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Aroma and compositional changes in wine with oxidation, storage and ageing

by

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Veränderungen des Aromas und der stofflichen Zusammensetzung von Wein durch Oxidation, Lagerung und Alterung

Z u s a m m e n f a s s u n g . — Mit Hilfe der "headspace"-Technik und der Gaschromatographie (G.C.) wurden bei Rieslingweinen die Veränderungen der Aromastoffzusammensetzung untersucht, die bei Oxidation und künstlicher Alterung stattfinden. Bei allen Behandlungsvarianten wurden Konzentrationsänderungen der Äthylester der C_6–C_{10}-Fettsäuren, von Hexylacetat, Äthylfuroat, Diäthylsuccinat, Hexan-1-ol-Äthyllactat und 2-Phenyläthanol beobachtet. Bei erhöhter Temperatur und oxidativer oder nichtoxidativer Lagerung war die Bildung von Vitispiran und 1,1,6-Trimethyl-1,2-dihydronaphtalin (TDN) begünstigt, während nennenswerte Mengen von Aldehyden einschließlich Benzaldehyd und Furfural nur unter oxidativen Bedingungen entstanden.

Die Konzentrationsänderungen der Hauptaromakomponenten reichten mit Ausnahme des Kohlenwasserstoffes TDN nicht aus, um die sensorischen Schwellenwerte zu überschreiten. Es wird jedoch angenommen, daß quantitative Veränderungen innerhalb einer Stoffklasse sowie die Bildung aromaintensiver Nebenkomponenten für einen Großteil der beobachteten Geruchs- und Geschmacksänderungen verantwortlich sind. Eine Abnahme der stärker aromabestimmenden Monoterpenalkohole und eine Zunahme im Gesamtgehalt der Aromakomponenten durch Oxidation und künstliche Alterung können den Verlust des fruchtigen Rieslingbuketts erklären.

Der Aldehydgehalt nahm ab, wenn der Wein unter Stickstoff erhitzt wurde, während oxidative Lagerung sowohl zu erhöhten als auch zu verminderten Aldehydkonzentrationen führen konnte. Hieraus ist ersichtlich, daß die Überwachung des Gesamtgehaltes an freiem Aldehyd (anders als die Konzentrationen einzelner Aldehyde) wenig Aufschluß über die vorangegangene Lagerung oder den derzeitigen Zustand eines Weines liefern kann.

Die "headspace"-Technik in Verbindung mit G.C. erwies sich als eine empfindliche Methode, um das Ausmaß der Oxidation und der Alterung eines Weines festzustellen.

Introduction

It is generally accepted that exposure to air is harmful to the aroma and taste of white table wine (Singleton and Esau 1969, p. 191). Loss of discernible fruit varietal bouquet occurs and excessive oxygen uptake leads to maderization, whereby colour is unfavourably affected (i.e. browning occurs) and cloudiness may develop (Cantarelli 1967). Oxidation favours the production of aldehydes and esters (Cantarelli 1967, Baro and Quiros Carrasco 1977), which, by their low flavour thresholds, are able to affect aroma even at low concentrations in the wine.

Certain white table wines benefit from long-term cellar storage (2—7 years) in the bottle where conditions are essentially anaerobic; during this time the wines develop deeper colour and richer bouquet (Singleton 1976). Various "quick-ageing"

techniques have been used and SINGLETON *et al.* (1964) have indicated that wine heated at ca. 50 °C for 15—30 d in the complete absence of oxygen can produce many of the changes associated with bottle-ageing.

In the studies now presented analytical headspace techniques have been used to examine the aroma volatiles of oxidised and quick-aged wines.

Materials and methods

1. Wines

Commercial white table wines made in 1977 from *Vitis vinifera* grapes (cultivars Riesling and Sultana) grown in the Barossa and Eden Valley districts of South Australia were used. These wines were sterile filtered at bottling using a membrane filter with 0.45 /'m pore size.

2. Treatment of wine samples

Riesling wine (160 ml) was placed in heat-sterilised 500 ml Sovirel reagent bottles (total capacity ca. 570 ml) having a screw cap lined with polytetrafluoro-ethylene. The samples were stored at constant temperature (15 and 50 °C); with quick-ageing the airspace was flushed with high-purity nitrogen before capping.

