

The Australian Wine Research Institute, Glen Osmond, South Australia

## Evolution of red wines

### I. Ambient influences on colour composition during early maturation

by

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#### Die Entwicklung von Rotweinen

##### I. Außeneinflüsse auf die Färbungskomponenten in der Frühphase der Weinreifung

**Zusammenfassung:** Bei zwei jungen Rotweinen wurden die Veränderungen der Farbstoffzusammensetzung und des Phenolgehaltes während der ersten 12 Monate nach der Lese verfolgt. Hierbei wurden die Auswirkungen der Lagerungstemperatur (3 und 25 °C), von Stickstoff und von Luft im Leerraum, der Pasteurisierung sowie der Kältestabilisierung auf die Spektraldaten erfaßt. Unter einer Stickstoffatmosphäre wurden zunehmend polymere Pigmente gebildet; bei 25 °C war die Reaktionsgeschwindigkeit wesentlich beschleunigt. Bei Anwesenheit von Sauerstoff liefen die Veränderungen der Färbungskomponenten schneller ab, die Meßwerte zeigten jedoch diskontinuierliche Schwankungen. Die Pasteurisierung hatte keinen Einfluß auf die Alterungsreaktion der Phenole, ebensowenig eine vorangegangene Kältestabilisierung.

Es werden zwei Möglichkeiten der Phenolkondensation während der normalen Rotweinalterung aufgezeigt. Die Untersuchungen liefern Hinweise darauf, wie die Reifung von Rotweinen beschleunigt und gleichzeitig die Alterungsreaktion der Phenole gesteuert werden kann.

**Key words:** red wine, maturation, pigment, phenol, post fermentation care, temperature, nitrogen, oxygen.

#### Introduction

The composition of red wine colour changes continuously during vinification and storage, with associated changes in sensory characteristics of the vintage. Thus the French words 'évolution' and 'élevage' are most apt in reference to the dynamic properties of young red wines, and to the need for their careful management during development into mature wines.

Progressive change is inevitable because of the reactivities of phenolic constituents extracted during primary fermentation, but the rate and course of phenolic interactions and degradations may be subject to many influences. Most rapid change in colour composition occurs during the first year (SOMERS 1971), when the wine is normally in bulk storage; it has been recently stated that this 'maturation phase' should be considered as being quite distinct from the latter 'ageing phase', when the wine is in bottle and well protected from any further contact with air (PONTALLIER and RIBÉREAU-GAYON 1983; RIBÉREAU-GAYON *et al.* 1983).

Although recognised influences on initial colour composition are amenable to control by the winemaker, the complex reaction system is susceptible to significant disturbance from conditions for favourable development of the wine; these matters are

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poorly understood in objective terms. Thus red wines do not always improve with age, their organoleptic properties may change unpredictably, and there are empirically established limits to what can be expected from any familiar vintage. There is, therefore, need for better definition of physico-chemical factors affecting the maturation of red wines.

The variable influences on phenolic (i. e. colour) composition, with related influences on other compositional aspects, are broadly of two sorts, viz. exterior or ambient, and those which are intrinsic to the initial wine composition.

In this paper, we report our observations, during the first year after vintage, of the relative effects of two different temperatures (3 and 25 °C) and of the presence or absence of oxygen on the colour composition of two red wines having typically low and high phenolic contents. The possibilities of influences from prior pasteurisation and from cold-stabilisation on subsequent maturation changes were also examined.

For obvious reasons, access to such data is hardly possible under commercial conditions; this investigation has been based on laboratory study of sterile wines stored in glass ampoules.

### Materials and methods

Two commercially produced wines (101 lots), fresh from fermentation in the Southern Vales district of South Australia, were used in this investigation, viz. a Grenache wine of low phenolic content ( $E_{280\text{ nm}}^{10\text{ mm}} = 33$ ) and a highly extracted Shiraz wine ( $E_{280\text{ nm}}^{10\text{ mm}} = 84$ ). No sulphur dioxide ( $\text{SO}_2$ ) had been used in making of the Grenache wine; total  $\text{SO}_2$  was 12 mg/l and free  $\text{SO}_2$  zero. The Shiraz wine contained 80 mg total  $\text{SO}_2$ /l and 0.6 mg free  $\text{SO}_2$ /l, determined by the spectral procedure (SOMERS and EVANS 1977). Wine pH values were 3.85 and 3.75, respectively. Malo-lactic fermentation had not occurred in either wine.

