Chapter

Phenolic Compounds of Grapes and Wines: Key Compounds and Implications in Sensory Perception

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Abstract

Phenolic compounds are a wide family of thousands of natural bioactives well-known for their overwhelming demonstrated health benefits. Particularly in wines, polyphenols and quality are closely interconnected. Indeed, these compounds possess a critical role due to their contribution to organoleptic wine quality as color, astringency, and bitterness. The profile or the composition of certain polyphenols has been even proposed as an analytical tool for authenticity certification. In this sense, although important progress has been achieved, the understanding of the relationship between the quality of a particular wine and its phenolic composition remains one of the major challenges in enology research. But why? If there is an adjective to define wine, it is "complex." This final complexity of a wine begins with the enormous polyphenolic variability that may be present in grapes influenced by ripening, genetic, or environmental factors, among others. Winemaking process (alcoholic and malolactic fermentation) and wine aging with or without wood contact produce endless reactions giving rise to complex transformations (copigmentation, cycloaddition, polymerization, and oxidation) of polyphenols. This chapter gathers the most relevant information about the composition, variations, and transformations of phenolic compounds from grape to wine including their influence on sensory properties.

Keywords: phenolic compounds, grapes, evolution, wine, oak wood, sensory perception

1. Introduction

Grape and wine phenols represent a large family of compounds with a great diversity of chemical structures and degrees of complexity. The term "polyphenols" or "phenolics" is used to define a group of plant secondary metabolites that presents one or more than one hydroxyl (–OH) groups attached to one or more benzene rings [1].

Polyphenols are synthetized by phenylpropanoid pathway, being the amino acid phenylalanine (a shikimate pathway product) their common precursor. They can be divided into flavonoid (anthocyanins, flavan-3-ols, flavonols, flavanones, flavanonols, flavones, and chalcones) and non-flavonoid (hydroxybenzoic and hydroxycinnamic acids and stilbenes) families [2].

These compounds are critically important for wine quality, due to their contribution to their sensory properties: color, taste, mouthfeel, flavor, astringency, and bitterness [3, 4]. For this reason, the understanding of the relationship between wine quality and its phenolic composition is considered, nowadays, one of the major challenges in enology research.

Furthermore, fermentation, maturation, and/or aging of wine may be performed in contact with oak wood. Spontaneous clarification, slow and continuous oxygen diffusion through the oak wood pores (for barrels and casks), and extraction of many volatile and nonvolatile (mainly ellagitannins) compounds are observed. As a result, wine undergoes a modulation of its quality and complexity with regard to aroma, structure, astringency, bitterness, persistence, and color stability [5].

The objective of this book chapter is to examine the key phenolic compounds in grapes and in oak wood used for the maturation of wine. Likewise, the evolution of these compounds during winemaking and wine aging and their impact in the sensory properties of wine will be discussed.

2. Key grape phenolic compounds

The most important grape polyphenols comprise anthocyanins, flavan-3-ols, proanthocyanidins and flavonols (flavonoid family), and phenolic acids and stilbenes (non-flavonoid family). Each family can be present in their free or conjugated forms, differing by their hydroxylation level and by the substitution of the hydroxy groups (methylation, glycosylation, acylation) and even forming adducts between them (e.g., phenolic acids with anthocyanins; condensed tannins). This fact explains the great chemical diversity of polyphenols in grapes [6].

It is noteworthy that polyphenolic composition in grapes is highly affected by different factors such as viticulture practices, environmental conditions (soil, climate), and pathogen attacks [7]. Although, one of the most important factors is undoubtedly the varietal or genetic differences [8] as well as the winemaking process.

2.1 Flavonoid grape polyphenols: Anthocyanins, flavan-3-ols, procyanidins, and flavonols

Flavonoids are basically formed by a structure of 15 carbons (C6-C3-C6) divided in 2 aromatic rings, A and B, which are joined by a 3-carbon chain that is part of a heterocyclic C ring (**Figure 1**). Depending on the oxidation state of C ring, this family can be subdivided in anthocyanins, flavan-3-ols, or flavonols.

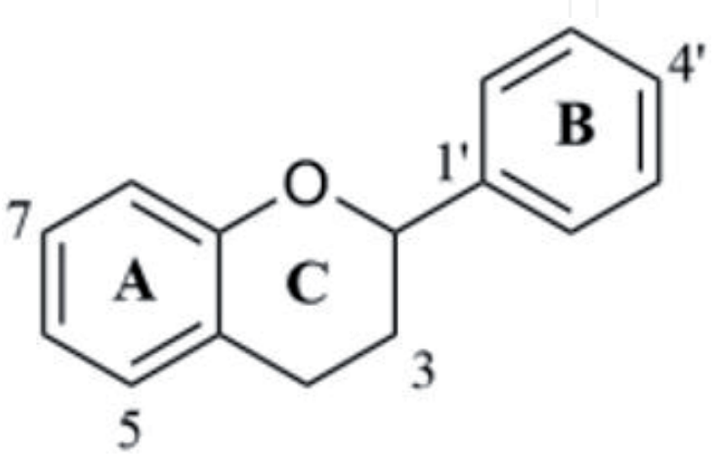


Figure 1.
General chemical structure of flavonoid family.

2.1.1 Anthocyanins

Structurally, anthocyanins are mainly present in nature in the form of heterosides. The aglycone form of anthocyanins, also called anthocyanidin, is based on the flavylium or 2-phenylbenzopyrilium ion having hydroxyl and methoxyl groups in different positions.

Anthocyanins are the most important natural pigments in wine grapes. These compounds are predominately accumulated in skins of red grapes during the ripening, and they are also present in the flesh of "teinturier" varieties [9]. In addition, it has been recently demonstrated that certain white grape cultivars (Sauvignon