Wine (300 ml) was freeze-dried to a syrup and then reconstituted with aqueous ethanol (12 % w/v). Part of this material (150 ml)was heated in the presence of air at 50 °C for 28 d.
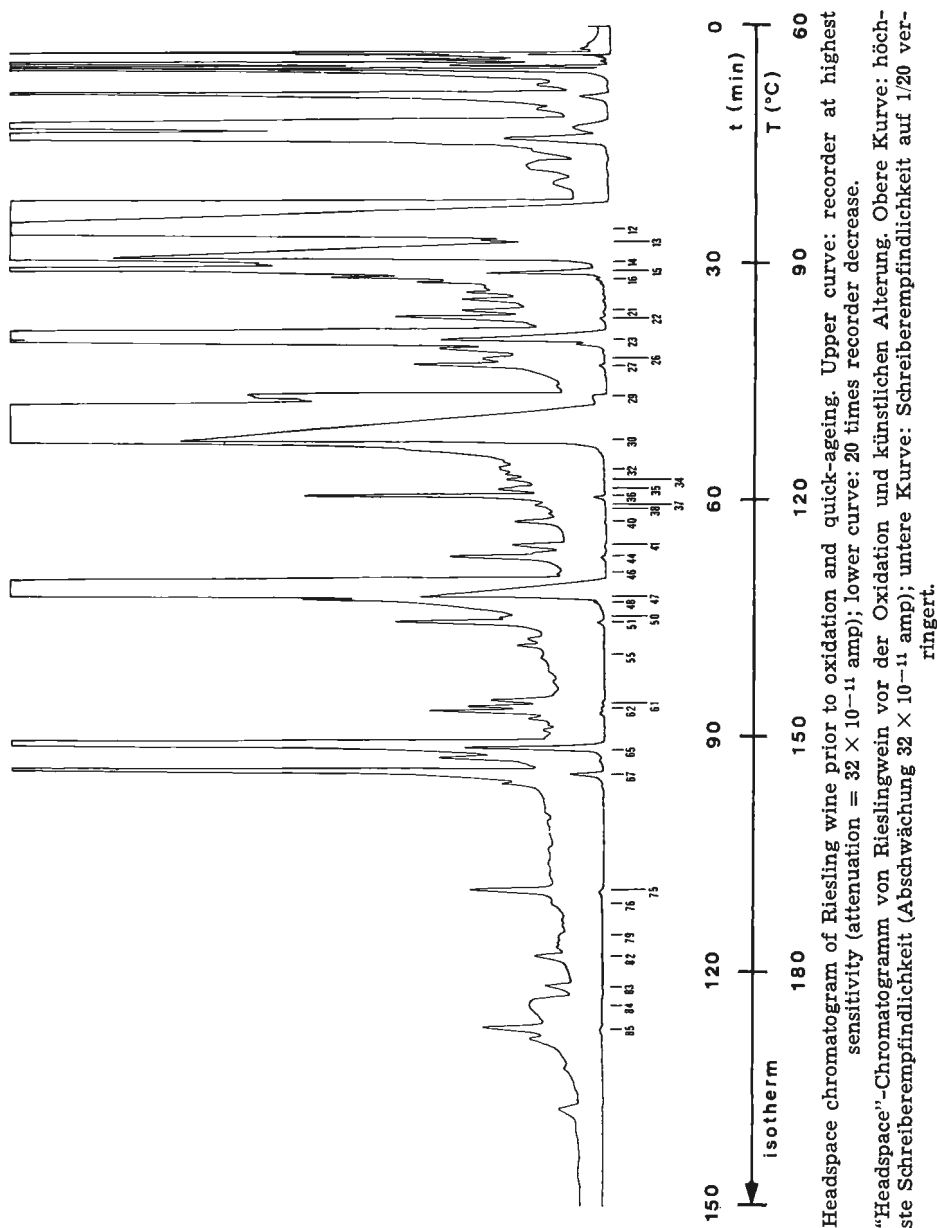
3. Headspace analysis

