applied sciences

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Review

Interactions between Polyphenols and Volatile Compounds in Wine: A Literature Review on Physicochemical and Sensory Insights

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Abstract: Wine polyphenols (PPhs) and volatile organic compounds (VOCs) are responsible for two of the main sensory characteristics in defining the complexity and quality of red wines: astringency and aroma. Wine VOCs' volatility and solubility are strongly influenced by the matrix composition, including the interactions with PPhs. To date, these interactions have not been deeply studied, although the topic is of great interest in oenology. This article reviews the available knowledge on the main physicochemical and sensory effects of polyphenols on the release and perception of wine aromas in orthonasal and retronasal conditions. It describes the molecular insights and the phenomena that can modify VOCs behavior, according to the different chemical classes. It introduces the possible impact of saliva on aroma release and perception through the modulation of polyphenols–aroma compounds interactions. Limitations and possible gaps to overcome are presented together with updated approaches used to investigate those interactions and their effects, as well as future perspectives on the subject.

Keywords: wine matrix; volatile organic compounds; polyphenols; interactions; volatility; hydrophobicity; orthonasal; retronasal; saliva; perception

Citation: Pittari, E.; Moio, L.; Piombino, P. Interactions between Polyphenols and Volatile Compounds in Wine: A Literature Review on Physicochemical and Sensory Insights. *Appl. Sci.* **2021**, *11*, 1157. https://doi.org/10.3390/app11031157

Academic Editor: Ioannis G. Roussis
Received: 31 December 2020
Accepted: 22 January 2021
Published: 27 January 2021

1. Introduction

Wine is composed of non-volatile and volatile chemical components, which are responsible for important oenological and sensory characteristics. Among them, polyphenols (PPhs) and volatile organic compounds (VOCs) are responsible for two of the main characteristics in defining complexity and quality of red wines and for the two main intrinsic drivers of red wine consumers' purchasing decisions: astringency and aroma [1–8].

Wine polyphenols are represented by non-flavonoids (i.e., small molecules such as benzoic and cinnamic acids) and flavonoids (i.e., flavan-3-ols, flavonols and anthocyanins) compounds. Among them, flavan-3-ols monomers [(+)-catechin and (-)-epicatechin], their oligomers and polymers (usually divided in condensed tannins or proanthocyanidins), and hydrolysable tannins (non-flavonoids polymers) are the most abundant in wine [9]. Condensed tannins are extracted from grapes and then modified during winemaking and aging processes [10]. Hydrolysable tannins are extracted from oak barrels or chips during aging or added as oenological tannins during winemaking processes [11].

The oenological interest in polyphenols is multifactorial, as they are responsible for wine color and its stability, for wine longevity thanks to their antioxidant activity, and for wine's oral characteristics.

The direct contribution of tannins to major oral sensations such as astringency and bitterness has been reviewed recently [12]. Being able to interact and precipitate proteins by forming noncovalent complexes, mostly correlated to conformationally accessible hydrophobic regions of both molecules [13–15], the interaction between astringent agents (i.e., tannins) and salivary proteins has been proposed as one of the main phenomena in

explaining wine astringency perception. Astringency is a complex sensation that involves several mechanisms. Initial steps imply a face-to-face stacking between the aromatic groups of polyphenols and the carbon–hydrogen skeleton of the pyranic rings of condensed tannins with surface-exposed amino acid residues of salivary proteins. These complexes, in subsequent aggregation and precipitation steps, cause a drying and grainy sensation in the mouth that decreases salivary lubrication between oral tissues and increases friction in the oral cavity [8,16–23]. This tactile nature of astringency has been investigated since 1954 [16]. Astringency has also been defined as a trigeminal sensation, since some phenolics are able to activate mechanosensors of somatosensory nerves located in the mouth and trigeminal nerve [24–27]. In addition to astringency, even if information is scarce [12], there is scientific evidence showing that polyphenols can be additionally responsible for the perception of bitterness in wine [8,28–32]. (Epi)catechin monomers are more bitter than dimers (procyanidins B3 more bitter than B4, and B6) and trimers (trimers C1 and C2) [29]. Recent results have suggested that several phenolic compounds, such as pentagalloylglucose hydrolysable tannins, (-)-epicatechin, procyanidin trimer C2, procyanidin B2-3-O-gallate, and some ellagitannins activate bitter taste receptors [31,32]. Aprioristically, astringency, and bitterness represent repulsive sensations for consumers, but when well balanced with the other oral sensations, they can add structure/body and persistence to red wines [33] and be perceived as strongly linked to its quality [6].

More than 800 VOCs have been identified in wines, with a concentration range varying from hundreds of mg/L to µg/L or ng/L levels [34]. However, only some of them work as odor-active molecules, mainly in concentrations above their sensory perception threshold but also because of synergistic or masking effects at peri/sub-threshold levels [35–40]. In wine, VOCs are divided in four groups, each of them containing several chemical classes: (i) grape and varietal VOCs, which are present in the cells of the berries as free volatile molecules (e.g., methoxypyrazines, varietal thiols, and monoterpenoids) or as glycosidic, aminoacidic/peptidic precursors (i.e., unsaturated fatty acids, phenolic acids, S-cysteine conjugates, dimethylsulfide precursors, carotenoids, and glycoconjugates); (ii) pre-fermentative VOCs, which are formed during the first processing steps such as crushing, pressing, and skin contact, or by thermal, chemical, and enzymatic reactions in the must (e.g., six carbon atoms (C6) aldehydes and alcohols); (iii) fermentative VOCs, which include yeasts and bacterial by-products responsible for the background aroma of any wine and obtained from the main biochemical transformations of alcoholic and/or malolactic fermentations (e.g., esters, higher alcohols, volatile fatty acids, aldehydes and ketones, fermentative sulfur aroma compounds); (iv) maturation/aging VOCs, which refer to the aroma bouquet that develops during wine aging and/or extracted from wood barrels (e.g., furanic compounds, lactones, phenolic aldehydes, volatile phenols, phenyl ketones).

When volatilized from the wine matrix, these molecules can reach—through the orthonasal (nose) and retronasal (mouth) paths—the olfactory bulbs and trigger receptors stimulating the perception of the corresponding odor whose intensity and quality mostly depend on their nature and concentration. The different chemical classes of volatiles are characterized by distinct chemical and physicochemical properties affecting their binding and release behavior. The volatility and solubility of aroma compounds represent the two main physicochemical properties driving the partitioning of the volatile substances between the liquid and the gas phases. This is strongly influenced by other wine constituents present in the medium, such as simple molecules (ethanol, sugars, glycerol) and macromolecules (proteins, polysaccharides, and polyphenols) [41–44]. Winemaking procedures and stabilization treatments (maceration, filtration, fining), as well as aging processes (polymerization and precipitation), or even the grape variety, impact on macromolecules involved in these interactions, with potential effects on mouthfeel balance and perceivable olfactory profile.

To date, the interactions between aromas and polyphenols are not deeply studied, even though the topic is of great interest in oenology. Moreover, the subject is of transversal concern in the food field, since polyphenols are largely present in other food matrices;

moreover, because of their antioxidant and healthy properties, knowledge about this family of compounds is of wide interest.

Nowadays, the population is more aware of health problems and there are new concerns about climate change, to the point that an ever-increasing number of consumers are advocating the reduction/elimination of consumption of animal products and turning toward healthier and more sustainable plant-based foods. These products can represent a valid alternative, but unfortunately, due to their bitterness/astringency characteristics, they are often discarded by the consumer. Consequently, all scientific knowledge that contributes to understanding how to smoothen/mask these sensations are welcomed by scientists and food technologists/engineers working in the food field.

Bilateral sensory effects have been suggested by different studies carried out with different approaches, estimating and/or measuring the sensory impact of the interactions between wine PPhs and VOCs both in orthonasal and retronasal conditions by in vitro or in vivo studies on aroma release. Exploring the influence of aromas on mouthfeel perceptions of Chardonnay wines, it was found that it is important to consider both volatile and non-volatile wine fractions when attempting to establish the relationship between chemical composition and mouthfeel as the volatile fractions, in some cases, influence the mouthfeel sensations [45].

From a sensory perspective, we recently explored the olfactory–oral cross-modal interactions through sensory and chemical characteristics of a wide set of Italian red wines showing different olfactory and oral features. The results suggested that olfactory cues might play modulation effects on the perceptions of in-mouth sensations, including some astringency sub-qualities, sweet and bitter tastes, supporting the expectations of multimodal sensory interactions between sensations elicited by VOCs and PPhs during red wine tasting [46].

From a physicochemical perspective, special attention has been paid, as of late, to understanding what happens in retronasal simulated and real conditions, reproducing—by model mouths or by real in vivo settings—the aroma release during wine tasting. These approaches are based on the evidence that, together with other in-mouth variables such as wine sip volume [47], salivary components can interact not only with wine polyphenols but also with VOCs, significantly affecting their release [48,49].

