Factors affecting the influence of oak chips on wine flavour

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INTRODUCTION
Demand for the flavour associated with oak maturation of wine has resulted in the continuation of oak barrel use, despite the inherent costs, associated labour requirements, and the availability of stainless steel storage vessels to the modern winemaker. Although maturation in oak casks remains the preferred form of oak usage with higher quality wine, cost effective alternatives are also available. These alternatives include oak chips, shavings and larger pieces of oak (e.g. DeGaris 1991, Hooper and Marks 1992). Off-cuts are commonly used, as they are of unsuitable dimensions for stave production in barrel manufacture (Spillman 1999).

The impact of oak on wine flavour is derived primarily from extraction of volatile aroma and flavour compounds from oak into wine. Some of these important compounds and their aroma thresholds and descriptors are listed in Table 1. Previously, we have published a table of similar data for 17 target oak compounds (Spillman et al. 2004b). Some oak-derived compounds, such as the cis-isomer of the oak lactones, are present in significant quantities in untreated oak, but others (e.g. vanillin, guaiacol, 4-methylguaiacol and furfural) are formed mainly from oakwood polymers that are broken down by heat (during cooperage), hydrolysis (by wine acids) or a combination of both (Reazin 1981, Chatonnet et al. 1989, Hale et al. 1999). Therefore, alternative oak products are often heated in order to mimic the sensory effect of oak barrel usage.

Apart from the origin and composition of raw oak products, a number of factors have the potential to determine the sensory outcome of using oak chips or oak barrels in winemaking. For oak fragments, these include chip size, chip heating time and temperature, timing of oak addition and the time in contact with wine, pre-treatment of chips with sulfur dioxide and shelf life of chips.

OAK CHIP SIZE
Numerous investigations, including a major study by us (Spillman et al. 1997, 1998, 2004a) have shown that the evolution of oak-derived flavour compounds in barrel-aged wines continues over a prolonged period, sometimes over several years. This is probably due, in part, to the time taken for wine to penetrate the oak staves and for flavour compounds to permeate back into the wine, but could also be due to a continual formation of these compounds in the wood matrix during maturation. With smaller oak pieces, we might expect extraction to take place much faster due to the large surface area, especially with fine shavings, and this expectation can be confirmed by experimental evidence. Thus, a comparison of extraction of cis-oak lactone into wine from larger oak fragments (average size of 15 x 15 x 5mm) with that extracted from the same quantity but smaller fragments (10 x 2 x 2mm) from the same sample of wood (Figure 1) shows that a greater amount of this compound was extracted from the finer fragments over a 30-day period. The extraction from the finer shavings was rapid during the first seven days, after which there was little increase in cis-oak lactone concentration in the wine. A

<table>
<thead>
<tr>
<th>Compound</th>
<th>Aroma descriptors</th>
<th>Threshold (µg/L)</th>
<th>Medium</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>guaiacol</td>
<td>smoky</td>
<td>20</td>
<td>white wine</td>
<td>1</td>
</tr>
<tr>
<td>4-methylguaiacol</td>
<td>smoky</td>
<td>65</td>
<td>red and white wines</td>
<td>2</td>
</tr>
<tr>
<td>cis-oak lactone</td>
<td>coconut, oak, vanilla, fruity, woody, caramel</td>
<td>20</td>
<td>white wine</td>
<td>3, 4, 5</td>
</tr>
<tr>
<td>(natural isomer)</td>
<td></td>
<td>54</td>
<td>red wine</td>
<td>3, 4, 5</td>
</tr>
<tr>
<td>trans-oak lactone</td>
<td>coconut, oak, weedy, woody, hay, jasmine</td>
<td>140</td>
<td>white wine</td>
<td>3, 4, 6</td>
</tr>
<tr>
<td>(natural isomer)</td>
<td></td>
<td>370</td>
<td>red wine</td>
<td>3, 4, 6</td>
</tr>
<tr>
<td>vanillin</td>
<td>vanilla, vanillin</td>
<td>400</td>
<td>white wine</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>320</td>
<td>red wine</td>
<td>2</td>
</tr>
</tbody>
</table>

Table compiled from the following references: Simpson et al. 1986 (1), Boidron et al. 1988 (2), Brown et al. 2006 (3), Spillman et al. 2004b (4), Wilkinson et al. 2004b (5), Günther and Mosandl 1986 (6).
similar trend was seen for this and other analytes in other oak samples previously analysed.

Although the evolution of volatile compounds from fine shavings into model wine was complete or near-complete after only a few days, the oak shavings were not entirely depleted of extractable material. When fine shavings were added at a dose of 10g/L, and repeatedly extracted with four successive volumes of fresh model wine, around 90 to 98% of the total extractable guaiacol and 4-methylguaiacol, but only 70 to 85% of the oak lactone isomers, was recovered in the first soaking. Most of the remainder was extracted into the second soak. At a dosage of 100g/L, extraction efficiency was even less, with only 45 to 60% of the total extractible analytes found in the first soak, and significant amounts (10 to 15% of the total extracted over the four successive soakings) were recovered in the final soak. Thus, preparing concentrated extracts of oak shavings in wine and then diluting these ten-fold with untreated wine will not have the same sensory effect as simply adding shavings to the total wine volume at one-tenth of the dosage.

