



# Astringency, bitterness and color changes in dry red wines before and during oak barrel aging: An updated phenolic perspective review

Si-Yu Li & Chang-Qing Duan

To cite this article: Si-Yu Li & Chang-Qing Duan (2018): Astringency, bitterness and color changes in dry red wines before and during oak barrel aging: An updated phenolic perspective review, Critical Reviews in Food Science and Nutrition, DOI: [10.1080/10408398.2018.1431762](https://doi.org/10.1080/10408398.2018.1431762)

To link to this article: <https://doi.org/10.1080/10408398.2018.1431762>



Accepted author version posted online: 30 Jan 2018.  
Published online: 16 Feb 2018.



Submit your article to this journal [↗](#)



Article views: 43



View related articles [↗](#)



View Crossmark data [↗](#)



# Astringency, bitterness and color changes in dry red wines before and during oak barrel aging: An updated phenolic perspective review

Si-Yu Li<sup>a,b</sup> and Chang-Qing Duan<sup>a,b</sup>

<sup>a</sup>Center for Viticulture & Enology, College of Food Science and Nutritional Engineering, China Agricultural University, Beijing, China; <sup>b</sup>Key Laboratory of Viticulture and Enology, Ministry of Agriculture, Beijing, China

## ABSTRACT

To understand effects of using oak barrels on the astringency, bitterness and color of dry red wines, phenolic reactions in wines before and after barrel aging are reviewed in this paper, which has been divided into three sections. The first section includes an introduction to chemical reactivities of grape-derived phenolic compounds, a summary of the phenolic reactions that occur in dry red wines before barrel aging, and a discussion of the effects of these reactions on wine astringency, bitterness and color. The second section introduces barrel types that determine the oak barrel constituents in wines (primarily oak aldehydes and ellagitannins) and presents reactions between the oak constituents and grape-derived phenolic compounds that may modulate wine astringency, bitterness and color. The final section illustrates the chemical differences between basic oxidation and over-oxidation in wines, discusses oxygen consumption kinetics in wines during barrel aging by comparing different oxygen consumption kinetics observed previously by others, and speculates on the possible preliminary phenolic reactions that occur in dry red wines during oak barrel aging that soften tannins and stabilize pigments via basic oxidation. Additionally, sulfur dioxide (SO<sub>2</sub>) addition during barrel aging and suitability of adopting oak barrels for aging wines are briefly discussed.

## KEYWORDS

Dry red wine; oak barrel aging; phenolic reactions; astringency; bitterness; color

## Introduction

Wine, one of the most popular beverages in the world, has thousands of years of history. Wine grape quality is largely determined by its terroir, grape variety and viticultural practices (Reynolds 2010; van Leeuwen 2010; Young et al. 2010). The organoleptic properties of wines (such as its smell, mouth-feel and color) are significantly dependent on the winemaking and aging techniques used (Ribéreau-Gayon et al. 2006b, c). The smell property of wines is correlated with the volatile compounds present, and the mouth-feel (primarily astringency and bitterness) and color properties of wines are generally conferred by the non-volatile compounds present in wines, especially the phenolic compounds (Monagas et al. 2005; Waterhouse 2002).

At present, dry red wines are the most consumed type of wine in the world. Although many of these wines can be enjoyed by consumers directly after fermentation, many dry red wines still require an aging period due to their inherent flavor characteristics and the desired wine styles of wine-makers. From a chemical viewpoint, red wines are mildly acidic aqueous solutions (pH 3.2–3.8) comprising various chemical compounds. These chemical compounds can react during aging and are thus able to modify the original organoleptic properties of wines. Oak woods have been considered resilient and impermeable to liquids and are used to make

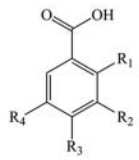
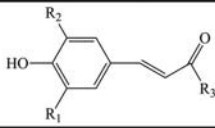
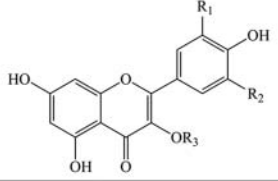
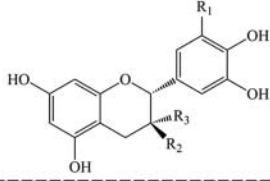
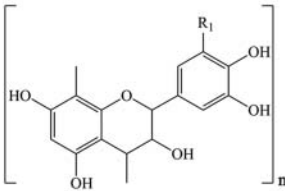
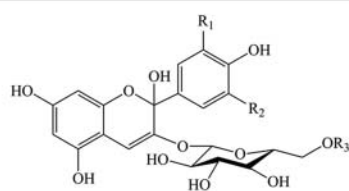
barrels for aging wines. Because oak barrels have special physicochemical properties, they affect the initial chemical reactions in wines during wine aging, contribute extractable oak constituents to wines and confer new flavor characteristics. Therefore, oak barrels are generally used in wine aging for making quality wines (Jackson 2008; Ribéreau-Gayon et al. 2006c; Waterhouse et al. 2016).

In dry red wines, the chemical reactions of the wine phenolic compounds that occur during barrel aging are complex. The aim of the present paper is to summarize the state of the art in relation to the primary phenolic reactions that occur in dry red wines before and during oak barrel aging and to discuss their impact on wine astringency, bitterness and color.

## Grape-derived phenolic compounds in red wines

### Classification

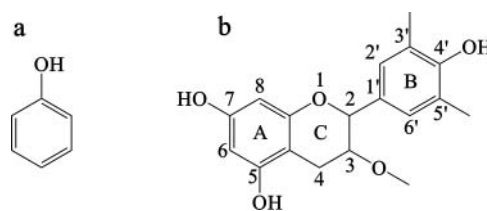
Phenolic compounds are a group of secondary metabolites in plants that possess a phenol ring consisting of an aromatic ring with at least one hydroxyl group. The major phenolic compounds in *Vitis vinifera* grapes include hydroxybenzoic acids, hydroxycinnamic acids, flavonols, flavanols and anthocyanins (Fig. 1) (Li and Sun 2017; Monagas et al. 2005; Waterhouse 2002). Generally, because of their structural

Basic structure	Hydroxybenzoic acids	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
	Salicylic acid	OH	H	H	H
	<i>p</i> -Hydroxybenzoic acid	H	H	OH	H
	Gentisic acid	OH	H	H	OH
	Protocatechuic acid	H	OH	OH	H
	Gallic acid	H	OH	OH	OH
	Vanillic acid	H	OCH <sub>3</sub>	OH	H
	Syringic acid	H	OCH <sub>3</sub>	OH	OCH <sub>3</sub>
Basic structure	Hydroxycinnamic acids	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>3</sub> modification
	<i>p</i> -Coumaric acid	H	H	OH	
	Caffeic acid	OH	H	OH	
	Ferulic acid	OCH <sub>3</sub>	H	OH	
	Sinapic acid	OCH <sub>3</sub>	OCH <sub>3</sub>	OH	(Tartaric acid)
Basic structure	Flavonols	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>3</sub> modification
	Kaempferol	H	H	H	
	Quercetin	OH	H	H	
	Myricetin	OH	OH	H	(Glucoside)
	Isorhamnetin	OCH <sub>3</sub>	H	H	
	Laricitrin	OCH <sub>3</sub>	OH	H	
	Syringetin	OCH <sub>3</sub>	OCH <sub>3</sub>	H	(Glucuronide)
Basic structure	Flavonols	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>3</sub> modification
	(+)-Catechin	H	OH	H	
	(-)-Epicatechin	H	H	OH	
	(+)-Gallocatechin	OH	OH	H	
	(-)-Epigallocatechin	OH	H	OH	(Gallate)
	Procyanidins	H			
	Prodelphinidins	OH			
Basic structure	Anthocyanins	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>3</sub> modification
	Delphinidin-3- <i>O</i> -glucoside	OH	OH	H	
	Cyanidin-3- <i>O</i> -glucoside	OH	H	H	
	Petunidin-3- <i>O</i> -glucoside	OCH <sub>3</sub>	OH	H	
	Peonidin-3- <i>O</i> -glucoside	OCH <sub>3</sub>	H	H	
	Malvidin-3- <i>O</i> -glucoside	OCH <sub>3</sub>	OCH <sub>3</sub>	H	
					(Acetyl)
					(Coumaroyl)

**Figure 1.** Major grape-derived phenolic compounds: hydroxybenzoic acids (a), hydroxycinnamic acids (b), flavonols (c), flavanol monomers (d), flavanol oligomers/polymers (e), and anthocyanins (f).

characteristics, hydroxybenzoic acids and hydroxycinnamic acids are classified as non-flavonoids, while flavonols, flavanols and anthocyanins are classified as flavonoids. The basic structural difference between these classes is non-flavonoids contain only one phenol ring and flavonoids contain two phenol rings (ring A and ring B). Furthermore, the two phenol rings of flavonoids are connected via an oxygen-containing central pyran ring (ring C) (Fig. 2). The phenolic compositions and concentrations of grapes and wines are dependent on many factors, such as the climatic and geographic conditions of the vineyards in which they were grown in addition to the viticultural practices, variety and maturation degree of the grapes, and the maceration and fermentation methods

used during winemaking (de Freitas et al. 2000; Reynolds 2010; Ribéreau-Gayon et al. 2006b; Spranger et al. 2004; Sun et al. 2001, 2011; Sun and Spranger 2005; van Leeuwen 2010;



**Figure 2.** Basic structures of non-flavonoids (a) and flavonoids (b).

**Table 1.** Concentration levels of different phenolic compounds present in red wines.

Phenolic compounds	Concentration level (mg/L)
Hydroxybenzoic acids <sup>a</sup>	8–54
Hydroxycinnamic acids <sup>a</sup>	11–164
Flavonols <sup>a</sup>	4–114
Flavanols <sup>b</sup>	436–3600
Anthocyanins <sup>c</sup>	185–895

<sup>a</sup>(Bautista-Ortín et al. 2007; García-Falcón et al. 2007; Gutiérrez et al. 2005; Kallithraka et al. 2006);

<sup>b</sup>(Bautista-Ortín et al. 2007; González-Centeno et al. 2016; Koundouras et al. 2013; Pérez-Lamela et al. 2007);

<sup>c</sup>(Bautista-Ortín et al. 2007; González-Centeno et al. 2016; Gutiérrez et al. 2005; Kallithraka et al. 2006; Koundouras et al. 2013; Pérez-Lamela et al. 2007).

Young et al. 2010). The general concentration levels of the various phenolic compounds present in red wines are listed in Table 1.

### Phenolic acids

Phenolic acids are present in fresh grapes and include hydroxybenzoic (Fig. 1a) and hydroxycinnamic acids (Fig. 1b). The major hydroxybenzoic acid present in red wines is gallic acid, which is found in its free form in grapes. However, gallic acid can also be released via the hydrolysis of gallate esters of tannins (Su and Singleton 1969; Waterhouse 2002). Although free hydroxycinnamic acids are not present in grapes, hydroxycinnamic acids exist as tartaric esters, which are hydrolyzed during winemaking and aging (Buiarelli et al. 2010; Singleton et al. 1986). Although hydroxybenzoic acids remain relatively stable in wines, hydroxycinnamic acids begin participating in both enzymatic and non-enzymatic reactions at the very start of the winemaking process and have been observed to affect wine color (Schwarz et al. 2003a, c; Somers et al. 1987).

### Flavonols

Flavonols are present in grape skins. Their biosynthesis is reported to be positively related to sunlight exposure (Price et al. 1995). In general, six types of flavanol aglycones (kaempferol, quercetin, myricetin, isorhamnetin, laricitrin, and syringetin) are present in grapes and wines. These aglycones exist in both simple and 3-*O*-glycosidic forms, and their sugar moieties are usually glucoside and glucuronide and occasionally galactoside (Fig. 1c).

### Flavanols

In general, five types of monomeric flavanols are found in grapes, namely, (+)-catechin, (-)-epicatechin, (+)-gallocatechin, (-)-epigallocatechin, and (-)-epicatechin-3-*O*-gallate (Fig. 1d). (+)-Catechin, (-)-epicatechin and (-)-epicatechin-3-*O*-gallate are found in both grape skins and grape seeds, whereas (+)-gallocatechin and (-)-epigallocatechin are only found in grape skins. This distribution leads to compositional differences in the flavanol oligomers/polymers present in grape skins and seeds (Escribano-Bailón et al. 1995; Su and Singleton 1969).

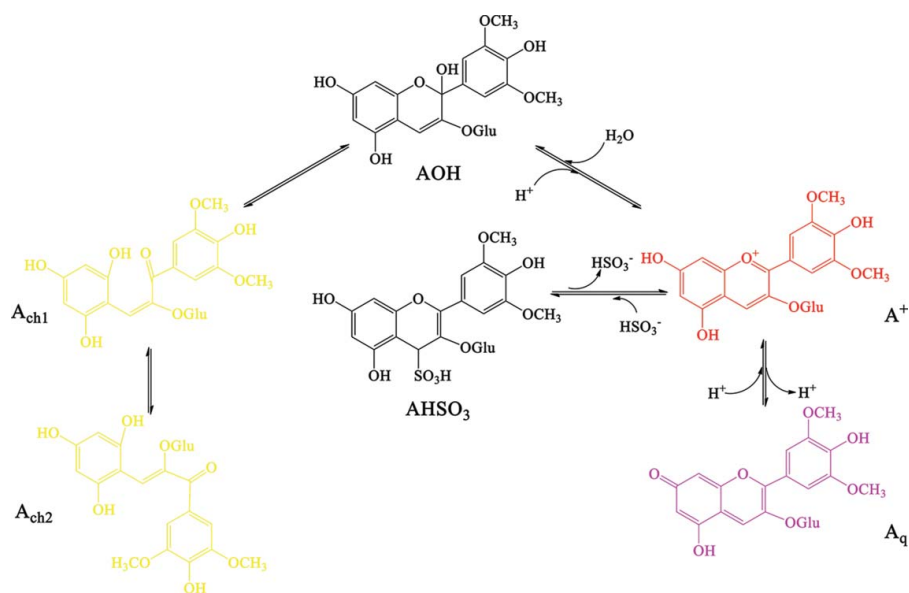
Flavanol oligomers/polymers are also referred to as proanthocyanidins and condensed tannins because of their abilities to release anthocyanidins under heated acidic conditions and to interact with and precipitate proteins (He et al. 2008; Porter et al. 1985). The most common structural characteristics of flavanol oligomers/polymers in grapes and wines are flavanol monomer units in which the C4 position of the top unit is linked to the C8 position of the lower unit (C4-C8-linked flavanols). Additionally, a small proportion of C4-C6-linked flavanols were detected in grapes and wines (Fig. 1e, Fig. 2b) (de Freitas et al. 1998, 2000; Escribano-Bailón et al. 1995; Mateus et al. 2001). The flavanol oligomers/polymers present in *V. vinifera* grapes are classified as either a procyanidin or prodelphinidin. The procyanidins comprise (+)-catechin and (-)-epicatechin, which are present in both grape seeds and skins. The prodelphinidins comprise (+)-gallocatechin and (-)-epigallocatechin, which are present only in grape skins. In red wines, the predominant flavanol monomer is usually (+)-catechin. In terms of the oligomers/polymers present in wines, (-)-epicatechin is the most abundant unit and (+)-catechin often acts as the terminal unit in the flavanol chain. In young red wines, flavanol oligomers/polymers account for 25–50% of the total phenolic compounds, and this proportion may be even higher in older wines (Waterhouse 2002).

Bitterness and astringency are taste and tactile sensations, respectively, perceived by the human mouth (Vidal et al. 2003; Soares et al. 2017). Flavanols play a significant role in the bitterness and astringency of wines. Many researchers acknowledged that the bitterness of a wine generally comes from low-molecular-weight flavanols, especially monomeric flavanols, while wine astringency is positively correlated with the degree of polymerization (DP) and the galloyl group number of flavanols (de Freitas and Mateus 2001, 2002; McRae et al. 2013; Sun et al. 2013).

### Anthocyanins

Anthocyanins are present primarily in grape skins and are responsible for the color of red wines. The anthocyanins present in *V. vinifera* grapes are usually the 3-*O*-glucosidic forms of five different anthocyanidins (delphinidin, cyanidin, petunidin, peonidin, and malvidin). Furthermore, in these five anthocyanidins, the hydroxyl group present at the C6 position of the glucose can also be esterified by acetic acid and phenolic acids, including *p*-coumaric acid, caffeic acid, and ferulic acid (Fig. 1f). In general, the predominant anthocyanins present in *V. vinifera* wines are malvidin-based anthocyanins (Bakker et al. 1997; Castañeda-Ovando et al. 2009; de Freitas and Mateus 2006).

In aqueous solution, different forms of anthocyanins coexist in a pH-dependent equilibrium, and the flavylium cation form of anthocyanins ( $A^+$ ) produces a red color ( $\lambda_{\max}$ : 515–530 nm). The red flavylium cation form is in equilibrium with the violet quinoidal base form ( $A_q$ ) and the colorless hemiketal form (AOH) via deprotonation and hydration, respectively. The colorless hemiketal form of anthocyanin is also in equilibrium with the yellow *cis/trans*-chalcone form ( $A_{ch}$ ) (Fig. 3) (Pina 1998). The proportion of each anthocyanin form changes with pH. At the pH of wine, the proportions of the flavylium cation,



**Figure 3.** Examples of anthocyanin equilibrium in wines and anthocyanin sulfite adducts generated from sulfite bleaching, including the hemiketal form (AOH), flavylium cation form ( $A^+$ ), quinoidal base form ( $A_q$ ), *cis*-chalcone form ( $A_{ch1}$ ), *trans*-chalcone form ( $A_{ch2}$ ), and anthocyanin sulfite adducts ( $AHSO_3$ ) (Castañeda-Ovando et al. 2009; Cheynier et al. 2006).

quinoidal base, hemiketal and chalcone forms of anthocyanin were determined to be approximately 12.2%, 15.0%, 45.2% and 27.6%, respectively (Glories 1984). Except for the pH change, the addition of sulfur dioxide ( $SO_2$ ) to wines for antimicrobial purposes can also affect the anthocyanin equilibrium because sulfite ( $HSO_3^-$ ) possesses the ability to react with flavylium cations and generate colorless sulfite adducts ( $AHSO_3$ ). The reaction between A and  $HSO_3^-$  is known as sulfite bleaching (Fig. 3).

#### Relationship between the structural characteristics and chemical reactivities of wine phenolic compounds

The chemical reactivities of phenolic compounds are dependent on their structural characteristics. On a phenol ring, carbons adjacent to and opposite the carbons bearing hydroxyl groups have a high electron density because the oxygen atoms on hydroxyl groups tend to transfer their electrons to the aromatic ring and because of the mesomeric effect of hydroxyl groups. Thus, these carbons are negatively charged and react easily with electrophiles. Phenol rings with the strongest nucleophilic ability are those with a phloroglucinol structure, such as the A rings of flavonoids (Fig. 2b, Fig. 4a) (Fulcrand et al. 2006). The C6 and C8 on the A ring shown in Fig. 2b can

function as nucleophilic sites; however, the C8 position is more prone to react with electrophiles due to its higher electron density.

The antioxidant characteristics of phenolic compounds are derived from the electron-donating ability of oxygen atoms on the hydroxyl groups. Furthermore, phenolic compounds with a catechol or a galloyl structure (Fig. 4bc) have been reported to be especially good antioxidants (Danilewicz 2003; Fulcrand et al. 2006; Singleton 1987; Waterhouse and Laurie 2006). Several non-flavonoids, including gallic acid and caffeic acid, and several flavonoids exhibiting a catechol or a galloyl structure on their B ring, including quercetin, (+)-catechin and delphinidin-3-O-glucoside, are all effective phenolic antioxidants.

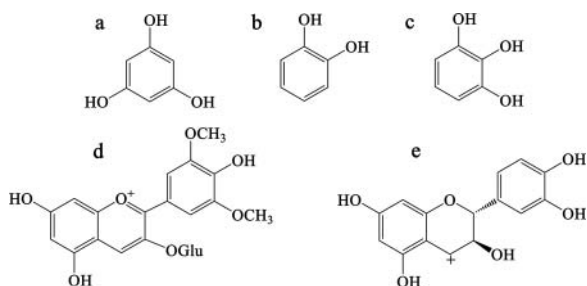
The C rings in anthocyanins and flavanols can be positively charged and can act as electrophiles in red wines. Anthocyanin cations include anthocyanin flavyliums (Fig. 4d) and flavanol cations produced by the acid cleavage of flavanol oligomers/polymers (Fig. 4e) (Haslam 1980; Vidal et al. 2002). In addition, the flavanols and hemiketal-formed anthocyanins present in red wines may exhibit nucleophilic reactivities.

As major phenolic compounds in dry red wines, flavanols and anthocyanins are directly responsible for the mouth-feel (primarily the astringency and bitterness) and color of wines. Because of their high concentrations (Table 1) and chemical reactivities, the reactions in which flavanols and anthocyanins participate during winemaking and aging play determinant roles in wine organoleptic properties.

#### Effects of the spontaneous chemical reactions of phenolic compounds on the astringency, bitterness and color of dry red wines

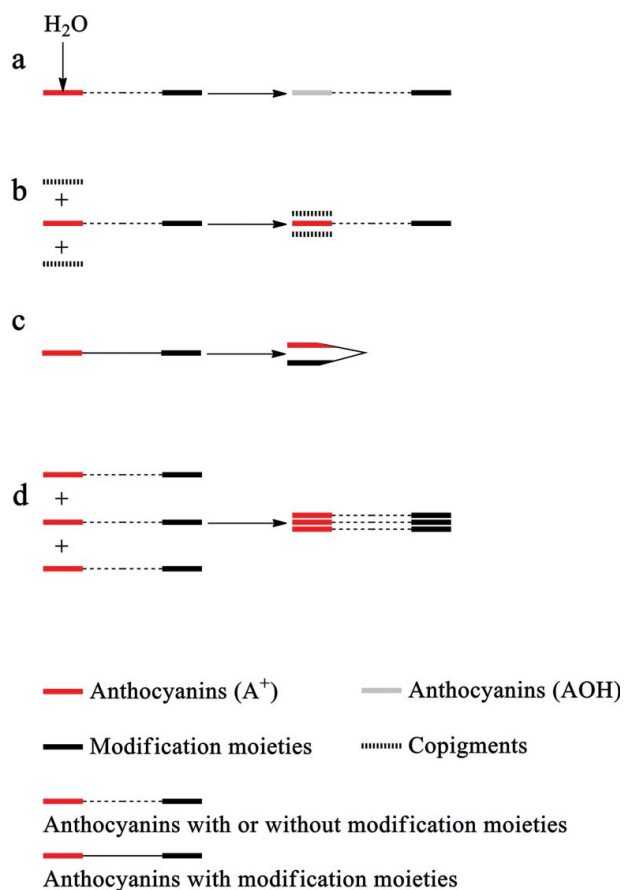
##### Copigmentation and self-association of anthocyanins

At the pH of wine (3.2–3.8), red flavylium cation-formed anthocyanins ( $A^+$ ) can be hydrated by water via nucleophilic attack, subsequently converting them into colorless hemiketal-



**Figure 4.** Basic structures of phloroglucinol (a), catechol (b), and galloyl (c) and examples of an anthocyanin flavylium cation (d) and a flavanol cation (e).





**Figure 5.** Examples of hydration (a), intermolecular copigmentation (b), intramolecular copigmentation (c) and self-association (d) of anthocyanins (Castañeda-Ovando et al. 2009; de Freitas et al. 2017; Escobedo-Bailón and Santos-Buelga 2012).

formed anthocyanins (AOH) (Fig. 5a). However, because of van der Waals interactions, hydrogen bonding and charge transfers between colored anthocyanins (the flavylium cation form or quinonoid form) and colorless copigments, non-covalent molecular complexes can be formed in a vertical  $\pi$ - $\pi$  stacking manner. These complexes have a sandwich-like structure, which aids in partially protecting the flavylium cations from hydration and stabilizes wine color. This phenomenon is referred to as copigmentation (Brouillard et al. 1989; Timberlake and Bridle 1976; Trouillas et al. 2016).

