrel maturation. Among the volatile phenols, the vinyl and ethyl phenols play the most important role. Emerging from the decarboxylation of hydroxycinnamic acids, these compounds are responsible for off-flavors of wines. Vinylphenols exhibit unpleasant odors. With thresholds of between 420 μg/L for a 10/1 mixture of 4-vinlyphenol and 4-vinylguaiacol in white wine and 720 μg/L for a 1/1 mixture of the ethyl-phenols in red wine, these compounds can easily spoil the wine. As reported by Chatonnet et al. (1989), the yeast *Saccharomyces cerevisiae* can only decarboxylate coumaric and ferulic acid.
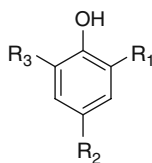
Phenols	R_1	R_2	R_3	MW
Ethyl phenol	H	C_2H_5	H	122
Vinyl phenol	H	C_2H_3	H	120
Guaiacol	OCH_3	OH	H	124
Methyl guaiacol	OCH_3	CH_3	H	122
Ethyl guaiacol	OCH_3	C_2H_5	H	136
Vinyl guaiacol	OCH_3	C_2H_3	H	134
Propyl guaiacol	OCH_3	C_3H_7	H	150
Allyl guaiacol	OCH_3	C_3H_5	H	148
Syringol	OCH_3	H	OCH_3	154
Methyl syringol	OCH_3	CH_3	OCH_3	152

Fig. 9C.4 Structures of volatile phenols in wine

More potent yeasts responsible for spoilages of wines with volatile phenols are of *Brettanomyces/Dekkerra* type that can produce the vinyl phenols and ethyl phenols of hydroxyl cinnamic acids. Ribéreau-Gayon et al. (2000) give an overview on this topic. Another source of volatile phenols is the oak wood of barrel and oak chips. These phenols are characterized by smoked and toasted aromas. Important volatile phenols in wine are depicted in Fig. 9C.4.

9C.3 Stilbenes

Stilbenes are a subclass of phenolic compounds naturally occurring in various families of plants, but grapes and wine are considered the most important dietary sources of these substances (Guebailia et al. 2006). Stilbenes can be biosynthesized by grapevines as a defence response to stress, such as microbial infection and UV irradiation, and they are transferred during the winemaking process into the must and wine. Due to their antioxidative, anticarcinogenic and antimutagenic potency, stilbenes are considered to play a central role in the human diet (Buiarelli et al. 2007).

Stilbenoids are derived from cinnamic acid and three acetate units from malonyl coenzym A. The first part of the biosynthesis is in common to flavonoids. The two biosynthetic routes are diverging at the point of cyclization of a styryl-3,5,7-triketoheptanoic acid. A C-acylation produces a chalcone and subsequent modifications lead to the flavonoids. An aldol condensation of the same intermediate polyketide produces a stilbene-2-carboxylic acid that is unstable and constitutes a range of structures known as stilbenoids. Figure 9C.5 shows an overview of the biosynthetic pathway (Gorham 1995).

One of the most relevant and extensively studied stilbene is *trans*-resveratrol (3,5,4'-trihydroxystilbene), a phytoalexin produced by grapevines in response to fungal infection, particularly *Botrytis cinerea*. Synthesis of resveratrol in grape berries is mainly located in the skin cells and is absent or low in the fruit flesh. In nature, resveratrol exists in two isomeric forms (*cis*- and *trans*-configured) in the free as well as in ß-glucoconjugated form. The 3-O-ß-D-glucosides of *cis*- and *trans*-resveratrol cis-and trans-configured are called piceids. The chemical structures of resveratrol and further stilbenes are depicted in Fig. 9C.6.

Stilbenes can also occur in oligomeric and polymeric forms, so-called viniferins. They are induced by oxidative polymerization of the monomer resveratrol through the activity of a peroxidase (Jean-Denis et al. 2006). Figure 9C.7 shows the biosynthesis of *trans-ε*-viniferin.