Techniques as described by WILLIAMS and STRAUSS (1977) were employed with benzyl alcohol (2 mg) as internal standard. Headspace materials were chromato-graphed on a S.C.O.T. High Performance Carbowax 20M column (purchased from Scientific Glass Engineering, Melbourne) in a Varian Aeorograph Series 1400 gas chromatograph, injector temperature 220 °C, detector 230 °C, temperature pro-grammed at 1 °/min from 60 to 180 °C, with ca 2.8 ml/min nitrogen or helium carrier gas and flame ionization detection. Peak areas were obtained using a Linear model 252A integrating chart recorder. Known amounts of purified reference materials were added to a base Sultana wine prior to headspace analysis to determine the concentrations in wine of the major components of the headspace collections. For quantitative determination of ethyl n-hexanoate, ethyl n-octanoate and ethyl n-decanoate the base wine was extracted with AR pentane prior to additions of known amounts of these compounds; this solvent removed the esters which were present initially. Acetic acid content was estimated from the measurement of peak heights.

Identifications of individual wine components were made by gas chromato-graphy-mass spectrometry (g.c.-m.s.) and from retention data.

4. Ethyl acetate content

Concentrations of ethyl acetate in the control and quick-aged wines were determined by g.c. (direct injection) after addition of n-butanol as internal standard. Assay conditions were: column, 15 % 1,2,3-tris(2-cyanoethoxy) propane on 60—80 mesh Chromosorb W, 3.7 × 3.18 mm stainless steel, injector temperature 180 °C, column temperature 70 °C (isothermal) with 30 ml/min nitrogen carrier gas and flame ionization detection.

Headspace chromatogram of Riesling wine prior to oxidation and quick-ageing. Upper curve: recorder at highest sensitivity (attenuation = 32 × 10⁻¹¹ amp); lower curve: 20 times recorder decrease.

"Headspace"-Chromatogramm von Rieslingwein vor der Oxidation und künstlichen Alterung. Obere Kurve: höchste Schreiberempfindlichkeit (Abschwächung 32 × 10⁻¹¹ amp); untere Kurve: Schreiberempfindlichkeit auf 1/20 verringert.

5. Flavour assessment and threshold values

Wine quality was assessed using a 20 point system: colour (3), aroma (7) and taste (10). The taste panelists were Institute staff members and were experienced in wine assessment. With oxidised wine samples, tastings were carried out using dark wine glasses and colour was scored separately. Flavour thresholds in wine were obtained by the method described by MEILGAARD (1975 a).

6. Visible spectral measurements

Optical densities were obtained using a Varian Techtron model 635D u.v.-visible spectrophotometer and 10 mm sample cells. Wines were filtered through a membrane filter with 1.2 μm pore size prior to measurement.

7. Aldehyde analysis

The airspace of oxidised wine samples was flushed with nitrogen and all samples were stored at —20 °C prior to assay. Free aldehyde content was determined by the method of GUYMON and CROWELL (1963).

Results

1. Compositional analysis

Composition of the aroma volatiles of Riesling wine prior to oxidation and quick-ageing is shown by the gas chromatogram (see figure).

Changes in composition with oxidation at 15 and 50 °C and quick-ageing (i.e. 50 °C in the absence of air) were determined as differences in peak heights, relative to the control wine or (within treatments) relative to the previous analysis (Table 1). All components showing a significant change in concentration are listed except for *act-* and isoamyl alcohols (peak 12) and compounds having shorter retention times; many of these compounds were poorly retained by the Chromosorb 105 traps used in concentrating the aroma volatiles (WILLIAMS and STRAÜSS 1977) and quantities could not be determined satisfactorily. Peak numbers refer to those shown in the figure.

(a) Accelerated oxidation (50 °C in the presence of air): Major changes in the aroma volatiles of Riesling wine were increases in the amounts of ethyl n-hexanoate, 1-hexanol/ethyl lactate, acetic acid, ethyl n-octanoate/furfural, benzaldehyde, vitispirane (which has been described previously (SIMPSON *et al.* 1977)), ethyl furoate, diethyl succinate, *a*-terpineol, 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), 2-phenethanol and components corresponding with peaks 21 and 22 (see figure). Hexyl acetate, linalool/ethyl n-nonanoate and components corresponding with peaks 34 and 41 showed an initial increase but subsequent decrease in concentration (Table 1).

