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Chapter

Chemistry and Technology of Wine Aging with Oak Chips

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Abstract

The use of wood chips is a common winemaking practice that has been permitted in Europe since the early 2000s. The use of oak chips, or other wood alternative products, has not always been favorably viewed by both producers and wine consumers. Beyond possible misuse, however, wood chips are a useful tool for the optimal achievement of numerous oenological objectives, including the extraction of certain volatile odor compounds from oak wood chips as well as compounds that will improve wine quality. This chapter deals with the main oenological uses of oak wood chips, the chemical transformations that underlie this practice and the effect of their utilization on wine quality. A final aspect concerns the main compositional and sensory differences between wines aged in barrel and those aged with alternative products, as well as the discriminative analytical methods used for this purpose.

Keywords: oak wood chips, alternative products, volatile compounds, tannins, wine aging

1. Introduction

The use of wood shavings in wine production has been documented in France since the nineteenth century. It was an unusual, but well-known, practice to improve the sensory characteristics of some wines using untoasted chips of oak wood or service trees [1]. The modern use of wood fragments in winemaking began in new winemaking countries in the early 1960s [2]. In 1993, the United States regulated the use of such products in oenology. In Europe, their use was opposed until the early 2000s, but finally in 2006, Regulation (EC) No. 1507/2006 of the Commission authorized the use of pieces of oak wood in oenology, enabling European producers to compete in a rapidly evolving world market. The new EU Delegated Regulation 2019/934 [3] currently regulates the use of oak wood chips in oenology, which are used for several technological purposes. The main objective is the release of desirable compounds, mainly aromas and polyphenolics, from the wood fragments into the wine during aging.

The main reason supporting the increased use of wood chips in wine production was essentially economic. The cost of wood chips is considerably lower than that of wooden casks. The production of wood fragments involves industrial-type technologies and therefore, is much cheaper than the artisanal processing of barrels. In addition, the wood, although from the same botanical species, in the case of barrels, is obtained from the most valuable part of the trunk, whereas woody fragments are usually recovered from less valuable parts or remnants of barrique production.
Nowadays, wood fragments represent an opportunity for wine producers to diversify their product in order to satisfy different market needs. From a technological point of view, the oenologist can choose the size of the wood pieces, the duration of the contact with the wine and the moment of application.

On the other hand, the same reasons that supported the spread of wood chips in wine production also prevented its acceptance from a regulatory point of view. Indeed, as mentioned above, there is a cost-reduction associated with the use of oak wood chips, obtained by giving a woody touch to the wine without the need to use barrels; however, without proper regulation, this could lead to fraud. If such wine is offered as barrel-aged wine [4, 5], the false use of quality indications on its label represents counterfeiting, which is detrimental to consumers and legitimate producers. Therefore, the challenge to distinguish between wines obtained using one refinement technique or another is particularly crucial, even if complicated by the multiplicity of variables involved. However, it is equally clear that, due to the need of control for both consumer protection and quality assessment, the continuous improvement of investigation methods is essential, either analytical or sensory, that allow distinguishing wines aged in barrels from those treated with chips or alternative woods.

2. Alternative products in oenology

2.1 The choice of wood

The current European legislation stipulates that the wood used in winemaking must come exclusively from the *Quercus* genus, so the use of alternative products, obtained from woods of other botanical origin is not permitted. From a technological point of view, oak wood is certainly the most suitable for the storage and aging of wine due to several positive technological characteristics such as natural durability, porosity, resistance, a high degree of impermeability, and low water content, as well as a good amount of extractable compounds useful for the positive evolution of wine. There are approximately 600 species of oak, but only a few of these are used for oenological purposes [6]. The most commonly used European species in oenology are *Q. sessilis* (or *petraea*) and *Q. robur* (or *pedunculate*), which usually grow mixed in the same area. More rarely, *Q. pyrenaica* belonging to the same genus and mainly spread between the Iberian Peninsula and western France [7] is used for winemaking purposes. American wood is mainly from *Q. alba* (White Oak) but also several other species namely, *Q. macrocarpa* and *Q. lylata* can be useful for winemaking purposes [6]. The differences among species essentially pertain to the content of extractable compounds from wood, the ellagitannins (generally higher in European oaks) and volatile aromatic compounds, namely whiskey lactone (present in a greater amount in American species). The compositional differences between individual trees, due to forestry conditions and anatomical localization of the wood or exposure, can have a greater impact than differences due to the botanical or geographical origin of the oak.

2.2 Types of alternative products and applications

The oak wood chips employed for oenological use are small pieces of wood with dimensions ranging from a minimum of 2 mm (sometimes called granulates, tabacs or wood rice) up to about 20 mm (sometimes called shavings, copeaux, or fragments) and are sold in single packs of a few kg. Following the Commission Delegated Regulation -EU- 2019/934 of 12 March 2019 - (Appendix 7) [3], manufacturers distinguish products based on the heating degree, suggesting their best use in different process phases. The doses vary, on average, between 0.5 and 4 g/L
for white winemaking and between 1 and 6 g/L for red winemaking, being 2 g/L a balanced and orientated usual dosage. The small dimensions guarantee a high exchange surface and consequently the refinement time is limited to a range of 4–6 weeks to a few months, depending on the size [8].

Currently, the market offers numerous alternatives to classic wood fragments. They are frequently larger products than typical chips, able to simulate aging in barrels more effectively. Commercially, they are called cubes, beans, blocks, dominoes, segments and so on. Xoakers are wooden spheres of small dimensions, measuring a few centimeters in diameter. The doses are variable, generally between 2 and 4 g/L. The infusion time varies from 1 to 6 months.

Oak staves, ministaves, and sticks are wooden slats or cylinders of variable size from a few centimeters to a meter long, width range of 25–75 mm and a thickness variable between 7 and 18/22 mm. Commercially, they are denominated in a variety of ways, but all these products share the same oenological objective, which is to optimally simulate aging in barrel. The recommended doses for the smaller ones are 1–5 g/L for about 6–12 months of contact time. Sometimes doses are reported as wood area/wine volume.

