

## **Wine Quality: Correlations with Colour Density and Anthocyanin Equilibria in a Group of Young Red Wines**

T. Chris Somers and Michael E. Evans

*The Australian Wine Research Institute, Glen Osmond, 5064 South Australia*

*(Manuscript received 19 February 1974 and accepted 7 May 1974)*

---

Following an exhibition of 32 current vintage red wines of two varieties from the Southern Vales district of South Australia, a correlation was observed between colour densities and the order of ranking previously assigned by a panel of experienced judges.

There was no relation between wine colour density and anthocyanin content. Amongst many wines having comparable levels of anthocyanins, the variation in colour density was as much as 3.6-fold, and the degree of ionisation of the anthocyanin component of wine colour was found to range from 6 to 25%. These latter values were also correlated with the quality ratings.

The data support the opinion that measurement of colour density and of the degree of ionisation of anthocyanins can provide an objective guide to organoleptic properties in young wines of the same variety and region. Confirmation for this view was obtained from other data concerning the subsequent vintage of Cabernet Sauvignon in the same district.

Factors likely to be responsible for the varying states of anthocyanin equilibria in these wines are discussed in terms of wine composition and oenological practice.

### **1. Introduction**

That a good red wine should be “rich in colour” is a firm principle in oenology. It is generally inferred that a deficiency of extractable pigment in the grape material will probably preclude the making of a high quality wine. Where there is adequate pigment available, the level of colour which the wine is allowed to attain is regarded as a matter for the empirical judgment of the winemaker. Quite apart from familiar regional variations in the pigment content of wine grapes, one would not expect that the colour densities of young red wines should vary greatly, for a single cultivar, within a region of apparently uniform characteristics.

It frequently happens, however, that new red wines have unaccountably low colour densities in comparison with other wines from the same area. Such variation in commercial wines could relate to actual variation in the pigment content, but colour density is also dependent upon pigment composition and the particular state of pigment equilibria, which may be subject to uncertain influences.

Anthocyanin content is the basis for red wine colour, and major secondary factors affecting colour density are known to be pH and sulphur dioxide (SO<sub>2</sub>) content. Investigations<sup>1–3</sup> of the pH-dependence of anthocyanin equilibria in model solutions

have indicated that, of total *Vitis vinifera* anthocyanins, 20 to 25% are in the coloured flavylum form in the pH range 3.4 to 3.6 and only about 10% at pH 4.0. The decolorisation of anthocyanins by  $\text{SO}_2$  has been shown to involve equimolar reaction of species such as  $\text{HSO}_3^-$  with the anthocyanin flavylum ion.<sup>4, 5</sup> The effect of  $\text{SO}_2$  on young wine colour is, however, complicated by the presence of other  $\text{SO}_2$ -binding compounds,<sup>6-8</sup> and by the gradual loss of  $\text{SO}_2$  from wine solution.

The changing nature of pigment composition during wine ageing, with progressively increasing contribution to colour density from non-anthocyanin polymeric pigment forms and accompanying decrease in anthocyanin colour, adds further complexity to the problem of interpreting red wine colour in chemical terms.<sup>3, 9-12</sup> The polymeric pigments are much less sensitive than the anthocyanins to  $\text{SO}_2$  and to changes in pH.<sup>3, 9</sup>

In this paper we report our interpretations of wine colour composition in a range of young red wines from a small viticultural area; there was very large variation in the state of anthocyanin equilibria in these wines. Our data also contain interesting implications in relation to wine quality.

## 2. Experimental

The Cabernet Sauvignon and Shiraz (syn. Syrah) wines used in this investigation were representative of the (March) 1972 vintage in the Southern Vales district of South Australia, and came from 18 different wineries. Grapes were grown under natural rainfall of 530 to 630 mm; yields were 4 to 5 tonnes/hectare for Cabernet Sauvignon and 5 to 6 tonnes/hectare for Shiraz. The wines were all made "on skins" in the traditional fashion. Our samples were taken from those presented at an exhibition of the district wines in November, 1972.