Compound	**g/kg dm**			**Grape variety**	**References**
	Pomace	Seeds	Skins		
Total polyphenol content[a]	19–40.5	36.6–88.7	20.2–52.3	Grenache, Syrah, Carignan noir, Mourvèdre, Counoise	[13]
Anthocyanins					
Total	11.47–29.82	11–47–29.82	ND	Cabernet Mitos, Lemberger, Spätburgunder, Schwarzriesling, Trollinger	[12, 14]
Delphidin-3-*O*-glucoside	0.44–1.11	0.44–1.11	ND		
Cyanidin-3-*O*-glucoside	1.51–3.81	1.51–3.81	ND		
Petunidin-3-*O*-glucoside	0.53–1.34	0.53–1.34	ND		
Peonidin-3-*O*-glucoside	0.99–2.49	0.99–2.49	ND		
Malvidin-3-*O*-glucoside	4.12–10.19	4.12–10.19	ND		
Total acetylated	3.88–10.88	3.88–10.88	ND		
Flavan-3-ols/proanthocyanidins					
Catechin	0–0.3	2.14–2.42	0–0.3	Grenache, Syrah, Carignan noir, Mourvèdre, Counoise Cabernet Sauvignon, Chardonnay, Sauvignon blanc, Moscatel de Grano Menudo, Gewürztraminer, Riesling, Viognier, Merlot, Cencibel	[13, 15–19]
Epicatechin	0–0.2	0.88–1.60	0–0.13		
Epigallocatechin	0–0.05	0.05	ND		
Epigallocatechin-3-*O*-gallate	0–0.007	0.06–0.07	ND		
Epicatechin-3-*O*-gallate	0.003	0.25–0.31	0.04		
Procyanidin B1	0.11–0.60	0.14–0.17	0.18–0.6		
Procyanidin B2	0.01–0.84	0.04–0.18	0.01–0.84		
Total tannins	39.1–105.8	62.3–167.8	44.9–73.0		
Flavonols					
Total	0.03–0.63	0.48–0.63	0.02–0.05	Merlot Weisser Riesling	[14]
Phenolic acids					
Total	0.03–8.31	0.10–0.11	0.17–8.23	Cabernet Sauvignon, Merlot, Cabernet Mitos	[12, 14, 19]
Gallic acid	0.03–0.11	0.03	0.01–0.11		
Coutaric acid	0–1.23	0.03–1.23	—		
Caftaric acid	0–6.97	0.11–6.97	—		

[a]*Gallic acid equivalents (GAE) per g dry weight.*

Table 1.
Main phenolic compounds in different grape parts (expressed in g/kg of dm).

Blanc, Riesling, and Chardonnay) can contain measurable traces of anthocyanins [10]. Several factors can influence the anthocyanin biosynthesis in grapes such as origin and type of the grape vine, degree of maturity, and weather conditions like temperature, water availability, or the light exposure and intensity [11].

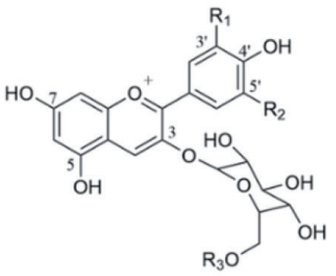
Regarding total anthocyanins, their quantities vary between 11.47 and 29.83 g/kg of dry matter (dm) in red grape skins [12] (**Table 1**). The principal individual anthocyanins in *Vitis vinifera* cultivars are the 3-*O*-monoglucosides (glucose linked through glucosidic bonds at the C3 positions of C ring) of delphinidin, cyanidin, petunidin, peonidin, and malvidin (**Figure 2**). Among these, malvidin-3-*O*-glucoside is generally the most abundant with values of 4.12–10.19 g/kg dm [14]. More recently, He and co-workers demonstrated for the first time the presence of pelargonidin-3-*O*-glucoside at trace levels on berry skins of Cabernet Sauvignon and Pinot noir cultivars [20]. Moreover, the monoglucoside forms can be acylated at the C6″ position of the glucose moiety with both aromatic (*p*-coumaric, caffeic, ferulic, and sinapic acid) or aliphatic acids (acetic, malic, malonic, oxalic, and succinic acid). The most common acylated anthocyanins in *V. vinifera* grape includes 3-*O*-(6″-*p*-coumaroyl)-glucosides, 3-*O*-(6″-acetyl)-glucosides, and 3-*O*-(6-caffeoyl)-glucosides of delphinidin, petunidin, peonidin, and malvidin [8, 12, 14, 21]. To go further, even anthocyanin dimers (malvidin-3-*O*-glucoside dimer and malvidin-3-*O*-glucoside-peonidin-3-*O*-glucoside) have been identified in grape skins [8, 22]. The presence of these acetylated forms is important for the color stabilization and intensity of wines [23]. The color intensity increases with the number of substituted groups on the B ring (di-oxygenated forms are redder, while tri-oxygenated are more purple) and with the replacement of hydroxyl by methoxyl groups (i.e., malvidin has the darkest color). Moreover, methoxylated anthocyanins (malvidin and peonidin) are more stable than hydroxylated ones to environmental and viticultural factors [24]. Additionally, anthocyanins can be found as 3,5-*O*-diglucosides or acylated 3,5-*O*-diglucosides, which are considered as marker compounds of non-*V. vinifera* species or hybrid red grapes [25].

In general, anthocyanin concentration is maximized under nonirrigated conditions in all cultivars, but anthocyanin profile and relative distribution of individual anthocyanins among irrigation treatments are influenced principally by the cultivar. In fact, Cabernet Sauvignon, Merlot, Syrah, and Tempranillo are characterized by a major proportion of malvidin forms, while in Nebbiolo (Italian cultivar) peonidin-3-*O*-glucoside is the most prevalent anthocyanin [11]. Other varieties, for example, Pinot noir, red Chardonnay, and pink Sultana (white red-colored mutants), are not able to synthetize acetylated anthocyanins [26]. In consequence, the anthocyanins profile in grapes can be used as an authentication tool of varietal wines [27].

2.1.2 Flavan-3-ols and proanthocyanidins (oligomeric proanthocyanidins or condensed tannins)

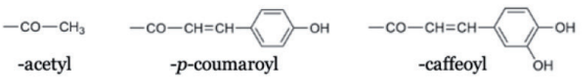
Flavan-3-ols are monomeric flavonoids formed by a benzopyran unit (rings A and C) with an aromatic cycle (ring B) linked to the carbon C-2 of the pyranic cycle (ring C). The presence of two chiral centers on the molecule (C2 and C3) gives rise to four possible configurations for a single monomer. These monomeric structures may be joined together forming dimers, oligomers (3–1o units of flavan-3-ols), and polymers (more than 1o units of flavan-3-ols). All these more complex structures are so-called condensed tannins. If they are formed by (+)-catechin and (−)-epicatechin and their gallic esters, they are named procyanidins, while when they are

Anthocyanins



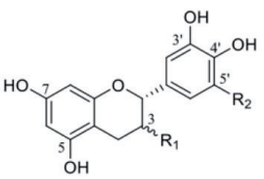
	R1	R2
Cyanidin-3-*O*-glucoside	OH	H
Delphinidin-3-*O*-glucoside	OH	OH
Peonidine-3-*O*-glucoside	OCH_3	H
Petunidin-3-*O*-glucoside	OCH_3	OH
Malvidin-3-*O*-glucoside	OCH_3	OCH_3

