

Wine

8. Wine

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Wine aroma is related to human cognition through multimodal stimuli, particularly in the case of volatile compounds detected by orthonasal and retronasal perception. In fine wines, aroma may be associated with associations of complexity, finesse, and elegance, sometimes attaining the level of uniqueness that makes them a source of a great pleasure. This chapter reviews the diversity of volatile components constituting wine aroma, including compounds originating from grapes, the metabolism of wine microorganisms during alcoholic and malolactic fermentations, implicating *Saccharomyces cerevisiae* and *Oenococcus oeni*, respectively, and oak barrels during wine aging. It will also address those associated with off-odors. The impact of all these compounds on wine aroma and quality is considered, including recently described perceptual interaction phenomena (i. e., masking, synergistic effects, and perceptual blend-

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ing) and the influence of nonvolatile compounds in the wine matrix on aroma perception.

The quality of wine aroma is a matter of great importance. The first sensory impressions of a wine are color, followed by aroma, via orthonasal, then retronasal sensations. Tasters are capable of detecting a broad palette of aromas, including spicy, woody, flowery, and fruity components originating from the grape variety, soil, and climatic conditions, as well as vinification and aging processes [8.1]. Sometimes, tasting a wine is a source of great pleasure and represents such a unique experience that it may be considered a veritable work of art [8.1].

Wine tasters may use either hedonic or analytical criteria, depending on their preferences and knowledge of wine tasting. In this context, they also appreciate the intensity and complexity of the aromatic nuances and assess overall wine quality [8.1]. Analysis of the language used by a group of professional wine tasters revealed that they focused less on describing wines than categorizing them in relation to types they have already memorized [8.2]. Tasters unconsciously seek wine aromatic components related to specificity and originality, in order to associate each wine with an ideotype (stored

reference). This aspect is related to the concept of typicality [8.3–5]. However, not all nuances are perceived in the same manner by different tasters; each taster has a unique personal sensitivity to aromas [8.6]. The context of the wine tasting may also have an impact on flavor perception [8.1, 7]. The perception of wine aroma and typicality is a complex cognitive process involving all the senses including somatosensory perceptions.

So, on what basis are a wine's aromatic nuances perceived? The aromatic palette is initially associated with the many – from one to several hundred – volatile compounds in the headspace above a glass of wine. Highly reputed wines usually have a complex composition consisting of a larger number of compounds. These compounds are stimuli for the human olfactory system, commencing with the olfactory epithelium before being transformed into nerve impulses in the olfactory bulb and becoming conscious sensations [8.8, 9]. However, volatile compounds do not contribute equally to wine aroma. Some, present in trace amounts (in the order of ng l^{-1} or pg l^{-1}), have a very low olfactory

detection or recognition threshold, while others, detected at higher concentrations (several mg l^{-1}), have much higher detection or recognition thresholds [8.10, 11]. This paradoxical situation is due to the specificity of detection by the human olfactory system. However, the perceived intensity of a compound usually increases at higher concentrations [8.12]. Also, the presence of other wine compounds (ethanol, polyphenols, acidity, etc.) may affect the composition of the volatiles present in the headspace above the wine [8.13–15] and, potentially, the sensory perception of its aromas.

Nevertheless, the aroma perceived by the brain is not an algebraic sum of all the volatile compounds, but is related to a complex combinatorial process in the unconscious stage of perception [8.16]. Thus, the ultimate perception and verbalization of aromas involve com-

plex, unconscious combinations of volatile compounds, as well as cognitive processes and memories of past experiences [8.10].

This chapter presents an overview of wine aroma components, including compounds originating from grapes (varietal compounds), those resulting from the fermentation metabolism of wine microorganisms, or associated with aging in oak barrels and bottles, and chemicals responsible for off-odors. The relationship between volatile compounds and their aromatic attributes in wine at each stage in tasting is discussed on the basis of recent research. The complex interaction of some key volatile compounds involved in overall perception is explored, focusing on combinatorial perception, as well as the impact of nonvolatile compounds on wine aroma.

8.1 Composition of the Wine Matrix

8.1.1 Fermentation Aroma

Compounds produced by the fermentation metabolism of yeasts (*Saccharomyces cerevisiae*, *Saccharomyces uvarum*) and lactic bacteria (*Enococcus oeni*, *Lactobacillus* sp.) contribute first to the vinous character of a wine and thus its sensory specificity in comparison to other fermented beverages, as well as, in some cases, its fruity character. These compounds are primarily alcohols, particularly higher or fusel alcohols, esters formed by the esterification of higher alcohols with the acetic acid produced during fermentation, such as acetate esters of higher alcohols, esters formed from fatty acids and ethanol, such as ethyl esters of fatty acids, and, finally, carbonyl and sulfur compounds.

The key higher alcohols are 3-methyl-butan-1-ol (isoamyl alcohol) and 2-methyl-butan-1-ol (bug-like and heavy solvent odor), 2-methylpropan-1-ol (heavy solvent odor), 2-propan-1-ol (heavy solvent odor), 2-phenylethanol (rose flower, *pot pourri*), and 3-methylthiopropan-1-ol (cooked cabbage). These compounds with high-odor detection thresholds (ranging from mg l^{-1} to tens of mg l^{-1}) can affect wine aroma, as concentrations may be as high as several tens or hundreds of mg l^{-1} . Total concentrations of these compounds vary between 100 and 550 mg l^{-1} [8.11, 17]. Overall, with the exception of 2-phenylethanol, these compounds are considered to have a detrimental effect on quality, due to their pungent aromas when concentrations in wines exceed 300 mg l^{-1} [8.11, 17].

Esters of fatty acids (mainly butanoic, hexanoic, octanoic, and decanoic acids) and acetic esters of higher alcohols contribute through fruity and flowery

nuances to the fermentation aroma of wines [8.11, 18]. The most significant acetic esters of higher alcohols in wine aroma are isoamyl acetate, responsible for the well-known banana aroma in some *primeur* wines, 2-phenylethyl acetate, which sometimes exhibits pungent, fruity, rose-like odors, and, less significantly, hexyl acetate (pear) and isobutyl acetate (banana). Globally, these compounds may be present at concentrations above the detection threshold (close to mg l^{-1}), sometimes masking the perception of varietal aroma nuances. Ethyl acetate (solvent *vinegar like*), also produced during alcoholic fermentation, may contribute to the fruity aroma of young wines at concentrations below 100 mg l^{-1} , while concentrations over 150 mg l^{-1} are always related to problems due to acetic or lactic bacteria, involving the esterification of ethanol with acetic acid [8.11].

Until 10 years ago, ethyl butanoate, ethyl hexanoate, ethyl octanoate, and ethyl decanoate, all known for their flowery aromas, were considered the most significant ethyl esters of fatty acids. The detection thresholds of these esters are in the $\mu\text{g l}^{-1}$ range in water, and mg l^{-1} in young wines, significantly exceeding their individual detection thresholds. The amount of esters in young wines depends mainly on parameters related to alcoholic fermentation: *S. cerevisiae* yeast strain, and fermentation temperature, as well as composition and turbidity of the grape must [8.19–21].

More recently, the contribution of branched esters was identified, usually with higher concentrations in red wines. These compounds include hydroxylated ethyl esters, including ethyl 3-hydroxybutanoate [8.22, 23], ethyl 4-hydroxy butanoate (ethyl leucate) [8.24],

ethyl 2-hydroxyhexanoate, and ethyl 6-hydroxyhexanoate [8.22, 23], keto esters, such as ethyl 4-oxopentanoate (ethyl levulinate) [8.22, 23], and methylated esters, such as ethyl 2-methylpropanoate (ethyl isobutyrate), ethyl 2-methylbutanoate, and ethyl 2-hydroxy-4-methylpentanoate. While the individual olfactory detection thresholds of these compounds are similar to those of conventional esters, their contribution to the fruity aromas of red wines through perceptual interaction phenomena was recently reported [8.23]. Ethyl 2-methylpropanoate and ethyl 2-methylbutanoate are implicated with ethyl propanoate in blackberry aromas, while ethyl 3-hydroxybutanoate, together with ethyl butanoate, ethyl hexanoate, and ethyl octanoate contribute to red berry aromas [8.23]. Moreover, ethyl 2-hydroxy-4-methylpentanoate, only recently identified, was demonstrated to be involved in blackberry aroma via perceptual interaction phenomena [8.25]. The organoleptic impact of the enantiomers of this compound has also been studied [8.26]. Branched ethyl esters present lower olfactory detection thresholds than nonbranched compounds [8.22].

Globally, the contribution of the fermentation esters to wine aroma is limited in time, as these compounds are quite quickly degraded through hydrolysis during aging [8.27, 28]. However, contradictory results were recently reported in red wines by *Antalick* et al. [8.29], who observed high ester levels in aged red wines. In fact, other ethyl esters of branched acids may also be formed via chemical esterification during aging, including ethyl 2-methylpentanoate, ethyl 4-methylpentanoate, ethyl cyclohexanoate [8.30, 31], ethyl isobutyrate, ethyl 2-methylbutyrate, ethyl 2-methylpropanoate, ethyl 2-methylbutanoate, ethyl isovalerate, butyl acetate, and ethyl phenylacetate [8.32, 33]. Their contribution to wine aroma has not yet been precisely qualified.

Chemical esterification mechanisms may also affect various acids present in wine, such as cinnamic acid, chemically esterified to ethyl cinnamate (reminiscent of cinnamon, sweet-balsam, sweet-fruit, plums, and cherries), which is also formed during alcoholic fermentation [8.36, 37]. Ethyl phenylacetate has a strong, flowery flavor and is formed from phenylacetic acid, produced by the oxidation of phenylacetaldehyde [8.38, 39].

8.1.2 Other Fermentation Compounds

Other volatile sulfur- and carbonyl-based compounds, produced by wine microorganisms during alcoholic and malolactic fermentation, may significantly impact wine aroma (Sect. 8.1.5). Among the latter, diacetyl (2,3-butanedione) and acetoin, an intermediate in diacetyl

formation, contributes to buttery, lactic aromas in both dry white and red wines following malolactic fermentation by *Enococcus oeni* [8.11, 18]. The olfactory detection threshold of diacetyl is in the $\mu\text{g l}^{-1}$ range in water and mg l^{-1} in model wine. A few mg l^{-1} diacetyl (2–3 mg l^{-1} in dry whites and 5 mg l^{-1} in reds) may contribute positively to wine aroma [8.11, 17, 40]. Another key volatile compound is acetaldehyde, but its contribution to wine aroma is generally limited, as it combines easily with the sulfur dioxide used as a preservative, except in oxidized wines. However, in specific situations, where wines are subjected to extreme oxidation during aging (e.g., Sherries from Xerez in southern Spain, Marsala, from Sicily, and *vin jaune* from the Jura region of France), acetaldehyde is present at concentrations of several hundreds of mg l^{-1} , contributing, with other volatile compounds (sotolon), to their typical oxidized apple and nut flavor [8.41].