### 2.1. Optical density measurements

The following measures were made on each wine; the cell compartment of the spectrophotometer was thermostatted at 25 °C. Measures at pH < 1.0 were corrected for the dilution used, and all readings were converted to  $E^{10\text{ mm}}$  values.

#### 2.1.1. At wine pH

As anthocyanins are immediately decolorised by an excess of  $\text{SO}_2$  at wine pH, comparative measures of colour composition<sup>3</sup> were easily obtained.

The visible spectrum of the wine in a 2 mm cell (0.65 ml) was first recorded. *Wine colour density* was the sum of  $E_{520\text{ nm}}^{10\text{ mm}}$  and  $E_{420\text{ nm}}^{10\text{ mm}}$ .

20% sodium metabisulphite (50  $\mu\text{l}$ ) was then added to the cell and the spectrum again recorded after about 1 min.  $E_{520}^{10\text{ mm}}$  of the partly bleached solution was used as a measure of the  $\text{SO}_2$ -resistant *polymeric colour*,<sup>3</sup> and the difference between this value and the original  $E_{520}^{10\text{ mm}}$  of *wine colour* as a measure of *anthocyanin colour*.

#### 2.1.2. At pH < 1.0

During earlier spectral studies of the polymeric pigment fractions of many young wines,<sup>3</sup> it was found that this component of total wine colour is much less sensitive to lowered pH than is the anthocyanin fraction;  $E_{520}$  of the polymeric pigments was increased by an

average factor of 5/3 at pH <1.0. Thus the estimated contribution of this fraction at pH <1.0 was  $5/3 \times (E_{520}^{10\text{mm}}$  of polymeric colour at wine pH). Anthocyanin colour at pH <1.0 was then the difference between  $E_{520}^{10\text{mm}}$  of the wine at pH <1.0 and the absorbance attributed to the polymer fraction.

The wine sample (1.0 ml) was diluted with 1.0 N-HCl (10.0 ml), and  $E_{520}$  was measured in a 5 mm cell after 4 to 6 h. Anthocyanin colour at pH <1.0 was calculated as above.

## 2.2. Total anthocyanins, degree of ionisation, ionised anthocyanins

Recent measures<sup>13, 14</sup> on recrystallised isolates of malvidin 3-glucoside, the principal anthocyanin of *V. vinifera*, have shown  $\epsilon$  values of 29 500 and 28 000, respectively, these being more than double the earlier estimates; our own later measures on crystalline pigment, isolated from Shiraz grapes by the method of Hrazdina,<sup>15</sup> have given similar high values. There is, however, some variation in the  $\epsilon$  values of anthocyanins<sup>14</sup> and there is also, in young red wines, considerable colour contribution from acylated anthocyanins having higher molecular weights.<sup>10</sup> For calculation of total anthocyanin content from the estimate of anthocyanin colour at pH <1.0, we have therefore chosen to use an  $E_{10\text{mm}}^{1\%}$  value of 500 at 520 nm.

The degree of ionisation of anthocyanins is the percentage ratio of anthocyanin colour at wine pH to that at pH <1.0. This figure was used to estimate the concentration of ionised anthocyanins from that found for total anthocyanins.

Note: some bleaching of the polymeric pigment fraction does occur with high levels of SO<sub>2</sub> addition,<sup>3</sup> and the level used in these analyses (10 000 parts/million) was probably grossly excessive. Although this makes little difference to estimates of the degree of ionisation of anthocyanins, as in the above, the present recommendation is that a 10  $\mu$ l addition of 20% sodium metabisulphite to a 2 mm cell (giving 2000 parts/million SO<sub>2</sub> in 0.65 ml of wine) is ample for immediate abolition of the anthocyanin component of wine colour.

## 2.3. Statistical analysis

Regression analyses were conducted on various relations. All regressions were approximately linear, and in each instance a test was made of the homogeneity of slope and position between the regressions obtained from data for the two varieties.

Where the slopes were not different, a regression line of the same slope was fitted to each varietal group and a test made for displacement. When the slopes were different, it was not relevant to test for displacement, and two regression lines are shown.

Where the slopes and position were not significantly different, a single regression line was used for all wines. A separate line for each variety, using common slope, is shown when the positions were significant.