R3

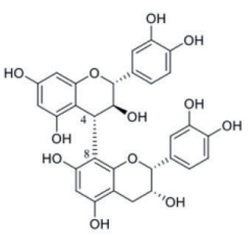


-acetyl -*p*-coumaroyl -caffeoyl

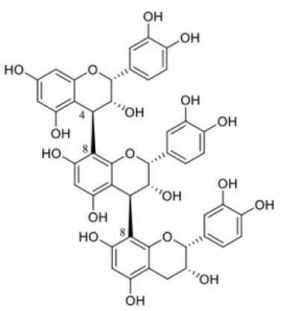
Flavan-3-ols and proanthocyanidins



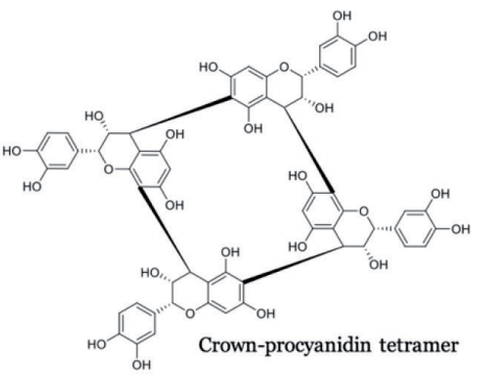
	R1	R2
Catechin	β-OH	H
Epicatechin	α-OH	H
Epigallocatechin	α-OH	OH
Epigallocatechin gallate	α-O-gallyl	OH
Epicatechin gallate	α-O-gallyl	H



Procyanidin B4

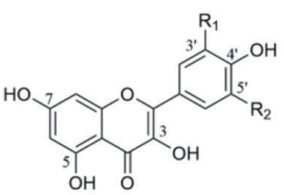


Procyanidin C1



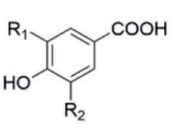
Crown-procyanidin tetramer

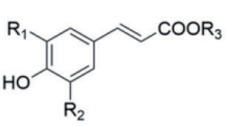
Flavonols



	R1	R2		R1	R2
Quercetin	OH	H	Isorhamnetin	OCH_3	H
Myricetin	OH	OH	Laricitrin	OCH_3	OH
Kaempferol	H	H	Syringetin	OCH_3	OCH_3

Phenolic acids

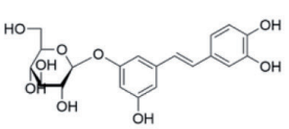




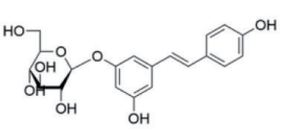
Hydroxybenzoic acids	R1	R2
p-hydroxybenzoic acid	H	H
protocatechuic acid	OH	H
vanillic acid	OCH_3	H
gallic acid	OH	OH
syringic acid	OCH_3	OCH_3

Hydroxycinnamic acids	R1	R2	R3
p-coumaric acid	H	H	H
caffeic acid	OH	H	H
ferulic acid	OCH_3	H	H
sinapic acid	OCH_3	OCH_3	H
p-coumaroyltartaric acid (coutaric acid)	H	H	$C_4H_5O_5$
caffeoyltartaric acid (caftaric acid)	OH	H	$C_4H_5O_5$
feruloytartaric acid (fertaric acid)	OCH_3	H	$C_4H_5O_5$

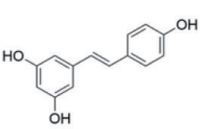
Stilbenes



E-astringin



E-piceid



E-resveratrol

Figure 2.
Chemical structures of major grape phenolic compounds.

constituted by (+)-gallocatechin and (−)-epigallocatechin and their galloylated derivatives, the term used is prodelphinidins [28].

They are located in all grape clusters solid parts (skins, seeds, stalks) and are responsible for the stabilization of wines' both color and sensory characteristics due to their astringent and bitter properties [29]. Five monomeric flavan-3-ols are commonly present in grapes (**Figure 2**): (+)-catechin and its stereoisomer (−)-epicatechin as the predominant ones in seeds (2.14–2.44 g/kg dm and 0.88–1.60 g/kg dm, respectively) (**Table 1**) (+)-gallocatechin, (−)-epigallocatechin, and (+)-catechin-3-*O*-gallate [13, 15–19].

As explained above, condensed tannins are oligomers of flavan-3-ol monomer units. These units can be linked by C-4 → C-6 or C-4 → C-8 bonds, so-called B-type proanthocyanidins. A-type condensed tannins are characterized by the presence of a second interflavonoid bond by C**–**O oxidative coupling (C-2 → O-7 on the basic flavan-3-ol unit) [28]. B-type proanthocyanidins, and in particular, dimers as B1, B2, B3, and B4 or trimer C1 are mainly located in grape skins (0.01–0.86 g/kg dm) and, in a lower extent, in seeds (0.04–0.18 g/kg dm) [16–18]. On the contrary, complex procyanidins (n > 3) are more abundant in seeds (58–163 g/kg dm) than in skins (45–71 g/kg dm) (**Table 1**).

Tannins' structure is characterized by the nature of its constitutive extension and terminal units, its mean degree of polymerization (mDP; average number of units in the polymer), and its degree of galloylation (%G; percentage of subunits bearing gallic acid esters). In the case of skins, the percentage of (−)-epigallocatechin (EGC) or also called the percentage of prodelphinidins (%P) is also used for characterization purposes. Condensed tannins with different mDPs may have different organoleptic properties. Generally, astringency increases with tannin concentration, molecular size, and %G [29]. Polymerized procyanidins are increasingly reactive with proteins and, therefore, have a more important astringent character [30]. Proanthocyanidins' molecular size could also affect bitterness since monomers are considered to be more bitter than oligomers and polymers. Therefore, the estimation of both mDP and %G of procyanidins could be a useful parameter to evaluate the type of procyanidins present in a sample.

The quantity of flavan-3-ols and proanthocyanidins varies during ripening being higher at flowering and lower as the grapes maturate [31]. Both flavan-3-ols and proanthocyanidins are the major polyphenolic compounds in *V. vinifera* grapes. The greatest content is observed in seeds (62–168 g/kg dm) followed by skins (45–73 g/kg dm) (**Table 1**). This amount can be also variable depending on the grape variety and vintage [13].

Very recently, a new condensed tannin called "crown" proanthocyanidin tetramer has been isolated for the first time in grape skins of Cabernet Sauvignon cultivar. This tetramer is totally absent in seeds differentiating it from the rest of proanthocyanidins. This name "crown" is associated to an unusual macrocyclic carbon skeleton that has never been characterized before in the plant kingdom [32].

2.1.3 Flavonols

Flavonols constitute a group of flavonoids, which have the peculiarity to present a double bound between C2 and C3 and a hydroxyl group in C3. They vary in color from white to yellow and possess an important role in the color stabilization of young red wines, through copigmentation interaction with anthocyanins [3], and in the sensory perception of astringency and bitterness [33].