Chip size does not just affect the rate and extent of extraction of oak volatiles into wine. Apart from purely practical considerations such as the greater combustibility of finer shavings, the greater surface area to volume ratio of shavings compared to larger oak pieces has a significant effect on the outcome of heating oak pieces, probably because of the importance of air contact to this process (Campbell et al. 2005). For oven-heated samples, we found that finer shavings gave a greater yield of volatile phenols. This was particularly the case with vanillin, as illustrated in Figure 2 (Campbell et al. 2005). Another study (Giménez Martínez et al. 2001) conducted under different conditions indicated that, for chips greater than 5mm in diameter, the concentrations of vanillin was also approximately inversely proportional to the particle size. However, for oak particles ranging in size from < 0.1mm up to 5mm in diameter, the opposite effect was observed. It is possible that the very small particles gave a greater evaporative loss of these volatiles in their study.

POST EXTRACTIVE FORMATION OF OAK-DERIVED VOLATILES

Singleton and Draper (1961) have reported that oak aroma in wine treated with oak chips appeared to increase over time after oak chips were removed. Such an observation could be due to one or both of the two following factors. The first is that the increase in oak aroma could have been stemming from a sensory ‘unmasking’ effect, that is, the aroma of a given concentration of oak components becomes more apparent with time as other aromas (fermentation or grape-derived) are muted by the ageing process. The second possibility is that the concentration of oak compounds in wine might continue to increase during wine maturation as a result of chemical formation from soluble precursors. This latter possibility has been suggested by several observations. Firstly, although both guaiacol and 4-methylguaiacol are considered to be primarily products of toasting and are significant components of wood smoke, these two compounds show quite different profiles of extraction from oak barrels over a two year period (Spillman et al. 1998). Guaiacol was extracted most rapidly in the first six weeks, but then continued to accumulate in a near-linear fashion for the remainder of the barrel storage period, whereas 4-methylguaiacol did not increase significantly in concentration beyond the first year of storage. The accumulation curve for vanillin was asymptotic during the
first 32 weeks and linear thereafter, indicating more than one mechanism for forming this compound in oak extracts. Finally, the accumulation curve for cyclotene was linear throughout the entire maturation period. This is consistent with this compound being generated by slow acid hydrolysis of precursors formed during coopering (Spillman et al. 1998). Although cyclotene itself is unlikely to have any major impact on wine aroma, this behaviour illustrates the importance of processes other than simple extraction in determining the composition of barrel-aged wines. None of these observations, however, demonstrate whether the precursors to these compounds were extracted into solution and then hydrolysed or remained bound to the wood and were hydrolysed within this matrix.

More recently, we showed that the time necessary for the ring-opened (odourless) precursor of cis-oak lactone to close completely to the lactone (odour-active) could be of the order of several weeks, depending on wine pH (Wilkinson et al. 2004a). Therefore, the aroma of any cis-oak lactone that might have been extracted from oak shavings as the ring-opened precursor would not necessarily reach full intensity until sometime after such shavings were removed from the wine and the lactonisation was completed.

In order to explore the possible importance of hydrolytic processes to the continued formation of oak-derived volatiles after the removal of oak shavings from wine, we prepared model wine extracts of both heated and unheated shavings of three oak samples, one French (Troncais, *Quercus sessile*), and two American (*Q. alba*). The shavings were then removed from the wine and the solutions stored at 50°C for 80 days, under air or with inert gas protection (Campbell 2001).

The evolution of guaiacol in model wine extracts after the oak had been removed was constant over the whole period, and a significant proportion (up to 25% of the total) was formed after the shavings were removed from the model wine. Smaller increases in 4-methylguaiacol were also observed, with maximum concentrations being reached after 10 to 20 days following removal of the shavings. There was a significant (25% of the total) evolution of cis- and trans-oak lactone in the first 10 days following removal of the shavings, only for a medium grained American oak sample. This sample was the only sample of the three that contained significant amounts of extractable oak lactone.

Vanillin showed the largest increase in concentration following removal of the shavings. The percentage of vanillin generated in model wine filtered oak extracts stored under inert gas cover after 40 days at 50°C varied considerably between the experiments (from 10 to 50% of the final vanillin concentration). The generation of vanillin was also enhanced by the presence of air in all of the extracts (Campbell et al. 2005). This effect of air was smaller for other analytes and not observed for all oak samples.

These results demonstrate that soluble precursors are capable of forming additional amounts of oak-derived volatiles in wine once alternative oak products are removed.

We next took samples of pre-extracted oak shavings and resuspended them in fresh model wine and heated the mixture for 80 days at 50°C. The amount of vanillin in the suspensions was, at first, low. However, the additional vanillin generated over time was substantial (e.g. Figure 3), and approximately three times that generated from extractable precursors following removal of the shavings. None of the other analytes (guaiacol, 4-methylguaiacol and the oak lactone isomers) were formed in significant quantity in the suspensions of the pre-extracted shavings.

