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EFFECT OF OAK AGING TREATMENTS ON THE PHENOLIC COMPOSITION AND SENSORY QUALITY OF SEYVAL BLANC WINES

The Ohio State University

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EFFECT OF OAK AGING TREATMENTS ON THE
PHENOLIC COMPOSITION AND SENSORY
QUALITY OF SEYVAL BLANC WINES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Karl Lawrence Wilker, B.S., M.S.

* * * * *

The Ohio State University
1986

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INTRODUCTION

The first recorded use of barrels for wine storage dates back to the Roman times (Amerine and Singleton, 1977). Barrels provided the possibility of storing large quantities of wine with minimal air contact. While the understanding of the effects of oxygen and microorganisms on wine was centuries away, the harmful effects of air were at least recognized (Amerine and Singleton, 1977).

In recent years, the percentage of wine stored in oak barrels has declined. This is primarily due to the increased use of stainless steel tanks. Stainless steel tanks have many advantages over barrels for wine storage. Advantages include lower long term costs, greater protection from oxygen, better utilization of cellar space and decreased losses due to evaporation. An instance where barrels may be preferred to stainless steel tanks is the aging of dry table wines. With these wines, the extraction of wood components, and the increase in oxygen exposure associated with barrel aging is often desired.

In an effort to achieve a barrel aged style wine while using stainless steel tanks, the use of oak chips has been suggested. The oak chips are either added directly to a large tank of wine or a wine is passed through a device packed with oak chips. Oak chips can also be used to extend the usable life of barrels by supplying depleted wood extract.
The concept of adding oak chips to wine as a means of imitating barrel aging has been met with some skepticism. A common criticism is that wines stored in stainless steel tanks do not undergo the slow uptake of oxygen associated with barrel aging. While the effect of oxygen on wine is an important aspect of barrel aging, there appears to be a lack of information concerning its movement into barrels and mode of action. There is also minimal information concerning the composition of oak chip extract versus oak barrel extract during wine contact.

The wood used for barrel construction is either slowly dried outdoors or quickly dried in wood kilns. Some concern has been expressed that barrels made from kiln dried wood have a different sensory impact on wine than those made from air dried wood. A comparison of these two forms of drying on wine composition would seem warranted considering the interest in kiln drying, for its shorter time of curing.

Traditionally, barrels received a slight scorching or toasting on the inside surface during assembly. This is a consequence of heating the staves with a small fire to facilitate their bending. Today, most mechanized cooper companies use steam in the stave bending process instead of a small fire. If toasting is desired additional heating with fire is required. This heating step may be important as some winemakers have shown a preference for toasted versus plain barrels. Many barrel manufacturers have responded to this by offering barrels with a choice of several degrees of toasting. Oak chips are also offered in both plain and toasted forms.

To further understand the use of oak barrels and oak chips in the aging of wines, the following studies were conducted.
1. Sensory quality and composition of Seyval blanc wine aged in barrels and stainless steel tanks with oak chips.

2. Phenolic analysis of kiln and air dried oak staves used in the aging of Seyval blanc wine.

3. Phenolic analysis of plain and toasted oak chips used in the aging of Seyval blanc wine.
GENERAL REVIEW OF LITERATURE

The Effects of Aging Wine in Oak Barrels

Evaporation. White oak is the most common type of wood used in wine barrel production. White oak is porous; however, this wood has a lower permeability than many other hard woods. The low permeability of white oak inhibits the movement of most gases and liquids through the sides of wine barrels (Guymon and Crowell, 1970). Guymon and Crowell (1970) attribute the low permeability of white oak to the fact that the void areas in the heartwood are discrete and evenly distributed, and the presence of tyloses. Tyloses are film like growths formed during the conversion of sapwood to heartwood. Tyloses block the conductive vessels common to hardwoods.

Two compounds capable of diffusing through stave wood and evaporating from the wood surfaces are ethanol and water (Guymon and Crowell, 1970). This is due to their low molecular weights. The relative rate of ethanol and water loss due to evaporation from barrels is influenced by the relative humidity of the surrounding air. Guymon and Crowell (1970) working with brandy found that if the surrounding air has a low relative humidity value the loss of water from a barrel will be greater than the loss of ethanol. If a barrel is kept in an area of high relative humidity, the evaporation of water is reduced. The diffusion rate of ethanol is less effected by humidity, and the concentration of ethanol will either increase or decrease depending on the rate of water loss.
The relative humidity which the concentration of ethanol remains stable is approximately 60 to 65 percent (Singleton, 1981).

The volume loss of wine due to evaporation is usually 2 to 5 percent per year in a 200 L barrel (Singleton, 1981). It would be greater for a smaller container and less for a larger barrel or cask. Nonvolatile as well as volatile compounds larger in molecular weight than ethanol are likely to concentrate as evaporation occurs. Evaporation loss is usually greater with red wines as they tend to be aged in barrels for longer periods of time than white wines.

**Oxygen Uptake.** Traditionally, the uptake of oxygen during the barrel aging of wine was thought to occur at a slow continuous rate through the barrel staves. This is still considered by some to be an important factor in wine aging (Pontallier et al., 1982). Others suggest that oxygen uptake is greater during the transfer operations than during storage in barrels (Peterson, 1976; Singleton, 1981). Work by Peterson (1976) appears to be responsible for this shift in thought. He found that full, tightly bunged, nonleaking barrels will form a vacuum as water and ethanol evaporate. The formation of vacuum in these barrels refutes the belief that air is capable of penetrating a full barrel due to the wood porosity. Peterson (1976) reported that only one barrel of six failed to form a vacuum during 28 weeks of wine aging. This barrel, although not visibly leaking wine, had two wine stained staves. The oxygen uptake by the wine in this barrel was likely greater than those stored in barrels which formed a vacuum.

Indirectly the porosity of the barrel staves may lead to an increase in oxygen uptake. This is due to the practice of opening barrels to
replace wine lost through evaporation (Singleton, 1981). Also, if enough evaporation occurs the ullage loss may become large enough to where the inside surface of a barrel is not fully wet. This could result in considerable oxygen uptake, for dry wood is quite permeable to oxygen (Singleton, 1981).

The necessity of oxygen uptake to occur at a slow rate during wine aging has also been questioned. Research by Wildenradt and Singleton (1974) indicated that air contact with wine immediately leads to the production of a strong oxidant. They stated that the effects of oxidation would be the same over a short or long period of time as long as the same amount of oxidation occurred and the wine was well mixed.

**Oak Extract.** One of the important aspects of aging wine in barrels is the extraction of wood components. Most of the research dealing with oak extractants has been with distilled beverages (Guymon and Crowell, 1968; Guymon and Crowell, 1972; Onishi et al., 1977; Puech, 1981, 1984; Reazin, 1981). However, recent studies have been conducted on oak extraction by wine (Aiken and Noble, 1984a; Quinn and Singleton, 1985; Rous and Alderson, 1983; Singleton et al., 1971). The extraction of wood components is influenced by the level of ethanol in the extracting liquid (Singleton and Draper, 1961). The optimum level of ethanol for the extraction of solids from oak wood is 55 percent in an aqueous solution (Singleton and Draper, 1961). Table wines which have lower ethanol levels than distilled beverages are likely to have slightly different extractive properties. Compounds extracted by ethanol solutions include phenolics (Singleton et al., 1971), fixed acids (Reazin, 1981), volatile

Phenolic compounds found in oak extracts are predominantly non-flavonoid phenols and include aromatic aldehydes, aromatic acids and hydrolyzable tannins. Examples of aromatic aldehydes found in oak extracts include vanillin, syringaldehyde, coniferaldehyde, and sinapaldehyde (Puech, 1981). Aromatic acids extracted from oak include sinapic, vanillic, ferulic, gallic, caffeic, syringic, cinnamic, benzoic, p-hydroxybenzoic and p-coumaric acid (Puech, 1981). Both the aromatic acids and aldehydes are thought to be derived from lignin (Puech, 1981). These compounds are either extracted from wood or extracted as ethanol-lignin compounds which are later degraded to simple phenolic compounds (Puech, 1981). Puech (1981) suggests that some aromatic acids are formed by oxidation of aromatic aldehydes. Aromatic acids and aldehydes may have relatively high individual taste thresholds in ethanol solutions. However, when they are in combination, there is often a synergistic effect producing lower taste thresholds (Maga, 1985).