Conventionally, flavonols are present in berry skins of both white and colored grapes, and their total flavonoid content varies notably depending on cultivars and ripening stage [34]. In relation with cultivars, more quantities of flavonols have

been reported, for example, in *V. vinifera* French varieties (Syrah, Petit Verdot, Cabernet Sauvignon, and Merlot), than with Spanish ones (Tempranillo, Garnacha, and Garnacha Tintorera) [35]. The total amount of flavonols in grapes varies from 1 to 80 mg/kg of fresh berry, being the red cultivars regularly richer than the white ones [35, 36].

Flavonols are found in grape berry skins in 3-*O*-glycoside forms. The main flavonols reported in red grapes are the dihydroxylated quercetin-3-*O*-glucoside and 3-*O*-glucuronide and the trihydroxylated myricetin 3-*O*-glucoside. In addition, other compounds such as kaempferol and the methylated isorhamnetin, laricitrin, and syringetin 3-*O*-glucosides have also been identified [35]. Furthermore, kaempferol and laricitin-3-*O*-galactosides, kampferol-3-*O*-glucuronide, and even quercetin and siringetin-3-*O*-(6″-acetyl)-glucoside have been identified in Cabernet Sauvignon grapes in lower quantities [37]. Interestingly and more recently, laricitrin-3-*O*-galactoside and syringetin-3-*O*-galactoside were reported in red grapes for the first time. With regard to white grapes cultivars, myricetin, laricitrin, and syringetin have not been identified [36].

2.2 Non-flavonoid grape polyphenols: phenolic acids and stilbenes

2.2.1 Phenolic acids

Phenolic acids can be classified in two main groups: hydroxybenzoic acids (C6-C1) and hydroxycinnamic acids (C6-C3). This family is found in skins, pulp, and seeds of grapes, being generally most numerous in skins (0.2–8.2 g/kg dm) (**Table 1**). The quantities of total hydroxycinnamic or hydroxybenzoic acids in grape skins vary depending on cultivar and origin. For example, hydroxycinnamic acids are more predominant in *V. vinifera* East Asian or North American grapes than in European grapes in which these phenolic acids are only present in trace levels. However, the hydroxybenzoic acid amounts are similar between cultivars [38].

Individually, the most important hydroxybenzoic acids in grapes are gallic, vanillic, and syringic acids. Predominantly present in grape seeds, gallic acid is considered the most important phenolic acid (100–230 mg/kg dm), being the precursor of all hydrolyzable tannins [39]. In lower quantities, protocatechuic acid and *p*-hydroxybenzoic acids are also present [39, 40] (**Figure 2**).

Regarding hydroxycinnamic acids, they are principally located in skins, being *p*-coumaric, caffeic, ferulic, and sinapic acids the most significant. It should be reminded that *p*-coumaric and caffeic acids can be found esterified by the glucose of the anthocyanin monoglucosides forming their acylated derivates. In grapes (mainly white) and also in wines, hydroxycinnamic acids are mainly esterified with tartaric acid forming caftaric, *p*-coutaric, or fertaric acids (from caffeic, *p*-coumaric, and ferulic acids, respectively) [18] (**Figure 2**).

Phenolic acids, and overall, hydroxycinnamic acids can act as copigments. Indeed, they are implicated on the formation of new more stable pigments (pyranoanthocyanins) in wine and, in consequence, are considered as color stabilizer agents of young red wines, through copigmentation with anthocyanins [3]. Moreover, they are also associated with the sensory perception of astringency and bitterness [41].

2.2.2 Stilbenes

Stilbenes (1,2-diphenylethylene) are formed from two phenyl rings linked together by an ethylene bridge generating a C6–C2–C6 structure. The aromatic rings are generally substituted by different functions such as hydroxyl, methyl, methoxyl, prenyl, or geranyl groups. Moreover, monomeric units (resveratrol) can

also be coupled, leading to the formation of more complex stilbenes. Their composition and content are extremely variable depending on different biotic (attack of plant pathogens) and abiotic factors including grape variety and ripening stage [42].

In grape berries, stilbenes are mainly concentrated in skins [43]; only trace amounts are reported in seeds [44]. In addition, red varieties seem to present higher stilbene content than white ones [45]. The major stilbenes in grapes are the glucosides piceid (mean 1.3 mg/kg fresh weight (fw)), resveratrol (mean 1.1 mg/kg fw), and astringin (mean 0.5 mg/kg fw) [46] (**Figure 2**). Furthermore, other minor monomers were identified such as pterostilbene and isorhapontigenin [47]. Finally, different dimers as pallidol, ε-viniferin and δ-viniferin, trimers such as miyabenol C and α-viniferin, and tetramers as hopeaphenol and isohopeaphenol have also been reported [46] (**Figure 2**).

3. Key phenolic compounds in oak wood

Oak wood is the preferred material for the manufacture of barrels, casks, or whatever derived wood product (chips, blocks, winewoods, tankstaves, etc.) used during fermentation and/or aging of wines. Resistance, flexibility, easy handling, and low permeability make oak wood particularly suitable for wine maturation and storage, in relation to mechanical, physical, and chemical properties provided by other woods [48].

Regardless of the species, oak heartwood is basically composed by cellulose, hemicelluloses, and lignin, representing approximately 90% of dry wood and acting as key structural polymers of wood matrix. The remaining 10% of dry wood corresponds to an extractable fraction, mainly consisting of phenolic compounds but also presenting low molecular weight compounds and volatile compounds. Lignans, coumarins, phenolic acids, and phenolic aldehydes may be found in the oak wood phenolic fraction, but hydrolyzable tannins are the major constituents [49].

Depending on the release of gallic or ellagic acid under acidic conditions, hydrolyzable tannins may be classified, respectively, as either gallotannins or ellagitannins [50]. Gallotannins are the simplest hydrolyzable tannins with a structure consisting of polygalloyl esters of glucose. The oxidative coupling of their galloyl groups converts gallotannins to the related ellagitannins [51].

Ellagitannins are the major nonvolatile extractives from oak heartwood (**Figure 3**). These oak phenolics have a specific structure, consisting of an glucose open-chain esterified at positions 4 and 6 by a hexahydroxydiphenoyl unit (HHDP) and a nonahydroxyterphenoyl unit (NHTP) esterified at positions 2, 3, and 5 with a *C*-glycosidic bond between the carbon of the glucose and position 2 of trihydroxyphenoyl unit [52]. Among ellagitannins, the monomers castalagin and vescalagin

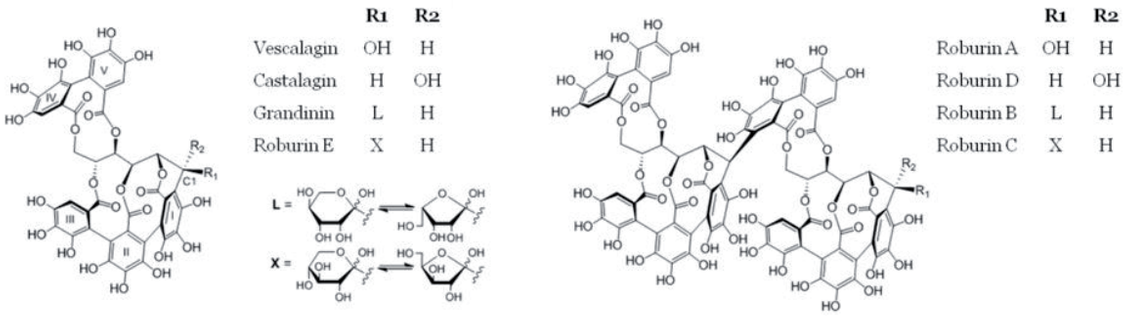


Figure 3.
Chemical structure of main ellagitannins present in oak wood.

