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Red wine quality and style: Diversities of composition and adverse influences from free SO_2

by

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Qualität und Nuance von Rotwein: Schwankungen der Zusammensetzung sowie nachteiliger Einfluß von freiem SO_2

Zusammenfassung. — Anhand der Analysen von 404 jungen Rotweinen — zwei Sorten aus drei aufeinanderfolgenden Jahrgängen — wurden die Beziehungen zwischen den Komponenten der Weinfärbung und der Gesamtnote der sensorischen Qualitätsprüfung untersucht. Die Weine, Shiraz und Cabernet Sauvignon, waren bei den Adelaide Wine Shows 1974/75/76 zur vergleichenden Beurteilung angestellt worden. Sämtliche Parameter des Phenolgehaltes, die Farbintensität und -tönung, der pH-Wert sowie der Gehalt an Gesamt-SO_2 und freiem SO_2 zeigten eine beträchtliche Variabilität. Das freie SO_2 beeinflußte das Pigmentgleichgewicht am stärksten, wobei der Ionisationsgrad der Anthocyane (α) bis zu 10fach schwanken konnte. Positive Qualitätsfaktoren waren: Farbintensität, der Parameter α, gefärbte Anthocyane, Gesamtpigmente sowie Gesamtphenole. Zu den negativen Faktoren gehörten Farbtönung, freies SO_2 und Gesamt-SO_2. Keinerlei Korrelation bestand zum Wein-pH. Die unterschiedlichen Qualitätsnoten der geprüften Rotweine dürften zum Gutteil kellertechnisch, durch die beträchtlichen Schwankungen der zugesetzten SO_2-Mengen und des Behandlungszeitpunktes, bedingt sein.

Introduction

The concept of wine quality as being a result of local ecological factors has fundamental acceptance in oenology. Thus the particular soil and climate characteristics are generally given emphasis in popular accounts of regional wines, and have indeed provided the basis, usually with stipulation of the grape varieties, for the many classifications of wines according to district of origin and year of vintage.

Such classifications involve assumptions about management of the winemaking process and of the subsequent conservation period in widely different situations, since they imply that the full potential of the harvest is normally realised in the finished wine. Oenological factors may however have over-riding influence on sensory properties of a wine. Large quality differences in commercial red wines have provided the background to extensive investigations at this Institute of relations between the composition of total wine phenolics and relative wine quality. The analytical data have referred exclusively to the phenolic content, the wine colour composition and to factors affecting both anthocyanin equilibria and colour composition.

In a study of young red wines from a single district, significant correlations had been shown between overall wine quality and the wine colour density (SOMERS and EVANS 1974). The surprising observation that there was no relation between colour density and anthocyanin content in those commercial wines focussed attention on fac-

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tors affecting the pigment equilibria; the major influences are pH and those arising from the use of sulphur dioxide. Much of the wide variation in colour density of those regional wines was due to corresponding variation in the state of anthocyanin equilibria i.e. in the degree of ionisation (α) of residual anthocyanins which was strongly correlated with wine quality.

More recent developments have helped towards interpretation of the significance of α values in relation to quality of young Australian red wines. Thus BURROUGHS (1975) showed how the levels of "free SO_2" in young red wines can be derived by manipulation of the pigment equilibria, and use of this procedure in investigations of young Beaujolais wines at Long Ashton (JACKSON *et al.* 1978, TIMBERLAKE *et al.* 1978) provided evidence that the generally higher α values of those French wines were due to much lower levels of free SO_2 than present in young Australian red wines.

In this paper we report data and interpretations of colour composition in relation to quality of young commercial red wines in the Australian vintages 1974—75—76.

Materials and methods

Wines

All wines were of commercial origin, coming from 20 widely dispersed viticultural regions of Australia. The wines were analysed within the week following sensory assessment at the Adelaide Wine Show, conducted by the Royal Agricultural & Horticultural Society of South Australia, in October of 1974—75—76. The wines had been presented in separate varietal classes, Shiraz and Cabernet Sauvignon, at 6—7 months after vintage. Five groups of such wines were examined, comprising Shiraz 94 (1975), 103 (1976) and Cabernet Sauvignon 53 (1974), 76 (1975) and 78 (1976).

Quality assessments

Scores were assigned by panels of three experienced wine judges appointed by the Show Committee. In the Australian system all wines presented in each class are put before each judge at one time, so that a comparative assessment is more readily made; maximum points that could be given were colour 3, aroma 7 and palate 10 (RANKINE 1974). The mean aggregate scores, as reported by the Show Committee, were used in our investigations.