Hydrolyzable tannins are the major nonflavonoids found in oak wood extract (Quinn and Singleton, 1985). The predominant type of hydrolyzable tannins in European and American oak extracts are ellagitannins (Quinn and Singleton, 1985). These hydrolyze easily under acidic conditions, yielding ellagic and gallic acid and a polyhydroxy substance (Quinn and Singleton, 1985). Quinn and Singleton (1985) suggested that hydrolyzable tannins are probably important in the astringency of oak treated wines. Their hydrolysis may be a major factor in decreasing the astringency of wines.
Acetic acid is usually the predominant acid responsible for increases in the volatile acidity of wines (Amerine and Ough, 1980). Reazin (1981) reported that increases in acetic acid of barrel aged whiskey may be attributed to the oxidation of ethanol as well as its extraction from wood. Aiken and Noble (1984a), studying wines aged in American and European barrels, suggested that the increases in volatile acidity were primarily due to the extraction from wood. Logically, acetic acid formation from ethanol becomes a major factor with increased oxygen exposure.

Titratable acidity values have also increased during the barrel aging of wines and distilled spirits (Aiken and Noble, 1984a; Reazin, 1981). While some increases may be attributed to higher levels of volatile acids and to the concentrating effects of evaporation, other increases are believed to be due to the extraction of fixed acids from barrel wood (Aiken and Noble, 1984a). The specific fixed acids extracted, other than phenolic acids, have not been fully elucidated.

Aiken and Noble (1984a) found the potassium contents to be significantly higher in Cabernet Sauvignon wines aged in American oak barrels than those aged in French oak barrels and control wines without wood contact. They attributed the potassium increases to the extraction from barrel aging. Potassium is an important constituent, because it effects both the pH and titratable acidity of wines (Boulton, 1980).

Slight increases in sugar levels of whiskey aged in American oak barrels were observed by Reazin (1981). The sugars that were found to increase included arabinose, xylose, glucose, galactose, fructose and rhamnose. The increased level of these sugars, excluding fructose, is
believed to be due to the breakdown of hemicellulose (Reazin, 1981). Glucose is also thought to increase due to the hydrolysis of ellagitannins (Quinn and Singleton, 1985). However, sensory changes in wine due to increases in these compounds during barrel aging is minimal for they occur in relatively small amounts.

Furfural and β-methyl-γ-octalactone ("oak" lactone) are nonphenolic compounds which are extracted from oak during wine aging. Both compounds may effect the sensory properties of wine and distilled spirits (Onishi et al., 1977). Furfural has a high odor threshold (5.8 mg/L) and is regarded to be only a small odor contributor in brandy, but is considered to cause an increase in the hotness of taste (Guymon and Crowell, 1972; Salo et al., 1972). Both the cis and trans forms of oak lactone have been found in oak extract with the trans configuration being predominant (Onishi et al., 1977). Oak lactone has a low odor threshold (0.5 mg/L) and a distinctive aroma characteristic similar to dried coconut (Guymon and Crowell, 1972; Salo et al., 1972).

Differences Among Wine Barrels

European Versus American Oak. The most widely accepted and documented variable in the construction of wine barrels is whether European or American white oak is used. American oak is primarily Quercus alba and related species (Singleton, 1974). European oak is from the species Quercus sessilis and Quercus robur (Singleton, 1974). European oak has been found to contribute considerably more solids and nonflavonoid phenols to wine than American oak (Singleton et al., 1971). American oak is lower in tannin and coloring compounds than European oak, but higher in furfural and oak lactone (Guymon and Crowell, 1972; Puech, 1984;
Onishi et al., 1977). The higher levels of oak lactone and furfural in American oak may explain why it is considered to have more odorous components than European oak.

Rous and Alderson (1983a) found the rate of nonflavonoid phenol extraction varied greatly between French and American barrels during their first and second fillings with wine. By the third filling of the French and American barrels, the extraction rates were almost identical. At this time, the easily extracted phenols were depleted, with hydrolyzable phenols being the main source of the phenolic increases (Rous and Alderson, 1983).

Aiken and Noble (1984a) compared a Cabernet Sauvignon wine aged in French versus American oak barrels and found the wines aged in the American barrels to be higher in potassium and lower in titratable acidity than those from French oak. A detectable sensory difference was also reported between the wines after 115 days of barrel aging but not after 239 and 338 days. The lack of a difference in the 239 and 338 day wines was attributed to the masking of oak flavor differences by the strong varietal character of the wine.

Rous and Alderson (1983) compared a white wine aged in French and American oak barrels at three fill intervals and found a detectable sensory difference at each fill interval. Although at the third filling interval, the sensory differences were subtle and made differentiation difficult.

It appears that the duration of barrel aging, number of previous extractions of a barrel, and the type of wine being aged have effects on the sensory differences of wines aged in French and American oak barrels.
Regional Variation. The specific origin of oak on a regional basis only applied to buying European barrels. Most French cooperage is differentiated by the forest or trade center from which the stave wood is obtained. The main causes of regional variations are soil differences, climate and the relative age of timber stands rather than species variation (Singleton, 1974). A good example of this variation is the differences reported between the oaks from the Limousin and Troncais regions in France (Pontallier et al., 1982). Limousin oak generally grows on poor rocky soil in small widely scattered forests in France. The trees grow wide and short and the wood has a wide grain. In contrast, Troncais oak commonly grows on deep and fertile loam soils where the trees grow close together. These trees grow tall and thin with a closer grain than Limousin oak. The width of grain effects the rate of extraction of phenolic compounds. A wide grained wood such as Limousin oak generally has a greater extraction rate than Troncais oak.

Most research that compares oaks for regional differences has been done using French oaks. Puech (1981) found variations in aromatic aldehydes extracted by Armagnac from several French oaks (Troncais, Limousin, Gascony and Columbia). Among these oaks, Limousin was found to release the highest level of aromatic aldehydes. Puech (1984) also compared the tannin levels of Armagnac aged in Troncais, Limousin and Gascony oak barrels and although he found that the tannin contents varied slightly, the means values were quite similar. Guymon and Crowell (1972) found the tannin level of brandy aged in Limousin, Troncais and Gascony barrels to be generally higher in the Limousin barrels. These results indicate that some regional variation of stavewood does exist. However,
Limousin type trees are likely to be found in the forests of Troncais and vice versa.

In general, regional distinctions have not developed for American oak barrels. Whether this is due to the inherent uniformity of American oak or just a greater mixing of stavewood by the American barrel industry has not been fully examined. Weil (1984) stated that the northern and mountain oaks generally have a finer grain than other American oaks. Considering this finding and the diverse production areas for white oak in America, the possibility of regional variations seems likely.