However, depending on the methodological approaches, the wine matrix or model solutions compositions (e.g., ethanol content), the tested VOCs, and tannins types and corresponding concentrations applied, different results were found. These results are not easy to compare and, apart from short sections on polyphenol impact on VOCs [43,50], no reviews focus on this topic.

With that in mind, the main aim of the present review is to build a comprehensive framework of the main physicochemical and sensory effects of polyphenols on the release and on orthonasal and retronasal sensory perception of wine volatiles. For this purpose, we also tried to highlight the limitations and possible gaps to overcome, as well as possible future perspectives.

2. Molecular Insights

The pioneering research conducted on wine PPhs–VOCs interactions and, consequently, on the effects of polyphenols on aromas release dates to the late 1990s [51]. The authors evaluated the influence of phenolic compounds such as (+)-catechin, epicatechin, and a highly condensed tannin fraction (extracted from wine) on some linear or aromatic wine aromas with different hydrophobicity, which were added in 10% hydroalcoholic or wine model solutions. A dynamic exponential dilution technique and ^{1}H NMR to probe the interactions at the molecular level were used. General decreases of volatility for isoamyl acetate, ethyl hexanoate, benzaldehyde, and limonene were correlated to increasing concentrations of (+)-catechin (0–12 g/L), with the latter less retained at low catechin concentrations (0–5 g/L). Unlike catechin, the tannin fraction induced a slight decrease of benzaldehyde release and a salting out of limonene with no effect

on the two esters, thus suggesting that monomeric or oligomeric/polymeric PPhs can differently impact volatility. At the molecular level, the NMR study focused on aromas–monomeric polyphenols interactions. Similar weak bimolecular bindings were reported for the intermolecular complexation of isoamyl acetate, ethyl hexanoate, and benzaldehyde with catechin. Both catechin and epicatechin showed a higher affinity to benzaldehyde than for 3,5-dimethoxyphenol. Monomers had a higher affinity for benzaldehyde than for themselves.

In subsequent work, Jung and collaborators [52], applying ^{1}H NMR spectroscopy analyses, have explained the supramolecular assembly at the base of specific VOCs–PPhs interactions by noncovalent bonds. The authors have shown that the addition of gallic acid to model solutions containing 2-methylpyrazine, vanillin, or ethyl benzoate has reduced their volatility mostly due to π–π stacking of the galloyl ring of the phenolic compound with the aromatic ring of the odorant molecule, with secondary hydrogen-bonding effects helping in stabilizing the complex and enhancing the specificity, as represented in Figure 1. Moreover, the supramolecular complexation also depends on the structural nature of the VOC, with 2-methylpyrazine and vanillin interacting more strongly than ethyl benzoate.

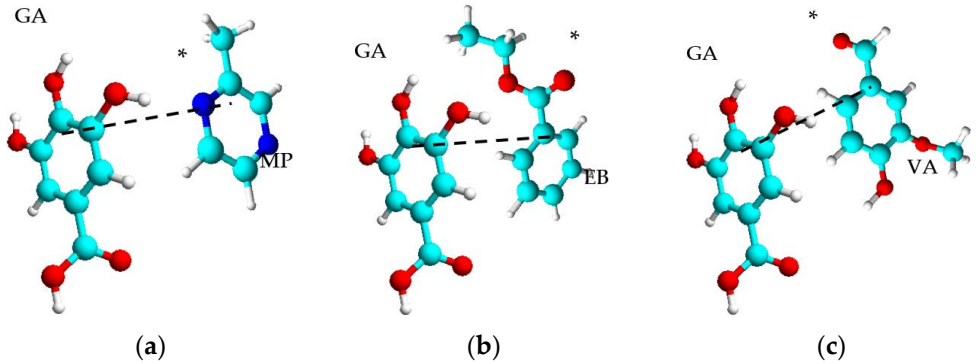

Figure 1. Proposed mechanisms illustrating π–π stacking interactions (black dotted line) and hydrogen bonding (* suggested involved atom) of the galloyl ring of the phenolic compound with the aromatic ring of the odorant molecule: (**a**) gallic acid (GA) and 2-methylpyrazine (MP); (**b**) gallic acid and ethyl benzoate (EB); (**c**) gallic acid and vanillin (VA) (adapted from Jung and co-workers [52]; created with ACD Labs, Freeware, 2020).

These molecular insights have represented the starting point for further research conducted in the last decades by means of updated approaches/methodologies, and they aimed at understanding how the volatility and sensory perception of wine aromas could be affected by the presence of polyphenols.

The two studies cited suggested the hydrophobicity of both PPhs and VOCs as a main driving force in explaining bimolecular aroma–phenolic compound interactions, which were then significantly involved in the modification of VOCs release. Supporting results were obtained by a different approach [53]. The authors prepared model solutions of ethyl benzoate (2 to 16 mg/L in 1% ethanol–water mixture) and 2-methylpyrazine (60 to 300 mg/L in water) and investigated their interactions with gallic acid (10 mM) through HS-SPME/GC-MS and sensory analysis. Their results are aligned to molecular evidence: the addition of gallic acid significantly decreased the headspace partitioning of the two VOCs and their perceived aromatic intensity.

The variation in VOCs response to polyphenols depends not only on the concentration or on the chemical characteristics of both VOCs and PPhs but also on other matrix characteristics such as ionic strength and ethanol content. These variables can impact polyphenols' structure, aggregation, solvation, colloidal state [54], and involvement in "salting-out" and/or hydrophobic phenomena that are likely to impact their interactions with VOCs. All the mentioned factors may affect how PPhs interact with VOCs and consequently, their release and perception.

3. Polyphenols Effects on VOCs Release

Different studies have investigated the effects of polyphenols on wine odor. In most of the studies, static or dynamic HS-SPME/GC-MS or FID analyses have been applied to investigate aroma release from the matrix. Some of them have combined chemical and sensory experiments to study and compare the two effects, while only a few studies performed GC-O (Gas Chromatography-Olfactometry) analysis, and no data regarding the use of electronic nose are reported in the literature.

The different analytical methodologies were applied to model solutions and real wines with significant compositional differences or deodorized/reconstituted wines.

These different approaches, notwithstanding their advantages and drawbacks, tested the behavior of several VOCs belonging to different chemical classes. Different results, sometimes contradictory and difficult to interpret, have been reported. To compare these results, they were summarized in Table 1, which was organized listing VOCs belonging to the same chemical class accordingly to their increasing hydrophobicity expressed as $\log P_{\text{octanol/water}}$.

Considering that ethanol can affect PPhs structure/colloidal state and solubility, as well as VOCs solubility, release, and perception, in Table 1, we have also reported its concentration used in the studies. However, since in all relevant studies, ethanol levels ranged between 10 and 12% (*v/v*), it is difficult to hypothesize a significant effect on both PPhs and VOCs chemical characteristics. In the literature, differences in PPhs particle size and colloidal state [54,55], as well as in VOCs solubility, release, and sensory perception have always been observed at different ethanol levels when higher than 2% (*v/v*) [56], and references there in.

As further information, in Table 1, we also specified the type of matrix as well as the nature and/or the content of PPhs that were tested in the different studies to consider different wine systems. Grape tannins and polyphenols extracted from grape skins or seeds are characterized by different properties. The highest concentration of tannins in grape berry derives from grape skins, which differ from seed tannins in terms of polymerization degree (DP) and amount of gallates [57]. The average DP for skin tannins is higher than the average DP for seed tannins, which tend to be in monomeric form rather than polymerized. In addition, real wines (i.e., white, young red, and old red wines) are widely different in terms of polyphenolic characteristics. They differ in terms of total phenolic content, which can vary from around 200 mg/l of gallic acid equivalents (GAEs) in white wines to 2000 mg/L in young-reds and 3500 mg/L or more in aged-red wines [10]. Moreover, older red wines are normally characterized by a decrease of several low molecular weight phenolic compounds and anthocyanins and higher concentrations of polymeric pigments, while younger wines have higher concentrations of anthocyanins and other phenolic compounds [58–60].

Considering all the described frameworks, in the following paragraphs, we attempted to link and critically discuss the observed effects of polyphenols on VOCs release.

3.1. Effects on Terpenoids

Terpenoids are varietal compounds essentially coming from grapes as enzymatically produced secondary metabolites of the terpenoid pathway and existing as saturated/unsaturated and cyclic/acyclic hydrocarbons that can contain alcohol, aldehyde, ketone, ester, ether, and acetal functionalities. These compounds are also present as terpene glycosides that can be hydrolyzed to free volatile aglycones in different phases of wine production and life, mainly by yeast glycosidases during fermentation, and by the acidic conditions during wine storage. From a sensory point of view, terpenes are largely responsible for citric, floral, and balsamic aromas [61]. The effect of polyphenols on monoterpenoids volatility has been mostly observed in deodorized/reconstituted real wines [62], and linalool in model wine solutions [63]. According to data reported in the literature and summarized in Table 1, a common trend can be noted. Indeed, independently from the VOC hydrophobicity within the tested range ($2.67 \leq \log P \leq 3.47$) and from

the type of matrix representative of different PPhs compositions, the release of the tested terpenoids decreases at increased tannin concentrations [62,63]. Interestingly, considering the real wine matrices, it can be noted that while the aged-red wine has significantly retained terpinen-4-ol, β-citronellol, and nerol, in the young-red wine, a significant retention effect has been observed for all the terpene compounds, including α-terpineol and linalool [62]. Based on results by Dufour and Bayonove [51] suggesting that monomeric or oligomeric/polymeric polyphenols can differently impact aromas volatility, this behavior could be linked to the lower concentration of polymeric polyphenols [64] of young-red wines compared to aged ones. Considering the sensory importance of these odorants and that they act in combination with each other [39], it could be hypothesized that the PPhs composition of wine could impact the olfactory perception of monoterpenes.

