**Chapter 22. Recent advances in the study of grape and wine volatile composition: Varietal, fermentative and ageing aroma compounds**

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**Abstract**

 Aromatic compounds are one of the most important substances present in grape and wines. Wine aroma does not depend on a particular compound, but on the aromatic profile and the interactions between the multiple active odorant compounds that are present in it. Wine aromatic potential also depends on the release of aromatic compounds from its non-odorous precursors, and the chemical modifications of the volatile substances during its maturation. The volatile compounds that compose the wine aroma can be classified into four main groups according to their origin: varietal aromas, typical to the grape variety; pre-fermentative aromas: formed from the harvest until the beginning of the alcoholic fermentation; fermentative aromas, produced during the alcoholic and malolactic fermentations by the action of yeasts and lactic acid bacteria, respectively; and ageing aromas, generated during the storage and ageing of the wines, highlighting especially the ones comes from the wood. This chapter describes the origin of the wine aroma, as well as the main factors that affect to their content in grapes and wines.

**22.1 Introduction**

 Wine aroma is of a great complexity due to the large amount of volatile compounds that it contains. More than 800 volatile compounds have been found in wine, and some of them provide a relevant response in the olfactory system, with a wide concentration, that varies from a few ng/L to more than hundreds of mg/L (de Castilhos, del Bianchi, Gómez-Alonso, García-Romero, & Hermosín-Gutiérrez, 2019). These compounds are widely known thanks to the large number of analytical techniques available (Flanzy, 2000). Wine aroma is important to determine the wine quality and therefore to determine wine value (Aleixandre-Tudo, Weightman, Panzeri, Nieuwoudt, & du Toit, 2015; Gambetta, Bastian, Cozzolino, & Jeffery, 2014; Mihnea, González-San José, Ortega-Heras, & Pérez-Magariño, 2015). In the wine can be distinguished various aromatic compounds that depend on several factors such as grape variety, season, terroir, grape maturity, viticultural practices, fermentation conditions, and conservation, being the grape maturity and the alcoholic fermentation the most critical stages. In addition, the release and the perception of the aroma largely depends on physical and environmental aspects, such as the wine temperature or the shape of the glass (Ayestarán et al., 2019; Gambetta et al., 2014; Styger, Prior, & Bauer, 2011).

 The constituents of wine aroma have been classified according to their origin in:

* Varietal aromas: they come from the grape.
* Pre-fermentative aromas: they are formed from the harvest until the beginning of the alcoholic fermentation.
* Fermentative aromas: they are formed by yeasts in the alcoholic fermentation or by lactic bacteria in the malolactic fermentation.
* Ageing aromas: they come from the wine conservation stage.

 This chapter is divided into three sections; the first corresponds to the primary aromas (varietal and pre-fermentative), the second one to the fermentative or secondary aromas and the third corresponds to the ageing or tertiary aromas, where their origin and the main factors that affect their content in grapes and wines are described.

**22.2 Varietal and pre-fermentative aromas**

 The varietal aromas of the wine are composed by the odorous compounds that come from the own grape metabolism. Therefore, they depend on the grape variety and are influenced by all the vineyard edaphic and climatic conditions and by the viticultural practices carried out. The grape aroma metabolites constitute a very complex group of substances that can be found in free form, i.e., as volatile molecules and therefore odorants, or in bound form, i.e., as non-volatile precursors and therefore odorless molecules. There are few wines whose varietal aromatic notes correspond to their grapes, among them highlight those from the Muscat varieties, in which the first odorant compounds of the terpenes family were identified.

 Thus, most of the wine grapes at harvest time are fruits that have no smell, and therefore the odorless precursors of the aroma are the most abundant and important compounds of the aroma pool of the grapes. These precursors begin their transformation in their corresponding odorant molecules from the moment in which the grapes are collected, throughout the different stages of the winemaking process, especially during the alcoholic fermentation, and during wine ageing. Aroma precursors are organic molecules of glycosidic, amino-acidic and lipidic nature, which provide the volatile compounds by means of enzymes of the grape itself or of the microorganisms that participate in the different stages of the winemaking, fundamentally the yeasts. Also, the wine chemical conditions, especially its pH and temperature, participate in the odorants hydrolysis from their precursors.

 The odorant compounds of the wines that come from the grapes, can be grouped according to their chemical family in: methoxypyrazines, terpenes, C13 norisoprenoids, benzenoids (phenylpropanoids), thiols, and C6 compounds. Among all of them, methoxypyrazines are found in grapes only as free volatiles and thiols only as precursors. The other compounds are found in the grape, as free volatiles or as precursors, being the bound form the predominant one.

 Methoxypyrazines exist in grape berries as volatile free compounds and have a vegetable aroma that is only acceptable in some white wines, but their presence is detrimental in some red wines, especially from Cabernet family (Ward, Petrie, Johnson, Boss, & Bastian, 2015). There are several types of methoxypyrazines, but particularly 3-isobutyl-2-methoxypyrazine (IBMP) is the most abundant, and exceeds its low olfactory perception threshold (OPT) (Table 22.1) in wines from cool climates, especially if they come from early harvests, since these compounds diminish considerably with maturation until they disappear (Sidhu, Lund, Kotseridis, & Saucier, 2015). Another factor that can affect the IBPM concentrations is the vine water status, having been shown that irrigation of the vines increase its content (Mendez-Costabel et al., 2014).

 The terpenes found in the most of the grape cultivars are alcohols and oxides of 10 carbon atoms, such as geraniol, linalool, citronellol, nerol and rose oxide, among others. They have floral aromas and low OPT (Table 22.1). Terpenes significantly exceed their OPT in grapes and wines of the Muscat family and have an important participation in the wine aroma from other white varieties, such as Albariño, Gewürztraminer and Chardonnay, but not in wines from red varieties. However, among them there are synergistic effects, which could make them effectively participate in the aroma, even without exceeding their OPT. They are synthesized during grape ripening and are located mainly in the grape skin. Although there is no unanimity in this regard, free volatiles accumulate before technological maturity, while precursors continue to increase until overripe (Hjelmeland & Ebeler, 2015). They are sensitive to viticultural practices, soil type, exposure to light, UV-B radiation, water deficit, basal leaf removal, crop thinning and pest (Robinson et al., 2014). In wine, they undergo chemical reactions and rearrangements to form other terpenes, that can explain the aroma ageing suffered by certain wines (Black, Parker, Siebert, Capone, & Francis, 2015).

 Although less studied, terpenes of 15 carbon atoms, or sesquiterpenes, are also present in grapes and wines. Among them, farnesol and nerolidol, linear sesquiterpenes, which have floral aromas, are the most abundant, but their OPT are higher than the C10 compounds, which make them less important for the wine aroma (Table 22.1). However, a recent research suggests that the content of farnesol and nerolidol, in acidic conditions, decreases during ageing, due to cycling, which may contribute to the balsamic and spicy aroma of Corvina grapes and wines (Slaghenaufi & Ugliano, 2018). The sesquiterpene more recently investigated has been rotundone, which is a powerful odorant of spiced aroma (black or white pepper). This compound was initially associated with the Australian cool climate Shiraz grapes, but also found in other red varieties, such as Cabernet Sauvignon, Graciano or Pinot Noir, among others (Mattivi et al., 2011).