From the limited number of samples studied so far, vanillin appears to be formed in sensorially significant quantities by mechanisms other than pure extraction, but this takes place primarily during the time period in which the wine typically remains in contact with the wood. Smaller amounts of guaiacol and cis-oak lactone could also be formed from soluble precursors for some samples. A larger study of many different oak samples needs to be conducted before we can determine whether additional oak aroma can be generated (following removal of shavings from the wine) in amounts that are significant in comparison to the normal variation in oak composition that results from different toasting levels or raw oak composition.

**THE EFFECT OF PRE-TREATMENT OF OAK SHAVINGS WITH SULFUR DIOXIDE**

Sulfur dioxide (SO$_2$) is widely used in wineries as an antimicrobial and antioxidation agent. Barrels are often soaked with an aqueous solution of SO$_2$ (approximately 4g/hL water of sulfur) prior to use, and after each use. An alternative barrel sanitising method, sometimes employed by coopering companies, is to gas barrels with SO$_2$ prior to sale and transportation (Boidron 1994).

To date, there has been little work completed that specifically examines the effects of sulfur dioxide on oak-derived volatiles in wine. Towey and Waterhouse (1996) briefly address this variable, having observed that increased levels of oak lactones in second use barrels result from barrel soaking in aqueous solutions containing SO$_2$. They suggested that SO$_2$ might aid in the dehydration of a postulated open

![Figure 3. Evolution of vanillin in model wine soakings of heated, then pre-extracted oak shavings. Soakings were stored at 50°C for 80 days.](image-url)
chain hydroxy acid precursor that results in the lactone form, but this speculation has been refuted by Wilkinson et al. (2004a). In a report on barrel maintenance (Boidron 1994), the effect of SO₂ soaking barrels prior to use appeared to increase levels of both cis- and trans-oak lactone.

In our trial, unheated and ‘medium’ heated (200°C for one hour) samples of French and American oak, contained in Schott bottles, were exposed to excess SO₂ gas to fill the Schott bottles, which were then sealed and kept for one hour at room temperature. Following this period, SO₂ treated and untreated samples were soaked in model wine under anaerobic conditions.

The largest effects were observed for vanillin. In all the oak wood types investigated, unheated and heated, of both French and American origin, vanillin was extracted to a larger extent (15 to 65% more) in the oak samples that had been treated with SO₂ (Figure 4) when compared to the control samples that had been exposed to air instead of SO₂. A possible mechanism for increased vanillin extraction from oak treated with SO₂ might be through the antioxidative action of this compound inhibiting vanillin degradation.

The heated American oak also showed the largest effects for other compounds (Figure 4), for example a small but significantly higher production of cis-oak lactone with SO₂ treatment. However, in the other wood samples, cis-oak lactone was always in greater concentrations in the wood not treated with SO₂, although none of these latter results were statistically significant.

Thus, pre-treatment of oak with SO₂ can result in increased extraction of cis-oak lactone and vanillin for some types of oak.

‘SHELF’ LIFE OF OAK CHIP SAMPLES
Oak chips are often left in plastic bags and other containers, for significant periods of time, before use in winemaking. We, therefore, conducted an experiment that was aimed at determining the effect of this prolonged storage on the concentration of extractable oak-derived volatile compounds.

For the experiment, model wine extracts of commercial French oak chips which had been toasted over an oak-fuelled fire (of the same oak) for increasing times, for ‘light’, ‘medium’ and ‘heavy’ toast, were analysed, along with a commercial sample of American oak chips which were oven-heated in our laboratory at 175°C for one hour or at 200°C for three hours.

The first analyses of the extracts of oak chips were completed immediately after the purchase of new chips, to best represent the initial sampling time, prior to storage. After six months, the chips were sampled a second time and extracted with model wine. At each sampling date, two dosage levels were used, and duplicate preparations were completed. Between the two sampling dates there was no significant difference in the concentration of guaiacol, 4-methylguaiacol, cis- and trans-oak lactone or vanillin after 28 days extraction. Thus, storage of these chips did not affect the level of extractable oak-derived volatiles measured.

CONCLUSIONS
Several experiments to determine the importance of some of the variables that could influence the impact of oak chip use on wine composition are described here. These studies are by no means exhaustive, and do not include experiments with larger, plank-sized oak pieces such as oak staves. We have also not investigated the effect of the timing of oak addition, although there is much evidence in the literature to indicate that most of the vanillin that is rapidly extracted will be converted to relatively odourless derivatives up to the end of primary fermentation.

It is not easy to predict, in more than a very general way, the outcome of using a particular batch of chips or shavings during winemaking because of the large number of variables that can determine the composition of oak pieces. One option is to treat a small volume of finished wine with various oak products (or blends of these products) and assess the results sensorially, but this is of limited use if the intention is to add the oak at the start of fermentation. An alternative is to determine the composition of oak extracts analytically. To make use of such data will require an understanding of the relationship between wine composition and sensory properties which can only be gained from experience and further research.

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