Evolution of red wines
III. Promotion of the maturation phase
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Die Entwicklung von Rotweinen
III. Beschleunigung der Reifungsphase


Es wurden stetige Veränderungen bei Komponenten festgestellt, die für Farbe, Geruch und Geschmack wesentlich sind; sie entsprachen den Veränderungen, die sich bei normaler Kühlage­ rung während eines viel längeren Zeitaumes einstellten. Die spektralen Veränderungen der Farb­ intensität und -tönung waren von einer raschen logarithmischen Abnahme der Anthocyankonzen­ tration bei Wärmebehandlung begleitet, während sich die Kontrollweine nur geringfügig veränder­ ten. In den behandelten Weinen stabilisierte sich die Färbung, bedingt durch die Zunahme oligomerer Farbstoffe.

Es gab keine analytischen oder sonstigen Hinweise auf den nachteiligen Einfluß einer derarti­ gen, zeitlich begrenzten Weinlagerung. Bei Shiraz-Weinen wurde die Entwicklung eines zarten Beerenaromas und -geschmackes festgestellt; gleichzeitig wurde zu Beginn der Wärmebehandlung die vermehrte Bildung von Damascenon beobachtet.

Key words: red wine, ageing, post fermentation care, heat, anaerobic storage, colour, anthocyanin, polyphenol, flavour, damascenone.

Introduction

Red wines of moderate to high phenolic extract are commonly conserved in oak barrels of casks for up to 2 years — the maturation phase — before their further development in bottle — the ageing phase. Typically, the purple tints of the young red wine are gradually lost, with colour change towards ruby red; and there is associated alteration of taste and flavour. This traditional process is in marked contrast with the modern technology for preparation of white wines, rosés and light red wines. Thus the use of stainless steel vessels, and of refrigeration, centrifugation and coarse to sterile filtration techniques enable the latter wine types to be made ready for marketing within a few weeks or months of vintage.

These technological differences are fundamentally due to the additional presence in red wines of pigments and tannins at high concentrations (2–4 g/l). There is then an intrinsic potential for progressive development of more complex taste and flavour characteristics during maturation and ageing. Such wines may have exceptional long­evitiy and value. Technology has had limited influence, however, on the production of the finest red wines, for, even in the absence of legislative constraints, the traditional methods survive and prosper as a sort of thriving anachronism in the modern wine industry. Yet wine styles have altered in response to economic pressures, and one
accepts that many good red wines are consumed well before reaching their optimal development. There is therefore much scope for technological change in this sector of the industry.

Spectral observations have shown that the rate of change in phenolic composition of young commercial red wines in bulk storage, as indicated by 'chemical age' indices, varies greatly, for reasons which could not be clearly defined (SOMERS et al. 1983). Mechanisms of phenolic change during wine ageing are matters for speculation rather than factual discourse, for there is continuous and irreversible reaction, with increasing chemical complexity and heterogeneity of molecular species (SOMERS 1983; SOMERS and VERETTE 1988).

The broadest description of such compositional change is that the (monomeric) anthocyanin pigments initially responsible for wine colour are progressively displaced by more stable oligomeric and polymeric pigment forms during fermentation, maturation and ageing. Subtle slow oxidative influences surely occur, but recent studies have indicated that the principal phenolic interactions, which begin in the early stages of vinification and continue through wine storage, are essentially anaerobic (SOMERS and EVANS 1986). In that investigation, which was based on spectral observations of young sterile wines in ampoules (25 ml) with controlled head-space gases, the rate of change in phenolic composition was much increased by higher temperature (25 °C vs 3 °C). Although there was vastly greater change in the presence of oxygen, colour instability and phenolic deposition occurred only under highly aerobic conditions. Lesser influences on rate of phenolic change (than temperature and oxygen access) are phenolic concentrations and free SO₂ level, and there is also widely variable involvement of acetaldehyde in the phenolic condensation reactions (SOMERS and WESCOMBE 1987).