Kiln Versus Air Drying of Stavewood. Several reasons for potential differences between air and kiln dried wood have been suggested. One difference most commonly mentioned is the leaching of tannins from air dried wood by rainwater (Pontallier et al., 1982). Singleton (1981) suggested that this is only a surface phenomenon, and the effect is small and probably unimportant. The condensation and polymerization of tannins during the air drying of staves is mentioned by Pontallier et al. (1982). These reactions are believed to be due to enzymes naturally occurring in wood and those secreted by microorganisms. Kiln drying is thought to reduce these reactions (Pontallier et al., 1982).

Pontallier et al. (1982) compared the effects of kiln and air drying of two French oaks (Allier, Limousin). With Allier oak, they found that kiln drying caused an increase in the phenolic acids extracted by wine. However, with Limousin oak, air or kiln drying had little effect on the phenolic acid contents. Also tastings of wines aged in barrels constructed of these woods indicated that Allier oak was greatly affected by the method of drying. Air dried Allier oak yielded wines with a powerful
woody vanilla character. In contrast, the kiln dried Allier oak gave the wines a less aggressive but sometimes resinous woody character. With Limousin oak, the method of stave drying had little effect on the sensory properties of the wines.

Markman (1974) compared oven drying, simulated kiln drying, and airdrying of wood from one American oak tree. She found that the oven dried wood was higher and the kiln dried wood was lower in phenolics than the air dried wood. Using paper chromatography, two unidentified compounds were found in the oven and kiln dried woods, but not in the air dried wood. Both unidentified compounds were present in low concentrations. Overall, she reported that the total amount of phenolics and the number of compounds were similar for air and heat dried woods.

**Effects of Toasting.** The changes that occur in a barrel due to toasting are similar to those by charring. Reazin (1981) found substantial increases in aromatic aldehydes extracted by 140 P neutral spirits from new charred versus new uncharred barrels. Recharring of used barrels was found to increase the levels of solids, fixed acids, and tannins extracted by neutral spirits (Reazin, 1981). However, the levels of these congeners were not as high as those for new barrels. Reazin (1981) suggested that charring caused a partial degradation of lignin, causing an increase in reactivity with ethanol. This increase in extractable phenolic compounds may be the reason why some winemakers request toasted barrels.
CHAPTER I
COMPARISON OF SEYVAL BLANC WINE AGED IN
BARRELS AND STAINLESS STEEL TANKS
WITH OAK CHIPS

Oak chips have been suggested as a means of supplying oak extract to
wine (Singleton, 1974). Their use is intended to simulate barrel aging
while avoiding the higher costs and management requirements of barrels.
While oak chips are being used to some extent by commercial wineries,
their use has been criticized as being less satisfactory than barrel
aging.

This study was undertaken to conduct a comparison of aging wine in
new oak barrels versus stainless steel tanks with the addition of oak
chips. In addition, wines aged in new oak barrels and used barrels
containing oak chips were compared, because barrel aging is exposed to
greater levels of oxygen. The level of extraction from the oak chips and
barrels was monitored by determining the nonflavonoid phenols as
suggested by Singleton et al. (1971). The various treatment wines were
compared for differences in chemical composition and sensory properties.

Materials and Methods

Barrels and oak chips. The four new and three used barrels used in
this experiment were constructed of American oak and were obtained from
the same cooperage firm in Missouri. The used barrels had been used once
for the aging of Chardonay wine. All barrels and the three stainless
Steel tanks were 190L in volume. One of the new barrels was disassembled and converted into oak chips by a commercial chip machine. The dimensions of the oak chips were approximately 0.2 to 0.5 cm thick, 1 to 3 cm long and 1 cm wide.

Wine. The wine used in this experiment was a 1983 Seyval blanc vinified by Chalet Debonne Vineyards in Madison, Ohio. The grapes were grown in the Finger Lakes region of New York. All containers were filled from a single stainless steel tank.

Chemical analysis. Total phenolics, titratable acidity, pH, reducing sugars, volatile acidity (Cash Apparatus), alcohol, and the presence of a malolactic fermentation were analyzed as described by Amerine and Ough (1980). Nonflavonoid phenols were analyzed according to Amerine and Ough (1980). This method included nitrogen sparging and closing the test tubes after the addition of formaldehyde (Kramling and Singleton, 1969).

Barrel extraction. The barrels and tanks were rinsed with cold water and filled with wine. Samples were taken periodically from each container to monitor the increases in nonflavonoid phenols. After 10 weeks storage, there was an average increase in nonflavonoid phenols of 45 mg/L and 19 mg/L for the new and used barrel wines, respectively. At this time, 19L samples were removed from each container and placed in a glass carboys at 17 C. For the control samples, an additional 19L sample was taken from each stainless steel tank. Potassium metabisulfite was added to the wines to maintain the free sulfur dioxide levels between 25 and 30 mg/L.
Oak chip extraction. Extraction trials were conducted to determine the amount of nonflavonoid phenols extracted from 1 g of oak chips. Results indicated that approximately 6.8 mg of nonflavonoid phenols (gallic acid equivalents) were extracted from 1 g of oak chips (13.4% moisture) in 1 L of wine in seven days.

To raise the level of nonflavonoid phenols in the used barrel and stainless steel tank wines to that of the new barrel wines, oak chips were added directly to each of the three used barrel and stainless steel tank carboys of wine which 1 L of wine was previously removed. The 1 L wine samples were returned to the containers. An average of 127 g of oak chips were added to each stainless steel tank carboy and 74 g to each used barrel carboy of wine. For the new barrel and control wines 1 L of wine was drawn off and then returned without the addition of oak chips. The chips were left in the wines for seven days and then all wines were racked into 11 L glass carboys. The wines were bottled 73 days after chip removal and stored at 17 C.

Ten week chip extraction. To determine if a higher level of volatile acids (acetic acid) are extracted from oak chips by wine in a ten week extraction versus a one week extraction, the following experiment was undertaken. Oak chips were added to six 750 mL bottles of Seyval blanc wine at a concentration of 5.1 g/L. Three bottles of wine without oak chips were used as controls. The wines were kept at 17 C. Three of the bottles of wine containing oak chips were analyzed for volatile acidity at one week. The remaining three bottles of wine containing oak chips and the control wines were analyzed for volatile acidity at ten weeks.
**HPLC analysis.** The phenolic acid analysis was conducted using a Hewlett Packard HP 1090 Liquid Chromatograph unit with gradient capabilities. The instrument was equipped with a 5.0 uL manual injector, uv detector and a 3392A integrator. The column used was a Waters micro-Bondapak C18 (3.9mm x 30cm). The solvents consisted of a 5% acetic acid solution (solvent A) and a 30% methanol solution acidified with 5% acetic acid (solvent B). Acetic acid was used to suppress ionization of the phenolic acids (Wulf and Nagel, 1976). An acidified methanol gradient was used starting with 0% solvent B and increasing linearly to 3% at 30 minutes, 45% at 75 minutes, remaining at 45% until 90 minutes then increasing to 50% at 95 minutes. The initial flowrate was 0.05 mL/min at 130 minutes. Detection was carried out at 280 nm.

Tentative identification of the phenolic acids was determined by comparing peak retention times with known standards and observing increases in peak areas of standards added to wine samples. Quantification of the phenolic acids was accomplished by using standard curves constructed from the peak areas of standards. These were analyzed under the same chromatographic conditions as the wine samples.

