

Interpretations of colour composition in young red wines

by

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Interpretation der Färbungskomponenten bei jungen Rotweinen

Zusammenfassung. — Neuere Erkenntnisse der Forschung über die Farbstoffzusammensetzung und das Anthocyangleichgewicht von Rotweinen ermöglichen eine objektivere Beschreibung und eine zweckmäßige Interpretation der verschiedenen Weintypen und -nuancen.

Durch die Anwendung einer neuen analytischen Methode konnte bei australischen Rotweinsorten eine beträchtliche Variabilität der Parameter, welche die Weinfärbung charakterisieren, aufgezeigt werden. Der Phenolgehalt kann über einen breiten Bereich variieren, wofür normalerweise entsprechende Schwankungen in der Zusammensetzung des Lesegutes verantwortlich sind; aber auch Wein-pH und Konzentration der freien schwefligen Säure stellen wesentliche Faktoren für die Ausprägung der Farbintensität und -tönung dar. Aus insgesamt 6 spektralphotometrischen Bestimmungen können leicht Daten über solche Einflüsse sowie Werte des Anthocyan- und Gesamtphenolgehaltes gewonnen werden.

Es wird vorgeschlagen, diese Methode für eine Art „anatomischer Beschreibung“ junger Rotweine zu benutzen, wobei Größen verwendet werden, die in Bezug sowohl der Zusammensetzung des Lesegutes wie zur Weintechnologie stehen. Die Brauchbarkeit dieser Vorstellungen wird dadurch erhärtet, daß Korrelationen zwischen einer Reihe von Parametern der Weinfärbung und den unabhängig davon gewonnenen Ergebnissen sensorischer Qualitätsprüfungen aufgezeigt werden konnten.

Introduction

The elaborate technology we have today is designed to give better or even optimal control of the winemaking process, along with more efficient and more hygienic handling of materials at all stages. While these are most important considerations for commercial operations, it is significant that some excellent red wines in particular are still being made with fairly simple equipment and facilities. This fact of oenological experience underlines the fundamental importance of the harvest composition in relation to that of the vintage product.

In wine making practice however, and particularly in relatively new viticultural districts where there is no legacy of wine experience, the quality of the product often does not come up to expectations from the harvest. In this paper, interpretations of wine colour composition are proposed as providing better appreciation of some of the factors affecting the quality of red wines.

As the pigments are generally localised in the skin vacuolar cells, one can make white or at least rosé-type wines from black grapes. This truism serves to emphasize the central fact that all of the many differences between red and white wines, whether sensory or determined by instrumental means, are due to these phenolic materials, i.e. they are the *very essence* of red wines.

However, in spite of numerous research studies over many years, the vital role of these minor constituents has not been well appreciated in oenology. This has been

largely due to the chemical diversity and reactive nature of the total wine phenolics, which have presented great difficulties in interpretation of wine colour (SINGLETON and ESAU 1969).

Very often therefore in laboratory control, the same analytical measures are applied to red wines as to white, and wine colour, the most obvious feature, is assessed in purely subjective terms. Instrumental measures are seldom made because they are deemed to be much less useful or even irrelevant to wine condition. Such omission has even been sometimes evident in elaborate research reports.

Recent developments have shown this attitude to be quite erroneous, as spectral measures of wine colour composition can in fact provide a unique appraisal of overall wine condition.

Diversity of type and style in red wines

Because of the complexity of grape and wine composition, each wine is uniquely different. Furthermore, the additional presence of the flavonoid phenolics in red wines gives them even greater scope for significant variation in composition and sensory effect. It is this "extra dimension" which accounts for the obvious diversity and for the ageing characteristics of red wines. The whites, in contrast, have no similar capacity for improvement during conservation.