### Storage conditions

All laboratory procedures were carried out under nitrogen to minimise oxygen contact. Half of each wine lot was cold-stabilised by storage at  $-4\text{ }^\circ\text{C}$  for 10 d; the other half of each lot was treated with bentonite (5 g/l) and retained at  $10\text{ }^\circ\text{C}$  under nitrogen. All four lots were then sub-divided by identical procedures as follows:

Each wine sample was filtered through  $8\text{ }\mu\text{m}$  and  $0.45\text{ }\mu\text{m}$  membranes into sterile vessels. The wines were then pumped through sterile tubing into sterile ampoules containing nitrogen, carbon dioxide or air. Each ampoule, swept out with gas before sealing, contained ca. 23 ml wine and 1–2 ml of the particular headspace. From each wine lot, ampoules prepared were approximately 120 under nitrogen, 16 under carbon dioxide and 20 under air. Sterility of a few samples was verified by plate counting.

Half of each set of ampoules were then pasteurised by immersion, with frequent inversion, in a water-bath at  $85\text{ }^\circ\text{C}$  for 80 s before rapid cooling to room temperature.

From each wine, four sets of ampoules were prepared, i. e. all combinations of cold-stabilised/non cold-stabilised and pasteurised/non-pasteurised, and each set included ampoules with nitrogen, carbon dioxide and air headspace. One half of each set was stored at  $3\text{ }^\circ\text{C}$ , the other at  $25\text{ }^\circ\text{C}$ , both in the dark. Thus there were initially 24 different groupings for each of the two wines. All ampoules were stored vertically without mixing.

## Analyses

A fresh ampoule was taken from storage for each analytical inspection. All cold-stabilised wines stored under nitrogen were examined 14 times during the period of observation, 10 of these during the first 6 months. Cold-stabilised wines stored under carbon dioxide and under air headspace were examined on 5—7 occasions during the year. Non cold-stabilised wines were not examined further after the first few months (see 'Results').

Analytical measures were by methods previously described (SOMERS and EVANS 1977). The various parameters of wine colour composition and of phenolic content are listed, using the same terminology as in the above report except for preferred description of the parameter ( $\alpha$ ) as 'degree of colouration of anthocyanins' and the use of percentage values as indices of 'chemical' age ( $\beta$ ,  $\gamma$ ):

- (a) Wine colour density,  $E_{420} + E_{520}$
- (b) Wine colour tint,  $E_{420}/E_{520}$
- (c) Degree of colouration of anthocyanins, %, ( $\alpha$ )
- (d) Total anthocyanins, mg/l
- (e) Coloured anthocyanins, mg/l
- (f) Total phenolics,  $E_{280} - 4$
- (g) Index of 'chemical age',  $E_{280}^{SO_2}/E_{520} \times 100$  %, ( $\beta$ )
- (h) Index of 'chemical age',  $E_{280}^{SO_2}/E_{520}^{HCl} \times 100$  %, ( $\gamma$ ).