 Norisoprenoids come from the oxidative degradation of the carotenoids, which give rise to compounds of 13 carbon atoms. Carotenoids share their biosynthetic onset with sesquiterpenes, having in common the compound farnesyl pyrophosphate, as a starting point, so usually the set of monoterpenes, sesquiterpenes and C13 norisoprenoids are called as terpenoids. The most important C13 norisoprenoids are those that have the megastigmane structure and have a wide range of odors, from floral and fruity to scents reminiscent of tobacco and kerosene, but the most abundant in grapes and in most wines are those with pleasant aromas, especially the oxygenated megastigmanes β-damascenone and β-ionone, both with very low OPT (Table 22.1). Recently, a positive correlation between C13 norisoprenoids and fruity aromas, especially β-damascenone, as an enhancer of this aroma, has been found (Sáenz-Navajas et al., 2015), and so they have been the focus of many current studies. C13 norisoprenoids are derived from photoactive carotenoids (Chen et al., 2017), and therefore, an increase in the penetration of light in canopy, achieved through various agronomic practices, influence their formation (Hernández-Orte et al., 2015), although this could also be attributed to the impact of temperature on the cluster that could confuse the effect of sunlight related effects.

 Although dependent on grape varieties, edaphic and climatic conditions as well as viticultural practices, the accumulation of norisoprenoids has been reported to begin earlier than the optimal technological ripening. This has been used to mitigate the effect of climate change on the quality of wines, since early-harvested grapes produce wines with lower alcohol content and optimum aromatic quality (Asproudi et al., 2018). Other important oxygenated C13 norisoprenoids are 3-oxo-α-ionol (tobacco aroma), β-damascone (tobacco and fruity), 3-hydroxy-β-damascone (tea and tobacco), but their content in wines are usually very low, and their OPT are not defined. However, it has recently been shown that a synergistic effect between 3-oxo-α-ionol, β-damascenone and TBP (the major representative of C13 norisoprenoids non-oxygenated) is responsible for the tobacco aroma of certain wines (Slaghenaufi & Ugliano, 2018).

 Terpenoids (monoterpenes, sesquiterpenes and C13 norisoprenoids) are found in grapes mainly as odorless precursors in glycosylated or bound form. The free aroma, or aglycone, joins a sugar moiety through the process of glycosylation, which is one of the predominant reactions in plants catalyzed by a group of enzymes called glycosyltransferases. Glycosylation is a mechanism used by plants to facilitate the solubilization, transport and accumulation of lipophilic compounds, as well as a detoxification process. In grapes, sugars are mainly glucoside, or disaccharide or trisaccharide glycosides, where the other sugars are arabinose, rhamnose, apiose and xylose conjugated to the glucose. All glycosides are not present in different cultivars, and differ in their proportions, therefore, they have been proposed for use in varietal differentiation (Ghaste et al., 2015). These glycoconjugates are of great importance in winemaking, since they are extracted from the grapes at the beginning of winemaking, and, in acidic conditions and reactions catalyzed by glycolytic enzymes, can release the volatile aglycones and participate in the wine aroma. The highest release of volatile aglycones takes place during the alcoholic fermentation, followed by the malolactic fermentation, although sugar and alcohol limit the glycosidase activity of yeasts and bacteria. However, this fact is favored by the acidic pH of the wine, which is why the hydrolysis takes place along ageing. The glycoconjugates hydrolysis yields volatile aglycones, but while in the case of glycosylated monoterpenes and sesquiterpenes this hydrolysis directly releases the free volatiles, in the case of the glycosilated C13 norisoprenoids, it produces non-odorous or less-odorous compounds, which require new chemical rearrangements to give the odorous compounds. This fact is well demonstrated for β-damascenone (Hjelmeland & Ebeler, 2015).

 The accumulation of glycosylated terpenoids begins at ripening, but few studies have shown a correlation between these compounds and the enological classical parameters of grapes at such stage. Possibly, this is due to the difficulty of its determination, since the glycoconjugate aromas are not analyzed as intact molecules, but this is done indirectly through the volatile aglycones. In particular, once the glycoconjugates are isolated, they are hydrolyzed to release the volatile aglycones, which are subsequently determined by gas chromatography (GC). However, if the hydrolysis is enzymatic, the specificity of the enzymes implies the release of only some aglycones, and if the hydrolysis is acidic, important structural changes occur in the aglycones that do not reflect the original chemical nature of the glycosides (Hjelmeland & Ebeler, 2015; Liu, Zhu, Ullah, & Tao, 2017). In recent years, a simple method has been developed to determinate the glycosylated aroma precursors of white and red grapes, musts and wines, taking as reference a previous method proposed several years ago by Williams et al. (1995). It is based on the analysis by high performance liquid chromatography-refractive index detection (HPLC-IR) of the glucose released by acidic hydrolysis of such precursors, called glycosyl-glucose (G-G), a moiety common in all grape aroma glycoconjugate compounds (Salinas, Serrano de La Hoz, Zalacain, Lara, & Garde-Cerdán, 2012) (Figure 22.1). Therefore, this G-G analysis allows to make an estimation of all these compounds, and the method has been adapted to be able to apply it in wineries using UV-VIS spectrometry (Serrano de la Hoz, Carmona, Zalacain, Alonso, & Salinas, 2014), which provides the varietal aroma potential index (IPAv). The evolution of the aroma glycoconjugate compounds by the IPAv parameter during three consecutive vintages have been estimated by Crespo et al. (2018). They have observed a high parallelism between the evolution of the IPAv and ºBrix, as well as its relation with the climatic fluctuations during the period of the grape ripening.

 In order to take place the glycosylation, it is necessary that the aglycones have an alcohol, phenol or acid function, so in grapes there are a large number of glycosylated precursors in addition to the terpenoids. Thus, many benzenoids, especially phenylpropanoids, which are present in grapes in very low concentrations as free volatiles, can be found in important levels in the form of glycosylated precursors. Glycosylated forms of volatile phenols such as eugenol, guaiacol, vanillin and their derivatives, can contribute to the spicy aroma of wines, without these have been subjected to a process of ageing in contact with oak wood (Table 22.1). It is also noted that the balsamic aroma associated with the "terroir" of many wines can be attributed to these phenylglycosylated compounds. The mechanism of glycosylation as a detoxifying process of plants has been recently demonstrated by Hayasaka et al. (2013) in relation to the effect that the smoke from forests fires next to vineyards produced in their wines. These wines showed a clear smoky odour, as a consequence of the hydrolysis of the glycosylated precursors generated by the plant with volatile phenols present in the smoke, especially syringol and guaiacol. The same effect was observed when vines were treated with oak lactones and with oak extracts (Pardo-Garcia et al., 2015), where a previous step to glycosylation was observed, consisting in the opening of the lactone ring to give the corresponding hydroxyacid. Coumaric and ferulic cinnamic acids, located mainly in the grape skins, are also precursors of volatile phenols, such as vinyl and ethylphenol and vinyl and ethylguaiacol, for which enzymes with decarboxylation activity are required. This activity is inhibited when there are catechins, therefore, the presence of these volatile phenols is more important in wines of short maceration, as white wines, than in those of long maceration, as it happens in red wines (Darriet, Thibon, & Dubourdieu, 2012).