Two general types of copigmentation are present in wines, namely, intermolecular copigmentation and intramolecular copigmentation (Brouillard 1981; Brouillard 1982). Intermolecular copigmentation occurs between anthocyanins and non-anthocyanin molecules in which the latter act as copigments (Fig. 5b). The effective copigments in wines include organic acids, amino acids, metals, and phenolic compounds (Baranac et al. 1996, 1997; Gómez-Míguez et al. 2006). Intramolecular copigmentation occurs when several modification moieties in the anthocyanin molecules fold and function as copigments (Fig. 5c). Representative modification moieties include the acylation of the glucose residues of anthocyanin molecules with phenolic acids and the addition of flavanol unit(s) to anthocyanins via an ethyl bridge (Atanasova et al. 2002; Cheynier et al. 2006; de Freitas and Mateus 2006; Timberlake and Bridle 1976). Except for these two types of copigmentation, the

anthocyanin self-association that occurs between independent anthocyanin molecules is also able to prevent the hydration of flavylium cations and stabilize wine color (Fig. 5d) (Timberlake 1980). Copigmentation can stabilize the flavylium cation chromophores as well as increase both the absorbance of these pigments (hyperchromic effect) and the visible absorption maximum (bathochromic effect) (Baranac et al. 1996, 1997).

The copigmentation effect in wines is dependent on the composition and concentration of the anthocyanins present, particularly those of the copigments. A more planar structure is preferred when forming a  $\pi$ - $\pi$  stacking sandwich-like structure. Therefore, in comparing the copigmentation effect of different phenolic compounds, flavonols are considered as effective copigments because of their planar structure (Baranac et al. 1996, 1997). Additionally, flavanols show poorer copigmentation behavior than other phenolic compounds (Gómez-Míguez et al. 2006). However, flavanols are the predominant phenolic compound present in red wines; therefore, their probability of interacting with anthocyanins is higher than that of any other compound present. Furthermore, their total copigmentation effect should not be overlooked. It was speculated that only flavanols free from copigmentation can bind to taste receptor and saliva proteins and contribute bitterness and astringency to wines. For this reason, copigmentation, which includes flavanols, may decrease the bitterness and astringency properties of red wines (Boulton 2001).

The hypothesis that phenolic compounds participating in copigmentation can partially avoid oxidation because oxidation reactions are closely related to free phenolic compounds is widely accepted (Boulton 2001; Escobedo-Bailón and Santos-Buelga 2012). However, scientists have not yet reached a consensus concerning the effects of copigmentation on the formation of polymeric pigments in wines. Several scientists believe that polymerization reactions only occur in free phenolic compounds and these compounds may be negatively affected by copigmentation (Somers 1971). Other scientists believe that copigmentation interactions are the first step in the formation of new polymeric pigments because phenolic compounds stacked within limited spaces may be more active (Brouillard et al. 2003; de Freitas et al. 2017).

In young red wines, copigmentation is reportedly responsible for 30–50% of the total wine color intensity (Boulton 2001; Darias-Martín et al. 2006; Levensgood and Boulton 2004; Schwarz et al. 2005). During wine aging, the concentrations of anthocyanins and copigments decrease due to the occurrence of various chemical reactions, resulting in the decreased influence of copigmentation on wine color expression. However, the number of new pigments derived from chemical reactions continue to increase and are becoming increasingly important in modifying red wine color during aging (Darias-Martín et al. 2006; Gutiérrez et al. 2005; Lorenzo et al. 2005).

### General oxidation

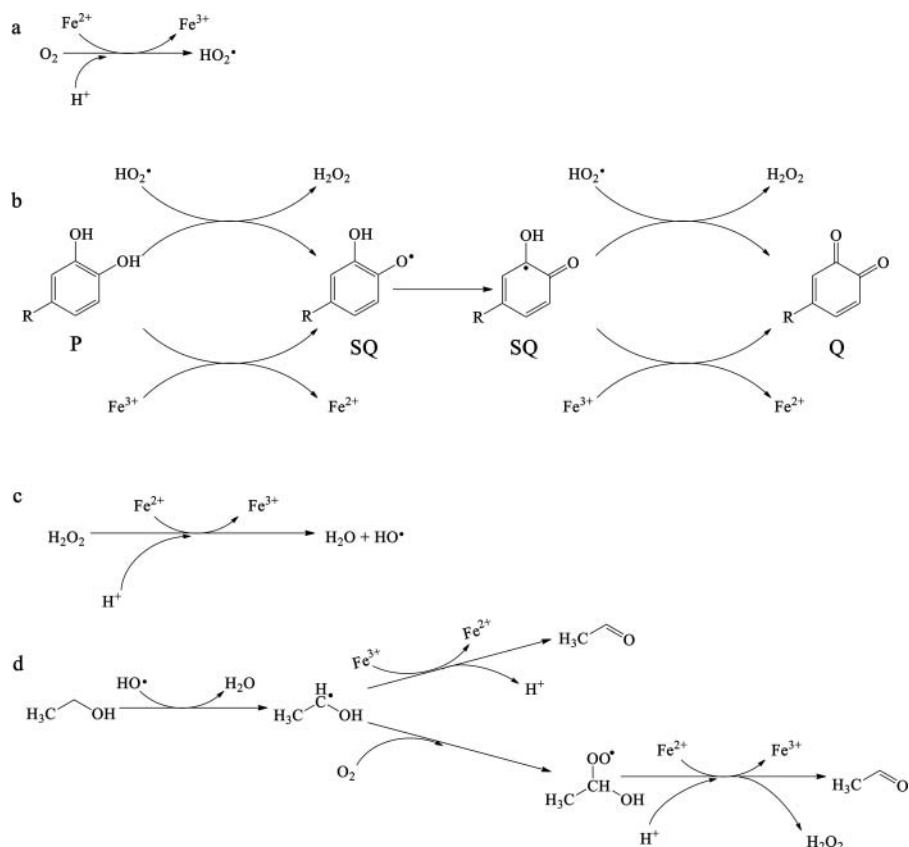
$O_2$  comprises approximately 21% of the atmosphere, and its solubility in air-saturated wines is 8.6 mg/L at room temperature and atmospheric pressure (Singleton 1987). Grape musts have been reported to be nearly saturated with  $O_2$  during crushing and pressing (Schneider 1991). During the

winemaking operations that follow crushing and pressing, including pumping, racking, centrifugation, filtration and bottling, oxygen is inevitably absorbed by wines. In fact, the absorption of oxygen during the fermentation procedure has been reported to reach 20 mg/L (Vidal et al. 2004a; Vivas 1999a, 1999b; Vivas et al. 2003). Wine contact with oxygen causes wine oxidation, which can be classified into enzymatic and non-enzymatic oxidation. Enzymatic oxidation occurs primarily in grape musts, and non-enzymatic oxidation prevails in wines (Li et al. 2008; Oliveira et al. 2011; Waterhouse and Laurie 2006). Herein, we discuss only the mechanism of non-enzymatic oxidation and its impacts on red wine astringency, bitterness and color.

Due to its triplet ground state,  $O_2$  cannot react with organic compounds directly. However, when dissolved in wine and with the aid of metal ions, such as  $Fe^{2+}$ ,  $O_2$  can be reduced and protonated to form a hydroperoxide radical ( $HO_2\cdot$ ) (Fig. 6a).  $HO_2\cdot$  is unable to oxidize the majority of the organic compounds present in wine except for phenolic compounds with catechol or galloyl structures. These phenolic compounds have good hydrogen-donating properties and can act as primary oxidation substrates (Fig. 6b) (Danilewicz 2003; Singleton 1987; Waterhouse and Laurie 2006). In addition to oxidation via  $HO_2\cdot$ , phenolic compounds can be oxidized via catalysis with metal ions, such as  $Fe^{3+}$  and  $Cu^{2+}$ , present in the soil and in winemaking equipment (Fig. 6b) (Danilewicz 2003; 2007, 2011; Danilewicz et al. 2008; Waterhouse and Laurie 2006).

During oxidation, phenolic compounds are oxidized into semiquinone free radicals and quinones, and metal ions and  $HO_2\cdot$  are reduced to less oxidative metal ion forms and hydrogen peroxide ( $H_2O_2$ ), respectively (Fig. 6b) (Danilewicz 2003; Waterhouse and Laurie 2006).  $HO_2\cdot$  is reduced to  $H_2O_2$  during the oxidation of phenolic compounds. Subsequently,  $H_2O_2$  is able to react in the presence of  $Fe^{2+}$  via a Fenton reaction, resulting in the formation of a hydroxyl radical ( $HO\cdot$ ) (Fig. 6c) (Fenton 1894).  $HO\cdot$  is a highly unstable radical able to oxidize almost any organic compound present in red wines. Moreover, because  $HO\cdot$  has no selectivity for antioxidants,  $HO\cdot$  reacts with organic compounds nearly proportionally with their concentrations (Danilewicz 2003; Elias and Waterhouse 2010; Laurie and Waterhouse 2006; Waterhouse and Laurie 2006; Wildenradt and Singleton 1974). Ethanol is the most abundant organic compound present in red wines and is considered to be the most common reaction substrate of  $HO\cdot$ . The resulting oxidation product of ethanol and  $HO\cdot$  is acetaldehyde (Fig. 6d). Additionally,  $HO\cdot$  can oxidize other organic compounds, such as tartaric acid, which yields glyoxylic acid (Fenton 1894). The effects of these oxidation products on red wine astringency, bitterness and color is discussed in other sections of this article.

A semiquinone free radical, one oxidation product of wine phenolic compounds, is able to form a covalent bond with another semiquinone free radical by each sharing their unpaired electron. Quinones are able to react with the electron-rich A rings of other flavonoids because of their electrophilic



**Figure 6.** Examples of wine oxidation reactions: formation of  $HO_2\cdot$  (a), oxidation of phenolic compounds (P) and formation of semiquinones (SQ) and quinones (Q) (b), Fenton reaction (c), and generation of acetaldehyde due to oxidation of ethanol (d) (Danilewicz 2003; Danilewicz et al. 2008; Karbowski et al. 2009; Waterhouse and Laurie 2006).

character. The reactions in which semiquinone free radicals and quinones participate are referred to as regenerative polymerization reactions (Guyot et al. 1996b; Singleton 1987). The products of regenerative polymerization include semiquinone-semiquinone and quinine-phenol dimers, which have lower redox potentials than their parent phenols and are thus much more easily oxidized. Therefore, these semiquinone-semiquinone and quinine-phenol dimers can participate in further oxidation and regenerative polymerization in wines to produce larger oligomers/polymers. This circulation continues until the polymers become so large that they finally precipitate (Fig. 7) (Li et al. 2008; Singleton 1987).

The products derived from phenolic oxidation and from the regenerative polymerization of semiquinone free radicals or quinones contribute a yellow-brown color to wines (Fig. 7) (Li et al. 2008). The participation of anthocyanins in oxidation and regenerative polymerization reactions also decreases the concentration of flavylum cations, resulting in a decrease in the red color of wines. Additionally, all flavanols in red wines have a catechol or a galloyl structure. The participation of these types of structures in oxidation and regenerative polymerization reactions produce more astringent flavanol oligomers/polymers, thus decreasing bitterness while enhancing astringency in wines (Guyot et al. 1996a). When these polymers become too large to dissolve in wines, the astringency will decrease due to their precipitation (Cheynier et al. 2006).

### Reactions of flavanols and anthocyanins

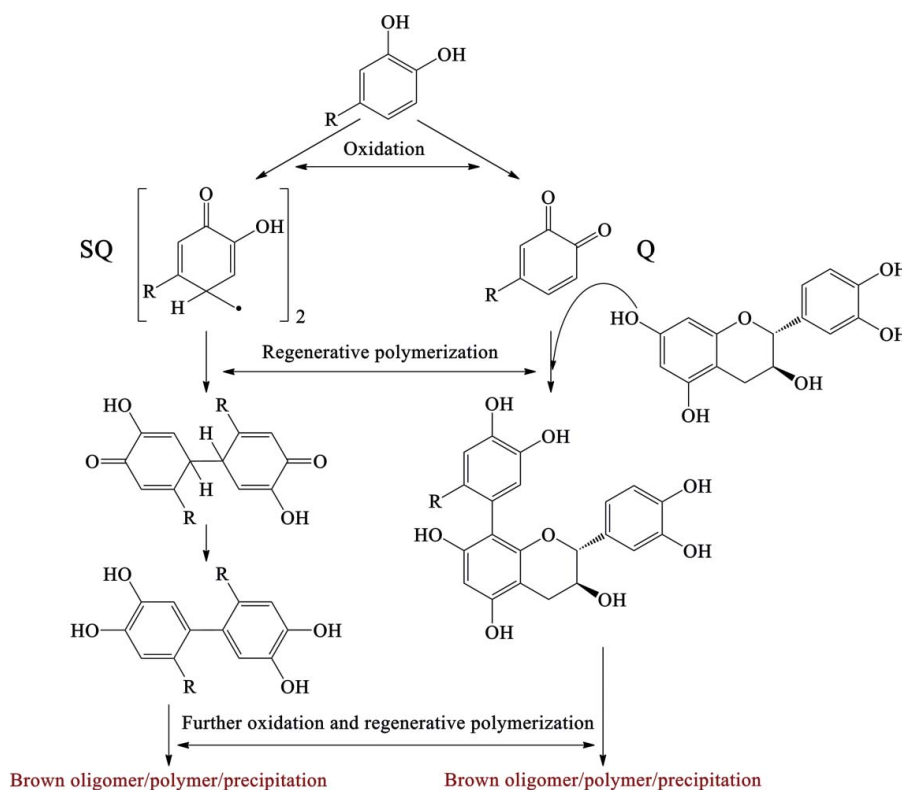
In this section, three primary types of reactions in which flavanols and anthocyanins participate are examined. The first

reaction type introduced comprises direct polymerization reactions that occur between anthocyanins and flavanols, including the acid-catalyzed cleavage of flavanol oligomers/polymers. The second reaction type includes indirect polymerization reactions that occur between anthocyanins and flavanols, primarily acetaldehyde-mediated polymerizations. Finally, reactions concerning the formation of pyranoanthocyanins are discussed.

### Direct polymerizations of flavanols and anthocyanins

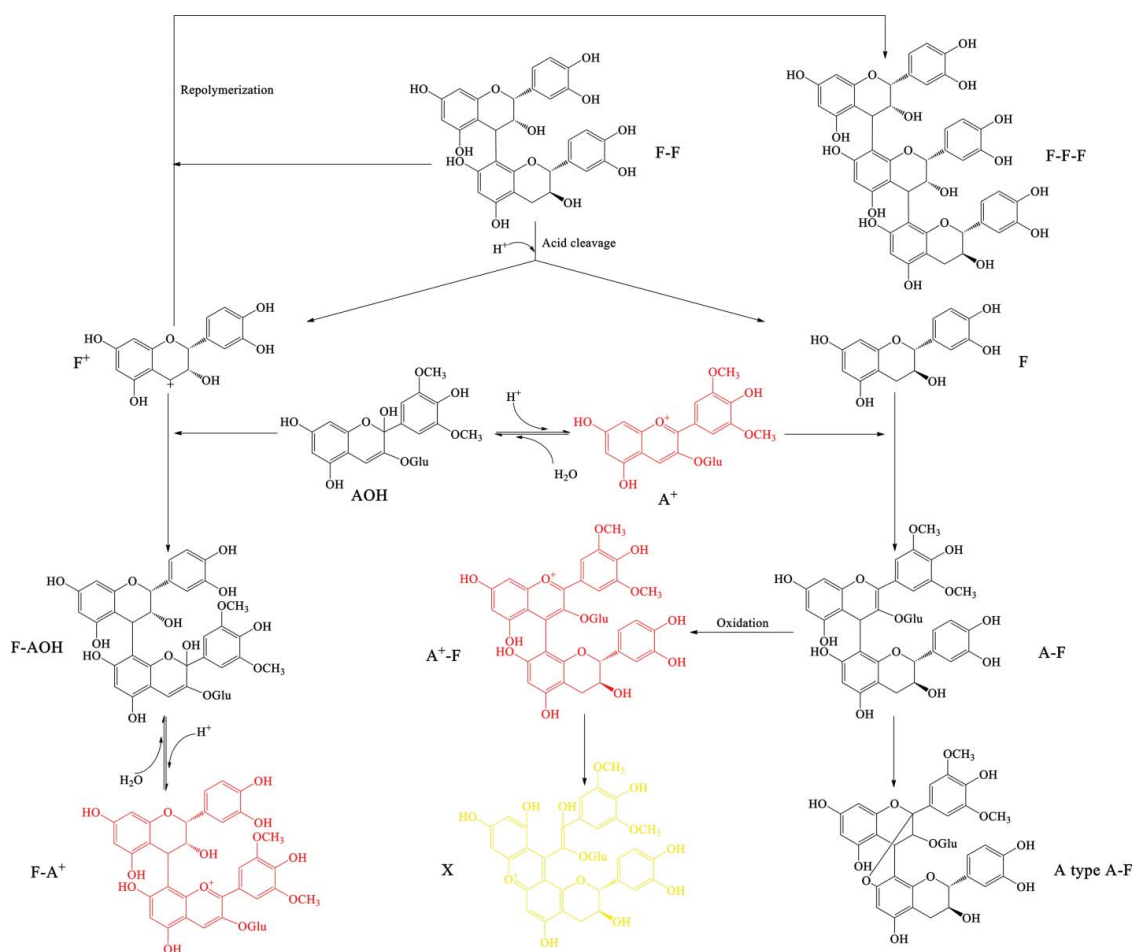
At the pH of wine, flavanol oligomers/polymers undergo acid-catalyzed cleavage and generate low-molecular-weight flavanol oligomers/polymers and flavanol cations (Fig. 8) (Haslam 1980; He et al. 2008; Salas et al. 2003; Vidal et al. 2002). Anthocyanins and flavanols undergo direct polymerizations via two possible mechanisms that are possible because of the electrophilic character of the C rings in flavylum cations and flavanol cations and the nucleophilic properties of the A rings in flavanol molecules and hemiketal-formed anthocyanins.

One possible mechanism concerning flavanol and anthocyanin direct polymerizations is a reaction that occurs between the positively charged C4 in a flavanol cation unit ( $F^+$ ) and the electron-rich C6 or C8 in a hemiketal-formed anthocyanin unit (AOH). This mechanism results in the production of a colorless flavanol-anthocyanin adduct (F-AOH) (Fig. 8) (Salas et al. 2003). This F-AOH complex is in equilibrium in wines and can partially transform into red flavanol-anthocyanin flavylum cations ( $F-A^+$ ), which includes their anthocyanin precursor (Fig. 5). Therefore, this reaction has little effect on wine color (Salas et al. 2004a; Salas et al. 2004b). However, because the flavanol cations are produced via the acid-catalyzed cleavage



**Figure 7.** Examples of phenolic oxidation and regenerative polymerization reactions of semiquinones (SQ) and quinones (Q) (Li et al. 2008; Singleton 1987).





**Figure 8.** Examples of the acid-catalyzed cleavage of flavanols, direct polymerizations of flavanols and anthocyanins, and other reactions (Cheynier et al. 2006; Fulcrand et al. 2006; Jurd 1969; Somers 1971).

reaction of flavanol oligomers/polymers, the formation of F-AOH or F-A<sup>+</sup> can promote the cleavage of flavanol oligomers/polymers and decrease wine astringency. Although flavanol cations can react with other flavanol molecules in wines via the same mechanism, they are also able to react with anthocyanins. The repolymerization reactions of flavanols are considered to be less influential than their acid-catalyzed cleavage reactions in wines due to the continuing decrease of the mean degree of polymerization (mDP) of flavanols during aging (Cheynier et al. 2006; Drinkine et al. 2007a; McRae et al. 2012; Salas et al. 2003; Vidal et al. 2002).

The second mechanism of flavanol and anthocyanin direct polymerizations discussed herein concerns the reaction between the positively charged C4 in a flavylium cation unit (A<sup>+</sup>) and the electron-rich C6 or C8 in a flavanol molecule unit (F). This mechanism results in the production of a colorless anthocyanin-flavanol adduct (A-F). The A-F complex can be further oxidized into a red anthocyanin-flavanol flavylium cation form (A<sup>+</sup>-F), which is able to rapidly transform into a xanthylum structure (X) due to structural rearrangement and emit a yellow color ( $\lambda_{\text{max}}$ : 430–460 nm) (Escribano-Bailón et al. 1996; Jurd 1969; Mateus et al. 2002; Remy et al. 2000; Salas et al. 2003; Somers 1971). The A-F complex is also able to transform into a colorless A-type A-F dimer (Fig. 8) (Remy-Tanneau et al. 2003). The reaction caused by the second mechanism decreases the concentration of the flavylium cations and

increases the xanthylum pigments present in wines, which decreases the red color of the wine while increasing its yellow color. Furthermore, the participation of flavanols and the formation of A-F complexes reduce the bitterness and astringency because these processes decrease the concentration of flavanol in wine (Dallas et al. 1996a).

### Indirect polymerizations between flavanols and anthocyanins

In dry red wines, the direct polymerizations of anthocyanins and flavanols occur very slowly, and the effects of these polymerizations on wine astringency, bitterness and color are less important than those of the indirect polymerizations between anthocyanins and flavanols (Dallas et al. 1996a, b). The reaction rates of the indirect polymerization of anthocyanins and flavanols are much faster than those of the direct polymerization of anthocyanins and flavanols due to the participation of mediating compounds, such as protonated acetaldehyde, which is very active toward flavanols (de Freitas and Mateus 2006; Es-Safi et al. 2002; Fulcrand et al. 2006; Li et al. 2008; Sun et al. 2008).

Acetaldehyde is produced from microbial activities during fermentation as well as from ethanol oxidation in wines (Fig. 6d) (Danilewicz 2003; Elias and Waterhouse 2010; Laurie and Waterhouse 2006; Waterhouse and Laurie 2006; Wildenradt and Singleton 1974). Under acidic conditions, such as those in wines,

indirect polymerizations between anthocyanins and flavanols begin with acetaldehyde protonation. The resulting protonated acetaldehyde is then added to an electron-rich C6 or C8 in a flavanol unit to form a flavanol-ethanol adduct (F-EtOH). This adduct is further protonated and dehydrated, finally yielding a new carbocation. This carbocation can suffer a nucleophilic attack from an electron-rich C6 or C8 in another flavanol unit or an electron-rich C8 in a hemiketal-formed anthocyanin unit to produce a flavanol-ethyl-flavanol adduct (F-ethyl-F) or a flavanol-ethyl-anthocyanin adduct (F-ethyl-AOH), respectively (Fig. 9) (Fulcrand et al. 1996a; Fulcrand et al. 2006; Pissarra et al. 2004; Rivas-Gonzalo et al. 1995; Timberlake and Bridle 1976).

Both F-ethyl-F and F-ethyl-AOH complexes can participate in further acetaldehyde-mediated polymerizations with other flavanols or anthocyanins in wines (Es-Safi et al. 1999a). With a sufficient acetaldehyde supply, the complexes may become too large to remain in solution and become insoluble, causing the solutions containing the complexes to become hazy or form precipitates and resultant instability problems (Es-Safi et al. 2002; 2003; Escribano-Bailón et al. 2001). In ethyl-bridged complexes that contain anthocyanin unit(s), each ethyl-bridged complex possesses no more than two anthocyanin units because anthocyanins only donate the electrons on C8 in polymerizations (Es-Safi et al. 1999a; Rivas-Gonzalo et al. 1995). These two anthocyanin units act as terminating units in the ethyl-bridged complex chain, which halts the increasing complex size and contributes to wine stabilization. To a large extent, the compositions and polymerization degrees of ethyl-bridged complexes in wines are determined by the flavanol/anthocyanin ratio and the acetaldehyde concentration in the wines (Bindon et al. 2014; Fulcrand et al. 2006; Schmidtke et al. 2011; Versari et al. 2013). An appreciable presence of acetaldehyde in its free form (>5 mg/L) has been reported to destabilize red wines by inducing phenolic hazes and precipitations (Somers 1998).

