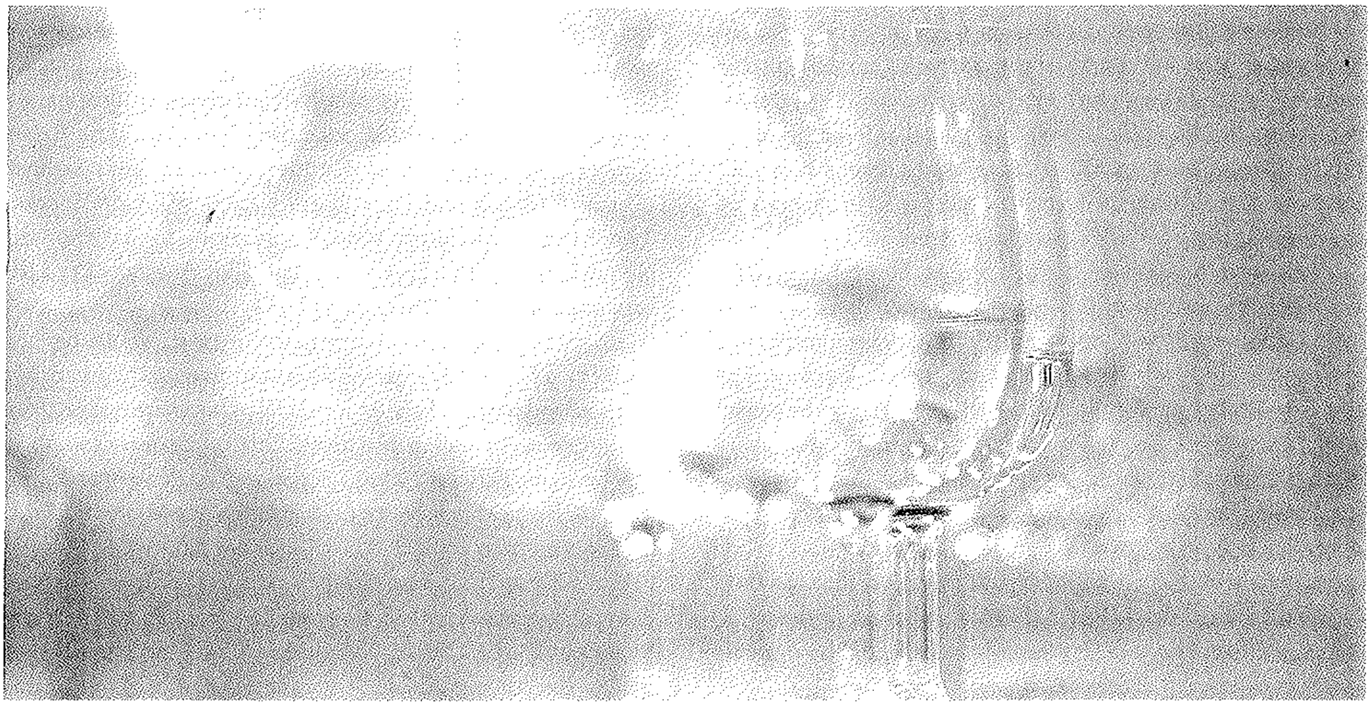

Flavour 'scalping' by wine bottle closures

— the 'winemaking' continues post vineyard and winery

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The AWRI Report
The Australian Wine Research Institute

OBJECTIVE MEASUREMENTS of winegrape quality are difficult to achieve, not the least because the relationship between winegrape composition and the final product that reaches the consumer depends on a myriad of influences beyond the vineyard. Nowhere is this more evident than with the volatile wine components that are responsible for a wine's aroma and also contribute in a major way to wine flavour.

A few wine flavour compounds that are formed in the grape remain largely unchanged for much of the lifetime of a wine. *iso*-Butylmethoxypyrazine, which is said to confer an 'herbaceous' or 'vegetative' character to wine and is particularly important to Sauvignon Blanc and Cabernet Sauvignon wines, is one such compound (Allan and Lacey 1999). However, for most of the volatile flavour components of wine, no more than a tiny proportion (if any) are present in the grape at harvest, and the composition of the volatile components of wine usually bears little resemblance to that of the fruit from which it was made.

Many volatile wine flavour compounds are released during vinification, maturation and storage from involatile grape-derived precursors, either by wine micro-organisms or by chemical reactions in the wine medium. Simple metabolites of wine micro-organisms as well as some volatile oak constituents can also have a major impact on wine flavour.

The flavour of wine continues to change while it is in the bottle. Some flavour compounds found in young wines will disappear over time mainly as a result of both oxidative and non-oxidative transformations, while new flavour compounds can also be generated by these chemical reactions. Even wine bottle closures can have an impact on wine flavour.