8.1.3 Compounds Originating from Grapes

Methoxypyrazines

Methoxypyrazines are nitrogen heterocycle compounds belonging to the pyrazine group, largely represented in both animals and plants [8.42]. Among the various methoxypyrazines, some alkylated methoxypyrazines, such as 2-methoxy-3-isobutylpyrazine (IBMP), 2-methoxy-3-sec-butylpyrazine, and 2-methoxy-3-isopropylpyrazine (IPMP) are highly volatile with very low-odor thresholds, in the nanogram per liter range in water (Table 8.1). The odors of these methoxypyrazines are vegetable-like, reminiscent of pea pods, green peppers and, depending on the concentration and the compound, earthy nuances. These same substances have also been identified in bell peppers, pea pods, potatoes, and carrots as well as blackcurrants, raspberries, and blackberries [8.43–45].

These compounds, particularly 2-methoxy-3-isobutylpyrazine (IBMP), have been identified in various grape varieties such as Cabernet Sauvignon, Cabernet Franc, Sauvignon blanc [8.46–49], Merlot, Carmenère, and Verdejo [8.45, 50–52]. IBMP has also been found in Pinot Noir, Chardonnay, Riesling, Chenin Blanc, Traminer, Syrah, and Pinotage [8.53, 54], but in very low concentrations. Among the most odorous methoxypyrazines, IBMP is proportionally the most abundant compound in grapes and wine. Its concentration in Sauvignon blanc wines varies from 0.5 to 40 ng l^{-1} and from 0.5 to 100 ng l^{-1} in Cabernet Sauvignon wines. This compound can be detected at the highest concentrations (up to 160 ng l^{-1}) in Carmenère wines, which are frequently marked by herbaceous flavors [8.45, 50]. In Sauvignon blanc, as in Cabernet Sauvignon, the pea-pod, pepper-like aroma of IBMP

Table 8.1 2-Methoxy-3-alkylpyrazines identified in grapes and wines

Name	Structure	Descriptors	Detection threshold (ng l ⁻¹)
			
2-Methoxy-3-isobutylpyrazine	R: CH ₂ CH(CH ₃) ₂	Greenpeper/pea pod	1 ^a
2-Methoxy-3-isopropylpyrazine	R: CH(CH ₃) ₂	Greenpeper/pea pod/earthy	2 ^a
2-Methoxy-3-sec-butylpyrazine	R: CH(CH ₃)CH ₂ CH ₃	Greenpeper/pea pod	1 ^a
2-Methoxy-3-ethylpyrazine	R: CH ₂ CH ₃	Greenpeper/pea pod	40 ^b
2-Methoxy-3-methylpyrazine	R: CH ₃	Greenpeper/pea pod	4000 ^c

^a Determined in water at ISVV, University of Bordeaux
^b Concentrations (after [8.34])
^c Concentrations (after [8.35])

contributes to their herbaceous expression. A negative effect has been noticed on Cabernet Sauvignon wine flavor at concentrations as low as 15 ng l⁻¹ [8.55]. IBMP can also affect the flavor of Tempranillo and Grenache grown in Spain [8.13]. On the other hand, IBMP can contribute, to some extent, to desirable varietal aromas in Sauvignon blanc wines [8.56, 57]. As noticed by Escudero et al. [8.58] and Pineau et al. [8.59], perceptual interaction phenomena between 2-methoxy-3-isobutylpyrazine and other compounds, β-damascenone, dimethylsulfide can modulate the perceived herbaceous flavor of this compound by tasters (Sect. 8.2).

During vinification, IBMP is easily extracted during pressing or prefermentation maceration [8.60, 61]. Neither alcoholic fermentation nor aging modify the original concentration of IBMP in the must by more than 30% [8.60, 61]. This means that conventional winemaking techniques do not contribute to a decrease of IBMP in must, from the original amounts in grapes to the finished wine. However, the settling of must during the fermentation of white or rosés wines can reduce IBMP levels by about 50% [8.60, 61]. As for red wines, thermo-vinification can lead to a decrease of IBMP by evaporation [8.60, 61]. During aging, and because this compound is nonoxidizable, oxygenation has no impact on its concentration [8.60, 61]. Moreover, IBMP content is very stable during aging and can affect wine aroma for many years [8.60, 61].

Furthermore, other methoxypyrazines, such as 2-methoxy-3-methylpyrazine [8.48] and 2-methoxy-3-ethylpyrazine [8.62, 63], have been identified in Sauvignon blanc grapes, but these compounds are much less odoriferous than IBMP (Table 8.1).

Also, numerous studies have been published concerning the impact of natural (climate, soil) and viticultural factors on IBMP concentrations in grapes and wine. Allen et al. [8.54] first noticed lower IBMP concentrations in wines obtained from grapes ripened at

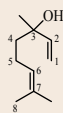



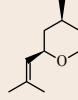
higher temperatures, whereas Falcao et al. [8.64] discovered varying IBMP levels in wines obtained from grapes grown at different altitudes. The sensitivity of IBMP to UV light and its resulting degradation, leading to the formation of 2-methoxy-3-methylpyrazine, a much less odoriferous compound [8.45, 65, 66] should be noted. Climate-related variations in IBMP content in grapes and wine thus represent a key factor [8.55, 67–69]. Moreover, other physiological parameters of grape vines, such as yields and the availability of water and nitrogen [8.45, 70] also impact IBMP development. IBMP content in ripe grapes may also vary significantly, depending on the clonal origin of the vines [8.50].

Terpenic Compounds

Terpenes are a very large widespread group of compounds. Working from an early hypothesis by Cordonnier [8.71], various enological research teams have conducted research to learn more about these compounds [8.72–75]. There are 40 main monoterpene compounds in grapes. The most important in terms of odor are certain monoterpene alcohols and oxides, such as linalool, geraniol, citronellol, (*E*)-hotrienol, (*E*) and (*Z*)-rose oxide and nerol (3,7-dimethyl-2(*Z*),6-octadien-1-ol), which develop floral aromas. The detection thresholds of these compounds are quite low, ranging from tens to hundreds of micrograms per liter (Table 8.2).

The monoterpene alcohols mentioned above play a major role in the aroma of grapes and wines from the Muscat family (Muscat de Frontignan, also called Muscat à Petits Grains or Muscat d'Alsace, Muscat of Alexandria, also called Muscat à Gros Grains, Muscat d'Otonel, White Muscat from Piemonte, etc.) as well as crosses between Muscat of Alexandria and other varieties (including such varieties as Muscat de Hambourg (crossed with Frankenthal [8.78]), and the Argentinian variety Torrontes (a cross with the Mission also called Pais variety [8.78]). The concentrations of

Table 8.2 Characteristics of some monoterpenes identified in grapes and wine

Name	Structure	Descriptors	Detection threshold ^a ($\mu\text{g l}^{-1}$)	Concentrations in Muscat wines (Min–Max) ^b ($\mu\text{g l}^{-1}$)
Linalol 3,7-Dimethyl-1,6-octadien-3-ol		Coriander seed-rose	20/3 ^c	170–815
Geraniol 3,7-Dimethyl-2(<i>E</i>),6-octadien-1-ol		Rose	90/9	223–1056
Citronellol 3,7-Dimethyl-6-octen-1-ol		Rose- lemongrass	20/15	nd-20
(<i>E</i>)-Hotrienol 3,7-Dimethyl-1,5(<i>E</i>)7-octatrien-3-ol		Linden-rose	300/70	5–300
(2 <i>S</i> , 4 <i>R</i>)-(–)- <i>cis</i> -Rose oxide		Floral-green	8 ^d /0.2 ^c	0.2–10 ^e

^a Determined in water at ISVV, University of Bordeaux
^b Concentrations (after [8.72–75])
^c Detection threshold in wine model solution and water, respectively
^d Determined on racemic mixture
^e Values (after [8.76, 77])

the main monoterpenes in these grapes and wines are much greater than the odor-detection threshold of these compounds. Monoterpenes also have a more or less pronounced impact in the flavor of Gewürztraminer, Albariño, Scheurebe, and Auxerrois grapes and wines, and to some extent those of Riesling, Muscadelle, and some clones of Chardonnay. These monoterpene alcohols are often found in many varieties (Sauvignon, Syrah, Cabernet Sauvignon, etc.) at levels generally below the olfactory perception threshold. In addition, as some monoterpenes have an asymmetric carbon, varying degrees of enantiomeric forms of monoterpenes can be found in grapes [8.79]. For example, linalool, hotrienol, *cis*-, and *trans*-rose oxide are predominantly present (88–97%) in a single enantiomeric form in the various varieties of Muscat that were analyzed (*S* form for linalool and (*E*)-hotrienol and (2*S*, 4*R*) and (2*R*, 4*S*) forms for (*Z*)-rose oxide, respectively). The abundance of one or the other enantiomer may contribute to modulating the strength of these odorous compounds in grape juice and wine, as well as aromatic expression. *R*-(–)-linalool, with an odor threshold of 0.8 $\mu\text{g l}^{-1}$, is described as having floral notes and overtones of woody lavender. It is more odoriferous than

S-(+)-linalool, which presents a floral, sweet scent with a detection threshold of 17 $\mu\text{g l}^{-1}$ [8.76]. However, the proportions of enantiomeric forms may change over the fermentation process, the most fragrant enantiomer, *cis*-(2*S*, 4*R*)-rose oxide or (*Z*)-(–)-rose oxide, being for example, between 38 and 76% in wine [8.76]. Other than rose oxide, oxides present in grapes, such as the oxides of linalool and nerol, have little olfactory impact (i. e., high-perception thresholds of 1–5 mg l^{-1}). However, the presence of linalool oxide contributes to the increased perception of linalool [8.77, 80].

Botrytis cinerea development on grapes can also alter the composition of grape monoterpenes by degrading the main monoterpene alcohols and their oxides into generally less odorous components [8.73, 81]. Also, fermentation significantly alters the monoterpene composition of grapes through chemical and microbiological processes. The most pronounced transformation concerns the degradation of nerol and geraniol by the yeast *S. cerevisiae* via an enzymatic reduction to form citronellol, alpha-terpineol, and linalool [8.82, 83]. The proportion of the above compounds depends on the yeast strain and grape juice composition [8.84]. Also, during fermentation, the enzymatic reduction of 3,7-