The quantity of total wine phenolics is a primary consideration. Whereas white wines from free-run juice contain minimal levels of mainly non-flavonoid phenolics (as little as 50 mg/l), red wines may contain as much as 4 g/l of reactive flavonoid phenolics, including the anthocyanins; the latter are present in amounts up to about 1 g/l in new red wine. At one extreme, with very low levels of anthocyanins and other phenolics, the wine is a rosé ready for drinking early in the current vintage, as are the dry white wines. At the other extreme of phenolic content, the wine is a deeply coloured astringent red, requiring perhaps years of conservation before attaining its full potential.

The level of such skin and seed extractives is obviously limited by the amount available, which refers both to the grape variety and to the vines from which the crop is harvested. Any lower level arises from less efficient extraction of the grape solids, which is very often intended by the winemaker.

However, while quantity of phenolic extract is the determinant of wine type, the qualitative state of these materials is a most critical feature in relation to wine style and sensory properties, and also to potential for improvement during conservation.

The nature of wine colour

The gist of it is that the anthocyanins and related phenolics contribute much more to wine appreciation than mere visual appearance. These minor constituents are entirely responsible for the initial astringency in new red wines, and for much of the dynamic character of such wines during ageing, referring both to colour composition and to sensory effect. This is to say that they are not simply colouring agents, but are an intrinsic part of the wine at all stages of development (SOMERS 1968, 1971).

It is important to note that the initial composition of wine colour and the course of the ageing reactions are dependent not only on the quantity of anthocyanins and other phenolics, but are very much influenced by other features of the harvest and by the particular oenological procedures or method. This is the lesson which has

been learned from studies of the anthocyanin equilibria (TIMBERLAKE and BRIDLE 1967 a and b, SOMERS 1971, BURROUGHS 1975), and of the compositional changes in wine colour which occur continuously during ageing (SOMERS 1968, 1971, RIBÉREAU-GAYON 1973, TIMBERLAKE and BRIDLE 1976 a).

Whereas the colour of new wine is almost entirely due to the monomeric grape anthocyanins, there is a steady shift, as a result of condensation reactions, towards predominantly polymeric pigment forms in aged wines, along with a progressive decline in the level of anthocyanins. Such changes are detectable immediately after vintage, which means that wine colour must generally be regarded as an integration of contributions from monomeric and polymeric pigment forms (SOMERS 1971).

The organoleptic benefits conferred upon a wine by good conservation practice are very largely due to the occurrence of favourable chemical changes in these total phenolics, and there are associated changes in the composition of wine colour, i.e. in the appearance of the wine. Needless to say, the same is true of unfavourable influences which may occur during conservation.

Spectral evaluation of young red wines

Thus, the older the wine the more complex is the chemistry of the total phenolics, posing problems which are considered to be too difficult to warrant their detailed study at this stage.

However, because of the progression of events which has been recognised in red wine ageing, and thanks also to notable differences in properties between the monomeric and polymeric pigment forms, the situation is quite different in consideration of young red wines. Furthermore, it is relevant to note that high quality material is the prerequisite for the making of good matured wines of whatever age.

On these bases, simple spectrophotometric methods have been recently developed for objective assessment of young red wines "as seen in the glass" i.e. the measures are made, as nearly as possible, upon the intact wine. Such analysis has been shown to provide remarkably comprehensive and useful information about the young wine at a critical stage of its development (SOMERS and EVANS 1974, 1977, SOMERS 1975).

In these measures, the states of the anthocyanin equilibria are of principal interest, and corrections are applied for the contributions of the polymeric pigments to wine colour. Essentially, the evaluation depends upon deliberate displacements of the pigment equilibria, enabling their states in the particular wine to be determined (see Appendix).

The two major influences upon anthocyanin colour are wine pH and free SO_2 content, both of which are variable features of wine composition. Thus, the degree of ionisation (α) of the anthocyanin component of wine colour (i.e. the percentage of anthocyanins in the coloured forms) has been found to vary from as low as 2% to over 30% in recent surveys of Australian red wines, with consequently large effect upon wine colour composition and colour density. This means that, in some situations, there may be no relation whatever between wine colour density and anthocyanin content, as was found in a survey of wines from the Southern Vales district of South Australia in 1972 (SOMERS and EVANS 1974).