The results of a recent study [65] referred to a possible sensory impact on terpenes perception as an effect of the presence of gallic and *p*-coumaric acids. Independent of phenolic acids composition and concentration, both acids tended to decrease the production and volatilization of free terpenes during fermentation, with *p*-coumaric acid showing a greater restraining effect. Studies of linalool and its terpene glycosides have shown that the main driving forces in their interactions with these phenolic acids are dispersive interactions and hydrogen bonding. Sensory analyses confirmed a decrease in the perception of some aromatic notes related to the presence of free terpenes (e.g., tropical, and sweet fruit aromas), albeit not enough to be statistically significant. The authors concluded that the matrix effect of phenolic acids can effectively control the release and modulate the global feature of wine aromas.

3.2. Effects on Esters

Esters are mainly produced by yeasts during alcoholic fermentation. Their concentration and relative proportion are strongly influenced by several fermentation parameters (i.e., oxygen level, fermentation temperature, yeast strain characteristics, yeast assimilable nitrogen levels). From a sensory point of view, they are considered as one of the most important families of compounds lending fruity characters in wines. In most of the GC-O studies present in the literature, esters are included in the list of the compounds with the highest odor active value (OAV) [10].

The influence of polyphenols on esters release and, in some cases, on their perception, has been investigated on several compounds belonging to this family, as reported in Table 1. Some observations can be made despite the absence of a clear and unique trend that could be explained by the wide range of polarity within the group of esters tested ($1.26 \leq \log P \leq 5.71$). Around 2.85 seems to be a cut-off log*P* value; indeed, there is a switch of esters behavior, depending on the PPhs levels in the matrix. Esters characterized by lower log*P*s tended to a lower release at smaller PPhs levels, while they were raised at higher ones. This suggests that for poorly hydrophobic esters, there is the prevalence of a retention phenomenon at low PPhs concentrations and a tendency of salting-out effects at higher PPhs concentrations. Alternatively, the release trend of esters characterized by higher log*P*s decreased independently from the PPhs level, suggesting that hydrophobicity represents the main driving force of highly hydrophobic esters release. The only exception to this behavior is the opposite trend observed for ethyl octanoate in oak barrel aged red wine. Both monomers, catechin and gallic acid, tested at 2 g/L, did not affect the release of the more polar esters (ethyl isobutanoate, ethyl butanoate, isoamyl acetate), while the release of the hydrophobic ethyl octanoate decreased in the presence of catechin ($\log P = 1.37$) but not in the presence of gallic acid ($\log P = 0.59$), suggesting that the hydrophobicity of PPhs could be significant [66]. In the case of ethyl 2-methyl butanoate, unlike ethyl butanoate, the sensory impact of release differences determined by GC-MS was confirmed by GC-O data. In fact, the olfactometric score increased when the volatile matrix of a white wine was replaced by the volatile extract of an aged red wine [67]. The results from sensory assessment are not completely in line with instrumental ones with ethyl octanoate,

ethyl isobutanoate, and ethyl butanoate being perceived as less intense in the presence of catechin at 2 g/L [66].

Based on results reported above and on the knowledge that esters act synergistically in imparting fruity notes to wine [39], the observed changes of most hydrophobic esters at increased levels of PPhs could have a significant sensory impact on wine fruity aroma. In addition, the observed decreases of isoamyl acetate, a molecule having an important olfactory role in wine, could be significant [39].

3.3. Effects on Alcohols

Alcohols are a group of volatile compounds mainly produced as fermentative by-products of yeasts amino acids metabolism via the Ehrlich pathway. Their production is strongly influenced by several fermentation parameters (e.g., fermentation temperature, yeast strain characteristics, yeast assimilable nitrogen levels, turbidity) [10]. From a sensory point of view, except for β-phenylethanol, which was described with floral/rose notes, the other alcohols are described in fusel, oily, alcoholic, ethereal terms. Some authors have suggested that alcohols may contribute not only to the vinous aroma but also to its aromatic complexity of wines. However, at high concentrations, they can mask certain aromas [39,68].

Based on results reported in the literature and schematized in Table 1, it seems difficult to draw trends or conclusions. The entire set of compounds shows low hydrophobicity ($0.76 \leq \log P \leq 2.03$), which could be a reason for other variables driving their interactions with PPhs. Looking at β-phenylethanol, a "salting-out" effect at high tannins concentrations and independently from their nature was observed [63]. Considering its relatively low hydrophobicity ($\log P = 1.36$) and the presence of an aromatic ring on its structure, the formation of π–π interactions of the galloyl ring of the phenolic compound with the aromatic ring of the odorant molecule might explain its reduction in volatility at low tannins concentration [51,52]. At high tannins concentrations, it could be possible that the decrease in the potential binding sites for odorants has occurred because of the low ethanol concentration (10% *v/v*) contained in the model solutions. Indeed, it has been shown that at relatively low ethanol concentrations (8–10% *v/v*), more tannins self-aggregation occurs, making them less available to interact with aroma compounds [54,55,69]. This could explain the two aromatic alcohols showing opposite trends at the corresponding lowest PPhs levels: benzyl alcohol raised over the headspace of a real matrix (oak barrel aged red wine) containing 12% *v/v* ethanol and TPC = 230 [62]; β-phenylethanol lowered in a model wine solution with 10% *v/v* ethanol and 0.5–1 g/L of skin tannins extract [63].

From a sensory perspective, it is not possible to speculate on the impact of the observed variations.

3.4. Effects on Volatile Phenols

Volatile phenols are a family of volatiles that comprise (i) volatile phenols formed during the fermentation process and released from grape-derived glycosides, (ii) volatile phenols formed during the fermentation process by the metabolism of hydroxycinnamic acids, precisely by yeasts of the genus *Brettanomyces/Dekkera*, through the decarboxylation of *trans* ferulic and *trans p*-coumaric acid, and (iii) volatile phenols extracted when storing wine in contact with toasted oak wood [70–72]. While some of them contribute positively to wines aroma complexity (i.e., guaiacol and eugenol), others (i.e., 4-ethylphenol, 4-vinylphenol, 4-ethylguaiacol, and 4-vinylguaiacol) might be involved in the appearance of unpleasant notes. In particular, while low concentrations of volatile phenols extracted when storing wine in contact with toasted oak wood by the metabolism of yeasts of the genus *Brettanomyces/Dekkera* (i.e., 4-ethylphenol and 4-ethylguaiacol) can contribute to wine aroma complexity, high concentrations of these two VOCs are indicative of Brett character, which is one of the most widespread red wine defects. However, depending on consumers' expectation of a particular wine, the presence of Brett character can be considered either negative or positive. For example, ethylphenols can be found at concen-

trations much higher than their detection thresholds in certain very expensive French red wines, where they may be considered part of the wine's style, as an expression of terroir and part of nature, rather than a fault [10]. Consequently, it is important for winemakers to manage the increase and/or the production of these VOCs and to understand which conditions favor their perception or otherwise. For this reason, the influence of polyphenols on the release of different volatile phenols ($1.32 \leq \log P \leq 2.61$) and in some cases on their sensory perception has been evaluated both in model solutions and real wines (Table 1). Except for guaiacol and eugenol, which are characterized by the lowest log*P* values and better volatilized in the presence of grape tannins at 0.5–1.5 g/L [69], the release of volatile phenols was essentially reduced by PPhs.

Important results regarding the effects of polyphenols on the two volatile phenols 4-ethylphenol and 4-ethylguaiacol in model solutions have been understood from a recent study [73]. The authors showed that at increasing polyphenols concentration, a significant and linear decrease in the volatility of these two VOCs has been observed due to π–π interactions. Additionally, performing sensory tests, they showed that the unpleasant and characteristic "phenolic" taint, due to the presence of 4-ethylphenols [70,74,75], has been significantly higher in the trials with lower polyphenol content, highlighting a consistent and significant masking effect of polyphenols on the perception of the Brett character. This result may be of great interest in winemaking, since controlling the concentration and the sensory impact of these compounds in wine is an always current topic in oenology.

Table 1. Aroma compounds affected by the presence of polyphenols in wine matrix with different characteristics: release and orthonasal sensory perception trends.