Numerous stilbenes such as *ε*-viniferin (Landrault et al. 2002) and *δ*-viniferin, two resveratrol dehydrodimers (Vitrac et al. 2005), the resveratrol dimer pallidol (Vitrac et al. 2001), *α*-viniferin, a trimer of resveratrol (Pryce and Langcake 1977)
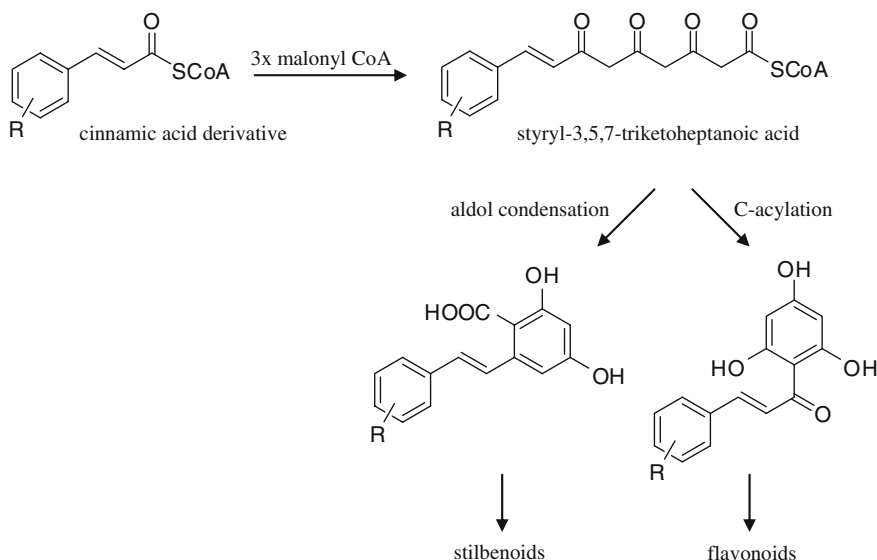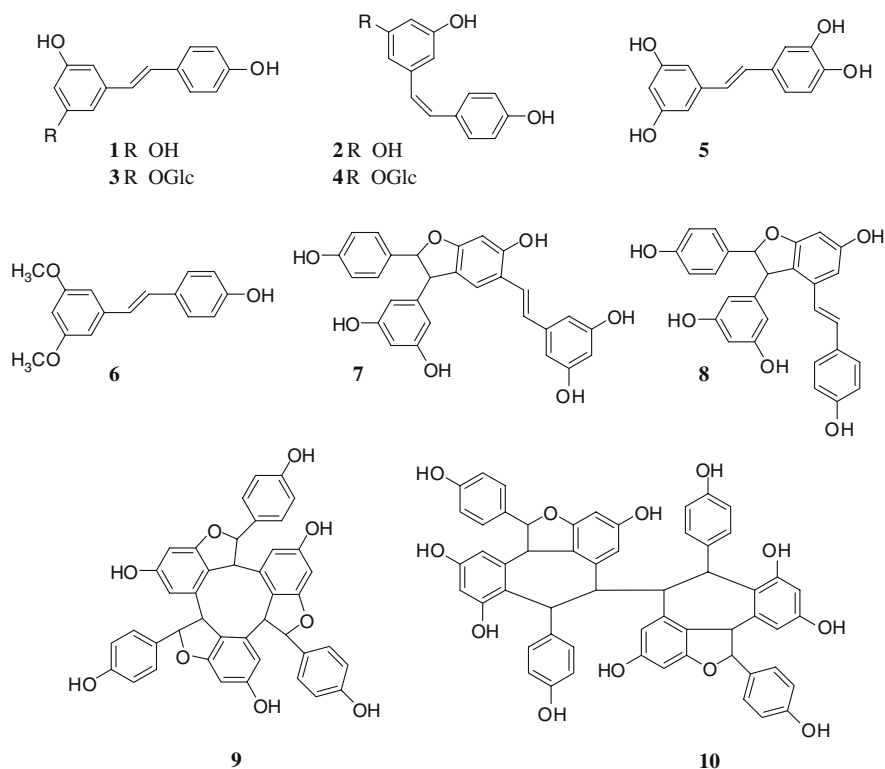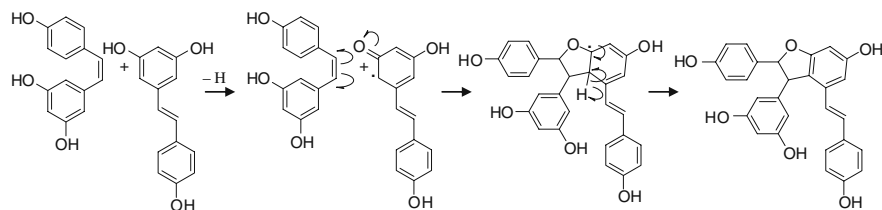

Fig. 9C.5 Common biosynthetic pathway of stilbenoids and flavonoids

Fig. 9C.6 Chemical structures of stilbenes: *trans*-resveratrol (1), *cis*-resveratrol (2), *trans*-piceid (3), *cis*-piceid (4), *trans*-piceatannol (5), *trans*-pterostilbene (6), *trans*-δ-viniferin (7), *trans*- ε-viniferin (8), α-viniferin (9), hopeaphenol (10)

Fig. 9C.7 Biosynthesis of *trans*-ε-viniferin

and the resveratrol tetramer hopeaphenol (Guebailia et al. 2006) have been identified in grapevine and wine. In addition, some oligomeric glucosides like *cis*- and *trans*-ε-viniferin diglucosides and pallidol-3-3″-diglucoside could be isolated and characterized from Riesling wine (Baderschneider and Winterhalter 2000).

The content of stilbenes in wine varies considerably and depends on several factors including climate, grape variety, fungal infections (Perrone et al. 2007; Jeandet et al. 1995), UV light, heavy metal ions (Püssa et al. 2006) and enological methods

(Cantos et al. 2003; Gambuti et al. 2004). It is also influenced by yeast enzymatic activities, in particular those of isomerase and glucosidase (Jeandet et al. 1994). Equally, activities of lactic acid bacteria, which are responsible for malolactic fermentation (Hernández et al. 2007), can also affect stilbene content in wine (Poussier et al. 2003). Aging of wine appears to have no important influence on the concentration of stilbenes (Jeandet et al. 1995).

Red wines usually contain higher stilbene concentrations than rosé or white wines. This depends on the more prolonged skin contact of the must during fermentation and the high phenolic content of red grape cultivars (Perrone et al. 2007).

Free *trans-* and *cis*-resveratrols are present in a concentration range of 0.2–13 mg/L in red wines and 0.1–0.8 mg/L in white wines. Consistently, high concentrations of *trans*-resveratrol are obtained in wines from Pinot noir. On the one hand, Cabernet Sauvignon wines cover a wide range of concentrations, with relatively high values in those from cool-climate countries such as Ontario and the Bordeaux region of France, whereas, on the other hand, wines from warmer climates like California, South America, and Australia tend to have much lower concentrations. In comparison to wine, grape juice offers a content of *trans*-resveratrol in a range of 0.09–0.18 mg/L (Stecher et al. 2001).

For piceid, the resveratrol-3-*O*-glucoside, concentrations are reported to be in a range of 0.3–9 mg/L in red and 0.1–2.2 mg/L in white wines (Goldberg et al. 1995, 1996a, b; Lamuela-Raventós et al. 1995; Sato et al. 1997; Naugler et al. 2007; Romero-Pérez et al. 1996). In Portuguese red wines piceids were even determined in concentrations up to 68 mg/L (Ribeiro de Lima et al. 1999). In comparison to wine, grapes were found to contain mainly *trans*-resveratrol glucoside in concentrations ranging from 1.5 to 7.3 μg/g (Burns et al. 2002).

In a survey of commercial wines from the South of France, levels of pallidol and viniferin have been reported. Viniferin was found to be present in red and botrytized sweet white wines with levels between 0.1 and 1.63 mg/L. Pallidol was not found in dry and sweet white wines but only in wines made by maceration with stems, with levels between 0.38 and 2.22 mg/L (Landrault et al. 2002).