Samples for HPLC analysis were prepared by adding 100ml of wine to a 250 mL erlenmeyer flask containing 55 g of ammonium sulfate crystals and 20 mL of ethanol. The ammonium sulfate was added for the purpose of salting out the ethanol into a separate phase (Singleton, 1961). The head space was flushed with nitrogen and the flask stoppered. The mixture was stirred for 30 minutes and allowed to separate into two layers. A portion of the top layer (ethanol) was filtered through a 0.45 um filter and then injected (5 uL) into the HPLC unit.
Sensory analysis. The taste panel for rating wine quality consisted of seven judges. Judges were asked to score each wine for aroma and taste on a nine point hedonic scale (nine being excellent). The wines were served in dark coded glasses, and each treatment was judged three times for a total of 21 ratings.

The taste panel for the triangle test for judging quality differences consisted of six judges. The wines were served in dark coded glasses, and each comparison was judged three times for a total of 18 trials.

The taste panel for the ranking preference of the wines consisted of 24 judges. The wines were served in clear coded glasses and each treatment was judged once for a total of 24 rankings.

Results and Discussion

For the phenolic acids examined (Table 1), only the level of gallic acid increased among the wood treatment wines. The greatest increases occurred in wines from new barrels followed by wines aged in used barrels and in stainless steel tanks with oak chips. Differences also existed in the percentage of the nonflavonoid phenol increases that can be attributed to the extraction of gallic acid. The highest percentage, 9.6%, occurred in the new barrel wines. This was followed by the used barrel wines at 8.0% and oak chip wines at 6.4%. Quinn and Singleton (1985) reported that the gallic acid content of a commercial oak flavoring preparation was relatively high (about 10% of the total extractable phenols). This level was attributed to the hydrolysis of wood under moist and high SO₂ conditions. The longer extraction period for the barrel wines (10 weeks vs. 1 week) may have allowed for an increase in
the hydrolysis of barrel wood. Hennig and Burkhardt (1962) found that gallic acid was absent during the first few days of a chip extraction, but later it became a major component. Possibly, the oak chip wines may have extracted a higher level of gallic acid, if the aging period had exceeded one week. The significance in gallic acid levels among the wood treatment wines is not clear. Gallic acid levels may be related to hydrolyzable tannins as gallic acid is one of the hydrolytic products of ellagitannins, a type of hydrolyzable tannin (Quinn and Singleton, 1985). Ellagitannins are contributors to astringency in wine (Quinn and Singleton, 1985). Therefore, an increase in gallic acid may indicate a decrease in astringency (Quinn and Singleton, 1985).

The concentrations of the phenolic acids examined (Table 1), other than gallic acid, showed little change between the control and wood treatment wines. These results seem to indicate that there was very little extraction of these compounds from the barrel or oak chip wood. Although little information is available concerning these acids and their extraction from American oak, some research has been conducted on French oak. Puech (1981) observed a slight increase in syringic, vanillic, ferulic and p-coumaric acid in Armagnac aged in French oak barrels for ten years. These results are in agreement with findings of this study as the differences in phenolic acid levels of the three wood treatments were small. However, slightly different results were obtained by Pontallier et al. (1982), who investigated three red wines aged in air and kiln dried French oak barrels. He found decreases in syringic and vanillic acid, slight increases in protocatechuic acid, and varying amounts of
p-coumaric acid in wines after barrel aging. Some of the wines showed an increase in p-coumaric acid, 15 mg/L or greater, while others exhibited only a small increase or slight decrease. Considering the high levels of phenolic compounds in red wines as compared to white wines and distilled spirits, red wines are likely to show a greater change in their phenolic acid contents during aging due to oxidation and hydrolysis. This may explain the greater differences in the phenolic acid contents of the wines studied by Pontallier et al. (1982).

The chromatograms for the wood treatment and control wines (Figures 1, 2, 3 and 4) were similar except for the peaks for gallic acid (peak 1) and three unknown compounds (peaks 2, 4 and 7). Peak 2 had its largest areas in the used and new barrel wines. Peak 4 had its greatest areas in the new barrel wines followed by the wines from the used barrel, oak chip and control treatments. Peak 7 was most prominent in the wines which had wood contact. Whether the changes in peak areas of these three unknown compounds are due to the extraction of wood components or to the oxidation of wine components is not known.

The oak chip, used barrel and new barrel wines had similar nonflavonoid as well as total phenol levels (Table 2). This was expected as oak chips were added to the oak chip and used barrel wines in amounts calculated to raise their nonflavonoid phenol contents to the same level of the new barrel wines. The used barrel wines received an average of 27 mg/L of nonflavonoid phenols from the extraction of oak chips and 19 mg/L from the extraction of their own wood. Oak chips supplied an average of 42 mg/L of nonflavonoid phenols to the oak chip wines.
Volatile acidity values for the used and new barrel wines were significantly higher than the oak chip and control wines (Table 2). Furthermore, the new barrel wines had volatile acidity values significantly higher than the used barrel wines. Considering the slight differences in volatile acidity between the oak chip and control wines, it appears that only a small increase of the volatile acidity was attributed to the extraction of wood. This finding was in contrast to the results obtained by Aiken and Noble (1984a). To determine the effect of the length of extraction period, wines in contact with oak chips for one week to ten weeks were compared. Results of this experiment revealed no significant differences in volatile acidity between the wines with a one week and ten week extraction (Table 3). Considering these results, it appeared that the increases in volatile acidity levels for the used and new barrel wines were due to oxidation and subsequent acetification. The differences in volatile acidity between the used and new barrel wines indicated different levels of oxygen exposure. The fact that the new barrels required more topping off of ullage than the used barrels tends to support this theory. None of the wines went through a malo-lactic fermentation.

The pH values for the wines from the new and used barrels were significantly lower than the oak chip and control wines (Table 2). Some decreases in pH of the new barrel wines may be due to an increase in titratable acidity (Table 2). However, this was not the case for the used barrel wines which had titratable acidity values similar to those of the oak chip and control wines. Some component or components other than
titratable acidity appeared to be responsible for the decrease in pH for the used barrel wines.

A higher level of titratable acidity for the new barrel wines is attributed to an increase in acetic acid and extraction of fixed acids from wood. Aiken and Noble (1984a) found a decrease in pH and an increase in titratable acidity for a red wine after barrel aging.

Wines from used and new barrels were similar in reducing sugar values which were significantly higher than the oak chip and control wines (Table 2). These slight increases may be due to the breakdown of hemicellulose and hydrolysable tannins in wood (Quinn and Singleton, 1985; Rezin, 1981). The longer exposure time for the used and new barrel wines probably allowed for a greater breakdown of these compounds. Sensory differences among the wines due to variations in their reducing sugar concentrations were likely small, because slight sugar level differences were found among the wines.

The color values for the oak chip, used barrel, and new barrel wines were not significantly different (Table 2). However, these wines had higher color values than the control wines. The increases in color for the wood treatment wines were predominantly due to an increase in coloring compounds extracted from wood. Increases in color during barrel aging were previously reported for brandy, whiskey and wine (Aiken and Noble, 1984a; Guymon and Crowell, 1970; Rezin, 1981).

Results indicated that only slight differences in the ethanol levels were found between the control and wood treatment wines (Table 2). Evaporation may have been the major factor lowering ethanol levels in the new barrel wines.
The results of the triangle test indicated a sensory difference between the oak chip and new barrel wines (Table 4). The differences in volatile acidity between these wines may have contributed to these sensory differences. However, other changes due to oxygen exposure were likely to have caused the sensory differences. The taste panel members were not able to distinguish between wines from the used barrel and either the oak chip or new barrel wines. This similarity may have been due to the fact that the used barrel wines had a level of oxygen exposure between the oak chip and new barrel wines, as indicated by the volatile acidity values.