Aromas Characteristics				Matrix Characteristics				Effects		Ref.
Compound	**Descriptors ***	**Concentration**	**logP (o/w) ***	**Type of Matrix**	**%Ethanol (*v*/*v*)**	**Added Tannins**	**Tannin Content**	**Effects on Release**	**Effects on Orthonasal Perception**	
MONOTERPENOIDS										
α-Terpineol	Pine, terpenic, lilac, citrus, woody, floral	0–0.433 mg/L	2.67	White wine Young-red wine Oak barrel aged-red wine	12		TPC = 230 TPC = 1820 TPC = 2142	↓ (ns) ↓ ↓ (ns)		[62]
Linalool	Citrus, floral, sweet, bois de rose, woody, green blueberry	1 mg/L	2.97	Model wine solution	10	Skin tannins extract Seed/Skin tannins mixture (4:1 *w*/*w*)	0.5–10 g/L 1–10 g/L	↓ ↓		[63]
		0–0.498 mg/L		White wine Young-red wine Oak barrel aged-red wine	12		TPC = 230 TPC = 1820 TPC = 2142	↑ (ns) ↓ ↓ (ns)		[62]
Terpinen-4-ol	Peppery, woody, earthy, musty, sweet	0–0.665 mg/L	3.26	White wine Young-red wine White wine	12		TPC = 230 TPC = 1820 TPC = 2142	↑ (ns) ↓ ↓		[62]
β-Citronellol	Floral, leathery, waxy, rose, citrus	0–1.563 mg/L	3.30	White wine Young-red wine Oak barrel aged-red wine	12		TPC = 230 TPC = 1820 TPC = 2142	↓ (ns) ↓ ↓		[62]
Nerol	Sweet, natural, citrus, magnolia	0–7.838 mg/L	3.47	White wine Young-red wine Oak barrel aged-red wine	12		TPC = 230 TPC = 1820 TPC = 2142	↓ ↓ ↓ (ns)		[62]

Table 1. *Cont.*

Aromas Characteristics				Matrix Characteristics				Effects		Ref.
Compound	**Descriptors ***	**Concentration**	**logP (o/w) ***	**Type of Matrix**	**%Ethanol (*v*/*v*)**	**Added Tannins**	**Tannin Content**	**Effects on Release**	**Effects on Orthonasal Perception**	
ESTERS										
Diethyl succinate	Fruity, apple, cooked apple, ylang	20 mg/L	1.26	Model wine solution	10	Skin tannins extract	0.5–3 g/L	↓		[63]
							3–10 g/L	↑		
						Seed/Skin tannins mixture (4:1 *w*/*w*)	1–10 g/L	↑		
Ethyl isobutanoate	Sweet, ethereal, fruity, alcoholic, fusel, rummy	200 µg/L	1.66	Model wine solution	12	Catechin	2 g/L	NA	↓	[66]
						Gallic acid	2 g/L	NA	NA	
Isobutyl acetate	Sweet, fruity, ethereal, banana, tropical	0–0.675 mg/L	1.78	White wine	12		TPC = 230	↓		[62]
				Young-red wine			TPC = 1820	↑ (ns)		
				Oak barrel aged-red wine			TPC = 2142	↑		
Butyl acetate	Ethereal, solvent, fruity, banana	0–0.713 mg/L	1.78	White wine	12		TPC = 230	↓ (ns)		[62]
				Young-red wine			TPC = 1820	↑ (ns)		
				Oak barrel aged-red wine			TPC = 2142	↑		
Ethyl butanoate	Fruity, fruit juice, pineapple, cognac	200 µg/L	1.80	Model wine solution	12	Catechin	2 g/L	NA	↓	[66]
						Gallic acid	2 g/L	NA	NA	
		-		Red wine non-volatile extract + white wine VOCs extract	12		TPI = 60.1	↓		[67]
		0–1.456 mg/L		White wine	12		TPC = 230	↓ (ns)		[62]
				Young-red wine			TPC = 1820	↑ (ns)		
				Oak barrel aged-red wine			TPC = 2142	↑		

Table 1. *Cont.*

Aromas Characteristics				Matrix Characteristics				Effects		Ref.
Compound	**Descriptors ***	**Concentration**	**logP (o/w) ***	**Type of Matrix**	**%Ethanol (*v*/*v*)**	**Added Tannins**	**Tannin Content**	**Effects on Release**	**Effects on Orthonasal Perception**	
Ethyl 2-methyl butanoate	Sharp, sweet, green apple, fruity	-	2.16	Red wine non-volatile extract + white wine VOCs extract	12		TPI = 60.1	↓ (ns)		[67]
		0–0.803 mg/L		White wine	12		TPC = 230	↓ (ns)		[62]
				Young-red wine			TPC = 1820	↑		
				Oak barrel aged-red wine			TPC = 2142	↑		
Isoamyl acetate	Sweet, fruity, banana, solvent	4 mg/L	2.25	Model wine solution	10	Skin tannins extract	0.5–10 g/L	↑		[63]
		200 µg/L		Model wine solution	12	Catechin Gallic acid	2 g/L 2 g/L	NA NA	NA NA	[66]
		-		Red wine non-volatile extract + white wine VOCs extract	12		TPI = 60.1	↓		[67]
		0–1.619 mg/L		White wine	12		TPC = 230	↓		[62]
				Young-red wine			TPC = 1820	↓ (ns)		
				Oak barrel aged-red wine			TPC = 2142	↓		
Ethyl hexanoate	Sweet, fruity, pineapple, waxy, green banana	-	2.85	Red wine non-volatile extract + white wine VOCs extract	12		TPI = 60.1	↓		[67]
		0–2.356 mg/L		White wine	12		TPC = 230	↓		[62]
				Young-red wine			TPC = 1820	↓ (ns)		
				Oak barrel aged-red wine			TPC = 2142	↓ (ns)		

Table 1. *Cont.*

Aromas Characteristics				Matrix Characteristics				Effects		Ref.
Compound	**Descriptors ***	**Concentration**	**logP (o/w) ***	**Type of Matrix**	**%Ethanol (*v*/*v*)**	**Added Tannins**	**Tannin Content**	**Effects on Release**	**Effects on Orthonasal Perception**	
Ethyl cinnamate	Sweet, balsamic, fruity, spicy, powdery, berry plum	0–0.825 mg/L	2.99	White wine Young-red wine Oak barrel aged-red wine	12		TPC = 230 TPC = 1820 TPC = 2142	↓ ↓ (ns) ↓		[62]
Ethyl octanoate	Fruity, winey, waxy, sweet, apricot, banana, brandy, pear	1 mg/L	3.84	Model wine solution	10	Skin tannins extract Seed/Skin tannins mixture (4:1 *w*/*w*)	0.5–10 g/L 1–10 g/L	↓ ↓		[63]
		600 µg/L		Model wine solution	12	Catechin Gallic acid	2 g/L 2 g/L	↓ NA	↓ NA	[66]
		-		Red wine non-volatile extract + white wine VOCs extract	12		TPI = 60.1	↓		[67]
		0–2.124 mg/L		White wine Young-red wine Oak barrel aged-red wine	12		TPC = 230 TPC = 1820 TPC = 2142	↓ ↓ (ns) ↑		[62]
Ethyl decanoate	Sweet, waxy, fruity, apple, grape, oily, brandy	1.5 mg/L	4.86	Model wine solution	10	Skin tannins extract Seed/Skin tannins mixture (4:1 *w*/*w*)	0.5–10 g/L 1–10 g/L	↓ ↓		[63]
		0–0.931 mg/L		White wine Young-red wine Oak barrel aged-red wine	12		TPC = 230 TPC = 1820 TPC = 2142	↓ ↓ (ns) ↓		[62]

Table 1. *Cont.*

Aromas Characteristics				Matrix Characteristics				Effects		Ref.
Compound	**Descriptors ***	**Concentration**	**logP (o/w) ***	**Type of Matrix**	**%Ethanol (*v*/*v*)**	**Added Tannins**	**Tannin Content**	**Effects on Release**	**Effects on Orthonasal Perception**	
Ethyl dodecanoate	Sweet, waxy, floral, soapy, clean	2 mg/L	5.71	Model wine solution	10	Skin tannins extract	0.5–10 g/L	↓		[63]
						Seed tannins extract	0.5–5 g/L	↑		
							5–10 g/L	↓		
						Seed/Skin tannins mixture (4:1 *w*/*w*)	1–10 g/L	↓		
ALCOHOLS										
Isobutanol	Ethereal, winey	80 mg/L	0.76	Model wine solution	10	Skin tannins extract	0.5–10 g/L	↓		[63]
						Seed/Skin tannins mixture (4:1 *w*/*w*)	1–10 g/L	↓		
Benzyl alcohol	Floral, rose, phenolic, balsamic	0–1.563 mg/L	1.10	White wine Young-red wine Oak barrel aged-red wine	12		TPC = 230	↑		[62]
							TPC = 1820	↓ (ns)		
							TPC = 2142	↑		
3-methyl-1-butanol	Fusel, alcoholic, whiskey, fruity, banana	50 mg/L	1.16	Model wine solution	10	Grape tannins	0.5–1.5 g/L	↓		[69]
2-methyl-1-butanol	Roasted, winey, onion, fruity, fusel, alcoholic, whiskey	150 mg/L	1.29	Model wine solution	10	Skin tannins extract	0.5–10 g/L	↑		[63]
						Seed/Skin tannins mixture (4:1 *w*/*w*)	1–10 g/L	slight ↑		