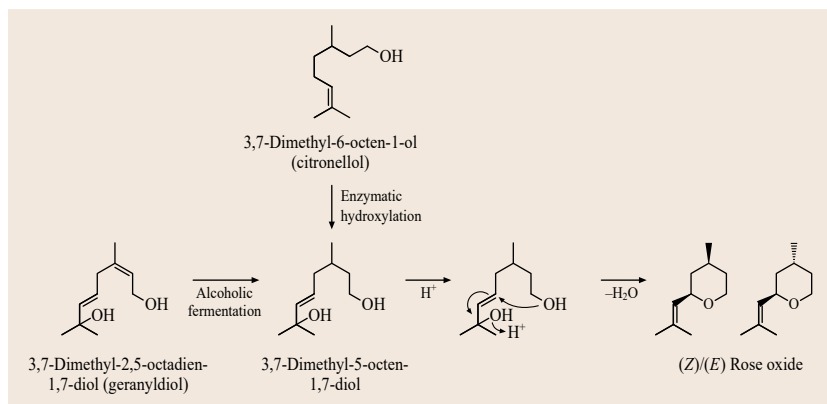


Fig. 8.1 Formation of rose oxide from various precursors in grape and during vinification (after [8.80])

dimethyl-2,5-octadien-1,7-diol or geranyldiol leads to the formation of a diendiol 3,7-dimethyl-5-octen-1,7-diol which is a precursor of rose oxide [8.80]. This diol is also derived from the enzymatic hydroxylation of citronellol in grapes [8.80]. These results illustrate the deep changes in the flavor of grapes that can result from the combination of fermentative metabolism of yeasts and wine acidic conditions (Fig. 8.1). Then during wine aging, the terpenols themselves may undergo rearrangements in acid to produce other monoterpene alcohols [8.85]. This is a classic chemical reaction involving the dehydration of alcohols in an acid medium. Thus, the alcohol dehydration of 3,7-dimethylocta-1,5-dien-3,7-diol, in the wine acidic medium, yields (*E*)-hotrienol, while (*E*)-2,6-dimethyl-6-hydroxyocta-2,7-dienoic acid has recently been identified as the precursor of the *wine-lactone* via stereoselective cyclization (Fig. 8.2) [8.86]. On the other hand, the concentrations of geraniol and nerol, which constitute part of the aroma of young wines, can rapidly decrease after 2–3 years of bottle aging (for instance in Muscat), and then no longer contribute in the same way to wine aroma. Linalool is more stable. Concentrations of this compound may even actually increase at the beginning of aging since it is formed from geraniol and nerol [8.87]. More specifically, cyclizing nerol produces α -terpineol; nerol is transformed into α -terpineol and linalool. Linalool is also converted into terpene hydrate over time [8.87]. These results account, at least partially, for the fact that the very intense young character of Muscat wine disappears during aging, acquiring a resinous odor.

Sesquiterpenoids

Sesquiterpenoids ((+)-aromadendrene, α -humulene, α -bisabolol, dehydro-aromadendrene, etc.) are secondary metabolites of grapes [8.88, 89] that do not generally contribute directly to wine flavor as their concentrations are usually in the $\mu\text{g l}^{-1}$ range, below the olfactory

perception threshold of these compounds. Nevertheless, the characterization of pepper nuances in Syrah wines led to the successful identification of (–)-rotundone, a powerful sesquiterpene with an olfactory perception threshold in the ng l^{-1} range (Table 8.3). Concentrations in Syrah range from 50 to 600 ng l^{-1} , and it is assumed that this compound can contribute to the black pepper flavor of this variety [8.88, 89].

C₁₃-Norisoprenoid Derivatives

The oxidative degradation of carotenoids, which belong to the family of terpenes with 40 carbon atoms (tetraterpenes), leads to many derivatives, including norisoprenoids with 13 carbon atoms (C₁₃-norisoprenoids) that may contribute to the aroma of wines. Three major groups each containing various volatile odoriferous compounds are concerned. The oxygenated megastigmane group includes powerful compounds, such as beta-damascenone [8.93, 94]. The smell of β -damascenone is reminiscent of apple sauce and tropical fruit. β -Damascenone has a very low-odor threshold in water (2 ng l^{-1}) and a threshold close to wine in model solution (60 ng l^{-1}) (Table 8.4). This compound, initially identified in grape juice from the Riesling and Scheurebe varieties by Schreier [8.93, 94] and then in many other varieties [8.93, 94] has maintained the myth of a major contribution to wine aromas given its very low olfactory threshold in water (2 ng l^{-1}). In fact, the perception threshold of β -damascenone in wine is between 2 and 7 $\mu\text{g l}^{-1}$, although this com-

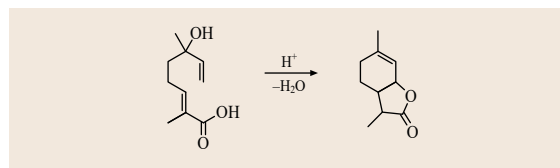


Fig. 8.2 Formation of wine lactone from (*E*)-2,6-dimethyl-6-hydroxyocta-2,7-dienoic acid (after [8.86])

Table 8.3 (–)-Rotundone a powerful sesquiterpenoid in wine (after [8.88, 89])

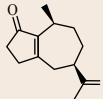
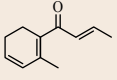
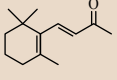
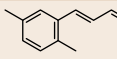
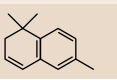
Name	Structure	Detection threshold ($\mu\text{g l}^{-1}$)	Concentrations in wines ($\mu\text{g l}^{-1}$)
(–)-Rotundone		0.016/0.008	0.05–0.6

Table 8.4 Characteristics of some C_{13} -norisoprenoids identified in wines

Name	Structure	Descriptors	Detection threshold ^a (ng/L)	Concentrations in wines (Min–Max) ^b (ng/L)
β -Damascenone		Applesauce rose	60/2 ^c	100–2500
β -Ionone		Violet	800/120	nd-2415
TPB		Geranium leaf	24/20	nd-120
TDN		Kerosene-like	2300/1000	nd-30000

^a Determined at ISVV, University of Bordeaux

^b Concentrations (after [8.59, 90–92])

^c Detection threshold in wine model solution and water, respectively

ound, usually found in concentrations of between 700 ng l^{-1} and $2.5 \mu\text{g l}^{-1}$ [8.93, 94], is rarely the only one involved in the aromatic composition of wines. However, β -damascenone can contribute by synergistic phenomena (Sect. 8.2). β -Ionone, with a distinctive smell of violet, has a perception threshold of 120 ng l^{-1} in water, 800 ng l^{-1} in model solution and $4 \mu\text{g l}^{-1}$ in white wine, and its influence has been demonstrated in various grapes and wine varieties [8.90, 93, 94]. Other C_{13} -oxygenated norisoprenoids, such as 3-oxo- α -ionol (tobacco), 3-hydroxy- β -damascone (tea, tobacco), and β -damascone (tobacco, fruit) can provide only a very weak potential contribution to wine aroma. The second group consists of non-oxygenated megastigmane compounds, with 1-(2,3,6-trimethylphenyl)buta-1,3-diene (TPB) as a major representative. The detection threshold of this compound, presenting a typical geranium leaf odor, is 40 ng l^{-1} in wine and 20 ng l^{-1} in water. Concentration ranges in some old Sémillon wines can reach 200 ng l^{-1} [8.93, 94]. The third group, composed of nonmegastigmanes, includes some odorous compounds as 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), which smells like kerosene and has a detection threshold of $1 \mu\text{g l}^{-1}$ [8.91, 93, 94], (*E*) and (*Z*)-vitispirane which have camphor/woody nuances, riesling acetal (fruity descriptor), and actinidol (woody). TDN is considered to account in large part for the *petroleum* aromas of aged Riesling wines [8.93, 94] while (*E*) and (*Z*)-vitispirane, riesling acetal, actinidol are considered

to have a limited contribution to wines aroma, particularly Riesling, as their concentration are usually much lower than their detection threshold [8.93, 94]. While megastigmane compounds from the first group can be detected in grape must and are present in the young wine, the representatives of the two other groups are only formed during wine aging. All these compounds originate from carotenoids present in grape, through enzymatic oxidative cleavage leading to hydroxylated C_{13} -norisoprenoid which then are submitted to several dehydration reactions in wine acidic media.

Impact of Volatile Thiols

In enology, many sulfur compounds in the thiol (sulfanyl) family are held responsible for olfactory defects. However, during the 1990s, several of these compounds were detected in wine and their positive contribution to wine flavor, particularly the varietal aroma of Sauvignon blanc wines and other white and red varieties, is now well documented. The three most important thiols in Sauvignon blanc aroma are 3-sulfanylhexanol (3SH), reminiscent of grapefruit flavor, 3-sulfanylhexyl acetate (3SHA), and 4-methyl-4-sulfanylpentan-2-one (4MSP) with box tree and broom aromas (Table 8.5) [8.95–98]. Descriptors, such as box tree and broom for 4MSP and grapefruit/passion fruit for 3SH match the occurrence of these compounds in box tree, broom, grapefruit, and yellow passion fruit, respectively. Several other odoriferous volatile thiols have also been

Table 8.5 Characteristics of some volatile thiols (sulfanyls) identified in wines

Name	Structure	Descriptors	Detection threshold ^a (ng l ⁻¹)	Concentration in wines ^b (ng l ⁻¹)
3-Sulfanylhexanol 3-SH		Passion fruit, grapefruit	60	100–10 000
3-Sulfanylhexylacetate 3SHA		Boxwood, passion fruit	4	0–1000
4-Methyl-4-sulfanylpentan-2-one 4MSP		Boxwood, broom	0.8	0–120
4-Methyl-4-sulfanylpentan-2-ol 4MSPOH		Citrus zest	55	0–150
3-Methyl-3-sulfanylbutan-1-ol 3MSB		Cooked leeks	1500	0–1500
3-Sulfanylpentan-1-ol 3SP		Citrus	900	0–400
3-Sulfanylheptan-1-ol 3SHp		Grapefruit	35	0–80
2-Methyl-3-sulfanylbutan-1-ol 2M3SB		Raw onion	nd	10–70

^a Threshold determined in wine model solution at ISVV, University of Bordeaux

identified in Sauvignon blanc wine, such as 4-methyl-4-sulfanylpentan-2-ol, with a grapefruit zest flavor, and 3-methyl-3-sulfanylbutan-1-ol, smelling of leeks [8.97, 98]. Although these varietal thiols were first identified in Sauvignon blanc wine, they have also been found to contribute to the varietal aroma of wines made from other *Vitis vinifera* varieties, both red and white, such as Gewürztraminer, Riesling, Sémillon, Manseng, and Arvine [8.99, 100], as well as Merlot and Cabernet Sauvignon [8.101, 102].

More recently, 3-sulfanylpentan-1-ol (3SP), 3-sulfanylheptan-1-ol (3SHp), 2-methyl-3-sulfanylbutan-1-ol (2M3SB), and 2-methyl-3-sulfanylpentan-1-ol (2M3SP) were identified in Bordeaux dessert wines [8.103] and additive effects between them have been reported (Sect. 8.2). Due to their functional SH-group, thiol compounds sometimes occur in (*R*)- and (*S*)-enantiomer form. The enantiomeric distribution of 3SH, which contains one chiral center, was initially studied in passion fruit [8.97, 98], and later investigated in wines made from Sauvignon blanc and Sémillon grapes by *Tominaga et al.* [8.104]. The (*R*)- and (*S*)-enantiomer ratios of these two thiols in dry white Sauvignon blanc and Sémillon wines are approximately 30 : 70 for 3SHA and 50 : 50 for 3-sulfanylhexanol. However, in white dessert wines made from botrytized grapes, the proportion of the *R* and *S* forms of 3SH is in the vicinity of 30 : 70. The aroma descriptors of the two enan-

tiomers of 3SH and 3SHA are quite different, although their perception thresholds are similar. Therefore, the enantiomeric distribution of 3SH and 3SHA in wine may have an impact on the perception and complexity of dry and sweet white wine aromas [8.104]. These varietal thiols originate from nonvolatile grape precursors, i. e., *S*-cysteine or glutathione conjugates, released during alcoholic fermentation [8.105]. 3-Sulfanylhexyl acetate (3SHA) is produced by enzymatic esterification of 3SH by *S. cerevisiae* yeast [8.106]. Accordingly, the formation of these compounds (thiols and esters) depends both on the yeast strain in alcoholic fermentation and the must matrix. Also, as thiols (sulfanyls) are highly reactive, they need to be preserved during winemaking and aging by protecting them from oxygen.