Treatment	Species	Monomers		Pentosylated monomers		Dimers		Pentosylated dimers		Total ellagitannins	References
		Castalagin	Vescalagin	Roburin E	Grandinin	Roburin A	Roburin D	Roburin B	Roburin C		
Untreated wood	*Quercus robur*	5.82–27.50	1.76–23.90	0.69–13.70	1.00–10.40	0.39–6.64	0.95–5.34	0.44–4.67	0.47–6.29	13.47–91.02	[54, 56–59]
	Quercus petraea	1.63–11.76	1.05–8.01	0.78–4.44	0.76–5.47	0.13–2.05	0.17–3.27	0.29–2.41	0.06–2.25	5.87–34.41	
	Quercus alba	1.19–5.29	0.70–2.83	0.29–1.38	0.38–2.17	0.31–0.70	0.08–0.67	0.13–0.83	0.04–0.54	3.48–13.14	
Seasoned wood	*Quercus robur*	1.43–13.00	0.85–10.60	0.77–9.20	0.36–6.15	0.09–1.91	0.18–2.52	0.09–0.48	0.14–1.72	3.93–43.97	[53, 55, 56, 60–62]
	Quercus petraea	0.90–15.91	0.39–11.76	0.39–7.98	0.12–5.80	0.05–2.73	0.02–2.58	0.04–1.84	0.01–1.97	1.98–39.77	
	Quercus alba	0.41–4.45	0.15–6.44	0.15–2.30	0.07–1.81	0.03–0.40	0.02–0.84	0.02–0.79	0.01–0.20	0.89–8.93	
Toasted wood	*Quercus robur*	3.60–5.44	0.89–1.15	1.80–2.39	0.28–0.66	0.41–0.47	0.45–0.50	0.17–0.20	0.12–0.19	7.72–11.00	[53, 60, 62, 63]
	Quercus petraea	1.75–3.79	0.36–1.46	0.09–2.23	0.13–0.59	0.20–0.50	0.16–0.44	0.10–0.22	0.03–0.17	3.53–8.96	
	Quercus alba	0.21–0.44	0.08–5.28	0.04	0.02	ND	0.04	ND	0.01	0.55–5.72	

All values are displayed in mg/g of wood. ND, not detected.

Table 2.
Ellagitannin concentration in untreated, seasoned, and toasted oak wood from the main Quercus *species used in cooperage.*

largely predominate in oak wood, representing from 40 to 65% by weight of total ellagitannins [53–58] (**Table 2**). Six additional ellagitannins have been identified in oak wood: the lyxose/xylose-bearing monomers grandinin and roburin E, the dimers roburins A and D, and the lyxose/xylose-bearing dimers roburins B and C [64].

Since ellagitannins are very soluble in wines and spirits, with a high reactivity, their levels in oak-aged beverages are much lower than what could be expected. When comparing both main monomers, vescalagin presents a more polar configuration that confers it a lower stability in hydro-alcoholic solutions [65]. From a sensory point of view, their level and profile may affect the astringency and bitterness of wine [66].

The level of ellagitannins in oak heartwood depends on the botanical species, the geographical origin, the single-tree variability, the sampling position in the tree, the grain, and the processing of wood in cooperage, notably the type and length of both seasoning and toasting periods.

3.1 Influence of botanical species

Among the more of 150 oak species classified in the genus *Quercus*, the most frequently used in cooperage for winemaking are *Quercus robur* (pedunculate oak) and *Quercus petraea* (sessile oak), both growing in Europe, and *Quercus alba*, commonly known as American white oak, growing in the United States [5]. American oaks differ from European species not only because of their mechanical properties (higher density and resistance and lower porosity and permeability) [60] but also for the chemical composition of their phenolic fraction. Ellagitannin concentration is generally lower in *Q. alba* than European species, which in turn show a greater ellagitannin content in pedunculate oak than in sessile oak (**Table 2**) [53, 55–58].

3.2 Influence of geographical origin

Until recently, French and American oak forests have been the quintessential source of wood for cooperage. Meanwhile, over the last few years, a huge number of studies on pedunculate and sessile oaks from different European origins (Hungary, Poland, Russia, Romania, Slovenia, Spain, Ukraine, and Moldova, among others) confirm their prospective use for maturation of quality wines [60]. Oaks from these new European origins appear to present ellagitannin concentrations halfway between French and American oaks [5, 58].

3.3 Influence of single-tree variability

The width of oak wood rings ("grain") is of great importance for the choice of oak wood for barrel and cask making, since it influences the wood chemical composition and affects the contribution of oak aging to wine quality. The higher the grain size, the larger the amount of ellagitannins released and the faster that release [67]. Furthermore, the grain size also exerts an effect on the oxygen transfer ratio (OTR): the smaller the grain size, the greater the OTR, and the faster the wine maturation [68].

3.4 Influence of cooperage operations

Fresh wood cannot be directly used in winemaking, due to the great percentage of humidity (up to 70%), an excess of phenolic compounds, and a shortage of aromatic constituents. Oak wood conditioning in cooperage includes two stages that will determine the enological quality of wood. Both seasoning and toasting affect

the structure and final chemical composition of the wood that is going to be in contact with wine.

Seasoning allows, not only reduction of humidity in wood, but also fiber contraction and wood maturation. During this process, an important decline of ellagitannin content is observed due to different physical, chemical, and biochemical mechanisms involved: stave leaching by rain, hydrolytic oxidative degradation, polymerization, and fungal enzymatic activity [56]. These phenomena occur particularly in the surface of wood and, in a lesser degree, but uniformly, in the inner wood [53]. Among the different oak wood seasoning methods, natural seasoning in open air seems to be more effective than mixed and artificial methods in reducing the excess of ellagitannins [56].

Toasting also induces an important modification of wood chemical composition, including an additional decline of the ellagitannin content. During toasting, castalagin is mainly oxidized in dehydrocastalagin, whereas its diastereomer vescalagin is reduced in deoxyvescalagin [69]. Similar deoxy- and dehydro-derivates have been observed for roburins A and D, respectively.