The quality ratings of the wines (aroma and taste) revealed no significant differences between the wood treatment wines (Table 5). However, these results were due to the score averages rather than the uniformity of the taste panel opinions. The preference panel produced similar results with each wood treatment wine being rated as most preferred, by the same number of judges (Table 6). There were no significant differences for the wine preferences. Comments by the taste panel members indicated that the new barrel wines were strongest in oak aroma and flavor with wines from oak chips having a stronger fruity aroma. Aiken and Noble (1984b) found that during the barrel aging of Cabernet Sauvignon, the intensity of the spicy, vanilla and oak blend aroma attributes increased while there was a dramatic increase in the vegetative aroma. These findings demonstrated that one effect of barrel aging is the loss of the vegetative or fruity aroma originally present in a wine.
In summary, taste panel members were able to distinguish between Seyval blanc wine aged in stainless steel tanks containing American oak chips versus wines aged in new American oak barrels. The greater oxygen exposure during aging in new barrels is speculated to be the major cause of these sensory differences. The main differences in chemical composition between the wood treatment wines were increases in volatile acidity and decreases in pH for the new and used barrel wines as compared to wines from oak chips. The potential for using oak chips seems to have promise during wine aging in used barrels. Wines aged in used barrels with over 50% of the phenolic extraction due to oak chips, were not distinguished from similar wines aged in new barrels. Additional research is needed to better understand the effects of oxygen on wine during barrel aging.
Table 1. Effect of several wood treatments on the phenolic acid content of Seyval blanc wine.

<table>
<thead>
<tr>
<th>Wood Treatment</th>
<th>Phenolic Acids (mg/L)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gallic acid(1)</td>
<td>proto-catechuic acid(3)</td>
<td>vanillic acid(5)</td>
<td>syringic acid(6)</td>
<td>p-coumaric acid(8)</td>
</tr>
<tr>
<td>Control</td>
<td>1.32 ± 3</td>
<td>0.9A</td>
<td>1.1A</td>
<td>1.3A</td>
<td>2.3A</td>
</tr>
<tr>
<td>Oak chips</td>
<td>4.0B</td>
<td>0.8A</td>
<td>1.1A</td>
<td>1.3A</td>
<td>2.2A</td>
</tr>
<tr>
<td>Used barrels</td>
<td>5.0C</td>
<td>0.7A</td>
<td>1.2A</td>
<td>1.3A</td>
<td>2.1A</td>
</tr>
<tr>
<td>New barrels</td>
<td>5.6C</td>
<td>0.7A</td>
<td>1.3A</td>
<td>1.4A</td>
<td>1.9A</td>
</tr>
</tbody>
</table>

1Peak No. for the HPLC chromatograms shown in Figures 1, 2, 3 and 4.
2Average of three replications.
3Mean separation within a column by Duncans New Multiple Range Test, .05 Level.
Table 2. Wine analysis of Seyval blanc wine aged using three different wood treatments.

<table>
<thead>
<tr>
<th>Wood Treatment</th>
<th>pH</th>
<th>Titratable acidity</th>
<th>Volatile acidity</th>
<th>Alcohol percent</th>
<th>Color</th>
<th>Reducing sugars (g/100mL)</th>
<th>Total phenols</th>
<th>Nonflavonoid phenols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>3.42</td>
<td>7.43B</td>
<td>.058C</td>
<td>12.7A</td>
<td>.073B</td>
<td>7.12B</td>
<td>267B</td>
<td>219B</td>
</tr>
<tr>
<td>Oak chips</td>
<td>3.42A</td>
<td>7.36B</td>
<td>.059C</td>
<td>12.6AB</td>
<td>.085A</td>
<td>7.12B</td>
<td>307A</td>
<td>261A</td>
</tr>
<tr>
<td>Used barrel</td>
<td>3.35B</td>
<td>7.43B</td>
<td>.074A</td>
<td>12.6AB</td>
<td>.084A</td>
<td>7.37A</td>
<td>309A</td>
<td>265A</td>
</tr>
<tr>
<td>New barrel</td>
<td>3.33B</td>
<td>7.66A</td>
<td>.093B</td>
<td>12.5B</td>
<td>.089A</td>
<td>7.36A</td>
<td>308A</td>
<td>264A</td>
</tr>
</tbody>
</table>

1 Titratable acidity as g/L tartaric acid.
2 Volatile acidity as g/100 mL acetic acid.
3 Color as absorbance at 420 nm.
4 Expressed as mg/L gallic acid.
5 Average of three replications.
6 Mean separation within columns by Duncan's New Multiple Range Test, .05 level.
Table 3. Volatile acidity values for Seyval blanc wine after one and ten weeks of oak chip extraction.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Volatile acidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>.0562B3</td>
</tr>
<tr>
<td>Oak chips (1 week)</td>
<td>.061A</td>
</tr>
<tr>
<td>Oak chips (10 weeks)</td>
<td>.060A</td>
</tr>
</tbody>
</table>

1Volatile acidity as g/100 mL acetic acid.  
2Average of three replications.  
3Mean separation by Duncan's New Multiple Range Test, .05 level.

Table 4. Results of a triangle test for measuring taste differences of Seyval blanc wine aged by three different wood treatments.

<table>
<thead>
<tr>
<th>Comparison</th>
<th>Total responses</th>
<th>Correct responses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oak chips vs. new barrels</td>
<td>18</td>
<td>10¹</td>
</tr>
<tr>
<td>Oak chips vs. used barrels</td>
<td>18</td>
<td>5</td>
</tr>
<tr>
<td>New barrels vs. used barrels</td>
<td>18</td>
<td>6</td>
</tr>
</tbody>
</table>

¹Significant at the .05 level.
Table 5. Aroma and taste ratings of Seyval blanc wine aged by three different wood treatments.

<p>| Wood Treatment | Sensory Ratings¹ |       |       |</p>
<table>
<thead>
<tr>
<th></th>
<th>Aroma</th>
<th>Taste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oak chips</td>
<td>6.5A²</td>
<td>6.8A</td>
</tr>
<tr>
<td>Used barrels</td>
<td>7.0A</td>
<td>7.0A</td>
</tr>
<tr>
<td>New barrels</td>
<td>6.8A</td>
<td>6.7A</td>
</tr>
</tbody>
</table>

¹ Each attribute was scored on a 9-point quality scale, 9 being excellent.

² Means within rows are not significantly different.

Table 6. Results for the ranking of taste preferences of Seyval blanc wine aged by three different wood treatments.

<table>
<thead>
<tr>
<th>Judges Preferences</th>
<th>Most preferred</th>
<th>Medium preference</th>
<th>Least preference</th>
<th>Mean normal scores</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood treatments</td>
<td>8¹</td>
<td>8</td>
<td>8</td>
<td>0A²</td>
</tr>
<tr>
<td>Oak chips</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Used barrels</td>
<td>8</td>
<td>10</td>
<td>6</td>
<td>+.072A</td>
</tr>
<tr>
<td>New barrels</td>
<td>8</td>
<td>6</td>
<td>10</td>
<td>−.072A</td>
</tr>
</tbody>
</table>

¹ Number of judges listing as most preferred.

