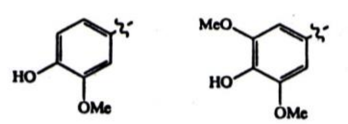
Wine/Enology
Grape Chemistry Group at Va Tech

BARRELS, BARREL ADJUNCTS, AND ALTERNATIVES

Section 2.

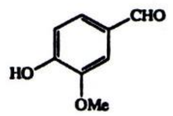
Volatile Phenols. Guaiacyl and syringyl (Figure 7) make up the largest portion of oak volatiles. These are products of the degradation of lignin. Most of the volatile phenols with low aroma and taste thresholds are guaiacyl derivatives. The syringyl derivatives have weak odors and probably have little impact on wine flavor (Boidron et al., 1988; Dubois, 1989). It is possible that they modify the impact of the more potent volatile phenols.

Figure 7. Structures of Guaiacyl (left) and Syringyl (right)



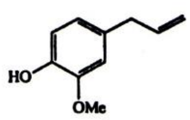
Vanillin (Figure 8) is a major component of oak extracts and the principal flavor volatile of natural vanilla, adding a vanilla character to wines. Dubois (1989), however, attributes the “vanilla oak” character to other products formed during the toasting. Levels of vanillin increase markedly with heating and toasting of barrels (Chatonnet et al., 1989; Nishimura et al., 1983). Seasoning also affects the level of vanillin.

Figure 8. Structure of Vanillin



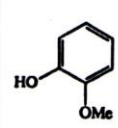
Eugenol (Figure 9) is a significant component of unheated oak with low flavor threshold and a spicy, clove-like aroma (Boidron et al., 1988). Levels decrease markedly during the first six months of seasoning, and then more slowly during the next 18 months, to less than half the concentration found in the green timber. A greater spicy character can frequently be attributed to higher levels of eugenol.

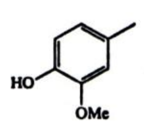
Figure 9. Structure of Eugenol



Guaiacol and 4-methylguaiacol (Figure 10) both have smoky aromas and are found in significant concentrations in barrel-aged wines (Boidron et al., 1988; Bubois, 1989; Chatonnet et al., 1990; Hoey et al., 1988). They are only present in trace quantities in un-toasted or moderately-heated oak wood (Sefton et al., 1990). They are generated by thermal degradation of lignin at the higher barrel toasting levels. The degree of toasting is, therefore, an important factor in imparting a smoky character to wines.

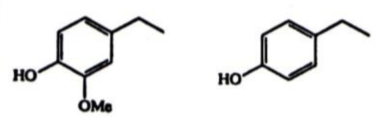
Figure 10. Structures of Guaiacol (left) and 4-Methylguaiacol (right)





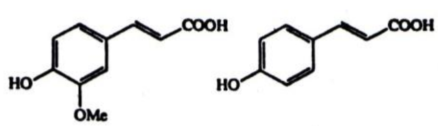
4-Ethylguaiacol and 4-ethylphenol (Figure 11) are found in concentrations above sensory thresholds in red wines matured in oak wood (Boidron et al., 1988). However, unlike the other volatile phenols, they are only trace components of oak wood and are not observed in barrel-aged white wines.

Figure 11. Structures of 4-Ethylguaiacol (left) and 4-Ethylphenol (right)



The mechanism of the formation appears to be of microbiological origin with precursors, ferulic acid and *p*-coumaric acid (Figure 12), mainly fruit-derived.

Figure 12. Structures of Ferulic (left) and *p*-Coumaric (right) Acids



Chatonnet et al. (1990) observed the highest levels of these two volatile phenols in red wines aged in used wood. Although small quantities have little influence on wine quality, the high levels associated with used oak are regarded as detrimental to the quality of the wines. Shaving of used oak barrels has been shown to significantly reduce the levels of these compounds (Chatonnet et al., 1990) due to the reduction in the spoilage yeast *Brettanomyces*.

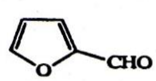
- 4-ethylguaiacol has a smoky, spicy, and somewhat medicinal character.
- 4-ethylphenol has been described as mainly “medicinal” and “horsey.”

It is not only the depletion of oak extractives which limits the useful life of a barrel. The absorption of undesirable compounds, such as the ethylphenols and ethylguaiacol, also contributes to depreciation of barrel quality.

Carbohydrate Degradation Products. Another class of volatile flavor components of oak is those derived from the thermal degradation of cellulose and hemicellulose, which account for more than 50% of the dry weight of oak. The carbohydrate-derived volatiles are only minor or trace components of unheated wood, but are dominant in extracts of heated or toasted oak (Nishimura et al., 1983; Sefton et al., 1990).

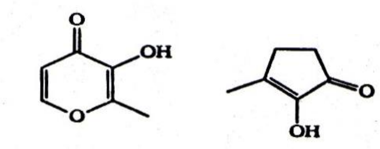
Furfural (Figure 13) and its methyl-derivatives are the predominant aldehydes playing a role in the flavor of wood-aged brandies or whiskies. In wines, they are reduced enzymatically to the corresponding hydroxymethyl analogues which have high flavor thresholds and, therefore, have a limited influence on wine flavor.

Figure 13. Structure of Furfural



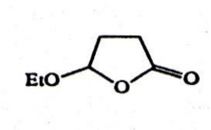
Maltol and cyclotene (Figure 14) have sweet and toasty aromas. These compounds appear to be the most important of the carbohydrate degradation products for oak-derived flavor.