 Some wines have pleasant aromas of sulfur nature, which exclusively exist in the grapes in the form of non-odorous precursors of cysteine and glutathione. They are located in the pulp or in the skin depending on the type of precursor. These compounds, called polyfunctional thiols, are absent in musts and are formed mainly during the alcoholic fermentation, as long as the yeasts possess a specific lyase activity for the S-cysteine and glutathione conjugates. The most important thiols are 3-mercaptohexan-1-ol (3MH), 3-mercaptohexyl acetate (3MHA) and 4-mercapto-4-methyl-pentan-2-one (4MMP), powerful odorants to which are attributed the typical aroma of some Sauvignon Blanc and Verdejo wines, with tropical notes reminiscent of grapefruit, boxwood and passion fruit. They have also been found in many other varieties, reds and whites, although they do not seem to define the aroma of their wines. It has been observed that they are dependent on the vine agronomic practices (Helwi et al., 2015) and that, although they are released at the beginning of the alcoholic fermentation, they are chemically unstable and very easily oxidized, and even in reducing environments, they can be transformed into undesirable aromas. Thus, for their preservation, a compromise between the oxygen content of the wine and the reduction conditions is necessary (Herbst-Johnstone, Nicolau, & Kilmartin, 2011).

 All the grapes have, as free volatiles, other type of compounds, the so-called C6 compounds, which are referred to as "green leaf volatiles", since they are characterized as "herbaceous" and "green" aroma. C6 compounds manly consist of alcohols and aldehydes, such as 1-hexanol, (Z)-3-hexenol, (E)-3-hexenol and (E)-2-hexenal. The alcohols have high OPT, so they are among the less grape odorant volatiles (Table 22.1). The evolution of these compounds in grapes is different, as aldehydes decreased toward the end of ripening, and alcohols increased, which is a positive aspect, because alcohols have a higher OPT than aldehydes, resulting in a less pronounced herbaceous character (Kalua & Boss, 2010). In addition, their content can be increased from the moment in which the berry is separated from the cluster and in all the other pre-fermentative stages, which is why they are called pre-fermentative volatiles. Since they come from the grape variety, many authors consider them as varietal aromas, however, they are common in all grapes, and therefore in this chapter they are considered pre-fermentative aromas. The main agent that triggers their formation is oxygen, which activates enzymatic systems that generate aldehydes and alcohols from polyunsaturated fatty acids, being these reactions favored by the temperature. In the grapes, C6 compounds can be also found as non-odorous glycosylated precursors, but their concentration is much lower than those of the free forms, since to be generated is necessary oxygen from the air as the initiator of their synthesis from fatty acids. The increase of C6 compounds in musts and wines can be avoided by reducing the contact of the harvest with the oxygen and keeping it at low temperatures. This is the reason why mechanical harvest increases herbaceous character. In the same way, the night harvesting and the use of the inert gases is being imposed to transport the harvest to the cellars, and to avoid uncontrolled oxidation in other pre-fermentative stages (Boselli, di Lecce, Alberti, & Frega, 2010). During the alcoholic fermentation, yeasts reduce these aldehydes to alcohols, which are much less odorous and normally in wines do not exceed their OPT, but if they do, it should be considered a wine defect.

 The amino acids of the grapes play a decisive role in the process of the alcoholic fermentation, since they are nitrogen sources for yeasts. Since the amino acid profile of the grapes is a varietal characteristic, the fermentative aromatic profile generated by the amino acids of the grapes is also a varietal characteristic. The amino acids of the grapes are therefore precursors of fermentative aromas; such will be studied in the next section.

**22.3 Fermentative aromas**

 Fermentative aromas are all those wine volatile compounds that are formed during the vinification. The first step in this process is the alcoholic fermentation, which is carried out by yeasts (*Saccharomyces* and *non-Saccharomyces*); and the second step is the malolactic fermentation, which is carried out by lactic bacteria. For the wine aroma, the alcoholic fermentation is a very important process, since it is responsible for the wine notes common to every wines. In addition, the volatile compounds formed during this stage quantitatively represent most of the constituents of the wine aroma. Conversely, the malolactic fermentation subtly modifies the wine aroma (Flanzy, 2000). The volatile compounds formed in the fermentative stage belong to the following groups: alcohols, acids, esters, carbonyl compounds, sulfur compounds, lactones and volatile phenols (Flanzy, 2000). Due to their contribution to the wine aroma, the higher alcohols and their acetates, and the fatty acids and their ethyl esters, are the most studied compounds (Molina, Swiegers, Varela, Pretorius, & Agosin, 2007; Wang, He, Pan, Duan, & Wang, 2018).

 Higher alcohols are quantitatively dominated by 2- and 3-methyl-1-butanol (known as isoamyl alcohols), n-propanol, isobutanol, n-butanol, n-pentanol, 2-phenylethanol, 3-methylthio-1-propanol, tyrosol, and tryptophol. Their average total content in the wine is of the order of 300-400 mg/L, above these values they can contribute in a negative way to the wine aroma. The formation of these compounds is linked to the sugars and amino acids metabolism, and therefore, strongly influenced by the grape nitrogen composition. In this way, the formation of these compounds depends on the yeast nitrogen demand (Flanzy, 2000). Isobutanol and isoamyl alcohol, suppress fruity and woody notes, but no leather, animal, and ink notes, and can impart to the wine a negative quality. The presence of 2-phenylethanol, that provides honey and rose notes, can contribute to the wine aroma (Wang et al., 2018). The most significant acetates are isobutyl acetate, which contributes to the fruity aroma, isoamyl acetate, which contributes to the banana flavor, and 2-phenylethyl acetate, which contributes to the floral aroma. These esters are derived from their corresponding higher alcohols, isobutanol (derived from the amino acid valine), isoamyl alcohol (derived from leucine), and 2-phenylethanol (derived from phenylalanine) (Garde-Cerdán & Ancín-Azpilicueta, 2008; Gutiérrez-Gamboa, Garde-Cerdán, Portu, Moreno-Simunovic, & Martínez-Gil, 2017).