Table 1. *Cont.*

Aromas Characteristics				Matrix Characteristics				Effects		Ref.
Compound	**Descriptors ***	**Concentration**	**logP (o/w) ***	**Type of Matrix**	**%Ethanol (*v*/*v*)**	**Added Tannins**	**Tannin Content**	**Effects on Release**	**Effects on Orthonasal Perception**	
β-phenylethanol	Floral, rose, dried rose	50 mg/L	1.36	Model wine solution	10	Skin tannins extract	0.5–1 g/L	↓		[63]
							1–10 g/L	↑		
						Seed/Skin tannins mixture (4:1 *w*/*w*)	1–10 g/L	↑		
trans-3-hexen-1-ol	Green, cortex, privet, leafy, floral, petal, oily, earthy	0–0.875 mg/L	1.61	White wine	12		TPC = 230	↓		[62]
				Young-red wine			TPC = 1820	↓ (ns)		
				Oak barrel aged-red wine			TPC = 2142	↑ (ns)		
Hexanol	Ethereal, fusel, oily, fruity, alcoholic, sweet, green	6 mg/L	2.03	Model wine solution	10	Seed tannins extract	0.5–10 g/L	↓		[63]
				Model wine solution	10	Grape tannins	0.5–1.5 g/L	↓		[69]
		0–2.200 mg/L		White wine	12		TPC = 230	↓ (ns)		[62]
				Young-red wine			TPC = 1820	↑ (ns)		
				Oak barrel aged-red wine			TPC = 2142	↑		
ACIDS										
Butyric acid	Sharp, acetic, cheesy, buttery, fruity	-	0.79	Red wine non-volatile extract + white wine VOCs extract	12		TPI = 60.1	↓		[67]
Hexanoic acid	Sour, fatty, sweaty, cheesy	-	1.92	Red wine non-volatile extract + white wine VOCs extract	12		TPI = 60.1	↓		[67]

Table 1. *Cont.*

Aromas Characteristics				Matrix Characteristics				Effects		Ref.
Compound	**Descriptors ***	**Concentration**	**logP (o/w) ***	**Type of Matrix**	**%Ethanol (*v*/*v*)**	**Added Tannins**	**Tannin Content**	**Effects on Release**	**Effects on Orthonasal Perception**	
Octanoic acid	Fatty, waxy, rancid, oily, vegetable, cheesy	200 mg/L	3.05	Model wine solution	10	Skin tannins extract	0.5–1 g/L	↓		[63]
							1–10 g/L	↑		
						Seed tannins	0.5–5 g/L	↑		
							5–10 g/L	↓		
						Seed/Skin tannins mixture (4:1 *w*/*w*)	1–10 g/L	↑		
		-		Red wine non-volatile extract + white wine VOCs extract	12		TPI = 60.1	↓		[67]
		0–4.656 mg/L		White wine	12		TPC = 230	↑		[62]
				Young-red wine			TPC = 1820	↑ (ns)		
				Oak barrel aged-red wine			TPC = 2142	↑ (ns)		
VOLATILE PHENOLS										
Guaiacol	Phenolic, smoky, spicy, vanilla, woody	4 mg/L	1.32	Model wine solution	10	Grape tannins	0.5–1.5 g/L	↑		[69]
Eugenol	Sweet, spicy, clove, woody	0.5 mg/L	2.27	Model wine solution	10	Grape tannins	0.5–1.5 g/L	↑		[69]
		0–0.400 mg/L		White wine	12		TPC = 230	↓		[62]
				Young-red wine			TPC = 1820	↓		
				Oak barrel aged-red wine			TPC = 2142	↓		
4-ethylguaiacol	Spicy, smoky, bacon, phenolic, clove	135 µg/L	2.43	Model wine solution	Not specified	Grape polyphenolic extract	0–3 g/L	↓	↓	[73]

Table 1. *Cont.*

Aromas Characteristics				Matrix Characteristics				Effects		Ref.
Compound	**Descriptors ***	**Concentration**	**logP (o/w) ***	**Type of Matrix**	**%Ethanol (*v*/*v*)**	**Added Tannins**	**Tannin Content**	**Effects on Release**	**Effects on Orthonasal Perception**	
4-ethylphenol	Phenolic, castoreum, smoky, guaiacol	440 µg/L	2.58	Model wine solution	Not specified	Grape polyphenolic extract	0–3 g/L	↓	↓	[73]
4-vinylphenol	Chemical, phenolic, medicinal, sweet	0–0.432 mg/L	2.61	White wine Young-red wine Oak barrel aged-red wine	12		TPC = 230 TPC = 1820 TPC = 2142	↓ ↓ ↓		[62]
KETONES										
1-octen-3-one	Herbal, mushroom, earthy, musty, dirty	1 mg/L -	2.18	Model wine solution Red wine non-volatile extract + white wine VOCs extract	10 12	Grape tannins	0.5–1.5 g/L TPI = 60.1	↑ ND		[69] [67]
α-ionone	Sweet, woody, floral, violet, orris, tropical, fruity	0–0.228 mg/L	3.99	White wine Young-red wine Oak barrel aged-red wine	12		TPC = 230 TPC = 1820 TPC = 2142	↑ (ns) ↓ (ns) ↓		[62]
β-damascenone	Natural, sweet, fruity, rose, plum, grape, raspberry, sugar	- 0–0.425 mg/L	4.04	Red wine non-volatile extract + white wine VOCs extract White wine Young-red wine Oak barrel aged-red wine	12 12		TPI = 60.1 TPC = 230 TPC = 1820 TPC = 2142	ND ↑ (ns) ↓ ↓		[67] [62]

Table 1. *Cont.*

Aromas Characteristics				Matrix Characteristics				Effects		Ref.
Compound	**Descriptors ***	**Concentration**	**logP (o/w) ***	**Type of Matrix**	**%Ethanol (*v*/*v*)**	**Added Tannins**	**Tannin Content**	**Effects on Release**	**Effects on Orthonasal Perception**	
OXYGEN HETEROCYCLES (FURANS/ LACTONES)										
Sotolon	Sweet, caramellic, maple, sugar, burnt sugar, coffee	-	−0.29	Red wine non-volatile extract + white wine VOCs extract	12		TPI = 60.1	ND		[67]
Furaneol	Sweet, cotton candy, caramellic, strawberry, sugar, brown sugar	-	−0.08	Red wine non-volatile extract + white wine VOCs extract	12		TPI = 60.1	ND		[67]
Ethyl furaneol	Sweet, caramellic, candy, butterscotch	-	0.43	Red wine non-volatile extract + white wine VOCs extract	12		TPI = 60.1	ND		[67]
5-methyl furfural	Spicy, caramellic, maple	0–1.475 mg/L	0.67	White wine Young-red wine Oak barrel aged-red wine	12		TPC = 230 TPC = 1820 TPC = 2142	↑ ↑ ↑		[62]
γ-nonalactone	Coconut, creamy, waxy, sweet, buttery, oily	0–0.413 mg/L	1.94	White wine Young-red wine Oak barrel aged-red wine	12		TPC = 230 TPC = 1820 TPC = 2142	↓ ↓ ↓		[62]

Table 1. *Cont.*

Aromas Characteristics				Matrix Characteristics				Effects		Ref.
Compound	**Descriptors ***	**Concentration**	**logP (o/w) ***	**Type of Matrix**	**%Ethanol (*v*/*v*)**	**Added Tannins**	**Tannin Content**	**Effects on Release**	**Effects on Orthonasal Perception**	
***trans*-whiskey lactone**	Spicy, coconut, clove, celery, incense	0–0.868 mg/L		White wine			TPC = 230	↑		[62]
				Young-red wine			TPC = 1820	↓ (ns)		
				Oak barrel aged-red wine			TPC = 2142	↓		
***cis*-whiskey lactone**	Sweet, spicy, coconut, vanilla	0–0.682 mg/L	2.63	White wine	12		TPC = 230	↑ (ns)		[62]
				Young-red wine			TPC = 1820	↓		
				Oak barrel aged-red wine			TPC = 2142	↓		

* The Good Scents Company; TPC = Total Polyphenol Content (it is expressed in mg/L gallic acid); TPI = Total Polyphenol Index; ↑ = increase; ↓= decrease; (ns) = not significant; NA = Not Affected; ND = Not Detected

3.5. Effects on Acids

Volatile aliphatic organic acids are compounds produced during alcoholic fermentation as by-products of fatty acids. As all the other fermentative aromas, acids production strongly depends on fermentation parameters. Fatty acids, such as butyric acid, isobutyric acid, hexanoic acid, octanoic acid, nonanoic acid, and decanoic acid, possess unpleasant aromas, are normally described with rancid, pungent, fatty, or cheese-like notes, and their sensory contribution in real wine is a general contribution to the vinous character [76]. However, volatile aliphatic organic acids concentration is usually correlated with their corresponding ethyl esters, with the latter being characterized by a more powerful odor. Indeed, as an example, acetic acid itself is described with pungent, vinegar-like descriptors; however, the off-odor associated with volatile acidity appears to be primarily due to the more powerful ethyl acetate, which is formed by the esterification of acetic acid [10].