Although ethyl-bridged flavanol complexes continue to contribute bitterness and astringency to wines (Cheynier et al. 2006; Vidal et al. 2004b), the acetaldehyde-mediated polymerization reactions are generally believed to intervene in the mouth-feel evolution of wines. These reactions are hypothesized to decrease the free flavanol level in wines and alleviate wine bitterness and

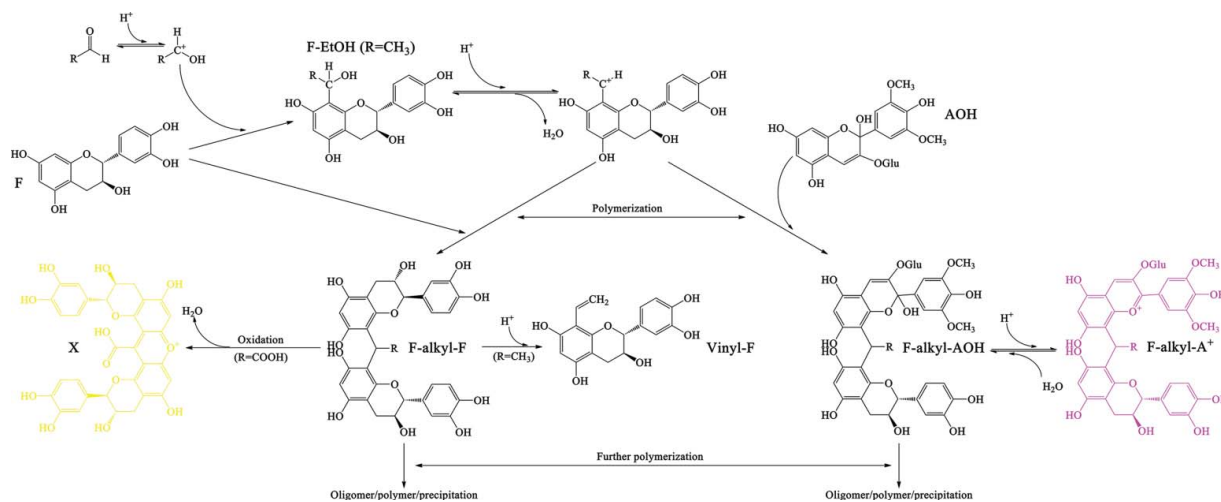
astringency (Es-Safi et al. 1999a; Fulcrand et al. 1996ab; Tanaka et al. 1994). Via the intramolecular copigmentation effect, the flavylium cation forms of F-ethyl-A complexes contribute a purple color to wines (F-ethyl-A<sup>+</sup>,  $\lambda_{\max}$ : 528–540 nm), and these complexes are more stable and less reactive to hydration and sulfite bleaching than their anthocyanin precursors (Fig. 5c, Fig. 9) (Atanasova et al. 2002; Cheynier et al. 2006; de Freitas and Mateus 2006; Escribano-Bailón et al. 2001; Timberlake and Bridle 1976).

Ethyl-bridged complexes, especially F-ethyl-F oligomers/polymers, are sensitive to degradation and may undergo hydrolytic cleavage to release vinylflavanol units (Vinyl-F). These units are responsible for the formation of orange-red flavanyl-pyranoanthocyanins in wines (Alcalde-Eon et al. 2006; Escribano-Bailón et al. 2001; Es-Safi et al. 1999a; He et al. 2010a; Pissarra et al. 2004). Acetaldehyde-mediated phenolic complexes have been reported to exhibit antioxidant activities as strong as those of their precursor phenolic compounds (Sun et al. 2009).

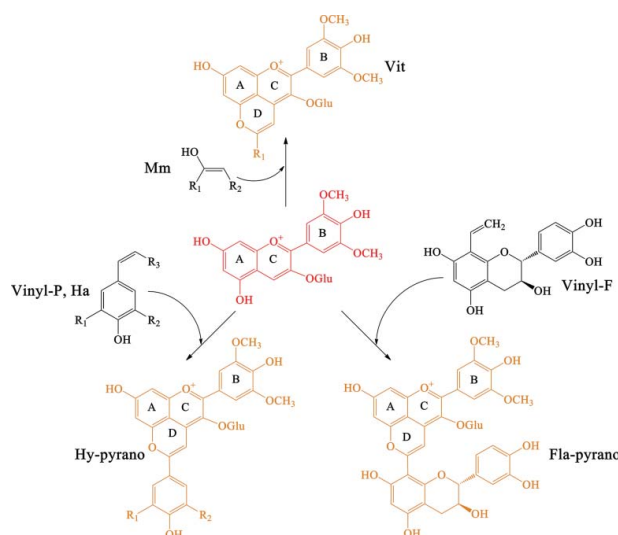
Except for acetaldehyde, the components in wines with aldehyde moieties can participate in the indirect polymerizations between anthocyanins and flavanols using the same acetaldehyde-mediated mechanism to produce other F-alkyl-F and F-alkyl-A complexes (Es-Safi et al. 2002; Pissarra et al. 2004; Pissarra et al. 2003). For example, glyoxylic acid, the oxidation product of tartaric acid, can play the same role that acetaldehyde plays in indirect polymerizations (Drinkine et al. 2005; Fulcrand et al. 1997). Glyoxylic acid is converted into a xanthylum structure (X) only when flavanol units participate in the reactions, contributing a yellow color to the wine ( $\lambda_{\max}$ : 430–460 nm). Alternatively, glyoxylic acid contributes a purple color to wines when the polymerized complexes contain anthocyanin unit(s) (Fig. 9) (Es-Safi et al. 1999bc, 2000b, 2003).

### Formation of pyranoanthocyanins

Flavylium cation-formed anthocyanins are vulnerable to nucleophilic attack at the C4 position by compounds with a polarizable double bond. These anthocyanins then undergo a cycloaddition and a subsequent oxidation step to form an



**Figure 9.** Examples of indirect polymerizations between flavanols and anthocyanins and associated reactions (Cheynier et al. 2006; Es-Safi et al. 1999a; Es-Safi et al. 2000b; Es-Safi et al. 1999b; Es-Safi et al. 1999c).



**Figure 10.** Examples of the formation reactions of three basic pyranoanthocyanins in dry red wines (Castañeda-Ovando et al. 2009; Cheynier et al. 2006; Fulcrand et al. 1996b, 1998, 2006; Mateus et al. 2002; Schwarz et al. 2003c). Mm: microbial metabolites (pyruvic acid:  $R_1=\text{COOH}$ ,  $R_2=\text{H}$ ; acetaldehyde:  $R_1=R_2=\text{H}$ ; acetoacetic acid:  $R_1=\text{CH}_3$ ,  $R_2=\text{COOH}$ ; acetone:  $R_1=\text{CH}_3$ ,  $R_2=\text{H}$ ). Vit: vitisins (A type vitisins:  $R_1=\text{COOH}$ ; B type vitisins:  $R_1=\text{H}$ ; methyl-pyranoanthocyanins:  $R_1=\text{CH}_3$ ). Vinyl-P: vinylphenols (4-vinylphenol:  $R_1=R_2=R_3=\text{H}$ ; 4-vinylguaiacol:  $R_1=R_3=\text{H}$ ,  $R_2=\text{OCH}_3$ ). Ha: hydroxycinnamic acids ( $\rho$ -coumaric acid:  $R_1=R_2=\text{H}$ ,  $R_3=\text{COOH}$ ; caffeic acid:  $R_1=\text{OH}$ ,  $R_2=\text{H}$ ,  $R_3=\text{COOH}$ ; ferulic acid:  $R_1=\text{OCH}_3$ ,  $R_2=\text{H}$ ,  $R_3=\text{COOH}$ ; sinapic acid:  $R_1=R_2=\text{OCH}_3$ ,  $R_3=\text{COOH}$ ). Hy-pyrano: hydroxyphenyl-pyranoanthocyanins. Vinyl-F: vinylflavanols. Fla-pyrano: flavanyl-pyranoanthocyanins.

additional oxygen-containing pyran ring, ring D, between the C4 position in ring C and the C5 hydroxyl group in ring A (Fig. 10) (de Freitas and Mateus 2011; Fulcrand et al. 1996b; Rentzsch et al. 2007a). These types of pigments result in an orange-red color in wines and are known as pyranoanthocyanins ( $\lambda_{\text{max}}$ : 480–510 nm). Pyranoanthocyanins can basically be classified into three types according to the compounds that react with anthocyanins.

The first group of pyranoanthocyanins discussed herein is referred to as vitisins, which include A-type vitisins, B-type vitisins and methyl-pyranoanthocyanins. Vitisins are formed via reactions between anthocyanins and microbial metabolites, including pyruvic acid, acetaldehyde, acetoacetic acid and acetone (Fig. 10) (Bakker and Timberlake 1997; Fulcrand et al. 1998; Lu and Foo 2001). In dry red wines, vitisins usually reach their maximum concentrations during fermentation because their formation is closely related to microbial activities. In wines, the formation of vitisins is suppressed due to  $\text{SO}_2$  addition, resulting in varying decreases in vitisin concentrations (Morata et al. 2016).

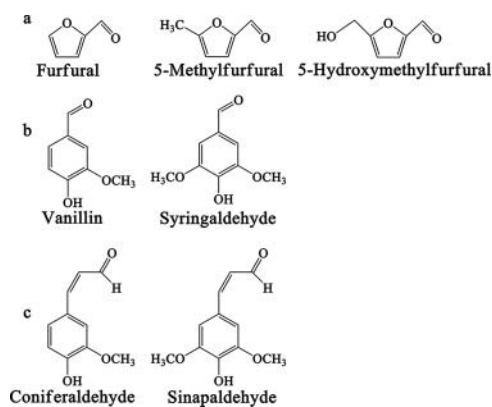
Anthocyanins react with vinylphenols and hydroxycinnamic acids to produce hydroxyphenyl-pyranoanthocyanins, the second group of pyranoanthocyanins discussed herein (Fig. 10) (Fulcrand et al. 1996b). Vinylphenols are produced from hydroxycinnamic acids (usually  $\rho$ -coumaric acid and ferulic acid) via enzymatic decarboxylation reactions via hydroxycinnamate decarboxylase, which is present in the majority of microorganisms (Chatonnet et al. 1993; Morata et al. 2007). However, because of their vinyl reductase activity, vinylphenols can react further to produce ethylphenols in the presence of yeast from the genera *Brettanomyces* and *Dekkera*. Ethylphenols are generally recognized as off-flavor compounds in wines

(Suárez et al. 2007). Reactions between anthocyanins and vinylphenols that generate hydroxyphenyl-pyranoanthocyanins usually occur during fermentation because the production of vinylphenols depends on microbial activities (Benito et al. 2011). In wines, anthocyanins can also directly react with all hydroxycinnamic acids present to produce hydroxyphenyl-pyranoanthocyanins. However, these reactions are slow for two reasons: the hydrolysis of the tartaric esters of hydroxycinnamic acids is slow during wine aging, and competing reactions between anthocyanins and other wine constituents are also present (Rentzsch et al. 2007b; Schwarz et al. 2003c; Schwarz and Winterhalter 2003). In wines, hydroxyphenyl-pyranoanthocyanins accumulate at a very slow rate, and these compounds are recognized as effective markers for analyzing wine age (Ivanova-Petropoulos et al. 2015; Schwarz et al. 2004).

Vinylflavanols are products of the cleavage of F-ethyl-F complexes or from the dehydration of flavanol-ethanol adducts. When vinylflavanols react with anthocyanins, the third type of pyranoanthocyanins, the flavanyl-pyranoanthocyanins, are produced (Fig. 10) (Cruz et al. 2008; Francia-Aricha et al. 1997; Mateus et al. 2003a). F-ethyl-F complexes are produced from acetaldehyde-mediated polymerizations of flavanols. Therefore, controlled oxygenation in wines might be beneficial in the production of flavanyl-pyranoanthocyanins. However, over-oxidation might cause haze from and precipitations of these ethyl-bridged complexes rather than produce vinylflavanols, which is disadvantageous in terms of the production of flavanyl-pyranoanthocyanins (Somers 1998). Many wine pigments only exhibit their maximum absorbance in aqueous solutions with pH values lower than the wine pH range, whereas many flavanyl-pyranoanthocyanins display a maximum absorbance value at a wine pH of approximately 3.6. In addition, flavanyl-pyranoanthocyanins were reported as more stable against hydration and bisulfite bleaching than their counterparts, the precursor anthocyanins, vitisin A and F-ethyl-A<sup>+</sup> compounds, which may be attributed to both C4 substitution and intramolecular copigmentation (Asenstorfer et al. 2001; He et al. 2010a; Vivar-Quintana et al. 2002).

Except for the three basic types of pyranoanthocyanins introduced herein, other pyranoanthocyanin compounds, including oxovitisins, portisins and pyranoanthocyanin dimers, were reported to contribute yellow ( $\lambda_{\text{max}}$ : 370 nm), blue ( $\lambda_{\text{max}}$ : 575 nm) and turquoise ( $\lambda_{\text{max}}$ : 680–730 nm) colors to wines, respectively. However, these special pyranoanthocyanins are mostly found in Port wines (He et al. 2010b; Mateus et al. 2003b, 2005, 2006; Oliveira et al. 2010).

Pyranoanthocyanins are more resistant to hydration and sulfite bleaching than their anthocyanin precursors and other pigments such as F-A<sup>+</sup>, A<sup>+</sup>-F, and F-ethyl-A<sup>+</sup> complexes because substitution at the C4 position decreases their electrophilicity (Chassaing et al. 2015; Cheynier et al. 2006; Timberlake and Bridle 1967). In addition, pyranoanthocyanins primarily exist in their colored forms (the flavylium cation and quinoidal base forms). Therefore, they have lower visual detection limits than their anthocyanin precursors and can contribute more color when all pigments present have the same concentration (Pina et al. 2015; Schwarz et al. 2003b; Schwarz and Winterhalter 2004). In dry red wines, pyranoanthocyanins play an increasingly important role in color expression as wine



**Figure 11.** Representative aldehydes from oak woods: furanic aldehydes (a), benzoid aldehydes (b) and cinnamic aldehydes (c).

age increases (Blanco-Vega et al. 2014; Ivanova-Petropulos et al. 2015; Quaglieri et al. 2017).

### Effects of using oak barrels on astringency, bitterness and the color of dry red wines during aging

The use of wood containers for wine conservation began thousands of years ago, and, at present, oak barrels are generally used globally for producing quality wines. Oak woods have been considered resilient and impermeable to liquids, and these woods gradually contribute both volatile and non-volatile compounds to dry red wines during aging. Volatile compounds primarily include furanic aldehydes, phenolic aldehydes, volatile phenols and lactones, which confer complex aromatic characteristics to wines. Furthermore, several volatile compounds (furanic aldehydes, phenolic aldehydes and several volatile phenols including 4-vinylguaiacol) can also react with phenolic compounds in wines and thus affect wine astringency, bitterness and color (Fig. 11). The non-volatile compounds present in wine are primarily ellagitannins, a group of phenolic compounds. Ellagitannins were not originally present in wines before barrel aging and affect wine astringency, bitterness and color due to their chemical reactivities (Fig. 12) (Díaz-Plaza et al. 2002; Garde-Cerdán and Ancín-Azpilicueta 2006; Jourdes et al. 2011; Prida and Chatonnet 2010; Prida and Puech 2006; Puech et al. 1999; Vivas

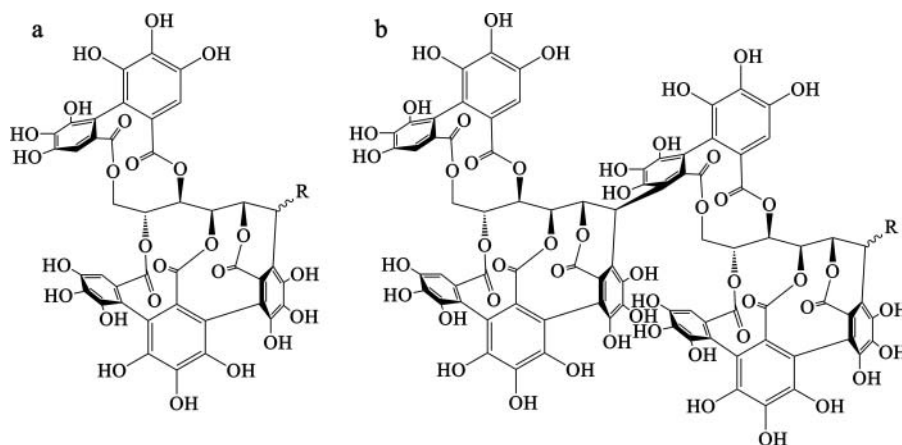
and Glories 1996a; Waterhouse and Towey 1994). Moreover, the porous properties of oak woods allow wines to continuously consume small quantities of  $O_2$ , leading to limited oxidation in wines and resulting in increased wine quality (del Alamo-Sanza et al. 2017; del Alamo-Sanza and Nevares 2014; Nevares and del Alamo-Sanza 2014; Puech et al. 1999).

### The barrel-making process and its effects on the chemical properties of barrels

Traditionally, three species of oak woods are used in cooperage, namely, *Quercus petraea*, *Q. robur* and *Q. alba*. The species *Q. petraea* and *Q. robur* are widely cultivated in Europe and are thus referred to as “European oak”. *Q. alba* is primarily found in America and is thus referred to as “American oak” (del Alamo-Sanza and Nevares 2017).

Raw oak woods primarily contain the following three types of substances, which are important in barrel-making: water (40–60% of the total wood weight), macromolecules (90% of the dry wood weight) and extractable compounds (10% of the dry wood weight). Macromolecules consist of a wood structure and primarily include cellulose (40–45% of the dry wood weight), hemicellulose (20–35% of the dry wood weight) and lignin (15–35% of the dry wood weight), while the extractable compounds primarily include hydrolyzable tannins (ellagitannins and gallotannins) as well as several phenolic compounds and lipids (Prida 2002; Puech et al. 1999; Rubio-Bretón et al. 2012).

In cooperage, two stages have the greatest effect on the chemical composition of oak woods, namely, seasoning and toasting. Seasoning is a process used to decrease the moisture content of wood in which coopers place the oak woods in the open air for at least 2 to 3 years or in the oven for a significantly shorter period of time. During the natural seasoning of oak woods, a constant decrease in hydrolyzable tannins and a slight increase in the phenolic aldehydes and volatile phenols due to microbial activities and oxidation have been observed (Cadahía et al. 2003; Cadahía et al. 2001; Hale et al. 1999; Mingshu et al. 2006; Vivas and Glories 1996b). However, changes in these volatile and non-volatile compounds are negligible compared with the effects of toasting.



**Figure 12.** Representative ellagitannins from oak woods: ellagitannin monomers (a) and ellagitannin dimers (b). a: Vescalagin (a, R=β-OH), castalagin (a, R=α-OH), granadinin (a, R=β-lyxose), roburin E (a, R=β-xylose); b: roburin A (b, R=β-OH), roburin B (b, R=β-lyxose), roburin C (b, R=β-xylose), roburin D (b, R=α-OH).



The purpose of toasting is to shape the oak staves into a more suitable form for making barrels and to reconstitute their chemical composition. During toasting, the inner surface temperature of the barrels can reach 200°C or even higher, which causes the macromolecules to degrade and produce volatile compounds, including furanic aldehydes, phenolic aldehydes and volatile phenols. Furanic aldehydes (furfural, 5-methylfurfural, and 5-hydroxymethylfurfural) are formed by the thermal degradation of cellulose and hemicellulose by Maillard reactions, and their concentrations are positively correlated with the toasting level (Cadahía et al. 2003; Cadahía et al. 2001; Haluk and Irmouli 1998). When the toasting temperature is between 120–165°C, phenolic aldehydes (primarily cinnamic aldehydes such as coniferaldehyde and sinapaldehyde) increase due to the thermal degradation of lignin. When the toasting temperature is above 165°C, a more intense thermolysis process could occur, resulting in the degradation of cinnamic aldehydes into benzoic aldehydes (vanillin and syringaldehyde) and hydroxybenzoic acids (vanillic acid and syringic acid) and the subsequent degradation of those products into volatile phenols (e.g., guaiacol, 4-methylguaiacol, 4-ethylguaiacol, and 4-vinylguaiacol) (Cadahía et al. 2003; Cadahía et al. 2001; Sarni et al. 1990). Hydrolyzable tannins are sensitive to high temperatures, and their decreasing concentration is positively correlated with the toasting level due to thermal degradation. During toasting, a 72–99% decrease in ellagitannins and a complete disappearance of gallotannins occurs (Chatonnet 1992; Chatonnet et al. 1989; Hale et al. 1999; Haluk and Irmouli 1998; Matricardi and Waterhouse 1999). Currently, no international standards for toasting during barrel making exist, and toasting methods vary whether they are performed by the same cooper or different coopers, primarily depending on the cooper's personal experience. Toasting levels are classified into the following general categories depending on temperature and toasting duration: light (inner surface temperature 100–180°C, approximately 5 minutes), medium (inner surface temperature >180°C, approximately 10–15 minutes) and heavy toasting (inner surface temperature >200°C, approximately 15–25 minutes) (Chatonnet 1992; Jackson 2008; Matricardi and Waterhouse 1999; Ribéreau-Gayon et al. 2006; Rubio-Bretón et al. 2012).

The grain is used to define the average width of the annual rings in oak woods. The grain levels of *Q. petraea*, *Q. robur* and *Q. alba* were reported as 1–3 mm, 3–10 mm and 1–5 mm respectively, and coopers empirically classify barrels into fine grain, medium grain and coarse grain (Chatonnet and Dubourdieu 1998; Vivas 1995). As the fineness of the grain increases, the reported tannin potential decreases and the volatile potential of the oak woods increases (Vivas 2000). French oak woods exhibit a higher tannin potential and lower volatile potential than American oak woods; tannin potential and volatile potential may be affected by both the geographic and species conditions of the trees (Chatonnet and Dubourdieu 1998; Díaz-Plaza et al. 2002; Mosedale et al. 1999; Prida and Puech 2006; Sefton et al. 1993; Waterhouse and Towey 1994). Because the oak constituents in newly made barrels are finite, the flavor pool of barrels is exhausted with their repeated use (García-Estévez et al. 2017b; Vivas and Saint-Cricq de Gaulejac 1998).

During barrel aging, oak constituent extraction from barrels into wines is dependent on the concentrations of these

constituents in the barrels and the extractability of these constituents, which is determined by the barrel structure. Previous work on new French barrels reported that the oak constituent extractability is primarily affected by the toasting level and wood grains used. Cracks produced inside staves during toasting permit the penetration of wines into the woods and the extraction of oak constituents. Thus, increasing the toasting level can increase oak constituent extraction, which could result in the production of a better wine (Prida 2002; Sarni et al. 1990). However, heavy toasting should be used with caution, as it leads to a dramatic decrease in hydrolyzable tannins and an over-production of volatile compounds, which may cause an unbalanced flavor profile in wines. Scientists have determined that as the grain coarsens, the ability of wines to penetrate oak woods increases when the toasting level is not considered. Therefore, the extraction of oak constituents can be improved by using barrels with a coarser grain (Michel et al. 2016; Moutounet et al. 1998). Tyloses are composed of small particles that block the vessels in oak woods, resulting in watertight woods ideal for making barrels. American oak woods generally contain more tyloses than European oak woods; thus, the penetration of wines into American oak woods is more difficult. This increased difficulty may, to some extent, increase the difficulty of extracting the oak constituents in American barrels (Chatonnet and Dubourdieu 1998; Moutounet et al. 1999). In old barrels, wood pores become blocked as a result of microbial activities over time and the obstruction of the wood during the precipitation and stabilization processes of wines. Thus, their use in oak constituent extraction is disadvantageous (Jackson 2008; Rubio-Bretón et al. 2012). In summary, the compositions and concentrations of the oak constituents present in wines extracted from oak barrels vary between the different indexes of oak barrels. The general concentrations of the oak constituents present in oak woods and in oak barrel-aged red wines are listed in Table 2.

