

## Oak Barrel Aging of Red Wines

Traditionally, great red wines are aged in oak barrels from the end of fermentation until bottling. The first motivation in choosing barrels was probably that they were easy for one man to handle and could also be used for shipping. It was not until some time later that their positive effect on wine development, in terms of color, clarity and flavor, came to be appreciated. However, the use of barrels involved a major financial commitment and entailed risks of microbial contamination, as well as the likelihood of communicating organoleptic faults to wine. For these reasons, the practice of aging even high-quality red wines in inert vats became widespread in the 1950's. At that time, the elimination of old barrels, responsible for moldy off-flavors, certainly resulted in improved quality. The red wines were perhaps less complex, but cleaner and fruitier.

Over the past few years, a more favorable economic climate has fostered a new interest in barrel aging. There is greater awareness of the role played by oak in wine development, and a concern to adapt barrel aging to the quality of each wine. Perfect control of the various parameters and techniques has made it possible to fine-tune the use of wood and its influence on wine quality. Firstly, clarity is easier to obtain when wine is aged in the barrel rather than in the vat, due to the smaller volume. Clarification is also facilitated by the adsorption phenomena that occur in oak. Furthermore, wine in the barrel is more sensitive to outside temperature, so the precipitation of salts, particles and colloidal coloring matter is much more likely to be triggered by winter cold.

Stabilization reactions affecting color, clarity and colloids, as well as modifications in the phenol structures (softening of the tannins), also occur in wine during aging, while aromas develop. Barrel aging promotes these reactions to a much greater extent than large airtight vats, which, being theoretically inert, are considered not to interact with the wine.

The phenol composition of wine is considerably modified by barrel aging, thanks to controlled oxidation. Color is intensified due to reactions between tannins and anthocyanins, as well as others involving ethanal. The free anthocyanin concentration decreases and the tannin structure evolves, as does its reactivity to gelatin. After ten months of barrel aging, wines have better color than those aged in the vat and this color remains more stable during bottle aging. The flavor is also more attractive, characterized by softer tannins.

Wine also acquires aromatic complexity as a result of the odoriferous substances extracted from wood. The oaky aroma must be carefully modulated, to ensure that it blends harmoniously with the wine's overall structure. Even though producers may wish to give their wines an oak character, this must not be overdone. It should never overpower the wine's intrinsic qualities. The barrels contribution to aroma and flavor may be adjusted by modifying the proportion of wine aged in oak, especially new barrels. Other important factors are the type of oak and the way the barrels are made (degree of toasting), as well as the duration of barrel aging.

Three factors related to this type of aging are responsible for the wine's development: oxidation-reduction reactions, as well as volatile and non-volatile compounds dissolved from the oak.

### Oxidation-Reduction

Oxygen in red wines may have various origins. Handling operations, treatments and regular winemaking tasks represent a major proportion (up to 50%), while barrel aging accounts for the remainder. The amount of oxygen absorbed by the wine depends on the origin of the barrels, as well as the type and position of the bung.

It is thought that oxygen passes through the wood (16%), mainly via gaps between staves (63%). Smaller amounts (21%) are admitted through the bunghole. The position of the bung affects the penetration of oxygen into the wine. Wooden bungs positioned on the side of the barrel and tight silicon bungs produce a vacuum effect on the order of 120 mbar, which increases the quantity of oxygen dissolved in the wine.

It is, however, difficult to determine the precise quantity of oxygen that penetrates into the wine, as measurements, even in model solutions, do not take into account the amounts consumed by ellagitannins in the oak. Dissolved oxygen constantly disappears by oxidizing various components in the wine. Quantities may vary by 100% (from 100 to 200 mg/L), depending on whether the wine is aged in the vat or in the barrel.

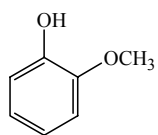
The oxidative phenomena involved in barrel aging are not exclusively due to increases in the wine's oxygen content.