Lactones

Both γ - and δ -lactones are important aroma compounds, present in a wide variety of foods, beverages, and fruits. Many of them have been detected in wines, but one of the main cited is γ -nonalactone (Table 8.6). This compound has been identified in many different types of wine, including dry red and white, as well as botrytized and fortified wines [8.39, 107, 108]. Concentrations are low in white wines ($\approx 5.9 \mu\text{g l}^{-1}$) and higher in botrytized and old red wines ($27\text{--}40 \mu\text{g l}^{-1}$) [8.109, 110]. This compound, smelling of cooked peach when diluted, may con-

tribute to the characteristic prune flavor of these old red wines [8.111]. However, this substance is unlikely to contribute individually and directly to the aroma of most red wines, but probably has a greater impact in synergy with other γ - and δ -lactones. As γ -nonalactone is also found in oak wood, higher levels are found in wines aged in barrel [8.112].

This lactone is also a chiral compound, with enantiomers that differ slightly in their odor descriptors and strongly in their odor thresholds. Analysis of its enantiomeric distribution in wines revealed that, with few exceptions, the (*R*) enantiomer was more prevalent than its (*S*) counterpart in all the botrytized white wines analyzed, whereas neither isomer was overwhelming predominant in red wines [8.113].

This lactone is detected at low levels in grapes, depending on maturity or the development of noble rot (*B. cinerea*) [8.114], but is mainly produced by yeast (*S. cerevisiae*) during alcoholic fermentation [8.115]. *S. cerevisiae* yeast has been shown to produce γ -nonalactone from linoleic acid by two biosynthetic pathways [8.116]. The first features 13-lipoxygenation of linoleic acid to (*S*)-13-hydroxyoctadecadienoic acid, followed by four β -oxidation cycles and finally α -oxidation to (*S*)- γ -nonalactone (40–80% ee). The second features 9-lipoxygenation of linoleic acid to (*R*)-9-hydroxyoctadecadienoic acid, followed by a Baeyer-Villiger type oxidation to 3-(*Z*)-nonen-1-ol, which is further metabolized to the (*R*)-enantiomer (40–60% ee). Finally, this enzymatic mechanism exhibits an unsteady optical purity. Another odoriferous lactone, 2-nonen-4-olide, implicated in perceptual interaction phenomena, was recently identified in dessert wines [8.117].

Furanones

The flavor of 4-hydroxy-2,5-dimethyl-3(*2H*)-furanone (Furaneol, HDMF) is influenced by its concentration; the pure compound is reminiscent of caramel, while it is described as cooked strawberry at low concentrations. This compound has a pK_a of 8,56 (20 °C) and, like many structurally related compounds, 3(*2H*) furanone is highly soluble in water (0.315 g mL⁻¹, 25 °C) [8.118]. It was first identified in grapes and wines made with certain fungus-resistant cultivars obtained by cross-breeding wild American vines (*Vitis labrusca*) with European cultivars (*Vitis vinifera*), marked by an intense strawberry flavor. For example, furaneol levels as high as 10 mg l⁻¹ have been measured in wines made from the Castor cultivar [8.119]. Since then, it has frequently been reported as contributing to the complexity and quality of red wines, while the lowest levels were found in dry white wines (10–40 μ g l⁻¹). On the contrary, concentrations may

reach 60 μ g l⁻¹ in young Cabernet Sauvignon wines and even 150 μ g l⁻¹ in Merlot. These values are well correlated with the caramel note found in certain Merlot wines [8.120]. High concentrations have also been reported in sweet fortified wines, reaching more than 620 μ g l⁻¹ in young wines but decreasing during aging suggesting that this compound is unstable at wine pH, degrading to form acetylformoin [8.121], buta-2,3-dione, and acetoin [8.122]. In wines, this furanone exists in free and odorous form, as well as bound to sulfur dioxide and catechols (mainly nonpolymerized forms). According to *Ferreira et al.* [8.123], this finding may explain the low free furaneol levels found in white wines.

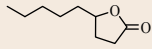
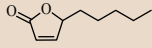

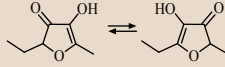
As demonstrated by *Guedes de Pinho et al.* [8.124], furaneol levels can be increased by using pectolytic enzymes with β -glucosidic secondary activities, suggesting the existence of glycosylated precursors. Also, while it is absent from grapes at maturity, high levels have been found in overripe grapes. As furaneol may be formed from pentose or hexose by a Maillard reaction, its presence in grapes may also be enhanced by high temperatures around maturity [8.125]. Besides these aspects, *Sarrazin et al.* [8.39] highlighted the fact that most of the furaneol found in wine is released or produced thanks to the yeast metabolism during alcoholic fermentation [8.39]. The use of toasted oak wood may also provide an additional source of this furanone.

Homofuraneol, HEMF (5 (or 2)-ethyl-4-hydroxy-2(or 5)-methyl-3(*2H*)-furanone), like furaneol, has a planar enol-oxo-configuration, but, due to the asymmetry of the molecule, both tautomeric forms have been identified and separated by GC on polar phase [8.126]. This compound was detected at the end of the 1990s in wines [8.77] and, like furaneol, is reminiscent of caramel and cooked strawberries. Concentrations in wines are lower compared to furaneol, ranging from 10 to 70 μ g l⁻¹ in dry red and white wines, and thus rarely exceed its perception threshold (Table 8.6) [8.39]. The lowest levels (a few μ g l⁻¹) were found in sweet fortified wines, whereas the highest values, around 320 μ g l⁻¹, were determined in botrytized wines. Moreover, owing to a strong synergistic effect between HDMF and homofuraneol, the fruity caramel note was increased, as evidenced in some rosé wines [8.127].

C₆ Aldehydes and Alcohols

Unsaturated fatty acids with 18 carbon atoms, such as linoleic acid and linolenic acid, are converted during prefermentation operations into the C₆ aldehydes hexanal and 2- and 3-hexenal with the aid of grape lipoxygenase [8.128, 129], and then further reduced to alcohol during fermentation. These C₆ aldehydes and

Table 8.6 Main furanones and lactones in wine

Name	Structure	Descriptors	Detection threshold
Racemic γ -nonalactone		Coconut, cooked peach	$30 \mu\text{g l}^{-1\text{b}}$
(<i>R</i>)-form soft coconut with fatty-milky aspects strong, sweet ^c			$284 \mu\text{g l}^{-1\text{a,c}}$
(<i>S</i>)-form fatty, moldy, weak coconut note ^c			$91 \mu\text{g l}^{-1\text{a,c}}$
2-Nonen-4-olide		Minty and fruity	$4.3 \mu\text{g l}^{-1\text{b}}$
Furaneol		Cooked strawberry, caramel	$60 \mu\text{g l}^{-1\text{b}}$
Homofuraneol		Cooked strawberry, caramel	$10\text{--}40 \mu\text{g l}^{-1\text{b}}$

^a Wine, ^b Wine model solution determined at ISVV, University of Bordeaux, ^c Cooke et al. [8.113]

alcohols smell like freshly cut grass, but, considering their detection thresholds in the mg l^{-1} range, when taken separately, they rarely contribute directly to the herbaceous character of musts and wines.

8.1.4 Aging Aroma and Oak Related Flavor Compounds

Aging of wine is an important aspect of wine connoisseurship and one which distinguishes wine from almost every other drink. Already, in Antiquity, Falernian, and Surrentine wines required 15–20 years aging before they were considered at their best and were sometimes kept for decades in sealed earthenware jars or amphorae. Moreover, the Greek physician Galen was probably the first to note that an *aged* wine need not necessarily be old, but might simply have the characteristics of age. In other words, it was possible to age wines prematurely by heating or smoking them.

Nowadays, when we age wine, we hope for changes that will cause the wine to mature well by gaining a complex mix of complementary flavors. This is why the reputation of white and red wines is always strongly associated with their aging potential. These wines are able to retain the flavor nuances of young wines while developing specific varietal nuances. This kind of aging results in what is known as a reduction *bouquet*. While this specific organoleptic character is highly prized by connoisseurs, ideal aging does not occur in every wine. Most of the time, wine flavor develops quickly, resulting in a loss of complexity and personality, i.e., the flavor found in every oxidized wine. This phenomenon, known as premature aging, is well known in white wines and has more recently been found in

red wines. Prematurely aged (Premox) white wines are reminiscent of honey, cider, and in certain cases, cooked vegetables, while red wines develop several aromatic nuances reminiscent of prunes and figs. In our experience of red wine tasting, the presence of these overriding odors affects the quality and subtlety of the wine flavor and may shorten its shelf life.

Wine aging generally consists of two phases: maturation (oxidative aging) and bottle aging (reductive aging). During maturation, wine is often stored in oak barrels. Continued aging in bottle is known as reductive aging, due to the small amount of oxygen inside the bottles.

Oak Wood Volatile Compounds in Wine Aroma

Oak (*Quercus* sp.) is currently the only wood used in making barrels for fermenting and aging quality wines. A fundamental aspect of aging wines in oak concerns the aromatic compounds extracted from the wood. When these compounds marry perfectly with a wine's intrinsic aromas, they make a significant contribution to the richness and complexity of the bouquet, as well as improving the flavor. Volatile extractive compounds from oak wood are responsible for important olfactory notes, such as coconut, wood, vanilla, caramel, and spice that play an essential role in wine aging in oak casks. They generally have low-aroma thresholds and may thus be detected by tasters in mature beverages at very low concentrations. Volatile content is strongly affected by natural factors, as well as botanical species (*Quercus robur*, *Quercus petraea*, *Quercus alba*), geographical origins, and cooperage techniques, such as seasoning and toasting (also known as hydrothermolysis). Hundreds of oak-derived volatile compounds have

Table 8.7 Oak volatile compounds

Name	Structure	Descriptors	Detection threshold ^a
(Z)-Oak lactone		Coconut, earthy	20 $\mu\text{g l}^{-1}$
(E)-Oak lactone		Spicy, coconut	110 $\mu\text{g l}^{-1}$
Vanillin		Vanilla	65 $\mu\text{g l}^{-1}$

^a In wine model solution determined at ISVV, University of Bordeaux

been identified in alcoholic beverages. One group of compounds is formed by the degradation of oak lignin. This releases a range of phenolic odorants, the most important being eugenol, guaiacol, and 4-methylguaiacol, which give wine smoky and spicy aromas. Many other odorants are also directly or indirectly associated with wood aging, increasing the complexity of wines aged in oak barrels [8.130–133].