Products with dimensions less than 2 mm are not permitted by European legislation [3] but can be used by New World manufacturers and take the commercial name of dust or flour. The small size of the wood considerably increases the exchange surface with the wine and consequently, the extraction processes of aromatic compounds and tannins are very rapid (15 days to 4 months). The cost of the treatment is therefore extremely low due to the low cost of the product and the limited quantities that are used. Oak powders have the advantage of being able to be pumped together with the wine during racking operations; however, it is much more difficult to remove from wine than chips or staves. The doses vary between 0.5 and 2 g/L of wine.

All these products can be used at different stages of winemaking and for various purposes. Generally, untoasted fresh chips or low toasted wood chips are used in the early stages of winemaking in order to allow color stabilization improving the anthocyanin extraction in young wines and their color characteristics during wine stabilization [9]. Toasted products can be used both during the alcoholic fermentation and after the end of malolactic fermentation.

The use of alternative products assumes that a huge array of variables must be considered including the type of wood, the size and shape of fragments, the mode of wood seasoning, the grade of toasting, the moment of use during winemaking, duration and the timing of contact as well as the interaction with yeasts and bacteria involved in winemaking. The main technological variables are examined below.

2.3 Technological factors driving product quality

Commonly, the wood used for alternative products is obtained from remnants of the barrel-making process, especially in the production of granulates or chips. This is not a negligible part of oak wood, but almost 50–75% of the total production, depending on the method used for barrel stave production, that is, traditional via splitting or by sawdust. Oak wood is otherwise obtained from trees with small diameters or presenting some physical defects [10]. Sometimes, for example, for high-quality alternative staves, the wood is the same as that used to produce barrels. In all cases, to obtain a high-quality product, it is necessary to pay particular attention to the seasoning phases that should occur in the best possible conditions [1]. Seasoning is a fundamental process useful in eliminating excess water present in the wood from 70% to about 14–18% [11]; it can be carried out naturally, alternatively, by forced drying.
During natural seasoning, the wooden planks are stacked outdoors in the open air for a variable period, which depends on the thickness, and ranges from about 2–3 years. Slats are periodically moistened to remove, via leaching, the excess astringent and bitter compounds, such as tannins and coumarins, present in the wood [12, 13]. Furthermore, the presence of unpleasant compounds is attenuated, primarily trans-2-nonenal which gives the wood a hint of fresh wet wood. From a microbiological point of view, this process allows the development of a varied micro-flora on the surface of the wood which promotes the formation of fungicidal substances, the transformation of phenolics of the wood and eventually the evolution of some aromatic wood precursors [14, 15]. In this regard, eugenol decreases significantly during this process, whereas other aromas such as vanillin or oak lactone (see Section 3.1.1) are subject to contrasting phenomena of neosynthesis from aromatic precursors and degradation or leaching during seasoning [16].

Artificial seasoning allows cost containment and a considerable reduction in processing time. However, natural seasoning leads to a greater accumulation of odorous compounds in the wood, in particular, volatile phenols, phenolic aldehydes, furanic compounds, and cis- and trans-β-oak lactones compared with artificial seasoning, it also appears to be more effective in reducing the excess tannins present in the wood [17]. The loss of some important compounds during artificial seasoning as polyphenolics and some aromatic compounds (lactones, phenols, fatty acids, and norisoprenoids), as well as the formation of furanic compounds deriving from the degradation of hemicellulose, is proportional to the initial moisture content of the wood along with the drying temperature [18]. Although these differences are certainly relevant, the influence of the wood piece size and the toasting intensity on the volatile composition of alternative products is higher than the method of seasoning, that is, natural or artificial [10].

After seasoning, it is necessary to eliminate residual sapwood and bark that have a very different composition to heartwood, which is the most precious part of the wood. Oak wood is then processed to reduce it to the most appropriate size and is eventually toasted. During toasting, numerous transformations take place such as, the partial degradation of the wood polyosides that leads, in turn, to the formation of numerous odorous compounds. At the same time, a large portion of the tannins undergoes degradation, with the extent depending upon the degree of toasting. Unlike the production of barrels, the toasting of alternative products is, generally, an easy, automatic process. The technological solutions for their toasting are varied and include: direct contact of the pieces of wood with a suitably heated surface; by means of a suitably heated air jet; by irradiation with IR rays, which does not allow deep toasting of the pieces; by direct contact with a flame, used almost exclusively for the production of alternative staves. Two main benefits must be considered: the first is reducing production costs; the second is standardization in terms of quality. The toasting degree of the alternative products follows that for wooden barrels; therefore, they can be distinguished as untoasted or with a light, medium or high (heavy) toasting level. However, this classification does not represent an absolute reference as the technologies used by individual companies may differ considerably [19].

3. Oak wood chips chemistry

3.1 The general composition of oak wood

From an oenological point of view, the oak heartwood is the wood of major interest. Its chemical composition includes three large groups of compounds.
The first one consists of certain polymers constituting the cell wall and the median lamella of the vegetal cells with supporting functions. The second group is composed of several extractable substances accumulated during the natural transformation from sapwood to heartwood, as well as tannin deposits which protect against plant parasites. The third group includes, in smaller quantities, several compound residues of cellular metabolism: amino acids, fatty acids, terpene compounds, carotenoids, and various minerals [20, 21].

From a quantitative point of view, the main components of oak heartwood are cellulose (40–45% of dry weight), hemicellulose (20–25%) and lignin (25–30%) and, overall, they represent by weight, the predominant portion of the wood. These polymers form a three-dimensional structure, trapping cellulose in an insoluble and rigid matrix of lignin and hemicellulose, which gives the wood its typical technological characteristics.