THE IMPACT OF CLOSURES ON WINE AROMA AND FLAVOUR

It has long been recognised that wine bottle closures play a role in the way wine flavour changes during bottle storage,

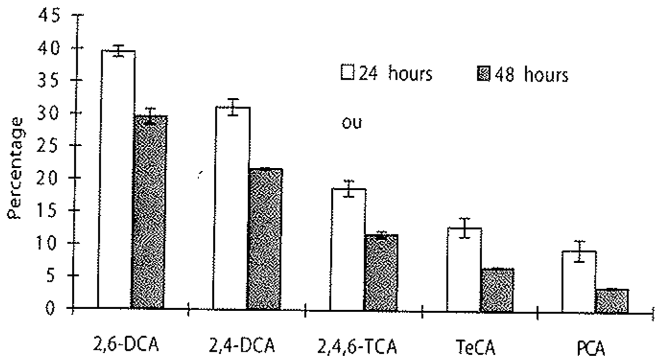

Figure 1. Proportions of chloroanisoles remaining in 200 mL of white wine following the immersion of four single piece straight wine corks for 24 or 48 hours (Capone et al. 1999). 95% confidence intervals are shown.

principally by acting as a partial barrier to the transmission of oxygen. The occasional extraction of 2,4,6-trichloroanisole (TCA) from cork bark closures into wine is well known as a means whereby an unwanted musty aroma can be imparted to wine, and there is some evidence that other constituents of closures can also be extracted into wine with various effects on wine aroma and flavour (Amon et al. 1989 [Institute publication #337], Simpson 1990 [Institute publication #375]).

Over the past several years, the AWRI has placed a strong focus on cork-derived wine taint research and the factors that influence the frequency and intensity of unwanted musty aromas in wine. Although not all cases of musty wine taint have their origin in wine corks (for example, mouldy barrels and wood products contaminated during shipping have also been implicated), it is clear from the various cases investigated by the Industry Services section of The AWRI that TCA derived from cork closures is responsible for the majority of such problems.

The fact that cork closure production mostly takes place on the other side of the world to Australia was an obvious barrier to our being able to conduct useful investigations into cork/oak forest management or cork bark handling in the factory. Instead, we chose to focus on the transmission of TCA between wine and cork closure in the bottle. There were many outcomes from this work; not the least was our ability to distinguish between cases in which TCA was derived from cork from those in which it was already present in the wine (Capone et al. 1999 [Institute publication 616]). It soon became obvious that, although wine could extract a small proportion of TCA from cork closures, corks could also absorb a much higher proportion of TCA and other chloroanisoles from wine (Figure 1) and, indeed, we observed one case in which wines that had become tainted with tetrachloroanisole through contact with contaminated oak were 'cleaned up' as a result of the cork closures absorbing this unwanted musty-smelling compound from the wine (Capone et al. 1999 [Institute publication #616]). This capacity for corks to absorb TCA from wine also had implications for the way many wineries and cork supply companies assessed batches of corks for possible TCA contamination prior to use.

Our observations of the absorptive capacity of cork closures for chloroanisoles led us to question whether 'normal' wine flavour components could also be absorbed. It was well known that packaging components for other food products can also modify product quality by absorbing aroma compounds from the product, a process sometimes known as 'flavour scalping'. We, therefore, set up a long term trial to study the absorptive capacity ('flavour scalping') of various wine bottle closures. The closures used in this trial were from the same batches used in the AWRI's earlier closure trial (bottling in May 1999) that focused on white wine oxidation and sensory properties (Godden et al. 2001 [Institute publication #666]). They comprised a Roll-On Tamper Evident screw cap (ROTE) (wadding material type: EPE30A faced with aluminium/PET at 2.0 mm caliper), two grades of natural bark cork (Reference 2 and 3), a technical cork closure, and seven synthetic closures. We also carried out some preliminary trials with 'bag-in-box' packaging which showed that certain wine flavour compounds could be partially removed by the packaging in an extremely short time frame (Pollnitz et al. 2002 [Institute publication #702]).

Absorption of flavour compounds can be determined in one of two ways—either directly, by extracting the closures themselves and analysing the extracts for absorbed compounds; or indirectly, by determining the decrease in concentration of these compounds in wine during storage. For technical reasons, the latter option is far more practical and was the approach taken in this study. In this case, it was also essential to have control samples stored with and without air in all-glass containers (sealed ampoules), so that the loss of wine components by chemical degradation could be distinguished from loss by absorption.