 The fatty acids and their ethyl esters are, together with the higher alcohols and their acetates, the main markers of the fermentative aroma. The fatty acids and their ethyl esters are produced in high quantities in wines, presenting a pleasant aroma, being the esters the principal responsible for the smells judged as pleasant, mainly fruity. Conversely, although the fatty acids have been related as not desirable odors, they are considered necessary for good balance of wine aroma (Flanzy, 2000). Hexanoic, octanoic and decanoic acids are common volatile fatty acids in wine, with octanoic acid being the most abundant. These fatty acids contribute to fatty, rancid and cheese flavors (Wang et al., 2018). The ethyl esters contribute to the pleasant aroma, and are formed during the alcoholic and malolactic fermentations, being those coming from the action of the yeasts in the alcoholic fermentation the most important for the wine aroma (Belda et al., 2017). The formation of esters, higher alcohols and fatty acids from sugars or amino acids (Ehrlich's pathway) are shown in Figure 22.2. There are different factors that can affect the volatile compounds content in wines. These factors include: viticultural practices, among them, the basal defoliation and the foliar application; pre-fermentative techniques, such as the enological tannins addition and different types of maceration; fermentative techniques, where the use of different strains of yeasts and lactic bacteria, as well as fermentation conditions; and, moreover, the grape nitrogen composition it is other important factor. Table 22.2 shows a summary of how the factors and practices studied affect the content of fermentative aromas. The viticultural practices are those carried out in the vineyard and that can affect the plant growth and the grape composition. Among these practices, the basal defoliation is one of the most common current viticulture practices management, in order to modify the effect of climate in the vineyard and that has been applied with the aim of improving the wine quality. The effects of basal defoliation in certain fermentative volatile compounds (2-phenylethanol, 2-phenylethyl acetate, decanoic acid and ethyl octanoate) mainly depend on the grape maturity, and to a lesser extent on the grape variety and the climatic conditions (Wang et al., 2018). The grape fatty acids and amino acids content is modified by environmental factors, such as exposure to sunlight, so that the basal defoliation would modify their content, and, therefore, the fermentative aromas content (Wang et al., 2018). In the same way, the sunlight exposure facilitate by the training system chosen in the vineyard could affect the wine volatile composition, as observed Vilanova et al. (2017) in Albariño wines. This fact may be related to the effective canopy surface area and the density that allows the training system. Thus, the wines from Geneva Double-Curtain training system had the highest total concentration of alcohols, ethyl esters, and lactones, while wines from Scott-Henry training system had the highest concentration of terpenes and C13 norisoprenoids.

 On the other hand, Ju et al. (2018) studied the effect of different regulated deficit irrigation (RDI) strategies on Cabernet Sauvignon grapes and wines volatile compounds. They observed that the RDI treatments increased the levels of aromatic compounds such as benzaldehyde, benzyl alcohol, and phenylethyl alcohol respect to the highest watered treatment (100% grapevine estimated evapotranspiration, ETc). Also detected increments of phenylethyl alcohol, 2-methyl-1-propanol and 3-methyl-1-butanol content in wines elaborated from the RDI treatments. They related these increases in the effects caused by the irrigation strategy used on the amino acids concentration, especially those precursors of volatile compounds. Also, García-Esparza et al. (2018) observed that the low watered treatments (rainfed or irrigation at 25 % or 50 % of ETc) would result in a more adequate strategy due to increasing of the volatile compounds content, unlike the most irrigated treatment which seems to produce an increase of herbaceous related aromas (hexanal and (E)-2-hexenal) not desirable for wines. Another viticultural technique widely used is the foliar application, which consists in enriching plants with different nutrients through the leaves. It has been shown that the application of different aqueous wood extracts increases the amino acids content, and therefore the formation of volatile compounds during the alcoholic fermentation (Sánchez-Gómez et al., 2016). However, the wine aromatic profile was scarcely affected by the application of several nitrogen sources as fertilizers (Rubio-Bretón, Gutiérrez-Gamboa, Pérez-Álvarez, Santamaría, & Garde-Cerdán, 2018). The pre-fermentative techniques are those that are made in the cellar before starting the winemaking. One of the most carried out pre-fermentation techniques is the addition of enological tannins. In this sense, it has been observed that treatments with tannins significantly improve the wine aromatic complexity, inhibiting the formation of higher alcohols in the alcoholic fermentation and increasing the isoamyl acetate (banana) and 2-phenylethanol (floral aromas) content (Chen et al., 2016). However, this technique affects the synthesis of methanol and diacetyl, which increased excessively. On the other hand, it has been seen that the addition of these compounds is negative for floral and fruity aromas, but positive for the formation of higher alcohols in fermentations involving *Saccharomyces cerevisiae* and less effective in those involving non*-Saccharomyces* yeasts (Chen et al., 2018). Another pre-fermentative technique that affects the content of fermentative aromas is the different maceration types, as several works have studied. The wines produced by carbonic maceration have a higher content of alcohols and carbonyl compounds, but lower content of C6 alcohols and volatile acids than conventionally produced wines (Ayestarán et al., 2019). On the other hand, it has been studied that the standard macerated wines contain higher amount of higher alcohols, that the cold maceration previous to the fermentation showed the highest levels of acetaldehyde and ethyl acetate and increased the content of esters with respect to the standard maceration, and that maceration at high temperature increased the amount of esters and fatty acids to a greater extent (Lukić, Budić-Leto, Bubola, Damijanić, & Staver, 2017). In another study, fermentation with the skins and contact with the skins before fermentation led to lower levels of terpenes, esters, acids and thiols, and higher levels of alcohols, compared to fermented wines without any type of contact with the skins (Aleixandre-Tudo et al., 2015). The fermentative techniques are those carried out during the fermentation. The most significant fermentative factors are the different types of yeast (Figure 22.3) and bacteria, and the fermentation conditions (temperature, pH, level of agitation...). The yeasts are responsible for the transformations that occur during the alcoholic fermentation. These microorganisms degrade the two fermentable sugars of grapes, glucose and fructose, to produce ethanol and carbon dioxide. During the fermentation, numerous yeast species can coexist, being the most common the *Saccharomyces cerevisiae* species. In recent years, the effect of these yeasts on the aromatic wine composition has been studied. A study reveals that wines fermented with *Torulaspora delbrueckii* had dry fruit and pastry aromas, and low intensities of fresh fruit aromas, which reduced the content of main esters and increased the content of lactones and some ethyl esters (Ramírez et al., 2016). Other study, in which two types of yeast were used, showed that the wines produced by *Metschnikowia* *pulcherrima* contained 1.0 % v/v less ethanol than the wines fermented with *Saccharomyces cerevisiae* and higher concentrations of ethyl acetate, total esters, total higher alcohols and total sulfur compounds, while wines fermented with *Saccharomyces uvarum* showed a reduction of 1.7 % v/v in ethanol and a higher total concentration of higher alcohols (Varela, Barker, Tran, Borneman, & Curtin, 2017). On the other hand, the impact on two white wines of different fermentative strategies was evaluated: inoculation with *Saccharomyces cerevisiae* yeast, sequential inoculation (*Torulaspora delbrueckii/Saccharomyces cerevisiae*) and spontaneous fermentation. The wines inoculated with *Saccharomyces cerevisiae* and *Torulaspora delbrueckii* showed nuances of ripe fruit improved and a higher content of ethyl propanoate, ethyl 2-methylpropanoate and ethyl dihydrocinnamate. Thus, the spontaneous fermentation wines presented improved nuances of “stone fruit” (peach, nectarine, apricot…) related to the higher contents of 2-phenylethyl acetate and 2-methylpropyl ethanoate (Puertas et al., 2018). It has also been shown that wines produced by a strain of *Saccharomyces cerevisiae*, as well as wines produced by spontaneous fermentation, produced high concentrations of esters, mainly ethyl 2-hydroxypropanoate, and fatty acids (Blanco, Mirás-Avalos, Pereira, & Orriols, 2013). In another work, volatile content was compared in fermentations carried out by *Saccharomyces cerevisiae* and mixed fermentations (*Pichia fermentants/Saccharomyces* *cerevisiae*). The results revealed that mixed fermentations increased the content of acetates, ethyl esters, fatty acids and many other volatile fermentative compounds (Ma, Yan, Wang, Zhang, & Tao, 2017).