Chemically, cellulose is a crystalline homopolymer consisting of units of glucose 1,4-β-bonded, which has an average molecular weight of 10^6 Da corresponding to 10,000–15,000 monosaccharide units. Hemicellulose is a complex polymer that may contain pentoses (β-d-xylene, α-L-arabinose), hexoses (β-d-mannose, β-d-glucose, α-d-galactose), and uronic acids [22]. Structurally, it has two roles: binding cellulose microfibers and strengthening the cell wall. It is worth noting that both the concentration and structure of this polymer differ between sapwood and wood. Finally, lignin, which from a structural point of view is a p-coumaryl alcohol polymer, is responsible for the typical mechanical properties of wood, making it more resistant to both chemical and biochemical degradation. As for the mechanical properties of wood, similarly to hemicellulose, structural differences have been found between sapwood lignin and heartwood lignin [22]. The average composition of structural polymers can vary significantly according to different factors. In this regard, it is worth mentioning that the wood composition within each tree is very different and depends on the location and anatomic position of tissues. In particular, the concentration of tannins is higher in the trunk and near the base of the tree [19]. The distance from the central part of the trunk influences the chemical composition and therefore, the technological characteristics of the wood [23]; the resistance to heat treatment for instance depends on whether the wood portions are central or radial. These aspects are very important from a technological point of view because the wood used for alternative products is generally obtained from different parts to those used for barrel production.

Finally, both the rate of growth and botanical origin affect strongly the chemical-physical characteristics of the wood. Slow growth leads to fine grains, less dense wood, which is of greater resilience and, most of all, richer in extractable compounds, whereas rapid growth leads to the formation of medium or coarse grain woods. As regards botanical origin the main differences concern the tannin content, generally higher in the heartwood of European origin and the volatile compounds (lactones, norisoprenoids, sesquiterpenes, and fatty acids), usually more abundant in *Q. alba* wood [19].

### 3.2 Volatile compounds

#### 3.2.1 Oak-derived volatile compounds

β-methyl-γ-octalactone is included among the minority aromatic compounds, but it has a crucial role from a sensory point of view. This is a natural lactone present in fresh oak wood, and it is characterized by intense notes of coconut, celery, and pastry with a very low perception threshold. Also called whiskey lactone or oak lactone, because it was discovered in the 1970s for the first time in whiskey and
shortly thereafter in the oak wood used for their processing [24, 25], oak lactone is formed from the cyclization of 3-methyl-4-hydroxyoctanoic acid. This compound is present in oak wood as a glycoconjugate precursor namely, galloylglucoside, glucoside, and a rutinoside derivative [26, 27] and can undergo hydrolysis during both seasoning and toasting operations or during the maturation of the wine in contact with the oak wood.

From a structural point of view, oak lactone is a molecule with two chiral carbons, therefore, four different optical configurations are possible. Only two stereoisomers of oak lactone are present in oak wood [28], the “cis” isomer with configuration (3S, 4S) and the “trans” isomer with configuration (3S, 4R). From a sensory point of view, the “cis/trans” ratio strongly influences the wine aroma, because the cis isomer is several times more odorous than the trans isomer [29]. The cis form is more abundant in Q. alba than in the European oaks, and among the latter, the cis isomer is more abundant in Q. petraea than in Q. robur [30]. The cis/trans lactone ratio was about 3.5 and 1 in American or French oak chip-treated wines, respectively [31]. It is interesting to note that the aging method (chips or barrels) did not influence this ratio which is related to the oak’s origin [32].

Generally, this compound is more abundant in American oak wood. A recent work showed that wines macerated with Q. pyrenaica chips presented levels of oak lactone and other wood-related compounds, more similar to those macerated with French oak wood chips and lower than American chips [33].

Among the aromatic compounds from fresh oak wood that have a significant impact on the aroma of wine can be included eugenol, which is characterized by typical clove notes and is present in small quantities, especially in sapwood [34]. Another important group of naturally occurring compounds is that of norisoprenoids [35]. These compounds originate from the degradation of carotenoids and xanthophylls present in the wood. Some of them have very low perception thresholds and perfumes that vary from floral to balsamic (see Section 3.4).

3.2.2 Compounds derived from the degradation of polysides

The degradation of wood polymers under an inert atmosphere proceeds gradually following the increase of temperature [36]. The decomposition of hemicellulose and cellulose takes place at 200–380°C and 250–380°C, respectively, while lignin decomposition occurs over the range of 180–900°C. Moreover in normal cooperage conditions, the degradation of cellulose occurs with great difficulty and the sensory impact of its derivatives remains negligible [22]. On the contrary, hemicellulose is more susceptible to hydrolysis, which can occur during both toasting and wine aging, and leads to an increase in the total content of galactose, fructose or xylose [37], up to a few hundred mg/L. From a microbiological point of view, this aspect should be considered carefully for the development of undesired microflora in wines, taking into account the ability of some spoilage microorganism, namely Brettanomyces spp. [38], to consume these sugars. The formation of monosaccharides during wood toasting leads to their thermodegradation and of odorous volatile compounds neogenesis. These compounds, named furanic aldehydes (mainly furfural and 5-hydroxymethylfurfural), are contained in negligible quantities in seasoned oak wood, used to produce barrels and chips, but their content increases dramatically passing from light to medium toasting level and tends to decrease with strong toasting. From a sensory point of view their importance is modest and linked primarily to a general increase in “overall oak” perceived intensity rating and decreased “fruity” aroma [39].

Other compounds, namely maltol and cyclotene, originating from hemicellulose degradation [22], are characterized by specific caramel notes. Like furanic
aldehydes, they have a limited impact on empyreumatic notes of wine aged using oak wood, because of their high perception threshold. Sugar condensation products such as DDMP (2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one), HDMF (4-hydroxy-2,5- dimethylfuran-3(2H)-one) and DHM (dihydromaltol), derived from glucose and proline condensation, seem to have a greater impact on the toasty/caramel aroma [40].

Finally, the thermodegradation of lignin leads to the formation of several key aromatic compounds including aromatic hydrocarbons, phenols (mainly monomethoxylated and dimethoxylated derivatives), aromatic aldehydes (benzoic aldehydes), and syringyl-derived compounds. Various factors such as the moisture of the wood, the intensity of the heat applied, the presence of other polymers such as cellulose can influence the chemical yield of these reactions [41]. Specially, the toasting intensity is the factor that most influences the final composition of these compounds in wine. Low/medium levels of heating lead to the formation of cinnamon and benzoic aldehydes as synapic aldehyde, coniferyl aldehyde, vanillin, and siringaldehyde. Among these, vanillin has an important aromatic impact thanks to its recognizable scent and low perception threshold [39]. More intense toasting levels lead to the formation of volatile phenols such as phenol, cresol isomers, guaiacol, 4-methylguaiacol, eugenol, isoeugenol and propiovanillone, some of them characterized by a low perception threshold and clear spiced or smoky notes.