Thus the ampoule experiments had suggested the feasibility of more deliberately structuring a wine (than normally occurs during bulk storage), while also promoting the maturation reaction processes. Accelerated ageing, logically by the judicious use of heat treatment, has always been a popular aim, generally in application to fortified rather than natural wines (CRUESS 1947; AMERINE et al. 1980), but results have often been unsatisfactory. For the finest red wines, none other than the proven, traditional methods are seriously considered, and there is little information about wine ageing reactions. From our experience, however, it did appear that it would be quite 'safe' to conduct anaerobic heat treatment of red wines on commercial premises, from which realistic data might be gained.

This report is an account of observations made, in the vintages 1986/87/88, from large scale experiments wherein new red wines were stored at elevated temperatures under inert gas for several weeks.

Materials and methods

The wines were from various commercial sources:
1986: Shiraz/Cabernet Sauvignon (4 : 1) from Blewett Springs, South Australia, 5000 l.
1987: Shiraz from Padthaway, S.A., 5000 l; Cabernet Sauvignon from Wagga Wagga, New South Wales, 1200 l.
1988: Shiraz, Malbec wines from Padthaway, South Australia, 250 l; Cabernet Sauvignon, Shiraz port from Roseworthy, South Australia, 250 l.

The Shiraz wines of 1986/87 were each heat-treated 14 d after primary fermentation. The Cabernet Sauvignon wine (1987), although 6 months old at the time of treatment, had been stored since vintage at 0—5 °C, and was like a new wine. When treated,
none of the wines had any free SO₂. Ethanol concentrations were in the range 11.7—13.5 % v/v, and pH 3.30—3.65. The untreated control wines were each in approximately equal volumes to those treated.

Cellar treatment

The new wine was cold-settled, racked and pad-filtered with earth, then heated to 46—47 °C via plate heat-exchange equipment before transfer to a well insulated stainless steel storage vessel (5 000, 1 200, 250 l). The wine was held in warm storage under a carbon dioxide blanket for up to 40 d. Maintenance of temperature within the range 42—45 °C was found to require further heat exchange after about 15 d. Samples were taken for sensory inspection and analysis every 2—3 d. Samples of the treated and control wines were bottled after addition of SO₂ (30 mg/l).

Analyses

Spectral measures, using a Varian DMS 200 spectrophotometer, were made as previously described (Somers and Evans 1977, Somers and Verette 1988). Anthocyanin concentrations were measured by higher performance liquid chromatography, with malvidin 3-glucoside as reference standard (Preston and Timberlake 1981).

Head-space analyses of flavour volatiles were conducted by GC-MS as described by Williams et al. (1980). Ethyl carbamate concentrations were also measured by GC-MS, using the method of Ough et al. (1988) but with an isotopically labelled reference standard according to Cairns et al. (1987).

Results and discussion

1. Wine storage parameters

The experimental aim was that the cellar treatment should promote only those reactions which may normally occur in young red wine under anaerobic storage conditions. The wines were part of commercial vintages, so that it was necessary to ensure that there were no heat-induced cooked or 'porty' flavours, and that microbiological activity was inhibited rather than stimulated. According to these constraints, 50 °C was considered to be too high a temperature for prolonged wine storage, and 40 °C was definitively too low. Temperatures < 40 °C would have smaller influence on reaction rates, and could encourage microbiological spoilage. Temperatures close to 45 °C were therefore chosen as being most suitable for long-term anaerobic storage, and it was found that the wines, when heated to 46—47 °C via heat exchange equipment before transfer to insulated stainless steel storage at about 45 °C, became effectively sterile within 24 h. Care was taken to maintain a CO₂ blanket over the warm wine. Because of these conditions, it was unnecessary (and also undesirable from the aspect of promoting wine ageing reactions) to have any free SO₂ in the trial wines. New wines direct from primary fermentation, and therefore containing no free SO₂, are most suitable for such treatment.