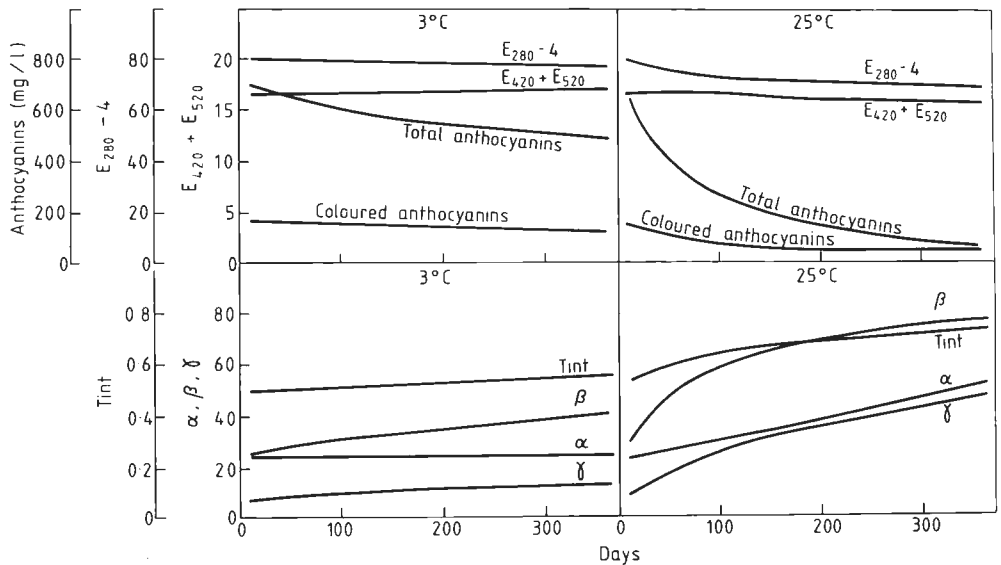
## Results

No essential differences were seen between data sets for cold-stabilised and non cold-stabilised wines, but as the latter all tended to throw precipitates, and were subject to slight variation in pH, data presented here refer only to wines which had been cold-stabilised. Although such treatment had involved loss of about 5 % absorbance at 280 nm in each wine, the benefits were stable pH and perfect wine clarity during the course of observation, except for a few samples under prolonged air headspace.

Comparative inspection of related sets of data by use of transparent plots enabled further reduction of the original information collated. As wines stored under nitrogen and under carbon dioxide developed in identical fashion, measures over the full term of the investigation were confined to those stored under nitrogen. Furthermore, close comparison of data for pasteurised and non-pasteurised (sterile-filtered) wines showed pasteurisation to have no influence on any of the subsequent analytical measures; the ageing patterns for wine colour composition, as indicated by the progressive indices of 'chemical age', were identical over the 1-year-period of observation. Data selected for presentation here, therefore, refer to the effects of temperature (3, 25 °C) and to the presence or absence of oxygen on the evolution of wine colour composition in each of the two sterile wines.

## Storage under nitrogen

Temperature, rather than the availability of oxygen was clearly the main ambient influence on progressive change in the composition of wine colour. Complete data for the Shiraz wine (of high phenolic extract) during storage under nitrogen at 3 and 25 °C are shown in the figure. Quantitative measures of total phenolic content ( $E_{280} - 4$ ), total anthocyanins, coloured anthocyanins and wine colour density ( $E_{420} + E_{520}$ ) are presented separately from measures of a qualitative nature, viz. wine tint, degree of colouration of anthocyanins ( $\alpha$ ), and the age indices ( $\beta$ ,  $\gamma$ ) which refer to the increasing



Changes in colour composition and phenolic content of a Shiraz wine stored under nitrogen at 3 and 25 °C.

Die Veränderung der Färbungskomponenten und des Phenolgehaltes eines Shiraz-Weines bei Lagerung unter einer Stickstoffatmosphäre und bei Temperaturen von 3 und 25 °C.

contribution of polymeric pigments to wine colour (SOMERS and EVANS 1977; see 'Materials and methods').

Rapid decrease in total anthocyanins during storage at 25 °C was accompanied by corresponding increase in  $\beta$ , the percentage measure of polymeric pigments at wine pH. Wine hue or tint at 25 °C changed perceptibly in the first months of observation when anthocyanin loss was greatest (Fig.). Despite these large changes in colour composition, the wine colour density remained virtually constant, slight decrease in  $E_{520}$  being compensated by a similar increase in  $E_{420}$ . Ageing effects were obviously much decreased by storage at the lower temperature (Fig.).

It is noted, however, that although the wines were only two weeks old when observations began, considerable change in pigment had already occurred. This is evident from the slope of the 'chemical age' index ( $\beta$ ) during wine storage at 25 °C (Fig.), i. e. this index had increased to 25 % from much lower values typically seen during and immediately after primary fermentation (SOMERS 1971).

During the period of observation, the age index ( $\beta$ ) increased from 25 to 78 % at 25 °C, but attained only 40 % at 3 °C. As rate of change in colour composition was greatest during the first 100 d of observation (Fig.), the use of  $\Delta$  values representing percentage change in the various parameters over this period is a convenient way of comparing all the relevant data. Thus for the Grenache wine (of low phenolic extract) there was generally similar development under nitrogen at 3 and 25 °C to that shown in the figure for the Shiraz wine, but the  $\Delta$  values were somewhat lower (Table), indicating slower ageing rates in this light red wine; this is attributed to the differing phenolic levels, as similar observations were made for the two wines under air headspace.

The data also serve to illustrate the utility of the qualitative measures ( $\beta$ ) and ( $\gamma$ ) in studies of this kind. These two age indices refer directly to the progressive displacement of the monomeric grape anthocyanins by more stable polymeric wine pigments, which are resistant to decolourisation by  $\text{SO}_2$  and to change in pH (SOMERS 1971). Each index approaches 100 % in aged red wines in which the polymeric pigments are almost entirely responsible for the wine colour (SOMERS and EVANS 1977).

