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Aroma composition of bottle aged white wine

by

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Die Aromazusammensetzung von flaschengereiftem Weißwein

Zusammenfassung. — Gaschromatographische Analysen der mit der „headspace"-Technik isolierten Aromakomponenten zeigten, daß in älteren Rieslingweinen höhere Konzentrationen von Furfural, Linalool- und Neroloxid, Äthylfuroat sowie 1,1,6-Trimethyl-1,2-dihydronaphthalin (TDN) und niedrigere Konzentrationen von Äthyl-n-decanoat vorliegen. Die beobachteten Unterschiede der Zusammensetzung stehen in Zusammenhang mit Veränderungen, die — wie in früheren Untersuchungen mittels künstlicher Alterung gezeigt wurde — während der Lagerung erfolgen.

Der Einfluß der unterschiedlichen chemischen Zusammensetzung auf das Aroma wurde geprüft. TDN und Dimethylsulfid werden als wichtige Komponenten des Aromas reifer Flaschenweine angesehen, während der erhöhte Gehalt an Monoterpenoxiden mit dem Verlust des frischen Rieslingbuketts in Verbindung gebracht werden kann.

Introduction

Some white table wines are capable of developing desirable bottle bouquet with cellar storage for 2—7 years. Colour of the wines increases with ageing and Singleton (1976) has referred to other changes including increased harmoniousness, decreased harshness, increased complexity and the development of flavour nuances. He also indicated that wines from certain *Vitis vinifera* cultivars (viz. Sauvignon blanc, Riesling and Semillon) are more likely to benefit from bottle ageing.

Conditions considered most suitable for bottle ageing are cool and constant temperatures, the latter being important in reducing the likelihood of leakage and ensuring that air contact is minimal. Singleton (1976) has estimated oxygen uptake through the cork is ca. 0.1 ml/l of wine per year demonstrating that bottle ageing occurs under essentially anaerobic conditions.

Various techniques for accelerating the bottle ageing process have been examined but heating the wine in the absence of oxygen has been most successful (Singleton 1962, Singleton *et al.* 1964). However, the differences in rates of reaction with traditional bottle ageing and "quick-ageing" may be responsible for producing significant differences in volatile aroma composition (Simpson 1978 a).

In the studies now presented headspace gas chromatography (g.c.) was employed to analyse the aroma composition of Riesling wines made under similar conditions during different vintages.

Materials and methods

1. Wines

Commercial white table wines were made in 1967—1977 from *Vitis vinifera* grapes (cultivar Riesling) grown in the Eden Valley district of South Australia.

Table 1

Analytical data for 1967—1977 Riesling wines[1])
Analysenwerte von Rieslingweinen, Jahrgänge 1967—1977[1])

	Vintage year				
	1967	1970	1973	1976	1977
Specific gravity (20/20 °C)	0.992	0.994	0.991	0.993	0.992
Ethanol (% v/v)	11.9	10.8	12.4	11.9	10.9
Reducing sugar (g glucose/l)	1.1	5.4	4.1	3.1	2.2
Titratable acidity (g tartaric acid)	7.4	6.6	6.3	6.7	6.7
pH	2.97	2.82	3.09	3.03	3.02
Volatile acidity (g acetic acid/100 ml)	0.41	0.47	0.71	0.54	0.49
Free SO_2 (mg/l)	25	28	18	24	21
	(4)[2])	(7)	(7)	(10)	(12)
Total SO_2 (mg/l)	124	156	133	154	115
	(81)[2])	(98)	(97)	(115)	(98)

[1]) Determined at bottling (July—October in the year of vintage).
[2]) Analysed December 1977.

Similar winemaking procedure was followed: Fermentations were carried out at 10—12 °C using *Saccharomyces cerevisiae* No. 729 Epernay strain. The wines were placed in 750 ml bottles during July—October in the year of vintage and subsequently stored at 12—15 °C.