### **Effects of oak constituents on the astringency, bitterness and color of wines**

The flavor contribution of oak constituents from barrels to wines cannot be considered as simple mathematical addition. Given their structural features, many constituents are chemically active toward phenolic compounds. Because the concentrations of oak constituents are generally low (Table 2), the potential products derived from the reactions between oak constituents and wine phenolic compounds are usually hard to detect. By using a mildly acidic model solution similar to that of most wines, scientists reacted oak constituents with wine phenolic compounds to determine their potential products and to examine their potential contribution to wine astringency, bitterness and color. Several of these products have been identified in barrel-aged dry red wines with recent advances in detection techniques, which are continuing to improve. The primary oak constituents capable of reacting with wine phenolic compounds are furanic aldehydes, phenolic aldehydes and ellagitannins.

### **Volatile constituents**

The chemical reactivities of volatile constituents from oak barrels toward wine phenolic compounds and their potential



**Table 2.** Mean concentrations of various oak constituents present in oak woods and oak barrel-aged red wines.

Sample type	Compounds present	Oak origin	Light toast	Medium toast	Heavy toast
Oak woods <sup>a</sup>	Furfural (mg/kg)	French	78	357	170
		American	41	681	61
	5-Methylfurfural (mg/kg)	French	16.5	42.3	25.1
		American	6.73	95.2	10.8
	5-Hydroxymethylfurfural (mg/kg)	French	37.2	58.3	44.2
		American	14.6	74.5	30.2
	Vanillin (mg/kg)	French	120	172	262
		American	27.4	120	244
	Syringaldehyde (mg/kg)	French	196	443	721
		American	57.4	343	768
	Coniferaldehyde (mg/kg)	French	179	293	283
		American	37.1	324	192
	Sinapaldehyde (mg/kg)	French	385	782	803
		American	49.1	902	490
	4-Vinylguaiacol (mg/kg)	French	0.33	1.24	0.66
Red wines <sup>b</sup>		American	0.17	1.64	0.4
	Ellagitannins (mg/kg)	French	1848	1118	12
		American	121	43	3
	Furfural ( $\mu$ g/L)	French	62.3	435.4	605
		American	55.7	88.2	738.2
	5-Methylfurfural ( $\mu$ g/L)	French	57.8	538.3	557.1
		American	38.9	201	715.6
	5-Hydroxymethylfurfural ( $\mu$ g/L)	French	80	121	137
		American	69.9	71.8	110.9
	Vanillin ( $\mu$ g/L)	French	438	491	330
		American	324	503	361
	Syringaldehyde ( $\mu$ g/L)	French	247	365	318
		American	205	391	407
	4-Vinylguaiacol ( $\mu$ g/L)	French	9.8	15.8	39.9
		American	9.6	13.7	35.1
	Ellagitannins (mg/L)	French	14.1	6.2	4.09
		American	2.46	1.07	0.58

<sup>a</sup>Oak chips manufactured from oak staves or wood remains obtained from barrel-making (Fernandez de Simon et al. 2010; Navarro et al. 2016b);

<sup>b</sup>Red wines aged in new 225 L oak barrels for 1 year (Navarro et al. 2016a, 2017).

impact on wine organoleptic properties are summarized in Table 3. Specifically, furanic aldehydes and several phenolic aldehydes (benzoic aldehydes: vanillin and syringaldehyde) can undergo aldehyde-mediated polymerizations with flavanols and/or anthocyanins similar to acetaldehyde to produce F-aryl-F or F-aryl-A oligomers/polymers (Fig. 9, Fig. 13) (Nonier et al. 2006; Sousa et al. 2007; Timberlake and Bridle 1976). When only flavanols are reacted with these aldehydes, an increase in the absorbance of the yellow region is observed, most likely due to the formation of xanthylum salts (X) derived from F-aryl-F complexes (Es-Safi et al. 2000a; Nonier et al. 2008). Because furanic aldehydes are more polar than benzoic aldehydes, they react with flavanols faster, and solutions that contain furanic aldehydes are more prone to becoming dark yellow and forming dark-colored precipitates (Es-Safi et al. 2002; Nonier et al. 2007; Vivas et al. 2008). When both flavanol and anthocyanin unit(s) participate in polymerization (except for the yellow xanthylum salts derived from F-aryl-F complexes), purple F-aryl-A complexes highly resistant to hydration and sulfite bleaching are also produced (Es-Safi et al. 2000a; Sousa et al. 2007; Nonier et al. 2011). These products both affect the color expression of model wine solutions. Furanic aldehyde-mediated polymerizations can confer a dominating orange hue to solutions and produce precipitates rapidly, whereas benzoic aldehyde-mediated polymerizations can produce a solution with a stable purple hue and form oligomers and precipitates rather than polymers. These differences may be attributed to the reactivity

differences between furanic aldehydes and benzoic aldehydes, of which the former are more active toward flavanols than the latter (Es-Safi et al. 2000a, 2002; Nonier et al. 2007, 2008, 2011; Vivas et al. 2008). The mechanisms of flavanol and anthocyanin polymerization reactions mediated by these oak aldehydes are similar to the acetaldehyde-mediated polymerization reactions. Thus, these reactions should also be capable of affecting the evolution of the mouth-feel of a wine by decreasing the free flavanol levels in wines and may, to some extent, alleviate wine bitterness and astringency (Es-Safi et al. 1999a, 2000a, 2002; Fulcrand et al. 1996ab; Nonier et al. 2007, 2011; Tanaka et al. 1994).

Cinnamic aldehydes (coniferaldehyde and sinapaldehyde) are phenolic aldehydes extracted from oak barrels and an exception to aldehyde-mediated polymerizations, as their aldehyde moieties do not undergo polymerization. Instead, these aldehydes react with flavanols to produce a new group of brick-red catechin-pyrylium pigments ( $\lambda_{\max}$ : 500 nm), oaklins. Oaklins have been synthesized in model solutions (de Freitas et al. 2004; Sousa et al. 2012) as well as identified as components of dry red wines in trace amounts (Sousa et al. 2005). The formation mechanism of this catechin-pyrylium structure is still unclear. One proposed mechanism is that under wine conditions, cinnamic aldehydes are first protonated to form carbocation intermediates, followed by the nucleophilic substitution of the electron-rich C8 or C6 in flavanols. The new products then undergo protonation, dehydration, intramolecular cyclization and oxidation reactions successively, finally generating a

**Table 3.** Chemical reactivities of volatile constituents from oak barrels toward wine phenolic compounds and their potential effects on wine organoleptic properties.

Volatile constituents	Phenolic compounds	Possible reaction products	Possible organoleptic impacts
Furanic aldehydes <sup>a</sup>	Flavanols	Flavanol-aryl-flavanol oligomers/polymers, xanthylum salts	Produce dark yellow pigments; decrease astringency and bitterness
Benzoic aldehydes <sup>b</sup>	Anthocyanins	Flavanol-aryl-anthocyanin oligomers/polymers	Produce purple pigments; decrease astringency and bitterness
	Flavanols	Flavanol-aryl-flavanol oligomers, xanthylum salts	Produce light yellow pigments; decrease astringency and bitterness
Cinnamic aldehydes <sup>c</sup>	Anthocyanins	Flavanol-aryl-anthocyanin oligomers	Produce purple pigments; decrease astringency and bitterness
4-Vinylguaicol <sup>d</sup>	Flavanols	Oaklins	Produce brick-red pigments; decrease astringency and bitterness
	Anthocyanins	Pyranoanthocyanins	Produce orange-red pigments

<sup>a</sup>(Es-Safi et al. 2000a, 2002; Nonier et al. 2007, 2008, 2011; Vivas et al. 2008);<sup>b</sup>(Nonier et al. 2007, 2008, 2011; Sousa et al. 2007; Vivas et al. 2008);<sup>c</sup>(de Freitas et al. 2004; Sousa et al. 2012, 2013, 2014);<sup>d</sup>(Fulcrand et al. 1996b; Schwarz et al. 2003c).

chromophore group with a pyrylium ring E that is associated with aromatic ring A (Fig. 14) (de Freitas et al. 2004; Sousa et al. 2005).

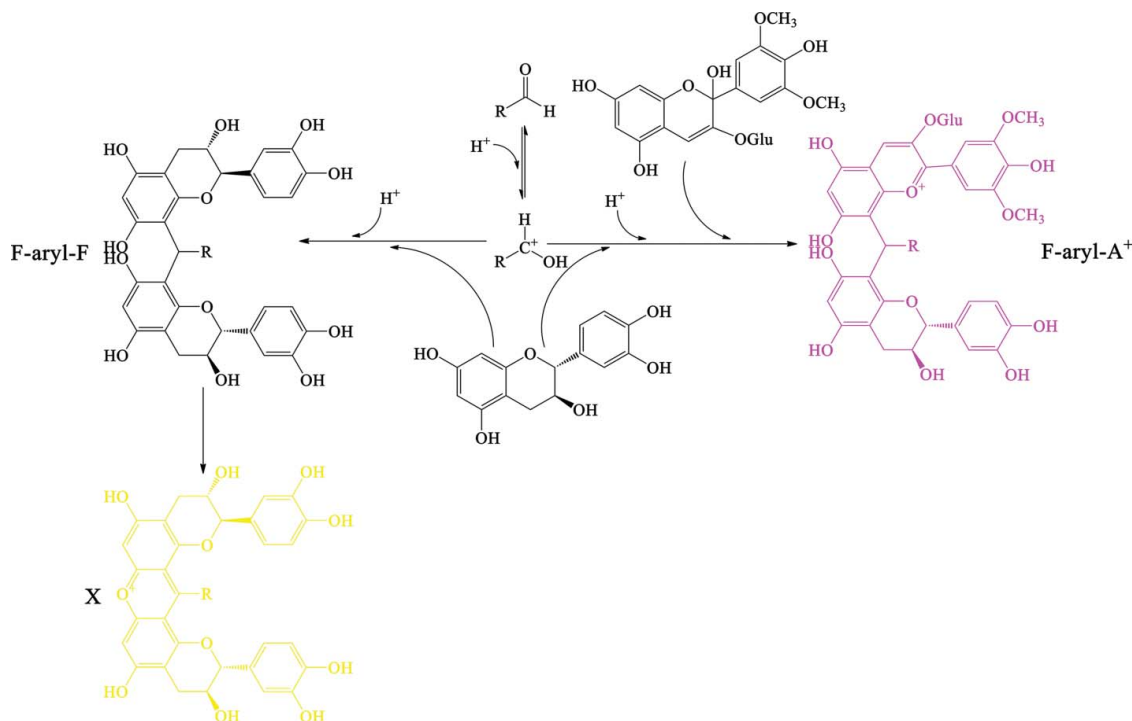
Oaklins are classified as deoxyanthocyanidins because they do not possess a glycosyloxy substituent at the C3 position of the C ring. Compared with the anthocyanins in dry red wines, they are more stable pigments. Their superior stability stems from their relatively higher  $pK'_a$  values, which increase the resistance of their flavylium cations to hydration, and their greater fraction of quinoidal base per mole (Sousa et al. 2013, 2014). The color of oaklins can also be stabilized by intermolecular copigmentation between oaklins and by several copigments present in wines, including flavanols (Sousa et al. 2014).

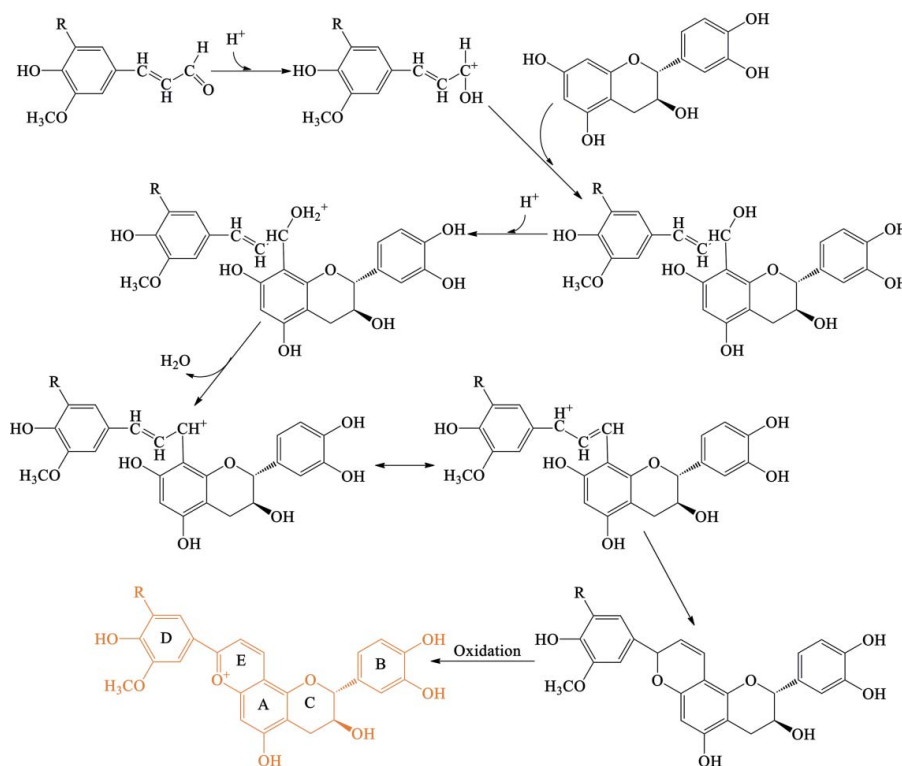
Most volatile phenols extracted from oak barrels only contribute aromatic attributes to wines. However, several other volatile phenols, such as 4-vinylguaicol, can react with anthocyanins to produce hydroxyphenyl-pyranoanthocyanins, thus contributing a stable orange-red color to wines (Fig. 10) (Fulcrand et al. 1996b).

### Ellagitannins

The basic structure of ellagitannins consists of a central glucosidic core esterified with ellagic acid (Jourdes et al. 2013). To date, the ellagitannins identified in barrel-aged dry red wines have primarily consisted of the monomers vescalagin and castalagin, which comprise nearly 50% of the total ellagitannins; their lyxose/xylose esterified monomers grandinin and roburin E; and the dimers roburin A, roburin B, roburin C and roburin D (Fig. 12) (Herve du Penhoat et al. 1991). After extraction into wine, ellagitannins undergo a series of reactions, which include reactions with wine components, oxidation, and hydrolysis (Chassaing et al. 2010; Jourdes et al. 2009, 2011; Quideau et al. 2003, 2010; Saucier et al. 2006). The products generated from these reactions affect wine astringency, bitterness and color.

Under acidic conditions, such as those of wines and wine-like model solutions, vescalagin can be protonated, dehydrated, and subsequently transformed into a carbocation intermediate,

**Figure 13.** Examples of indirect polymerizations between flavanols and anthocyanins mediated by oak aldehydes (Es-Safi et al. 2000a, 2002, 2003).



**Figure 14.** The proposed mechanism for the formation of oaklins (de Freitas et al. 2004; Sousa et al. 2005).

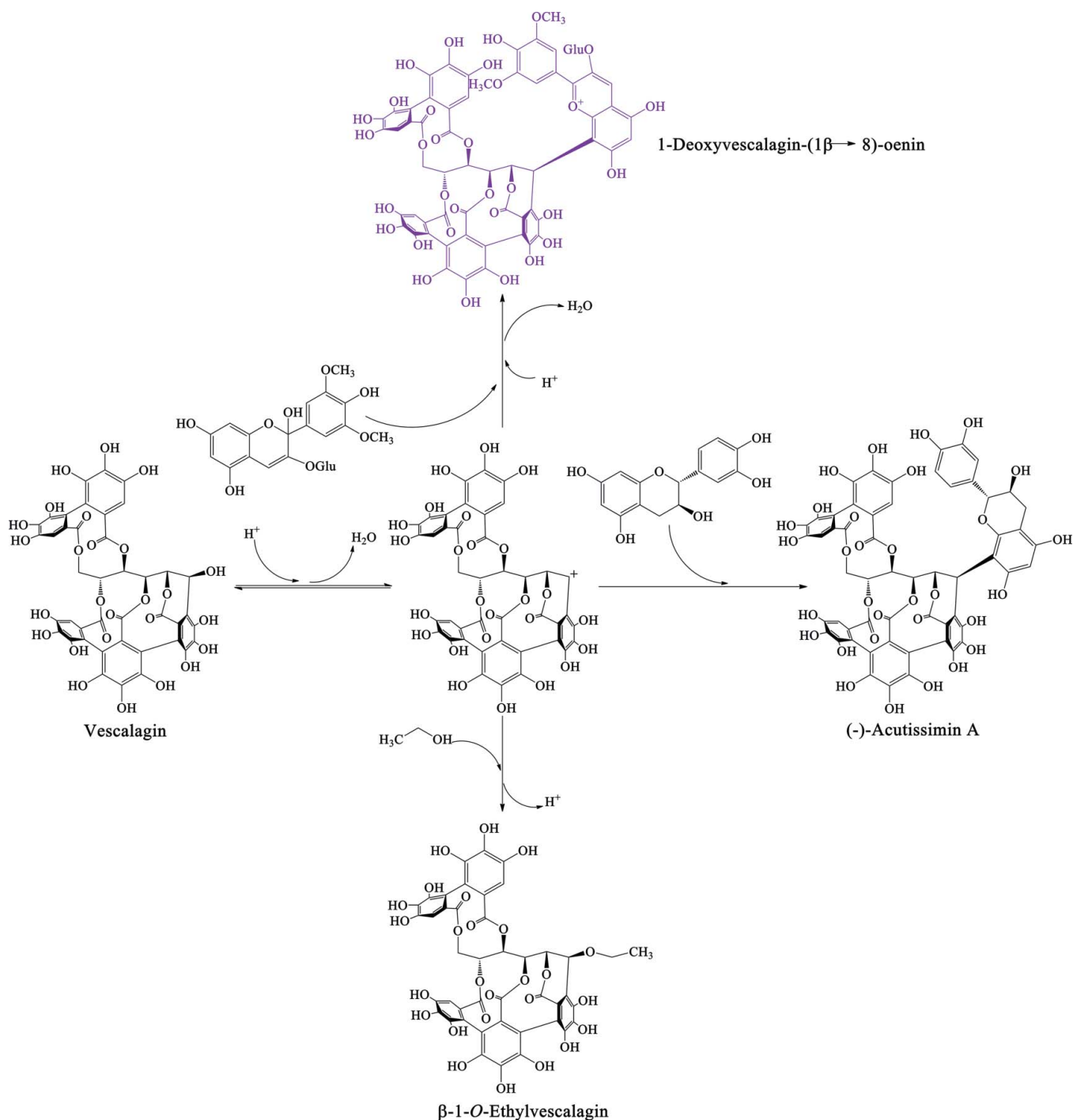
which then undergoes nucleophilic substitution in wine (Fig. 15) (Jourdes et al. 2009). The representative products found in dry red wines are flavano-ellagitannins such as (-)-acutissimin A, (-)-acutissimin B, (-)-epiacutissimin A and (-)-epiacutissimin B. The formation of (-)-acutissimin A and (-)-acutissimin B is achieved via reactions between a carbocation intermediate with the electron-rich C8 and C6 of (+)-catechin, respectively. (-)-Epiacutissimin A and (-)-epiacutissimin B are produced via the same mechanism, but (-)-epicatechin replaces (+)-catechin in the reaction (Fig. 15) (Quideau et al. 2003). In addition to attack by flavano-ellagitannins, the carbocation intermediate can also be attacked by ethanol to form  $\beta$ -1-*O*-ethylvescalagin (Fig. 15) (Quideau et al. 2005). Flavano-ellagitannins and  $\beta$ -1-*O*-ethylvescalagin, together with their ellagitannin precursors, are astringent and bitter compounds. Compared with the rough and puckering flavanols in wines, they exhibit much lower astringency thresholds and different astringent characteristics, which have been described as smooth (Glabasnia and Hofmann 2006; Hufnagel and Hofmann 2008; Stark et al. 2010). However, because flavanols are the predominant phenolic compounds in wines and flavano-ellagitannins,  $\beta$ -1-*O*-ethylvescalagin and other ellagitannins have usually been reported in concentrations below their astringency thresholds; their potential to affect wine astringency is quite limited (Table 4, Table 5).

Hemiketal-formed anthocyanins can also react with the carbocation intermediate derived from vescalagin by donating their electron-rich C8 or C6 to generate anthocyano-ellagitannin hybrid pigments such as 1-deoxyvescalagin-(1 $\beta$ →8)-oenin, 1-deoxyvescalagin-(1 $\beta$ →8)-myrtillin and 1-deoxyvescalagin-(1 $\beta$ →6)-myrtillin, which exhibit a purple color resulting from intramolecular copigmentation ( $\lambda_{\text{max}} > 540$  nm) (Fig. 15).

Scientific reports on these anthocyano-ellagitannins are the only hemisynthesis experiments in model solutions to date (Chassaing et al. 2010; García-Estévez et al. 2013). The absence of these anthocyano-ellagitannins in red wines may be due to competition from flavanols and ethanol or because they are present in wines in only trace amounts. Polymerizations between anthocyanins and vescalagin indicate that ellagitannins have the potential to modulate wine color.

The chemical reactivities of ellagitannins are strictly dependent on their chemical structures. Although reactions between vescalagin and wine components can easily occur under mildly acidic conditions, very extreme conditions are required for castalagin to react with these wine components (Jourdes et al. 2013). The only difference between vescalagin and castalagin is the orientation of the hydroxyl moiety in R1: vescalagin has a  $\beta$ -oriented hydroxyl moiety whereas castalagin has an  $\alpha$ -oriented hydroxyl moiety (Fig. 12). Upon investigating the chemical reactivities of different ellagitannin monomers, roburin E was reported to be the most affected by oxygen-independent reactions, followed by grandinin and vescalagin, whereas castalagin showed higher stability than the other three ellagitannin monomers (García-Estévez et al. 2017a). This result suggested that ellagitannins with a  $\beta$ -oriented hydroxyl moiety in R1, including vescalagin, grandinin, and roburin E as well as roburin A, roburin B and roburin C, may be active ellagitannins, whereas ellagitannins with an  $\alpha$ -oriented hydroxyl moiety in R1, such as castalagin and roburin D, may be inactive ellagitannins. American oak woods generally exhibit higher castalagin/vescalagin ratios than French oak woods (Navarro et al. 2016a).

Ellagitannins are excellent antioxidants due to their galloyl structure, except in reactions with wine components (Fig. 12).



**Figure 15.** Examples of reactions that occur between vescalagin and other wine constituents (Chassaing et al. 2010; García-Estévez et al. 2013; Jourdes et al. 2009; Quideau et al. 2003, 2005).

Ellagitannins exhibit better antioxidant properties than those of flavanols because they have more reactive hydroxyl groups capable of being oxidized per mole (Vivas and Glories 1996a). During barrel aging, because of the porous structure of oak staves,  $O_2$  can diffuse through oak woods and be consumed by wines, which causes a decrease in the concentration of grape-derived phenolic compounds in wines because they undergo oxidation. During the aging of wine oak barrels, scientists found that when the inner surface of oak woods are impregnated with wines, ellagitannins (especially vescalagin) can be extracted by wines that penetrate into oak woods and can

function as an effective barrier against  $O_2$  (García-Estévez et al. 2015, 2017a; Michel et al. 2016; Puech et al. 1999; Vivas and Glories 1996a). The oxidation of ellagitannins protects other phenolic compounds from undergoing unwanted reactions and results in the production of acetaldehyde. Both roles are very important for the indirect polymerizations of flavanols and anthocyanins, alleviating wine bitterness and astringency, and producing stable pigments. Furthermore, ellagitannins can also convert  $O_2$  into reactive oxygen species, which might favor the production of A-type vitisins (Vivas et al. 1996; Vivas and Glories 1996a).

**Table 4.** Astringency and bitterness thresholds of various flavanol and ellagitannin compounds detected in bottled water with an adjusted pH of 4.5.

Family	Compounds present	Astringency threshold (mg/L)	Bitterness threshold (mg/L)
Flavanols <sup>a</sup>	(+)-Catechin	119–174	290
	(-)-Epicatechin	232–270	232–270
	Procyanidin B1	139	231
	Procyanidin B2	110	280
	Procyanidin C1	260	347
Ellagitannins and their adducts <sup>b</sup>	Vescalagin	1.03	1578.5
	Castalagin	1.03	1578.5
	Roburin A	5.37	1535.5
	Roburin B	12.09	1159.5
	Roburin C	12.49	1199.1
	Roburin D	5.55	1372.7
	Roburin E	0.21	437.1
	Grandinin	0.21	655.6
	(-)-Acutissimin A	1.09	nr <sup>c</sup>
	(-)-Acutissimin B	1.93	nr
	(-)-Epiacutissimin A	1.81	nr
	(-)-Epiacutissimin B	2.9	nr
	$\beta$ -1-O-ethylvescalagin	2.7	>1446.55

<sup>a</sup>(Hufnagel and Hofmann 2008; Stark et al. 2010);<sup>b</sup>(Glabasnia and Hofmann 2006; Stark et al. 2010);<sup>c</sup>nr (not reported).