Of all the volatile compounds in oak wood, oak lactones, (*E*)/(*Z*)- β -methyl- γ -octalactone, particularly the *cis*-isomer, are considered the most important oak-derived compounds in wine. The structure of oak lactone, which is reminiscent of coconut, features two stereocenters, giving a total of four possible stereoisomers and two enantiomeric pairs of diastereoisomers. However, it has been established that oak wood contains only the (4*S*, 5*S*)-*cis*-1 and (4*S*, 5*R*)-*trans*-2 isomers of oak lactone [8.134]. The concentration of oak lactone (*cis*+*trans*) in untoasted wood ranges from 30 to 150 $\mu\text{g g}^{-1}$. In wines, the concentration of *cis*-oak lactone (the most odorous compound, Table 8.7), was found to be greater (under 20 $\mu\text{g l}^{-1}$ to over 1000 $\mu\text{g l}^{-1}$) than that of the *trans*-isomer (under 20 $\mu\text{g l}^{-1}$ to over 400 $\mu\text{g l}^{-1}$). The two isomers may be present at levels considerably higher than their perception thresholds [8.134]. Above a certain concentration, excessive amounts of this lactone may have a negative

effect on wine aroma, giving it a strong woody or even resinous odor. Even when alcoholic fermentation takes place in barrels, the yeast metabolism has no impact on concentrations in wine. By analyzing the ratio of *cis*- and *trans*-isomers, it is possible to determine the source of wood used for barrel aging. This finding has been supported by results showing that American oak (*Quercus alba*) has only approximately 10% of the *trans*-isomer, while French oak (*Quercus robur*, *Quercus sessilis*) was found to have an almost equal amount of both stereoisomers. Moreover, this lactone is specific to oak wood. Only trace levels have been found in acacia, cherry, and chestnut woods, other species potentially used by coopers [8.135]. Detected in fresh oak woods, the two isomers of β -methyl- γ -octalactone are also formed during the air-drying process and during toasting at high temperature (150–200 °C) through dehydration of several precursors naturally present in oak wood. The precursors identified in oak wood are *cis*-3-methyl-4-galloyloxyoctanoic acid (ring-opened *cis*-oak lactone gallate, *R*=4), (3*S*,4*S*)- and (3*S*,4*R*)-3-methyl-4-*O*- β -D-glucopyranosyloctanoic acid (ring-opened *cis*- and *trans*-oak lactone glucoside *R*=1) [8.136], (3*S*,4*S*)-3-methyl-4-*O*-(6'-*O*-galloyl)- β -D-glucopyranosyloctanoic acid (ring-opened *cis*-oak lactone galloylglucoside, *R*=2) and 3-methyl-4-*O*-(6'-*O*- α -L-rhamnosyl)- β -D-glucopyranosyloctanoic acid (*R*=3) [8.137, 138] (Fig. 8.3). Concerning the glycoconjugate precursors, Wilkinson et al. [8.138] reported concentrations of the galloylglucoside (*R*=2) in French oak woods ten times higher (110–354 $\mu\text{g g}^{-1}$) than those of the others forms (*R*=1, *R*=3). Finally, knowledge of precursors indicated that the formation of oak lactone from oak lactone precursors could occur in two steps: liberation of the ring-opened oak lactone from oak lactone precursor by either pyrolysis (toasting) or enzymic activity and acid hydrolysis, followed by ring closure (lactonization) to yield oak lactone [8.139].

Vanillin plays an active part in the oaky and vanilla odors that barrels release into wine. However, its organoleptic contribution is a matter of debate. It may be direct or indirect according to its concentra-

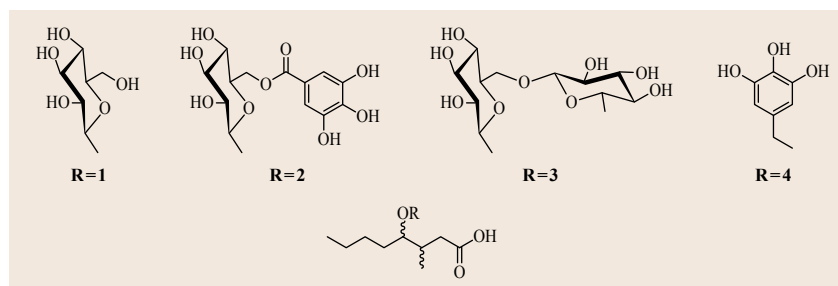


Fig. 8.3 Structure of the precursors of oak lactone identified in oak wood

tion and, more importantly, the type of wine (white or red) [8.140]. Only traces of vanillin are detected in grapes and wines, but much higher concentrations are released by toasted oak wood into wines during barrel aging. Though it is detected in nontasted wood, toasting significantly increases the concentration. Vanillin accumulates quickly in wine: 70% of the final concentration of a 9 month storage period is reached during the three first months [8.141]. According to the aging period (≈ 6 –24 months) and the type of wood, the highest level ($\approx 5 \text{ mg l}^{-1}$) was systematically found in red wines. Indeed, traditionally, white wines undergo alcoholic fermentation in oak barrels to limit the organoleptic impact of wood compounds. This is mainly due to a biochemical transformation of vanillin into the barely fragrant vanillyl alcohol (perception threshold: 50 mg l^{-1}), vanillyl ethyl ester (2.5 mg l^{-1}), and, finally, flavorless vanillyl ethyl ether. Moreover, yeast lees are capable of fixing and continuing to transform certain volatile compounds as they are released from the wood [8.142]. In general, the extraction of vanillin from wood is greater than its conversion, so it accumulates in the wine. During malolactic fermentation (MLF) in wood barrels, an increase in vanillin is associated with the secondary metabolism of lactic acid bacteria (*O. oeni*) [8.143]. It has been demonstrated that these bacteria are able to hydrolyze glycosylated compounds released by oak wood; but, to date, specific precursors have not yet been identified. Ferulic acid was demonstrated to produce vanillin in the presence of *O. oeni*, but yields were low, resulting in amounts too small to explain the concentrations found in wines after MLF [8.144].

Reduction-Related Flavor Compounds: Reduction Bouquet

Empyreumatic aromas originate from greek empyreume, *εμπυρευμα* (which is burned), the reminiscent of smoke and burnt wood odors, often feature in descriptors used by wine tasters. *Tominaga et al.* [8.145, 146] investigated the sensory impact of several volatile thiols on the reduction bouquet of wine aroma.

One potent thiol, 2-furanmethanethiol (2FM), develops a strong roast-coffee aroma and has been identified in Jurançon white dessert wines made from Petit Manseng grapes, as well as red Bordeaux wines (made from Merlot, Cabernet Franc, and Cabernet Sauvignon). These wines contain a few several dozen ng l^{-1} 2FM (Table 8.8). The highest amount (500 ng l^{-1}) was assayed in red wines at the end of 12 months aging in new oak barrels. Taking into account its very low-perception threshold (0.4 ng l^{-1}), 2FM can therefore contribute to the roast-coffee aroma of certain barrel-aged red and white wines [8.145, 147]. This compound

has also been reported in some old Champagnes, where it may be produced during bottle aging [8.148].





Traces of 2FM have been found in toasted oak used in barrel-making [8.149]. Furfural, released by toasted oak wood, plays a major role in 2FM formation in barrel-fermented white wines, where it is closely related to the yeast's (*S. cerevisiae*) sulfur metabolism. In barrel-aged red wines, a biochemical pathway involving furfural and a secondary metabolism of lactic bacteria (*O. oeni*) may promote a chemical route, involving furfural and H_2S . However, its formation mechanisms in bottle have not yet been elucidated.

Benzenemethanethiol (BM) contributes to the smoky/gunflint odor in several varietal wines. BM was detected systematically in white wines, including young (20 – 30 ng l^{-1}) and old Champagnes (200 – 400 ng l^{-1}), Sauvignon blanc (10 – 20 ng l^{-1}), and Chardonnay (20 – 40 ng l^{-1}). The lowest levels were found in red wines ($< 10 \text{ ng l}^{-1}$) [8.146]. This sulfur-containing compound has an extremely low-detection threshold (0.3 ng l^{-1}) and makes a significant sensory contribution to the aroma of white wine. Together with 2-furanmethanethiol, these thiols contribute to the empyreumatic nuances in the bouquet of old Champagne wines [8.148]. The precursors of this thiol have not yet been identified.

2-Methyl-3-furanthiol (2M3F), the reminiscent of cooked meat, was identified for the first time in wine by *Bouchilloux et al.* [8.150]. Despite its instability, assaying 2M3F demonstrated its ubiquitous properties in young, as well as older wines (3–8 years old). It was detected systematically in red and white wines from different appellations at concentrations up to 100 ng l^{-1} , i. e., significantly above the olfactory perception threshold for this compound in model dilute alcohol solution (2 – 8 ng l^{-1}). The highest values (reaching 200 ng l^{-1}) were found in Champagnes. At this level, it contributes to the overall *toasty* aroma in these wines [8.147]. The formation mechanisms of this compound, produced by Maillard reactions when food is cooked, have been studied in food, as well as in a model medium containing cysteine and pentose [8.151, 152]. In wine, its origin remains unclear. It has not been detected in must and is probably produced by yeast during alcoholic fermentation or brought in by dry yeasts [8.153].

Another important sulfur compound in the flavor of aged wines is dimethyl sulfide (DMS), identified by *Marais* [8.154]. It elicits odors described as *asparagus*, truffles, and molasses and plays an ambiguous role in wine aroma. Indeed, its influence on wine aroma was perceived either positively or negatively, depending on the DMS content and type of wine [8.155]. For example, it produces synergistic effects for fruity odors at subthreshold concentrations

Table 8.8 Volatile sulfur compounds related to aging aroma

Name	Structure	Descriptors	Detection threshold ^a
Dimethyl sulfide		Quince, truffle	25 $\mu\text{g l}^{-1}$ (white wine) and 65 $\mu\text{g l}^{-1}$ (red wine)
Benzenemethanethiol		Gunflint, smoky	0.3 ng l^{-1}
2-Furanmethanethiol or 2-Furfurylthiol		Roasted coffee	0.4 ng l^{-1}
2-Methyl-3-furanthiol		Cooked meat	2–8 ng l^{-1}

^a In wine model solution determined at ISVV, University of Bordeaux

(10 $\mu\text{g l}^{-1}$) in mixtures containing fruity esters, C_{13} -norisoprenoids, and linalool [8.156, 157]. Moreover, DMS is considered a beneficial compound at low concentrations, contributing to the aroma of bottle-aged wines. DMS concentrations found in wine range from a few $\mu\text{g l}^{-1}$ to 480 $\mu\text{g l}^{-1}$, well above the sensory threshold (27 $\mu\text{g l}^{-1}$) [8.158]: levels in freshly bottled wines are low and increase during aging, depending on storage temperature [8.159]. The DMS formation mechanism in wine is not clear. It may be formed in a similar way to other mercaptans. It appears during aging, via a yeast mechanism, by cleavage of *S*-methyl-*L*-methionine to form homoserine and dimethyl sulfide, and is also variously linked to the cysteine, cysteine, or glutathione metabolism in yeast.

Recently a strong correlation was established between the appreciation of reduction bouquet in aged great Bordeaux wines with the level of abundance of 2-methanefuranethiol and DMS [8.160]. Also, other thiol (sulfanyl) derivatives associated with ageing bouquet have been identified as vanillylthiol resulting from vanillin transformation and several thiopyrroles in aged Chardonnay wines from Burgundy [8.161].