The degree of ionisation (α) is obviously a most important variable of young red wines. Other information which can be routinely obtained from the 6 absorbance readings made in each evaluation includes the following: measures of colour density and hue, total phenolics as well as anthocyanin content, free and molecular SO_2 ,

indices of "chemical age". It is noteworthy that, because of interaction between SO_2 and anthocyanins, the level of free SO_2 in red wines cannot be determined by procedures applicable to white wines (BURROUGHS 1975). The age indices refer to the extent of polymerisation of the total wine phenolics, and to the wine's potential for improvement during conservation (SOMERS and EVANS 1977).

The range of such analytical measures in Australian wines has been very large, some typical data being shown in Table 1, in which pH values are also listed.

Table 1
Typical data for young Australian red wines
Typische Meßwerte junger australischer Rotweine

Analytical measure	Current vintage wines (1975 Shiraz)					
	1	2	3	4	5	6
Colour density	10.8	3.5	12.0	5.5	12.7	6.6
Colour hue	0.54	0.64	0.67	0.86	0.59	0.75
Actual degree of ionisation (α)	26	7	16	5	24	9
Natural degree of ionisation (α') ¹⁾	28	25	17	15	23	20
Free SO_2 (mg/l)	0.28	9.10	0.22	1.27	0	5.10
Molecular SO_2 ($\mu\text{g/l}$)	5.0	156	1.1	5.5	0	56
Total anthocyanins (mg/l)	371	381	486	390	460	408
Ionised anthocyanins (mg/l)	97	28	78	21	109	36
Total phenolics (absorbance units)	47	40	62	55	66	55
"Chemical age" index (i)	0.30	0.13	0.45	0.40	0.32	0.33
"Chemical age" index (ii)	0.10	0.03	0.11	0.08	0.09	0.08
pH	3.50	3.52	4.07	4.13	3.75	3.70

¹⁾ α' is the value found after abolition of the bleaching effect of SO_2 .

Correlations with wine quality

Thus, the new spectral method provides data interpreted as being pertinent both to wine type and to wine style or condition.

The utility of this approach to assessment of young red wines was first indicated by the finding of statistically sound correlations between wine colour densities and independently made sensory ratings of wines from the Southern Vales district of South Australia in 1972 (SOMERS and EVANS 1974). In that investigation, the significant qualitative feature was found to be the degree of ionisation (α) of the anthocyanin component of wine colour, the value of which is determined principally by the wine pH and by the level of free SO_2 (SOMERS and EVANS 1974, 1975, 1977).

Subsequently, these and other correlations were found in more elaborate surveys of red varietal wines in the Australian vintages 1974, '75 and '76 (SOMERS, EVANS and CELLIER, unpublished work). In these later surveys, of several hundred wines, extremely wide ranges of all the various colour factors were noted. The data for Shiraz and Cabernet Sauvignon wines of the 1976 vintage are presented in Table 2. The large variabilities are thought to be collectively responsible for much of the range in wine quality, and for the correlations which emerged from the surveys.

Details of the vintage survey data, which refer to statistically demonstrated viticultural and oenological requirements for reasonable standards of red wine quality in the Australian vintage, will be reported elsewhere. However, the validity of this analytical approach to assessments of relative wine quality has recently been

Table 2
 Variability in wine colour composition — 1976 vintage
 Variabilität der Färbungskomponenten von Weinen — Weinjahrgang 1976