#### Storage under air

Whereas data plots for wines stored under inert gas were quite smooth and continuous, as shown in the figure, there were evident discontinuities in sequential measures during storage under air headspace. Although patterns of change were similar for nitrogen and air (Table), the presence of oxygen resulted in more rapid decline in total anthocyanins and faster increase in the qualitative parameters of colour composition (tint,  $\alpha$ ,  $\beta$ ,  $\gamma$ ). The most immediate influence of air contact was significant increase in wine colour density at both 3 and 25 °C within the first week. Generally, this early increase in colour density under air was followed by gradual decline to values only slightly above those observed under nitrogen.

The erratic effects of air contact are attributed to the considerable variation in oxygen levels available in the headspace of each ampoule (1–2 ml air/22–23 ml wine, corresponding to 12–24 mg available oxygen/l). Although these previously cold-stabilised wines remained clear during the 1-year-period of observation, the destructive effect of excessive exposure to oxygen was easily demonstrated in related trials. Thus red wines ampouled under large oxygen headspace (4–5 ml oxygen/18–20 ml wine) also showed early increases in colour density, but there was then increasing turbidity and deposition of pigments. Even at 3 °C storage, there was 40 % loss in colour density over 6 months. During storage under oxygen at 25 °C, there was 70 % loss in colour density over 6 months with age indices attaining over 90 % in the residual wine solutions.

### Discussion

The ubiquitous presence of oxygen obviously has important bearing upon the nature of progressive phenolic interactions during normal ageing of red wines. However, whereas oxidative influences are generally injurious to sensory properties of white wines and care is taken for their avoidance, the traditional maturation processes for red wines permit wide variation in the uptake of oxygen before final bottling. Principal sources of increase in dissolved oxygen are racking and pumping operations and ullage space during storage. Until recently, it had long been assumed that wine maturation in wood inevitably involves slow but continuous oxygen absorption by diffusion through the staves. This notion appears to be generally untrue for sound oak barrels, in which the frequency and method of wine transfer procedures are likely to be the most significant factors in relation to levels of dissolved oxygen (PETERSON 1976).

The fundamental questions about the role of oxygen in the making of red wines appear to be:

- (i) Whether or not its presence is essential for the wine maturation, of which progressive change in colour composition is a most prominent feature.
- (ii) To what extent and by what means should oxidative influences be controlled, for excessive oxidation is well known to depreciate red wine quality.

Effects of temperature and of headspace gas on colour composition and phenolic content during the first 100 d of wine storage · Results are given as percentage increase or decrease in relation to the initial measures

Der Einfluß von Temperatur und Leerraumgas auf die Färbungskomponenten und den Phenolgehalt während der ersten 100 d der Weinlagerung · Die Ergebnisse sind als prozentuale Zu- oder Abnahme der Ausgangswerte angegeben

Analytical measure	Shiraz wine				Grenache wine			
	Nitrogen		Air		Nitrogen		Air	
	3 °C	25 °C	3 °C	25 °C	3 °C	25 °C	3 °C	25 °C
Colour density	0	0	+10	+10	0	0	+15	+20
Total phenols	-2	-10	-2	-10	0	-5	0	-10
Total anthocyanins	-10	-60	-15	-75	-10	-50	-15	-65
Coloured anthocyanins	-10	-50	0	-50	0	-40	0	-40
Colour tint	0	+30	0	+30	0	+15	0	+15
Degree of colouration ( $\alpha$ )	0	+30	+10	+60	0	+30	+5	+80
Age index ( $\beta$ )	+30	+140	+30	+160	+15	+80	+40	+110
Age index ( $\gamma$ )	+30	+320	+40	+500	+20	+240	+100	+350

The first question has been answered affirmatively in recent reports from Bordeaux which propose that the phenolic interactions are initiated and further promoted by the absorption of oxygen (PONTALLIER and RIBÉREAU-GAYON 1983; RIBÉREAU-GAYON *et al.* 1983). From their data, the authors infer a need for frequent racking of wines in bulk tank storage to approximate oxygen uptake during ageing in barrel.