Spectral evaluations

The spectral methods and interpretations used in analysis of wine colour composition and determination of the various wine parameters have been described previously (SOMERS and EVANS 1977, SOMERS 1978). Data for each wine were derived from various spectrophotometric readings at 280, 420 and 520 nm using cells of appropriate path length.

Other analyses

Measures of potassium content, by flame photometry, were made for all wines because of our special interest in the wide range of wine pH and of high correlations found between these two parameters (SOMERS 1977). Total SO_2 contents were determined by the standard aspiration procedure.

Statistical treatment

Correlation coefficients were calculated between all variables in each of the five wine groups. As all the matrices showed similar correlations, the values were pooled within varieties to give two composite matrices for the total data concerning Shiraz and Cabernet Sauvignon wines.

Results and discussion

Variability of wine colour and phenolic composition

The analytical and sensory data are summarised in Table 1, in which a division has been made between actual measures of phenolic content and those having modifying influences on colour density and composition. There is great diversity in every analytical aspect for all five wine groups, but it is significant that they cannot all be attributed to variation in grape composition or to varying extent of extraction during vinification. Thus these two factors would certainly be responsible for the several-fold ranges in concentrations of total anthocyanins, total pigments (E_{520}^{HCl}) and total phenolics (E_{280}), but it is now evident that high levels of free SO_2 have been the cause of abnormally low α values in many wines, with large effects on the level of coloured anthocyanins and on wine colour density and tint.

Correlations of analytical parameters with wine quality

In our earlier report of relationships between wine colour composition and quality in wines from a single region (SOMERS and EVANS 1974), it was noted that, although the "inbuilt colour correlation" appeared to be insignificant in relation to overall quality rating (as most wines actually received the maximum 3 points for colour out of the total 20), the data nonetheless implied significant interrelations between parameters of wine colour and the sensory assessment of aroma and flavour. From our own observations, there have always been good indications that this was so — thus the aroma was often odd or otherwise unsatisfactory in wines having low α values, with related influence on the palate. However, detailed sensory data were not available in the later surveys, which were conducted with reference only to the average gross quality rating of each wine.

The existence of such interrelationships between colour, aroma and flavour in young red wines was subsequently confirmed by JACKSON *et al.* (1978) in the course of an investigation of quality variation in Beaujolais wines. That report and others (TIMBERLAKE *et al.*, 1978, TIMBERLAKE 1981) have supported the original concept that analysis of wine colour composition can provide objective guidelines to the overall quality of young red wines.

Correlations between quality rating and various analytical parameters of young Shiraz and Cabernet Sauvignon wines from three successive vintages are shown in Table 2. Strong positive correlations were consistently found with colour density, the level of coloured anthocyanins, the content of total phenolics and with the degree of ionisation (α) of anthocyanins. Strong negative correlations were found with SO_2 content and with measures of wine hue or tint. It is noteworthy that despite the generally wide range of pH, no relation was found between pH and quality rating in any of the five groups.

Correlation matrices showing statistical data for all 197 Shiraz wines (two vintages) and 207 Cabernet Sauvignon wines (three vintages) are shown in Table 3; corre-