² Means are not significantly different.
Figure 1. Chromatogram (HPLC, 280nm) of Seyval blanc control wine (see Table 1 for identification of individual peaks, peaks 2, 4 and 7 are unidentified compounds).
Figure 2. Chromatogram (HPLC, 280nm) of Seyval blanc wine aged with oak chips.
Figure 3. Chromatogram (HPLC, 280nm) of Seyval blanc wine aged in used American oak barrels with the addition of oak chips.
Figure 4. Chromatogram (HPLC, 280nm) of Seyval blanc wine aged in new American oak barrels.
LITERATURE CITED


CHAPTER II

PHENOLIC ANALYSIS OF KILN AND AIR DRIED OAK STAVES USED IN AGING SEYVAL WINE

The wood used in wine barrel construction is either dried naturally outdoors or artificially in a wood kiln. Drying outdoors usually takes one to two years. Drying in a kiln greatly shortens the time requirement to a few months. As a matter of economics, more cooperages are using kilns for drying oak staves (Weil, 1984).

Some concern has been expressed that barrels constructed of kiln dried wood have a different sensory effect on wine than barrels from air dried wood. Pontallier et al. (1982) found sensory and compositional differences between wines aged in air dried and kiln dried Allier oak barrels. Wines stored in Limousin oak barrels were less affected by whether the barrel wood was kiln or air dried (Pontallier et al., 1982). There is little information available comparing the aging of wine in air dried and kiln dried American oak barrels.

In an effort to determine detectable differences between wines aged with air and kiln dried American white oak the following experiment was undertaken. Seyval blanc wines aged with oak chips made from air dried and artificially dried American white oak staves were compared for sensory and compositional differences.

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Materials and Methods

Oak staves. Eight white oak logs from sites in three states (Ohio, Kentucky, and West Virginia) were used as replications. Logs from several areas were included to compensate for possible regional variation to the effects of kiln and air drying. The bottom 4 foot segment of each log was cut lengthwise into quarters. Each quarter was then quarter-sawn into staves with two staves being retained per quarter. The staves were coded to identify the log and quarter. One stave per quarter was air dried and the second stave was dried in a drying oven.

Drying procedures. The initial moisture contents of the staves were 39.4 percent (Ohio), 44.8 percent (Kentucky) and 38.4 percent (West Virginia). The moisture contents were determined by measuring the weight loss of a 60 to 80 g. block of wood, cut from the center section of each stave. One stave per state was examined. The samples were dried in an oven at 103 C for 36 hours.

The staves for air drying were stacked, with spaces between the staves, and were stored in a three sided covered shed. This arrangement allowed for good air movement. The staves remained outdoors for 20 months time.

The staves that were artificially dried were placed in a forced air drying oven. No provisions were made for controlling the relative humidity in the drying oven. However, the increases in temperature were made according to a normal kiln schedule (Table 7). The initial oven temperature was 38 C. Selected staves from each state were weighed periodically to monitor the rate of moisture loss. The length of time to lower the moisture levels to approximately 10 percent was 36 days.
After the staves were dried, they were converted into chips by a commercial chip machine. Chips from the same dried staves, cut from the identical log, were mixed together. This produced two composite samples per log, one naturally dried and one artificially dried. The dimensions of the oak chips were about 0.2 to 0.5 cm thick, 1 to 3 cm long and 1 cm wide.

The moisture contents of the oak chip samples were determined by measuring the weight loss of 20 to 30 g samples of oak chips. Samples were dried in an oven at 103 C for 36 hours. The average moisture contents for air and kiln dried oak chips were 12.4 and 8.7 percent respectively.

Wine. The wine used in this experiment was a 1983 Seyval blanc vinified by Chalet Debonne Vineyards in Madison, Ohio. The grapes were grown in the Finger Lakes region of New York. All containers were filled from the same tank.

Oak chip extraction. Oak chips were added to 1.9 L glass containers containing Seyval blanc wine at a concentration of 5.13 g/L, on a dry weight basis. There were two chip samples extracted separately per tree, one air dried and one dried in a drying oven. The chips were extracted for six weeks at 17 C. Two 1.9 L glass containers of wine, without the addition of oak chips, were used as controls.

Chemical analysis. Color and total phenols were analyzed as described by Amerine and Ough (1980). Nonflavonoid phenols were analyzed according to Amerine and Ough (1980). This method included nitrogen sparging and closing the test tubes after the addition of formaldehyde (Kramling and Singleton, 1969).
Oak chip variation. To determine the variability in nonflavonoid phenols among the wood chips from individual logs, three air dried and kiln dried oak chip samples (West Virginia A log) were examined. Oak chips were added to 1.9 L glass containers containing Seyval blanc wine at a concentration of 5.35 g/L on a dry weight basis. The chips were extracted for six weeks at 17 C.

HPLC analysis. The gallic acid analysis was conducted using a Hewlett Packard HP 1090 Liquid Chromatograph unit with gradient capabilities. The instrument was equipped with a 5.0 uL manual injector, uv detector and a 3392A integrator. A Waters micro-Bondapak C18 (3.9mm x 30cm) column was used. The eluting solvent consisted of 5 percent acetic acid and 2.1 percent methanol in water. An acetic acid-methanol solution, for the separation of phenolic acids on a C18 column, was suggested by Wulf and Nagel (1976). The flow rate was increased linearly from 0.05 mL/min to .25 mL/min in 65 minutes. Detection was carried out at 280nm.

Tentative identification of gallic acid was obtained by comparing the peak retention time of a known gallic acid standard to an unknown peak in the wine samples. Also, spiking of wine samples and determining which peak increased was used to identify gallic acid. Quantification of gallic acid was accomplished by using a standard curve constructed from chromatograms of various concentrations of gallic acid (2.5, 5.0, 7.5 and 10 mg/L). Samples for HPLC analysis were prepared and injected in the same manner as described in Chapter I.

Sensory analysis. Sensory evaluation was performed by five judges who were experienced in judging oak aged wines. A triangle test was used
to determine taste differences of the various wines. Wines from air
dried staves of a single log were compared to those of the artificially
dried staves, all from the same log. Each set of samples from an
individual log equaled one replication, for a total of eight replica-
tions. The wines were served in dark coded glasses.

Results and Discussion

Results for the chemical analyses of the kiln and air dried oak
wines are presented in Table 8. These results indicated that there was a
9.5% difference between the average nonflavonoid phenol increase for the
kiln dried oak wines (55 mg/L) compared to that for the air dried oak
wines (50 mg/L). However, no statistical difference was obtained between
the mean values for nonflavonoid phenols of both treatments. This lack
of significant difference was due to varying amounts of nonflavonoid
phenols extracted from the kiln and air dried oak chip samples, for the
individual tree replications (Table 9). A higher level of nonflavonoid
phenols was extracted from some log samples if they were kiln dried (Ohio
A, Kentucky A, Kentucky C and West Virginia A), while others had a
slightly higher level extracted from the air dried wood (Kentucky B and
West Virginia B). Furthermore, some of the log samples showed very
little difference between drying treatments (Ohio B and Ohio C).

To determine if differences between the air and kiln dried samples
were due to the variability among the wood chips from individual logs,
three air dried and kiln dried oak chip samples (West Virginia A log)
were examined. This particular log was selected because of the large
difference in the concentration of nonflavonoid phenols between the kiln
and air dried oak wines (17 mg/L). The results of the nonflavonoid
phenol analyses are shown in Table 10. The mean values of the nonflavonoid phenol contents of replicated extractions reduced the differences between the kiln and air-dried oak wines. Thus, most of the variation between samples was likely caused by phenolic differences within the individual trees rather than the method of stave drying. The mean value for nonflavonoid phenols for the three replications of kiln-dried oak wines was 3 mg/L higher than the air-dried oak wine samples. While this was much smaller than the 17 mg/L difference for the original analysis, it still indicated a slight trend towards higher levels of nonflavonoid phenols in the wines aged with kiln-dried wood. Presumably the use of eight trees as replications, in the original experiment, helped to reduce the variation due to differences among the wood chips from the same tree.