Finally, some heterocyclic compounds present in small quantities, such as pyrazine, pyrrole pyridine, and triazole derivatives have been identified in toasted wood extracts. These compounds could be generated by Maillard’s reaction during the toasting operations [42].

3.2.3 Factors affecting xylovolatiles compounds during winemaking

The type of alternative wood has an important influence on the diffusion kinetics of aromatic compounds. Generally volatile compound accumulation is faster using wood chips than staves, on the other hand, staves lead to a greater accumulation of aromas, in all cases, the extraction seems to be complete after 3–12 months of aging [10, 43].

The botanical origin of wood has great importance in defining the transfer of aromatic compounds namely, oak lactone to wine. Wines aged in contact with American oak chips showed a significant increase of cis-oak lactone and guaiacol [31]. On the other hand, wines aged with French oak chips exhibited a major increase of furfural, 5-methylfurfural, 4-vinylguaiacol and trans-oak lactone.

The aging time was related to a higher content of esters [44]; the type of wood pieces was correlated to cis-oak lactone levels, octanal and 5-methyl furfural, and cis-oak lactone with the toasting degree.

The accumulation of phenols depends on the degree of toasting but, in general, a higher accumulation of these compounds occurs in wines aged with staves compared with those aged with chips [45]. For guaiacol, 4-methylguaiacol and eugenol, the maximum accumulation has been registered between 6 and 12 months.

The main variations during wine aging involve furan aldehydes; these changes are certainly decisive for wine quality. During the first months of storage, a high accumulation of furan aldehydes is observed [45], more remarkable in aging with staves than with chips; then their content decreases sharply, similar to that occurring in wines aged in barrique [46, 47]. This reduction is likely due to microbiological rather than chemical reactions. The notable reductase activity of yeasts and bacteria leads to the formation of furanic alcohols from their respective aldehydes. The observed decrease of furan aldehydes in wine during aging is also due to their involvement in reactions with polyphenols and, in particular, to the formation of
condensation compounds with polyphenols, mainly flavanols [48]. Vanillin and syringaldehyde exhibit accumulation and degradation curves during wine aging similar to those described for furan aldehydes [45].

Yeasts can also transform furfural to 2-furanmethanethiol (2-FMT), through the addition of hydrogen sulfide present during fermentation to furfural [49]. 2-FMT, with a very low perception threshold (0.4 ng/L) and its distinguishable odor of coffee [50], is the key aroma compound of the boisée aroma of wines. A similar biosynthetic mechanism has been hypothesized for the formation of benzenemethanethiol, characterized by subtle mineral notes, starting from benzaldehyde [51] and for vanillylthiol, a chemical compound reminiscent of cloves, and smoke originating from vanillin [52].

### 3.3 Tannins and micro-oxygenation

The “extractable fraction” of wood represents up to 10–15% of dry heartwood. Certainly, ellagitannins are the most abundant components in this fraction and, together with other compounds, are the source of many of the interesting sensory characteristics found in aged wines [53]. Eight ellagitannins have been identified in traditional oak species: castalagin, vescalagin, granidin, and roburins (A, B, C, D, and E), with the two most abundant compounds being the stereoisomers, vescalagin and castalagin [53–55]. Ellagitannins are transferred to the wine during aging, contributing to sensations of bitterness and astringency and behaving as antioxidants due to their capacity to consume oxygen [15, 53–55]. Moreover, ellagitannins directly affect wine color via reactions with anthocyanins forming red orange anthocyanin-ellagitannin complexes that are much more stable over time than free anthocyanins [55]. They often also occur in association with flavonoids to form flavano-ellagitannin derivatives (such as acutissimins A and acutissimins B) detected in aged wine and are also involved in tannin condensation [54]. Variation in ellagitannin concentration in the same wood, due to the different cooperage processes has been reported in various papers [53]; focusing on ellagitannin and alternative products, a recent study [56] performed with model wine showed that French oak chips released significantly higher amounts of ellagitannins than American oak chips at any toasting level. Their release by oak chips decreased as the toasting level increased in the French oak but this trend was not so clear in American oak.

Oxidation, condensation and polymerization reactions, in which phenolic compounds are involved, are oxygen dependent. During the aging of the wine in barrels, oxygen intake may promote, disappearance of reduction off-flavors and reduction of vegetal characteristics, but also color intensity and stabilization. This process, in barrels, is not a controlled process, but depends on wood characteristics. On the contrary, a monitored oxygenation process in stainless steel tanks can control the changes in the phenolic structure and aroma of the wine by managing oxygen-requiring reactions [57, 58].

Oxidation of wine, which is defined as the diffusion of air or oxygen into the wine, is an authorized oenological practice in the International Code of Oenological Practices of the OIV [59]. Micro-oxygenation (MOX), consisting of dispensing micro quantities of oxygen in a controlled way, was developed in France by Patrick Ducournau at the beginning of the 1990s, then Ducournau and Laplace registered a patent for the MOX method [60, 61]. Several researches have experimented MOX combined with the application of oak alternative products with the purpose to simulate the evolution and stabilization of the phenolic compounds that spontaneously takes place in barrel.

The formation of acetaldehyde from ethanol oxidation during wine MOX favors the creation of ethyl bridges between flavanols and between flavanols and
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Anthocyanins leading to an increase of both color intensity and color stability [62]. Ellagitannins contribute to the formation of ethylidene-bridged anthocyanin-tannin adducts through the formation of hydroperoxy radicals [63]. Moreover, MOX generally favors the formation of pyranoanthocyanins rising from the reaction of anthocyanins with small molecules, namely acetaldehyde. These compounds are likely to contribute to the red/orange hues observed in red wines during aging [64]. Acetaldehyde can also form bridges between tannin molecules, creating macromolecular structures that precipitate, leading to a decrease in astringency [65].