Analytical measure	Shiraz (103 wines)			Cabernet Sauvignon (79 wines)		
	Min.	Mean	Max.	Min.	Mean	Max.
Colour density	2.7	7.6	16.5	2.5	7.6	15.7
Actual degree of ionisation (α)	3	15	33	4	14	32
Natural degree of ionisation (α') ¹⁾	10	21	36	11	20	36
Free SO ₂ (mg/l)	0	2.4	17.5	0	2.5	11.5
Total anthocyanins (mg/l)	125	357	733	107	366	620
Ionised anthocyanins (mg/l)	12	52	171	12	49	150
Total phenolics (absorbance units)	26	50	96	23	50	67
“Chemical age” index (i)	0.16	0.35	0.58	0.19	0.36	0.58
“Chemical age” index (ii)	0.03	0.10	0.19	0.04	0.10	0.18
pH	3.38	3.79	4.34	3.37	3.81	4.40
Quality rating	10.0	14.5	18.5	9.6	14.3	18.5

¹⁾ Cf. footnote in Table 1.

supported by similar studies of Beaujolais wines, in which the same spectral procedures were used as in the earlier Australian investigations (TIMBERLAKE and BRIDLE 1976 b).

The concept of wine description

Such analysis of red wine colour is therefore seen to provide a sort of “anatomical description” of a young wine in terms which refer not merely to its appearance but also to vital aspects of the vintage, viz. phenolic content, acidity, SO₂ level. The method and concept now serve as a basis for technical advice from this Institute on matters pertaining to red wine composition.

For example, one feature of the analysis is that any positive value of the spectral measure of free SO₂ is indicative of SO₂ addition to that wine after fermentation (SOMERS and EVANS 1975, 1977); the wide-ranging influence of SO₂ upon the degree of ionisation of anthocyanins, and therefore upon wine colour composition and density, is shown in Table 1 (compare data for wines 1 and 2). Another novel feature is that the indices of “chemical age” appear to be related to the longevity or potential for improvement of the wine, as has been indicated by such measures of older wines (SOMERS and EVANS 1977).

It is suggested that this spectral method of wine description is sufficiently simple to have general application in the routine recording and exchange of oenological data, whether in quality control, commercial transactions or research. There are obvious advantages in the adoption of such a standard procedure.

Summary

Recent developments in research on pigment composition and anthocyanin equilibria in red wines have enabled more objective description, and some useful interpretation, of the various wine types and styles.

Very large variations in recognised parameters of wine colour have been shown in varietal Australian wines by application of a new analytical method. While there are wide ranges in phenolic content, which normally arise from corresponding variation in the harvest composition, the wine pH and the level of free SO₂ are also significant determinants of wine colour density and hue. Data on such influences together with measures of the anthocyanin and total phenolic content, are readily obtained from a set of 6 spectrophotometric observations.

The method is proposed as providing a kind of "anatomical description" of a young red wine in terms which relate both to the harvest composition and the wine making method. The utility of this concept in oenology has been emphasized by the showing of correlations between several parameters of wine colour and independent assessments of wine quality.

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Appendix

The analytical method has been recently described (SOMERS and EVANS 1977). Cells of appropriate path-length (1, 2, 5 or 10 mm) are used, and the particular spectrophotometric readings are:

- (i) absorbancies at 420 and 520 nm,
- (ii) the absorbance at 520 nm after bleaching of anthocyanin colour by addition of excess SO₂ to the cell used in (i),
- (iii) the absorbance at 520 nm after restoration of SO₂-bleached anthocyanins by addition of excess acetaldehyde to a fresh wine sample,
- (iv) the absorbance at 520 nm of a highly diluted acid solution of the wine (1 + 50 or 1 + 100 with 1 M HCL),
- (v) the absorbance at 280 nm of the above solution.

All 6 absorbance readings are then converted to values for the intact wine in 10 mm path-length. The derivation of the various wine parameters from the spectral data has been explained in the above paper.

The quality ratings included in Table 2, and referred to in the text, are mean

scores of 3 wine judges, who sought to provide comparative sensory measures of commercial wines submitted for appraisal at official exhibitions. As is customary in Australian Wine Shows, the wines in each group were all before each judge at one time. Scores were separately assigned on a 20 point scale (3 for colour and clarity, 7 for bouquet and 10 for palate) before determination of the mean value for each wine.

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