The difference was not significant between the mean gallic acid values for the kiln and air-dried oak wines. Since gallic acid is a breakdown product of ellagitannins, a large increase in this acid would tend to indicate the hydrolysis of these tannins (Quinn and Singleton, 1985). Ellagitannins, believed to be the major tannin in cooperage oak wood, are of interest, for they are astringent while their hydrolytic products are not (Quinn and Singleton, 1985). Considering the lack of a statistical difference between the mean values for gallic acid, these results would seem to indicate that either method of stave drying had little effect on the breakdown of hydrolysable tannins. However, changes in the level of tannins, which do not release gallic acid as a breakdown product, cannot be ruled out.

The difference was not significant between the mean color values for the kiln and air-dried oak wines (Table 8). Also, the difference was not
significant between the mean total phenol values for the kiln and air dried oak wines (Table 8). These two parameters were apparently not affected by whether a wine was aged with kiln or air dried oak.

Results of the triangle test for taste differences between the kiln and air dried oak wines are shown in Table 11. The taste differences between the kiln and air dried oak wines were not significant. However, one exception to this was found, wines from the Kentucky C log samples. All five judges were able to distinguish between the kiln and air dried oak wines from this log. The difference was not due to spoilage, but to a stronger oak aroma of the kiln dried oak wines. Results also indicated that there was a 12 mg/L nonflavonoid phenol difference between the kiln and air dried oak wine samples, Kentucky C log (Table 9). This difference in phenolic content may be the reason for the sensory quality differences between the two wines. Two other replications (Ohio A and West Virginia A samples) also were found to have differences in nonflavonoid phenol concentrations of 12 mg/L or higher between the kiln and air dried oak wines. When the taste panel results for these three replications were examined together, 10 correct judgments were obtained from 15 total responses. At this level, the number of correct decisions was statistically significant at the 1 percent level. Singleton (1971) found a minimum difference threshold of 11 mg/L for nonflavonoid phenols extracted from American oak chips in a port wine. This supports the findings of the sensory differences found in this study, for these wines.

In summary, small differences in phenolic composition and sensory characteristics were found between the wines containing extract from air dried and kiln dried white oak chips. However, the results indicated
that the level of nonflavonoid phenols tended to be higher in wines from kiln-dried wood. In addition, the variability in nonflavonoid phenol content among the wood chips from individual logs appeared to be greater than that due to the method of drying wood staves.
Table 7. Schedule for increasing the drying temperatures of oak staves as related to decreases in moisture.

<table>
<thead>
<tr>
<th>Moisture Content (%)</th>
<th>Oven Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>≥ 40</td>
<td>38</td>
</tr>
<tr>
<td>≥ 30</td>
<td>43</td>
</tr>
<tr>
<td>≥ 25</td>
<td>49</td>
</tr>
<tr>
<td>≥ 20</td>
<td>54</td>
</tr>
<tr>
<td>≥ 15</td>
<td>77</td>
</tr>
</tbody>
</table>

Table 8. Wine analysis of Seyval blanc wine after aging with oak chips made from kiln and air dried staves.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Color 1</th>
<th>Total phenols 2</th>
<th>Nonflavonoid phenols</th>
<th>Gallic acid (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>.072</td>
<td>282</td>
<td>207</td>
<td>1.2</td>
</tr>
<tr>
<td>Air dried oak</td>
<td>.096A</td>
<td>327A</td>
<td>257A</td>
<td>2.6A</td>
</tr>
<tr>
<td>Kiln dried oak</td>
<td>.099A</td>
<td>329A</td>
<td>262A</td>
<td>3.1A</td>
</tr>
</tbody>
</table>

1 Absorbance at 420nm.
2 Total phenols and nonflavonoid phenols listed as mg/L gallic acid.
3 Not included in statistical analysis.
4 Means within columns are not significantly different.
5 Average of three replications.
Table 9. Increases of the concentrations of nonflavonoid phenols in Seyval blanc wine aged with wood chips made from kiln and air dried oak staves of several wood samples.

<table>
<thead>
<tr>
<th>Drying Treatment</th>
<th>Increases (^1) of the concentrations of nonflavonoid phenols by wood samples (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air dried</td>
<td>44</td>
</tr>
<tr>
<td>Kiln dried</td>
<td>56</td>
</tr>
</tbody>
</table>

\(^1\) Individual wine value minus control wine value (207).
\(^2\) Ohio, Kentucky and West Virginia sites; replications A, B and C.

Table 10. Variability in the extraction of nonflavonoid phenols from oak chips from the same log\(^1\) by Seyval blanc wine.

<table>
<thead>
<tr>
<th>Drying Treatment</th>
<th>Nonflavonoid phenols Mean values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Air dried (rep. 1)</td>
<td>244 (\pm 4.6)</td>
</tr>
<tr>
<td>Air dried (rep. 2)</td>
<td>235</td>
</tr>
<tr>
<td>Air dried (rep. 3)</td>
<td>241</td>
</tr>
<tr>
<td>Kiln dried (rep. 1)</td>
<td>246 (\pm 2.9)</td>
</tr>
<tr>
<td>Kiln dried (rep. 2)</td>
<td>241</td>
</tr>
<tr>
<td>Kiln dried (rep. 3)</td>
<td>241</td>
</tr>
</tbody>
</table>

\(^1\) Oak chips from the West Virginia A log.
\(^2\) Mean separation by L.S.D., 0.05 level.

Table 11. Results for the triangle test for taste differences in Seyval blanc wine aged with kiln and air dried oak chips.

<table>
<thead>
<tr>
<th>Difference between kiln and air dried oak</th>
<th>Total responses</th>
<th>Correct responses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40</td>
<td>16*</td>
</tr>
</tbody>
</table>

\(^*\) N.S.
LITERATURE CITED


CHAPTER III
PHENOLIC ANALYSIS OF PLAIN AND TOASTED WHITE OAK
CHIPS USED IN AGING SEYVAL BLANC WINE

Charring the insides of whiskey barrels has been shown to increase the level of color, solids, fixed acids, tannins and aromatic aldehydes extracted by ethanol solutions (Reazin, 1981). Toasting the interiors of wine barrels is a milder heat treatment than charring and is likely to have a similar effect upon wine characteristics. Changes in the extractive properties of wine barrels due to toasting is suggested by the wide range of toast levels available. Oak chips are also available in a toasted form.

In an effort to determine if toasting has a similar effect on the extractive properties of white oak as charring, toasted white oak chips were compared to plain white oak chips. Chips of both plain and toasted oak were extracted with Seyval blanc wine for one week. The wines were analyzed for color, nonflavonoid phenols, total phenols and gallic acid.