Ellagitannins from the oak are dissolved in wine (castalagin, vescalagin, see Plant Phenolic Metabolism) and concentrations may reach 200 mg/l. They decrease regularly, due to oxidative phenomena catalyzed by these same substances. Even in the absence of oxygen, ellagic tannins are capable of modifying the tannin structure of a wine, as well as combining with anthocyanins and, consequently, stabilizing color.

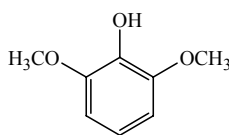
### Non-Volatile Compounds Extracted from Oak Barrels

In addition to ellagitannins, the oak releases a certain number of other compounds, mainly lignins with a high guaiacyl (ferulate → coniferyl alcohol → guaiacol) and syringyl (sinapate → sinapyl alcohol → syringol) content. Coumarins are also present in oak. The concentration in wine depends on the type of wood and the way it is seasoned. These compounds may be dissolved in wine as the glycoside (scopoline, esculin) or the aglycone (scopoletin, esculetin). See Plant Phenolic

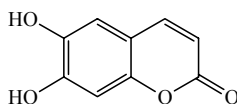
Metabolism. Phenolic acids are also extracted from oak and they are probably produced by the transformation of ellagitannins and possibly lignin. Gallic acid, at a concentration of about 50 mg/L is the major one.



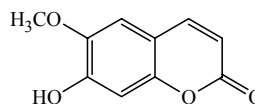
guaiacol



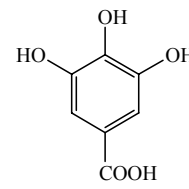
syringol



esculetin



scopoletin



gallic acid

In terms of flavor, studies investigating the organoleptic characteristics of these components produced the following findings:

1. Phenol acids (gallic acid) have an acid taste.
2. Coumarins (aglycones) seem acid and have a harsh character. Their glycosides are very bitter.
3. Ellagitannins (from oak) are astringent as compared to gallotannins (from grapes), which give a bitter, acidic impression.

### Volatile Compounds

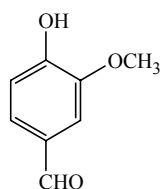
Untreated oak contains a certain number of volatile substances with specific odors.

Eugenol, with its characteristic odor reminiscent of cloves, is the main volatile phenol. Other volatile phenols are present in relatively insignificant quantities.

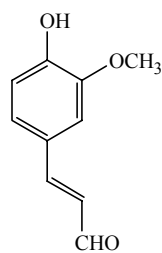
Phenol aldehydes are present in relatively small quantities. Vanillin and syringaldehyde have been identified, as well as coniferaldehyde and sinapaldehyde. Vanillin plays an active part in the oak and vanilla odors that barrels communicate to wine.

$\beta$ -methyl- $\gamma$ -octalactone, also known as oak lactone or whiskey lactone has two chiral centers and consequently four stereoisomers. The *cis* (-) isomer has an earthy, rather herbaceous character with hints of coconut, and is 4-5 times more odoriferous than the *trans* (+) isomer. The latter not only smells of coconut, but is also very spicy. Above a certain concentration, excessive amounts of this lactone may have a negative effect on wine aroma, giving it a strong woody or even resinous odor.

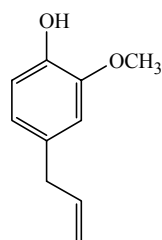
Concentrations of *trans*-non-2-enal vary a great deal from one oak sample to another. Together with *trans*-oct-2-enal and decanal, this molecule is responsible for the odor known as plank smell that wines may acquire during barrel aging. This unpleasant smell is attributed to unseasoned wood and may be attenuated by toasting the inside of the barrels more intensely.