# 3. Results

## 3.1. Colour density and wine quality

The wines had been scored, prior to exhibition, by a panel of three experienced wine judges, who acted quite independently of the authors. All wines in each class were examined by the judges at one time, so that a comparative ranking of overall wine quality

was obtained. Maximum points that could be assigned were colour 3, aroma 7 and palate 10.

Subsequently, we inspected the wines in  $\frac{1}{2}$ -inch test tubes, and noted a correlation between colour density and tasting score, with the more deeply coloured wines all scoring high. None of the wines were unacceptably light in colour and variations in colour density were more easily detected in test tubes than in wine glasses.

There was a linear relation between quality rating (the judges' mean score) and wine colour density (Figure 1). As there was no significant difference in slope or position

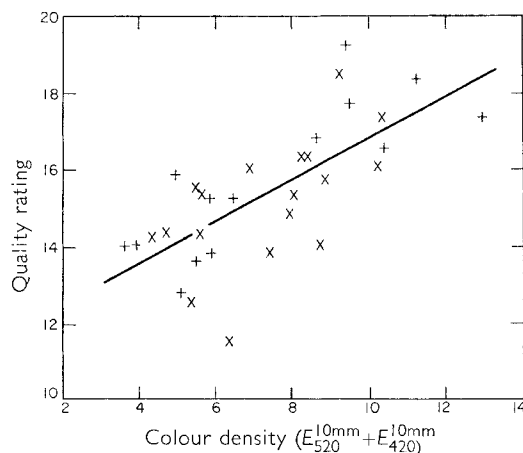


Figure 1. Relation between quality rating and wine colour density in 1972 Southern Vales wines. The regression line ( $P < 0.001$ ) applies to the total data.

In this and subsequent figures, Cabernet Sauvignon wines are shown as (+) and Shiraz (x). Where separate regression lines for each varietal group were appropriate, the line for Cabernet Sauvignon is shown as (—) and for Shiraz (-----).

between the regression lines for Cabernet Sauvignon and Shiraz wines, a single regression line ( $P < 0.001$ ) is given for all 32 wines.

### 3.2. Degree of ionisation of anthocyanins in wine

It was then of special interest to investigate the pigment content and colour composition of the individual wines. The data from which our interpretations have been made are presented in Table 1, in which the wines are listed according to the judges' comparative ratings.

The increase in absorbance at 520 nm on acidification of the wines varied from 3.1 to 8.8 times. Estimates of anthocyanin content and of the "degree of ionisation" of total anthocyanins in each of the exhibition wines were obtained. "Degree of ionisation" is intended to mean the percentage of total anthocyanins which are in the coloured or flavylium ion form; the values ranged from 6 to 25%.

Figure 2 emphasises the fact that there was no apparent relation between wine colour density and anthocyanin content in these wines. A Shiraz wine with the highest anthocyanin content, 0.63 g/l, had only moderate colour density; many wines had anthocyanin

TABLE 1. Analytical data and quality ratings for 1972 vintage Cabernet Sauvignon and Shiraz wines from Southern Vales, S.A.