Ellagic acid can be produced by the degradation (during natural seasoning or toasting) and hydrolysis (after being extracted into wines) of ellagitannins (Cadahía et al. 2003; Cadahía et al. 2001; Matricardi and Waterhouse 1999; Quideau et al. 2010). Researchers have reported that adding ellagic acid to wines can enhance wine copigmentation to some extent and protect other wine phenolic compounds from oxidation due to their galloyl structures (Jordão et al. 2006; Liu et al. 2016; Magalhães et al. 2014; Zhang et al. 2017).

### **Oxidation of wines during oak barrel aging and its effect on wine astringency, bitterness and color**

Many factors contribute to the determination of the oxygen transfer rates (OTRs) of oak barrels. The latest research reports that the average annual OTRs of new American medium grain oak barrels (*Q. alba*), new American fine grain oak barrels (*Q. alba*) and new French fine grain oak barrels (*Q. petraea*) are approximately 11.3 mg/L/year, 11.62 mg/L/year and 8.18 mg/L/year, respectively (del Alamo-Sanza and Nevares 2014). Another study showed that during the aging of wine oak barrels, the barrel OTRs decrease due to the increase in the free water content

in the oak woods (del Alamo-Sanza and Nevares 2014; del Alamo-Sanza et al. 2017; Nevares et al. 2014, 2016; Vivas and Glories 1997). Except for the origin species and duration, other factors that influence barrel OTRs are the anatomical characteristics of the oak wood, including earlywood density, latewood density, tylose content and the type and orientation of the medullary rays (del Alamo-Sanza et al. 2016). Because the topic of our paper is a discussion of the effects of oak barrel aging on the phenolic and organoleptic properties of red wines, we do not present a more detailed introduction to oak barrel OTRs here; however, readers interested in this research can read the latest review by del Alamo-Sanza and Nevares (2017).

### **Basic oxidation and over-oxidation: effects of phenolic and organoleptic properties on wines**

Oxidation is a double-edged sword in terms of wine quality. Here, we define the wine oxidation process artificially as having two degrees, namely, basic oxidation and over-oxidation.

When a small amount of O<sub>2</sub> is dissolved in wines in the presence of metal ions, such as Fe<sup>2+</sup>, wine phenolic compounds can be oxidized into (semi)quinones, and they will transform into larger oligomers via regenerative polymerizations (Singleton 1987). Simultaneously, a limited number of acetaldehydes can be generated from ethanol oxidation; these molecules can react rapidly with acetaldehyde-reactive-polyphenols (ARPs) such as flavanols and anthocyanins, resulting in the increased production of F-ethyl-F and F-ethyl-A oligomers (de Freitas and Mateus 2006; Fulcrand et al. 2006; Li et al. 2008). This process is referred to as basic oxidation, and the primary products of this period are limited amounts of small oligomers produced from regenerative polymerizations and indirect polymerizations mediated by acetaldehyde. The formation of ethyl-bridged complexes can alleviate wine astringency and bitterness to some extent due to the resulting decrease in the free flavanol level of wines (Es-Safi et al. 1999a; Fulcrand et al. 1996a; Tanaka et al. 1994). In addition, F-ethyl-F oligomers are not stable, as they can undergo cleavage to produce vinylflavanol units. Vinylflavanols participate in the formation of orange-red flavanyl-pyranoanthocyanins, which stabilize wine color (Cruz et al. 2008; Francia-Aricha et al. 1997; Mateus et al. 2003a). F-ethyl-A oligomers emit a purple color and are more resistant to hydration and sulfite bleaching compared with their anthocyanin precursors (Cheynier et al. 2006). Therefore, limited basic oxidation is beneficial for softening tannins and stabilizing pigments in wines (Fig. 16).

Supplying wines with an excess amount of O<sub>2</sub> activates the potential phenolic compounds to undergo basic oxidation and lead the oxidation intensity in a different direction, toward over-oxidation. Because the oligomers of (semi)quinones produced from regenerative polymerizations have lower redox potentials than their parent phenols, they are more easily oxidized (Singleton 1987). After these oligomers are generated primarily due to an excess of O<sub>2</sub>, they are then preferentially oxidized in the oxidation reactions that follow, and their molecular sizes will increase even more due to subsequent regenerative polymerizations. These oligomers contribute a yellow-brown color to wines, and they may be converted into polymers that eventually precipitate (Li et al. 2008). A significant amount of basic oxidation aids in regenerative polymerizations,

**Table 5.** Concentrations of different ellagitannins and their adducts in dry red wines aged in a new French oak barrel for 12 months (mg/L)<sup>a</sup>.

Compounds	Concentration
Vescalagin	3.78
Castalagin	0.43
(-)-Acutissimin A	0.17
(-)-Acutissimin B	0.1
(-)-Epiacutissimin A	0.05
(-)-Epiacutissimin B	0.04
$\beta$ -1-O-ethylvescalagin	1.31

<sup>a</sup>(Stark et al. 2010).



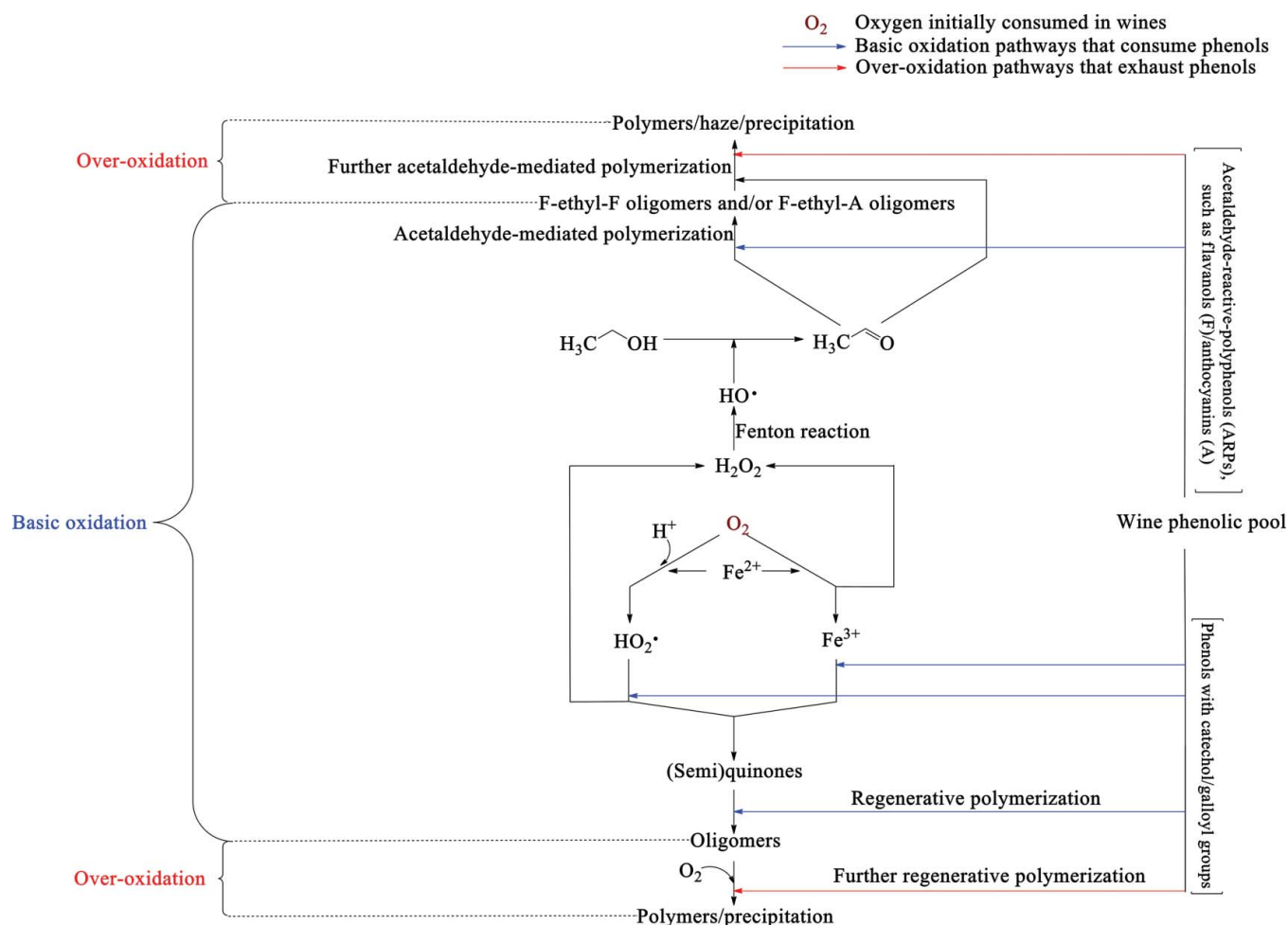


Figure 16. Different oxidation degrees in wines and their effects on wine composition.

decreases the concentration of wine phenolic compounds (including ARPs), and aids in the production and accumulation of a large amount of acetaldehyde. Excess acetaldehyde promotes an excessive amount of acetaldehyde-mediated polymerizations and increases wine turbidity (Es-Safi et al. 2002, 2003). Therefore, over-oxidation is considered disadvantageous for the production of quality wines (Fig. 16).

### Wine oxidation in barrel aging

A standard equilibrium point has not yet been established for assessing the oxidation degree of wines because the oxygen consumption potential of wine is determined by its chemical composition, which primarily includes metals (such as Cu and Fe) and phenolic compounds, and constituent concentrations (Carrascón et al. 2018; Ferreira et al. 2015; Marrufo-Curtido et al. 2018; Nevares et al. 2017). However, an excessive supply of oxygen to wines is more likely to cause over-oxidation than a limited supply of oxygen, whereas a limited amount of oxygen supplied to wines at a rate lower than the wine oxygen uptake rate guarantees a higher degree of wine oxidation than when oxidation reactions are confined to limited basic oxidation (Gómez-Plaza and Cano-López 2011; Schmidtke et al. 2011). A previous study has reported that when wines are treated with consecutive air-saturation cycles, the wine oxygen consumption

rates (OCRs) can be characterized into two statuses, namely, the initial OCRs and the average OCRs (Ferreira et al. 2015). Initial OCRs are observed during the first air-saturation cycle, whereas the average OCRs are observed during the subsequent air-saturation cycles (Table 6). The initial OCRs of wines are determined by the chemical compositions of the wines and demonstrate a positive relationship with chromatic parameters, such as the absorbance values observed at 520 nm (Abs520) and 620 nm (Abs620), and a negative relationship with the acetaldehyde content (Carrascón et al. 2018). The positive relationship between Abs520/620 and the initial OCRs indicates that the initial oxygen consumption stage results in an increase in desirable wine color properties. The negative role that acetaldehyde plays in affecting the initial OCRs may be explained by the increase in the acetaldehyde concentration, suggesting the exhaustion of ARPs active toward wine oxidation. During the oxidation period, wines with fewer ARPs are more prone to accumulating acetaldehyde, and thus, it is easier for these wines to leave the initial oxygen consumption stage and move to the average oxygen consumption stage (Carrascón et al. 2018). In combination with the phenolic and organoleptic changes we proposed for basic oxidation and over-oxidation, we believe that basic oxidation and over-oxidation may occur more easily during the initial oxygen consumption and average oxygen consumption stages, respectively.

**Table 6.** Oxygen consumption kinetics in wines treated with consecutive air-saturation cycles and oak barrel aging and possible explanations.

Wine samples	Treatment	Oxidation duration	Oxygen consumption kinetics	Possible reasons for the oxygen consumption kinetics
Bottled commercial wines <sup>a</sup>	Five consecutive air-saturation cycles	First air-saturation cycle	Initial oxygen consumption stage	Abundant amounts of phenolic compounds (such as ARPs) and oxygen
		Second air-saturation cycle	Average oxygen consumption stage	Exhaustion of phenolic compounds (such as ARPs) and sufficient supply of oxygen
		Third air-saturation cycle Fourth air-saturation cycle Fifth air-saturation cycle		
Wines directly after fermentation <sup>b</sup>	Aging in new French oak barrels ( <i>Q. robur</i> and <i>Q. petraea</i> )	0–8 days of aging	Similar to initial oxygen consumption stage	Abundant amount of phenolic compounds (such as ARPs) and limited supply of oxygen
		9–105 days of aging		
		≥106 days of aging		

<sup>a</sup>(Ferreira et al. 2015);<sup>b</sup>(Michel et al. 2016).

Studies on the OCRs of wines during barrel aging are quite limited. When wines are transferred to different new French oak barrels (*Q. robur* and *Q. petraea*), wine OCRs behave differently than the OCRs of wines treated with consecutive air-saturation experiments (Table 6) (Michel et al. 2016). Rapid OCRs have been observed in wine within the first eight days of barrel aging: the study by Michel et al. reports the average oxygen concentrations in all the barrels decreased from  $5.138 \pm 0.341$  mg/L to  $0.187 \pm 0.025$  mg/L. Over the next 97 days, the OCRs decreased, and the average oxygen concentrations in all the barrels decreased from  $0.187 \pm 0.025$  mg/L to  $0.074 \pm 0.004$  mg/L. Afterward, the dissolved oxygen levels in the wines fell below the detection limit (1  $\mu$ g/L), suggesting that after 105 days of barrel aging, the OCRs of the wines become very close to the OTRs of the barrels. The rapid OCRs recorded during the first eight days are primarily due to the presence of a significant amount of antioxidants, such as grape-derived phenolic compounds in wines and ellagitannins in barrels, the large amount of dissolved oxygen in the wines from their contact with the air prior to barreling, and the rapid OTRs of the barrels at the beginning of barrel aging. The much slower OCRs recorded after the first 8 days are likely due to the rapid decrease in the initial dissolved oxygen concentration in the wines and to the limited supply of oxygen from the barrels. Mathematically, the oxygen consumed by the wines during the first 105 days of barrel aging should be approximately  $5.055 \pm 0.069$  mg/L. During this period, we believe the oxygen consumption kinetics may be similar to those of the initial oxygen consumption stage observed in the consecutive air-saturation treatments of wines. Unlike the consecutive air-saturation experiments that cause wines to deliberately become saturated with oxygen, the oxygen in barrel-aged wines is naturally dissolved prior to barreling and, thus, the exhaustion of ARPs in barrel-aged wines is less dramatic than that during the first air-saturation cycle. Regarding the barrel aging period following the first 105 days, we deduce that the OCRs of the wines became quite close to the OTRs of the barrels because the dissolved oxygen in wines was below the detection limit. According to a previous report, the OTRs of new American barrels

fluctuate at approximately 20  $\mu$ g/L/day even after being filled with model wines for approximately 40 days (del Alamo-Sanza and Nevares 2014). Because French barrels have been found to have lower oxygen doses than American barrels, the OCRs of wines aged in French barrels may be below 20  $\mu$ g/L/day, which was far lower than the OCRs of wines exposed to air. Therefore, compared with the wines in the first air-circulation cycle and during the first 105 days of barrel aging, the ARPs in red wines during the subsequent aging period would not have been exhausted too quickly and may have participated in oxidation reactions at a slow rate. Furthermore, the oxygen consumption kinetics in the next barrel aging period should be similar to the initial oxygen consumption stage, which consisted of continuous limited basic oxidation, and a much longer time may be needed to exhaust the phenolic pool of wines to allow the wines to reach oxygen consumption kinetics similar to those in the average oxygen consumption stage.

According to previous reports of the oxygen consumption kinetics of air-saturated wines and barrel-aged wines (Carrascón et al. 2018; Ferreira et al. 2015; Michel et al. 2016), and given our definition of basic oxidation and over-oxidation and our speculation on the oxygen consumption kinetics of barrel-aged wines (Table 6), we believe that the oxidation that occurs in barrels during wine aging is continuous basic oxidation with a limited intensity. Scientists have reported that dry red wines with a long period of barrel aging contain low levels of F-ethyl-F and F-ethyl-A<sup>+</sup> oligomers, suggesting that these ethyl-bridged products undergo further reaction and participate in the formation of more stable pigments (Alcalde-Eon et al. 2006; Boido et al. 2006; Drinkine et al. 2007ab). During the barrel aging of wines, due to the continuous production of small quantities of acetaldehyde, wine tannins and pigments become softer and more stable, respectively (Fig. 17).

### Effects of the addition of SO<sub>2</sub> during barrel aging

The barrel aging of dry red wine begins at the moment the barrels have become completely filled with wine. The length of aging ranges from several months to many years and is

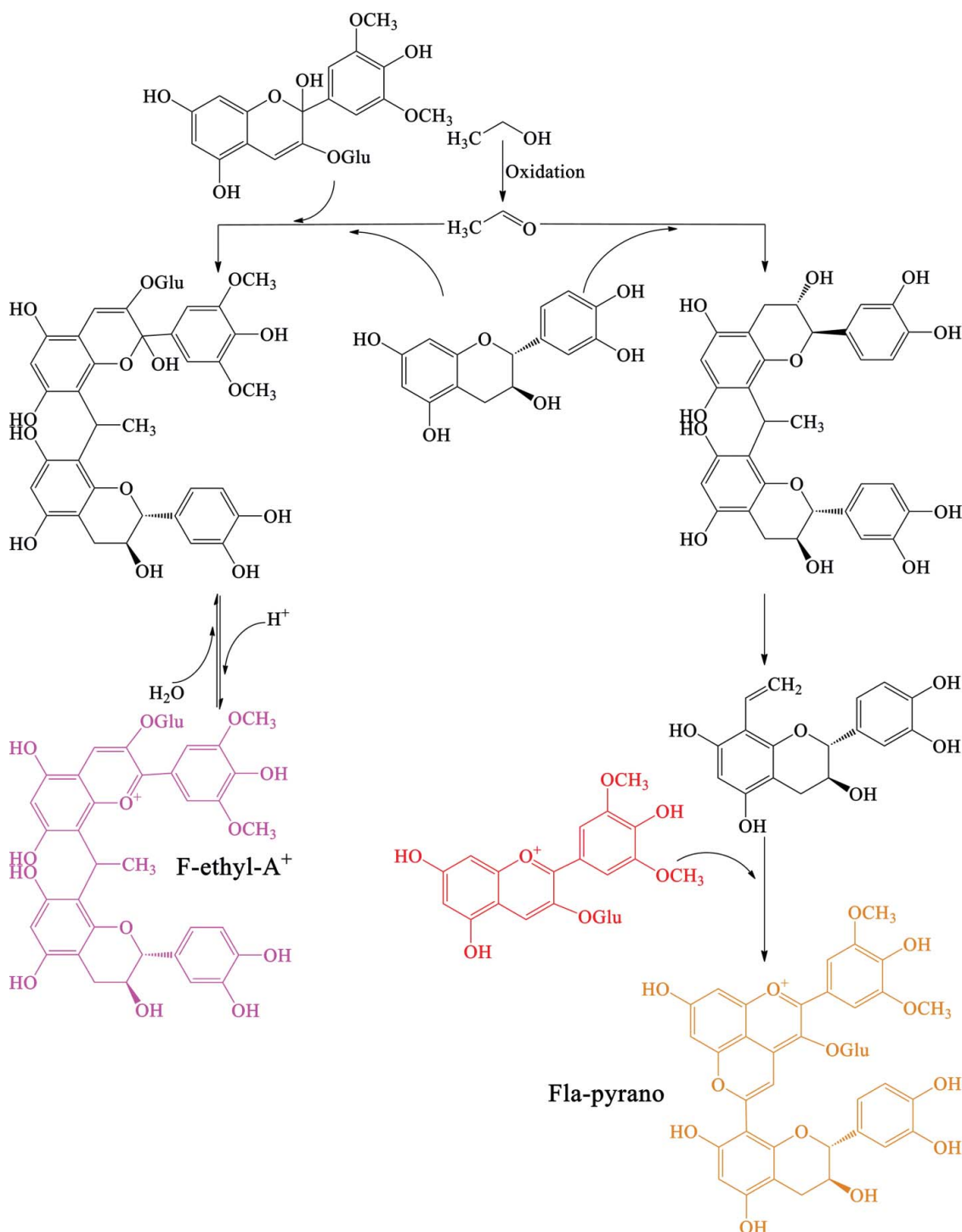


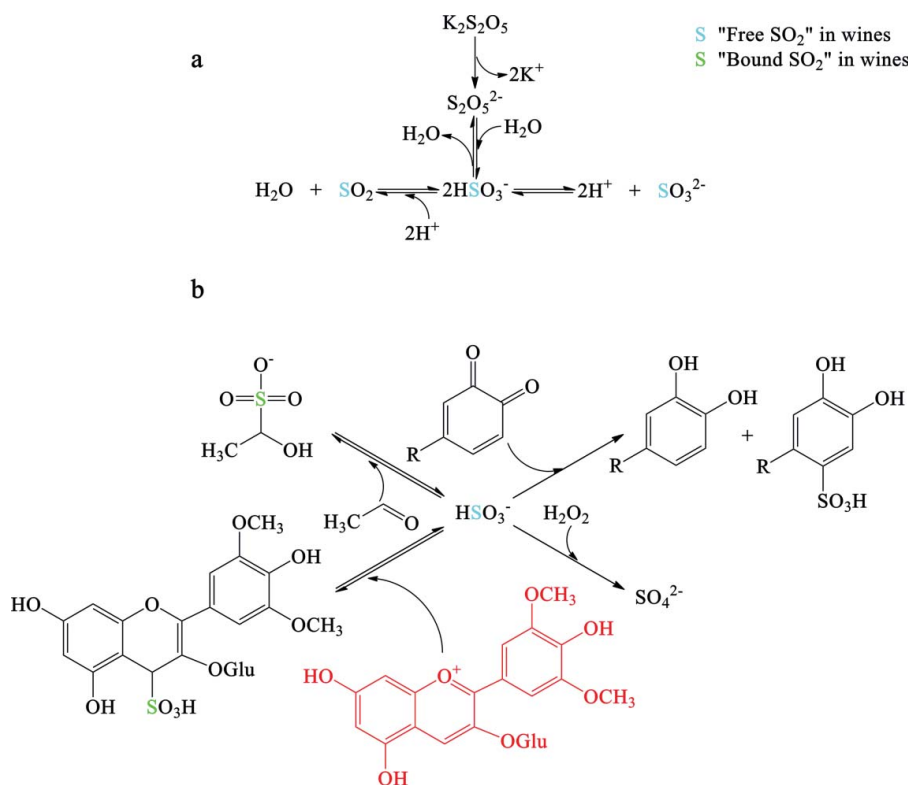
Figure 17. Possible preliminary phenolic reaction trends of dry red wines during their barrel aging period.

primarily determined by the winemakers' plans for the desired wine style. During this period, winemakers will add SO<sub>2</sub> (usually in the form of potassium metabisulfite tablets, K<sub>2</sub>S<sub>2</sub>O<sub>5</sub>) to barrel-aged wines periodically to prevent microbial spoilage, for example, from contamination by *Brettanomyces* and *Dekkera* (Guerrero and Cantos-Villar 2015; Suárez et al. 2007).

When K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> is dissolved in wines, the predominant free SO<sub>2</sub> species is HSO<sub>3</sub><sup>-</sup> (>90%) (Fig. 18a). HSO<sub>3</sub><sup>-</sup> is quite vulnerable to reacting with electrophiles (primarily anthocyanin flavylum cations and acetaldehyde) present in wines, which convert free SO<sub>2</sub> into bonded SO<sub>2</sub> adducts, result in a sulfite bleaching

effect on anthocyanins, and produce a dramatic decrease in the free acetaldehyde content in wines. Due to its strong antioxidant ability, HSO<sub>3</sub><sup>-</sup> can reduce quinones to their parent phenolic forms, thus regenerating the wine phenolic pools. Additionally, HSO<sub>3</sub><sup>-</sup> can react with H<sub>2</sub>O<sub>2</sub> to prevent Fenton reactions and avoid the generation of HO· (Fig. 18b). Therefore, adding SO<sub>2</sub> during the barrel aging of dry red wines can protect wines from oxidation to some extent and postpone subsequent chemical reactions (Waterhouse et al. 2016).