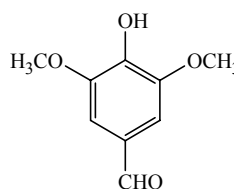
vanillin



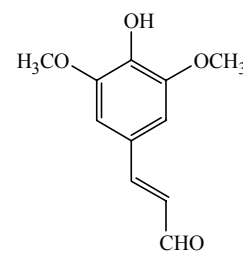
coniferaldehyde



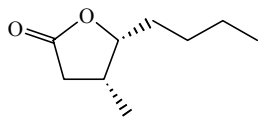
eugenol



syringaldehyde

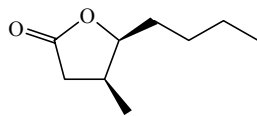


sinapaldehyde



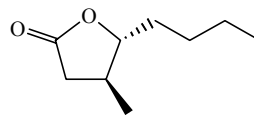
*cis* (+)  
(3R,4R)

sweet, woody, fresh, coconut



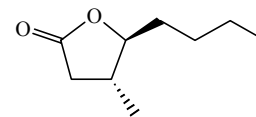
*cis* (-)  
(3S,4S)

earthy, herbaceous, coconut, dry



*trans* (+)  
(3S,4R)

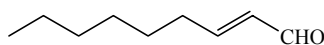
spicy, coconut, green walnut



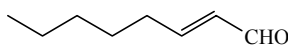
*trans* (-)  
(3R,4S)

strong coconut, leather, woody

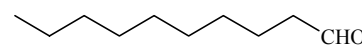
$\beta$ -methyl- $\gamma$ -octalactone or oak lactone



*trans*-non-2-enal



*trans*-oct-2-enal



decanal

## EFFECT OF THE TYPE OF BARREL ON THE DEVELOPMENT OF RED WINE

Phenomena affecting oxidation and aromas that occur in wine during barrel aging depend on many parameters, such as the type of barrels and the way they are made.

### Origins of the Wood

In France, wood for cooperage comes primarily from forests located in four main regions (Limousin, Centre, Bourgogne (Burgundy) and Vosges). Two species are unevenly distributed in these regions:

1. Pedunculate oaks (*Quercus robur* or *Quercus pedunculata*) grow most widely in the Limousin. They are also present in Bourgogne, as well as the south of France. They have a high relatively low concentration of methyloctalactone.
2. Sessile or durmast oaks (*Quercus petraea* or *Quercus sessilis*) are prevalent in the Centre and Vosges regions. They have high levels of extractable ellagitannins. Remember the types of tannins; hydrolysable tannins (gallotannin & ellagitannins) and condensed tannins (catechic tannins).

In the USA, the dominant species is American white oak (*Quercus alba*). This species has a high concentration of aromatic substances, especially methyloctalactone, which strongly affect the flavor of wine during aging.

Another characteristic of American white oak is that staves may be sawed thanks to the natural blocking of longitudinal vessels which prevents leaks. French oak, however, must be split along the grain, split again into the staves used to make barrels. This technique is more complex than sawing and results in considerable wastage. This is, however, the only way to avoid leaks due to vessels running through the width of the staves.

Table 1 examines the concentrations of the extractives from the three types of oak wood. Note that oak wood is high in hydrolysable tannins (ellagitannins).

**Table 1: Compounds Extracted from the Three Types of Oak by Dilute Alcohol**

|                                       | Sessile oak | Pedunculate oak | American white oak |
|---------------------------------------|-------------|-----------------|--------------------|
| methyloctalactone ( $\mu\text{g/g}$ ) | 77          | 16              | 158                |
| eugenol ( $\mu\text{g/g}$ )           | 8           | 2               | 4                  |
| vanillin ( $\mu\text{g/g}$ )          | 8           | 6               | 11                 |
| ellagitannins ( $\mu\text{g/g}$ )     | 8000        | 15000           | 6000               |
| catechic tannins ( $\mu\text{g/g}$ )  | 300         | 600             | 450                |

### Influence of Seasoning Conditions

The oak's humidity level should be in equilibrium with that of the surrounding atmosphere, on the order of 14-18% in temperate regions, to ensure the barrels' mechanical strength.