	pH	Total SO <sub>2</sub> (parts/million)	Quality rating <sup>a</sup>	At Wine pH			At pH < 1.0			Degree of ionisation of anthocyanins (%)	Ionised anthocyanins (g/l)
				Colour density ( $E_{520}^{10\text{mm}} + E_{420}^{10\text{mm}}$ )	Wine colour ( $E_{520}^{10\text{mm}}$ )	Polymeric pigment colour ( $E_{520}^{10\text{mm}}$ )	Anthocyanin colour ( $E_{520}^{10\text{mm}}$ )	Wine colour ( $E_{520}^{10\text{mm}}$ )	Anthocyanin colour ( $E_{520}^{10\text{mm}}$ )		
Cabernet Sauvignon	3.85	66	19.2	9.35	5.65	2.40	3.25	20.7	16.7	19	0.065
	3.73	79	18.3	11.15	6.95	3.15	3.80	23.3	18.0	21	0.076
	3.88	73	17.7	9.40	5.75	2.10	3.65	23.3	19.8	18	0.073
	3.86	99	17.3	12.85	7.70	3.90	3.80	23.8	17.3	22	0.076
	3.98	75	16.8	8.55	5.05	2.05	3.00	27.7	24.3	12	0.060
	3.85	61	16.5	10.30	6.20	2.50	3.70	23.1	18.9	20	0.074
	3.93	66	15.8	4.90	2.75	1.20	1.55	16.7	14.7	11	0.031
	3.66	86	15.2	6.40	4.00	1.50	2.50	15.8	13.3	19	0.050
	3.91	78	15.2	5.80	3.30	1.40	1.90	22.4	20.1	9	0.038
	3.47	178	14.0	3.60	2.25	0.75	1.50	19.8	18.5	8	0.030
	3.91	81	14.0	3.90	2.15	1.00	1.15	17.8	16.1	7	0.023
	3.75	108	13.8	5.80	3.20	1.60	1.60	21.6	18.9	8	0.032
	3.90	92	13.6	5.40	2.85	1.55	1.30	24.4	21.8	6	0.026
	3.92	96	12.8	5.00	2.70	1.40	1.30	20.0	17.7	7	0.026
Shiraz	3.87	89	18.5	9.15	5.60	1.95	3.65	26.4	23.2	16	0.073
	3.97	59	17.3	10.25	6.10	2.40	3.70	23.8	19.8	19	0.074
	3.76	22	16.3	8.20	5.00	1.85	3.15	15.6	12.5	25	0.063
	3.76	77	16.3	8.35	5.05	1.90	3.15	18.6	18.6	17	0.063
	3.98	58	16.0	10.15	6.00	2.60	3.40	23.1	18.8	18	0.068
	3.88	85	16.0	8.85	4.10	1.50	2.60	18.9	16.4	16	0.052
	3.75	120	15.7	8.80	5.50	1.85	3.65	22.7	19.6	19	0.073
	3.98	94	15.5	5.45	3.05	1.50	1.55	22.9	20.4	8	0.031
	3.69	122	15.3	8.00	5.05	1.90	3.15	16.7	13.5	23	0.063
	3.77	144	15.3	5.60	3.35	1.10	2.25	20.0	18.2	12	0.045
	3.74	10	14.8	7.90	4.75	1.95	2.80	15.6	12.4	23	0.056
	3.76	100	14.3	5.55	3.25	1.15	2.10	19.1	17.2	12	0.042
	3.91	73	14.3	4.65	2.70	0.95	1.75	19.4	17.8	10	0.036
	3.60	301	14.2	4.25	2.40	1.25	1.15	22.9	20.8	6	0.023
	3.76	104	14.0	8.70	5.10	2.25	2.85	20.7	17.0	17	0.057
	3.90	67	13.8	7.40	4.40	1.60	2.80	25.1	22.4	13	0.056
	3.80	89	12.5	5.35	3.15	1.20	1.95	17.8	15.8	12	0.039
	3.65	192	11.5	6.35	3.90	1.25	2.65	33.4	31.3	8	0.053

<sup>a</sup> Mean score of 3 individual ratings. Standard errors were  $\pm 0.39$  for Cabernet Sauvignon,  $\pm 0.56$  for Shiraz.

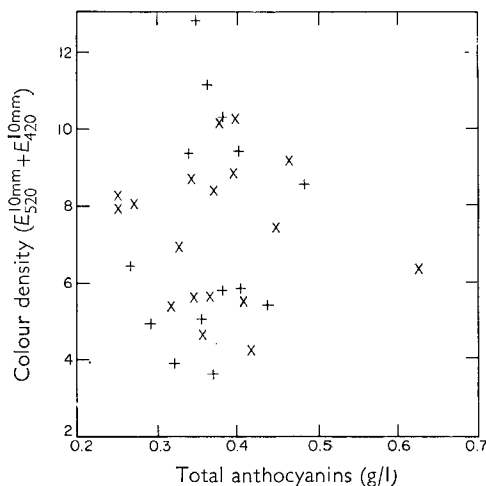


Figure 2. Plot of wine colour density against content of total anthocyanins.

levels in the range 0.35 to 0.45 g/l, but there was a three-fold variation in colour density within this group. This is a consequence of the widely variable degree of ionisation of anthocyanins in the different wines, and of the related variation in actual colour contribution from the polymeric pigment fraction (see below).