Figure 14. Structures of Maltol (left) and Cyclotene (right)



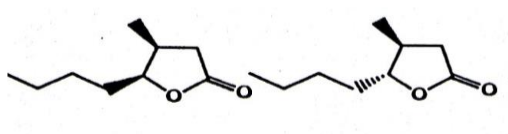
Ethoxylactone (Figure 15) is a major component of toasted oak and a carbohydrate degradation product. It is thought to have sweet and fruity aroma (Sefton et al., 1990).

Figure 15. Structure of Ethoxylactone



"Oak" Lactones. Two isomeric *gamma*-lactones, the so-called "oak" or "whisky"-lactones (Figure 16) have been identified as oak wood constituents. The *cis*-isomer has a much lower aroma and taste threshold than the *trans*-isomer. The oak lactones are found at concentrations in excess of their threshold in barrel-aged wines (Boidron et al., 1988; Chatonnet et al., 1990). Chatonnet et al. (1990) demonstrated that, at lower concentrations, these lactones impart a woody aroma which improves the quality of the wine, but at higher concentrations, resinous, varnish, and coconut-like aromas, which were seen as undesirable, become dominant.

Figure 16. *Cis*- (left) and *Trans*- (right) Gamma-Lactone Isomers



Levels of the oak lactones in oak wood appear to vary widely; this has been attributed to variations in oak origin (Gymon and Crowell, 1977; Otsuka et al., 1974). The concentrations of oak lactone increase with toasting (Maga, 1989). Seasoning American oak under dry conditions increases the levels of oak lactones approximately 1.5-fold during the first two years, and 4- to 5-fold after seasoning for six years (Maga, 1989). Studies have confirmed the importance of seasoning to oak lactone concentration, and variations depending upon the seasoning environment. For example, oak seasoned in a relatively hot and dry climate had approximately twice the level of *cis*-oak lactone of the wood seasoned under wetter and milder conditions.

Terpenes. Monoterpenes, sesquiterpenes and 9-, 11-, and 13-carbon norisoprenoids have been identified as oak wood constituents, although their role in oak-derived flavor has not been established (Nabeta et al., 1986; Nishimura et al., 1983; Sefton et al., 1990). These compounds, which are thought to be degraded carotenoids (Wahlberg and Enzell, 1987) are important to the flavor of tobacco, tea, and some fruits, and also occur mainly as glycoconjugates in both black and white grape varieties and in wines (Sefton et al., 1989; Winterhalter et al., 1990).

Among all the oak volatiles (Figure 17) observed in American and European oak extracts, the greatest variety is in norisoprenoids, with a higher overall concentration and greater variety of these compounds in the American oak.

Figure 17. Chemical Analysis of Oak and Wine

Tannin breakdown	Steam-volatile phenols ("smoke")
gallic acid	phenol
ellagic acid	guaiacol
castalagin	*o*-cresol
vescalagin	*m*- and *p*-cresol
Hemicellulose caramelization	4-ethylphenol
5-hydroxymethyl furfural	4-methylguaiacol
furfural	4-ethylguaiacol
5-methyl furfural	Oak lactones
Wine phenolics	*trans*-lactone
protochatechuic acid	*cis*-lactone
catechin	Other
epicatechin	scopoletin
chlorogenic acid	Volatile esters
myricetin	acetaldehyde
quercetin	diethyl acetal
Lignin degradation	ethyl acetate
vanillic acid	ethyl butyrate
syringic acid	ethyl hexanoate
vanillin	hexyl acetate
syringealdehyde	ethyl octanoate
coniferaldehyde	ethyl decanoate
sinapaldehyde	phenethyl acetate

Phenolic Taint. Wine stored in barrels, particularly used barrels, may develop elevated levels of ethylphenols (Chatonnet, 1993). These compounds provide "phenolic odors" reminiscent of barnyard and sweaty saddles. Chatonnet (1993) suggested that *Brettanomyces* spp. is the primary source of phenolic taint in aged wines.

Factors Impacting Red Wine Color

Color is an important wine attribute, because humans are visually oriented. As such, wine color can certainly bias evaluations. A classic example of color bias is to change the color of a white wine, such as Chardonnay, with red food coloring. In blind (but not blind-folded) evaluations, the color-adjusted wine frequently receives a different sensory rating for attributes such as fullness, body, and complexity.

As such, richly-colored wines are assumed to have high volume or body, and softer tannins. Conversely, a wine with less color is automatically assumed to have "green" or "harsh" tannins. Spectral color in wine is a function of these three elements:

- anthocyanin concentration
- concentration of cofactors, or certain non-colored compounds, which bind with anthocyanins
- polymeric pigments

Hyperchromicity, also known as copigmentation, is an interesting phenomenon that allows more visible red color, than would be expected due to the anthocyanin concentration alone. Cofactors are non-colored compounds that have the ability to bind with anthocyanins, creating more color than the unbound pigment, hence the term *hyperchromicity.*

The concentration and type of cofactors vary greatly from variety to variety, and season to season, but include some non-flavonoid phenols, flavonols, and the amino acid arginine. Oak components, such as gallic acid found in untoasted wood, can act as a color cofactor.

Barrel Preparation and Sanitation

New-barrel preparation options include the following:

- hot water rinse
- cold water rinse

- steam
- ozonated water
- bisulfite rinse

The simplest method is to fill the barrel upon receipt at the winery. However, due to the changing environmental conditions that the wood can experience from the cooper to the winery, the barrel may need to be swelled prior to filling. A common swelling method is the addition of a small quantity of hot water (about 5 gallons) for several hours.

In addition to the concern for swelling, most wineries rinse new barrels with a limited volume of water to remove easily extractable, harsh ellagic acid tannins. Most methods used for treating new barrels will not significantly alter the aromas/flavors imparted from the wood.

Used barrel cleaning and sanitation involves the above list of options, and others, including the following:

- high-pressure dry ice
- ultrasound
- high-power ultrasound (HPU)