Analytical data for these wines are given in Table 1.

2. Instrumental analyses

Methods used were as previously described (Simpson 1978 a). Quantities of furfural and the monoterpene oxides were determined and calibrations made by collecting and analysing a second 30 l headspace sample.

3. Determination of dimethyl sulphide in wine

The method was adapted from that described by Grigsby and Palamand (1977) in which the DMS content of beer was measured after extraction into carbon tetrachloride and colorimetric assay with sodium nitroprusside. In the modified procedure the visible spectra (400—700 nm) of the reaction mixtures from the untreated wine and the same wine sparged with nitrogen for 48 h were recorded. The deviation at 520 nm from a smooth curve for each of the samples was measured. The difference between the two values was taken as being due to the absorbance by the DMS-sodium nitroprusside complex.

4. Quality assessment

Bottle age aroma, grape bouquet and oxidised aroma were scored individually (0—7 points) and an overall rating was obtained using a 20 point system: colour (3), aroma (7) and taste (10). The taste panelists were personnel from commercial wineries and were experienced in wine assessment.

Results

1. Compositional analysis

Compositions of the aroma volatiles of 1967, 1970, 1973, 1976 and 1977 Riesling wines, isolated by headspace techniques and pre-concentration on the porous

Table 2

Aroma compositions of 1967—1977 Riesling wines[1]) (in mg/l)
Aromazusammensetzung von Rieslingweinen (mg/l), Jahrgänge 1967—1977[1])

Component	Vintage year				
	1967	1970	1973	1976	1977
Dimethyl sulphide	0.117	0.072	0.056	0.033	0.028
Isoamyl acetate	0.28	0.31	0.21	0.23	0.57
Ethyl n-hexanoate	0.83	0.97	0.87	0.76	0.83
Hexyl acetate	0.00	0.01	0.01	0.00	0.06
1-Hexanol (+ethyl lactate)	4.19	1.97	2.24	1.49	2.18
Acetic acid	270	250	400	370	380
Ethyl n-octanoate	1.40	1.38	1.33	1.32	1.62
Furfural	8.5	10.3	3.0	1.2	0.0
Linalool oxide, *trans*-isomer, 5-membered ring	1.5	1.2	0.7	0.5	0.0
Nerol oxide	1.2	1.3	1.1	1.1	0.8
Benzaldehyde	0.02	0.02	0.01	0.01	0.01
Vitispirane	0.32	0.29	0.15	0.08	0.02
Ethyl furoate	0.18	0.09	0.02	0.01	0.00
Ethyl n-decanoate	0.21	0.21	0.31	0.34	0.48
Diethyl succinate	1.2	1.1	0.8	0.6	1.0
Ethyl 9-decenoate	0.01	0.03	0.00	0.00	0.01
1,1,6-Trimethyl-1,2-dihydronaphthalene	0.042	0.031	0.022	0.010	0.001
1,1,6-Trimethyl tetrahydronaphthalene isomer	0.003	0.003	0.001	0.001	0.001
Ethyl n-dodecanoate	0.00	0.00	0.01	0.01	0.04
2-Phenethanol	8.8	11.2	9.2	7.7	12.5

[1]) Analysed December 1977.

polymer Chromosorb 105 (see WILLIAMS and STRAUSS 1977) are shown in Table 2. 3-Methyl-1-butanol and 2-methyl-1-butanol were major components but could not be determined quantitatively by this procedure.

Quantities of furfural and the monoterpene oxides were readily measured in the second 30 l headspace sample because of the reduced quantities of ethyl n-octanoate. The presence of the *trans*-isomer of the 5-membered ring linalool oxide and nerol oxide were confirmed by g.c. and g.c.-mass spectrometry; FELIX *et al.* (1963) had shown that the *trans*-linalool oxide eluted first on both polar and non-polar columns. The corresponding *cis*-isomer may have been present in small amounts but this compound would have been poorly resolved from nerol oxide under the conditions of analysis.