SO<sub>2</sub> addition may be the only artificial interference intentionally conducted during the barrel aging of wines. Because of



**Figure 18.** Interference of  $SO_2$ : dissolution of potassium metabisulfite and generation of different forms of  $SO_2$  (a); the role of bisulfite in affecting wine oxidation and phenolic reactions (b) (Waterhouse et al. 2016).

the potential allergic effects of  $SO_2$  on human health (Freedman 1980) and its pungent, irritating smell, the amount of  $SO_2$  added to wines during barrel aging should be carefully considered. The recommended free  $SO_2$  concentration in dry red wines during barrel aging is 20–30 mg/L (Ribéreau-Gayon et al. 2006a).

### Adoption of oak barrel aging

Although the benefits of oak barrel aging on wines have been studied by many scientists who have addressed its effects on the phenolic profile and astringency, bitterness and color properties of wines, which were all reviewed in this paper, not all dry red wines benefit from oak barrel aging. From a phenolic perspective, the added values of oak barrel aging include softening the tannins and stabilizing the pigments present in wines (Fig. 17). Therefore, for wines with low concentrations of flavanols and/or anthocyanins that have reached the stage directly after fermentation, the contribution of oak barrel aging is quite limited. For wines that have reached the stage directly after fermentation and have already exhibited desirable mouth-feel (primarily astringency and bitterness) and color properties making them good enough to drink, the adoption of oak barrel aging should be carefully considered. Because the continuous softening of wine tannins may cause wines to become structureless and the process that converts wine anthocyanins into more stable pigments (such as flavanyl-pyranoanthocyanins) changes the wine color from purple-red to yellow-orange, barrel-aged wines may be no better or even worse than wines that have not been barrel-aged.

At present, the adoption of oak barrel aging (including the choice of using this technique or not, the choice of barrel type, and selection of the oak barrel aging duration) is primarily dependent on the experiences of winemakers, which include their consideration of the following factors: the effects of oak barrels on wine phenolic profiles, mouth-feel and color properties; the aroma character that oak barrels contribute to wines; and winery budgets (Jackson 2008; Ribéreau-Gayon et al. 2006c; Waterhouse et al. 2016).

### Conclusions

Flavanols and anthocyanins are the major phenolic compounds present in dry red wines responsible for the mouth-feel (primarily its astringency and bitterness) and color properties, respectively, of these wines. Their chemical reactivities are closely related to their potential nucleophilic character in the A ring, antioxidant character in the B ring, and electrophilic character in the C ring. Phenolic reactions in wines during oak aging are confined to several specific types compared with the ones that occur spontaneously in wines directly after fermentation. Oak barrel aging contributes extractable oak constituents to wines, which can react with wine components to influence the astringency, bitterness and color of wines in different ways. Additionally, oak barrel aging guarantees the limited basic oxidation of dry red wines. Limiting this type of oxidation promotes the acetaldehyde-mediated polymerization of flavanols and anthocyanins and the formation of flavanyl-pyranoanthocyanins, which is beneficial for the modulation of mouth-feel and color stabilization.  $SO_2$  addition is the only artificial interference that may be intentionally conducted during barrel



aging, which protects wines from oxidation as well as postpones several phenolic chemical reactions. Although the benefits of oak barrel aging in wine-making have been studied by many scientists, not all dry red wines benefit from oak barrel aging. The suitability of a wine is determined by its basic phenolic profile and organoleptic properties directly after fermentation and speculation concerning the added value of barrel aging to the wine.

## Acknowledgments

This work was supported by the China Agriculture Research System (Grant No. CARS-29 to Chang-Qing Duan). The authors declare no conflict of interest.

## Funding

China Agriculture Research System.

## References

- Alcalde-Eon, C., M. T. Escribano-Bailón, C. Santos-Buelga, and J. C. Rivas-Gonzalo. 2006. Changes in the detailed pigment composition of red wine during maturity and ageing. *Analytica Chimica Acta* 563 (1–2):238–54. doi:10.1016/j.aca.2005.11.028.
- Asenstorfer, R. E., Y. Hayasaka, and G. P. Jones. 2001. Isolation and structures of oligomeric wine pigments by bisulfite-mediated ion-exchange chromatography. *Journal of Agricultural and Food Chemistry* 49 (12):5957–63. doi:10.1021/jf011261a.
- Atanasova, V., H. Fulcrand, C. Le Guernevé, V. Cheynier, and M. Moutouret. 2002. Structure of a new dimeric acetaldehyde malvidin 3-glucoside condensation product. *Tetrahedron Letters* 43 (35):6151–53. doi:10.1016/S0040-4039(02)01294-7.
- Bakker, J., P. Bridle, T. Honda, H. Kuwano, N. Saito, N. Terahara, and C. F. Timberlake. 1997. Identification of an anthocyanin occurring in some red wines. *Phytochemistry* 44 (7):1375–82. doi:10.1016/S0031-9422(96)00707-8.
- Bakker, J., and C. F. Timberlake. 1997. Isolation, identification, and characterization of new color-stable anthocyanins occurring in some red wines. *Journal of Agricultural and Food Chemistry* 45 (1):35–43. doi:10.1021/jf960252c.
- Baranac, J. M., N. A. Petranović, and J. M. Dimitrić-Marković. 1996. Spectrophotometric study of anthocyan copigmentation reactions. *Journal of Agricultural and Food Chemistry* 44 (5):1333–36. doi:10.1021/jf950420l.
- Baranac, J. M., N. A. Petranović, and J. M. Dimitrić-Marković. 1997. Spectrophotometric study of anthocyan copigmentation reactions. 2. Malvin and the nonglycosidized flavone quercetin. *Journal of Agricultural and Food Chemistry* 45 (5):1694–97. doi:10.1021/jf9606114.
- Bautista-Ortín, A. B., J. I. Fernández-Fernández, J. M. López-Roca, and E. Gómez-Plaza. 2007. The effects of enological practices in anthocyanins, phenolic compounds and wine colour and their dependence on grape characteristics. *Journal of Food Composition and Analysis* 20 (7):546–52. doi:10.1016/j.jfca.2007.04.008.
- Benito, S., A. Morata, F. Palomero, M. C. González, and J. A. Suárez-Lepe. 2011. Formation of vinylphenolic pyranoanthocyanins by *Saccharomyces cerevisiae* and *Pichia guilliermondii* in red wines produced following different fermentation strategies. *Food Chemistry* 124 (1):15–23. doi:10.1016/j.foodchem.2010.05.096.
- Bindon, K. A., M. G. McCarthy, and P. A. Smith. 2014. Development of wine colour and non-bleachable pigments during the fermentation and ageing of (*Vitis vinifera* L. Cv.) Cabernet Sauvignon wines differing in anthocyanin and tannin concentration. *LWT-Food Science and Technology* 59 (2):923–32. doi:10.1016/j.lwt.2014.05.051.
- Blanco-Vega, D., S. Gomez-Alonso, and I. Hermosin-Gutierrez. 2014. Identification, content and distribution of anthocyanins and low molecular weight anthocyanin-derived pigments in Spanish commercial red wines. *Food Chemistry* 158:449–58. doi:10.1016/j.foodchem.2014.02.154.
- Boido, E., C. Alcalde-Eon, F. Carrau, E. Dellacassa, and J. C. Rivas-Gonzalo. 2006. Aging effect on the pigment composition and color of *Vitis vinifera* L. Cv. Tannat wines. Contribution of the main pigment families to wine color. *Journal of Agricultural and Food Chemistry* 54 (18):6692–704. doi:10.1021/jf061240m.
- Boulton, R. 2001. The copigmentation of anthocyanins and its role in the color of red wine: A critical review. *American Journal of Enology and Viticulture* 52 (2):67–87.
- Brouillard, R. 1981. Origin of the exceptional colour stability of the zebrina anthocyanin. *Phytochemistry* 20 (1):143–45. doi:10.1016/0031-9422(81)85234-X.
- Brouillard, R. 1982. *Chemical structure of anthocyanins*. In: *Anthocyanins as Food Colors*, Ed. Markakis, P., 1–38. New York: Academic Press.
- Brouillard, R., S. Chassaing, and A. Fougerousse. 2003. Why are grape/fresh wine anthocyanins so simple and why is it that red wine color lasts so long? *Phytochemistry* 64 (7):1179–86. doi:10.1016/S0031-9422(03)00518-1.
- Brouillard, R., G. Mazza, Z. Saad, A. M. Albrecht-Gary, and A. Cheminat. 1989. The co-pigmentation reaction of anthocyanins: A microprobe for the structural study of aqueous solutions. *Journal of the American Chemical Society* 111 (7):2604–10. doi:10.1021/ja00189a039.
- Buiarelli, F., F. Coccioli, M. Merolle, R. Jasionowska, and A. Terracciano. 2010. Identification of hydroxycinnamic acid-tartaric acid esters in wine by HPLC-tandem mass spectrometry. *Food Chemistry* 123 (3):827–33. doi:10.1016/j.foodchem.2010.05.017.
- Cadahía, E., B. Fernández de Simón, and J. Jalocho. 2003. Volatile compounds in Spanish, French, and American oak woods after natural seasoning and toasting. *Journal of Agricultural and Food Chemistry* 51 (20):5923–32. doi:10.1021/jf0302456.
- Cadahía, E., L. Muñoz, B. Fernández de Simón, and M. C. García-Vallejo. 2001. Changes in low molecular weight phenolic compounds in Spanish, French, and American oak woods during natural seasoning and toasting. *Journal of Agricultural and Food Chemistry* 49 (4):1790–98. doi:10.1021/jf0006168.
- Carrascón, V., A. Vallverdú-Queralt, E. Meudec, N. Sommerer, P. Fernandez-Zurbano, and V. Ferreira. 2018. The kinetics of oxygen and SO<sub>2</sub> consumption by red wines. What do they tell about oxidation mechanisms and about changes in wine composition?. *Food Chemistry* 241:206–14. doi:10.1016/j.foodchem.2017.08.090.
- Castañeda-Ovando, A., M. Pacheco-Hernández, M. E. Páez-Hernández, J. A. Rodríguez, and C. A. Galán-Vidal. 2009. Chemical studies of anthocyanins: A review. *Food Chemistry* 113 (4):859–71. doi:10.1016/j.foodchem.2008.09.001.
- Chassaing, S., G. Isorez-Mahler, M. Kueny-Stotz, and R. Brouillard. 2015. Aged red wine pigments as a source of inspiration for organic synthesis—the cases of the color-stable pyranoflavylum and flavylum-(4→8)-flavan chromophores. *Tetrahedron* 71 (20):3066–78. doi:10.1016/j.tet.2014.10.058.
- Chassaing, S., D. Lefeuvre, R. Jacquet, M. Jourdes, L. Ducasse, S. Galland, A. Grelard, C. Saucier, P. L. Teissedre, O. Dangles, and S. Quideau. 2010. Physicochemical studies of new anthocyan-ellagitannin hybrid pigments: About the origin of the influence of oak C-glycosidic ellagitannins on wine color. *European Journal of Organic Chemistry* 2010 (1):55–63. doi:10.1002/ejoc.200901133.
- Chatonnet, P. 1992. Les composés aromatiques du bois de chêne cédés aux vins. Influence des opérations de chauffe en tonnellerie. En “le bois et la qualité des vins et des eaux-de-vie”. *Journal International des Sciences de la Vigne et du Vin* 81–91.
- Chatonnet, P., J. N. Boidron, and M. Pons. 1989. Incidence du traitement thermique du bois de chêne sur sa composition chimique. 2e partie: volution de certains composés en fonction de l'intensité de brûlage. *OENO One* 23 (4):223–50. doi:10.20870/oenone.1989.23.4.1722.
- Chatonnet, P., and D. Dubourdieu. 1998. Comparative study of the characteristics of American white oak (*Quercus alba*) and European oak (*Quercus petraea* and *Q. robur*) for production of barrels used in



- barrel aging of wines. *American Journal of Enology and Viticulture* 49 (1):79–85.
- Chatonnet, P., D. Dubourdieu, J. N. Boidron, and V. Lavigne. 1993. Synthesis of volatile phenols by *Saccharomyces cerevisiae* in wines. *Journal of the Science of Food and Agriculture* 62 (2):191–202. doi:10.1002/jsfa.2740620213.
- Cheyrier, V., M. Dueñas-Paton, E. Salas, C. Maury, J. M. Souquet, P. Sarni-Manchado, and H. Fulcrand. 2006. Structure and properties of wine pigments and tannins. *American Journal of Enology and Viticulture* 57 (3):298–305.
- Cruz, L., N. Teixeira, A. M. Silva, N. Mateus, J. Borges, and V. de Freitas. 2008. Role of vinylcatechin in the formation of pyranomalvidin-3-glucoside-(+)-catechin. *Journal of Agricultural and Food Chemistry* 56 (22):10980–87. doi:10.1021/jf8021496.
- Díaz-Plaza, E. M., J. R. Reyero, F. Pardo, G. L. Alonso, and M. R. Salinas. 2002. Influence of oak wood on the aromatic composition and quality of wines with different tannin contents. *Journal of Agricultural and Food Chemistry* 50 (9):2622–26. doi:10.1021/jf010521l.
- Dallas, C., J. M. Ricardo-da-Silva, and O. Laureano. 1996a. Interactions of oligomeric procyanidins in model wine solutions containing malvidin-3-glucoside and acetaldehyde. *Journal of the Science of Food and Agriculture* 70 (4):493–500. doi:10.1002/(SICI)1097-0010(199604)70:4<3493::AID-JSFA528%3e3.0.CO;2-7.
- Dallas, C., J. M. Ricardo-da-Silva, and O. Laureano. 1996b. Products formed in model wine solutions involving anthocyanins, procyanidin B2, and acetaldehyde. *Journal of Agricultural and Food Chemistry* 44 (8):2402–07. doi:10.1021/jf940433j.
- Danilewicz, J. C. 2003. Review of reaction mechanisms of oxygen and proposed intermediate reduction products in wine: Central role of iron and copper. *American Journal of Enology and Viticulture* 54 (2):73–85.
- Danilewicz, J. C. 2007. Interaction of sulfur dioxide, polyphenols, and oxygen in a wine-model system: Central role of iron and copper. *American Journal of Enology and Viticulture* 58 (1):53–60.
- Danilewicz, J. C. 2011. Mechanism of autooxidation of polyphenols and participation of sulfite in wine: Key role of iron. *American Journal of Enology and Viticulture* 62:319–28. doi:10.5344/ajev.2011.10105.
- Danilewicz, J. C., J. T. Secombe, and J. Whelan. 2008. Mechanism of interaction of polyphenols, oxygen, and sulfur dioxide in model wine and wine. *American Journal of Enology and Viticulture* 59 (2):128–36.
- Darias-Martín, J., M. Carrillo-López, J. F. Echavarri-Granado, and C. Díaz-Romero. 2006. The magnitude of copigmentation in the colour of aged red wines made in the Canary Islands. *European Food Research and Technology* 224 (5):643–48. doi:10.1007/s00217-006-0352-7.
- de Freitas, V., A. Fernandes, J. Oliveira, N. Teixeira, and N. Mateus. 2017. A review of the current knowledge of red wine colour. *OENO One* 51 (1):1001–1021. doi:10.20870/oeno-one.2017.51.1.1604.
- de Freitas, V., Y. Glories, G. Bourgeois, and C. Vitry. 1998. Characterisation of oligomeric and polymeric procyanidins from grape seeds by liquid secondary ion mass spectrometry. *Phytochemistry* 49 (5):1435–41. doi:10.1016/S0031-9422(98)00107-1.
- de Freitas, V., Y. Glories, and A. Monique. 2000. Developmental changes of procyanidins in grapes of red *Vitis vinifera* varieties and their composition in respective wines. *American Journal of Enology and Viticulture* 51 (4):397–403.
- de Freitas, V., and N. Mateus. 2001. Structural features of procyanidin interactions with salivary proteins. *Journal of Agricultural and Food Chemistry* 49 (2):940–45. doi:10.1021/jf000981z.
- de Freitas, V., and N. Mateus. 2002. Nephelometric study of salivary protein-tannin aggregates. *Journal of the Science of Food and Agriculture* 82 (1):113–19. doi:10.1002/jsfa.1016.
- de Freitas, V., and N. Mateus. 2006. Chemical transformations of anthocyanins yielding a variety of colours (review). *Environmental Chemistry Letters* 4 (3):175–183. doi:10.1007/s10311-006-0060-3.
- de Freitas, V., and N. Mateus. 2011. Formation of pyranoanthocyanins in red wines: A new and diverse class of anthocyanin derivatives. *Analytical and Bioanalytical Chemistry* 401 (5):1463–73. doi:10.1007/s00216-010-4479-9.
- de Freitas, V., C. Sousa, A. M. S. Silva, C. Santos-Buelga, and N. Mateus. 2004. Synthesis of a new catechin-pyrylium derived pigment. *Tetrahedron Letters* 45 (51):9349–52. doi:10.1016/j.tetlet.2004.10.132.
- del Alamo-Sanza, M., L. M. Carcel, and I. Nevares. 2017. Characterization of the oxygen transmission rate of oak wood species used in cooperage. *Journal of Agricultural and Food Chemistry* 65 (3):648–55. doi:10.1021/acs.jafc.6b05188.
- del Alamo-Sanza, M., I. Nevares, T. Mayr, J. A. Baro, V. Martínez-Martínez, and J. Ehgartner. 2016. Analysis of the role of wood anatomy on oxygen diffusivity in barrel staves using luminescent imaging. *Sensors and Actuators B: Chemical* 237:1035–43. doi:10.1016/j.snb.2016.08.075.
- del Alamo-Sanza, M., and I. Nevares. 2014. Recent advances in the evaluation of the oxygen transfer rate in oak barrels. *Journal of Agricultural and Food Chemistry* 62 (35):8892–99. doi:10.1021/jf502333d.
- del Alamo-Sanza, M., and I. Nevares. 2017. Oak wine barrel as an active vessel: A critical review of past and current knowledge. *Critical Reviews in Food Science and Nutrition* 1–16. doi:10.1080/10408398.2017.1330250.
- Drinkine, J., Y. Glories, and C. Saucier. 2005. (+)-catechin-aldehyde condensations: Competition between acetaldehyde and glyoxylic acid. *Journal of Agricultural and Food Chemistry* 53 (19):7552–58. doi:10.1021/jf0504723.
- Drinkine, J., P. Lopes, J. A. Kennedy, P. L. Teissedre, and C. Saucier. 2007a. Analysis of ethylidene-bridged flavan-3-ols in wine. *Journal of Agricultural and Food Chemistry* 55 (4):1109–16. doi:10.1021/jf0626258.
- Drinkine, J., P. Lopes, J. A. Kennedy, P. L. Teissedre, and C. Saucier. 2007b. Ethylidene-bridged flavan-3-ols in red wine and correlation with wine age. *Journal of Agricultural and Food Chemistry* 55 (15):62–99. doi:10.1021/jf070038w.
- Elias, R. J., and A. L. Waterhouse. 2010. Controlling the Fenton reaction in wine. *Journal of Agricultural and Food Chemistry* 58 (3):1699–1707. doi:10.1021/jf903127r.
- Es-Safi, N. E., V. Cheyrier, and M. Moutounet. 2000a. Study of the reactions between (+)-catechin and furfural derivatives in the presence or absence of anthocyanins and their implication in food color change. *Journal of Agricultural and Food Chemistry* 48 (12):5946–54. doi:10.1021/jf000394d.
- Es-Safi, N. E., V. Cheyrier, and M. Moutounet. 2002. Role of aldehydic derivatives in the condensation of phenolic compounds with emphasis on the sensorial properties of fruit-derived foods. *Journal of Agricultural and Food Chemistry* 50 (20):5571–85. doi:10.1021/jf025503y.
- Es-Safi, N. E., V. Cheyrier, and M. Moutounet. 2003. Implication of phenolic reactions in food organoleptic properties. *Journal of Food Composition and Analysis* 16 (5):535–53. doi:10.1016/S0889-1575(03)00019-X.
- Es-Safi, N. E., H. Fulcrand, V. Cheyrier, and M. Moutounet. 1999a. Studies on the acetaldehyde-induced condensation of (–)-epicatechin and malvidin 3-O-glucoside in a model solution system. *Journal of Agricultural and Food Chemistry* 47 (5):2096–2102. doi:10.1021/jf9806309.
- Es-Safi, N. E., C. Le Guernevé, V. Cheyrier, and M. Moutounet. 2000b. New phenolic compounds formed by evolution of (+)-catechin and glyoxylic acid in hydroalcoholic solution and their implication in color changes of grape-derived foods. *Journal of Agricultural and Food Chemistry* 48 (9):4233–40. doi:10.1021/jf000283e.
- Es-Safi, N. E., C. Le Guernevé, H. Fulcrand, V. Cheyrier, and M. Moutounet. 1999b. New polyphenolic compounds with xanthylum skeletons formed through reaction between (+)-catechin and glyoxylic acid. *Journal of Agricultural and Food Chemistry* 47 (12):5211–17. doi:10.1021/jf990424g.
- Es-Safi, N. E., C. Le Guernevé, B. Labarbe, and M. Moutounet. 1999c. Structure of a new xanthylum salt derivative. *Tetrahedron Letters* 40 (32):5869–72. doi:10.1016/S0040-4039(99)01156-9.
- Escribano-Bailón, M. T., M. Álvarez-García, J. C. Rivas-Gonzalo, F. J. Heredia, and C. Santos-Buelga. 2001. Color and stability of pigments derived from the acetaldehyde-mediated condensation between malvidin 3-O-glucoside and (+)-catechin. *Journal of Agricultural and Food Chemistry* 49 (3):1213–17. doi:10.1021/jf001081l.
- Escribano-Bailón, M. T., O. Dangles, and R. Brouillard. 1996. Coupling reactions between flavylum ions and catechin. *Phytochemistry* 41 (6):1583–92. doi:10.1016/0031-9422(95)00811-X.