Natural seasoning is an operation that takes several years, generally 24 months for 21 mm staves and 36 months for 28 mm staves. This length of time is necessary to obtain wood that is properly suited to the aging and improvement of wine. Seasoning takes place in the open air, in large, level spaces. It has been estimated that oak seasons at a rate of about 10 mm per year. In fact, intense dehydration takes place during the first 10 months. This is followed by a period when the wood actually matures, thus improving its physical, aromatic and organoleptic qualities. Seasoning is, however, heterogeneous, depending on the position of the wood in the pile. The outside of the pile is most intensively washed out, while the center is hardly touched by rain, or even sprinkling, and always has a lower humidity level. Enzymic reactions are also involved, caused by enzymes secreted by the fungal microflora that develop on the wood.

The following observations have been made of phenol composition during natural seasoning:

1. An alcoholic extract of the oak becomes less astringent and lighter-colored as the wood seasons. The quantities of ellagitannins extracted decrease. The reduction in ellagitannins is due to chemical and enzymic hydrolysis as well as oxidation of any ellagic acid that may be released.
2. Bitter-tasting glycosylated coumarins (esculin and scopoline) are hydrolyzed to form aglycones (esculetin and scopoletin) with relatively neutral or slightly acid flavors with a loss of bitterness and harshness generally observed during the seasoning and aging of wood.

Natural seasoning leads to an increase in the concentrations of various aromatic compounds: eugenol, syringic and vanillic aldehydes produced by the breakdown of lignin, as well as both isomers of  $\beta$ -methyl- $\gamma$ -octalactone, with a higher proportion of the more odoriferous *cis* form.

Artificial seasoning consists of keeping split oak in a ventilated drying oven at 40-60°C for approximately 1 month. This technique considerably reduces seasoning time, without altering the oak's physical properties. It also eliminates the financial investment tied up in a wood seasoning lot. However, green wood must be seasoned gradually, to avoid shrinkage cracks. This entails alternating seasoning times of varying lengths with stabilization periods in a dry, ventilated place. Nevertheless, this type of seasoning has certain effects on the development of the compounds in the oak. In particular, most of the reactions described in the preceding paragraphs do not occur under these conditions. Compared to naturally seasoned wood, oven-dried wood has a higher content of astringent tannins and bitter coumarins. It contains less eugenol, vanillin and methyloctalactone.

### **Barrel Toasting**

Once the stave wood is considered to be dry and seasoned, a cooper makes it into staves that are assembled (in groups of 18-25) with metal hoops to form barrels. The oak is then subjected to heating and toasting, both fundamental stages in barrel manufacture. The two stages can be summarized as follows:

1. Heating facilitates the bending of the staves to produce the characteristic barrel shape. It affects the plasticity of the lignin, but has little impact on the glucide polymers (cellulose and hemicellulose), as these compounds are protected by the humidity they absorb. The combination of heat and humidity makes it possible to bend barrels into shape without breaking the staves. Barrels, usually open at both ends, are heated for 20-30 minutes, with regular increases in temperature, while the staves are gradually bent into shape. At the end of the operation, the inside temperature of the barrel is approximately 200°C, while it is only 50°C on the outside.
2. The second operation, toasting, gives the barrel its final shape, while at the same time modifying the oak's structure and composition.

Barrel quality depends on successful toasting. This has a major impact on the later development of the wine during aging, as well as the organoleptic characteristics it acquires. However, toasting conditions vary a great deal from one cooperage to another, and even within the same cooperage. The human element, performed by true craftsmen, makes it impossible to control all the parameters in this operation. Factors include: the type and intensity of the heat source (wood, gas or electricity), whether the top of the barrel is open or closed, heating homogeneity and final temperature, as well as duration (risk of the wood charring and blistering), how often the wood is moistened and to what extent it changes color.

All of these toasting operations affect the surface and internal structure of the oak. There are three levels of toasting:

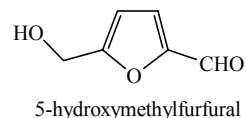
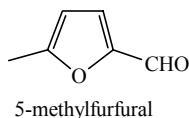
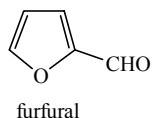
1. Light toast indicates a toasting time of approximately 5 minutes, with a surface temperature between 120 and 180°C. The inside of the barrel has a spongy appearance, due to modification of the lignins and hemicelluloses, while the cellulose structure remains intact.
2. Medium toast corresponds to a toasting time of approximately 10 minutes, producing a surface temperature of approximately 200°C. The parietal surface components disappear by fusion.
3. Heavy toast corresponds to a toasting time of more than 15 minutes, resulting in a surface temperature of approximately 230°C. The cell structure is considerably disorganized, while the surface is blistered and covered with tiny cracks.