The isomer of 1,1,6-trimethyl tetrahydronaphthalene (TTN), identified on the basis of mass spectral evidence (see LIEBICH *et al.* 1970), was well resolved from and had a longer retention time than 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN).

The method used to determine DMS in wines gave satisfactory results and for DMS added to wine the standard deviation was 0.007 mg/l. Values for the 1967—1977 wines (Table 2) are the means of two determinations.

Table 3

Flavour and overall quality assessments of 1967—1977 Riesling wines[1])
Geschmacks- und Gesamtqualitätsbeurteilung von Rieslingweinen, Jahrgänge 1967—1977[1])

	Vintage year					LSD (P = 0.05)
	1967	1970	1973	1976	1977	
Bottle age aroma (7 max)	5.0	4.7	4.0	2.7	1.7	0.8
Grape bouquet (7 max)	2.4	3.0	2.8	3.6	4.2	1.3
Oxidised aroma (7 max)	1.8	1.6	1.6	1.0	1.0	NS
Quality						
a) Colour (3 max)	2.6	2.7	2.4	2.7	2.6	NS
b) Aroma (7 max)	5.3	5.7	5.4	4.9	5.1	0.8
c) Taste (10 max)	7.2	7.8	7.1	6.7	6.6	0.8
Total (20 max)	15.1	16.2	14.9	14.3	14.3	1.4

[1]) Mean scores, 10 tasters.

Table 4

Optical densities of 1967—1977 Riesling wines
Optische Dichte von Rieslingweinen, Jahrgänge 1967—1977

Wavelength (nm)	Vintage year				
	1967	1970	1973	1976	1977
400	0.295	0.280	0.260	0.170	0.183
410	0.245	0.234	0.217	0.139	0.152
420	0.210	0.198	0.185	0.118	0.129
500	0.058	0.043	0.045	0.027	0.030
600	0.013	0.008	0.009	0.005	0.006
700	0.005	0.003	0.003	0.002	0.003

2. Flavour evaluation

Statistical analyses of the results (Table 3) were made according to Amerine and Roessler (1976). Bottle age aroma was more intense in the older wines but minor differences in grape bouquet, oxidised aroma and quality assessments were observed.

3. Optical density measurements

The colour of the older wines was deeper as shown by the higher absorbance readings (Table 4). Colour of the wines varied from straw coloured to deep yellow; there was no suggestion of browning in any of the wines.

Discussion

1. Aroma composition of 1967—1977 Riesling wines

The aroma compositions of the older wines were more complex with the presence of additional major components. Higher concentrations of furfural, the *trans*-isomer of the 5-membered ring linalool oxide, nerol oxide, vitispirane (see SIMPSON *et al.* 1977), ethyl furoate, TDN and lower concentrations of ethyl n-decanoate were found in the older wines (Table 2).

The presence of larger amounts of furfural in the older wines was consistent with its formation from carbohydrates, which is catalysed by heat and acid (PIGMAN and ANET 1972). The 1967 wine contained less furfural and less reducing sugar (see Table 1) than the 1970 wine. Ethyl furoate, which was present at consistently higher levels in the more aged wine, is also derived from carbohydrates.

Higher concentrations of the linalool oxide and nerol oxide in the older wines should correspond with a loss of the monoterpene alcohols. These terpene oxides are relatively stable compounds and have been found in appreciable quantities in 20 year Riesling wine whereas the monoterpene alcohols present in young wine (see SCHREIER *et al.* 1977) could not be detected (SIMPSON, unpublished data).

Concentrations of vitispirane and TDN were consistently higher in the older wines as expected from earlier observations of the changes in aroma composition with accelerated ageing (SIMPSON 1978 a).