In addition, Guebailia et al. (2006) have investigated the concentration of hopeaphenol in North African wines. Ksarwine presented the highest concentration of hopeaphenol (3.8 mg/L), followed by Muscat (3.06 mg/L), Guerrouane (2.68 mg/L), Merlot (2.1 mg/L), Cabernet Sauvignon (1.48 mg/L), Sidi-Brahim (0.61 mg/L), Amjad (0.34 mg/L), and Gris d'Algérie (0.3 mg/L).

Since Siemann and Creasy (1992) described the presence of *trans*-resveratrol in wines, many different methods have been developed to determine this compound and its derivatives (Romero-Pérez et al. 1996). Various methods use RP18-HPLC and gradient elution with UV detection (Lamuela-Raventós et al. 1995; Naugler et al. 2007; Ribeiro de Lima et al. 1999; Vitrac et al. 2005).

Trans-configured stilbenes such as *trans*-resveratrol, *trans*-pterostilbene and *trans*-ε-viniferin show two characteristic bands corresponding to high absorbances from 308 to 336 nm and from 281 to 313 nm. Cis-configured stilbenes like *cis*-resveratrol, *cis*-pterostilbene and *cis*-ε-viniferin exhibit a UV maximum at 285nm (Jeandet et al. 1997).

In addition, stilbenes are fluorescent compounds which are easily detected by fluorometry. For resveratrol, fluorescence detection is highly selective and even twice as sensitive as UV detection (Stecher et al. 2001). Due to this potential, methods by using HPLC coupled with absorbance and fluorescence detection were developed (Jeandet et al. 1997; Vitrac et al. 2002). Otherwise identification of stilbenes in wine by HPLC-DAD can be limited by coelution of two or more compounds. Therefore application of modern mass-spectrometry techniques is important to confirm the structure of stilbenes and to detect novel compounds in wine (Monagas et al. 2005b; Buiarelli et al. 2007; Careri et al. 2004; Jean-Denis et al. 2006; Kammerer et al. 2004; Mark et al. 2005; Püssa et al. 2006; Stecher et al. 2001). Table 9C.1 shows an overview on stilbenoid molecular ions and fragments identified in wine and grapevine by mass spectrometry.

It is widely accepted that polyphenols in wine are responsible for beneficial health effects (Sun et al. 2006). Particularly *trans*-resveratrol has been intensively studied and marked biological activities with regard to the prevention of cardiovascular disease and cancer have been reported (Ito et al. 2003). Other stilbenes also have properties similar to those of *trans*-resveratrol. Therefore, monitoring new stilbene derivatives in wine is of particular relevance (Guebailia et al. 2006).

9C.4 Miscellaneous Compounds

In addition to phenolic acids, volatile phenols, and stilbenes, other non-flavonoid phenolic compounds are also known to occur in wine. Marinos et al. (1992) were able to identify the lignans isolariciresinol-4′-*O*-ß-D-glucopyranoside and seco-isolariciresinol-ß-D-glucoside in an Australian Riesling wine as first representatives of a new category of wine phenols. By applying preparative all-liquid chromatographic techniques (i.e. countercurrent chromatography), Baderschneider and Winterhalter (2001) succeeded in isolating and fully characterizing nine additional lignans and neolignans from a German Riesling. Their structures are depicted in Fig. 9C.8. Nurmi et al. (2003) reported lignan concentrations in red wines in the range of 0.8-1.4 mg/L, with isolariciresinol being the main compound. Until now, it has not been clearly distinguished as to which extent these compounds are genuine grape constituents or rather formed during aging of wines in oak barrels. Clearly oak-wood derived are the coumarins which can be considered as cinnamic acid derivatives. The coumarins umbelliferone, 4-methyl-umbelliferone, esculin, and scopoletin have been extracted from oak wood (Puech and Moutounet 1988), and scopoletin (7-hydroxy-6-methoxycoumarin) has been reported as marker for the storage of wine in oak barrels (Tricard et al. 1987). More recently, oak-derived ellagtannins were reported to react with various nucleophilic wine constituents, such as catechin, epicatechin, anthocyanins, glutathione, and ethanol during barrel aging, giving rise to a formation of condensation products including ß-1- *O*-ethylvescalin and the potent antitumor agent Acutissimin A (Quideau et al. 2003, 2005; Saucier et al. 2006).

Table 9C.1 Stilbenoids identified in wine and grapevine by mass spectrometry

Compounds	[M-H]⁻	Fragment *m/z*	Technique	Sample	Reference
Monomers					
Resveratrol	227 [M-H]⁻	185, 183, 159, 157, 143	HPLC-ESI-MS/MS	Grapevine	Püssa et al. (2006)
Piceatannol	243 [M-H]⁻	225, 201, 200, 199, 175	HPLC-ESI-MS/MS	Grapevine	Püssa et al. (2006)
Astringin	405 [M-H]⁻	243, 173, 159	HPLC-TIS-MS/MS	Red wine	Buiarelli et al. (2007)
Piceid	389 [M-H]⁻	305, 289, 227, 175	HPLC-ESI-MS/MS	Grapevine	Püssa et al. (2006)
Dimers					
ε-Viniferin	453[M-H]⁻	435, 411, 369, 359, 347	HPLC-ESI-MS/MS	Grapevine	Püssa et al. (2006)
Pallidol	455 [M+H]⁺		FAB-MS (+)	Red wine	Vitrac et al. (2001)
Pallidol-3-*O*-glucoside	634 [M + NH₄]⁺		DCI-MS	White wine	Baderschneider and Winterhalter (2000)
Pallidol-3-3''-O-glucoside	777[M-H]⁻	615	HPLC-ESI-MS/MS	White wine	Baderschneider and Winterhalter (2000)
ε-Viniferin diglucoside	777	615	HPLC-ESI-MS/MS	White wine	Baderschneider and Winterhalter (2000)