Statistical analysis showed a significant difference in slope ( $P < 0.05$ ) of the regression lines relating wine colour density to degree of ionisation of anthocyanins in Cabernet Sauvignon and Shiraz wines [Figure 3(a)]. For the relationship between colour density

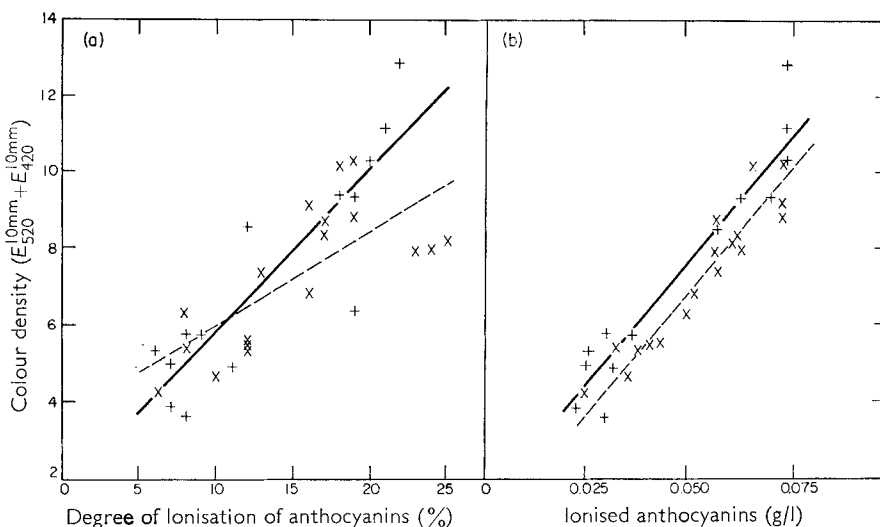


Figure 3. Relations between (a) wine colour density and degree of ionisation of anthocyanins and (b) wine colour density and content of ionised anthocyanins.

and content of ionised anthocyanins [Figure 3(b)] there was no significant difference in slope of the regression lines, but there was a difference ( $P < 0.05$ ) in position of the lines. The significance of each regression line was  $P < 0.001$ .

### 3.3. Polymeric pigments

Approximate measures of the contributions of polymeric pigments to wine colour were obtained by measurement of residual colour after addition of a large excess of  $\text{SO}_2$ . The percentage of absorbance at 520 nm due to these non-anthocyanin pigment forms was found to vary from 30 to 50%, and there was a fivefold range in the actual level of residual colour in these wines.

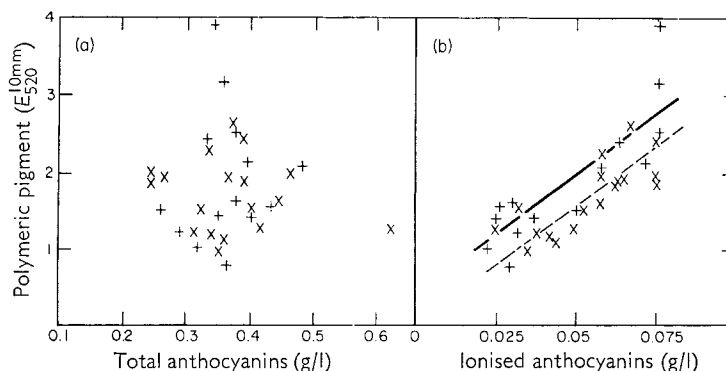


Figure 4. Plot of polymeric pigment component of wine colour against anthocyanin content (a), and relation between this component and the content of ionised anthocyanins (b).

Figure 4(a) shows the absence of any relation between colour due to polymeric pigments and total anthocyanin content, whereas good correlations ( $P < 0.001$ ) were obtained between polymeric pigment colour and the content of ionised anthocyanins [Figure 4(b)]. There was no difference in slope, but a significant difference in position, ( $P < 0.01$ ) between the regression lines for Cabernet Sauvignon and Shiraz wines.