We were interested to observe the effects of bottle closures on a range of flavour compounds, and since no one

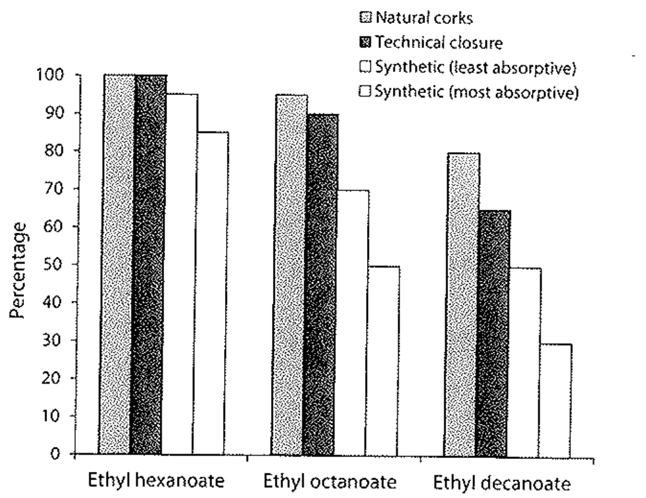

Figure 2. Proportions of ethyl esters remaining in white wine stored in 750 mL bottles sealed with various closures for two years. The proportions are expressed as the mean concentration of esters in five replicate treatments per closure type, as a percentage of the mean concentration in three control wines stored in glass ampoules for the same period.

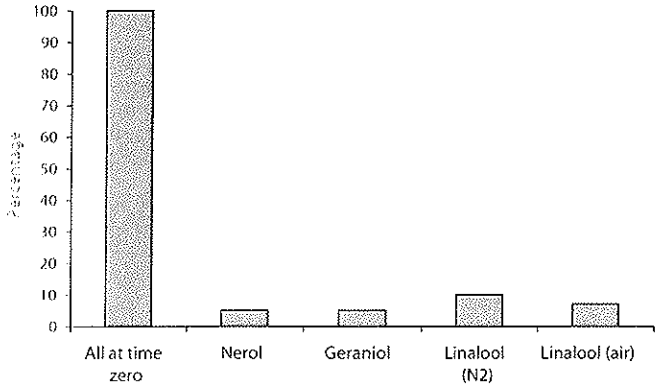

Figure 3. Proportion of monoterpenes remaining in white wine stored in sealed glass ampoules for two years. Proportions are a percentage of the concentration of the monoterpenes at the time the ampoules were sealed (time zero).

wine contains all flavour compounds in measurable concentrations, we spiked a Semillon wine with each of the volatile compounds we wished to study. The wine was then bottled and the bottles sealed with the closures listed above. The bottles were then stored in an inverted position in a near constant temperature storage facility also used for the AWRI's original closure trial (Godden et al. 2001 [Institute publication #666]).

After two years of bottle storage, the concentration of some, but not all, of the flavour compounds added to the wine changed significantly. Some of these changes can be attributed to absorption by the closures, and others to chemical modification which took place regardless of how the wine was sealed.

In no case was there any evidence of absorption of any of the flavour compounds from the wine sealed under ROTE closure. Where the concentration of compounds had decreased during the storage period in wine sealed under ROTE, similar decreases in concentration was observed for control samples sealed in glass ampoules.

Neither *iso*-butylmethoxypyrazine nor the oak-related components (guaiacol, 4-methylguaiacol, vanillin, *cis*- and *trans*-oak lactone, 4-ethylphenol and 4-ethylguaiacol) changed concentration significantly in either the controls or bottled wines over the two year period. All of these compounds were chemically stable in this white wine (including control wines stored under air) and were not affected by bottle closures.

The concentration of the simple fermentation esters changed in the control wines presumably as a result of competing hydrolysis and esterification reactions in the wine. Some esters increased in concentration while others decreased. These changes cannot be extrapolated from this wine to others, because the factors affecting such changes (relative starting concentrations of esters and their corresponding acids) varies from one wine to another. Some esters were also affected by the closures (other than ROTE) to varying degrees. The short chain ethyl isobutyrate, ethyl butyrate and ethyl isovalerate were unaffected by the closures. Ethyl hexanoate, ethyl octanoate and ethyl decanoate were all partially absorbed by the closures, and for each closure type, the amount of absorption increased with increasing ester chain length (Figure 2).

Both natural closure types (Reference 2 and 3 corks) absorbed no ethyl hexanoate, 5% of ethyl octanoate and 20% of ethyl decanoate. The technical closure absorbed slightly more of these last two compounds (10% and 35% respectively). The synthetic closures showed significantly greater absorption of these esters. For ethyl hexanoate the absorption was slight, ranging from 5% (in three closures) to 15% (in two closures). Ethyl octanoate absorption varied from 30% (two closures) to 50% (one closure), and ethyl decanoate from 50% (two closures) to 70% (one closure).