In each storage trial, the wine was closely monitored by frequent inspection up to a maximum period (in 1986) of 40 d. The overall experience (1986/87/88) has been that 20—25 d may be optimal for such treatment of young red wines. There was gradual change in all aspects of wine composition in comparison with control wines (stored at 10—12 °C), as indicated by appraisal of colour, nose and palate. Analytical data from trials conducted in the 1986 and 1987 vintages are presented here. (Observations from the 1988 trials were similar.)
2. Effects on colour and phenolic composition

Progressive change in wine colour during heat treatment was observed to correspond with effects normally seen over a much longer period of wine storage in large vessels — as much as 2 years, depending on ambient cellar temperatures. Spectral measures altered in predictable fashion (e.g. Fig. 1) with shift in colour from the purple hues of young red wines (characterized by low $E_{420\text{ nm}}/E_{520\text{ nm}}$) to the ruby red appearance (high $E_{420}/E_{520}$) of more mature wines. $\lambda_{\text{max}}$ shifted from 528 to 523 nm. These effects were accompanied by decrease in concentration of total anthocyanins from 81 mg/l to 17 mg/l after 28 d vs 80 mg/l in the control wine, which had been stored at 0—5 °C.

![Spectral changes during anaerobic storage of a young Cabernet Sauvignon wine (1987) over 28 d at 42—45 °C. Samples were taken at 0, 2, 4, 8, 11, 15, 19, 23, and 28 d. Light pathlength 2 mm.](image)

Fig. 1: Spectral changes during anaerobic storage of a young Cabernet Sauvignon wine (1987) over 28 d at 42—45 °C. Samples were taken at 0, 2, 4, 8, 11, 15, 19, 23, and 28 d. Light pathlength 2 mm.


These and other similar trial data are construed as confirmation of earlier indications that red wine maturation rate is highly dependent on the ambient cellar temperature. In traditional practice, cool storage has been mandatory because of the need to prevent microbiological spoilage, but such storage is more favourable to white wine composition than to red.

Direct spectral measures, particularly the use of 'chemical age' indices, enable convenient monitoring of dynamic change in pigment composition whereby there is gradual transition from monomeric to oligomeric pigment forms (Somers and Evans 1986).
The significant analytical factor is the decreasing concentration of anthocyanins, and Bakker et al. (1986) have shown that such decrease is logarithmic with time at constant temperature. The same has been observed in all of our heating trials, best illustrated by data for a young Shiraz wine showing steep decline in anthocyanins during the first few weeks of heat treatment, vs little change in the control at 10—20 °C (Fig. 2).

Fig. 2: Decrease in total anthocyanins (●) and in malvidin 3-glucoside (○) during anaerobic storage of a Shiraz wine (1986) at 42—45 °C for 40 d. Residual concentrations after 120 d are shown for the control wine (●, ○) and for the treated wine.


The experience of these trials, concerning pairs of different wines which were initially identical, has led to a simple means for quantification of colouration effects which are largely responsible for the dynamic nature of red wine colour during maturation. As these phenomena, known as self-association and co-pigmentation, are primarily dependent on the concentration of total anthocyanins (as in flower colouration), there is then a maximal colour synergism in very young wines of high phenolic content (Sommers and Verette 1988). Thus the extent of these concentration effects on colour density is indicated by the decline in corrected absorbance at 520 nm after serial dilution with a model wine solution of the same pH. The extreme differences in this significant aspect of pigment composition between a young Shiraz wine and the same wine after heat treatment (the wines of Fig. 2) are shown in Fig. 3. Whereas more than half of E520 in the new (untreated) wine was due to anthocyanin concentration effects, with large deviation from Beer's Law, the colouration phenomena were hardly operative in the heat-treated wine. Such dilution response, with much closer adherence to Beer's Law, is characteristic of aged red wines in which residual anthocyanin levels are typically less than 20 mg/l.
Fig. 3: Effects of dilution on pigment concentration in a young Shiraz wine (●, 430 mg/l total anthocyanins) and in the wine after heat treatment (○, 30 mg/l total anthocyanins). Serial dilutions were made with 12% aq. ethanol saturated with potassium hydrogen tartrate.