ESI-MS/MS: Electro spray ionization-tandem mass spectrometry; TIS-MS/MS: Turbo Ion Spray interface-tandem mass spectrometry; FAB-MS: Fast atom bombardment-mass spectrometry; DCI-MS: Desorption chemical ionization-mass spectrometry
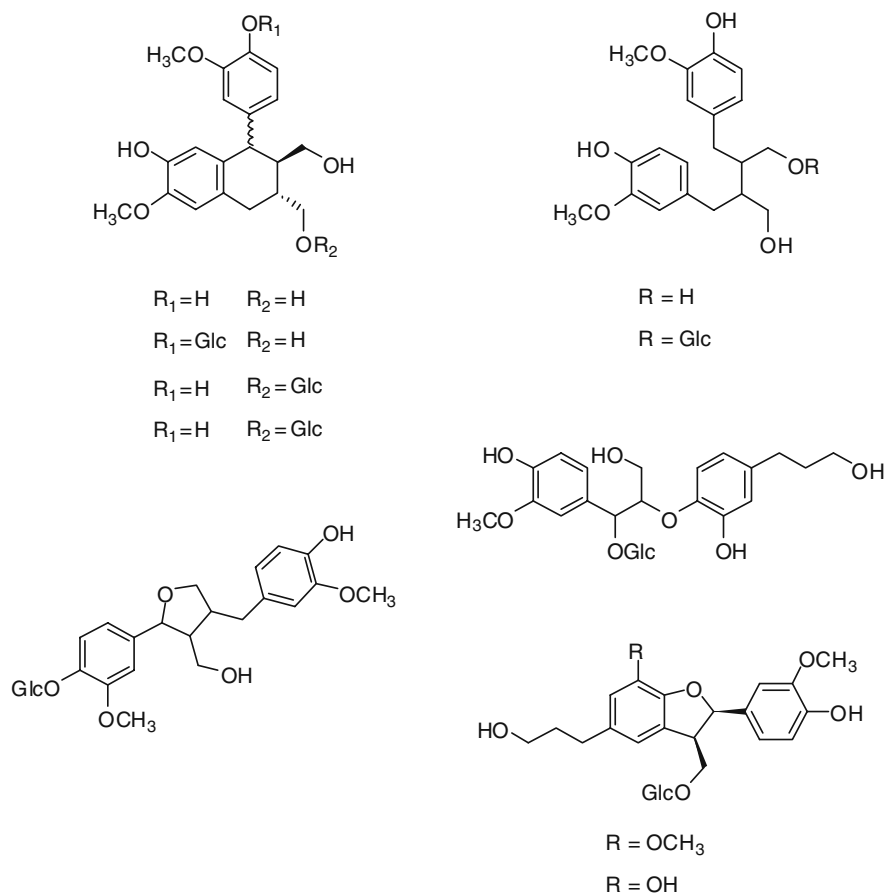
Fig. 9C.8 Structures of lignans and neolignans isolated from a German Riesling wine

References

Andres-Lacueva, C., Lamuela-Raventós, R. M., Buxadera, S., Torre-Bonat, M. C. (1996). Polyphenol content in sparkling wines (Cava) at different aging period. In J. Vercauteren, C. Chèze, M.C. Dumon, J.F. Weber (Eds.), *Polyphenols communications 96/XVIIIth International Conference on Polyphenols* (Vol. 2, pp. 305–306). Bordeaux: Secrétariat du Groupe Polyphénols.

Baderschneider, B., & Winterhalter, P. (2000). Isolation and characterization of novel stilbene derivatives from Riesling wine. *J. Agric. Food Chem., 48*, 2681–2686.

Baderschneider, B., & Winterhalter, P. (2001). Isolation and characterization of novel benzoates, cinnamates, flavonoids, and lignans from Riesling wine and screening for antioxidant activity. *J. Agric. Food Chem., 49*, 2788–2798.

Baldi, A., Romani, A., Mulinacci, N., & Vincieri, F. F. (1993). Composés phenoliques dans les cépages de Toscane de *Vitis vinifera* L. *J. Int. Sci. Vigne Vin, 27*, 201–215.

Baranac, J. M., Petranovic, N. A., & Dimitric-Markovic, J. M. (1996). Spectrophotometric study of anthocyan copigmentation reactions. *J. Agric. Food Chem., 44*, 1333–1336.

Betés-Saura, C., Andrés-Lacueva, C., & Lamuela-Raventós, R. M. (1996). Phenolics in white free run juices and wines from Penedès by High-Performance Liquid Chromatography: Changes during vinification. *J. Agric. Food Chem., 44*, 3040–3046.

Boulton, R. (2001). The copigmentation of anthocyanins and its role in the color of red wine: A critical review. *Am. J. Enol. Vitic., 52*, 67–87.

Boursiquot, J. M., Sapis, J. C., & Macheix, J. J. (1986). Les esters hydroxycinnamiques chez le genre *Vitis*. Essais d'application taxonomique premiers résultats. *C.R. Acad. Sci. Serie Iii- Life Sciences, 302*, 177–180.

Buiarelli, F., Coccioli, F., Jasionowska, R., Merolle, M., & Terracciano, A. (2007). Analysis of some stilbenes in Italian wines by liquid chromatography/tandem mass spectrometry. *Rap. Commun. Mass Spectrom., 21*, 2955–2964.

Burns, J., Yokota, T., Ashihara, H., Lean, M. E. J., & Crozier, A. (2002). Plant foods and herbal sources of resveratrol. *J. Agric. Food Chem., 50*, 3337–3340.

Cantos, E., Espín, J. C., Fernandez, M. J., Oliva, J., & Tomas-Barberan, F. A. (2003). Postharvest UV-C-irradiated grapes as a potential source for producing stilbene-enriched red wines. *J. Agric. Food Chem., 51*, 1208–1214.

Careri, M., Corradini, C., Elviri, L., Nicoletti, I., & Zagnoni, I. (2004). Liquid Chromatography-Electrospray Tandem Mass Spectrometry of *cis*-resveratrol and *trans*-resveratrol: Development, validation, and application of the method to red wine, grape, and winemaking byproducts. *J. Agric. Food Chem., 52*, 6868–6874.