Table 1

Summary of data for Shiraz and Cabernet Sauvignon wines in year of vintage

Die Werte der Shiraz- und Cabernet-Sauvignon-Weine im Jahr der Ernte

Variable [1]	Shiraz				Cabernet Sauvignon					
	1975 Mean	(n=94) Range	1976 Mean	(n=103) Range	1974 Mean	(n=53) Range	1975 Mean	(n=75) Range	1976 Mean	(n=79) Range
E_{520}	5.1	2—16	4.6	1—11	4.1	2—8	4.9	2—10	4.9	1—10
$E_{520}+E_{420}$	8.2	3—25	7.6	3—16	7.3	3—15	8.1	3—17	7.6	2—16
α (%)	16.5	5—34	14.9	3—33	11.4	3—21	14.1	4—27	13.7	4—32
α' (%)	23.3	14—40	21.2	10—36	16.8	10—25	20.0	12—31	20.2	11—36
Coloured anthocyanins (mg/l)	60	20—180	50	10—170	40	10—110	60	10—140	50	10—150
Total anthocyanins (mg/l)	380	120—700	360	120—730	380	90—660	410	110—780	370	110—620
E_{280}	51.9	28—104	54.4	30—100	53.1	34—84	54.3	35—86	53.9	27—71
E_{520}^{HCl}	—	—	21.0	8—43	—	—	—	—	21.0	6—34
pH	3.7	3.4—4.2	3.8	3.4—4.3	4.0	3.6—4.4	3.8	3.5—4.1	3.8	3.4—4.4
K (m.eq/l)	37.0	22—56	38.7	17—63	44.7	27—60	36.9	23—51	38.7	12—64
Total SO_2 (mg/l)	59.2	0—226	—	—	83.0	3—315	54.2	0—192	—	—
Free SO_2 (mg/l)	2.2	0—10	2.4	0—17	2.6	0—12.5	2.2	0—6.8	2.4	0—12.0
Molecular SO_2 (μg/l)	25.7	0—170	24.1	0—185	17.2	0—99	21.6	0—93	26.2	0—162
$E_{520}^{SO_2}/E_{520}$	0.40	0.25—0.73	0.45	0.23—0.70	0.51	0.32—0.69	0.42	0.23—0.68	0.47	0.22—0.71
$E_{520}^{SO_2}/E_{520}^{CH_3CHO}$	0.31	0.13—0.54	0.35	0.16—0.58	0.40	0.27—0.63	0.33	0.22—0.54	0.36	0.19—0.58
$E_{520}^{SO_2}/E_{520}^{HCl}$	0.09	0.04—0.23	0.10	0.03—0.19	0.09	0.05—0.19	0.08	0.03—0.17	0.10	0.04—0.18
E_{420}/E_{520} (tint)	0.65	0.48—0.92	0.70	0.45—1.0	0.79	0.51—1.1	0.69	0.50—1.0	0.72	0.48—0.99
Quality rating	14.9	11.0—18.7	14.5	10.0—18.5	14.6	8—18.8	14.9	9—18	14.3	9.6—18.5

[1]) All E values are in absorbance units corrected for 10 mm pathlength in intact wine.

Table 2

Correlations of quality rating with analytical variables of 404 commercial red wines in 3 vintages

Korrelationen zwischen der Qualitätsbeurteilung und den analytischen Größen von 404 käuflichen Rotweinen aus 3 Jahrgängen

Variable	1974	1975		1976	
	Cab. Sauv.	Shiraz	Cab. Sauv.	Shiraz	Cab. Sauv.
E_{520}	0.49	0.31	0.33	0.44	0.71
$E_{420} + E_{520}$	0.51	0.28	0.33	0.43	0.72
α	0.33	0.39	0.23	0.30	0.43
α'	0.14	0.23	0.04	0.22	0.30
Coloured anthocyanins	0.44	0.35	0.34	0.44	0.66
Total anthocyanins	0.27	0.08	0.24	0.28	0.44
E_{280}	0.47	0.09	0.23	0.33	0.46
E_{520}^{HCl}	—	—	—	0.31	0.52
pH	0.03	−0.19	−0.07	−0.08	−0.13
K	0.11	−0.22	−0.08	−0.09	0.01
Total SO_2	−0.27	−0.40	−0.25	—	—
Free SO_2	−0.30	−0.46	−0.32	−0.31	−0.43
Molecular SO_2	−0.32	−0.36	−0.26	−0.26	−0.32
$E_{520}^{SO_2}/E_{520}$	−0.23	−0.25	−0.17	−0.32	−0.40
$E_{520}^{SO_2}/E_{520}^{CH_3CHO}$	0.11	0.08	−0.02	−0.06	−0.06
$E_{520}^{SO_2}/E_{520}^{HCl}$	0.14	0.18	−0.01	0.04	0.10
E_{420}/E_{520} (tint)	−0.21	−0.41	−0.25	−0.39	−0.52
Degrees of freedom (n−2)	51	92	73	101	77
r value for significance					
at 0.1 % level	0.44	0.34	0.38	0.32	0.36
at 1 % level	0.35	0.27	0.30	0.25	0.28

lations which were not significant at the 1 % level have been excluded. Many of the higher coefficients refer to logical relationships between analytical variables, but the other data are also similar in all aspects for the two varieties. Positive interrelationships are grouped in sections A and C of the matrices, with negative interrelationships in section B (Table 3).

As stated earlier, correlations involving quality rating fall into two categories, referring to positive and to negative aspects of the wine composition (section D, Table 3). It is evident from Table 1 that the range of values for each of the phenolic variables is quite large, and that the range is enormously large in consideration of the spectral measure of free SO_2, which was negatively correlated with quality rating. In distinction from all other wine parameters investigated, there was skew distribution of free SO_2 levels in all groups, with measures ranging from zero to very high values in relation to the means.