Einfluß der Verdünnung auf die Farbstoffkonzentration eines jungen Shiraz-Weines (●, 430 mg/l Gesamtanthocyane) und eines wärme behandelten Weines (○, 30 mg/l Gesamtanthocyane). Die Verdünnungsserie wurde mit 12%igem wäßrigem, mit Kaliumhydrogentartrat gesättigtem Ethanol hergestellt.

Other spectral measures provide further appreciation of the extensive yet apparently systematic change occurring during the rapid maturation process. For example, other data are presented for the Cabernet Sauvignon wine, which was already 6 months old when heat treated in October 1987. That wine had, however, been deliberately conserved in cold storage (0—5 °C) and was still undeveloped in sensory terms. The rapid alteration in colour density and hue during anaerobic warming of this wine (at 42—45 °C) for 28 d has been already shown (Fig. 1). Spectral measures taken at high dilution in 1 M HCl, while showing little change in E420 (a measure of total phenolic components), show a progressive decrease in total pH-responsive pigments (Fig. 4).

This phenomenon, which is a consequence of structural change in pigment composition, is a distinctive feature of normal red wine ageing. Thus the ratio $E_{420}^{HCl}/E_{520}^{HCl}$, as an index of the phenolic composition, decreases from about 0.8 in new red wines of this type to about 0.15 in well aged wines (10 years or so) having good red colour (i.e. $E_{420}/E_{520} < 1.0$) (Somers and Verette 1988). The index declined from 0.50 to 0.30 during the Cabernet Sauvignon trial (Figs. 1, 4), measures which appear to indicate the intermediate status of the wine development during heat treatment.

Other evidence of profound structural change in phenolic composition was the progressive increase in $SO_2$-resistant pigments from 26 to 58% during the course of this same trial (Fig. 5) vs no change in the control. This percentage ratio ($E_{420}^{SO_2}/E_{520}^{SO_2}$) increases from an initial value of zero early in the primary fermentation to about 90% in aged wines (Somers 1971; Somers and Verette 1988).

Thus the central phenomenon of red wine maturation and ageing is that of dynamic change in wine colour and phenolic composition — in which the monomeric anthocyanin pigments, initially present as molecular pigment aggregates, are displaced by oligomeric structures which are much less responsive to pH change and to free $SO_2$. All of these effects and properties are promoted by anaerobic heat treatment.
3. Effects on taste and flavour

In their studies of storage effects on the volatile composition of bottled white wines, MARAIS and POOL (1980) observed that storage time (up to 12 months) and temperature (0, 10, 20, 30 °C) each caused similar trends in the concentrations of various components. Most esters decreased with time and temperature, but increases were noted in other esters (as concentrations of alcohols, acids and esters approached chemical equilibrium). More recent research developments have included investigations of the trace components associated with varietal flavour. These are the 'impact flavourants' such as the C₁₀ monoterpenes (STRAUSS et al. 1986; RAPP 1988) and the C₁₃ nor-isoprenoids (STRAUSS et al. 1987). Particular attention is now being given to the presence, in juices and wines, of glycosidically bound and other involatile flavour precursors, from which the impact flavourants may be released during maturation and ageing (WILLIAMS et al. 1988).