Chatonnet, P., Dubourdieu, D., & Boidron, J. N. (1989). Effects of certain factors on yeast phenolic acid decarboxylation. *Conn. Vigne* Vin., *23*, 59–62.

Chatonnet, P., Dubourdieu, D., Boidron, J.-N., & Lavigne, V. (1993). Synthesis of volatile phenols by *Saccharomyces cerevisiae* in wines. *J. Sci. Food Agric., 62*, 191–202.

Cheynier, V. F., Trousdale, E. K., Singleton, V. L., Salgues, M. J., & Wylde, R. (1986). Characterization of 2-*S*-glutathionylcaftaric acid and its hydrolysis in relation to grape wines. *J. Agric. Food Chem., 34*, 217–221.

Cheynier, V., Rigaud, J., Souquet, J. M., Barillere, J. M., & Moutounet, M. (1989). Effect of pomace contact and hyperoxidation on the phenolic composition and quality of Grenache and Chardonnay wines. *Am. J. Enol. Vitic., 40*, 36–42.

Cheynier, V., Rigaud, J., Souquet, J. M., Duprat, F., & Moutounet, M. (1990). Must Browning in relation to the behavior of phenolic compounds during oxidation. *Am. J. Enol. Vitic., 41*, 346–349.

Cilliers, J. J. L., & Singleton, V. L. (1990). Caffeic Acid Autoxidation and the Effects of Thiols. *J. Agric. Food Chem., 38*, 1789–1796.

Cooper, H. J., & Marshall, A. G. (2001). Electrospray Ionization Fourier Transform Mass Spectrometric Analysis of Wine. *J. Agric. Food Chem., 49*, 5710–5718.

Dallas, C., Ricardo-da-Silva, J. M., & Laureano, O. (1996a). Interactions of oligomeric procyanidins in model wine solutions containing malvidin-3-glucoside and acetaldehyde. *J. Sci. Food Agric., 70*, 493–500.

Dallas, C., Ricardo-da-Silva, J. M., & Laureano, O. (1996b). Products formed in model wine solutions involving anthocyanins, procyanidin B$_2$, and acetaldehyde. *J. Agric. Food Chem., 44*, 2402–2407.

Darias-Martín, J., Martín-Luis, B., Carrillo-López, M., Lamuela-Raventós, R., Díaz-Romero, C., & Boulton, R. (2002). Effect of caffeic acid on the color of red wine. *J. Agric. Food Chem., 50*, 2062–2067.

Dimitric Markovic, J. M. D., Petranovic, N. A., & Baranac, J. M. (2000). A Spectrophotometric study of the copigmentation of malvin with caffeic and ferulic acids. *J. Agric. Food Chem., 48*, 5530–5536.

Dimitric Markovic, J. M. D., Petranovic, N. A., & Baranac, J. M. (2005). The copigmentation effect of sinapic acid on malvin: A spectroscopic investigation on colour enhancement. *J. Photochem. Photobiol. B: Biol., 78*, 223–228.

Drawert, F., Schreier, P., & Scherer, W. (1974). Gaschromatographisch-massenspektrometrische Untersuchung flüchtiger Inhaltsstoffe des Weines III. Säuren des Weinaromas. *Z. Lebensm. Unters. Forsch., 155*, 342–347.

Es-Safi, N.-E., Fulcrand, H., Cheynier, V., & Moutounet, M. (1999). Studies on acetaldehyde-induced condensation of (-)-epicatechin and malvidin 3-*O*-glucoside in a model solution system. *J. Agric. Food Chem., 47*, 2096–2102.

Fernandéz de Simon, B., Pérez-Ilzarbe, J., Hernández, T., Gómez-Cordovés, C., & Estrella, I. (1992). Importance of phenolic compounds for the characterization of fruit juices. *J. Agric. Food Chem., 40*, 1531–1535.

Figueiredo, P., George, F., Tatsuzawa, F., Toki, K., Saito, N., & Brouillard, R. (1999). New features of intramolecular copigmentation by acylated anthocyanins. *Phytochemistry, 51*, 125–132.

Fulcrand, H., Cameira dos Santos, P.-J., Sarni-Manchado, P., Cheynier, V., & Favre-Bonvin, J. (1996a). Structure of new anthocyanin-derived wine pigments. *J. Chem. Soc. Perkin Trans. 1: Organic and Bio-Organic Chemistry*, 735–739.

Fulcrand, H., Doco, T., Es-Safi, N.-E., Cheynier, V., & Moutounet, M. (1996b). Study of the acetaldehyde induced polymerisation of flavan-3-ols by liquid chromatography-ion spray mass spectrometry. *J. Chromatogr. A, 752*, 85–91.

Gambuti, A., Strollo, D., Ugliano, M., Lecce, L., & Moio, L. (2004). *trans*-Resveratrol, quercetin, (+)-catechin, and (-)-epicatechin content in south italian monovarietal wines: Relationship with maceration time and marc pressing during winemaking. *J. Agric. Food Chem., 52*, 5747–5751.

Garcia-Viguera, C., & Bridle, P. (1995). Analysis of non-coloured phenolic compounds in red wines. A comparison of High-Performance Liquid Chromatography and Capillary Zone Electrophoresis. *Food Chem., 54*, 349–352.

Goldberg, D. M., Yan, J., Ng, E., Diamandis, E. P., Karumanchiri, A., Soleas, G., & Waterhouse, A. L. (1995). A global survey of trans-resveratrol concentrations in commercial wines. *Am. J. Enol. Vitic., 46*, 159–165.

Goldberg, D. M., Tsang, E., Karumanchiri, A., Diamandis, E. P., Soleas, G., & Ng, E. (1996a). Method to assay the concentrations of phenolic constituents of biological interest in wines. *Anal. Chem., 68*, 1688–1694.

Goldberg, D. M., Ng, E., Karumanchiri, A., Diamandis, E. P., & Soleas, G. J. (1996b). Resveratrol glucosides are important components of commercial wines. *Am. J. Enol. Vitic., 47*, 415–420.