Table 3

Correlation matrices for analytical and sensory data; 404 young red wines · Upper lines: pooled correlation coefficients for Shiraz 1975—76 (n = 197); lower lines: for Cabernet Sauvignon 1974—75—76 (n = 207) [1])

Korrelationsmatrizen der analytischen und sensorischen Werte von 404 jungen Rotweinen · Obere Zahlenreihen: Zusammengefaßte Korrelationskoeffizienten für Shiraz, 1975/76 (n = 197); untere Zahlenreihen: Cabernet Sauvignon, 1974/75/76 (n = 207)

	E_{520}	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
(1) $E_{520}+E_{420}$	0.99 0.99														
(2) α	0.66 0.70	0.61 0.65													
(3) α'	0.56 0.55	0.50 0.49	0.75 0.74												
(4) Coloured anthocyanins	0.95 0.95	0.92 0.91	0.74 0.76	0.61 0.59											
(5) Total anthocyanins	0.59 0.56	0.61 0.57			0.56 0.54										
(6) E_{280}	0.69 0.68	0.74 0.72		**A**	0.57 0.53	0.73 0.64									
(7) E_{520}^{HCl}	0.65 0.58	0.68 0.59			0.60 0.54	0.99 0.98	0.78 0.62								
(8) pH	−0.21 −0.29		−0.60 −0.58	−0.83 −0.85	−0.36 −0.40										
(9) $E_{520}^{SO_2}/E_{520}$	−0.34 −0.48	−0.27 −0.40	−0.56 −0.58	−0.40 −0.42	−0.57 −0.69	−0.21 −0.35		−0.27 −0.38	0.56 0.47						
(10) K			−0.40 −0.36	−0.55 −0.49	−0.26 −0.27				0.76 0.67	0.51 0.38					
(11) Total SO_2	−0.21 −0.36		−0.53 −0.50		−0.37 −0.41		**B**			0.63 0.42	0.42 0.26				
(12) Free SO_2	−0.47 −0.50	−0.45 −0.50	−0.72 −0.72	−0.24 −0.21	−0.51 −0.53					0.47 0.48	**C**	0.66 0.58			
(13) Molecular SO_2	−0.39 −0.34	−0.39 −0.35	−0.53 −0.48		−0.39 −0.35					0.24 0.26		0.49 0.54	0.85 0.83		
(14) E_{420}/E_{520}	−0.66 −0.63	−0.60 −0.57	−0.76 −0.63	−0.70 −0.56		−0.29 −0.33		−0.35 −0.43	0.66 0.56	0.75 0.69	0.49 0.33	0.46 0.26	0.54 0.45		
(15) Quality rating	0.36 0.50	0.35 0.51	0.35 0.33		0.39 0.47	**D**	0.22 0.37	0.31 0.52		−0.29 −0.27		−0.39 −0.26	−0.37 −0.35	−0.31 −0.29	−0.40 −0.26

[1]) Only r values > 0.20, significant at 1 % level or better, are shown.

Interpretations

As in the first investigation (SOMERS and EVANS 1974), strong correlations between overall wine quality and the colour parameters α were a consistent feature of these analytical surveys. In the earlier work, the phenomenon of widely variable colouration in the anthocyanin fraction was not explicable from the available data, even though pH and SO_2 were known to be major influences on the state of anthocyanin equilibria.

Analytical survey methods were subsequently improved by inclusion of measures of free SO_2 (spectral), total phenolics (as E_{280}) and indices of "chemical age" (SOMERS and EVANS 1977). For the much larger groups of wines examined in the present work, strong negative correlations were established between α and free SO_2, and between α' ("natural" degree of ionisation) and pH (Table 3). The quality rating was correlated negatively with free SO_2, but there was no correlation between quality and wine pH in any wine group (Tables 2 and 3). Though correlations with wine colour density (positive) and tint (negative) have been consistently shown, it became evident that, in the context of Australian red wines at least, the SO_2 content is a major variable affecting the relative wine quality. The level of free SO_2 in particular was indicated because of its negative influence on the colouration of anthocyanins (α) with which quality was consistently correlated in the Australian wines (Tables 2 and 3).

Contrary to our findings, however, JACKSON *et al.* (1978) found no correlation between α and quality in a similar investigation of young French wines. We consider that it is the differences between the two sets of data, rather than their many similarities, which are of most importance; for there have typically been a much greater range and variability in α values of the Australian wines, e. g. 3—33 %, mean 15 % for the 1976 Shiraz wines vs. 18—43 %, mean 26 % for the young French wines studied by JACKSON *et al.* Thus the divergent results concerning α and relative wine quality can be attributed to the fact that free SO_2 levels in the Australian wines have varied enormously, e. g. 0—17 mg/l (spectral), mean 2.4 mg/l for the 1976 Shiraz; which is in marked contrast with the corresponding French data, range 0.1—4.0 mg/l, mean 0.6 mg/l (spectral).