- Escribano-Bailón, M. T., M. T. Guerra, J. C. Rivas-Gonzalo, and C. Santos-Buelga. 1995. Proanthocyanidins in skins from different grape varieties. *Zeitschrift für Lebensmitteluntersuchung und-Forschung A* 200 (3):221–24. doi:10.1007/BF01190499.
- Escribano-Bailón, M. T., and C. Santos-Buelga. 2012. Anthocyanin copigmentation-evaluation, mechanisms and implications for the colour of red wines. *Current Organic Chemistry* 16 (6):715–23. doi:10.2174/138527212799957977.
- Fenton, H. J. H. 1894. Oxidation of tartaric acid in presence of iron. *Journal of the Chemical Society, Transactions* 65:899–910. doi:10.1039/CT8946500899.
- Fernandez de Simon, B., I. Muino, and E. Cadahia. 2010. Characterization of volatile constituents in commercial oak wood chips. *Journal of Agricultural and Food Chemistry* 58 (17):9587–96. doi:10.1021/jf101301a.
- Ferreira, V., V. Carrascon, M. Bueno, M. Ugliano, and P. Fernandez-Zurbano. 2015. Oxygen consumption by red wines. part I: consumption rates, relationship with chemical composition, and role of SO<sub>2</sub>. *Journal of Agricultural and Food Chemistry* 63 (51):10928–937. doi:10.1021/acs.jafc.5b02988.
- Francia-Aricha, E. M., M. T. Guerra, J. C. Rivas-Gonzalo, and C. Santos-Buelga. 1997. New anthocyanin pigments formed after condensation with flavanols. *Journal of Agricultural and Food Chemistry* 45 (6):2262–66. doi:10.1021/jf9609587.
- Freedman, B. J. 1980. Sulphur dioxide in foods and beverages: Its use as a preservative and its effect on asthma. *British journal of diseases of the chest* 74:128–34. doi:10.1016/0007-0971(80)90023-6.
- Fulcrand, H., C. Benabdeljalil, J. Rigaud, V. Cheynier, and M. Moutounet. 1998. A new class of wine pigments generated by reaction between pyruvic acid and grape anthocyanins. *Phytochemistry* 47 (7):1401–07. doi:10.1016/S0031-9422(97)00772-3.
- Fulcrand, H., V. Cheynier, J. Oszmianski, and M. Moutounet. 1997. An oxidized tartaric acid residue as a new bridge potentially competing with acetaldehyde in flavan-3-ol condensation. *Phytochemistry* 46 (2):223–7. doi:10.1016/S0031-9422(97)00276-8.
- Fulcrand, H., T. Doco, N. E. Es-Safi, V. Cheynier, and M. Moutounet. 1996a. Study of the acetaldehyde induced polymerisation of flavan-3-ols by liquid chromatography-ion spray mass spectrometry. *Journal of Chromatography A* 752 (1–2):85–91. doi:10.1016/S0021-9673(96)00485-2.
- Fulcrand, H., P. J. dos Santos, P. Sarni-Manchado, V. Cheynier, and J. Favre-Bonvin. 1996b. Structure of new anthocyanin-derived wine pigments. *Journal of the Chemical Society, Perkin Transactions 1* 7:735–39. doi:10.1039/p19960000735.
- Fulcrand, H., M. Dueñas, E. Salas, and V. Cheynier. 2006. Phenolic reactions during winemaking and aging. *American Journal of Enology and Viticulture* 57 (3):289–97.
- Gómez-Míguez, M., S. González-Manzano, M. T. Escribano-Bailón, F. J. Heredia, and C. Santos-Buelga. 2006. Influence of different phenolic copigments on the color of malvidin 3-glucoside. *Journal of Agricultural and Food Chemistry* 54 (15):5422–29. doi:10.1021/jf0604586.
- Gómez-Plaza, E., and M. Cano-López. 2011. A review on micro-oxygenation of red wines: Claims, benefits and the underlying chemistry. *Food Chemistry* 125 (4):1131–40. doi:10.1016/j.foodchem.2010.10.034.
- García-Estévez, I., C. Alcalde-Eon, L. Le Grottaglie, J. C. Rivas-Gonzalo, and M. T. Escribano-Bailón. 2015. Understanding the ellagitannin extraction process from oak wood. *Tetrahedron* 71 (20):3089–94. doi:10.1016/j.tet.2014.10.047.
- García-Estévez, I., C. Alcalde-Eon, A. M. Martinez-Gil, J. C. Rivas-Gonzalo, M. T. Escribano-Bailón, I. Nevares, and M. del Alamo-Sanza. 2017a. An approach to the study of the interactions between ellagitannins and oxygen during oak wood aging. *Journal of Agricultural and Food Chemistry* 65 (31):6369–78. doi:10.1021/acs.jafc.7b02080.
- García-Estévez, I., M. T. Escribano-Bailón, J. C. Rivas-Gonzalo, and C. Alcalde-Eon. 2017b. Effect of the type of oak barrels employed during ageing on the ellagitannin profile of wines. *Australian Journal of Grape and Wine Research* 23 (3):334–41. doi:10.1111/ajgw.12292.
- García-Estévez, I., R. Jacquet, C. Alcalde-Eon, J. C. Rivas-Gonzalo, M. T. Escribano-Bailón, and S. Quideau. 2013. Hemisynthesis and structural and chromatic characterization of delphinidin 3-O-glucoside-vescalagin hybrid pigments. *Journal of Agricultural and Food Chemistry* 61 (47):11560–568. doi:10.1021/jf4033188.
- García-Falcón, M., C. Perezlamela, E. Martinezcarballo, and J. Simalgandara. 2007. Determination of phenolic compounds in wines: Influence of bottle storage of young red wines on their evolution. *Food Chemistry* 105 (1):248–59. doi:10.1016/j.foodchem.2006.11.006.
- Garde-Cerdán, T., and C. Ancín-Azpilicueta. 2006. Review of quality factors on wine ageing in oak barrels. *Trends in Food Science & Technology* 17 (8):438–47. doi:10.1016/j.tifs.2006.01.008.
- Glabasnia, A., and T. Hofmann. 2006. Sensory-directed identification of taste-active ellagitannins in American (*Quercus alba* L.) and European oak wood (*Quercus robur* L.) and quantitative analysis in bourbon whiskey and oak-matured red wines. *Journal of Agricultural and Food Chemistry* 54 (9):3380–90. doi:10.1021/jf052617b.
- Glories, Y. 1984. La couleur des vins rouges: 2e. Partie: Mesure, origine et interpretation. *Connaissance de la Vigne et du Vin* 18:253–71.
- González-Centeno, M. R., K. Chira, and P. L. Teissedre. 2016. Ellagitannin content, volatile composition and sensory profile of wines from different countries matured in oak barrels subjected to different toasting methods. *Food Chemistry* 210:500–511. doi:10.1016/j.foodchem.2016.04.139.
- Guerrero, R. F., and E. Cantos-Villar. 2015. Demonstrating the efficiency of sulphur dioxide replacements in wine: A parameter review. *Trends in Food Science & Technology* 42 (1):27–43. doi:10.1016/j.tifs.2014.11.004.
- Gutiérrez, I., E. Lorenzo, and A. Espinosa. 2005. Phenolic composition and magnitude of copigmentation in young and shortly aged red wines made from the cultivars, Cabernet Sauvignon, Cencibel, and Syrah. *Food Chemistry* 92 (2):269–83. doi:10.1016/j.foodchem.2004.07.023.
- Guyot, S., J. M. Pellerin, Brillouet, and V. Cheynier. 1996a. Inhibition of  $\beta$ -glucosidase (*Amygdalae dulces*) by (+)-catechin oxidation products and procyanidin dimers. *Bioscience Biotechnology and Biochemistry* 60:1131–35. doi:10.1271/bbb.60.1131.
- Guyot, S., J. Vercauteren, and V. Cheynier. 1996b. Structural determination of colourless and yellow dimers resulting from (+)-catechin coupling catalysed by grape polyphenoloxidase. *Phytochemistry* 42 (5):1279–88. doi:10.1016/0031-9422(96)00127-6.
- Hale, M. D., K. McCafferty, E. Larmie, J. Newton, and J. S. Swan. 1999. The influence of oak seasoning and toasting parameters on the composition and quality of wine. *American Journal of Enology and Viticulture* 50 (4):495–502.
- Haluk, J. P., and M. Irmouli. 1998. Les constituants polymères fixes du chêne de tonnellerie: Cellulose, hémicelluloses et lignine. *Journal des Sciences et Techniques de la Tonnellerie* 4:1–82.
- Haslam, E. 1980. In vino veritas: Oligomeric procyanidins and the ageing of red wines. *Phytochemistry* 19 (12):2577–82. doi:10.1016/S0031-9422(00)83922-9.
- He, F., Q. H. Pan, Y. Shi, and C. Q. Duan. 2008. Chemical synthesis of proanthocyanidins *in Vitro* and their reactions in aging wines. *Molecules* 13 (12):3007–32. doi:10.3390/molecules13123007.
- He, J., A. R. Carvalho, N. Mateus, and V. de Freitas. 2010a. Spectral features and stability of oligomeric pyranoanthocyanin-flavanol pigments isolated from red wines. *Journal of Agricultural and Food Chemistry* 58 (16):9249–58. doi:10.1021/jf102085e.
- He, J., J. Oliveira, A. M. Silva, N. Mateus, and V. de Freitas. 2010b. Oxoviti-sins: A new class of neutral pyranone-anthocyanin derivatives in red wines. *Journal of Agricultural and Food Chemistry* 58:8814–19. doi:10.1021/jf101408q.
- Herve du Penhoat, C. L., V. M. Michon, P. Shuyun, C. Viriot, A. Scalbert, and D. Gage. 1991. Structural elucidation of new dimeric ellagitannins from *Quercus robur* L. roburins AE. *Journal of the Chemical Society. Perkin transactions. I* 7:1653–60. doi:10.1039/P19910001653.
- Hufnagel, J. C., and T. Hofmann. 2008. Orosensory-directed identification of astringent mouthfeel and bitter-tasting compounds in red wine. *Journal of Agricultural and Food Chemistry* 56 (4):1376–86. doi:10.1021/jf073031n.
- Ivanova-Petropulos, V., I. Hermosín-Gutiérrez, B. Boros, M. Stefova, T. Staflov, B. Vojnoski, Á. Dörnyei, and F. Kilár. 2015. Phenolic compounds and antioxidant activity of macedonian red wines. *Journal of Food Composition and Analysis* 41:1–14. doi:10.1016/j.jfca.2015.01.002.

- Jackson, R. S. 2008. *Oak and cooperage*. In: *Wine Science. Principles and Applications*, Ed. Taylor, S. L., 452–472. New York: Academic Press.
- Jordão, A. M., J. M. Ricardo-da-Silva, and O. Laureano. 2006. Effect of oak constituents and oxygen on the evolution of malvidin-3-glucoside and (+)-catechin in model wine. *American Journal of Enology and Viticulture* 57 (3):377–81.
- Jourdes, M., D. Lefeuvre, and S. Quideau. 2009. C-Glycosidic ellagitannins and their influence on wine chemistry. In: *Chemistry and Biology of Ellagitannins: An Underestimated Class of Bioactive Plant Polyphenols*, Ed. Quideau, S., 320–365. Bordeaux: World Scientific Publishing Co.
- Jourdes, M., J. Michel, C. Saucier, S. Quideau, and P. L. Teissedre. 2011. Identification, amounts, and kinetics of extraction of C-glucosidic ellagitannins during wine aging in oak barrels or in stainless steel tanks with oak chips. *Analytical and Bioanalytical Chemistry* 401 (5):1531–39. doi:10.1007/s00216-011-4949-8.
- Jourdes, M., L. Pouysegue, D. Defieux, P. L. Teissedre, and S. Quideau. 2013. Hydrolyzable tannins: gallotannins and ellagitannins. In: *Natural Products: Phytochemistry, Botany and Metabolism of Alkaloids, Phenolics and Terpenes*, Eds. Ramawat, K. G., and Merillon, J. M., 1975–2010. Berlin: Springer.
- Jurd, L. 1969. Review of polyphenol condensation reactions and their possible occurrence in the aging of wines. *American Journal of Enology and Viticulture* 20 (3):191–5.
- Kallithraka, S., E. Tsoutsouras, E. Tzourou, and P. Lanaridis. 2006. Principal phenolic compounds in greek red wines. *Food Chemistry* 99 (4):784–93. doi:10.1016/j.foodchem.2005.07.059.
- Karbowiak, T., R. D. Gougeon, J. B. Alinc, L. Brachais, F. Debeaufort, A. Voilley, and D. Chassagne. 2009. Wine oxidation and the role of cork. *Critical Reviews in Food Science and Nutrition* 50 (1):20–52. doi:10.1080/10408390802248585.
- Koundouras, S., I. Kanakis, E. Drossou, S. Kallithraka, and Y. Kotseridis. 2013. Effects of postveraison water regime on the phenolic composition of grapes and wines of cv. Agiorgitiko (*Vitis vinifera* L.). *OENO One* 47 (2):115–28. doi:10.20870/oeno-one.2013.47.2.1542.
- Laurie, V. F., and A. L. Waterhouse. 2006. Oxidation of glycerol in the presence of hydrogen peroxide and iron in model solutions and wine. Potential effects on wine color. *Journal of Agricultural and Food Chemistry* 54 (13):4668–73. doi:10.1021/jf053036p.
- Levengood, J., and R. Boulton. 2004. The variation in the color due to copigmentation in young Cabernet Sauvignon wines. In: *Red Wine Color. Revealing the Mysteries*, Eds. Waterhouse, A. L., Kennedy, J. A., 35–52. Washington DC: American Chemical Society.
- Li, H., A. Guo, and H. Wang. 2008. Mechanisms of oxidative browning of wine. *Food Chemistry* 108 (1):1–13. doi:10.1016/j.foodchem.2007.10.065.
- Li, L., and B. Sun. 2017. Grape and wine polymeric polyphenols: Their importance in enology. *Critical Reviews in Food Science and Nutrition* 1–17. doi:10.1080/10408398.2017.1381071.
- Lorenzo, C., F. Pardo, A. Zalacain, G. L. Alonso, and M. R. Salinas. 2005. Effect of red grapes co-winemaking in polyphenols and color of wines. *Journal of Agricultural and Food Chemistry* 53 (19):7609–16. doi:10.1021/jf050848c.
- Lu, Y., and L. Y. Foo. 2001. Unusual anthocyanin reaction with acetone leading to pyranoanthocyanin formation. *Tetrahedron Letters* 42 (7):1371–73. doi:10.1016/S0040-4039(00)02246-2.
- Magalhães, L. M., I. I. Ramos, S. Reis, and M. A. Segundo. 2014. Antioxidant profile of commercial oenological tannins determined by multiple chemical assays. *Australian Journal of Grape and Wine Research* 20 (1):72–79. doi:10.1111/ajgw.12058.
- Marrufo-Curtido, A., V. Carrascón, M. Bueno, V. Ferreira, and A. Escudero. 2018. A procedure for the measurement of oxygen consumption rates (OCRs) in red wines and some observations about the influence of wine initial chemical composition. *Food Chemistry* 248:37–45. doi:10.1016/j.foodchem.2017.12.028.
- Mateus, N., E. Carvalho, A. R. Carvalho, A. Melo, A. M. González-Paramás, C. Santos-Buelga, A. M. Silva, and V. de Freitas. 2003a. Isolation and structural characterization of new acylated anthocyanin-vinyl-flavanol pigments occurring in aging red wines. *Journal of Agricultural and Food Chemistry* 51 (1):277–82. doi:10.1021/jf020695i.
- Mateus, N., S. Marques, A. C. Gonçalves, J. M. Machado, and V. de Freitas. 2001. Proanthocyanidin composition of red *Vitis vinifera* varieties from the Douro Valley during ripening: Influence of cultivation altitude. *American Journal of Enology and Viticulture* 52 (2):115–121.
- Mateus, N., J. Oliveira, A. M. González-Paramás, C. Santos-Buelga, and V. de Freitas. 2005. Screening of portisins (vinylpyranoanthocyanins pigments) in port wine by LC/DAD-MS. *Food Science and Technology International* 11 (5):353–58. doi:10.1177/1082013205057940.
- Mateus, N., J. Oliveira, J. Pissarra, A. M. González-Paramás, J. C. Rivas-Gonzalo, C. Santos-Buelga, A. M. S. Silva, and V. de Freitas. 2006. A new vinylpyranoanthocyanin pigment occurring in aged red wine. *Food Chemistry* 97 (4):689–95. doi:10.1016/j.foodchem.2005.05.051.
- Mateus, N., A. M. Silva, J. C. Rivas-Gonzalo, C. Santos-Buelga, and V. de Freitas. 2003b. A new class of blue anthocyanin-derived pigments isolated from red wines. *Journal of Agricultural and Food Chemistry* 51 (7):1919–23. doi:10.1021/jf020943a.
- Mateus, N., A. M. Silva, C. Santos-Buelga, J. C. Rivas-Gonzalo, and V. de Freitas. 2002. Identification of anthocyanin-flavanol pigments in red wines by NMR and mass spectrometry. *Journal of Agricultural and Food Chemistry* 50 (7):2110–16. doi:10.1021/jf0111561.
- Matricardi, L., and A. L. Waterhouse. 1999. Influence of toasting technique on color and ellagitannins of oak wood in barrel making. *American Journal of Enology and Viticulture* 50 (4):519–26.
- McRae, J. M., R. G. Damberg, S. Kassara, M. Parker, D. W. Jeffery, M. J. Herderich, and P. A. Smith. 2012. Phenolic compositions of 50 and 30 year sequences of Australian red wines: The impact of wine age. *Journal of Agricultural and Food Chemistry* 60 (40):10093–102. doi:10.1021/jf301571q.
- McRae, J. M., A. Schulkin, S. Kassara, H. E. Holt, and P. A. Smith. 2013. Sensory properties of wine tannin fractions: Implications for in-mouth sensory properties. *Journal of Agricultural and Food Chemistry* 61 (3):719–27. doi:10.1021/jf304239n.
- Michel, J., W. Albertin, M. Jourdes, A. Le Floch, T. Giordanengo, N. Mourey, and P. L. Teissedre. 2016. Variations in oxygen and ellagitannins, and organoleptic properties of red wine aged in French oak barrels classified by a near infrared system. *Food Chemistry* 204:381–90. doi:10.1016/j.foodchem.2016.02.129.
- Mingshu, L., Y. Kai, H. Qiang, and J. Dongying. 2006. Biodegradation of gallotannins and ellagitannins. *Journal of Basic Microbiology* 46 (1):68–84. doi:10.1002/jobm.200510600.
- Monagas, M., B. Bartolome, and C. Gomez-Cordoves. 2005. Updated knowledge about the presence of phenolic compounds in wine. *Critical Reviews in Food Science and Nutrition* 45 (2):85–118. doi:10.1080/10408690490911710.
- Morata, A., C. Gonzalez, and J. A. Suarez-Lepe. 2007. Formation of vinylphenolic pyranoanthocyanins by selected yeasts fermenting red grape musts supplemented with hydroxycinnamic acids. *International Journal of Food Microbiology* 116 (1):144–52. doi:10.1016/j.ijfoodmicro.2006.12.032.
- Morata, A., I. Loira, J. M. Heras, M. J. Callejo, W. Tesfaye, C. Gonzalez, and J. A. Suarez-Lepe. 2016. Yeast influence on the formation of stable pigments in red winemaking. *Food Chemistry* 197 (Pt A):686–91. doi:10.1016/j.foodchem.2015.11.026.
- Mosedale, J. R., J. L. Puech, and F. Feuillat. 1999. The influence on wine flavor of the oak species and natural variation of heartwood components. *American Journal of Enology and Viticulture* 50 (4):503–12.
- Moutounet, M., J. P. Mazauric, B. Saint-Pierre, and J. F. Hanocq. 1998. Gaseous exchange in wines stored in barrels. *Journal des Sciences et Techniques de la Tonnelerie* 4:131–45.
- Moutounet, M., J. L. Puech, R. Keller, and F. Feuillat. 1999. Les caractéristiques du bois de chêne en relation avec son utilisation en oenologie. Le phénomène de duramisation et ses conséquences. *Revue Française d'Enologie* 174:12–17.
- Navarro, M., N. Kontoudakis, S. Gómez-Alonso, E. García-Romero, J. M. Canals, I. Hermosín-Gutiérrez, and F. Zamora. 2016a. Influence of the botanical origin and toasting level on the ellagitannin content of wines aged in new and used oak barrels. *Food Research International* 87:197–203. doi:10.1016/j.foodres.2016.07.016.



- Navarro, M., N. Kontoudakis, S. Gómez-Alonso, E. García-Romero, J. M. Canals, I. Hermosín-Gutiérrez, and F. Zamora. 2017. Influence of the volatile substances released by oak barrels into a Cabernet Sauvignon red wine and a discolored Macabeo white wine on sensory appreciation by a trained panel. *European Food Research and Technology* 199:822–827.
- Navarro, M., N. Kontoudakis, T. Giordanengo, S. Gomez-Alonso, E. Garcia-Romero, F. Fort, J. M. Canals, I. Hermosin-Gutierrez, and F. Zamora. 2016b. Oxygen consumption by oak chips in a model wine solution; influence of the botanical origin, toast level and ellagitannin content. *Food Chemistry* 199:822–27. doi:10.1016/j.foodchem.2015.12.081.
- Nevares, I., and M. del Alamo-Sanza. 2014. Oxygène et barriques actualisation des connaissances quantité et voies de pénétration de l'oxygène dans la barrique. *Revue Des Oenologues Et Des Techniques Vitivinicoles Et Oenologiques* 41:41–44.
- Nevares, I., R. Crespo, C. Gonzalez, and M. del Alamo-Sanza. 2014. Imaging of oxygen transmission in the oak wood of wine barrels using optical sensors and a colour camera. *Australian Journal of Grape and Wine Research* 20 (3):353–60. doi:10.1111/ajgw.12104.
- Nevares, I., V. Martínez-Martínez, A. Martínez-Gil, R. Martín, V. F. Laurie, and M. del Alamo-Sanza. 2017. On-line monitoring of oxygen as a method to qualify the oxygen consumption rate of wines. *Food Chemistry* 229:588–596. doi:10.1016/j.foodchem.2017.02.105.
- Nevares, I., T. Mayr, J. A. Baro, J. Ehgartner, R. Crespo, and M. del Alamo-Sanza. 2016. Ratiometric oxygen imaging to predict oxygen diffusivity in oak wood during red wine barrel aging. *Food and Bioprocess Technology* 9 (6):1049–59. doi:10.1007/s11947-016-1695-0.
- Nonier, M. F., I. Pianet, M. Laguerre, N. Vivas, and N. Vivas de Gaulejac. 2006. Condensation products derived from flavan-3-ol oak wood aldehydes reaction. *Analytica Chimica Acta* 563 (1–2):76–83. doi:10.1016/j.aca.2005.09.036.
- Nonier, M. F., N. Vivas, C. Absalon, C. Vitry, E. Fouquet, and N. Vivas de Gaulejac. 2008. Structural diversity of nucleophilic adducts from flavanols and oak wood aldehydes. *Food Chemistry* 107 (4):1494–1505. doi:10.1016/j.foodchem.2007.10.012.
- Nonier, M. F., N. Vivas, V. de Freitas, N. Vivas de Gaulejac, and C. Absalon. 2011. A kinetic study of the reaction of (+)-catechin and malvidin-3-glucoside with aldehydes derived from toasted oak. *The Natural Products Journal* 1 (1):47–56.
- Nonier, M. F., N. Vivas, N. Vivas de Gaulejac, I. Pianet, and E. Fouquet. 2007. A kinetic study of the reactions of (+)-catechin with aldehydes derived from toasted oak. *Journal of the Science of Food and Agriculture* 87 (11):2081–91. doi:10.1002/jsfa.2968.
- Oliveira, C. M., A. C. Ferreira, V. de Freitas, and A. M. Silva. 2011. Oxidation mechanisms occurring in wines. *Food Research International* 44 (5):1115–26. doi:10.1016/j.foodres.2011.03.050.
- Oliveira, J., J. Azevedo, A. M. Silva, N. Teixeira, L. Cruz, N. Mateus, and V. de Freitas. 2010. Pyranoanthocyanin dimers: A new family of turquoise blue anthocyanin-derived pigments found in port wine. *Journal of Agricultural and Food Chemistry* 58 (8):5154–59. doi:10.1021/jf9044414.
- Pérez-Lamela, C., M. S. García-Falcón, J. Simal-Gándara, and I. Orriols-Fernández. 2007. Influence of grape variety, vine system and enological treatments on the colour stability of young red wines. *Food Chemistry* 101 (2):601–606. doi:10.1016/j.foodchem.2006.02.020.
- Pina, F. 1998. Thermodynamics and kinetics of flavylium salts malvin revisited. *Journal of the Chemical Society, Faraday Transactions* 94 (15):2109–116. doi:10.1039/a802602e.
- Pina, F., J. Oliveira, and V. de Freitas. 2015. Anthocyanins and derivatives are more than flavylium cations. *Tetrahedron* 71 (20):3107–14. doi:10.1016/j.tet.2014.09.051.
- Pissarra, J., S. Lourenço, A. M. González-Paramás, N. Mateus, C. Santos-Buelga, and V. de Freitas. 2004. Formation of new anthocyanin-alkyl/aryl-flavanol pigments in model solutions. *Analytica Chimica Acta* 513 (1):215–21. doi:10.1016/j.aca.2003.09.039.
- Pissarra, J., N. Mateus, J. Rivas-Gonzalo, C. Santos Buelga, and V. Freitas. 2003. Reaction between malvidin 3-glucoside and (+)-catechin in model solutions containing different aldehydes. *Journal of Food Science* 68 (2):476–81. doi:10.1111/j.1365-2621.2003.tb05697.x.
- Porter, L. J., L. N. Hrstich, and B. G. Chan. 1985. The conversion of procyanidins and prodelphinidins to cyanidin and delphinidin. *Phytochemistry* 223 (230):223–30. doi:10.1016/S0031-9422(00)94533-3.
- Price, S. F., P. J. Breen, M. Valladao, and B. T. Watson. 1995. Cluster sun exposure and quercetin in Pinot Noir grapes and wine. *American Journal of Enology and Viticulture* 46 (2):187–94.
- Prida, A. 2002. Use of oak wood in manufacture of barrels for preparing and aging wines. In: *Review: Oak; Ecology, Types and Management*, Eds. Cláudio, A. C., Abrahán, B. G., 173–193. New York: Nova Science Publishers, Inc.
- Prida, A., and P. Chatonnet. 2010. Impact of oak-derived compounds on the olfactory perception of barrel-aged wines. *American Journal of Enology and Viticulture* 61 (3):408–13.
- Prida, A., and J. L. Puech. 2006. Influence of geographical origin and botanical species on the content of extractives in American, French, and East European oak woods. *Journal of Agricultural and Food Chemistry* 54 (21):8115–26. doi:10.1021/jf0616098.
- Puech, J. L., F. Feuillat, and J. R. Mosedale. 1999. The tannins of oak heartwood: Structure, properties, and their influence on wine flavor. *American Journal of Enology and Viticulture* 50 (4):469–78.
- Quagliari, C., M. Jourdes, P. Waffo-Teguo, and P. L. Teissedre. 2017. Updated knowledge about pyranoanthocyanins: Impact of oxygen on their contents, and contribution in the winemaking process to overall wine color. *Trends in Food Science & Technology* 67:139–149. doi:10.1016/j.tifs.2017.07.005.
- Quideau, S., M. Jourdes, D. Lefeuvre, D. Montaudon, C. Saucier, Y. Glories, P. Pardon, and P. Pourquier. 2005. The chemistry of wine polyphenolic C-glycosidic ellagitannins targeting human topoisomerase II. *Chemistry-A European Journal* 11 (22):6503–13. doi:10.1002/chem.200500428.
- Quideau, S., M. Jourdes, D. Lefeuvre, P. Pardon, C. Saucier, P. L. Teissedre, and Y. Glories. 2010. Ellagitannins—an underestimated class of bioactive plant polyphenols: chemical reactivity of C-glucosidic ellagitannins in relation to wine chemistry and biological activity. In: *Recent Advances in Polyphenol Research*, Eds. Santos-Buelga, C., Escribano-Bailon, T., Lattanzio, V., Vol. 2, 81–137. Singapore: Blackwell Publishing Ltd.
- Quideau, S., M. Jourdes, C. Saucier, Y. Glories, P. Pardon, and C. Baudry. 2003. DNA topoisomerase inhibitor acutissimin A and other flavanoglycosidic ellagitannins in red wine. *Angewandte Chemie International Edition* 42 (48):6012–14. doi:10.1002/anie.200352089.
- Remy-Tanneau, S., C. Le Guernevé, E. Meudec, and V. Cheynier. 2003. Characterization of a colorless anthocyanin-flavan-3-ol dimer containing both carbon-carbon and ether interflavanoid linkages by NMR and mass spectrometry. *Journal of Agricultural and Food Chemistry* 51 (12):3592–97. doi:10.1021/jf021227b.
- Remy, S., H. Fulcrand, B. Labarbe, V. Cheynier, and M. Moutounet. 2000. First confirmation in red wine of products resulting from direct anthocyanin-tannin reactions. *Journal of the Science of Food and Agriculture* 80 (6):745–51. doi:10.1002/(SICI)1097-0010(20000501)80:6%3c745::AID-JSFA611%3e3.0.CO;2-4.
- Rentzsch, M., M. Schwarz, and P. Winterhalter. 2007a. Pyranoanthocyanins—an overview on structures, occurrence, and pathways of formation. *Trends in Food Science & Technology* 18 (10):526–34. doi:10.1016/j.tifs.2007.04.014.
- Rentzsch, M., M. Schwarz, P. Winterhalter, and I. Hermosín-Gutiérrez. 2007b. Formation of hydroxyphenyl-pyranoanthocyanins in grenache wines: Precursor levels and evolution during aging. *Journal of Agricultural and Food Chemistry* 55 (12):4883–88. doi:10.1021/jf0702491.
- Reynolds, A. G. 2010. Viticultural and vineyard management practices and their effects on grape and wine quality. In: *Managing Wine Quality (Volume 1), Viticulture and Wine Quality*, Ed. Reynolds, A. G., 365–444. Cambridge: Woodhead Publishing.
- Ribéreau-Gayon, P., D. Dubourdieu, B. Donèche, and A. Lonvaud. 2006a. The use of sulfur dioxide in must and wine treatment. In: *Handbook of Enology (Volume 1, 2nd Edition): The Microbiology of Wine and Vinifications*, 193–221. Chichester: John Wiley & Sons Ltd.
- Ribéreau-Gayon, P., D. Dubourdieu, B. Donèche, and A. Lonvaud. 2006b. Red winemaking. In: *Handbook of Enology (Volume 1, 2nd Edition):*