There appeared to be little effect of the closure type on the concentration of the monoterpenes linalool, geraniol and nerol. The overwhelming factor affecting the concentration of these compounds in the wines was chemical degradation. At wine pH, nerol and geraniol are converted mainly to linalool which is in turn converted to the relatively weak-smelling alpha terpineol and terpin hydrate. In these trial wines, less than 5% of the added nerol and geraniol and 10% of the added linalool remained after two years. In the control samples, headspace had some effect, with a reduction of linalool concentration of approximately 30% in control wines stored under air compared to those stored under nitrogen (Figure 3).

The monoterpene rose oxide, which gives a 'lychee' character to some white wines, was partially absorbed by the synthetic closures only. This absorption ranged from 15% to 45%.

The taint compound naphthalene (added to give an indication of the absorption of structurally similar compounds) was substantially absorbed, particularly by the synthetic closures. The least absorptive of these removed 75%, while 90% was removed by the most absorptive synthetic closure. The natural and technical corks absorbed less of these compounds (30% and 40% respectively) (Figure 4).

The grape-derived hydrocarbon known as TDN can give a kerosene-like flavour to some white wines. It can some-

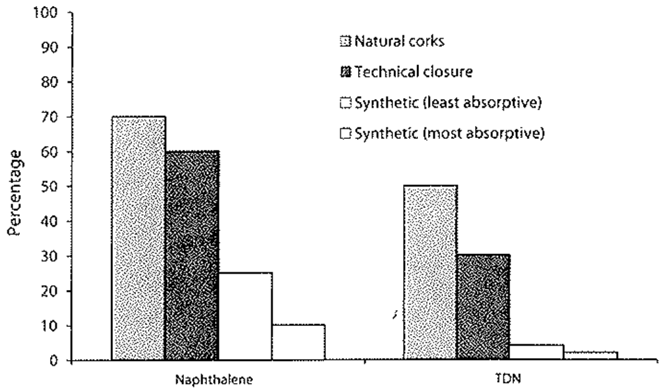

Figure 4. Proportions of naphthalene and 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) remaining in white wine stored in 750 mL bottles sealed with various closures for two years. The proportions are expressed as the mean concentration of naphthalene or TDN in five replicate treatments per closure type, as a percentage of the mean concentration in three control wines stored in glass ampoules for the same period.

times be found in relatively high concentrations in Riesling wines, particularly those that have been in bottle for two years or more. This compound was the most strongly affected by the closures (with the exception of the ROTE) (Figure 4). All of the synthetic closures had removed between 96% and 98% of the TDN after two years. The natural corks and technical closures removed 50% and 70% respectively, while the ROTE closures removed none at all. TDN is sometimes regarded as undesirable when present in high concentration, so the capacity of closures to remove this particular flavour compound (and perhaps others) from wine is certainly not always deleterious to wine quality.

In summary, relatively non-polar volatile compounds were absorbed by synthetic and natural cork closures, but not by ROTE screw caps. The more polar compounds were not absorbed at all by any closure. Synthetic closures showed a much greater capacity to absorb non-polar compounds than did natural cork bark or technical closures. The technical closure behaved in a similar fashion to the natural corks but had a slightly higher capacity for absorption. Among the synthetic closures, some consistently appeared to have had a higher capacity for absorption than others. Some compounds (oak components, *iso*-butylmethoxypyrazine, 4-ethylphenol, TDN) were completely stable in wine, even with an air headspace, while others (monoterpenes, damascenone) were substantially degraded in the wine whatever the closure.

Further data analyses and interpretation of the data fron this study are currently under way. At this point in time, i appears clear that the choice of closure may have a dramat ic effect on wine sensory characteristics not only due t(gross oxidative changes and transfer of taint compound: described earlier (e.g. Godden et al. 2001 [Institute publica tion #666]) but also through direct absorption of com pounds to the closure material. As closure manufacturin technologies and materials are likely to change due to ongo ing commercial developments, winemakers must at al times conduct their own trials to make informed choice: about the closures most suited to their preferred styles o: wine and commercial objectives.

CONCLUSIONS

The results of this trial so far make it clear that modificatior of wine flavour in the bottle is not just as a result of chemical and microbiological transformations of wine components, but also partly due to the sorptive capacity of bottle closures. The observations made on TDN are a good case in point. Attempts to modify TDN concentration in Riesling wine by carrying out particular vineyard practices (Marais et al. 1992) are pointless if the wine is to be bottled and sealed with synthetic closures. On the other hand, if the wine bottles are sealed with ROTE closure then the outcome of viticultural practices intended to modulate the concentration of this compound in the finished wine will be magnified, compared to if the wine is bottled and sealed with natural cork closures.

ACKNOWLEDGMENTS

This project is supported by Australia's grapegrowers and winemakers through their investment body the Grape and Wine Research and Development Corporation, with matching funds from the Federal Government. We thank Alan Pollnitz for his expert technical advice and help in preparing the figures for this manuscript.

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