Ellagitannin degradation, and in turn their sensory impact on wines, may be modulated by changing the toasting thermal profile (temperature and length) [5]. In this sense, an ever-widening range of toasting levels is available at cooperages for all oak wood products. The higher the toasting level, the greater the ellagitannin decomposition, via dimerization and hydrolysis reactions, as well as formation of copolymers with cell-wall components [64].

Recently, new compounds that showed [M-H]-ion peak at *m/z* 1055.0631 (compound A) and at *m/z* 1011.0756 (compound B) have been identified as a result of thermodegradation of ellagitannins. The A compound corresponds to castacrenin E which is the oxidation product of castacrenin D, a vescalagin with an additional aromatic ring (gallic acid) to the C-1 through a C–C bond. The levels of these compounds, found under experimental conditions and further searched in commercial oak wood, are dependent on both oak wood size and toasting method [70].

But, the extraction of oak phenolics into wine depends not only on the pool of potential extractible compounds originally present in wood, determined by the abovementioned factors, but also on the wine matrix, the aging length, and the exposed wood area to wine volume ratio.

4. From grapes to wine aging: phenolic compound evolution

During the grape ripening phase, the physiological and biochemical changes determine grape quality. The first period of grapes growth consists mostly of cell division and expansion, followed by a rapid growth phase during which the berry is formed and the seed embryos are produced. In this period, several compounds are accumulated in the berries, especially the tartaric and malic acids, conferring the acidity of the future wine. During the first growth period, several polyphenolic compounds increased like hydroxycinnamic acids in grapes' pulp and skin and tannins and catechins in the skin and seed. The most important changes in grapes composition happen during the second growth phase (the ripening stage). Grapes switch from small, hard, and acidic berries to larger, softer, sweeter, less acidic, flavored, and colored ones. The majority of the solutes accumulated during the first growing phase remain at harvest. During the second period, the malic acid is metabolized and used as an energy source, its proportion decreasing toward the tartaric acid concentration, which remains almost unchanged. In general, the chemical

composition of the final product is much more complex than in the raw material, due to the formation of new compounds [71].

4.1 Phenolic compound changes during winemaking

Winemaking techniques involve the extraction of juice from ripe grapes, fermentation with yeast, and changes in polyphenolic composition that occur due to the participation of these compounds in various reactions such as copigmentation, cycloaddition, polymerization, and oxidation. These reactions begin after grape crushing, followed by fermentation and aging, contributing to the sensory properties of wines, mainly color and mouthfeel sensation. The total extractable phenolic content in grapes is encountered in seeds (60–70%), in the skin (28–35%), and in the pulp (about 10% or less). In the seeds, the phenolic content may range between 5 and 8%, by weight [72].

The understanding of the relationship between the quality of a particular wine and its phenolic composition remains one of the major challenges in enological research. For example, the anthocyanin fingerprints of varietal wines are proposed as an analytical tool for authenticity certification [27]. Patterns of some classes of flavonoids are under strict genetic control, and their distribution varies considerably among different grape cultivars [73, 74].

Several factors impact the wine phenolic composition, including the "terroir," the grape variety and its degree of maturation before harvesting, or the winemaking process with its specific conditions of fermentation or aging [75]. Certain technological procedures, such as addition of sulfur dioxide (SO_2) and/or ascorbic acid prior to crushing the grapes, maceration, yeast strain utilization and alcoholic fermentation, oxidation, or adsorption, can also influence the levels of phenolics during the winemaking process [76]. The addition of SO_2 and pectolytic enzymes before fermentation caused an increase in color intensity, color stability, total phenolics, anthocyanins, catechin, and epicatechin in a red Italian wine [77].

In white grape musts, the predominant phenolic compounds are hydroxycinnamic tartaric acid esters as catechins and proanthocyanidins which are found mainly in their skins. The must fermentation of red wines is realized in the presence of both grape skins and seeds. During this process, phenolic compounds such as anthocyanins are subjected to various reactions, such as enzymatic oxidation, nucleophilic substitution, degradation, and cycloaddition of the carbonyl compounds leading to the formation of vitisins (A and B). These pyranoanthocyanins in red wine are mainly orange pigments. Moreover, the red wine color evolution and stabilization are mainly induced by the formation of polymerized pigments. The acidic hydrolysis of proanthocyanidins leads to the formation of flavan-3-ol unit or tannin oligomers with a carbocation in C4 position which can be attacks by positions C6 and C8 of another proanthocyanidins or an anthocyanin. This reaction will induce the modification of the condensed tannin polymerization degree or the formation of the polymerized pigment. These newly formed purple pigments induce the color modification of the young red wine. Moreover, polymerization through acetaldehyde between two condensed tannins or between condensed tannins and anthocyanins also occurs during the winemaking process and aging. The formation of these ethyl bridge compounds will also produce modification in the organoleptic properties of the wine and the color stabilization since the ethyl-bridged anthocyanin-tannin compounds also exhibit purple color [72]. During the red wine maturation in bottles, all these newly formed purple polymerized pigments will undergo slight oxidative reaction to slowly form some more orange pigments which together with pyranoanthocyanins are forming the color of old wine.

4.2 Using oak wood during winemaking

The winemaking process involves the alcoholic fermentation of must, often followed by malolactic fermentation (MLF). When MLF is completed, the wine is subjected to different clarification and stabilization treatments and/or is stored in oak barrels for aging for a variable period of time. MLF and aging in oak barrels are two enological processes which modify the composition and sensory characteristics of the wines [5, 78–80]. When oak wood derivatives like chips are added after fermentation, wines seem to have a greater aging potential compared to the wines fermented with chips due to their higher ellagitannin content and enhanced condensation reactions. On the other hand, color stabilization and tannin polymerization occur faster when chips are added during fermentation, resulting in shorter aging periods suitable for early consumed wines [81]. MLF in tanks may simplify the control of the process; however, the use of oak wood during the MLF stage affects the chemical and sensory attributes of wines. In red wines, MLF container plays an important role on proanthocyanidin and anthocyanin concentration and evolution as oxygen in small quantities favors polymerization reactions among anthocyanins and tannins. Wines performing MLF in tanks present a higher total proanthocyanidin concentration (5.8 g/L wine) than that of those which accomplished MLF in medium-toasted barrels (4.9 g/L wine). The major wine glucosidic anthocyanin, malvidin, showed as well greater levels in wines carrying out their MLF (33 and 26 mg/L wine, respectively, for tank and barrel MLF). Regarding ellagitannin concentration, their content is strongly influenced by both barrel toasting and MLF container. For instance, in the case of medium-toasting barrels, castalagin was found at concentrations twofold times higher (19 mg/L wine) when MLF was performed in barrels [79]. Concerning sensory results, the MLF strengthens the organoleptic preference of wine when it takes place in barrels [79, 80, 82]. In white wines, total ellagitannin concentration varied from 7.8 to 17.4 mg castalagin equivalents/L for wines performing MLF in tanks and barrels, respectively [83].