 Another factor of great importance in the production of fermentative volatile compounds is the fermentation conditions. One of the conditions that most affects is the temperature of fermentation, but there are also other factors, such as pH or agitation speed. Regarding the temperature of fermentation, its effect has been evaluated and it has been found that at lower temperatures, higher concentrations of compounds related to fresh and fruity aromas were found, while at higher temperatures, higher concentrations of floral aromas (Molina et al., 2007) and esters were found (Rollero et al., 2015). The agitation speed during fermentation is another factor that influences the production of volatile aromas, it was found that 80 rpm was more effective than 125 rpm and 40 rpm for the production of fermentative aromas (Rollero, Roberts, Bauer, & Divol, 2018). The factors exposed until now are the most important, but there are other factors that can modify the content of fermentative volatile aromas in wine, some of these are the changes in the winemaking process, where wines that have been previously dried, presented a relevant note of marmalade, possibly due to the presence of 2-phenylethyl acetate (de Castilhos et al., 2019), and supplementation with oxygen and lipids, where the addition of lipids increased the concentration of esters, higher alcohols and volatile acids, the addition of oxygen increased the concentration of higher alcohols, and the addition of oxygen together with lipids, showed an additive effect on the concentration of higher alcohols, but oxygen suppressed the potentiating effect of lipids in the formation of volatile esters and acids (Varela, Torrea, Schmidt, Ancín-Azpilicueta, & Henschke, 2012). After alcoholic fermentation, some wines may undergo malolactic fermentation. The agents of these malolactic transformations are the lactic bacteria, mainly of the *Oenococcus oeni* species and to a lesser extent *Pediococcus damnosus* and *Lactobacillus* species. It has been found that bacteria can influence the aroma, producing volatile metabolites and modifying the aroma compounds derived from grapes and yeast metabolism (Styger et al., 2011). In general, it has been found that the malolactic fermentation can improve the fruity aroma and the note of butter, being able to reduce the green aroma of the wine (Styger et al., 2011). Finally, the amount of nitrogen compounds in must can affect the volatile composition of the wine, since amino acids (the main source of nitrogen for yeasts), are precursors of volatile fermentative compounds (Sánchez-Gómez et al., 2016). The availability and utilization of nitrogen by *Saccharomyces cerevisiae* significantly influence the fermentation kinetics (Arias-Gil, Garde-Cerdán, & Ancín-Azpilicueta, 2007) and the production of volatile compounds important for wine aroma (Garde-Cerdán & Ancín-Azpilicueta, 2008). It has been shown that the concentration of volatile compounds in the wine was directly related to the amount of amino acids present in the must, and that nitrogen has a double role, promoting the yeast growth to carry out the alcoholic fermentation, and producing volatile compounds (Fairbairn, McKinnon, Musarurwa, Ferreira, & Bauer, 2017).