In the literature, the effect of polyphenols has been reported on butyric, hexanoic, and octanoic acids (Table 1). When analyzed in a reconstituted sample made of the volatile extract of an aged-red wine and a non-volatile extract of a Chardonnay white wine, the release of the three compounds decreased [67]. The intensity of butyric acid, tested by GC-O analyses, was negatively affected. Octanoic acid, having a higher log$P$ = 3.05 compared to the other two, showed different behaviors depending both on the concentration and the nature of PPhs.

No conclusions can be drawn on this class of VOCs, due to the scarcity of results.

3.6. Effects on Ketones

Ketones are mainly derived from lipid oxidation, as well as from the citrate and glucose metabolism. This group of VOCs is characterized by a wide array of odors varying from baked/dehydrated fruits to earthy and floral, among others. Norisoprenoidic ketones such as β-damascenone and α-ionone provide fruity/baked fruit or floral notes. Acetoin and diacetyl mostly result in a buttery flavour, while other compounds such as 1-octen-3-one have herbaceous, mushroom, and earthy aromas.

The two VOCs α-ionone and β-damascenone are characterized by similar log$P$ values (3.99 and 4.04, respectively), which are higher compared to that of 1-octen-3-one (log$P$ = 2.18). Both the norisoprenoidic ketones showed similar trends: at high tannins concentrations, and in presence of the high polymerized ones, their release decreased [62]. Conversely, the release of 1-octen-3-one, at high grape tannins concentrations, increased in model wine solutions. However, results from HS-SPME-GC–O techniques carried out by trained panelists show lower GC-O scores for 1-octen-3-one in the presence of tannins [67]. Furthermore, at high ethanol (14% *v/v*), fructose (2 g/L), and tannins concentrations (1.5 g/L), odor thresholds have been seen to be higher for β-damascenone and 1-octen-3-one [69].

The observed results on β-damascenone and 1-octen-3-one could be interesting from a sensory point of view. β-damascenone is reported as a compound that is able to enhance the fruity character due to ethyl esters in red wine. Thus, considering the observed negative impact at increasing levels and the polymerization of PPhs on the release of esters and β-damascenone [62], it can be argued that this could correspond to a significant diminution of the fruity character of red wines, especially in aged and/or woody ones. Concerning 1-octen-3-one, a compound involved in the cork taint [77,78], it could be interesting to test if the concentration and the nature of PPhs could be useful in managing the sensory impact of this off-flavor.

3.7. Effects on Oxygen Heterocycles (Furans/Lactones)

Furans and lactones are VOCs normally related to wine aging. Furans in wines are generated by the thermal degradation of sugars due to acid-catalyzed reactions, or even through Maillard reaction. Lactones are essentially formed by yeasts during alcoholic fermentation, although significant odorant lactones are usually accumulated during wine aging. They can impart powerful nuances to wines, especially in oxidative conditions [79].

Oxygenated heterocycles reported in Table 1 have different functionalities such as ketonic, aldehydic, or alcoholic and range from very polar compounds such as sotolon (4,5-dimethyl-3-hydroxy-2,5-dihydrofuran-2-one) with log*P*= −0.29, to the more hydrophobic cis-whiskey lactone with log*P* = 2.63. Data suggest that at increasing tannins concentrations, VOCs with log*P* values higher than 1 show a decrease in volatility. More specifically, the retention effect of the real wine matrices was higher for the oak-barrel aged one compared to the young-red one for γ-nonalactone (log*P* = 1.94), trans-whiskey lactone (log*P* = 1.97), and cis-whiskey lactone (log*P* = 2.63). On the contrary, VOCs with lower log*P* values (i.e., 5-methyl furfural with log*P* = 0.67), independently from the matrix type, have shown a "salting-out" effect [62]. Furthermore, GC-O data have shown that the most hydrophilic and polar VOCs, sotolon (log*P*= −0.29), furaneol (log*P*= −0.08), and ethyl furaneol (log*P*= 0.43), even if not instrumentally detected by GC-MS, were characterized by higher GC-O scores in the presence of a red wine non-volatile extract compared to a white one [67]. These results could be linked to the very low detection thresholds characterizing these furans, all in the order of μg/L, with sotolon having the lowest (1–6 μg/L).

A sensory implication of these observations could be that the perception of these molecules involved in oxidative notes of wines could be favored in the presence of PPhs. On the contrary, coconut/woody-spicy/sweety odors due to lactones could be less perceivable at increasing concentrations of PPhs. However, there are no scientific data supporting this hypothesis, since no works have been conducted on the hypothetical sensory effects of polyphenols on these VOCs, which could be an interesting aspect to consider for future research.

4. Polyphenols Effects on Aromas Release in Oral Conditions: The Role of Saliva

When considering PPhs–VOCs interactions in oral modality, the effects described above for orthonasal conditions can change. During wine tasting, and in general during food consumption, aroma compounds are transported to the nasal cavity by following the retronasal route (nasopharynx). Along this path, there is a dilution and a change in VOCs repartition between the condensed and the gas phases due to the mixing of wine with saliva and their interaction with the oral/pharyngeal cavity during the transfer to the olfactory receptors through the breath airflow. Several factors (e.g., anatomical, physicochemical, physiological, mechanical, etc.) can be implicated in VOCs release and perception in retronasal conditions [80]. Individual oral physiology characteristics, such as salivary flow rate, protein content and composition, antioxidant capacity, temperature, mucosa, swallowing and tongue force, oral volume, respiratory flow, and other oral physiological components could vary amongst individuals and with matrix composition, affecting wine aromas release [49,81–85]. However, among all, saliva can be considered as a main factor so that its effects on food and beverages flavor perception have been frequently investigated in the last decades.

Saliva can directly play a modulating role on polyphenols perception (PPhs–saliva interactions) and on aroma release and perception (VOCs–saliva interactions) during wine tasting, so we can argue that saliva could play a further indirect role by affecting PPhs–VOCs interactions [7,8,22,49,86–90]. While the first evidence on the molecular mechanisms explaining astringency as the sensation elicited by the interaction and precipitation of salivary proteins by tannins was published around 50 years ago [16], the direct impact of saliva on VOCs release and perception has started to be shown more recently [91–95]. Numerous phenomena have been proposed to explain the changes in release amount, kinetic, and nature of VOCs in the presence of saliva. Salivary proteins have binding sites available to trap volatiles. In fact, mucin and other salivary proteins can directly bind specific aroma compounds through covalent and non-covalent interactions (hydrophobic and electrostatic interactions, Van der Waals forces, formation of Schiff bases), inducing a modification in their release [7,92,93,96,97]. Salivary enzymes present in human saliva can catalyze reactions, are able to transform some volatile molecules into other odorants, and can hydrolyze bound volatiles from non-volatile precursors [7,94–96,98,99]. More-

over, saliva can directly impact VOCs dilution, affecting their release to the oral cavity, since the repartition of molecules within the system wine–saliva–air is different compared to the wine–air system [7]. The first works hypothesizing a role played by saliva on PPhs–VOCs interactions during white and red wine tasting have been conducted using model mouth systems, in in vitro conditions, with either human saliva, artificial saliva, or comparing both types [48,63]. In recent years, the development of procedures and methodologies allowing the quantification of aroma release in real in vivo conditions has improved results useful to understand how saliva–polyphenols interactions could impact the release and the perception of wine aroma. Different innovative approaches were used, such as the application of retronasal trapping devices that allowed entrapping the exhaled breath of the panelists [83], or intra-oral SPME (Solid Phase Micro Extraction) procedures [100–102], or the monitoring of the nasal cavity exhalations through PTR-ToF-MS (Proton Transfer Reaction-Time of Flight-Mass Spectrometry) (during real wine tasting sessions [103].

Impact of Saliva on Aroma through the Modulation of Polyphenols–VOCs Interactions

The contradictory results available in the current literature could be at least partially due to the different approaches that were used (i.e., model solutions or real wines, artificial or real human saliva, different aromas and polyphenols concentrations, different analytical methods), so that it is difficult to get general conclusions on causes and effects of aromas–saliva–polyphenols interactions. Therefore, as already observed [100], the effect of polyphenol–salivary proteins interactions on aroma release is little known. Some hypotheses have been presented as possible causes of the different VOCs release behaviour in retronasal conditions compared to orthonasal ones, in the presence of different polyphenols at different concentrations. In the PPhs–VOCs–saliva systems, not only dilution, interaction, and salting-out effects can occur, but also the balance among the following phenomena should be considered: inhibition by PPhs of salivary enzymes activity in "metabolizing" VOCs; competitions between PPhs and VOCs in interacting with salivary proteins; hydrophobic VOCs inclusion in PPhs–saliva complexes. These phenomena have been argued based on results from in vivo trials and mainly observed on wine volatile esters.