### 3.4. pH and sulphur dioxide

These are two variable features of red wines known to have important influence upon anthocyanin equilibria. It has not been possible to interpret their separate effects in consideration of this group of commercial wines.

The range of total  $\text{SO}_2$  content was very large (10 to 301 parts/million), and the several wines at the extremes of this range did have correspondingly high and low degrees of ionisation (Table 1). There was, however, a three-fold range in the degree of ionisation of anthocyanins, with consequent variation in wine colour density, for 26 wines having 60 to 120 parts/million total  $\text{SO}_2$  and also for 14 wines having 75 to 100 parts/million total  $\text{SO}_2$ . It is noteworthy that none of the first six rated wines in either variety contained more than 100 parts/million total  $\text{SO}_2$ .

### 3.5. Wine quality and degree of ionisation

From Figures 1, 3 and 4 it is evident that the particular content of ionised anthocyanins is a variable feature of wine colour composition which relates to the quality of these wines.

Even though the actual anthocyanin concentrations varied more than twofold in the wines examined, there was a good correlation between quality rating and degree of ionisation (Figure 5); the significance of the parallel regression lines was  $P < 0.001$  for Cabernet Sauvignon and  $P < 0.05$  for Shiraz wines.

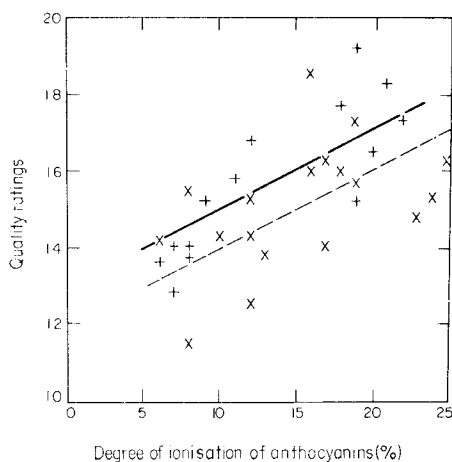


Figure 5. Relation between quality rating and degree of ionisation of anthocyanins.

### 3.6. Data from the 1973 vintage

Similar analyses were conducted on wines of the subsequent vintage in the Southern Vales, exhibited in October 1973. For the 15 Cabernet Sauvignon wines, excellent correlations were again obtained between quality rating and wine colour density ( $P < 0.001$ ), and between quality rating and degree of ionisation of anthocyanins ( $P < 0.001$ ). There were, however, no such statistical correlations for the group of 22 Shiraz wines.

## 4. Discussion

### 4.1. General comment

Following the chance observation of an evident correlation between quality rating and colour density in these young red wines, our purpose has been to recognise the responsible features of wine colour composition in an attempt to show a much needed link between instrumental measurement and sensory appraisal of such wines.

It does indeed seem surprising that variation in the degree of ionisation of anthocyanins in wines of uniform pH has not been previously established as being a significant factor in red wine composition. However, following identification and description of grape anthocyanins and accompanying phenolics by Ribéreau-Gayon,<sup>1</sup> much of the



experimentation on wine colour composition would now seem to have been needlessly elaborate and indirect. Chromatographic and gel column procedures are essential for investigations of phenolic composition, but interpretations from such data of the actual chromophoric components of wine colour have been uncertain. Also, the long established use of various colorimetric analyses for categories of constituent phenolics<sup>16</sup> seems to have directed attention away from the state of the anthocyanin fraction in wine solution.

Considerations of "grape tannin", assumed to be extracted into the wine during vinification, have obscured the issue further, but it is now clear that such materials are artifacts of extraction and that, although some phenolic components are extremely labile and condense rapidly in new wines, the initial wine colour is due very largely to anthocyanins alone.<sup>3</sup> This being so, it should then be a simple matter to account the colour of a new wine in terms of anthocyanin content and of the equilibria between colourless forms and coloured flavylum ions. However, by the time a wine has been clarified and finished, the usually considerable contribution to colour density of the polymeric pigment forms<sup>3</sup> requires that due allowance be made for this in determination of the state of residual anthocyanins.