Gorham, J. (1995). *The Biochemistry of the Stilbenoids*. London: Chapman & Hall.

Guebailia, H. A., Chira, K., Richard, T., Mabrouk, T., Furiga, A., Vitrac, X., Monti, J. P., Delaunay, J. C., & Mérillon, J. M. (2006). Hopeaphenol: The first resveratrol tetramer in wines from North Africa. *J. Agric. Food Chem., 54*, 9559–9564.

Güntert, M., Rapp, A., Takeoka, G. R., & Jennings, W. (1986). HRGC and HRGC-MS Applied to wine constituents of lower volatility. *Z. Lebens. Unter. Forsch., 182*, 200–204.

Håkansson, A. E., Pardon, K., Hayasaka, Y., de Sa, M., & Herderich, M. (2003). Structures and colour properties of new red wine pigments. *Tetrahedron Lett., 44*, 4887–4891.

Hayasaka, Y., & Asenstorfer, R. E. (2002). Screening for potential pigments derived from anthocyanins in red wine using nanoelectrospray tandem mass spectrometry. *J. Agric. Food Chem., 50*, 756–761.

Hernández, T., Estrella, I., Pérez-Gordo, M., Alegría, E. G., Tenorio, C., Ruiz-Larrrea, F., & Moreno-Arribas, M. V. (2007). Contribution of malolactic fermentation by *Oenococcus oeni* and *Lactobacillus plantarum* to the changes in the nonanthocyanin polyphenolic composition of red wine. *J. Agric. Food Chem., 55*, 5260–5266.

Herrick, I. W., & Nagel, C. W. (1985). The caffeoyl tartrate content of white Riesling wines from California, Washington, and Alsace. *Am. J. Enol. Vitic., 36*, 95–97.

Herrmann, K. (1989). Occurrence and content of hydroxycinnamic and hydroxybenzoic acid compounds in foods. *Crit. Rev. Food Sci. Nutr., 28*, 315–347.

Holbach, B., Marx, R., & Zimmer, M. (2001). Bedeutung der Shikimisäure und des Anthocyanspektrums für die Charakterisierung von Rebsorten. *Lebensmittelchemie, 55*, 32–34.

Ito, T., Akao, Y., Yi, H., Ohguchi, K., Matsumoto, K., Tanaka, T., Iinuma, M., & Nozawa, Y. (2003). Antitumor effect of resveratrol oligomers against human cancer cell lines and the molecular mechanism of apoptosis induced by vaticanol C. *Carcinogesis, 24*, 1489–1497.

Jean-Denis, J. B., Pezet, R., & Tabacchi, R. (2006). Rapid analysis of stilbenes and derivatives from downy mildew-infected grapevine leaves by Liquid Chromatography-Atmospheric Pressure Photoionisation Mass Spectrometry. *J. Chromatogr. A*, *1112*, 263–268.

Jeandet, P., Bessis, R., Sbaghi, M., & Meunier, P. (1994). Occurrence of a resveratrol b-D-glucoside in wine: Preliminary studies. *Vitis, 33*, 183–184.

Jeandet, P., Bessis, R., Sbaghi, M., Meunier, P., & Trollat, P. (1995). Resveratrol content of wines of different ages: Relationship with fungal disease pressure in the vineyard. *Am. J. Enol. Vitic., 46*, 1–4.

Jeandet, P., Breuil, A. C., Adrian, M., Weston, L. A., Debord, S., Meunier, P., Maume, G., & Bessis, R. (1997). HPLC analysis of grapevine phytoalexins coupling Photodiode Array Detection and Fluorometry. *Anal. Chem., 69*, 5172–5177.

Kammerer, D., Claus, A., Carle, R., & Schieber, A. (2004). Polyphenol screening of pomace from red and white grape varieties (*Vitis vinifera* L.) by HPLC-DAD-MS/MS. *J. Agric. Food Chem., 52*, 4360–4367.

Lamuela-Raventós, R. M., Romero-Pérez, A. I., Waterhouse, A. L., & de la Torre-Boronat, M. C. (1995). Direct HPLC analysis of *cis-* and *trans*-resveratrol and piceid isomers in Spanish red *Vitis vinifera* wines. *J. Agric. Food Chem., 43*, 281–283.

Landrault, N., Larronde, F., Delaunay, J.-C., Castagnino, C., Vercauteren, J., Mérillon, J.-M., Gasc, F., Cros, G., & Teissédre, P.-L. (2002). Levels of stilbene oligomers and astilbin in French varietal wines and in grapes during Noble Rot development. *J. Agric. Food Chem., 50*, 2046–2052.

Lao, C., López-Tamames, E., Lamuela-Raventós, R. M., Buxaderas, S., Torre-Bonat, M. C. (1996). Effect of grape pectic enzyme treatment on phenolics of white musts and wines. In J. Vercauteren, C. Chèze, M. C. Dumon, J. F. Weber (Eds.), *Polyphenols communications 96/XVII-Ith International Conference on Polyphenols* (Vol. 2, pp. 303–304). Bordeaux: Secrétariat du Groupe Polyphénols.

Lee, C. Y., Jaworski, A. (1989). Major phenolic compounds in ripening white grapes. *Am. J. Enol. Vitic., 40*, 43–46.

Marinos, V. A., Tate, M. E., Williams, P. J. (1992). Lignan and phenylpropanoid glycerol glucosides in wine. *Phytochemistry, 31*, 4307–4312.

Mark, L., Nikfardjam, M. S. P., Avar, P., & Ohmacht, R. (2005). A validated HPLC method for the quantitative analysis of *trans*-resveratrol and *trans*-piceid in Hungarian wines. *J. Chromatogr. Sci., 43*, 445–449.

Mazza, G., Miniati, E. (1993). *Anthocyanins in fruits, vegetables, and grains*. Boca Raton: CRC Press.

Miniati, E., Damiani, P., & Mazza, G. (1992). Copigmentation and self-association of anthocyanins in food model systems. *It. J. Food Sci., 4*, 109–116.