Saliva contains several enzymes (e.g., esterases, aldehyde dehydrogenases, aldose reductases, peroxidases, etc.) originating from salivary glands, oral tissues, and microbiota [104,105]. These enzymes may be able to catalyze biochemical reactions, metabolizing certain classes of aromas (e.g., esters, aldehydes, ketones, alcohols, thiols) by transforming them into different odorants. Oral enzymes can also hydrolyze odorless aroma precursors (glycosidic or aminoacidic) with the consequent production of odorous aglycones [7,94–96,98,99,106,107]. In the presence of phenolic compounds, it has been shown that some enzymatic activities may be inhibited [108,109]. In the specific case of esters, it has been hypothesized that the activity of carboxyl esterase involved in their metabolism might be inhibited in the presence of phenolic compounds, thus leading to a lower hydrolysis of esters in solutions and, consequently, to a higher concentration of molecules that can be released. This hypothesis is supported by results obtained in both in vitro [48] and in vivo [83] conditions. Genovese and co-workers investigated the influence of human and artificial saliva on the release of white and red wine VOCs by SPME/GC-MS analyses using a model mouth system called retronasal aroma simulator (RAS). In the experiment with human saliva, containing salivary enzymes, the authors observed a significant lower decrease of some VOCs concentrations (i.e., ethyl butanoate, 3-mehtylbutyl acetate, ethyl hexanoate, hexyl acetate, and ethyl dodecanoate) in red wine headspace compared to the white one. Successively, interesting results have been pointed out in a more recent study involving a panelists' group that was classified as a lower releaser based on their real-time breathing profile monitored by a tailor-made retronasal aroma trapping device (RATD) that allowed entrapping the exhaled breath of the panelists and consequent GC-MS analysis [83]. The authors have shown a higher release of ethyl hexanoate during the consumption of a young-red wine, which was characterized by the highest polyphenolic content, in comparison with a white, an aged-red, a sparking,

and a sweet wine [83]. Since the same effect was not observed on the other analyzed ester (i.e., isoamyl acetate), the presence of tannins could have played an inhibition activity on certain salivary enzymes implicated in the metabolism of ethyl esters in the mouth. Similar phenomena have been observed by using a more innovative in vivo PTR-ToF-MS approach monitoring the nasal cavity of nine subjects after they rinsed their mouths with three different samples (a control wine and the same wine with two different commercial oenological tannins added). The presence of tannins (50 mg/L) corresponded to a higher release of ethyl decanoate, which was significant at the first and fourth minute of monitoring after swallowing [103], in the prolonged aroma release condition, and it was responsible for the aroma persistence [110–113]. The authors suggested that "the presence of tannins could have inhibited certain salivary enzymes implicated in the metabolism of aroma compounds, such as ethyl esters, in the mouth" [103].

Moreover, a modification of VOCs release might be due to competitions between PPhs and VOCs in interacting with salivary proteins. Salivary proteins (e.g., mucins, α-amylases, etc.) have demonstrated their ability to interact with aroma compounds through hydrophobic and other kinds of non-covalent interactions (electrostatic interactions, Van der Waals forces) [114], modifying their release and perception [87]. However, phenolic compounds have shown to strongly interact with mucin [24,115], likely competing with aromas in their interaction with saliva. For example, in in vitro conditions and investigating the influence of the presence/absence of saliva on the release of red and white wine VOCs, a lower decrease for some alcohols (i.e., 2-methyl-1-propanol, 3+2-ethyl-1-butanol, 3-methyl-1-pentanol, and 1-hexanol) was found with human or artificial saliva in red wine compared to the white wine [48]. In addition, Mintropoulou and co-authors [63] showed a different modulating effect of artificial saliva (with no added enzymes) on some VOCs release in model solutions with added tannins. Following interaction with saliva, the authors observed a lower decrease for isoamyl acetate, ethyl hexanoate, octanoate, decanoate, dodecanoate, 2-methyl-1-butanol, and linalool, in the presence of tannins.

However, in the presence of tannins, some VOCs, due to their ability to participate in the formation of large complexes with salivary proteins and wine carbohydrates [63], might be encapsulated, leading to a lower retronasal release. This phenomenon has been observed for some hydrophobic esters (i.e., isoamyl acetate and ethyl hexanote) in different works [100,101], such as for guaiacol and, to a lesser extent, for β-ionone [101]. These authors suggested an interaction of these VOCs with salivary proteins–PPhs complexes, resulting in a lower immediate release in red wines [100] or in wines added with different types of phenolic extracts [101].

A further aspect possibly affected by the PPhs–VOCs–saliva interactions could be the flavor persistence during wine tasting [103]. Polyphenols are responsible for astringency and bitterness perception, which are two oral sensations characterized by an extended persistence as showed by TDS (temporal dominance of sensations) studies [116]. Based on some evidence, the long time of development and the dynamic persistence might be at least partially linked to the multistage mechanism underpinning PPhs–saliva interactions [20]. The results presented by Jöbstl and co-workers show that polyphenol–protein binding produces a more cross-linked and hydrophobic protein, which could enhance the hydrophobic trapping/inclusion of small molecules such as VOCs. Moreover, specific aroma compounds–mucosa interactions occurring after swallowing could contribute to the formation of a coating on the throat and pharynx, which could increase the liquid/air free surface, thus modulating some VOCs release over time [7], under the expiration flows in specific in vivo conditions. This phenomenon, together with the inhibition by PPhs of salivary enzymes activity in "metabolizing" VOCs, could explain the higher ethyl decanoate release over time once the wine was expectorated [103]. In addition, Perez-Jiménez and co-workers [101] have suggested a modification in VOCs behavior over time. After the fourth minute from the expectoration, in prolonged aroma release conditions, the behavior of some VOCs release changed for some individuals. For three of the six subjects participating in the study, a higher release of ethyl hexanoate and isoamyl acetate has

been observed when tasting the wine added with the red wine phenolic extract mainly composed of anthocyanins. For two individuals, a higher release of guaiacol has been shown for all the investigated phenolic extracts. However, some of these cited results are in contradiction with data from a very recent study [102] that showed, through an intra-oral SPME procedure and consequent GC-MS analysis, a lower immediate and prolonged esters' retronasal release (i.e., ethyl butanoate, isoamyl acetate, ethyl pentanoate, hexanoate, octanoate, and decanoate) in the wine added with a moderate total polyphenol content (TPC) compared to the wine with a low TPC, 661 ± 33 and 402 ± 10 mg gallic acid/L, respectively.

All of this highlights the high complexity and scarce knowledge of PPhs–VOCs–saliva interactions and their effects on VOCs release and perception in retronasal settings. Current research is paying attention to individual salivary characteristics and composition (e.g., flow, protein content, antioxidant capacity) and interindividual differences, trying to understand if the interindividual diversity could modulate the in-mouth aroma release by affecting PPhs–VOCs interactions [101,103].

5. Polyphenols Effects on Aromas Sensory Perception

Few experiments have been conducted to measure the sensory impact of polyphenols on aromas perception in orthonasal and retronasal conditions.

In orthonasal conditions, Lund and co-workers [117] investigated the effects of three polyphenols naturally present in white wines on the perception of four key aroma compounds from a Sauvignon Blanc wine. Their results showed that the perception of isobutyl methylpyrazine and ethyl decanoate was suppressed by catechin, caffeic acid, and somehow by quercetin or its degradation products. Regarding the two former phenolic compounds, noncovalent bonds (π–π interaction and hydrogen bonding) between their large-OH groups and the aroma compound might have reduced its perception [51,52]. The perception of 3-mercaptohexanol (described as passionfruit skin/stalk) was suppressed when catechin and quercetin were added, while it was enhanced by caffeic acid. 3-Mercaptohexyl acetate was the least affected volatile, suggesting that the acetate group was less suitable to interact with phenolics compared to the indoxyl. Considering red wine aroma perception in orthonasal conditions, some authors have found that in wines characterized by high polyphenols concentrations (5.4–7.2 g/L), the intensity of perceived fruity, citrus, strawberry, cooked fruit, and floral odors was significantly lower compared to wines with low polyphenols concentrations (1.4–3.2 g/L). A tendency, even if not significant, to the accentuation of spicy, herbaceous, and sweet pepper notes was also observed. However, neither changes in headspace (HS-SPME-GC-MS analyses) nor in matrix concentration (physicochemical composition) showed results that were significantly related to the relative changes in sensory intensity [118].