Sensory inspection of the Shiraz wines had shown, along with softening of the tannin astringency, the development of a distinct berry bouquet and flavour after about the first 10 d of warm anaerobic storage. Comparison of head-space volatiles from the treated and control wines (1987) showed many compositional changes, with appearance
of new minor volatiles in the treated wine (Fig. 6). One of these, having $M^+ 190$, was shown to be damascenone, a most potent flavour volatile of the C$_7$ nor-isoprenoid category (Fig. 7). Damascenone has a flavour threshold near to the $\mu g/l$ level and has been considered to arise from the degradation of carotenoids (OHLOFF 1978). Its presence in various alcoholic beverages has been demonstrated, and its concentration in grapes and wine has been shown to be increased by heating (MASUDA and NISHIMURA 1980). Damascenone is probably present in all wines at varying concentration above and below threshold (BAUMES et al. 1986). It contributes to floral flavour notes and to the acceptability of wine, but is possibly not responsible for the berry character, reminiscent of raspberry, in the Shiraz wines. The Cabernet Sauvignon (1987) and Malbec wines (1988) responded differently to heat treatment in this aspect of composition — wine flavour was altered, with loss of young wine aroma, but berry flavour was not particularly evident.

Concerning Shiraz, the same berry characteristics did later appear in the untreated control wines, but this feature was not consistently seen in the latter group; reduced sulphur aroma and flavour were then sometimes prominent sensory notes, particularly after malolactic fermentation (m.l.f.). Thus both Shiraz wines (1986/87) had been successfully inoculated with *Leuconostoc oenos* after heat treatment and before.

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![Absorption spectrum showing colour change and increase in SO$_2$-resistant pigments during anaerobic storage of the Cabernet Sauvignon wine (1987) at 42–45 °C.](image)

Fig. 5: Spectra showing colour change and increase in SO$_2$-resistant pigments during anaerobic storage of the Cabernet Sauvignon wine (1987) at 42–45 °C. Light pathlength 2 mm.
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Transfer to oak barrels. Induced berry flavours were retained in the treated wines (with and without m.l.f.) during 10 months of wood storage and subsequently in bottle, but were sometimes overshadowed by a suggestion of sulphur volatiles in the control wines. This latter feature was gradually lost during wine exposure to air, but the wines remained different from those which had been treated.

This experience, with just a few wines made under controlled cellar conditions, has served to underscore the importance of trace impact volatiles (µg/l) in relation to acceptability and quality. It also shows actual advantage, in the practical sense of wine quality control, for the mild heat treatment process. Along with the more rapid generation of mature wine flavour from physiologically inert precursor components, there must also be rapid turnover, and loss by volatilisation, of undesirable reduced sulphur flavours. That the latter occurs during warm anaerobic wine storage is indicated by our observations that ethanol concentration was decreased by 0.2—0.3 % v/v during a 25 d period at 42—45 °C.

4. Checks for adverse influence

Such marginal loss of ethanol is of no importance in wines from warm viticultural regions. Analyses for detection of possibly unfavourable influences were as follows:

![Chromatogramme der im Dampfraum von Shiraz-Weinen enthaltenen Aromastoffe. Der Vergleich zeigt den Einfluß der anaeroben Lagerung bei 42—45 °C im Verlauf von 25 d. IS: innerer Standard. Die eingekreisten Abschnitte sind in Fig. 7 in gespreizter Form dargestellt.](image)

Fig. 6: Comparative chromatograms of headspace volatiles from Shiraz wines, showing the effects of anaerobic storage at 42—45 °C for 25 d. IS is internal standard. The portions circled have been expanded in Fig. 7.
(i) Hydroxymethyl furfural: The concentration of this compound, which may attain 90 mg/l in port wines during normal ageing, serves as a marker for the formation of undesirable reaction products during heat treatment (Amerine et al. 1980). The concentration found in the processed wines was about 0.5 mg/l, compared with zero in the control wines. The amounts found in a random selection of commercial wines ranged from 0 to 4 mg/l.

(ii) Ethyl carbamate: Recent concern about the possibility of ethyl carbamate formation during vinification (ough et al. 1988) prompted such analysis of the trial wines. Concentrations found ranged from 1 to 12 µg/l (mean 4 µg/l) in control and treated wines, there being no significant influence of this sort from the treatments described.