Materials and Methods

Oak chips. The oak chips used in this experiment were obtained from a composite sample of white oak chips having an average moisture content of 15 percent. The moisture contents of the oak chips in this experiment were determined in the same manner as in Chapter II. The dimensions of the oak chips were approximately 0.2 to 0.5 cm thick, 1 to 3 cm long and 1 cm wide.
Heating treatments. For toasting, chips were placed in a rotating drum heated by a gas flame. Two toasting levels were achieved by removing the oak chips after 25 and 45 minutes. The normal commercial heating period was 45 minutes. The moisture contents for both heated chip samples were about 1 percent after heating, and increased to approximately 2 percent before adding to the wine. The oak chip samples which were heated for 25 minutes appeared to be similar to the unheated chips except having a slightly darker tan color. The oak chips heated for 45 minutes turned a dark brown color throughout; however, no evidence of charring was noted. These chips also acquired a smoky odor. This odor was probably due to the formation of compounds which are common to wood smoke. Wood smoke compounds have been found in white oak charred during the formation of whiskey barrels (Maga, 1985).

Wine. The wine used in this experiment was a 1983 Seyval blanc vinified by Chalet Debonne Vineyards in Madison, Ohio. The grapes were grown in the Finger Lakes region of New York. All containers were filled from a single tank.

Oak chip extractions. Plain and toasted oak chips were added to 1.9 L glass containers containing Seyval blanc wine at a concentration of 5.13 g/L on a dry weight basis. Containers containing Seyval blanc without the addition of oak chips were kept as controls. The oak chips were extracted for one week at 17 C. There were three replications per treatment.

Chemical analysis. Color and total phenols were analyzed according to Amerine and Ough (1980). Nonflavonoid phenols were analyzed according to Amerine and Ough (1980). This method included nitrogen sparging and
closing the test tubes after the addition of formaldehyde (Kramling and Singleton, 1969).

**HPLC analysis.** The same equipment and analysis procedure listed for the determination of gallic acid in Chapter II was employed.

**Results and Discussion**

The results for the chemical analysis of the experimental wines are presented in Table 12. There was a similar increase in color, gallic acid, nonflavonoid phenols and total phenols, with the addition of oak chips, for the plain and 25 minute chip treatment wines. Heating the oak chips for 25 minutes apparently had little effect on these parameters.

The 45 minute chip treatment wines had increases in color, nonflavonoid phenols and total phenols which were approximately 50 percent less than those found for the plain and 25 minute chip treatment wines (Table 12). There was no appreciable increase in gallic acid for the 45 minute chip treatment wines (Table 12). During the experiment, a slower saturation process was observed for the 45 minute oak chips (4 to 5 days) than the other oak chips (1 to 2 days). This was measured by the amount of time required for the chips to drop to the bottom of a container of wine. This suggests that the slower saturation process for the 45 minute chips caused the reduction in color, nonflavonoid phenols and total phenols extracted by wine. However, this observation does not totally explain the lack of an increase in gallic acid in the wines which had contained the 45 minute chips. Hennig and Burkardt (1962) found that gallic acid was absent during the first few days of an oak chip extraction, but later it was a major component. It appears that a longer time
period was needed to saturate the 45 minute chips with wine and to extract gallic acid.

The reduced reactivity of the oak chips to the extraction of phenols by wine, after being heated for 45 minutes, was not expected, considering the effect of charring on whiskey barrels (Reazin, 1981). Although toasting for 45 minutes did change certain chip characteristics (browning, slower moisture uptake), an actual charring process may be needed to increase the level of phenolic compounds extracted by wines. The use of higher alcohol concentrations in the extraction solution and a longer extraction period may have provided results similar to those found for distilled beverages aged in charred barrels (Reazin, 1981).

Whether or not differences in the type of compounds extracted from toasted and plain oak chips do exist is not known. Considering the lower levels of gallic acid extracted from the 45 minute chips and their smoky odor, qualitative differences seem likely for certain constituents in wines which are treated with plain and toasted oak chips.

In summary, the level of phenolic compounds extracted by wine from oak chips was reduced by toasting the chips to a brown color. This was in contrast to the findings for charred whiskey barrels extracted by distilled spirits (Reazin, 1981). In this study, results indicated that the lower levels of phenolic compounds extracted from the toasted oak chips may be due to their greater resistance to moisture uptake. The formation of wood smoke compounds is thought to have occurred in the oak chips after heating for 45 minutes, as they developed a smoky odor.
Table 12. Wine analysis of Seyval blanc wine after aging with plain and toasted oak chips.

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Color 1</th>
<th>Total phenols 2</th>
<th>Nonflavonoid phenols 2</th>
<th>Gallic acid (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 3</td>
<td>.077A 4,5</td>
<td>262A</td>
<td>211A</td>
<td>1.2A</td>
</tr>
<tr>
<td>No heating</td>
<td>.101C</td>
<td>295C</td>
<td>249C</td>
<td>2.3B</td>
</tr>
<tr>
<td>25 min. heating</td>
<td>.103C</td>
<td>301C</td>
<td>247C</td>
<td>2.2B</td>
</tr>
<tr>
<td>45 min. heating</td>
<td>.092B</td>
<td>279B</td>
<td>231B</td>
<td>1.3A</td>
</tr>
</tbody>
</table>

1 Absorbance at 420 nm.
2 Expressed as mg/L gallic acid.
3 Wine without the addition of oak chips.
4 Mean separation within columns by Duncan's New Multiple Range Test, .05 level.
5 Average of three replications.
LITERATURE CITED


GENERAL DISCUSSION AND CONCLUSIONS

Through history, the main purpose of oak barrels has changed from providing a means of storing wine with minimal oxygen exposure to producing wines with specific flavors and bouquets. There appears to be a lack of available information which provides a good understanding of the phenomena occurring in wine barrel aging. Specifically, more information is needed concerning those factors which influence the extraction of compounds from oak, and the functional properties of oxygen during barrel aging of table wines.

Recently, the use of oak chips has been suggested as a means of adding oak extract to wine without investing in oak barrels. In this study, taste panelists were able to distinguish between wines aged in stainless steel tanks with oak chips and similar wines aged in new oak barrels. Variations in oxygen exposure between these wines may in fact be the primary cause for the sensory quality differences. Results of this study indicated that the addition of chips to increase oak extractants in wines aged in used barrels may be a useful vinification procedure. Wines aged by this technique were found to be similar to wines aged in new barrels, when compared by sensory tests. This also suggests that oxygen exposure rather than the extraction of oak components was the major cause for quality differences between wines aged in new barrels and stainless steel tanks with oak chips. Additional studies are needed to better understand the effect of oxygen exposure on the composition and
quality of wines aged in oak barrels. This research is essential before developing and recommending the aging of wines in stainless steel tanks with oak chips to simulate the use of new oak barrels.

Kiln drying of wood staves is popular, for this process requires less time to dry than air drying outdoors. Results of previous research have indicated possible differences between extracts from kiln and naturally dried oak staves (Pontallier et al., 1982). In this study, kiln and naturally dried oak staves were compared for sensory and phenolic differences, when extracted by wine. Although these differences were not significant, there was a slight trend for a higher level of phenolic compounds extracted from kiln dried staves. Further investigations concerning wine differences from barrels constructed of kiln and air dried wood would be important. Particularly, the determination of any structural differences between kiln and air dried wood and their effect on wine quality.

Recently, wine barrels of different toasting levels have been made available to the industry. While some information is available about charring, few studies have been made on relating wine composition and quality to toasting of barrels. In this study, toasted oak chips, to simulate toasted barrels, were extracted by wines for one week. Results indicated that toasting the oak chips until they browned reduced the level of color, total phenols, nonflavonoid phenols and gallic acid extracted by wine. This reduction was possibly due to the longer time required for the 45 minute chips to become saturated with wine than plain oak chips. Changes in the type of compounds extracted from oak chips due to toasting was suspected, for the 45 minute chips developed a smoky odor.