These propositions and conclusions were based on the fact that absorption of oxygen by wine leads to formation of acetaldehyde from ethanol by coupled autoxidation with phenolic components (WILDENRADT and SINGLETON 1974). Acetaldehyde then induces co-polymerisation of anthocyanins in Baeyer condensation reactions, with formation of  $-\text{CH}(\text{CH}_3)-$  bridges between phenolic units. Model reactions of this type (e. g. between malvidin 3-glucoside, acetaldehyde and (+)-catechin), showing increase in colour density and formation of polymeric pigments, have been demonstrated, though such structures are not yet proven (TIMBERLAKE and BRIDLE 1976; BARONOWSKI and NAGEL 1983). In experimentation with red wines to which acetaldehyde had been added, decreasing acetaldehyde concentration was accompanied by decrease in anthocyanins, increase in colour density and in the level of polymeric pigments; with high acetaldehyde additions, there was subsequent decrease in colour density and precipitation of pigments (RIBÉREAU-GAYON *et al.* 1983).

Prevalence of the Baeyer reaction, promoted by oxygen uptake, does not however constitute evidence that it is fundamentally responsible for pigment phenomena during evolution of red wines. Nor can our data (Fig.), showing continuous development in wine pigment composition during one year under nitrogen, be construed as convincing evidence to the contrary. However, since every effort was made to exclude oxygen from the new wines, it seems clear that any oxygen requirement for such ageing reactions to proceed is actually minimal. Obviously, it is *temperature* which is the major influence on reaction rates leading to formation of polymeric pigments in red wines (Table).

For wines under air ullage, the amount of oxygen initially available in the ampoule headspace (12–24 mg/l) was up to 3 times wine saturation level; these figures are in the middle range of estimates for total oxygen consumption which may occur in red wines during the 1st year after vintage (PRILLINGER 1965). It is noteworthy that such oxidative storage conditions did not result in any actual browning, tint indices being the same as in wines stored under nitrogen (Table).

As mentioned, however, data lines for wines under air were not smooth, probably because of the 2-fold range in available oxygen levels, with varying effect on phenolic composition by way of acetaldehyde production and interaction. Discontinuities were most evident in measures of residual anthocyanins and of the age indices ( $\beta$ ) and ( $\gamma$ ). Unrealistically high values for the degree of colouration of anthocyanins ( $\alpha$ ) have been previously noted in aged red wines, a trend indicated in the figure and the table for wines stored at 25 °C, and particularly under air head-space (Table). This suggests changing properties of the polymeric pigments (i. e. resistance to bleaching by  $\text{SO}_2$  and colour response to lower pH), assumptions about which provide the basis for determination of ( $\alpha$ ) values in young red wines (SOMERS and EVANS 1977).

The facts that acetaldehyde is a normal component of new wines, that it may be generated by aeration of wine, and that it is depleted by interaction with phenolics, all contribute to present uncertainties in interpretation of pigment phenomena during wine ageing. However, it seems significant that patterns of change for the two wines under nitrogen were essentially the same (Table) even though the initial acetaldehyde levels were quite different. These were respectively 55 mg/l for the Shiraz wine and 8 mg/l for the Grenache, calculated from the stoichiometric relationship with total  $\text{SO}_2$

in new wines (SOMERS and WESCOMBE 1982). Here it should be noted that acetaldehyde present at completion of primary fermentation is strongly bound to  $\text{SO}_2$ , whereas any subsequent oxidative influences result in formation of free acetaldehyde.

Our observations indicate that the phenolic condensation reactions do not depend on formation of acetaldehyde by continuing oxidative influences on the wine composition, and that the rate of natural progression from monomeric to polymeric pigment forms depends largely upon ambient temperature. The general interpretation is that two types of phenolic condensations are normally operative during maturation of red wines:

1. The first of these, which is considered to be intrinsic to the phenolic composition of new red wines and fundamental to wine ageing reactions, involves direct condensations between anthocyanins and other flavonoid components; likely mechanisms have been previously proposed (JURD 1967, 1972; SOMERS 1971). These mechanisms require formation of colourless flavenyl intermediates and their oxidative conversion to coloured flavylum structures; involvement of the phenolics in wine redox systems is indicated here, but any oxygen requirement should be slight.
2. Baeyer condensations by which interactions with acetaldehyde result in formation of  $-\text{CH}(\text{CH}_3)-$  bridges between anthocyanins and other flavonoids (SOMERS 1971; TIMBERLAKE and BRIDLE 1976, 1977) and between polymeric structures already formed by direct condensations.

Kinetic evidence for the occurrence of these two types of condensation has been recently obtained from study of model systems (BARONOWSKI and NAGEL 1983). Whereas direct condensation to polymeric pigments appears to be a property of the total phenolic extractives in red wines, the extent of Baeyer reactions must depend on the availability of free acetaldehyde.