![Chromatogram showing formation of damascenone](image)

Fig. 7: Comparative chromatograms showing formation of damascenone (scans 659–660) and other changes during treatment of the Shiraz wine (cf. Fig. 6).

Chromatogramme von Shiraz-Weinen: Bildung von Damascenon (659–660) und andere Veränderungen im behandelten Wein im Vergleich mit Kontrollwein (vgl. Fig. 6).

Conclusions

The sole purpose of this or any other variation in winemaking method is improved quality control and/or better wine quality. On both counts, judging by the attitudes and opinions of the winemakers directly involved in the commercial trials, warm anaerobic storage is an extremely safe and effective procedure for young red wines:

- The wine maturation is promoted along numerous reaction pathways, with acceleration of compositional changes affecting colour, nose and palate. The reactions are, however, constrained by the absence of oxygen from minimal headspace.
As anticipated, all microbiological activity is eliminated by the conditions of wine storage. Thus there was no change in volatile acidity or in malic acid concentration, such as may commonly occur in normal bulk storage. (The inoculation of sterile wines from heat treatment with \textit{L. oenos} starter culture, after cooling to about 28 °C, has been mentioned as a further winemaking option.)

There is no evidence of any adverse influence on wine composition from warm anaerobic storage for limited term. A period of 20—25 d at about 45 °C is near to optimal in sensory terms.

Although the method appears to be incompatible with the concurrent use of oak cooperage, oak flavour notes could be imposed by suspension of oak chips or shavings in the heated wine.

No scale limitation for such wine treatment is likely, so that the procedure appears to be well suited to very large volumes of wine, for which insulation would be less important than for the small batches described herein.

The nature and extent of sensory change must depend on particular reactive aspects of the wine composition. This is to say that, given a suitable balance of alcohol and acidity, a satisfactory result from such cellar treatment (as from normal long-term storage) will depend on phenolic concentrations and on the range of flavour volatiles and precursor compounds.

Whereas it did at first seem important that strictly anaerobic conditions should be maintained during the warm storage trials, it is noted that red wines, much more than white, normally have some limited access to oxygen during vinification and bulk maturation. Thus it has been evident that temperature is the primary influence on phenolic reaction rates, but that oxidative influences impose greater chemical complexity; they may also be quite destructive in chemical and sensory terms (Simers and Evans 1986; Simers and Wescombe 1987). The same applies to consideration of the flavour volatiles (Simpson 1978; Marais and Pool 1980). The widely variable extent to which oxygen may participate in wine ageing reactions does therefore provide for enormous range in the detail of wine composition. From these considerations, speculation about reaction mechanisms seems to be rather futile, except in very general terms.

Because of present uncertainty about the role of oxygen in red vinification, further investigations of rapid maturation should explore the added influence of strictly limited oxygen access during warm bulk storage, with the aim of establishing the optimal head-space regime for such treatment.

**Summary**

On the basis that initial wine ageing reactions are essentially anaerobic and that they are susceptible to acceleration by higher temperatures, the influence of anaerobic storage at 42—45 °C was monitored over periods of 25—40 d in comparison with controls at normal cellar temperatures. The trials were conducted with batch lots of young red wines (Shiraz, Cabernet Sauvignon, Malbec) in insulated stainless steel tanks (250, 1200, 5000 l).

Progressive change in aspects of composition affecting colour, nose and palate was noted as corresponding to that occurring over a much lower period in normal cool storage. Spectral change in colour density and tint was accompanied by rapid, logarithmic decrease in anthocyanin concentration during heat treatment compared with marginal alteration in the controls. There was corresponding decline in operation of colouration phenomena and increase in the contribution of more stable oligomeric pigments to wine colour.
There was no analytical or other evidence of any adverse influence from such wine storage for limited term. Development of a subtle berry aroma and flavour in Shiraz wines was noted, along with the accelerated formation of damascenone during the early stages of heat treatment.

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References


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