4.3 Evolution of phenolic compounds during aging

The phenolic composition of wine changes along the wine aging process reflects in the color and astringency level of the final product. From 1978 to 2005 vintage for Cabernet Sauvignon wine, phenolic compounds, total tannins, and total anthocyanins varied from 1735 to 2903 mg/L, from 1.3 to 2.2 g/L, and from 15 to 123 mg/L, respectively [29]. In general, the relative anthocyanin content decreases upon aging although this chemical modification is associated with a very clear change in color. This characteristic is often used as a quality standard for aged wines. One of the main factors responsible for anthocyanin loss is the storage temperature [84]. The majority of red wines aged are in contact with oak wood, whether in form of barrels or in form of oak wood derivatives. As a consequence, their phenolic composition changes due to the addition of oak wood extracted compounds. These compounds include hydrolyzable tannins (*C*-glucosidic ellagitannins), aromatic carboxylic acids, and several aldehydes. Regarding wine-air interactions, barrel structure allows a controlled entrance of oxygen, which is essential to the polymerization and the slight oxidative reactions between different types of flavonoids, leading to a modification of the organoleptic properties of the wine. Indeed, wood can affect wine composition and, consequently, organoleptic properties through different mechanisms. On the one hand, wine compounds can be adsorbed onto wood surface. On the other hand, compounds, such as ellagitannins, can be extracted from wood to the wine due to the hydro-alcoholic nature of the latter. Ellagitannins can take

part in oxidation reactions that may favor the polymerization reactions between flavanols and between flavanols and anthocyanins. Furthermore, they can directly react with these types of compounds giving rise to flavano-ellagitannins or anthocyano-ellagitannins [85]. The formation of flavano-ellagitannins and the *β*-1-*O*-ethylvescalagin in red wines aged in oak barrels has been reported. The ellagitannin concentrations fluctuated between 4 and 8 mg/L, being castalagin the ellagitannin with the highest concentration, followed by mongolicain A [86]. As a consequence, ellagitannins can modulate wine astringency and color through interactions with these compounds. Strong correlations have been observed between ellagitannin concentration and both antioxidant capacity and astringency sensation [5, 63, 78]. The amount of ellagitannins released into the wine depends on the content in the oak wood barrel, which in turn is dependent on several factors (Section 3). For instance, after 12-month aging with woods, the total ellagitannin level revealed a large diversity of concentrations ranging from 6.3 to 26.1 mg of ellagic acid/L wine. The wine with heavy toast woods and the wine with low toast woods presented, respectively, the less and the highest ellagitannin concentrations [78]. Storage with oak can also cause a decrease in anthocyanins, catechin, and epicatechin but an increase in total phenolic content and a stabilizing effect on color [77].

Besides the winemaking process, and oak wood aging, wine can be further exposed to oxygen during aging in the bottle, depending on the oxygen permeability of the closure. Because of the extremely low rates of oxygen ingress through a closure, this form of oxygen exposure has been referred to as nano-oxygenation. Oxygen transmission rates (OTR) of wine closures may vary widely depending on closure type and strongly influence the evolution of white and red phenolic composition and astringency during bottle aging [87].

5. Sensory impact of phenolic compounds in wine

"In-mouth" sensory properties of red wines encompass multiple interacting sensations such as acidity, sweetness, bitterness, retronasal aroma perception (flavor), viscosity, warmth, and astringency. Among these, the sensation of astringency and the taste of bitterness are related to phenolic compounds.

Bitterness perception is a taste recognition mediated by taste buds present in the tongue papillae. Each taste bud, consisting of approximately 50–100 taste receptor cells, is innervated by multiple taste fibers that transmit nervous signals to the brain [88]. In humans, each bitter receptor cell contains approximately 25 bitter G protein-coupled receptors encoded by a TAS2R gene family. It was evidenced by Soares and colleagues [89] that different phenolic compounds activate distinguished combination of TAS2Rs: epicatechin stimulated three receptors whereas procyanidin trimer only one. In general, in wines containing a large number of polyphenols, the taste of bitterness is attributed to flavan-3-ols and their polymers, although it is also able to be elicited by some flavonols [90], hydroxycinnamates, and benzoic acid derivatives [91].

While bitterness is a gustatory sense recognized by nervous signals, astringency is an oral sensation involving dryness and puckering [92]. According to the American Chemical Society, astringency refers to "the complex of sensations due to shrinking, drawing or puckering of the epithelium as a result of exposure to substances such as alums or tannins" [93]. It has been classically postulated that tannins possess the ability to interact with salivary proteins, with or without precipitation of the corresponding complexes [94]. In fact, the name of "tannins," originating from "tanning" of leather, has been used over decades for their

capability of binding with proteins. The mechanisms of tannin-protein interactions involved different types of interaction such as the hydrophobic interactions, which are the predominant mechanisms involving the hydrophobic nature of the condensed tannin carbon skeleton and the apolar regions of the proteins. Together with hydrophobic interactions, some hydrogen interactions also occur between the carbonyl function of proline and the hydroxyl functions of phenols as well as some ionic interactions. This mechanism and thus the final astringency of wine are influenced by many factors, such as the structure and amount of condensed tannins in the wine as well as the composition of the wine matrix [95]. Indeed, the intensity and the quality of the astringency perception are influenced by the concentration of condensed tannins [96], their degree of polymerization [97], their percentage of galloylation [98], and prodelphinidins [99]. The matrix, on the other hand, impacts the perception according to its acidity [100], its ethanol concentration [101], and the presence of macromolecules such as polysaccharides. Fontoin and co-workers demonstrated that the astringency sensation of grape-seed oligomer tannins decreased with increasing pH and the percentage of ethanol [100]. For example, Cabernet Sauvignon wines having a mDP between 2.0 and 4.0 were characterized as mellow and slight astringent. Meanwhile, a rougher sensation (tannic) was perceived for wines with a mDP higher than 4.0. [102]. The analytical determination of the proanthocyanidin content and the type of subunit that is dominant in tannin chains might be a valuable tool for astringency estimation during wine aging [103]. Astringency intensity is influenced by the source of proanthocyanidin (seed or skin) and by well-defined proanthocyanidin fractions (oligomeric or polymeric). Polymeric seed fraction was perceived more astringent than the monomeric/oligomeric one, whereas polymeric skin fraction was characterized less tannic than the monomeric/oligomeric skin fraction, indicating a negative relationship between astringency intensity and % of prodelphinidins [104]. The presence of epigallocatechin units in the proanthocyanidins has been shown to lower the "coarse" perception through the increase of the degree of B-ring trihydroxylation. Furthermore, seed fraction with a higher proportion of galloyl group and a lower mDP was perceived to be bitterer than the skin fraction [105]. Both the interflavanoid bonds and stereochemistry of subunits impact bitterness sensation: catechin-(4–6)-catechin dimer was bitterer than both catechin-(4–8)-catechin and catechin-(4–8)-epicatechin [91].