**22.4 Ageing aromas**

 The ageing period for a wine involves developing a series of processes which determine the properties of the end product. The wine can be subjected to some of the various processes during this maturing period, such as contact with wood, storage in containers of different characteristics (stainless steel, concrete, granite, wood…), in bottles or all of these. Ultimately, this is the final and longest period involved in producing a wine, in which the traits acquired in the prior processes are consolidated and new properties, especially if the wine is kept in contact with wood, are added. During the conservation of the wine, the tertiary aromas are generated, which can be produced in the course of traditional oak barrel ageing technology, or with innovative ageing technologies, as the conservation of wine in contact with wood fragments, ageing on lees, or application of micro-oxygenation. The main groups of volatile substances that the wood provide to wine are (Table 22.3): furanic compounds (furfural, 5-methylfurfural, 5-hydroxymethylfurfural, and their corresponding alcohols); phenolic aldehydes (vanillin and syringaldehyde); lactones (*cis* and *trans-*β-methyl-γ-octalactone); volatile phenols (eugenol, guaiacol, 4-methylguaiacol, 4-propilguaiacol, isoeugenol, 4-vinylguaiacol, syringol and 4-alilsyringol); and acetic acid, which is not positive regarding the aromatic quality of the wine, and leads to an increase in volatile acidity. Most of these compounds are specific substances of the wood that are not found practically in the base wine (guaiacol, 4-methylguaiacol, and oak lactones). But some compounds, such as vanillin, syringaldehyde, and eugenol can be present in the wine in traces and their concentration can significantly increase due to the wood contribution (Flanzy, 2000). Furfural and 5-methylfurfural have, on their own, a minor impact. However, furfural has been reported to have an important modifying effect on the aroma perception of oak lactones, decreasing wood aroma as the levels of furfural are increased (Chira & Teissedre, 2015). Oak lactones contribute to olfactory characteristics of wine with coconut, woody and oak notes, whereas vanillin is related to vanilla and coffee smells, and volatile phenols to spicy and smoked flavors (Prida & Chatonnet, 2010). Therefore, during the process of conservation and ageing of the wines, the fruity aromas characteristic of young wines, coming from esters, alcohols and terpenes decrease, appearing more complex aromas with other sensory characteristics. The extraction process of volatile compounds that takes place in oak barrels depends on many factors, among which stand out: the oak species, the oak geographical origin, the silvicultural treatment of the tree, the wood processing in cooperage (seasoning method and oak toasting intensity during barrel’s manufacturing), the contact time between wood and wine, and the number of times that the barrels have been used previously (González-Centeno, Chira, & Teissedre, 2016; Navarro et al., 2018).Besides the characteristics of barrel, the grape variety and wine composition have a real impact on the extractive capacity of wine. On this way, several authors (Garde-Cerdán, Torrea-Goñi, & Ancín-Azpilicueta, 2004; González-Centeno et al., 2016) suggest that the extraction of woody aroma compounds from barrels increased with increasing the wine alcoholic degree. Moreover, according to other authors (Garde-Cerdán et al., 2004; Rodríguez-Rodríguez & Gómez-Plaza, 2012), a high alcohol content and acidity could favor the alcoholysis of lignin and a higher amount of guaiacol and 4-methylguaiacol could then be released. These same authors (Rodríguez-Rodríguez & Gómez-Plaza, 2012) also observed a significant negative correlation between the lactones concentration and the alcohol content, titratable acidity, and volatile acidity; as well as a significant positive correlation between the vanillin and the alcohol content and titratable acidity. Oak barrels are the most used for the wine ageing process. Oak species and their geographical origins affect considerably the volatile composition of wines. The most widely species used in cooperage are *Quercus alba* from America and *Q. petraea* and *Q. robur* from Europe, mainly from France. Martínez-Gil et al. (2018) observed that the wines macerated in contact with *Q. alba* oak chips showed greater content of furfural, guaiacol, vanillin, syringol, and *cis-*oak lactone than the one macerated with *Q. petraea* oak chips. Also, other authors (Chira & Teissedre, 2015; Spillman, Sefton, & Gawel, 2004b) suggested than *Q.* *robur* oak contain less eugenol than *Q.* *petraea*. Moreover, it is well known that wines aged in American oak barrels have a higher *cis*/*trans*-oak lactone ratio than those aged in French oak barrels (Chira & Teissedre, 2015; Garde-Cerdán & Ancín-Azpilicueta, 2006b, 2006a; Gómez-Plaza, Pérez-Prieto, Fernández-Fernández, & López-Roca, 2004). Aromatic composition of other oak geographical origins and wood species have been studied, showing an interesting oenological potential as alternative species for coopering: Colombian oak (*Q. humboldtii*) (Martínez-Gil et al., 2018); Spanish oak (*Q.* *pyrenaica*) (Gallego et al., 2012); Slavonia oak (*Q. petraea* and *Q. robur*)(Chira & Teissedre, 2015); acacia (*Robinia pseudoacacia*) (Fernández de Simón et al., 2014; Kyraleou et al., 2015); cherry (*Prunus* *avium*) (Fernández de Simón et al., 2014); chestnut (*Castanea* *sativa*) (Fernández de Simón et al., 2014) and ash (*Fraxinus excelsior*) (Fernández de Simón et al., 2014). Wood seasoning in cooperage affects the final chemical composition of the wood and therefore, the volatile composition of aged wines in barrels. The effect of various oak wood seasoning methods, natural seasoning in open air, artificial seasoning in a kiln, and a mixed method that combines open air and kiln drying was studied by Martínez et al. (2008). These authors observed that the natural seasoning wood had larger concentrations of volatile phenols, phenolic aldehydes, furanic compounds, and *cis*- and *trans-*oak lactones, than mixed or artificial methods. The toasting degree of barrels can be classified as light, medium or high. Several authors (Dumitriu, López de Lerma, Zamfir, Cotea, & Peinado, 2017; Herrero et al., 2016) observed that wines aged in barrels with high toasted level showed the highest concentration of volatile aroma compounds highlighting those aromas extracted from the wood. Guaiacol and 4-methylguaiacol have smoky aromas and are indicators of the wood toasting level, since they are formed by the thermal degradation of lignin during the toasting process. As it has been observed in many works (Chira & Teissedre, 2013b; Gómez García-Carpintero et al., 2012; Guchu, Díaz-Maroto, Pérez-Coello, González-Viñas, & Cabezudo, 2006; Herrero et al., 2016; Vichi et al., 2007),higher toasting levels correspond to higher concentrations of these compounds, due to exposure of the wood to heat and fire. On the other hand, several authors (Bosso et al., 2008; Chira & Teissedre, 2013b; Herrero et al., 2016) have observed that the maximum concentrations of syringaldehyde, vanillin, furfural, and guaiacol were found in wines in contact with medium toasting level woods. Moreover, toasting process significantly affects lactone levels, obtaining more oak lactones content in light than in medium toasted barrels (Bosso et al., 2008; Chira & Teissedre, 2015), probably due to the thermodegradation of these heat-sensitive compounds or their loss by volatilization when the oak wood is subjected to high temperatures or even charring (Chira & Teissedre, 2013b). Moreover, watering process during toasting enhances furanic compounds, vanillin, and oak lactones extraction (Chira & Teissedre, 2015). Because oak extractives in a barrel is finite, the volatile composition of aged wines in used barrels have studied by several authors (Garde-Cerdán, Rodrı́guez-Mozaz, & Ancín-Azpilicueta, 2002; Gómez-Plaza et al., 2004).The quantity of these compounds and their rate of extraction diminish with the utilization of the barrel during successive years. The concentrations of volatile aromatic compounds found in wines matured in second-fill barrels are lower than in new barrels, even if the maturing time is longer. Another factor that affects the concentration of aromatic compounds in wines is the contact time with the wood. Many works (Chira & Teissedre, 2013b; González-Centeno et al., 2016; Herrero et al., 2016) show how the concentration of main volatile compounds extracted from wood to wine (vanillin, furfural, guaiacol, eugenol and lactones) increases over time. In several studies (Chira & Teissedre, 2013a; Rodríguez-Rodríguez & Gómez-Plaza, 2012), the extraction rate of furanic compounds in wines in contact with wood was maximum after 3 or 6 months of maceration, and after 12 months these compounds were exhausted. This is due to the biochemical reduction of furfural and 5-methylfurfural to the corresponding alcohols can be higher than their extraction from wood. Moreover, the maximum concentrations for the vanillin and guaiacol were at 9 or 12 months, and in the case of eugenol, isoeugenol, and both lactones, an increase during all the oak maturation period was observed. According Herrero et al. (2016) only methyl vanillate and vinylphenols decreased over time. Methyl vanillate decreased over time because it can be easily degraded during ageing (Jarauta, Cacho, & Ferreira, 2005), while vinylphenols may decrease during the ageing period, with the presence of *Bretanomyces/Dekkera* yeasts, which promote their transformation to ethylphenols (4-ethylguaiacol and 4-ethylphenol). These compounds contribute negatively to wine aroma due to the odor associated with them described as phenolic, horse sweat, or stable odors (Table 22.3). The moment of the addition of the oak fragments also influences the concentration of wine tertiary aromas. Thus, Kyraleou et al. (2016) observed that the addition of wood chips after fermentation enhanced the levels of guaiacol, 4-methylguaiacol and vanillin, compared with the wines fermented with chips. On the other hand, the presence of lees during ageing can modify the wine aromatic properties. Thus, the conservation of white wine on yeast lees in oak barrels significantly reduces the concentration of volatile compounds that can be extracted from wood. For example, during the ageing on lees, the biochemical reduction of vanillin, with a high contribution to wine aroma due to its low detection threshold (Table 22.3), to vanillyl alcohol, a very little aromatic compound (Flanzy, 2000). Besides, the addition of lees to the wine aged in oak wood decreases the concentration of phenols, furanic compounds, phenolic aldehydes and lactones, due to their binding by the lees, being the compounds with the most affinity for the lees eugenol, 4-propylguaiacol, 4-methylguaiacol, furfural and 5-methylfurfural. This retention is incremented with increased concentration of lees. On the other hand, guaiacol and γ–nonalactone were the only compounds that were not bound by the lees (Jiménez-Moreno & Ancín-Azpilicueta, 2007). For all this, ageing wine in oak barrels in presence of lees attenuates the impact of wood on wine aroma (Liberatore, Pati, Nobile, & Notte, 2010; Loira et al., 2013). Moreover, during the ageing on lees of red wines in oak barrels can be detected furfurylthiol, with coffee aroma, which comes from the reaction between furfural from wood and hydrogen sulfide, originating from the lees (Blanchard, Tominaga, & Dubourdieu, 2001).