Oxidation-Related Flavor Compounds

Sotolon (4,5-dimethyl-3-hydroxy-2(5H)-furanone) is an important five-branched lactone belonging to the isotetronic acid family (Table 8.9). The pure compound possesses an intense odor of curry, but develops honey and nutty flavors when diluted. NMR revealed that only the enolic tautomer of sotolon was observed in aqueous solution [8.162]. It is stable at the pH of wine, but unstable under basic conditions and in apolar organic solvent. Furthermore, this thermolabile, highly polar compound is susceptible to irreversible adsorption in GC-MS and is difficult to extract from wine samples (poor yields). However, methodologies have been optimized for its quantification and SIDA approaches (^{13}C label) gave the best results [8.162, 163].

Sotolon contributes to the aromas of *vins jaunes* from the Jura and sherries [8.164, 165], as well the *dried fig* and *rancio* nuances in French fortified wines (Vins doux naturels – VDN) and port [8.166, 167]. Concentrations in white wines made from grape varieties like Savagnin increase during aging with yeast *flor*, as well as during the barrel aging of sweet wines [8.167–169]. Wines of this type, over 20 years old, may contain up to 1 mg l^{-1} sotolon that contributes to the typicality of these wines, made under oxidative conditions.

This furanone has also been detected in white wines made from botrytized grapes [8.170] but is rarely found in red wines. More recently, several authors determined the contribution of sotolon to the oxidation aromas of prematurely aged dry white wines [8.171–173]. The highest concentration found in these dry wines was 15–20 $\mu\text{g l}^{-1}$. Oxidation phenomena are involved in generating sotolon in wine. In wines that are made traditionally under reductive conditions, sotolon is considered an off-flavor.

Both enantiomers are detected in white wines, but due to its low-perception threshold, only (*S*)-sotolon contributes to the characteristic aroma of prematurely aged (premo) dry white wines. According to the wines, the maximum enantiomer excess (ee) ranged from 56 to 50 for the *R* and *S* forms, respectively [8.174, 175].

According to several studies, amino acids and, more precisely, threonine constitute a potential source of this furanone in wines. Its enzymatic or chemical deamination to 2-ketobutyric acid, followed by an aldol condensation with acetaldehyde, led to the formation of racemic sotolon (Fig. 8.4) [8.177]. Acetaldehyde and 2-ketobutyric acid are found in every wine as by-products of *S. cerevisiae*. 2-Ketobutyric acid has also been identified as an oxidative degradation product of ascorbic acid, a natural antioxidant present in small quantities in grapes and added during white wine vinification as well as at bottling (from 50 to 100 mg l^{-1}) to protect the wine from oxidative phenomena. A stereoselective pathway producing enantiopure sotolon has

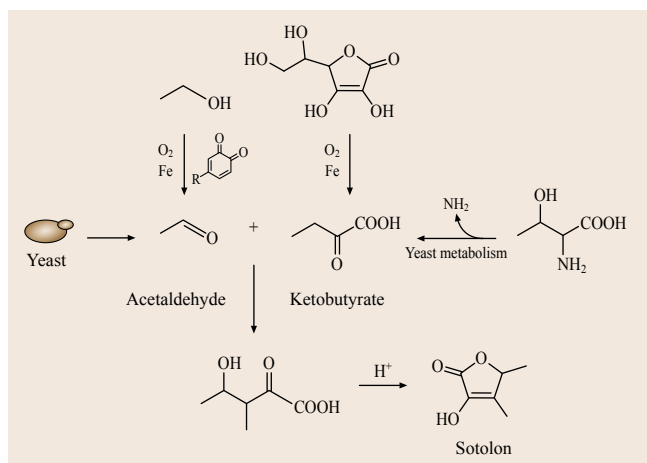


Fig. 8.4 Chemical and biochemical production of sotolon in wines (after [8.166, 176, 177])

not yet been identified. However, such a mechanism is not ruled out; low enantiomeric excess (ee) may be partly explained by the slow racemization kinetics (20 months) of optically active sotolon. Abhexon, an analogue of sotolon, with very similar organoleptic properties, has been identified in old Sauternes and flor sherry wines [8.178].

Among the oxidation-related aroma compounds, aldehydes, methional, and phenylacetaldehyde have attracted the most attention, due to their supposedly greater aroma impact and possible contribution to the aromas of red and white wines [8.179]. Reminiscent of boiled potatoes and old rose, respectively, their perception thresholds in wine model solution are 0.5 and 1 $\mu\text{g l}^{-1}$ [8.180]. These aldehydes are commonly found in all wines: white and red, port and sherry. Methional concentrations range from a few hundred ng l^{-1} to 4.9 $\mu\text{g l}^{-1}$ in white wines and, in exceptional cases, 140 $\mu\text{g l}^{-1}$ [8.179], according to the oxidation level. Phenylacetaldehyde concentrations range from a few $\mu\text{g l}^{-1}$ to 53 $\mu\text{g l}^{-1}$ in white wines, sometimes exceeding 90 $\mu\text{g l}^{-1}$ in red [8.180] and botrytized white wines [8.39]. These compounds contribute directly to the flavors of oxidized white wines and are the reminiscent of cooked vegetables, cider, liquor, and honey. In oxidized red wines, they add nuances of figs and dried prunes and their direct contribution is not so clear. For example, *San-Juan et al.* [8.181] showed that the addition of methional to a young red wine transformed fresh fruit nuances into dried fruit aromas. According to these authors, this effect is particularly strong in the presence of C₁₃ norisoprenoids.





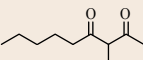
It has been proposed that these aldehydes are formed from methionine and phenylalanine amino

acids, respectively, via the Strecker reaction, involving the presence of a dicarbonyl compound. Wine contains two possible sources of dicarbonyl compounds able to induce the Strecker reaction. The first requires a reaction involving wine ortho-diphenols, forming ortho quinones [8.182] and are, in turn, able to induce the Strecker reaction with the amino acid [8.183]. Wine also contains dicarbonyls produced by microbial metabolisms. These include diacetyl, glyoxal, and methylglyoxal. The formation of aldehydes involving these carbonyls and the corresponding amino acids has been demonstrated in a wine-like medium and may play a role in the formation of aldehydes during bottle aging [8.184].

Another ketone involved in red wine flavor modifications is 3-methyl-2,4-nonanedione (MND) (Table 8.9). This β -diketone, the reminiscent of hay and anise, was recently identified in prematurely aged red wines with a marked prune flavor [8.111]. These descriptors may be concentration dependent. Indeed, at low concentrations, MND smells different from the pure compound (i.e., fruit pit, prune) and is rather reminiscent of prematurely aged (premo) red wine. Its perception threshold in wine model solution is 16 ng l^{-1} [8.185]. MND content was shown to be lower in nonoxidized red wines than oxidized red wines, where it systematically exceeded the perception threshold (62 ng l^{-1}). The keto-enol equilibrium, in which tautomers with the same odor and perception threshold in air [8.186] are only partially interconverted according to the temperature and polarity of the solvent, was first described by *Guth* [8.187].

Concentrations up to 340 ng l^{-1} were determined in most oxidized red wines. High concentrations of this compound can be found in various wines i.e., rosé, botrytized wines and fortified wines made with overripe grapes. The lowest levels (2.9 ng l^{-1}) were found in nonoxidized white wines and the highest concentrations in oxidized botrytized wines (293.8 ng l^{-1}). From a sensory standpoint, the presence of MND alone significantly modifies the flavor of a red wine. The fresh fruit flavor in unadulterated red wine contrasts with the aromatic expression of *rancio* (old walnut flavor characteristic of oxidative aged Port wine) in wines spiked with high concentrations of MND (308.9 ng l^{-1}). Oxidation mechanisms are responsible for its presence in wines. *Guth* found that certain furan fatty acids (10,13-epoxy-11,12-dimethyloctadeca-10,12-dienoic acid and 12,15-epoxy-13,14-dimethyleicosa-12,14-dienoic acid) were precursors of this compound in soybean oil [8.188]. These fatty acids have not previously been identified in wine, so the origin of 3-methyl-2,4-nonanedione in red wine is still unknown.

Table 8.9 Characteristics of volatile compounds involved in oxidation-related wine flavors

Name	Structure	Descriptors	Detection threshold ^a
Sotolon		Curry	Racemic 2 μg l ⁻¹ . (S) 0.8 μg l ⁻¹ (R) 89 μg l ⁻¹
Abhexon		Curry	4.5 μg l ⁻¹
Methional		Boiled potatoes	0.5 μg l ⁻¹
Phenylacetaldehyde		Honey, old rose	1 μg l ⁻¹
3-Methyl-2,4-nonanedione		Dried parsley, fruit pit, anise	16 ng l ⁻¹

^a In wine model solution determined at ISVV, University of Bordeaux

Other Age-Related Flavor Compounds

TDN (1,1,6-trimethyl-1,2-dihydronaphthalene), previously described (Sect. 8.1.2) as grape-derived C₁₃-norisoprenoid, sometimes imparts an undesirable *petroleum* or *kerosene* note to Riesling wine during aging (Table 8.10). Despite that, TDN is found in several red and white varieties, e.g., Cabernet Sauvignon, Cabernet Franc, and Sauvignon blanc, and is considered to have a strong, specific impact on Riesling wines. *Sponholtz* et al. [8.189] reported that TDN concentrations below 20 μg l⁻¹ were considered to make a positive contribution to the varietal aroma of young Riesling wines and Riesling wine quality in general, up to a maximum of 4 μg l⁻¹, but recent work by *Schüttler* et al. [8.92] did not find any link between TDN concentrations in Riesling wines and the appreciation of their aroma uniqueness. TDN may be formed during alcoholic fermentation, but develops mainly during bottle storage. TDN is chemically stable in wine. Lutein, a carotenoid was shown to be a possible precursor for TDN via chemical thermal degradation in a sulfuric acidic medium. It is also generated from megastigm-4-ene-3,6,9-triol and megastigm-4,7-diene-3,6,8-triol, possibly bound as glycosides, by hydrolytic cleavage in acidic media [8.190, 191]. More recently, *Daniel* [8.192] demonstrated that Riesling acetal is a precursor of TDN in wine.



2-Aminoacetophenone is known as the aroma impact compound responsible for *untypical aging off-flavor* (UTA) in *Vitis Vinifera* wines [8.193]. This off-flavor may develop in bottle or in barrel within a few months after fermentation. UTA is associated with descriptors such as furniture polish, mothballs, or acacia blossom, combined with a loss of varietal character. Below its odor threshold in grape berries, must, and wine after alcoholic fermentation [8.194], 2-AAP concentra-

tions increase significantly during storage. It has been detected in all wines irrespective of the grape variety, at concentrations ranging from 0.02 to 10 μg l⁻¹ [8.195]. Concentrations in Sauvignon blanc range from 0.05 to 0.9 μg l⁻¹, rarely exceeding its sensory threshold, between 0.7 and 1 μg l⁻¹. Red wines contain the lowest concentrations. The 2-AAP content in wines without UTA is below 0.3 μg l⁻¹. Indole-3-acetic acid (IAA), a naturally occurring grape phyto-hormone, is considered a potential precursor of 2-AAP in wines [8.196]. A nonenzymatic mechanism is involved in its formation, when IAA reacts with sulfite, which requires superoxide radicals [8.197], generated by the aerobic oxidation of sulfured wine during storage. UTA has not yet been detected in red wines; the degradation of IAA to 2-AAP is probably blocked due to the presence of phenolic radical scavengers (Table 8.10).