Moreover, astringency sensation perceived always reduces with the increasing saliva volume flow rate. A linear correlation was found between protein concentration and tannin-binding affinity. The saliva proteins, including PRP family (acidic, basic, and glycosylated), α-amylase, statherin, histatins, and mucins, show diversified ability to interact with tannins [106]. Some proteins are specifically bound to astringents. For instance, tannins and alum precipitated PRPs, while acid and alum precipitated mucins [107, 108].

Ellagitannins (hydrolyzable tannins) impart an oral sensation described as astringent at relatively low threshold concentrations spanning from 0.2 to 6.3 mmols by means of the half-tongue test in bottled water (pH 4.5). Due to their lower astringent taste thresholds, hydrolyzable tannins are usually perceived as more astringent than condensed tannins (1.1 μM for both castalagin and vescalagin, compared to 410 μM for catechin, 930 μM for epicatechin, 240 μM for procyanidin B1, 190 μM for procyanidin B2, and 200 μM for procyanidin B3) [66, 69, 109]. Among ellagitannins, the monomers grandinin and roburin E exhibited an astringent mouthfeel at the lowest taste thresholds (0.2 μM), whereas values for dimers ranged between 2.9 and 6.3 μM. Thus, the *C*-glycation of castalagin and vescalagin seems to favor the astringent sensation, while dimerization seems to reduce it [66].

When the same concentration of ellagitannins and skin and seed tannins was tested, the ellagitannins were perceived softer [104].

Interaction of ellagitannins with salivary proteins has been poorly investigated up to now, probably because of their lower wine content compared to condensed tannins. Even if perceived as more astringent, ellagitannins have been noted as poorer protein precipitants than condensed tannins [94]. Soares and co-workers [110] stated that ellagitannins act as multidentate ligands cross-linking different salivary protein units, via their galloyl moieties. It is noteworthy to mention that these units are responsible for the antioxidant ability of hydrolyzable tannins; thus when complexed with salivary proteins, the antioxidant capacity of ellagitannins may be significantly impaired. At higher concentration levels, the main eight oak ellagitannins have also been observed to provide the wine with a bitter taste [66].

Apart from tannins, other polyphenolic compounds present in wine have been related with the overall perception of astringency sensation or bitterness. Very recently, some works have provided evidence about the interaction of anthocyanins and pyranoanthocyanins with salivary proteins. Indeed, malvidin-3-*O*-glucoside, the major anthocyanin of wine, has demonstrated to interact with acidic proline-rich proteins (aPRPs) showing dissociation constants (K_D) calculated by NMR of 1.88 mM [111] that can be compared to those obtained for procyanidins (dimers B1–4 and trimer C2) (between 0.4 and 8 mM) [112]. In addition, Paissoni and colleagues [113] tested the interaction with saliva proteins of the three representative of wine anthocyanins (glucosides, acetylated, and cinnamoylated) proving that cinnamoylated anthocyanins are the most reactive and also those that present the lowest perception threshold in wine model solutions. More recently, another work showed that pyranoanthocyanins (pyranomalvidin-3-glucoside, pyranolmalvidin-3-glucoside-catechol, and pyranomalvidin-3-glucoside-epicatechin) can also able to interact aPRPs with K_D even lower (more affinity) than for anthocyanins (between 0.87 and 1.73 mM) [114].

Concerning bitter taste, malvidin-3-*O*-glucoside has also demonstrated to stimulate one member of the bitterness receptor family (TAS2R7) at micromolar levels (12.6 μM) [89]. With regard to flavanols, the addition of quercetin-3-*O*-glucoside (0.25–2 g/L) to white and red wines resulted in a noticeable increase of astringency and bitterness evaluated by sensory analysis. In general, wines were described as smooth-tasting before the flavonol addition and became more astringent, rough, green, dry, bitter, and persistent in presence of quercetin-3-*O*-glucoside [33].

6. Conclusions

There is no doubt that wine is an extremely complex medium and that polyphenolic compounds play an essential role on its final sensory properties. There is an inestimable chemical diversity of polyphenols in both grapes and wines. Each family can be present in free or conjugated forms, with different hydroxylation levels and substitutions or even forming adducts between them. Starting with the raw material, phenolic compounds in grapes can vary substantially depending on several factors as ripening, viticulture practices, environmental conditions, and varietal or genetic differences. Such is the case that each cultivar may be considered as "exclusive" and consequently, the resulting wine too. Anthocyanins (mainly present in skins) and flavan-3-ols and condensed tannins (mainly present in skins and seeds) are the most abundant polyphenols in grapes. On the one hand, anthocyanins are responsible of the color of red wines, and their profile can be used as an analytical tool for authenticity certification. On the other hand, flavan-3-ols and condensed tannins are key compounds due to their implication on color

stabilization and astringent and bitter properties. Finally, other phenolics as flavonols and hydroxycinnamic acids are mainly known for acting as copigments. Oak wood is commonly used during fermentation and/or aging of wines. The phenolic composition of oak wood will vary depending on species, geographical origin, and grain or wood processing. In quantitative terms, ellagitannins are the major phenolic constituents of oak wood, and their level and profile may affect the astringency and bitterness of wine. Winemaking produces important changes in polyphenolic composition. In fact, phenolics participate in several reactions such as copigmentation, cycloaddition, polymerization, and oxidation. Thus, new compounds as vitisins, ethyl-bridged anthocyanin-flavanol derivatives, or pyroanthocyanins are formed. Furthermore, wine aging in contact with oak wood affects the degree of complexity of phenolic compounds. In this sense, ellagitannins are actively engaged in oxidation reactions that favor the polymerization between flavanols and between flavanols and anthocyanins.

Overwhelming evidence has demonstrated that tannins (mostly condensed tannins), thanks to their ability to precipitate salivary proteins, are implicated on wine astringency. Astringency intensity, even if it is a multifaceted sensation complicated by a number of variables, is more influenced by the source of proanthocyanidin (seed or skin) and by well-defined proanthocyanidin fractions (oligomeric or polymeric). Up to now, ellagitannins' direct impact on astringency and bitterness sensation remains still unknown. One of the major limitations of the half-tongue test used to evaluate their sensory impact is the absence of contact between the ellagitannins and the entire oral cavity. Further studies are needed under wine conditions. Additionally, recent studies highlight that other phenolic compounds such as anthocyanins/pyranoanthocyanins or flavanols may also interact with salivary proteins and bitterness receptors. Thus, a new research line in the field of sensory properties linked to wine phenolic compounds sensory properties is opened.

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