In general, MOX in combination with ellagitannins increased color intensity, even after 5 months of bottle aging due to increase of polymeric pigments including ethylidene-bridged compounds. These compounds contributed to the red and violet color range, but reduced hue levels, due to larger contributions to the 520 nm range [66] as shown for the treatment MOX with added tannin.

The oxygen consumption rate was clearly related to the level of released ellagitannins. Therefore, oak chips should be chosen considering their potential to release ellagitannins, not only because they can have a direct impact on the flavor and body of the wine, but also as they can protect against oxidation. Moreover, the origin and size of the oak chips seem to influence results when their addition is combined with MOX technique. The effect of American, French and Spanish oak chips or staves on in combination with MOX during red wine aging was researched; wine treated with staves (larger pieces of wood) and also aged with French oak products consumed more oxygen [67]. Finally, grape variety and especially MOX had more influence on phenolic composition and wine color than the type of oak chips which did not modify the chromatic characteristics of the red wines [68].

### 3.4 Secondary compounds found in oak wood

Various isoprenoid compounds and derivatives have been isolated and described in oak wood. Among them terpenes are compounds with a very low perception threshold and remarkable olfactory pleasantness; however their contribution of wood to wine is rather limited [69]. On the contrary, the presence of carotenoids is an important factor to consider for barrel production. The content of carotenoids in oak wood is found to be generally low and considerably variable between samples, depending mainly on the color of the piece of wood. Pinkish woods are mostly considered for barrel making being significantly richer in carotenoids than other colored woods. In particular, the molecules responsible for the pinkish hue of woods are found to be principally β-carotene and lutein [70]. Carotenoid compounds are highly sensitive to oxygen, light and temperature.

Pyrolysis/Gas Chromatography/Mass Spectrometry (PY/GC/MS) used on samples of French oak, to simulate the heating of barrels demonstrated that the thermal degradation products obtained after pyrolysis of β-carotene and lutein respectively were essentially norisoprenoids and sesquiterpenes [71]. During the natural seasoning the wood barrels are exposed to light and oxidation, then to heat during toasting and new aromatic compounds could be produced. With regard the norisoprenoids, over 30 different highly odorous compounds derived from the degradation of carotenoids, have been highlighted in oak wood, among which the main ones are 3-oxo-a-ionol, and dehydrovomifoliol [35]. American oak wood seems to be richer in norisoprenoids than that of European origin, while numerous compounds are common to both oak and grapes.

Finally, several pyrazines and pyridine derivatives have been detected in toasted oak wood [72]. Among them 2,5-disubstituted pyrazines seem to be responsible for rancid butter off-flavor [73]. Moreover 2-methoxy-3,5-dimethylpyrazine is linked
to “corky,” potato, green hazelnut, and dusty odor [74]. However this compound, synthesized by some proteobacteria, degrades at temperatures above 220° C, consequently the wood toasting reduces significantly its content.

Other extractable compounds present in smaller quantities in oak wood are amino acids, fatty acids and minerals.

4. Sensory profile of wines refined with alternative products

Several research studies have highlighted the effects of the application of wood fragments on the sensory profile of wines. Some findings on the topic are reported below.

Generally, the oak-chip treatment favors the polymerization of anthocyanins and tannins, leading to a reduction of monomers in wines. In a research involving two Italian red wines, Aglianico and Montepulciano, after 1 year of aging, the content of polymeric phenols in both red wines was about 40% higher in oak-treated samples compared with the control wines. This effect, however, strongly depends on grape variety and on the polyphenolic profile of each cultivar. The same oak chip-treated samples showed attenuation of floral and fruity descriptors and the introduction of oak notes (woody, vanilla, spicy notes, and black pepper), accompanied by a higher astringency. After 1 year of aging, the flavor complexity decreased, especially the spicy notes and astringency, which were even more reduced in the oak-treated samples than in the control wines [75].

The sensory profile of wine also depends on the phase of the winemaking process at which the oak chips are added, as well as on the oak chip dose. A study on the red wine Bobal [76] showed that the wines with oak wood chips added during alcoholic fermentation had a similar sensory profile to control wines with olfactory attributes of red fruits, liquorice, pepper, leather, tobacco, and cassis, but with some woody notes. On the other hand, wines with oak chips added during malolactic fermentation showed higher intensities for the oak descriptors than wines with the oak chips added when the malolactic fermentation had finished. The intensity of woody attributes was higher when the chips were added in higher doses (6 g/L).

Another experiment with white wines, Verdejo, showed the different effects of medium-toasted oak chips added during the alcoholic fermentation or aging stage [75]. With respect to the control (no chips were added), oak-treated wines showed a decrease of the descriptors fresh, green apple, fruity, tropical fruit, and citrus and higher intensities for “ripe fruit” and “sweet” and for new attributes like coconut, sweet spices, woody (oak), and toasty in the oak chip-treated wines. Specifically, the wines with oak chips added during the alcoholic fermentation presented a lower content of volatile oak-extractable compounds, thus intensity of wood-related sensory attributes, but higher concentrations of fermentative volatile substances than the new wines aged with oak chip. The toasting status of oak chips (toasted or not toasted) seemed to be more relevant than the origin of oak in a study carried out on Chardonnay wine [77]. The differences highlighted among wines with added oak chips of different origin, did not influence the preference of the panel. On the other hand, the level of toasting was more important than the origin of the oak chips (German or French) [78]. Finally, the quantity of oak chips can have greater impact than the origin of the oak [79]. The sensory profile of the white wines Listan blanco, indeed, was mainly influenced by the amount of oak chips, less by the geographical origin of the oak, which was more relevant only in the case of comparing oak chips and barrels.