8.1.5 Off Flavors in Wine

Many examples show how wine tasting can be affected by volatile compounds associated with organoleptic deviations. Also, it is important to characterize the com-

Table 8.10 Characteristics of volatile compounds involved in undesirable aging-related flavors in wine

Name	Structure	Descriptors	Detection threshold ^a
2-Aminoacetophenone		Mothball, acacia blossom	0.7–1 μg l ⁻¹
TDN		Kerosene-like	2.3 μg l ⁻¹

^a In wine model solution determined at ISVV, University of Bordeaux

pounds responsible for off-odors in order to develop control strategies, as well as protocols to address the problem and improve wine quality. Acetic spoilage, resulting in the production of acetic acid and ethyl acetate, constitutes an historical example where deviation due to sugars being metabolized by acetic bacteria, converts wine into an unpleasant-tasting vinegary beverage [8.11]. Other off-odors in wine aroma can be traced back to the pollution of wine by contaminated materials, such as a cork stoppers (cork taint due to the release of 2,4,6-trichloroanisole and 2,3,4,6-tetrachloroanisole, formed by *Ascomycetes* fungi (*Penicillium* sp., and *Trichoderma* sp.)) [8.11] or bushfire smoke [8.198], as well as undesirable metabolic by-products of grape and wine microorganisms, and, finally, chemical mechanisms responsible for transforming non-odorous compounds into defects. These off-odors may originate from grapes, as well as during winemaking and aging in tanks, oak barrels, and bottles.

Concerning the contribution of each compound to the off-odor, it is necessary to bear the following three points in mind:

1. Firstly, the perception of an off-odor depends on both the concentration of the compound responsible and its olfactory detection (or recognition) threshold. However, at a given concentration, the perception of an off-odor is highly dependent on individual sensitivity.
2. Secondly, the perception of an off-odor may be modulated by the presence of other volatile compounds.
3. Thirdly, the recognition of an off-odor depends on the wine tasters' capacity, depending on their level of experience, to distinguish a particular odor among the complex aromas of wine (*Tempere* et al. [8.199]).

Off-Odors Related to the Metabolism of Wine Microorganisms


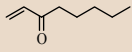
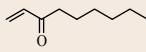
Many unpleasant odors in wine result from the development of unwanted microorganisms or are related to metabolic modifications in wine microorganisms. Among the microorganisms concerned, over the past 20 years, spoilage due to *Brettanomyces* sp contaminant yeast has increasingly deteriorated the aromatic appreciation of red wines [8.200]. This off-odor is due to volatile phenolic compounds, mainly 4-ethylphenol and 4-ethylguaiacol, which originate from the decarboxylation of hydroxycinnamic acids in grapes, ferulic, and p-coumaric acid, respectively, by *Brettanomyces* sp. [8.201, 202]. The development of *Brettanomyces* sp. is favored, particularly in oak barrels, when wine is not sufficiently protected by sulfur dioxide due to high pH.

4-Ethylphenol and 4-ethylguaiacol present a heavy phenolic flavor likely to spoil red wine aroma, particularly attenuating their fruity character, with horse sweat, leather, and phenolic descriptors, all recognized as *Brett* character [8.181, 201–203]. In model solution similar to wine, the olfactory detection thresholds of 4-ethylphenol and 4-ethylguaiacol are $440\ \mu\text{g l}^{-1}$ and $135\ \mu\text{g l}^{-1}$, respectively. They are usually present in a ratio of around 10 : 1. As *Brett* character is not always clearly detected at concentrations above the detection threshold of ethylphenols in red wines, several studies have reconsidered the sensory perception implication of these compounds in red wine aroma [8.6]. A psychophysical study with 134 wine professionals highlighted that the distribution of individual olfactory detection thresholds for a mixture of 4-ethylphenol and 4-ethylguaiacol (in a 10 : 1 ratio) varied by a factor of 100 between the persons with the lowest and highest sensitivity. Moreover, the detection threshold of these compounds in red wine may be modulated by the presence of other wine volatile constituents (Sect. 8.2). In recent studies, *Tempère* et al. [8.199] investigated the analysis of perceptual skills and socio-professional parameters implicated in the recognition of *Brett* character. An initial experiment tested the hypothesis that expertise in terms of age and qualifications could affect the assessment of *Brett* character.

Vinyl phenols also affect the *finesse* of dry white and rosé wines [8.204]. These compounds originate from the decarboxylation of hydroxycinnamic acids by *S. cerevisiae*. 4-Vinylphenol has a strong odor, described as phenol, pharmaceutical, or gouache, that is, heavy odor of painting used by painters-, while 4-vinyguaiacol elicits the smell of cloves. Various enological parameters influence vinylphenol formation in white and rosé wines, particularly the strain of *S. cerevisiae* yeast used for alcoholic fermentation.

Lactic acid bacteria belonging to *O. oeni* and *Lactobacillus* sp contribute to wine stabilization by fermenting malic acid during malolactic fermentation, a key step for numerous premium red and white wines. However, the development of these bacteria in wines may sometimes result in off odors detrimental to the aromatic quality of the wine. This is the case when sorbic acid (2,4-hexadienoic acid), a fungistatic agent used in some dessert wines to reduce the risk of refermentation, is degraded by lactic bacteria to form 2-ethoxyhexa-3,5-diene, a strongly odoriferous compound reminiscent of geranium leaves (*Pelargonium* sp [8.205]. Also, *L. hilgardii* and *L. brevis* may be implicated in the production of potent nitrogen-heterocyclic compounds (2-acetyltetrahydropyridine, 2-acetyl-1-pyrroline, or 2-ethyltetrahydropyridine) that contribute to an off odor in red wines identified as mousy taint [8.206–208].

Table 8.11 Characteristics of some compounds contributing to fungal and mushroom off-odors in wines

Name	Structure	Descriptors	Detection threshold ^a
(-)-Geosmin		Table beet, earth	10 ng l ⁻¹
1-Octen-3-one		Fresh mushroom	30 ng l ⁻¹
1-Nonen-3-one		Fresh mushroom	8 ng l ⁻¹

^a In wine model solution determined at ISVV, University of Bordeaux

Fungal, Mushroom, and Herbaceous Off-Odors

Some of these off-odors in wines are related to fungal notes, the reminiscent of damp earth, camphor, mold, and fresh mushrooms (Table 8.11). The presence of these aromatic nuances is sometimes attributed to contact between must or wine and materials (tanks, oak-barrels, or stoppers) that have been polluted during vinification, or barrel or bottle aging. These off-odors may originate from grape bunch rot when the harvest is spoiled by poorly timed rain, persistent morning mists, or hail. Analysis of these off-odors has led to the identification of several compounds with detection thresholds in the ng l⁻¹ range, including 1-octen-3-one and 1-nonen-3-one (fresh mushroom odors), (-)-geosmin (powerful *damp earth* and *beetroot* odor) and the less common 2-methylisoborneol, with its camphor and earthy off-odors [8.209, 210]. These fungal off-flavors are related to grapes with bunch rot complexes involving *Botrytis cinerea* and secondary saprophytic invaders belonging to various species especially the *Penicillium* genus [8.211, 212]. Due to the potent odor of (-)-geosmin (perception threshold in water: 10 ng l⁻¹), less than 1% infection of a plot in the vineyard is enough to contaminate the entire harvest [8.209]. Particular care in the prevention and control of gray mold caused by *B. cinerea* in the vineyards concerned, together with careful sorting and removal of affected grapes, is recommended, in view of this compound's strong sensory impact [8.209]. Herbaceous off-odors have been shown to originate from the presence of high concentrations of 2-methoxy-3-isopropylpyrazine, due to the contamination of grapes during harvesting by the Asian Lady Beetle, *H. axyridis*, an insect introduced for the biological control of aphids [8.213].

Reduction Defects Caused by Volatile Sulfur Compounds

The impact of trace amounts of highly odorous volatile thiols on a wine's varietal aroma was established in the

early 1990s (Sect. 8.1.3, *Impact of Volatile Thiols*), and in the wine aging bouquet. However, in enology, sulfur compounds are first considered to be responsible for organoleptic defects due to the irritating odor of sulfur dioxide or the *reduced* character related to the presence of some thiol or sulfide compounds. Winemakers have, therefore, always sought to minimize the impact of these compounds.

Historically, the first sulfur compound used in the elaboration of wine likely to cause a deterioration in quality is sulfur dioxide. This compound, naturally produced during alcoholic fermentation by *S. cerevisiae* at concentrations around 10 mg l⁻¹, is added to grape must and wine after fermentation and during aging, to prevent the development of undesirable microorganisms (bacteria and yeasts) and limit oxidative phenomena. Sulfur dioxide has been used systematically for its protective antioxidant and antimicrobial properties since at least the early 17th century. Its irritating odor, rarely perceived today in commercial wine, is considered detrimental to wine quality.

Off-odors known as *reduction* defects, evocative of rotten egg, garlic, onion, rubbery, or sometimes metallic character, are associated with volatile sulfur compounds:

1. Sulfides
2. Thiols
3. Thiophenes
4. Thiazoles.

Two groups of compounds have been distinguished according to their volatility: Highly volatile sulfur compounds (VSC) (boiling point < 90 °C), including hydrogen sulfide (H₂S), methanethiol (MeSH), ethanethiol (EtSH), dimethyl sulfide (DMS), diethyl sulfide (DES), dimethyl disulfide (DMDS) and *heavy* sulfur compounds, with boiling points above 90 °C. VSC compounds have a strong impact on wine aroma, due to their high volatility and low-odor thresholds. The main *light* sulfur compounds hydrogen sulfide, methyl mercaptans, and, less frequently, ethanethiol, dimethyl disulfide, and carbon disulfide, play a key role in reduction defects. In *reduced* wines, levels of these compounds are always above the olfactory detection threshold [8.214, 215]. The origins of these compounds are diverse, depending on vinification and aging conditions, as well as grape and wine contaminants. However, on the other hand, the absence of a small amount of oxygen, either enclosed at bottling or as a result of oxygen seeping through the closures, results in undesirable *reduction* aromas. Nitrogen deficiency in grape must and the presence of sulfur residues from pesticide treatments may also have a significant effect on the formation of these compounds

by *S. cerevisiae* yeast, as well as photochemical degradation during the wine aging (degradation of vitamin B2) [8.11].