Highest contents of isoamyl acetate and hexyl acetate were found in the 1977 wine; ethyl n-decanoate appeared to decrease with wine ageing. However, for many of the esters shown in Table 2 there were no trends evident with concentrations and the extent of ageing. PEYNAUD (1937) had shown that the content of volatile esters in wine generally increased with time as esterification and hydrolysis reactions occurred and the system tended towards chemical equilibria. Consistent differences in concentrations of ethyl n-hexanoate, ethyl n-octanoate and diethyl succinate with age of the 1967—1977 Riesling wines were not observed but concentrations of these esters (and also isoamyl acetate and hexyl acetate) in newly vintaged wine are strongly influenced by characteristics of the grape material used and fermentation parameters. Apparently there was sufficient variability in the initial concentrations of the individual esters to mask the changes described by PEYNAUD (1937). In earlier studies (SIMPSON 1978 a) clear trends were generally observed for changes in volatile ester concentrations and extent of "quick-ageing" with the same wine.

Concentrations of DMS in the 1967—1977 wines varied from ca. 0.03—0.12 mg/l and the older wines consistently showed higher levels of this component (Table 2). DMS formed in the presence of free SO_2 which was retained by the wines during storage (see Table 1).

2. Flavour considerations

The 1967—1977 wines examined were noted for their ability to develop desirable bottle bouquet. Assessment of this particular aroma characteristic revealed distinct differences between the wines (Table 3), whereas overall quality assessments such as with the 20 point system used (see Table 3) are not able to reflect the changes in wine style that occurred.

Of those compounds showing considerable differences in concentration with ageing, furfural could not be expected to influence aroma. It was present at subthreshold values in these wines as indicated from the flavour threshold in beer reported as 150 mg/l (MEILGAARD 1975).

Concentrations of vitispirane were less than its flavour threshold value of 0.80 mg/l (SIMPSON 1978 a). However, concentrations of the hydrocarbon TDN in the 1967, 1970 and 1973 wines exceeded the flavour threshold of this compound (0.02 mg/l, SIMPSON 1978 b), which was shown to be a major contributor to bottle age bouquet. The TTN isomer which also appeared to increase with age of the wine, was present in insufficient quantities to significantly affect wine aroma.

Observed differences in concentrations of the major volatile esters, including isoamyl acetate and hexyl acetate with flavour thresholds in wine of 1.0 (SIMPSON, unpublished data) and 2.4 mg/l (SIMPSON 1978 a), respectively, were unlikely to influence flavour in the 1967—1977 wines examined.

LOUBSER and DU PLESSIS (1976) measured DMS in wine and provided evidence for the development of this compound in "Late Harvested" and Riesling wines. Reported flavour threshold values for DMS are: in water 0.01—0.02 (STAHL 1973), carbonated beer 0.05 (MEILGAARD 1975) and uncarbonated beer 0.06 mg/l (HARRISON 1970). The latter values should provide an indication of the flavour threshold in wine. Therefore, DMS especially at the higher concentrations present in the 1967, 1970 and 1973 wines must be expected to contribute significantly to the overall aroma.

Grape aroma was less evident in the older wines and a loss in grape aroma with storage is expected (AMERINE *et al.* 1967, SIMPSON 1978 a). Reduced quantities of the more aroma-intense monoterpene alcohols such as linalool, geraniol and nerol can not be compensated by increased concentrations of the monoterpene oxides which have considerably higher flavour thresholds (RIBÉREAU-GAYON *et al.* 1975).

Summary

Analyses by headspace gas chromatography revealed the presence of higher concentrations of furfural, linalool and nerol oxides, ethyl furoate and 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) and lower concentrations of ethyl n-decanoate in the older wines examined. The observed differences in composition were consistent with changes occurring during storage as shown by previous studies using accelerated ageing techniques.

Influences on aroma of the compositional differences were examined. TDN and dimethyl sulphide were considered to be important to the development of bottle age bouquet whereas higher contents of the monoterpene oxides can be related to loss of grape aroma in wine.

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