In retronasal conditions and focusing on PPhs effects on the prolonged aroma release, a sensory study conducted on a Syrah wine adjusted to two concentrations of ethanol and tannins has pointed out that the duration (length in mouth) of bell pepper flavor (due to the presence of 3-isobutyl-2-methoxypyrazine) was longer at higher tannin concentrations. A possible explanation could be found in a change in release kinetic: the formation of 3-isobutyl-2-methoxypyrazine-tannins complexes [52,53], which could have resulted in this aroma compound being retained in solution, yielding to a more gradual release of its bell pepper flavor over time [119]. Finally, in the same study cited above [101], a sensory descriptive analysis was performed to compare intra-oral SPME data with sensory assessments. The results showed that wines added with phenolic extracts exhibited lower retronasal intensity for the attributes "banana" and "apple", which are aromatic notes associated with isoamyl acetate and ethyl hexanoate. At the contrary, the attribute "honey", which is correlated to β-phenylethanol, was scored slightly higher in the wines with phenolic extracts, while the attribute "chemical" correlated to guaiacol—however, without a relationship to a higher oral release of this latter VOC. The authors suggested that the phenolic extracts that were tested might exert an effect on the prolonged aroma release.

This seems an interesting research perspective to approach by means of dynamic sensory methods coupled with real-time instrumental techniques to test over time if polyphenols might induce a modification on the long-lasting aroma perception of aroma attributes.

6. Conclusions and Future Perspectives

Wine VOCs–PPhs interactions and their effects on aromas release, headspace partitioning, and sensory perception represent an actual research topic in oenology. Even if some molecular insights at the base of these interactions (π–π interaction and hydrogen bonding) and the importance of VOCs and PPhs hydrophobicity have been proposed around 20 years ago, the mechanisms and the effects of these interactions are still unclear. Results of studies conducted using a variety of methods, detection modes, solutions or wines, tannin additions, or manipulation of VOC concentrations have been seen to be very different, contradictory, or difficult to interpret Moreover, results from orthonasal and retronasal studies show different behaviors, suggesting that oral factors, such as saliva, can affect the interactions.

Regarding orthonasal conditions, while for some VOCs chemical classes (e.g., terpenoids, esters, volatile phenols, oxygen heterocycles), it was possible to extrapolate a trend, for others (e.g., alcohols and acids), the poor data available made it difficult to draw a coherent conclusion on phenolic compounds effects on their release. To summarize, the release of all the tested terpenoids decreases at increasing tannin concentrations. For esters, around 2.85 seemed to be a cut-off log*P* value: esters characterized by lower log*P*s diminished at smaller PPhs levels, while they were raised at higher ones, suggesting that for poorly hydrophobic esters, there is the prevalence of retention phenomena at low PPhs concentrations and the prevalence of salting-out effects at higher PPhs concentrations. Conversely, the release of esters characterized by higher log*P*s, except for ethyl octanoate, decreased independently from the PPhs level, suggesting that hydrophobicity represents the main driving force of highly hydrophobic esters release. Except for guaiacol and eugenol, the release of volatile phenols (e.g., 4-ethylphenol and 4-ethylguaiacol) was essentially reduced by PPhs. At increasing tannins concentrations, oxygen heterocycles VOCs with log*P* values higher than 1 (e.g., γ-nonalactone, trans-whiskey lactone, and cis-whiskey lactone), show a decrease in volatility. To the contrary, VOCs with lower log*P* values (i.e., 5-methyl furfural), independently from the matrix type, have shown a "salting-out" effect. Globally, the observed trends seem to suggest that in orthonasal conditions, for VOCs with a greater hydrophilic character, an increase in PPhs determines a greater release (salting-out), which is probably because this increase reduces the solvating capacity that the water molecules have toward VOCs. On the contrary, VOCs with a greater hydrophobic character are more retained at increasing PPhs concentration, likely in reason of hydrophobic intermolecular interactions occurring between them.

Considering retronasal conditions, it has been observed that in the presence of phenolic compounds, some salivary enzymatic activities may be inhibited (e.g., carboxyl esterase), thus leading to a lower hydrolysis of some VOCs (e.g., esters) in solutions and, consequently, to a higher release. Moreover, phenolic compounds have shown to strongly interact with mucin, "competing" with aromas in their interaction with saliva and resulting in some VOCs being characterized by a lower decrease in volatility. Finally, in the presence of tannins, some VOCs, for their ability to participate in the formation of large complexes with salivary proteins and wine carbohydrates, might be encapsulated, leading to a lower retronasal release. Despite these observations, the impact of PPhs–VOCs–saliva interactions on aroma release during wine consumption deserves further investigation and, in this context, additional research is needed to clarify the contribution of interindividual differences in terms of saliva composition (i.e., studies with a higher number of subjects will be necessary), since it seems that in these systems, salivary characteristics and interindividual differences may play a crucial role on VOCs release and perception.

A simplified schematic representation of the main variables potentially involved in the PPhs–VOCs interactions that may occur in wine is pictured in Figure 2.

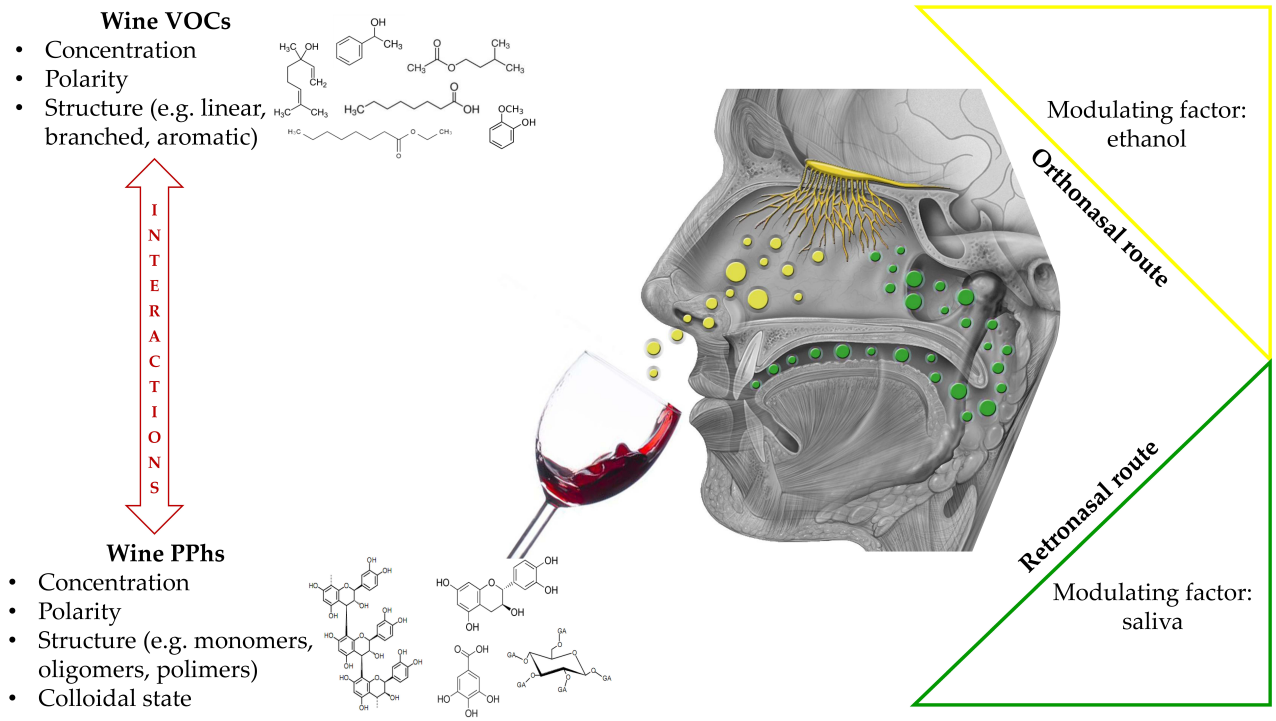

Figure 2. Simplified schematic representation of the main variables potentially involved in the polyphenols (PPhs)–volatile organic compounds (VOCs) interactions that may occur in wine.

As a future perspective at the molecular level, the interactions mechanisms should be investigated deeply, since hydrophobic and π–π interactions do not yield comprehensive explanations, and they correspond to wide concepts; therefore, they should be better described. A further chemical aspect that should be addressed is how the colloidal state of polyphenols—in relation to wine alcohol content, to other wine macromolecules (e.g., polysaccharides, proteins), to wine age—can affect their interactions with VOCs, as well as their release and perception.

The studies involving the effects of tannins on wine aroma persistence is a new field of research. Its scope of understanding could be improved with a new multidisciplinary approach combining in-mouth processes and dynamic sensory studies involving neuroscience, as well as the investigation of the role played by the oral microbiota. Furthermore, employing a wide range of real wines with a variety of different polyphenolic profiles might also be useful in future studies.

Author Contributions: Conceptualization, P.P.; writing—original draft preparation, E.P. and P.P.; writing—review and editing, E.P., L.M. and P.P.; visualization, E.P. and P.P.; supervision, P.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

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