The physical changes are accompanied by modifications in the oak's chemical composition. The parietal polymers (cellulose, hemicellulose and lignin) have different fusion points and give rise to a wide variety of decomposition products. Analysis of toasted oak extracts shows a break-down of the ellagitannins, especially after medium toasting.

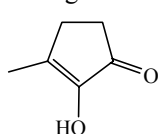
Heating oak also leads to the formation of volatile compounds that may have several origins. Firstly, thermal degradation of polysaccharides produces furanic aldehydes from carbohydrate polymers (mainly hemicelluloses). The resulting compounds include: furfural, 5-methyl-furfural (toasted almond aromas) and hydroxymethyl furfural (odorless). Table 2 shows the concentrations (mg/L) of the furanic aldehydes extracted by an alcoholic solution from oak. However, these furanic aldehydes are present in wine at concentrations well below their olfactory perception thresholds, so they have little impact on the aroma.

**Table 2: Impact of Toasting Intensity on the Formation of Furanic aldehydes**

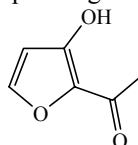
| Compounds (mg/L)        | Toasting Intensity |       |        |       |
|-------------------------|--------------------|-------|--------|-------|
|                         | None               | Light | Medium | Heavy |
| furfural                | 0.3                | 5.2   | 13.6   | 12.8  |
| 5-methylfurfural        | 0                  | 0.6   | 1.3    | 1.5   |
| 5-hydroxymethylfurfural | 0                  | 3.6   | 6.9    | 4.8   |



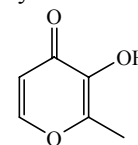
Heating also produces compounds with a caramel-toasty character (cyclohexene, maltol and isomaltol) derived from hexoses in the presence of nitrogenated substances. Their olfactory impact is greater than that of furanic aldehydes.



2-hydroxy-3-methyl-cyclopent-2-enone



isomaltol

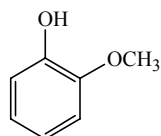


maltol

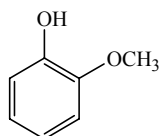
Thermal degradation of lignin and polyols produces volatile phenols and phenol aldehydes. Volatile phenols have smoky, spicy odors. Both monomethoxyylated (guaiacyl series) and dimethoxyylated (syringyl series) derivatives are also present (Table 3). The concentration of syringyl derivatives increases with heating intensity.

**Table 3: Impact of Toasting Intensity on the Formation of Volatile Phenols**

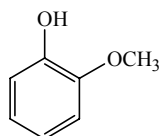
| Compounds ( $\mu\text{g/L}$ ) | Toasting Intensity |       |        |       |
|-------------------------------|--------------------|-------|--------|-------|
|                               | None               | Light | Medium | Heavy |
| guaiacol                      | 1                  | 5.2   | 27.7   | 30.3  |
| 4-methylguaiacol              | 2                  | 10    | 38.7   | 24.7  |
| 4-ethylguaiacol               | 0                  | 0     | 0      | 7.7   |
| 4-propylguaiacol              | 0                  | 0     | 0      | 6.3   |
| eugenol                       | 20                 | 17.7  | 71.7   | 44.3  |
| phenol                        | 5                  | 12    | 11.7   | 20    |
| o-cresol                      | 0                  | 0     | 0      | 1.7   |
| m-cresol                      | 0                  | 0     | 0      | 1.3   |
| p-cresol                      | 0                  | 0     | 0      | 2     |
| syringol                      | 0                  | 78.3  | 310.7  | 313.3 |
| 4-methylsyringol              | 0                  | 17.3  | 80.7   | 193.3 |
| 4-allylsyringol               | 0                  | 60.3  | 298.7  | 204.3 |