Monagas, M., Bartolomé, B., & Gómez-Cordovés, C. (2005a). Updated knowledge about the presence of phenolic compounds in wine. *Cr. Rev. Food Sci. Nutr., 45*, 85–118.

Monagas, M., Suárez, R., Gómez-Cordovés, C., & Bartolomé, B. (2005b). Simultaneous determination of nonanthocyanin phenolic compounds in red wines by HPLC-DAD/ESI-MS. *Am. J. Enol. Vitic., 56*, 139–147.

Naugler, C., McCallum, J. L., Klassen, G., & Strommer, J. (2007). Concentrations of *trans*-resveratrol and related stilbenes in Nova Scotia wines. *Am. J. Enol. Vitic., 58*, 117–119.

Nurmi, T., Heinonen, S., Mazur, W., Deyama, T., Nishibe, S., & Adlercreutz, H. (2003). Lignans in selected wines. *Food Chem., 83*, 303–309.

Okamura, S., & Watanabe, M. (1981). Determination of phenolic cinnamates in white wine and their effect on wine quality. *Agric. Biol. Chem., 45*, 2063–2070.

Ong, B. Y., & Nagel, C. W. (1978). High-Pressure Liquid-Chromatographic analysis of hydroxycinnamic acid - tartaric acid esters and their glucose esters in *Vitis vinifera*. *J. Chromatogr., 157*, 345–355.

Otteneder, H., Holbach, B., Marx, R., & Zimmer, M. (2002). Rebsortenbestimmung in Rotwein anhand der Anthocyanspektren. *Mitt. Klosterneuburg, 52*, 187–194.

Peña-Neira, A., Hernández, T., García-Vallejo, C., Estrella, I., & Suarez, J. A. (2000). A Survey of phenolic compounds in Spanish wines of different geographical origin. *Eur. Food Res. Technol., 210*, 445–448.

Perrone, G., Nicoletti, I., Pascale, M., De Rossi, A., De Girolamo, A., & Visconti, A. (2007). Positive correlation between high levels of ochratoxin A and resveratrol-related compounds in red wines. *J. Agric. Food Chem., 55*, 6807–6812.

Poussier, M., Guilloux-Benatier, M., Torres, M., Heras, E., & Adrian, M. (2003). Influence of different maceration techniques and microbial enzymatic activities on wine stilbene content. *Am. J. Enol. Vitic., 54*, 261–266.

Pozo-Bayón, M. A., Hernández, M. T., Martín-Álvarez, P. J., & Polo, M. C. (2003). Study of low molecular weight phenolic compounds during the aging of sparkling wines manufactured with red and white grape varieties. *J. Agric. Food Chem., 51*, 2089–2095.

Pryce, R. J., & Langcake, P. (1977). α-Viniferin: An antifungal resveratrol trimer from grapevines. *Phytochemistry, 16*, 1452–1454.

Puech, J. L., & Moutounet, M. (1988). Liquid chromatographic determination of scopoletin in hydroalcoholic extract of oak wood and in matured distilled alcoholic beverages. *J. Assoc. Off. Anal. Chem., 71,* 512–514.

Püssa, T., Floren, J., Kuldepp, P., & Raal, A. (2006). Survey of grapevine *Vitis vinifera* stem polyphenols by Liquid Chromatography-Diode Array Detection-Tandem Mass Spectrometry. *J. Agric. Food Chem., 54*, 7488–7494.

Quideau, S., Jourdes, M., Saucier, C., Glories, Y., Pardon, P., & Baudry, C. (2003). DNA Topoisomerase Inhibitor Acutissimin A and Other Flavano-Ellagitannins in Red Wine. *Angew. Chem. Int. Ed., 42*, 6012–6014.

Quideau, S., Jourdes, M., Lefeuvre, D., Montaudon, D., Saucier, C., Glories, Y., Pardon, P., & Pourquier, P. (2005). The chemistry of wine polyphenolic *C*-glycosidic ellagitannins targeting human topoisomerase II. *Chem. Eur. J., 11*, 6503–6513.

Rentzsch, M., Schwarz, M., Winterhalter, P., & Hermosin-Gutiérrez, I. (2007a). Formation of hydroxyphenyl-pyranoanthocyanins in Grenache wines: precursor levels and evolution during aging. *J. Agric. Food Chem., 55*, 4883–4888.

Rentzsch, M., Schwarz, M., & Winterhalter, P. (2007b). Pyranoanthocyanins – an overview on structures, occurrence, and pathways of formation. *Trends Food Sci. Technol., 18*, 526–534.

Ribeiro de Lima, M. T., Waffo-Téguo, P., Teissédre, P. L., Pujolas, A., Vercauteren, J., Cabanis, J. C., & Mérillon, J. M. (1999). Determination of stilbenes (*trans*-astringin, *cis*- and *trans*-piceid, and *cis*- and *trans*-resveratrol) in Portuguese wines. *J. Agric. Food Chem., 47*, 2666–2670.

Ribéreau-Gayon, P., Glories, Y., Maujean, A., & Dubourdieu, D. (2000). *Handbook of Enology. Volume 2: The chemistry of wine: stabilization and treatments*. Chichester: Wiley

Ricardo-da-Silva, J. M., Cheynier, V., Samsom, A., & Bourzeix, M. (1993). Effect of pomace contact, carbonic maceration, and hyperoxidation on the procyanidin composition of Grenache Blanc wines. *Am. J. Enol. Vitic., 44*, 168–172.

Rigaud, J., Cheynier, V., Souquet, J. M., & Moutounet, M. (1991). Influence of must composition on phenolic oxidation kinetics. *J. Sci. Food Agric., 57*, 55–63.

Rivas-Gonzalo, J. C., Bravo-Haro, S., & Santos-Buelga, C. (1995). Detection of compounds formed through the reaction of malvidin 3-monoglucoside and catechin in the presence of acetaldehyde. *J. Agric. Food Chem., 43*, 1444–1449.