The erroneous identification of colour density in young wines with anthocyanin concentration has been an implicit feature of most of the oenological literature. Berg<sup>17</sup> had speculated about differences in response of wine pigments from those of anthocyanins in model solutions, but the techniques used were too complicated to permit any clear interpretations, and the averaging of data from many wines of different varieties prevented recognition of any significant variation in anthocyanin equilibria between individual wines. From data based upon pigment profiles of young varietal wines, Somers<sup>10</sup> also concluded that colour density was not explicable in simple terms of pigment content and Ribéreau-Gayon<sup>12, 18</sup> has recently reported similar observations on young Bordeaux wines. It would seem that the phenomenon of variable ionisation, as observed in the Southern Vales wines, has quite general relevance to the oenology of red wines.

The correlations of quality rating with colour density and degree of ionisation imply a significant inter-relation between these features of wine colour and the aroma and palate characteristics; all but one wine (mean 2.7) had received the maximum of 3 points for colour, so that the lighter coloured wines lost relatively more points for aroma (7) and palate (10). It may be that the concentration of flavylum ions and/or the related level of SO<sub>2</sub>-resistant polymeric pigments [cf. Figure 4(b)] play a functional role in the inhibition of incipient spoilage yeasts or bacteria, resulting in a lower ranking for wines in which these factors are small. Reports of the bactericidal activity of anthocyanins and other wine phenolics have been reviewed by Singleton and Esau,<sup>16</sup> and yeast inhibition by a synthetic flavylum salt has been recently demonstrated.<sup>19</sup>

The identical slope of regression lines for the two varieties suggests that the significance of the relations could hold over a range of varieties of which these two are samples, the shift in position of the regression lines being an effect of varietal differences in composition. We conclude that use of the observed correlations may provide a valuable objective guide to relative assessment of the present, and possibly future, merit of sound young wines *of the same variety and style*.

The absence of any correlation with quality rating of Shiraz wines in 1973 could have been due to the fact that this exhibition was conducted a month earlier than that in 1972, allowing a lesser time for proper preparation of the young wines. Some of those in the Shiraz group were "out of condition", being slightly "spritzig" because of malolactic fermentation.

#### 4.2. Possible influences upon degree of ionisation

Several variable features of wine composition, other than pH, could be involved in the equilibria of anthocyanins in wine solution, as follows.

##### 4.2.1. Oxidation-reduction effects

Ribéreau-Gayon,<sup>12, 18</sup> in reporting observations during ageing of the same wine conserved in wood and in stainless steel and also on the effect on colour density of exposing red wines to air, found evidence of pH-independent variation of anthocyanin equilibria, and proposed that oxidation-reduction mechanisms were involved. As the oxidation-reduction potentials of wines are known to be poorly poised,<sup>20, 21</sup> the influence of such factors may well be at least partially responsible for the variation in degree of ionisation of anthocyanins in the Southern Vales wines. There are, however, no data on the intervention of such mechanisms on anthocyanin equilibria.

##### 4.2.2. Self-association, copigmentation

Asen, Stewart and Norris<sup>22</sup> have shown that anthocyanins can undergo self-association in aqueous solutions at pH 3 and above, with a disproportionate increase in visible absorbance at higher concentrations. They also reported<sup>22</sup> model experiments on the copigmentation of cyanidin 3,5-diglucoside with many other plant constituents, mainly phenolics and amino acids. Although these effects were concentration-dependent and the copigment complexes less stable in the presence of ethanol, their possible influence on colour composition in *V. vinifera* wines can not easily be discounted. Appreciable copigmentation in those non-*vinifera* wines and juices in which the principal pigments are anthocyanin 3,5-diglucosides seems very likely, because of the low pK values<sup>2</sup> of those anthocyanins. In the absence of some such large effect on the state of anthocyanin equilibria, such wines should be extremely light in colour.