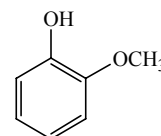
guaiacol



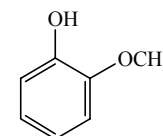
4-methylguaiacol



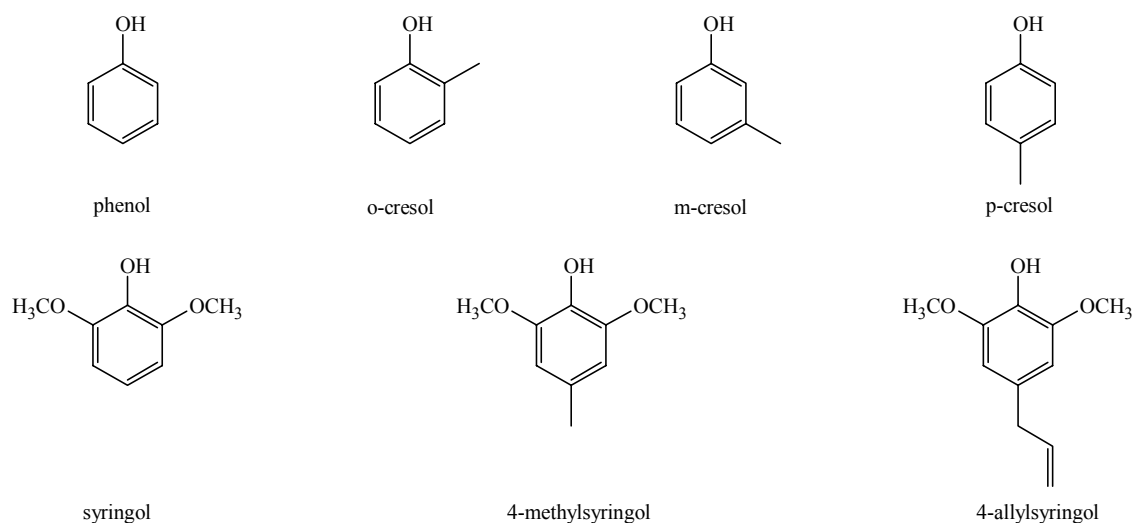
4-ethylguaiacol



4-propylguaiacol



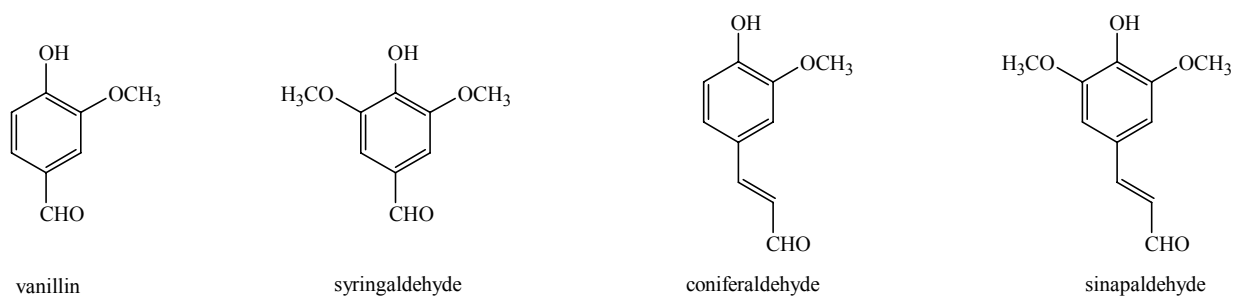
eugenol



The phenol aldehydes present after oak has been toasted (Table 4) include: the guaiacyl series (vanillin and coniferaldehyde) and the syringyl series (syringaldehyde and sinapaldehyde) aldehydes. Maximum quantities are formed when the oak is medium toasted.