Nevertheless, other research results have shown sensory differences attributed to the origin of the oak chips [31]. The wines (Romanian red wines Fetească neagră)
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aged in contact with American oak chips had a higher intensity of vanilla, toasty and cacao aromas compared with the wines aged using French oak chips, which had a higher intensity of smoky, licorice, and toasty aromas. The degree of toasting of the wood chips or staves also influenced aromas in the same Romanian red wine [44]. A woody attribute was more evident in wines aged with oak pieces with a low degree of toasting, whereas medium plus toasted wood increased the fruity aroma descriptors.

With the aim of simulating the effect of an oak barrel, the wood pieces can be added to wine in combination with micro-oxygenation [80]. This technique (oak chips or staves combined with micro-oxygenation) can produce wines with sensory characteristics very similar to those of products aged in new American and French oak barrels for 6 months [57].

5. Oak wood chips vs. barrel

5.1 Sensory differences and consumer preferences

As previously described, the quantity of oak chips, their dimensions and shape, their degree of toasting, contact time, and the stage of the winemaking process of their application can influence the sensory characteristics of the wine in numerous ways. Moreover, traditional refinement in wooden containers can lead to different results based on factors such as the time of contact, the use of new woods or used barrels, the period and frequency of an eventual batonnage, together with the possibility of using containers of different sizes. Therefore, the challenge to distinguish between wines obtained using barrel or chip-aged wines is particularly complicated due to the multiplicity of variables involved.

From a sensory point of view, wines refined with chips in steel containers are not clearly different from those long preserved in new barrels [81]. On the other hand, young wines made with chips are almost sensorially indistinguishable from those stored in new barrels for short periods (about 3 months); both are characterized by light boisé olfactory notes. Moreover, considering the effects of oak wood chip size, wood contact time (3, 6, and 9 months) and type of container (tank or used wood barrel) in wines analyzed after 6 months of bottling [82], some evident sensory differences were observed. The sensory effect of the addition of oak wood chips was more evident for the wines in tanks than for those in used barrels. Moreover, wines in used wood barrels with wood chips were not easily distinguishable from wines with no added wood chips. Considering wines treated with alternative products, the more appreciated were those aged in contact with cubes for 3 or 6 months. The authors suggested to use oak wood chips for short-aged wines and to reuse wood barrels still in good condition, pointing out that new wood barrels give wines of higher quality [82].

The sensory differences between wines aged in wood barrels or with oak wood fragments do not always reflect significant differences regarding consumer preference [83]. In a survey on consumer preferences, a large disparity of preferences was found among the participants that traditionally consume quality wines. A large proportion of respondents (55%) said that they would not buy wines produced using oak wood chips, whereas others declared that they would buy them only if, after tasting they had perceived the same quality as the wines in wood barrels. However, young people seemed to be less traditional and more open to buy a wine produced using oak wood fragments. Another online survey [84] involving Australian wine consumers reached similar conclusions.

Finally, the use of oak wood fragments could be an interesting alternative to barrels in emerging wine countries, such as Mexico [85] or Brazil [86], due to their
lower costs. Nevertheless, before using oak wood in winemaking, local producers should investigate the preferences of their potential consumers.

5.2 Main analytical techniques that can be used for the discrimination and evaluation of product quality

The challenge of explaining the sensory differences described previously from a chemical point of view, is not easy. Considerable works have addressed the chemical characterization of wines aged with alternative products. However, only some of these studies have directly compared the composition of a barrel-aged wine and that of a wine in contact with wood oak fragments [45, 87–91]. Nevertheless, it is equally clear that, because of the need of control for consumer protection and quality assessment, it is essential to develop methods of investigation that allow distinguishing wines arising from barrel aging from those that used alternative woods. To our knowledge, the main techniques that have been used so far for this purpose are: (i) methods examining differences in phenolic composition (based on High Performance Liquid Chromatography (HPLC) or on classical phenolics determination) and color analyses; (ii) chromatographic techniques investigating.

5.2.1 Discrimination methods based on phenolics and color profiles

A primary work in 2004 analyzed changes in phenolic compounds, phenolic acids, aldehydes, and the color of wine aged for 5 months in order to determine the influence of the type of aging and oak wood origin used for storage. A discriminant analysis was performed with the aging system as the discriminant factor, using over 66 samples. Wines aged in wood barrels differed considerably in their characteristics with respect to wines aged with wood chips. Based on the obtained model, 94 and 83% of the samples aged in barrel and chips, respectively, were correctly assigned [88]. A further, comprehensive study was carried out to discriminate wine aged in wood barrels from those aged with alternative products, both during the wood contact period and bottling stage [89]. During the first 6 months of aging, wines treated with wood staves obtained characteristics that were halfway between wines with chips and those aged in wood barrels [89]. However, as the wood contact period increased so did the differences between wines stored in traditional and alternative systems (staves or chips): after a 2-year bottling period, the wines from the three systems became unique enough to tell them apart. Discriminant analysis revealed the most meaningful variables: the yellow color component, anthocyanins (cyanidin-3-glucoside, vitisin A and sum of p-coumaryl derivates), vanillic acid, protocatechuic aldehyde, and epicatechin.

The factorial analysis performed during the investigation of both phenolic and sensory profile of red wines aged in wood barrels (French and American) and wines aged with oak wood chips, [81] highlighted several differences; wines aged with wood chips showed characteristics closer to the wines aged in wood barrels for 3 months. Moreover, total and polymeric anthocyanins, together with acetylated and glucoside anthocyanins and pigments from the direct condensation
of anthocyanin flavonol, seem to be the main variables able to differentiate wines [81]. Authors also pointed out the strong effect of grape variety on the discriminant variables associated with “alternative” or “traditional” wines.

A recent study [91], aimed to characterize the flavonoid and non-flavonoid phenolic composition of wines in contact with wood barrels, chips and staves during a 12-month aging period has hypothesized that the effect of wood on the phenolic composition was mostly associated with the original and intrinsic characteristics of each grape variety. Therefore, this work concluded that the extraction of phenolic compounds from oak wood during wine aging is closely related to the wood format, to grape variety and aging time. Consistent with papers previously presented, the study confirmed that the final effect of wood on wine is not related only to the transference of polyphenols from wood, but also to structural modifications of grape polyphenols.