 Oxygen is a decisive factor in all the steps involved in the wine maturing process since, the wine receives oxygen, in a controlled way or not, during its storage in contact with wood or containers made of other materials, like stainless steel, concrete, granite or polyethylene, and then, the oxygen added to the wine via the closure system, when is stored in the bottles (del Álamo-Sanza, Laurie, & Nevares, 2015; Nevares & del Álamo-Sanza, 2018). The role of oxygen in modifying the wine aroma during ageing is an aspect widely studied during the bottle storage process (Caillé et al., 2010; Ferreira, Bueno, Franco-Luesma, Culleré, & Fernández-Zurbano, 2014; Lopes et al., 2009; Ugliano, 2013; Ugliano et al., 2012; Vasserot, Jacopin, & Jeandet, 2001). However, few papers evaluating its effect on the aroma of wines aged in oak barrels or in contact with oak alternatives have been found (del Álamo-Sanza, Nevares, Gallego, Fernández de Simón, & Cadahía, 2010; Fernández de Simón, Cadahía, Muiño, del Álamo-Sanza, & Nevares, 2010; Gallego et al., 2012; Oberholster et al., 2015) and none assessing the effect of oxygen on the aroma of wines stored in granite or concrete. The interaction between the compounds responsible for the wine aroma and the oxygen available during ageing is determined by the type of wood used in the process, the environmental conditions of storage and the quantity of oxygen consumed by the wine. Thus, when red wine is aged in oak barrels for 6 months using the alternatives and micro-oxygenation (MOX), those treated with *Q. alba*, *Q. petraea* or *Q. pyrenaica* oak staves, together with MOX, consume more oxygen (25.7, 19.8 and 12.5 mg/L, respectively) than those aged with *Q. alba*+MOX, *Q. petraea*+MOX or *Q. pyrenaica*+MOX (16.8, 9 and 6.7 mg/L, respectively) oak chips (del Álamo-Sanza et al., 2010).That paper stated that the volatile compounds content from the wood was closely related to oxygen consumption in the wine. So, the higher oxygen consumption by wines treated with staves+MOX was related to the higher 5-methylfurfural, furfural, 2-furanmethanol, *cis* and *trans*-oak lactones, maltol, guaiacol, 4-ethylphenol, 4-ethylguaiacol, vanillin, and syringaldehyde content in all the wines studied, regardless of the type of oak used: *Q. alba*, *Q. petraea* or *Q. pyrenaica* (del Álamo-Sanza, Nevares, Martínez-Gil, Rubio-Bretón, & Garde-Cerdán, 2019; Fernández de Simón et al., 2010)*.* Different studies confirm that oxygen reaches the wine in a barrel via the joins between the staves and via the wood (Nevares et al., 2016; Nevares & del Álamo-Sanza, 2014). This oxygen transfer (OTR) follows a dynamic trend by decreasing with ageing time, basically due to the wine impregnating the wood (del Álamo-Sanza, Cárcel, & Nevares, 2017; del Álamo-Sanza & Nevares, 2014; del Álamo-Sanza & Nevares, 2017; Nevares & del Álamo-Sanza, 2014). The type of wood chosen and the cooperage treatments determine the wine-wood interaction and therefore the final traits of the wine. The UVaMOX group is working on the relationships existing between woods of varying permeability to oxygen and aromatic composition, as both aspects are decisive to the characteristics of wine matured in wood. Wood grain is normally selected according to its direct relationship with the aromatic profile which the wood will potentially transfer to the wine, depending on cooperage treatments. Collins et al. (2015) showed that during toasting, there are specific differences in the temperature profiles of each oak barrel, and these differences probably result in differences in the composition of each barrel. Therefore, the effect of temperature gradients is crucial to controlling the aromatic potential of a wood. Nevertheless, without a doubt, the wood, its anatomy and properties determine the aromatic potential, which will be transferred to the wine. Recent studies by the UVaMOX group has shown that the OTR entering the wine through French oak barrels determines the volatile compounds quantity ceded to the wine during maturation. This could be explained by considering the mechanisms that regulate the oxygen transfer through the wood: this is a process whereby oxygen is diffused through the structure of the wood into the wine. Therefore, the anatomy of the wood (proportion of early and latewoods, the medullary radius and its inclination), as well as the density, are the main factors defining its OTR. As the structure of high oxygenation woods differs significantly from that of low oxygenation ones, the volatile compounds profile that will potentially be transferred to the wines will also differ greatly (data not shown).

**22.5 Conclusions**

 Aromatic composition is a key aspect in the wine quality. Varietal and pre-fermentative aromas are mainly influenced by the grape variety and its state of maturity, as well as by viticultural practices, and edaphic and climatic conditions. For its part, fermentative aromas content depends on the handling of the technologies during pre-fermentation and alcoholic and malolactic fermentations. The choice and management of every of these aspects are a fundamental feature in the final balance of wine aroma.Besides, knowledge concerning type of wood and oxygen during wine maturation is essential to control the process, since they determine the final aromatic traits obtained. It is crucial to highlight that, the choice of a wood according to its physico-chemical properties and capacity for oxygenating wine, is also a factor decisive to the aromatic profile acquired by a wine during the ageing process.

**Acknowledgements**

 P. R.-B., E. P. P.-Á. and T. G.-C. thank MINECO for funding her doctoral contracts. S. M.-S. thanks Gobierno de La Rioja for her pre-doctoral contract. M. A.-S. and I. N. thank Junta de Castilla y León (VA315P18), MINECO (AGL2017-87373-C3-2-R), FEDER, and the Interreg España-Portugal Programme (Iberphenol) for the funding.