The nature and extent of such compositional problems in Australian red wines had not been suspected before these several analytical surveys. As the data had provided good indications that the quality of future vintages could be generally improved by better management of the SO_2 regime, study of the role of SO_2 during vinification and conservation has been of primary concern. As part of this program, elaborate surveys of actual vintage procedures and of conservation practice in many commercial wineries were conducted during 1979—80—81 (SOMERS and WESCOMBE 1982). The investigations showed that the metabolic fate of acetaldehyde, the principal SO_2 binding component, can be a major influence during red wine conservation, as unfavorable disturbance of the SO_2 equilibria may then occur during malo-lactic fermentation, i. e. bacterial catabolism of acetaldehyde releases bound SO_2, with consequent decline in α and changes in colour density and tint. These events occurred in a majority of the commercial wines monitored, and there may well be an association between excessively high acetaldehyde depletion (with release of high free SO_2) and particular strains of bacteria. Such uncertain influences during conservation can be restricted by ensuring low levels of total SO_2 at the end of primary fermentation, with minimal additions of SO_2 after early completion of malo-lactic fermentation. SOMERS and WESCOMBE (1982) also noted that an association existed between higher levels of free SO_2 and taints "on nose and palate" developing during conservation, strongly suggestive of reduced sulphur compounds. In this regard, an apparent link between SO_2 and formation of higher sulphides in finished beers is of special interest (WILLIAMS and GRACEY 1982). Such observations, fur-

ther to statistical evidence of interrelationships between sensory scores of colour, nose and palate in red wines, and of negative influence on red wine quality from added SO_2 (JACKSON *et al.* 1978, TIMBERLAKE 1981), provide some explanation of the connection between the overall wine quality and analytical measures of wine colour density and composition.

Thus the present data show pigment content and wine colour density, rather than the actual level of total anthocyanins, to be positive features of red wine quality, and there are negative correlations with hue or tint (Tables 2 and 3). The matrices in Table 3 direct attention to responsible factors of wine composition, the most significant being consistent correlations involving the colour parameter α, along with the strongly negative correlations involving SO_2 with α and with wine quality rating.

Though the fundamental importance of the wine pH to sound oenological practice has been better appreciated in more recent years, with climate-induced deficiencies in natural acidity being normally corrected before and sometimes during the vinification process, it is again remarked that no significant correlation of pH with overall quality rating was found in any of the five wine groups examined (Table 2). This is despite the prime determining influence of pH on α' ($r = -0.83, -0.85$, Table 3) and the wide range of pH in those wines of 1974—75—76 (Table 1).

It is rather the role of SO_2, now seen to be a most variable winemaking factor when evaluated as free SO_2 by the spectral procedure, which has come under special scrutiny; for inadequate management and excessive use of SO_2 can apparently lead to adverse sensory effect on all aspects of the wine composition, regardless of the pH. There is therefore the prospect of improved wine quality in all districts, approaching a situation in which the natural wine characteristics emerge from each vintage, with the more satisfactory recognition of regional wine styles.

Of the data compiled in these analytical surveys (Table 1), only those for actual pigment and phenolic content refer directly to the grape harvest composition, i. e. to viticultural rather than to oenological factors. A notable feature is that the levels of these essential extractives, which are the obvious determinants of red wine type, ranged 6-fold for residual anthocyanins and 4-fold for total phenolics. Thus the positive correlations involving these factors with overall quality (Tables 2 and 3) suggest the possibility of using such measures in evaluation and classification of regional wine characteristics for particular grape varieties.

Summary

Relationships between wine colour composition and the overall quality rating were investigated by analyses of 404 young red wines in two varietal classes from three successive vintages. The wines, of Shiraz and Cabernet Sauvignon from 20 viticultural regions of Australia, had been presented for comparative assessment at the Adelaide Wine Shows of 1974—75—76. There was a large variability in all aspects of phenolic content, in wine colour density and tint, in pH, and in levels of total SO_2 and free SO_2. The latter was the major influence on pigment equilibria, in which there was up to 10-fold variation in the degree of ionisation of anthocyanins (α). Positive quality factors were wine colour density, the parameter α, coloured anthocyanins, total pigments and total phenolics. Negative factors included colour tint, free SO_2 and total SO_2. There was no correlation with wine pH. Wide variation in winemaking practice concerning the amount and timing of SO_2 additions is considered to have been responsible for much of the range in quality within these groups of wines.

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