5.2.2 Discrimination methods based on volatile compounds

As a matter of fact, GC-MS is successfully used for the characterization and quantitative determination of volatile and semi-volatile compounds directly issued from oak wood [92, 93].

Among the many research studies using GC-MS in order to distinguish wines aged with alternative products or barrels, the work presented by Triacca et al. [94] stands out for the number of samples analyzed. A database made up of 352 new barrel wines, 665 used barrel wines and 600 chip wines, was created in order to verify compliance with laws and regulations prohibiting the use of chips in Switzerland. Wood-related volatiles (xylovolatiles) were elaborated using chemometrics techniques (logistic regression analysis). The authors were able to assign new unknown samples, with good certainty, to the chips or barrel group [94].

A research study carried out in 2008 [95] reported the influence on aroma compounds of adding oak wood chips either in stainless steel tanks or in used barrels, comparing these wines with those aged in new barrels. Both the size of the oak chips and the contact time were considered. To separate the samples according to wood format, three discriminant functions were obtained (81.5% correct classification). Wines in new wood barrels were separated from wines with wood chips, and lactones and 5-methylfurfural were the variables with the highest discriminant power. In a recent comprehensive study [90], 75 volatile compounds were determined by applying GC-MS and flame ionization detection (GC-FID) to a wide set of wines with differing aging processes. The authors found that compounds directly related to wood have greater discriminative power for separating wines aged in barrels from those macerated with oak fragments, but no single compound permits flawless classification. Therefore, they studied the overall effect of the addition of oak fragments on a set of 231 samples and compared them to those same wines aged in oak barrels. Thus, they developed a set of criteria that enables distinguishing, with a high degree of accuracy. The application of these criteria allowed the correct classification in over 90% of cases. It was found that out of the 75 analyzed compounds, those which best enable discrimination are the following: oak lactone isomers, vanillin, acetovanillone, syringaldehyde, furfural, furfuryl alcohol, 5-methylfurfural, 5-hydroxymethylfurfural, eugenol, methyl vanillate, and ethyl vanillate. Vanillin, acetovanillone, and syringaldehyde are the compounds that were present in higher concentrations in wines fermented or macerated with wood fragments than in wines aged in barrels. Eugenol (significantly higher) and oak lactone isomers are the compounds that explain the variance in wines aged in barrels. The authors also point out that the extraction of wood-derived compounds is affected by many factors such as the age of the barrel, the application during
fermentation or maceration and the dose. Nevertheless, the vanillin + acetovanil-
lone/eugenol ratio was an essential marker for discrimination.

A more recent study [96] focused on the characterization of xylovolatile
aromatic compounds using GC-MS of wines aged in barrels and those produced
using oak chips. Approximately 200 Italian wines aged using oak chips or wood
barrels were analyzed and 60 xylovolatile compounds were identified. Wines aged
in barrels had a higher concentration of ethylvanillate, 4-ethylphenols, eugenol
and whiskey-lactones than wines aged with chips, which were characterized by a
generally higher concentration of furanic compounds and hydroxybenzaldehyde
derivatives. The presence of 4-ethylphenols at higher concentrations in barrel-aged
wines indicated that there is still, in general, a higher risk of contamination from
Brettanomyces bruxellensis compared with chip refinement. Overall, promising
perspectives arose from applying DA (discriminant analysis) to classify wines
depending on the aging method (barrels vs. chips) with >96.5% success.

On the other hand, other work has demonstrated that discrimination based
on VOCs is not always easy and generalized patterns are hard to establish [97].
The analytical profile of the wood-related volatiles would be expected to exhibit
large variations, precluding the detection of a generalized pattern in several cases.
Moreover, the aging of red and white wines would certainly follow quite different
evolution routes, in terms of the enrichment in wood-related volatiles.

An innovative approach recently proposed in some papers [32, 45] couples VOC
analyses with other analytic techniques to overcome the problems described above.
Indeed, most previous studies investigating the influence of the type and length of
the aging process have dealt with a particular subgroup of compounds (volatile or
phenolic), which has recently been considered to be a limiting condition to obtain
a more comprehensive view of the subject [45]. Therefore, a study carried out in
2008 on Spanish wines [45] followed the evolution of both aromatic and phenolic
composition of wine during the contact time with oak wood: chips and staves, with
and without micro-oxygenation. These aging procedures were compared with the
traditional oak barrel aging method. Two canonical discriminant analyses were
carried out to classify the different treatments based on the volatile compounds
from oak wood and low-molecular weight phenols. A good separation was achieved
between the three treatments (chips, staves and barrels) for both groups of comp-
ounds. In the case of VOCs, 100% of cases were correctly classified. Wines aged in
barrels were correlated with a high concentration of 5-hydroxymethylfurfural and
5-methylfurfural; wines in contact with staves were correlated with a high content
of vanillin and trans-isoeugenol. As for low-molecular weight polyphenols, 100%
of the cases were also correctly classified. The variables with the highest discrimi-
nant power were syringic acid and quercetin (related to staves) and caftaric acid
(associated with barrels). On the other hand, the discriminant function 2 correlates
caffaric acid with the wines aged in barrels and with fragments and gallic acid with
the wines treated with chips.

The main aim of another research was to evaluate the same wine after 10 years
in bottles when aged in barrels and when treated with alternative products and oxy-
gen, by means of volatile compound quantitation and color analyses [32]. Overall,
the traditionally aged wines suffered a smaller decrease in color intensity, hue,
significance of reds and blues, followed by wines treated with staves + MOX and
chips + MOX. Furthermore, the highest concentration of cis-oak lactone was found
in wines aged in barrels. While, generally, oak-related compounds were found at
lower concentrations in barrel-wines than in alternative-products wines, except for
eugenol.

It is worth noting that the GC-MS technique and VOCs analyses have been used
in several studies on wood alternatives, although without direct comparison with
barrel aging, investigating various technological implications: the impact of time of the addition of chips during winemaking [98, 99]; the effect of wood toasting degree and contact time with oak fragments [31, 44]; and the geographical origin of oak wood from which alternative products are issued [77, 100].