### Conclusions

Interpretations of the spectral data are summarised as follows:

- (i) Reactions fundamentally responsible for progressive formation of polymeric pigments during maturation of red wines are essentially anaerobic.
- (ii) In commercial practice, however, the normal presence of dissolved oxygen imposes varying and uncertain influence on phenolic composition because of the intervention of acetaldehyde arising from autoxidation of ethanol.
- (iii) Most rapid change in phenolic composition occurs during the first few months after vintage.
- (iv) Temperature is the major influence on rates of reactions leading to formation of polymeric pigments.
- (v) Pasteurisation has no influence on the course of phenolic ageing reactions.

Thus there is the possibility of more deliberately 'structuring' a red wine during the critical early stage of maturation, i. e. ageing may be accelerated in a controlled fashion by bulk storage of cold-stabilised sterile wine at an elevated temperature under inert gas for several weeks after vintage, before proceeding with maturation by traditional methods. This subject warrants closer examination, as does the obviously varying role of acetaldehyde during evolution of red wines.

### Summary

Observations of changing colour composition and phenolic content of two new red wines were made during the 12-month period after vintage. Spectral data were plotted



with reference to two storage temperatures (3 and 25 °C), storage under nitrogen and under air headspace, pasteurised and non-pasteurised wines, cold-stabilised and non cold-stabilised wines. Progressive formation of polymeric pigments occurred under nitrogen headspace with much faster reaction rates at 25 °C. The presence of oxygen increased rate of change in colour composition, but data points were erratic. Pasteurisation had no influence on phenolic ageing reactions, nor did prior cold-stabilisation.

Two types of phenolic condensation reactions during normal wine ageing are indicated. Interpretations suggest the feasibility of accelerating red wine maturation, while at the same time directing phenolic ageing reactions along controlled lines.

### References

- BARONOWSKI, E. S.; NAGEL, C. W.; 1983: Kinetics of malvidin 3-glucoside condensation in wine model systems. *J. Food Sci.* **48**, 419—421, 429.
- JURD, L.; 1967: Anthocyanidins and related compounds. XI. Catechin-flavylium salt condensation reactions. *Tetrahedron* **23**, 1057—1064.
- —; 1972: Anthocyanidins and related compounds. XVI. Dimerisation of flavylium salts in aqueous solutions. *Tetrahedron* **28**, 493—504.
- PETERSON, R. G.; 1976: Formation of reduced pressure in barrels during wine aging. *Amer. J. Enol. Viticult.* **27**, 80—81.
- PONTALIER, P.; RIBÉREAU-GAYON, P.; 1983: Influence de l'aération et du sulfitage sur l'évolution de la matière colorante des vins rouges au cours de la phase d'élevage. *Connaiss. Vigne Vin* **17**, 105—120.
- PRILLINGER, F.; 1965: Uso dell'acido solforoso e dell'acido ascorbico per impedire l'ossidazione dei vini. *Riv. Viticult. Enol.* **18**, 99—108.
- RIBÉREAU-GAYON, P.; PONTALIER, P.; GLORIES, Y.; 1983: Some interpretations of colour changes in young red wines during their conservation. *J. Sci. Food Agricult.* **34**, 505—516.
- SOMERS, T. C.; 1971: The polymeric nature of wine pigments. *Phytochemistry* **10**, 2175—2186.
- —; EVANS, M. E.; 1977: Spectral evaluation of young red wines: Anthocyanin equilibria, total phenolics, free and molecular SO<sub>2</sub>, 'chemical age'. *J. Sci. Food Agricult.* **28**, 279—287.
- —; WESCOMBE, L. G.; 1982: Red wine quality: The critical role of SO<sub>2</sub> during vinification and conservation. *Austral. Grapegrower Winemaker* (220), 68, 70, 72, 74.
- TIMBERLAKE, C. F.; BRIDLE, P.; 1976: Interactions between anthocyanins, phenolic compounds and acetaldehyde and their significance in red wines. *Amer. J. Enol. Viticult.* **27**, 97—105.
- —; — —; 1977: Anthocyanins: Colour augmentation with catechin and acetaldehyde. *J. Sci. Food Agricult.* **28**, 539—544.
- WILDENRADT, H. L.; SINGLETON, V. L.; 1974: The production of aldehydes as a result of oxidation of polyphenolic compounds and its relation to wine ageing. *Amer. J. Enol. Viticult.* **25**, 119—126.

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