Romero-Pérez, A. I., Lamuela-Raventós, R. M., Waterhouse, A. L., & de la Torre-Boronat, M. C. (1996). Levels of *cis*- and *trans*-resveratrol and their glucosides in white and rosé *Vitis vinifera* wines from Spain. *J. Agric. Food Chem., 44*, 2124–2128.

Salagoïty-Auguste, M. H., & Bertrand, A. (1984). Wine phenolics - analysis of low molecular weight components by High-Performance Liquid-Chromatography. *J. Sci. Food Agric., 35*, 1241–1247.

Santos-Buelga, C., Bravo-Haro, S., & Rivas-Gonzalo, J. C. (1995). Interactions between catechin and malvidin-3-monoglucoside in model solutions. *Z. Lebens. Unters. Forsch., 201*, 269–274.

Sarni-Manchado, P., Fulcrand, H., Souquet, J.-M., Cheynier, V., & Moutounet, M. (1996). Stability and color of unreported wine anthocyanin-derived pigments. *J. Food Sci., 61*, 938–941.

Sato, M., Suzuki, Y., Okuda, T., & Yokotsuka, K. (1997). Contents of resveratrol, piceid, and their isomers in commercially available wines made from grapes cultivated in Japan. *Biosci. Biotechnol. Biochem., 61*, 1800–1805.

Saucier, C., Jourdes, M., Glories, Y., & Quideau, S. (2006). Extraction, detection, and quantification of flavano-ellagtannins and ethylvescalagin in a Bordeaux red wine aged in oak barrels. *J. Agric. Food Chem., 54*, 7349–7354.

Schwarz, M., Wabnitz, T. C., & Winterhalter, P. (2003). Pathway leading to the formation of anthocyanin-vinylphenol adducts and related pigments in red wines. *J. Agric. Food Chem., 51*, 3682–3687.

Schwarz, M., Hofmann, G., & Winterhalter, P. (2004). Investigations on anthocyanins in wines from *Vitis vinifera* cv. Pinotage: Factors influencing the formation of pinotin A and its correlation with wine age. *J. Agric. Food Chem., 52*, 498–504.

Siemann, E. H., & Creasy, L. L. (1992). Concentration of the phytoalexin resveratrol in wine. *Am. J. Enol. Vitic., 43*, 49–52.

Singleton, V. L. (1987). Oxygen with phenols and related reactions in musts, wines, and model systems: observations and practical implications. *Am. J. Enol. Vitic., 38*, 69–77.

Singleton, V. L., Timberlake, C. F., & Lea, A. G. H. (1978). The phenolic cinnamates of white grapes and wine. *J. Sci. Food Agric., 29*, 403–410.

Singleton, V. L., Zaya, J., & Trousdale, E. K. (1986). Caftaric and coutaric acids in fruit of *Vitis. Phytochemistry, 25*, 2127–2133.

Sladkovský, R., Solich, P., & Urbánek, M. (2004). High-Performance Liquid Chromatography determination of phenolic components in wine using off-line Isotachophoretic pretreatment. *J. Chromatogr., A, 1040*, 179–184.

Somers, T., Vérette, E., & Pocock, K. (1987). Hydroxycinnamate esters of *Vitis vinifera*: Changes during white vinification, and effects of exogenous enzymic hydrolysis. *J. Sci. Food Agric., 40*, 67–78.

Stecher, G., Huck, C. W., Popp, M., & Bonn, G. K. (2001). Determination of flavonoids and stilbenes in red wine and related biological products by HPLC and HPLC-ESI-MS-MS. *Fresenius J. Anal. Chem., 371*, 73–80.

Sun, B., Ribes, A. M., Leandro, M. C., Belchior, A. P., & Spranger, M. I. (2006). Stilbenes: Quantitative extraction from grape skins, contribution of grape solids to wine and variation during wine maturation. *Anal. Chim. Acta, 563*, 382–390.

Timberlake, C. F., & Bridle, P. (1976). Interactions between anthocyanins, phenolic compounds, and acetaldehyde and their significance in red wines. *Am. J. Enol. Vitic., 27*, 97–105.

Tricard, C., Salagoity, M. H., & Sudraud, P. (1987). Scopoletin: A marker of storage in oak barrels. *Conn. Vigne Vin, 21*, 33–41.

Vanhoenacker, G., De Villiers, A., Lazou, K., De Keukeleire, D., & Sandra, P. (2001). Comparison of High-Performance Liquid Chromatography – Mass Spectroscopy and Capillary Electrophoresis – Mass Spectroscopy for the analysis of phenolic compounds in diethyl ether extracts of red wines. *Chromatographia, 54*, 309–315.

Vitrac, X., Castagnino, C., Waffo-Téguo, P., Delaunay, J.-C., Vercauteren, J., Monti, J.-P., Deffieux, G., & Mérillon, J.-M. (2001). Polyphenols newly extracted in red wine from Southwestern France by centrifugal partition chromatography. *J. Agric. Food Chem., 49*, 5934–5938.

Vitrac, X., Monti, J.-P., Vercauteren, J., Deffieux, G., & Mérillon, J.-M. (2002). Direct liquid chromatographic analysis of resveratrol derivatives and flavanonols in wines with absorbance and fluorescence detection. *Anal. Chim. Acta, 458*, 103–110.

Vitrac, X., Bornet, A., Vanderlinde, R., Valls, J., Richard, T., Delaunay, J.-C., Mérillon, J.-M., & Teissédre, P.-L. (2005). Determination of stilbenes (δ-viniferin, *trans*-astringin, *trans*-piceid, *cis-* and *trans*-resveratrol, ε-viniferin) in Brazilian wines. *J. Agric. Food Chem., 53*, 5664–5669.

Wildenradt, H. L., & Singleton, V. L. (1974). The production of aldehydes as a result of oxidation of polyphenolic compounds and its relation to wine aging. *Am. J. Enol. Vitic., 25*, 119–126.

Würdig, G., & Woller, R. (1989). *Chemie des Weines.* Stuttgart: Eugen Ulmer