5.2.3 Discrimination based on spectroscopy methods

In the last decade, vibrational spectroscopy, namely infrared-based techniques (IR), supported by chemometric methods, was found to be a powerful technique because of its widespread use in analytical laboratories, its versatility and low economic impact. Moreover, IR technology requires minimal sample processing prior to analysis [5].

Certainly, IR spectroscopy coupled with multivariate data analysis has been used for the determination of oak volatile compounds [101–103] and for classifying barrels [104]. Subsequently, in recent years, this method has been proposed for discriminating wines aged in different types of wood containers and for different time periods [96, 105, 106], taking advantage on PLS-based calibration between GC-MS and near infrared spectroscopy (NIR).

The first publication appeared in 2012 [107], which investigated two different levels of information on fusion of NIR spectra and midinfrared (MIR) spectra from red wines aged in different ways. A total of 96 red wines, including wines aged in oak barrels, wines aged in stainless steel tanks with oak chips and without, were analyzed. Discriminant models of the three different aged wines were established, and the FDA method was applied to build the classification models of three different aged wines using the NIR, MIR and the merged spectra, reaching up to 98% correct classification with the latter. The results suggest that the spectral fusion of NIR and MIR is a promising technology for discriminating different aged wines.

A recent paper aimed to identify if spectroscopic techniques allow discriminating wines aged with alternative oak products (chips and staves) from different oak woods (American, French and Spanish) and floating micro-oxygenation (20 μg/L), compared with those aged in barrels, after 10 years of bottling [108]. The spectral information and analysis were performed in an FTIR-ATR (Fourier-transform IR-Attenuated Total Reflection). The results indicated that with this technique it is possible to clearly separate the wines aged by the three systems (chips, staves, and barrels) in the case of American oak. In the case of French oak, wines aged with chips were clearly differentiated for wines from a single grape variety and with similar oenological features.

The most recent paper on this topic [96] analyzed approximately 90 red wines issued from the same wine appellation in Italy, including commercial barrel-aged wines and wines aged using different types of commercial oak chips. Wines were analyzed in transmittance using NIR. In order to test if combined explanatory variables made it possible to discriminate treatments, an orthogonal partial least squares discriminant analysis (OPLS-DA) was carried out. Several factors were considered, including the aging process, the type of oak used for aging (wood barriques, big barrels or chips) and the wine typologies (differing for some oenological parameters). OPLS-DA application reached >96.5% success in classifying wines depending on the aging process (no wood, barrel/barrique and chips) in the internal validation check and > 90% in an external test. Certainly, further studies are needed to validate the potential of the technique in order to improve it for wine authentication, enlarging both the array of wine types (e.g., testing different appellations and grape varieties), and the range of oak alternatives (staves, cubes, blocks, and other sizes of product) to be tested, possibly in the presence of micro-oxygenation.

It is worth noting that IR spectroscopy has been used in other studies on wine aging, although without direct comparison between wood alternatives and barrel
aging. For instance, FT-IR and UV-visible (UV-Vis) spectroscopic techniques combined with multivariate analysis were used to obtain regression models to study the aging level of high-quality Sherry wines [106]. Moreover, [105] wines aged in barrels made from different wood species and in stainless steel tanks, were analyzed. A complete differentiation of the samples was achieved according to grape variety, the container type and the aging time based on two spectral regions of their FT-IR spectra. The overall significance of these studies is still provisional because of the restricted data sets and the inhomogeneity of spectral ranges analyzed in the different papers. However, the results show the potential of IR spectroscopy and chemometric analysis for discriminating wines issued from different aging processes. In this regard, identifying discriminating algorithms and creating robust databases is a necessary condition to obtain a method that can be used routinely in a laboratory for quickly acquiring specific information about the type of wood used for wine aging.

Finally, nuclear magnetic resonance (NMR) is a powerful tool for analysis, quality control and authentication of wines. The main advantage of non-targeted wine analysis by $^1$H NMR spectroscopy is the ability to collect, relatively simply and fastly, a huge amount of compositional information relating to a single sample [109]. Unlike other analytical techniques, however, it requires complex instrumentation and specialized personnel to be realized, but thanks to its versatility and reproducibility, this analytical technique seems to be very promising for the purposes described in this chapter.

6. Conclusions

In modern winemaking, oak products alternative to barrels are useful and flexible tools for wineries, enabling them to meet the needs of an increasingly wide and varied market. The compounds from oak wood impart a typical aromatic profile to wine and contribute to the increased polyphenolic patrimony of the final wine. Recently, the use of wood fragments has expanded, and new formats of alternative products have been added to those already known, significantly improving wine quality and dramatically increasing the opportunities of choice. Major advantages associated with the use of these products concern the reduction of both costs and production times. Furthermore, it enables the possibility of obtaining standardized wines whose compositional and sensory characteristics are very close to those defined in the phase of product design; in addition, the reduction of microbiological risks associated with the use of barrels is not negligible. Among the factors that most influence the sensory quality of the final wine, the dose of oak chips, the level of toasting and the moment of application must be considered. The different geographical and botanical origin of the chips seems to secondarily affect the result.

From a sensory point of view, it is not easy to distinguish products obtained by aging with chips from those obtained traditionally. Considering the consumer preference between oak chips and barrel wines, the variability among tasters is very high depending on the age and experience (e.g., young tasters and experienced tasters) and winemakers could take in consideration the specific preferences of different consumer groups. The distinction of the two different products is therefore mainly possible through laboratory investigation techniques: analytical methods allow expanding the compositional differences between the two products both for commercial purposes, but also for the control of fraudulent activities if necessary. Among the analytical techniques used, the spectroscopic ones are certainly those that, combined with multivariate statistics techniques, allow to obtain the best results in this field.
The possibility of refining wines with chips, staves or other alternative products, does not therefore oppose the use of barrels, but represents an additional option and a further opportunity for winemakers to obtain high-quality products. The two types of wines can today coexist in the wine global market, appreciated by different segments of consumers.
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