**Table 4: Impact of Toasting Intensity on the Formation of Phenol Aldehydes**

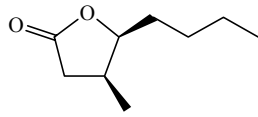
| Compounds (mg/L) | Toasting Intensity |       |        |       |
|------------------|--------------------|-------|--------|-------|
|                  | None               | Light | Medium | Heavy |
| vanillin         | <0.1               | 2.1   | 4.8    | 3.1   |
| syringaldehyde   | 0.2                | 5.6   | 12.9   | 12.2  |
| coniferaldehyde  | trace              | 3.1   | 6.2    | 2.1   |
| sinapaldehyde    | trace              | 1.9   | 4.9    | 2.6   |



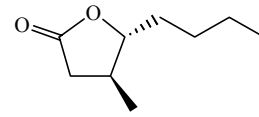
Toasting barrels also causes the thermal degradation of certain lipids or fatty acids, forming isomers of methyl-octalactone. This reaction increases in proportion to heating intensity (Table 5). The more odoriferous *cis* isomer, which already predominates in non-toasted wood, represents an even higher proportion of the isomers in toasted oak.

**Table 5: Impact of Toasting Intensity on the Formation of  $\beta$ -Methyl- $\gamma$ -octalactone Isomers**

| Compounds (mg/L)                       | Toasting Intensity |       |        |       |
|--|--------------------|-------|--------|-------|
|  | None               | Light | Medium | Heavy |
| <i>trans</i> -methyl-octalactone       | 0.16               | 0.11  | 0.11   | 0.14  |
| <i>cis</i> -methyl-octalactone         | 0.64               | 0.57  | 1.38   | 1.59  |
| <i>(cis+trans)</i> -methyl-octalactone | 0.8                | 0.68  | 1.49   | 1.73  |
| Ratio of <i>cis/trans</i>              | 4                  | 5.3   | 12.7   | 11.2  |



*cis*- $\beta$ -methyl- $\gamma$ -octalactone



*trans*- $\beta$ -methyl- $\gamma$ -octalactone

### Adapting the Type of Oak to Different Wines

Another problem raised by aging wines in oak is that of choosing the right barrels to suit the type of wine. Barrel aging must enable wines to develop their full character, yet remain in balance. If the oak/wine match is not perfect, there is a risk of acquiring a dominant woody character that overpowers the wine and dries it out rapidly.

The following list of criteria for selecting barrels is based on the preceding data, taking into account the variable characteristics of wines and barrels:

1. Naturally seasoned oak is generally better for red wines than artificially seasoned wood.
2. Fine-grained oak releases smaller amounts of phenols than coarser-grained oak. This slow, regular release may continue for several years.
3. Toasting eliminates green wood and plank faults, while producing very pleasant vanilla and spicy aromas. Heavy toasting gives a marked burnt, toasty character, making the aroma different, but without any major faults.
4. If a wine has a rich tannic structure, but is lacking in body and roundness, lower density wood (e.g. Vosges and Limousin) tends to reinforce the wine's astringency, but this effect may be partially alleviated by heavy toasting. High-density wood (such as Allier) is better suited to this type of wine, as it releases smaller quantities of phenols. A medium or heavy toast produces aromatic qualities that counteract herbaceous tendencies and attenuate bitterness.
5. The effect of barrel aging is more limited when wines are fine and well-balanced, with good structure and body, as well as powerful, fruity aromas. These wines can handle the phenols extracted from the oak, but care must be taken to avoid bitterness and plank odors, as well as intense, smoky, toasty overtones that are likely to make the wine seem rather coarse. Under these conditions, too much toasting should be avoided, especially when the barrel has already been closed at the top. Fine-grained wood and a medium toast would be just right.
6. Wines that have a light tannic structure or not very well developed aromas with herbaceous overtones need barrels that can enhance the wine's structure, without any aggressiveness. The right kind of oak contributes aromatic complexity without overpowering the fruit. Heavily toasted barrels are most appropriate in this instance and the density of the oak should be suited to the characteristics of the wine.