##### 4.2.3. Effect of added SO<sub>2</sub>

The most certain influence on the content of ionised anthocyanins in young red wines is that of added SO<sub>2</sub> (together with that of any SO<sub>2</sub> formed during the fermentation). Interpretations of the actual effect on anthocyanin colour in a particular wine would require knowledge not merely of anthocyanin and SO<sub>2</sub> concentrations, but also of the accompanying levels of acetaldehyde, pyruvic acid,  $\alpha$ -ketoglutaric acid and other SO<sub>2</sub>-binding compounds. Burroughs and Sparks<sup>8</sup> have shown how the SO<sub>2</sub>-binding power of white wines and ciders may be accounted from such information by use of equilibrium constants for the various SO<sub>2</sub>-binding reactions.

Because of the variable content in wines of the principal SO<sub>2</sub>-binding carbonyl compounds,<sup>23</sup> the same level of total SO<sub>2</sub> could have quite different effects upon antho-

cyanin colour in different wines. In the absence of any added SO<sub>2</sub>, it is probable that there would have been much smaller variation in the degree of ionisation of anthocyanins and also, therefore, of colour density, in the Southern Vales wines; except perhaps for the uncertain influences of oxidation-reduction mechanisms and copigmentation upon anthocyanin colour. It is evident that these are critical matters for further enquiry in the oenology of red wines.

### Acknowledgements

Our thanks are due to the winemakers of the Southern Vales, and to the panel of wine judges (Dr B. C. Rankine, Messrs. R. W. Hesketh and K. Sobels) for their parts in providing the unique circumstances of this investigation. We are also grateful to Mr K. M. Cellier, of the Division of Mathematical Statistics, C.S.I.R.O. for statistical analysis of data.

### References

1. Ribéreau-Gayon, P. *Les Composés Phénoliques du Raisin et du Vin* Institut National de la Recherche Agronomique, Paris 1964.
2. Timberlake, C. F.; Bridle, P. *J. Sci. Fd Agric.* 1967, **18**, 473.
3. Somers, T. C. *Phytochemistry* 1971, **10**, 2175.
4. Jurd, L. *J. Fd Sci.* 1964, **29**, 16.
5. Timberlake, C. F.; Bridle, P. *J. Sci. Fd Agric.* 1967, **18**, 479.
6. Burroughs, L. F.; Sparks, A. H. *J. Sci. Fd Agric.* 1973, **24**, 187.
7. Burroughs, L. F.; Sparks, A. H. *J. Sci. Fd Agric.* 1973, **24**, 199.
8. Burroughs, L. F.; Sparks, A. H. *J. Sci. Fd Agric.* 1973, **24**, 207.
9. Somers, T. C. *Nature, Lond.* 1966, **209**, 368.
10. Somers, T. C. *Vitis* 1968, **7**, 303.
11. Ribéreau-Gayon, P.; Stonestreet, E. *Bull. Soc. chim. Fr.* 1965, **9**, 2649.
12. Ribéreau-Gayon, P. *Vitis* 1973, **12**, 119.
13. Koeppen, B. H.; Basson, D. S. *Phytochemistry* 1966, **5**, 183.
14. Niketić-Aleksić, G. K.; Hrazdina, G. *Lebensmittel. Wiss. u. Technol.* 1972, **5**, 163.
15. Hrazdina, G. *J. Agric. Fd Chem.* 1970, **18**, 243.
16. Singleton, V. L.; Esau, P. *Phenolic Substances in Grapes and Wine and their Significance*, Academic Press, New York, 1969.
17. Berg, H. W. *Annls. Technol. agric.* 1963, **12**, 247.
18. Ribéreau-Gayon, P. *Connaissance Vigne Vin* 1971, **5**, 87.
19. Whiteley, L. A.; Bridle, P.; Timberlake, C. F.; Beech, F. W. *Long Ashton Report* (University of Bristol) 1971, p. 192.
20. Ribéreau-Gayon, J.; Peynaud, E. *Traité d'Oenologie*, Béranger, Paris 1961, Vol. 2.
21. Amerine, M. A.; Joslyn, M. A. *Table Wines* University of California Press, Berkeley. 1970.
22. Asen, S.; Stewart, R. N.; Norris, K. H. *Phytochemistry* 1972, **11**, 1139.
23. Rankine, B. C.; Pocock, K. F. *J. Sci. Fd Agric.* 1969, **20**, 104.