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**Table 22.1** Some varietal and pre-fermentative aroma compounds in wines.

|  |  |  |  |
| --- | --- | --- | --- |
|  | **Compounds** | **Aromatic descriptor**  | **ODT****(µg/L)** |
| **Methoxypyrazines** | 3-Isobuthy-2-methoxypyrazine (IBMP) | Green pepper, pea pod | 0.001a |
| 3-Isopropyl-2-methoxypyrazine (IPMP) | Green pepper, pea pod, earthy | 0.002a |
| **Monoterpenes** | Geraniol | Geranium, rose | 30b |
| Linalool | Coriander seed, rose | 15b |
| Nerol | Floral, orange flowers | 15c |
| Citronellol | Rose, lemongrass | 100c |
| *Cis*-Rose oxide | Floral, green | 8a |
| **Sesquiterpenes** | Farnesol | Floral | 1000d |
| Nerolidol | Floral | 15b |
| Rotundone | Black or white pepper | 0.016e |
| **C13 norisoprenoids** | β-Damascenone | Apple sauce, rose | 0.05b |
| β-Ionone | Violet | 0.09f |
| (E)-1-(2,3,6-Trimethylphenyl)butan-1,3-diene (TBP) | Geranium leaf | 0.024a |
| **Benzenoids** | Benzyl alcohol | Sweet, fruity, chemical | 200000b |
| 2-Phenylethanol | Floral, rose | 10000b |
| Methyl vanillate | Honey, vanilla | 3000c |
| Ethyl vanillate | Sweet, honey, vanilla | 990c |
| Syringol | Smoky | 2000f |
| **Thiols** | 3-Mercaptohexan-1-ol (3MH) | Passion fruit, grapefruit | 0.06a |
| 3-Mercaptohexyl acetate (3MHA) | Boxwood, passion fruit | 0.004a |
| 4-Mercapto-4-methylpentan-2-one (4MMP) | Boxwood, broom | 0.0008a |
| **C6 compounds** | (E)-2-Hexenal | Bitter almond | 4f |
| (Z)-3-Hexenol | Herbaceous | 400f |
| 1-Hexanol | Herbaceous | 8000f |

Olfactory detection threshold (in wine or model solution): ODT; aDarriet et al. (2012); bGuth (1997); cEtievant (1991); dFranco et al. (2004); eWood et al. (2008); fFerreira et al. (2000).

Table 22.2 Summary of the factors and practices that can affect the content of the wine fermentative volatile compounds.

|  |  |  |  |
| --- | --- | --- | --- |
| **Factors** | **Practices** | **Volatile compounds improved** | **Reference** |
| Viticultural Techniques | Basal defoliation | 1-Hexanol, 2-phenylethanol, 2-phenylethyl acetate, decanoic acid, ethyl octanoate | (Wang et al., 2018) |
| Foliar application | Amino acids | (Sánchez-Gómez et al., 2016) |
| Sunlight exposure | Alcohols, ethyl esters, lactones, terpenes, C13 norisoprenoids | (Vilanova et al., 2017) |
| Regulated deficit irrigation (RDI) | Benzaldehyde, benzyl alcohol, phenylethyl alcohol, 2-methyl-1-propanol, 3-methy-l-butanol, amino acidsVolatile compounds | (Ju et al., 2018)(García-Esparza et al., 2018) |
| Pre-fermentative Techniques | Addition of tannins | Higher alcohols, isoamyl acetate, 2-phenylethanol | (Chen et al., 2016) |
| Higher alcohols | (Chen et al., 2018) |
| Maceration | Alcohols, carbonyl compounds | (Ayestarán et al., 2019) |
| Acetaldehyde, ethyl acetate, C6 compounds, esters | (Lukić et al., 2017) |
| Alcohols, ethyl vanillate | (Mihnea et al., 2015) |
| Alcohols | (Aleixandre-Tudo et al., 2015) |
| Fermentative Techniques | Type of yeast | Lactones, minor ethyl esters | (Ramírez et al., 2016) |
| Ethyl acetate, esters, higher alcohols, sulfur compounds | (Varela et al., 2017) |
| Ethyl propanoate, ethyl 2-methylpropanoate, ethyl hydrocinnamate, 2-phenyl acetate, 2-methylpropyl ethanoate | (Puertas et al., 2018) |
| Higher alcohols, 2-phenylethanol, esters (ethyl 2-hydroxypropanoate) and fatty acids | (Blanco et al., 2013) |
| Acetates, ethyl esters, fatty acids | (Ma et al., 2017) |
| Type of bacteria | Compounds related to fruity aroma and butter note | (Styger et al., 2011) |
| Nitrogen compounds | Volatile compounds in general | (Fairbairn et al., 2017) |
| Esters | (Rollero et al., 2015) |
| Fermentation conditions (Tª, pH, agitation) | 15º C: compounds related to fresh and fruity aroma28º C: compounds related to floral aromas | (Molina et al., 2007) |
| 80 rpm: optimal for the production of fermentative aromas | (Rollero et al., 2018) |
| Others (grape pre-drying, submerged cap, supplementation with O2 and lipids) | 2-phenylethyl acetate, C6 alcohols | (de Castilhos et al., 2019) |
| Lipids: esters, higher alcohols, volatile acidsOxygen: higher alcoholsLipids + Oxygen: higher alcohols | (Varela et al., 2012) |

**Table 22.3** Main volatile odorant compounds added to wine by oak, aromatic descriptors and perception thresholds in red wine(μg/l).

|  |  |  |  |
| --- | --- | --- | --- |
|  | **Compound** | **Aromatic descriptor** | **ODT****(µg/L)** |
| **Furanic compounds** | Furfural | almond | 20000a,c,e |
| 5-Methylfurfural | toasted almond | 45000a,c,e |
| 5-Hydroxymethylfurfural | almond | 100000d |
| **Phenolic aldehydes** | Vanillin | vanilla | 320a |
| Syringaldehyde | spices, smoke | 50000a |
| **Lactones** | *cis*-Oak lactone | wood, coconut, vanilla | 74c,e /54b |
| *trans*-Oak lactone | wood, coconut, spices | 320c,e / 370b |
| **Volatile phenols** | Eugenol | spices (clove) | 500a,c,e |
| Guaiacol | smoke, toasted | 75a,c,e |
| 4-Methylguaiacol | smoke, burnt | 65a,c,e |
| 4-Propilguaiacol | leather, animal | 10d |
| Isoeugenol | spices | 6d |
| 4-Vinylguaiacol | carnation, pepper | 380a,c,e |
| Syringol | smoke | 2000c |
| **Ethylphenols** | 4-Ethylphenol | horse stable, medicinal | 620c |
| 4-Ethylguaiacol | leather, phenolic | 150a,c,e |

Olfactory detection threshold (in wine or model solution): ODT; aBoidron et al. (1988) ; bBrown et al. (2006); cChatonnet et al. (1992); dSáenz-Navajas et al. (2010); eSpillman et al. (2004a).



**Figure 22.1** Hydrolytic breakdown of the glycosidic bonds of the glycosylated precursor of linalool and release of sugars and the volatile aglycone. Glucose and the glycosyl-glucose moiety (G-G) are shown in red.



**Figure 22.2** Simplified metabolic map of ester formation. Genes that codify enzymes involved in ester formation are indicated. The substrate availability depends mainly on carbon, nitrogen, and fatty acid metabolism, while the ester synthase activity is mainly determined by the activity of the corresponding genes. Thus, factors that affect yeast metabolism or ester synthase gene regulation will influence ester synthesis (Belda et al., 2017).



**Figure 22.3** Aromatic compounds formed by yeasts during the alcoholic fermentation (Styger et al., 2011).