- The Microbiology of Wine and Vinifications*, 327–95. Chichester: John Wiley & Sons Ltd.
- Ribéreau-Gayon, P., Y. Glories, A. Maujean, and D. Dubourdieu. 2006c. Aging red wines in vat and barrel: phenomena occurring during aging. In: *Handbook of Enology (Volume 2, 2nd Edition): The Chemistry of Wine Stabilization and Treatments*, 387–428. Chichester: John Wiley & Sons Ltd.
- Rivas-Gonzalo, J. C., S. Bravo-Haro, and C. Santos-Buelga. 1995. Detection of compounds formed through the reaction of malvidin 3-monoglucoside and catechin in the presence of acetaldehyde. *Journal of Agricultural and Food Chemistry* 43 (6):1444–49. doi:10.1021/jf00054a006.
- Rubio-Bretón, P., C. Lorenzo, M. R. Salinas, J. Martínez, and T. Garde-Cerdán. 2012. Influence of oak barrel aging on the quality of red wines. In: *Review: Oak; Ecology, Types and Management*, Eds. Cláudio, A. C., Abrahán, B. G., 59–86. New York: Nova Science Publishers Inc.
- Salas, E., V. Atanasova, C. Poncet-Legrand, E. Meudec, J. P. Mazauric, and V. Cheynier. 2004a. Demonstration of the occurrence of flavanol-anthocyanin adducts in wine and in model solutions. *Analytica Chimica Acta* 513 (1):325–32. doi:10.1016/j.aca.2003.11.084.
- Salas, E., H. Fulcrand, E. Meudec, and V. Cheynier. 2003. Reactions of anthocyanins and tannins in model solutions. *Journal of Agricultural and Food Chemistry* 51 (27):7951–61. doi:10.1021/jf0345402.
- Salas, E., C. L. Guernevé, H. Fulcrand, C. Poncet-Legrand, and V. Cheynier. 2004b. Structure determination and colour properties of a new directly linked flavanol-anthocyanin dimer. *Tetrahedron Letters* 45 (47):8725–29. doi:10.1016/j.tetlet.2004.09.127.
- Sarni, F., M. Moutounet, J. L. Puech, and P. Rabier. 1990. Effect of heat treatment of oak wood extractable compounds. *Holzforchung-International Journal of the Biology, Chemistry, Physics and Technology of Wood* 44 (6):461–66.
- Saucier, C., M. Jourdes, Y. Glories, and S. Quideau. 2006. Extraction, detection, and quantification of flavano-ellagitannins and ethylvescalagin in a bordeaux red wine aged in oak barrels. *Journal of Agricultural and Food Chemistry* 54 (19):7349–54. doi:10.1021/jf061724i.
- Schmidtke, L. M., A. C. Clark, and G. R. Scollary. 2011. Micro-oxygenation of red wine: Techniques, applications, and outcomes. *Critical Reviews in Food Science and Nutrition* 51 (2):115–31. doi:10.1080/10408390903434548.
- Schneider, V. 1991. Comportement des vins obtenus par oxygénation des moûts blancs. *Revue Française d'Oenologie* 31 (130):33–42.
- Schwarz, M., G. Hofmann, and P. Winterhalter. 2004. Investigations on anthocyanins in wines from *Vitis vinifera* cv. Pinotage: Factors influencing the formation of pinotin A and its correlation with wine age. *Journal of Agricultural and Food Chemistry* 52 (3):498–504. doi:10.1021/jf035034f.
- Schwarz, M., G. Jerz, and P. Winterhalter. 2003a. Isolation and structure of Pinotin A, a new anthocyanin derivative from Pinotage wine. *Vitis* 42 (2):105–6.
- Schwarz, M., J. J. Picazo-Bacete, P. Winterhalter, and I. Herminos-Gutiérrez. 2005. Effect of copigments and grape cultivar on the color of red wines fermented after the addition of copigments. *Journal of Agricultural and Food Chemistry* 53 (21):8372–81. doi:10.1021/jf051005o.
- Schwarz, M., P. Quast, D. von Baer, and P. Winterhalter. 2003b. Vitisin A content in Chilean wines from *Vitis vinifera* cv. Cabernet sauvignon and contribution to the color of aged red wines. *Journal of Agricultural and Food Chemistry* 51 (21):6261–67. doi:10.1021/jf0346612.
- Schwarz, M., T. C. Wabnitz, and P. Winterhalter. 2003c. Pathway leading to the formation of anthocyanin-vinylphenol adducts and related pigments in red wines. *Journal of Agricultural and Food Chemistry* 51 (12):3682–87. doi:10.1021/jf0340963.
- Schwarz, M., and P. Winterhalter. 2003. A novel synthetic route to substituted pyranoanthocyanins with unique colour properties. *Tetrahedron Letters* 44 (41):7583–87. doi:10.1016/j.tetlet.2003.08.065.
- Schwarz, M., and P. Winterhalter. 2004. Novel aged anthocyanins from Pinotage wines: isolation, characterization and pathway of formation. In: *Red Wine Color: Revealing the Mysteries*, Eds. Waterhouse, A. L., and Kennedy, J. A., 179–97. Washington DC: American Chemical Society.
- Sefton, M. A., I. L. Francis, K. F. Pocock, and P. J. Williams. 1993. The influence of natural seasoning on the concentrations of eugenol, vanillin, and *cis*- and *trans*- $\beta$ -methyl- $\gamma$ -octalactone extracted from French and American oakwood. *Sciences des Aliments* 13 (4):629–643.
- Singleton, V. L. 1987. Oxygen with phenols and related reactions in musts, wines, and model systems: Observations and practical implications. *American Journal of Enology and Viticulture* 38 (1):69–77.
- Singleton, V. L., J. Zaya, and E. Trousdale. 1986. Compositional changes in ripening grapes: Caftaric and coumaric acids. *Vitis* 25 (2):107–17.
- Soares, S., E. Brandao, N. Mateus, and V. de Freitas. 2017. Sensorial properties of red wine polyphenols: Astringency and bitterness. *Critical Reviews in Food Science and Nutrition* 57 (5):937–48. doi:10.1080/10408398.2014.946468.
- Somers, T. C. 1971. The polymeric nature of wine pigments. *Phytochemistry Reviews* 10 (9):2175–86. doi:10.1016/S0031-9422(00)97215-7.
- Somers, C. 1998. *The Wine Spectrum: An Approach Towards Objective Definition of Wine Quality*. Adelaide: Hyde Park Press.
- Somers, T. C., E. Vêrette, and K. F. Pocock. 1987. Hydroxycinnamate esters of *Vitis vinifera*: Changes during white vinification, and effects of exogenous enzymic hydrolysis. *Journal of the Science of Food and Agriculture* 40 (1):67–78. doi:10.1002/jsfa.2740400109.
- Sousa, A., P. Araujo, L. Cruz, N. F. Bras, N. Mateus, and V. de Freitas. 2014. Evidence for copigmentation interactions between deoxyanthocyanidin derivatives (oaklins) and common copigments in wine model solutions. *Journal of Agricultural and Food Chemistry* 62 (29):6995–7001. doi:10.1021/jf404640m.
- Sousa, A., A. Fernandes, N. Mateus, and V. de Freitas. 2012. Synthesis and structural characterization of oaklin-catechins. *Journal of Agricultural and Food Chemistry* 60 (6):1528–34. doi:10.1021/jf204408p.
- Sousa, A., V. Petrov, P. Araujo, N. Mateus, F. Pina, and V. de Freitas. 2013. Thermodynamics, kinetics, and photochromism of oaklins: A recent family of deoxyanthocyanidins. *Journal of Physical Chemistry B* 117 (6):1901–10. doi:10.1021/jp3110216.
- Sousa, C., N. Mateus, J. Perez-Alonso, C. Santos-Buelga, and V. de Freitas. 2005. Preliminary study of oaklins, a new class of brick-red catechin-pyrylium pigments resulting from the reaction between catechin and wood aldehydes. *Journal of Agricultural and Food Chemistry* 53 (32):9249–56. doi:10.1021/jf051970e.
- Sousa, C., N. Mateus, A. M. S. Silva, A. M. González-Paramás, C. Santos-Buelga, and V. de Freitas. 2007. Structural and chromatic characterization of a new malvidin 3-glucoside-vanillyl-catechin pigment. *Food Chemistry* 102 (4):1344–51. doi:10.1016/j.foodchem.2006.04.050.
- Spranger, M. I., M. C. Climaco, B. Sun, N. Eiriz, C. Fortunato, A. Nunes, M. C. Leandro, M. L. Avelar, and A. P. Belchior. 2004. Differentiation of red winemaking technologies by phenolic and volatile composition. *Analytica Chimica Acta* 513 (1):151–61. doi:10.1016/j.aca.2004.01.023.
- Stark, T., N. Wollmann, K. Wenker, S. Losch, A. Glabasnia, and T. Hofmann. 2010. Matrix-calibrated LC-MS/MS quantitation and sensory evaluation of oak ellagitannins and their transformation products in red wines. *Journal of Agricultural and Food Chemistry* 58 (10):6360–69. doi:10.1021/jf100884y.
- Su, C. T., and V. L. Singleton. 1969. Identification of three flavan-3-ols from grapes. *Phytochemistry Reviews* 8 (8):1553–58. doi:10.1016/S0031-9422(00)85929-4.
- Suárez, R., J. A. Suárez-Lepe, A. Morata, and F. Calderón. 2007. The production of ethylphenols in wine by yeasts of the genera *Brettanomyces* and *Dekkera*: A review. *Food Chemistry* 102 (1):10–21. doi:10.1016/j.foodchem.2006.03.030.
- Sun, B., T. Barradas, C. Leandro, C. Santos, and I. Spranger. 2008. Formation of new stable pigments from condensation reaction between malvidin 3-glucoside and (-)-epicatechin mediated by acetaldehyde: Effect of tartaric acid concentration. *Food Chemistry* 110 (2):344–351. doi:10.1016/j.foodchem.2008.02.009.
- Sun, B., M. de Sa, C. Leandro, I. Caldeira, F. L. Duarte, and I. Spranger. 2013. Reactivity of polymeric proanthocyanidins toward salivary proteins and their contribution to young red wine astringency. *Journal of Agricultural and Food Chemistry* 61 (4):939–46. doi:10.1021/jf303704u.
- Sun, B., A. C. Neves, T. A. Fernandes, A. L. Fernandes, N. Mateus, V. de Freitas, C. Leandro, and M. I. Spranger. 2011. Evolution of phenolic composition of red wine during vinification and storage and its contribution to wine sensory properties and antioxidant activity. *Journal of*



- Agricultural and Food Chemistry* 59 (12):6550–57. doi:10.1021/jf201383e.
- Sun, B., I. Spranger, F. Roque-do-Vale, C. Leandro, and P. Belchior. 2001. Effect of different winemaking technologies on phenolic composition in Tinta Miúda red wines. *Journal of Agricultural and Food Chemistry* 49 (12):5809–16. doi:10.1021/jf010661v.
- Sun, B., I. Spranger, J. Yang, C. Leandro, L. Guo, S. Canario, Y. Zhao, and C. Wu. 2009. Red wine phenolic complexes and their in Vitro antioxidant activity. *Journal of Agricultural and Food Chemistry* 57 (18):8623–27. doi:10.1021/jf901610h.
- Sun, B., and M. I. Spranger. 2005. Changes in phenolic composition of Tinta Miúda red wines after 2 years of ageing in bottle: Effect of winemaking technologies. *European Food Research and Technology* 221 (3–4):305–12. doi:10.1007/s00217-005-1165-9.
- Tanaka, T., R. Takahashi, I. Kouno, and G. I. Nonaka. 1994. Chemical evidence for the de-astringency (insolubilization of tannins) of persimmon fruit. *Journal of the Chemical Society, Perkin Transactions 1* 20:3013–22. doi:10.1039/p19940003013.
- Timberlake, C. F. 1980. Anthocyanins-occurrence, extraction and chemistry. *Food Chemistry* 5 (1):69–80. doi:10.1016/0308-8146(80)90065-5.
- Timberlake, C. F., and P. Bridle. 1967. Flavylum salts, anthocyanidins and anthocyanins II.-reactions with sulphur dioxide. *Journal of the Science of Food and Agriculture* 18 (10):479–85. doi:10.1002/jsfa.2740181009.
- Timberlake, C. F., and P. Bridle. 1976. Interactions between anthocyanins, phenolic compounds, and acetaldehyde and their significance in red wines. *American Journal of Enology and Viticulture* 27 (3):97–105.
- Trouillas, P., J. C. Sancho-Garcia, V. de Freitas, J. Gierschner, M. Otyepka, and O. Dangles. 2016. Stabilizing and modulating color by copigmentation: Insights from theory and experiment. *Chemical Reviews* 116 (9):4937–82. doi:10.1021/acs.chemrev.5b00507.
- van Leeuwen, C. 2010. Terroir: the effect of the physical environment on vine growth, grape ripening and wine sensory attributes. In: *Managing Wine Quality (Volume 1): Viticulture and Wine Quality*, Ed. Reynolds, A. G., 273–315. Cambridge: Woodhead Publishing.
- Versari, A., W. du Toit, and G. P. Parpinello. 2013. Oenological tannins: A review. *Australian Journal of Grape and Wine Research* 19 (1):1–10. doi:10.1111/ajgw.12002.
- Vidal, J. C., J. C. Boulet, and M. Moutounet. 2004a. Les apports d'oxygène au cours des traitements des vins. Bilan des observations sur site, 3ème partie. *Revue Française d'Enologie* 205:25–33.
- Vidal, S., D. Cartalade, J. M. Souquet, H. Fulcrand, and V. Cheynier. 2002. Changes in proanthocyanidin chain length in winelike model solutions. *Journal of Agricultural and Food Chemistry* 50 (8):2261–66. doi:10.1021/jf011180e.
- Vidal, S., L. Francis, S. Guyot, N. Marnet, M. Kwiatkowski, R. Gawel, V. Cheynier, and E. J. Waters. 2003. The mouth-feel properties of grape and apple proanthocyanidins in a wine-like medium. *Journal of the Science of Food and Agriculture* 83 (6):564–73. doi:10.1002/jsfa.1394.
- Vidal, S., L. Francis, A. Noble, M. Kwiatkowski, V. Cheynier, and E. Waters. 2004b. Taste and mouth-feel properties of different types of tannin-like polyphenolic compounds and anthocyanins in wine. *Analytica Chimica Acta* 513 (1):57–65. doi:10.1016/j.aca.2003.10.017.
- Vivar-Quintana, A. M., C. Santos-Buelga, and J. C. Rivas-Gonzalo. 2002. Anthocyanin-derived pigments and colour of red wines. *Analytica Chimica Acta* 458 (1):147–55. doi:10.1016/S0003-2670(01)01619-1.
- Vivas, N. 1995. The notion of grain in cooperage. *Journal des Sciences et Techniques de la Tonnellerie* 1:17–32.
- Vivas, N. 1999a. Modelisation et calcul du bilan des apports d'oxygène au cours de l'élevage des vins rouge. III -interpretation des bilans et maitrise des apport d'oxygène. *Progrès Agricole et Viticole* 116 (1):16–18.
- Vivas, N. 1999b. Modelisation et etimation du bilan des apports d'oxygene au cours de l'élevage des vins rouge. IV-elevage des vins rouge en conditions d'oxygenations menagees controlees. *Progrès Agricole et Viticole* 116:305–11.
- Vivas, N. 2000. On the composition and quality of *Q. robur* L. From different regions in south-west Europe (fagales, fagaceae). *Journal des Sciences et Techniques de la Tonnellerie* 6:27–32.
- Vivas, N., G. Bourgeois, C. Vitry, Y. Glories, and V. De Freitas. 1996. Determination of the composition of commercial tannin extracts by liquid secondary ion mass spectrometry (LSIMS). *Journal of the Science of Food and Agriculture* 72 (3):309–17. doi:10.1002/(SICI)1097-0010(199611)72:3%3c309::AID-JSFA658%3e3.0.CO;2-U.
- Vivas, N., H. Debeda, F. Menil, N. Vivas de Gaulejac, and M. F. Nonier. 2003. Mise en évidence du passage de l'oxygène au travers des douelles constituant les barriques par l'utilisation d'un dispositif original de mesure de la porosité du bois. *Premiers résultats. Sciences des Aliments* 23 (5–6):655–78. doi:10.3166/sda.23.655-678.
- Vivas, N., and Y. Glories. 1996a. Role of oak wood ellagitannins in the oxidation process of red wines during aging. *American Journal of Enology and Viticulture* 47 (1):103–7.
- Vivas, N., and Y. Glories. 1996b. Study and optimization of phenomena involved in natural seasoning of oak wood. *Revue Française d'Enologie* 158:28–35.
- Vivas, N., and Y. Glories. 1997. Modélisation et calcul du bilan des apports d'oxygène au cours de l'élevage des vins rouges. II. Les apports liés au passage d'oxygène au travers de la barrique. *Progrès Agricole et Viticole* 114 (13–14):315–6.
- Vivas, N., M. F. Nonier, C. Absalon, V. L. Abad, F. Jamet, N. V. de Gaulejac, C. Vitry, and E. Fouquet. 2008. Formation of flavanol-aldehyde adducts in barrel-aged white wine-possible contribution of these products to colour. *South African Journal of Enology and Viticulture* 29 (2):98–108.
- Vivas, N., and N. Saint-Cricq de Gaulejac. 1998. Influence de la durée d'utilisation des barriques sur leurs apports aux vins. In: *Actes du Colloque Sciences et Techniques de la Tonnellerie*, 65–74. Bordeaux: Vigne et Vin Publications Internationales.
- Waterhouse, A. L. 2002. Wine phenolics. *Annals of the New York Academy of Sciences* 957:21–36. doi:10.1111/j.1749-6632.2002.tb02903.x.
- Waterhouse, A. L., and V. F. Laurie. 2006. Oxidation of wine phenolics: A critical evaluation and hypotheses. *American Journal of Enology and Viticulture* 57 (3):306–13.
- Waterhouse, A. L., G. L. Sacks, and D. W. Jeffery. 2016. Sulfur dioxide. In: *Understanding Wine Chemistry*, 140–148. Chichester: John Wiley & Sons.
- Waterhouse, A. L., and J. P. Towey. 1994. Oak lactone isomer ratio distinguishes between wines fermented in American and French oak barrels. *Journal of Agricultural and Food Chemistry* 42 (9):1971–74. doi:10.1021/jf00045a026.
- Wildenrad, H. L., and V. L. Singleton. 1974. The production of aldehydes as a result of oxidation of polyphenolic compounds and its relation to wine aging. *American Journal of Enology and Viticulture* 25 (2):119–26.
- Young, P. R., and M. A. Vivier. 2010. Genetics and genomic approaches to improve grape quality for winemaking. In: *Managing wine quality (Volume 1): Viticulture and Wine Quality*, Ed. Reynolds, A. G., 316–64. Cambridge: Woodhead Publishing.
- Zhang, B., F. He, Y. Liu, J. Cai, and C. Q. Duan. 2017. Impact of adding ellagic acid to red grapes on the phenolic composition and chromatic quality of cabernet sauvignon wines from a warm climate. *Journal of Food Processing and Preservation* 41 (4):1–11. doi:10.1111/jfpp.13080.