Among the many *heavy* VSCs identified in wines, only a few contribute significantly to reduction defects. The most important of these is 3-methylthiopropyl-1-ol or methionol, which smells strongly of fermented cabbage (odor threshold $1200 \mu\text{g l}^{-1}$). The 2-mercaptoethanol content in some *reduced* wines may also approach the odor threshold. Thiophene and 2-methyl-tetrahydro-thiophenone, act rather as odor-masking substances at concentrations exceeding $90 \mu\text{g l}^{-1}$, thereby masking other aroma compounds with positive impact on the global wine aroma [8.216]. Recently, a malodorous sulfur metabolite perceived as *baked beans* and *Fritillaria sp. bulbs*, affecting dry white and rosé wine aroma, was identified as ethyl 2-sulfanylacetate [8.217]. This compound is not associated with the sulfur metabolites produced during

alcoholic fermentation of grape juice containing solids, nor excessive addition of sulfur dioxide in the must. It is produced during alcoholic fermentation, particularly in wines made from hard-pressed juices and oxygenated musts. Depending on the wine matrix, concentration at which aroma is affected in dry Sauvignon blanc wines doted with this substance varies from 300 to 500 ng l^{-1} , while the detection thresholds of ethyl 2-sulfanylacetate in water and hydro-alcoholic solution are 70 ng l^{-1} and 200 ng l^{-1} , respectively. Moreover, concentrations of this compound increase during bottle-aging of white wine. The knowledge of this compound facilitates informed choice of pressing and juice selection, as well as white wine vinification techniques that preserve aroma. Particular care is recommended in situations where this malodorous compound is likely to be produced, with grape pressing under a nitrogen atmosphere as a key strategy for minimizing the oxidation of the grape juice [8.217].

8.2 Perceptual Interaction Phenomena

The uniqueness and complexity of wine aroma depends on the presence of key volatile compounds. Characterization of these volatile compounds constitutes the heart of research into wine aroma. Indeed, the chemical characterization of impact aroma compounds and analysis of their contribution to wine aroma provides an opportunity to consider various aspects of winemaking technology, including wine microorganisms and grape ripening conditions. Despite substantial progress toward identifying unique varietal aromas, the construction of olfactory *images* in the brain is so complex that the key compounds alone are often unable to explain all the nuances perceived in wine aromas. Well-known experiments by the *Laing* group [8.218, 219] revealed the limited capacity of human beings to identify odors correctly in a mixture consisting of only three or four compounds. In fact, in considering wine aroma perception, at least two main types of perception should be considered: analytical and elemental perception, where the odors of specific compounds are clearly perceived in the wine among other volatile odoriferous compounds and synthetic or configural perception, involving perceptual interaction phenomena, where the perceived odors result from a combination of several volatile compounds, modified by masking phenomena and additive or synergistic effects, possibly resulting in new aromas.

8.2.1 Masking Effects

In enology, research into wine volatile compounds, conducted mainly in the last decade, has shown the im-

portance of such sensory phenomena. Thus, it seems that the detection of off-odors in wine is likely to be related to analytical perception, while specific wine aromas more generally result from combinatorial effects involving several volatile compounds. In fact, empirical observations concerning the perception of *Brett* off-odor have indicated an indirect relation between the ethylphenol content in wines and the perception of this defect [8.199, 202]. For example, *Romano* et al. [8.220] showed that the detection threshold of a mixture of 4-ethylphenol and 4-ethylguaiaicol (in a 10:1 ratio) in wine was higher (i.e., reduced perception) when other volatile compounds related to *Brettanomyces* sp. metabolism, such as isobutyric and isovaleric acids, were present, indicating that a masking phenomenon was involved.

8.2.2 Additive and Synergistic Effects

In contrast, as early as 1970, *Ribéreau-Gayon* and *Boidron* demonstrated that a mixture of the main terpenols had a significantly lower odor-detection threshold than each one taken separately, thereby highlighting a synergistic action [8.74]. This effect was also observed for wine γ -lactones by *Jarauta* et al. [8.221], who reported that the detection threshold of a mixture of wine lactones was four times lower than that expected on the basis of their individual thresholds. *Sarrazin* et al. [8.103] also noticed that chemically similar sulfanylalcohols, for example, 3-sulfanylpentan-1-ol, and 3-sulfanylheptan-1-ol, which have a similar cit-

rus aroma to 3-sulfanylhexasan-1-ol, may contribute to dessert wine aromas at concentrations lower than their olfactory detection thresholds through additive phenomena.

More recently, the additive properties of some ethyl esters of fatty acids and fusel alcohol acetates in the fresh, fruity aromas of red wine have been extensively studied by several authors [8.22, 23, 26, 222, 223]. In combination, these compounds make a significant contribution to red wine fruity aroma, even at concentrations below their odor-detection thresholds, while each one added separately has no effect [8.13, 23, 23]. Ethyl butyrate, ethyl hexanoate, and ethyl octanoate were found to enhance the expression of *fresh fruit* and *red fruit* aromas, while ethyl propionate was implicated in the notion of *candied fruit* and *black fruit* [8.13, 23, 23]. By way of example, ethyl 2-hydroxy-4-methylpentanoate, also known as ethyl leucate, was recently demonstrated to enhance the fruity aroma of red wine [8.25, 26].

Both ethyl esters of fatty acids and fusel alcohol acetates are considered to impact the typical fruity character of red wines, through synergistic effects and perceptive interactions [8.13, 23, 23]. Using omission tests in model media (dilute alcohol solutions), Lytra et al. [8.223] highlighted the importance of ethyl propanoate, ethyl-3-hydroxybutanoate, butyl acetate, and 2-methylpropyl acetate in a fruity mixture containing 12-ethyl esters of fatty acids and fusel alcohol acetate, although these compounds were only present at subthreshold concentrations. Also, ethyl esters of fatty acids, such as butanoic, hexanoic, octanoic, decanoic, and, to a lesser extent, dodecanoic acids are involved in perceptive interactions with other aromatic compounds, including β -damascenone [8.13, 23, 23], β -ionone [8.13, 23, 23], and dimethylsulfide [8.13, 155, 157] even at concentrations below their odor thresholds.

Synergistic effects have also been revealed between monoterpenes and β -damascenone; for example, the orthonasal detection thresholds of linalool and geraniol are lowered by the presence of β -damascenone. This phenomenon has also been identified and measured with lab mice in the Pasteur Institute through psychophysical tests using a specific behavioral methodology [8.224]. Moreover, β -damascenone contributes, via synergistic phenomena, to reducing the detection thresholds of ethyl hexanoate and ethyl cinnamate and raising the detection threshold of 2-methoxy-3-isobutylpyrazine [8.59].

8.2.3 Perceptual Blending

Not many examples in the literature report the situation where a mixture of compounds triggers the percep-

tion of a different aroma from those of the compounds taken separately. A 30/70 mixture of ethyl isobutyrate (strawberry flavor) and ethylmaltol (caramel) induced the perception of pineapple [8.225]. In another situation, a mixture of six compounds (β -damascenone, β -ionone, frambinone, vanillin, isoamyl acetate, and ethyl acetate) had a flavor reminiscent of red cordial (grenadine), unlike any of the compounds taken individually [8.226].

Another example of perceptual interaction phenomena was revealed during a study on compounds involved in the *candied citrus* and *orange* aromas of dessert wines [8.117]. Emphasis was placed on the study of the phenomenon of perceptual interactions; consequently, *aromatic recovery* was an important research approach: while fractionating an extract of premium Sauternes dessert wine, one fraction was recognized as having these characteristic citrus aromas. This fraction was not present in lower quality wines. Analytical chemistry coupled with sensory analysis identified the compounds present in the fraction associated with this odor as whisky lactone (*coconut*), eugenol (*clove*), and a newly identified lactone, 2-nonen-4-olide, associated with noble rot, which has *minty* and *fruity* odors. None of these compounds considered alone at concentrations close to those assayed in wines produced an orange aroma. Subsequent omission and reconstitution tests demonstrated that these four compounds together, particularly the two lactones (one originating from oak wood and the other from botrytized grapes), generate the perception of *orange* aroma. Moreover, the importance of enantioselective distribution of 2-nonen-4-olide on this perceptual phenomena was recently evidenced (Stamatopoulos et al. [8.227]) The correlation of whisky lactone with wine fruitiness has also been reported [8.228, 229]. This sensory phenomenon, well known in perfumery, appears to contribute substantially to the uniqueness and complexity of wine and opens up new perspectives for understanding wine aroma perception.

8.2.4 Interactions Between the Wine Matrix and Aroma Compounds

The wine matrix contains numerous nonvolatile compounds, at concentrations in the g l^{-1} range, that may have a significant impact on aroma perception during wine tasting. Those compounds include acids (tartaric, malic, citric, and acetic acids), ethanol (at concentrations ranging from 70 to 160 g l^{-1}), polysaccharides, proteins, and polyphenols (pigments, such as anthocyanins, and flavonoids). One aspect of this subject concerns the impact of pigments (anthocyanins) on the

appreciation of aromatic nuances. Briefly, when nonexpert wine tasters were asked to assess a dry white wine colored with anthocyanins, they used red wine descriptors [8.7].

Another aspect of the impact of wine matrix composition on aroma compounds concerns physico-chemical interactions between volatile compounds and other key compounds in wine (glucose or fructose, polyphenols, polysaccharides, proteins, etc.) and in vivo retronasal perception in the mouth. Specifically, several authors have reported the impact of interactions between non-volatile and volatile compounds in wine on the partitioning of volatile compounds [8.10, 15, 230, 231]. First, *Dufour* et al. described the impact of (+)-catechin ($2\text{--}10\text{ g l}^{-1}$) on reducing the volatility of several fermentation esters:

1. Isoamyl acetate (banana flavor)
2. Ethyl hexanoate
3. Benzaldehyde.

The sensory effect of such phenomena, studied more recently [8.14] regarding other esters (ethyl butyrate and ethyl octanoate), indicated that their olfactory detection threshold increased (at least doubled) in the presence of (+)-catechin (2 g l^{-1}), but not in the presence of another phenolic compound, gallic acid (2 g l^{-1}) [8.14]. Also, the attenuating impact of ethanol on the volatility and fruitiness of several wine components has been illustrated by several authors [8.13,

15]. Considering a range of volatile compounds in wine [monoterpenes (linalool, nerol), C_{13} -norisoprenoids (β -damascenone, β -ionone), and ethyl esters], *Robinson* et al. [8.15] reported an increase in volatility in the presence of glucose ($160\text{--}320\text{ g l}^{-1}$) and the reverse for ethanol ($> 10\%$ vol.), whereas proline had no effect. Also, the presence of ethanol affected perceptual interaction phenomena in binary odor mixtures of isoamyl acetate and whisky lactone, [8.232]. The effect of these phenomena on the aromatic profile of wines has not yet been investigated in detail. The impact of (+)-catechin supplementation at concentrations ranging from 25 to 200 mg l^{-1} on the aromatic profiles of three Sauvignon blanc wines was studied through triangular tests. The experiment revealed significant differences between supplemented and non-supplemented wines at concentrations between 50 mg l^{-1} and 200 mg l^{-1} but not at lower levels [8.233].

The perception of volatile compounds during wine tasting is not only orthonasal but also retronasal. One recent study used an in vivo approach to measure aroma compound concentrations directly in exhaled breath after wine consumption, revealing the importance of the wine matrix, particularly the presence of polyphenols, on the volatility of odoriferous compounds, such as isoamyl acetate, ethylhexanoate and linalool and also the impact of oral mucosa [8.234–236]. Further research is required to elucidate the importance of these phenomena during wine consumption.

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