(b) Oxidation at cellar temperature (15 °C in the presence of air): The compositions of the headspace volatiles of wine stored at 15 °C for 28 and 56 d as shown by g.c. analysis closely resembled those obtained by accelerated oxidation after 3 and 7 d, respectively (see Table 1).

(c) Quick-ageing (28 d at 50 °C under nitrogen): The composition of the headspace volatiles of quick-aged wine appeared almost identical except for the absence of benzaldehyde and a higher content of 2-phenethanol (see Tables 1 and 2) with that of wine subjected to accelerated oxidation for a similar time.

(d) Examination of the origin of components forming with accelerated oxidation: The hydrocarbon TDN and vitispirane were major components in the aroma volatiles of Riesling wine that had been freeze-dried, reconstituted and subjected to accelerated oxidation over 28 d; these compounds were absent from the reconstituted wine prior to oxidation. Other components which developed in the reconstituted wine (with oxidation) included ethyl lactate, furfural (both of which gave well-resolved peaks because of the reduced quantities of 1-hexanol and ethyl n-octanoate), ethyl furoate and diethyl succinate.

Table 1

Changes in composition of the headspace volatiles of oxidised and quick-aged wine[1]

Veränderungen in der Zusammensetzung der "headspace"-Aromakomponenten bei oxidiertem und künstlich gealtertem Wein[1]

Peak No.[2]	Component	15 °C in the presence of air		Storage conditions 50 °C in the presence of air Duration (d)					50 °C under nitrogen
		28[3]	56	1[3]	3	7	14	28	28[3]
13	Unknown	— — — —		— — — —		—			— — — —
14	Ethyl n-hexanoate	+ + + +	— — — —	+ + + +	+ + + +	+ + + +	+ + + +		+ + + +
15	Hexyl acetate	+ + + +	— — — —	+ +	— —	— — —	— — — —	— — — —	— — — —
16	Unknown	— —		— —					— —
21	Unknown		+ +	+			+		+ + +
22	Unknown	+ +	+ + +	+ +	+	+ + +	+ + +	+ +	+ + + +
23	1-Hexanol/ethyl lactate	+ + + +		+ + + +	+ + + +	+ + + +	+ + +	+ +	+ + + +
26	trans-3-Hexenol		+						
27	cis-3-Hexenol			—					—
29	Acetic acid	+ + +	—	+ +	+		+ +		+ + +
30	Ethyl n-octanoate/ furfural	+ + + +	+ + + +	+ + + +	+ + + +	+ + + +	+ + + +	+ + + +	+ + + +
32	Benzaldehyde	+ + + +	+ + + +	+		+	+	+ + +	
34	Unknown			+ +	+ +	+	— —		
35	Vitispirane		+ +	+ +	+ + + +	+ + + +	+ + + +	+ + + +	+ + + +
36	Linalool/Ethyl n-nonanoate	+ + +	+ + +	+ + + +	— —	— — —	— — —		
37	Unknown		+						
38	Unknown		+ +						
40	Unknown		—						
41	Unknown		+ +	+ + +	+ +	+	— —	— —	+ +

Table 1 (contd.)

Peak No.[2]	Component	15 °C in the presence of air		Storage conditions 50 °C in the presence of air					50 °C under nitrogen
				Duration (d)					
		28[3]	56	1[3]	3	7	14	28	28[3]
44	Ethyl furoate	++	++	+	+	+	+	++	+++
46	Unknown					+			++
47	Ethyl n-decanoate	++++	++++	----	++++	++++	++++	++++	+++
48	Diethyl succinate	++	++			+	++	++++	++++
50	α-Terpineol			+	+	+			++
51	Ethyl 9-decenoate	++	++						
55	TDN[4]	+	++	++	+++	++++	++++	++++	++++
62	2-Phenethyl acetate	+	++	+					
67	2-Phenethanol	++	++++	+++	+	+	+		----
75	Ethyl n-tetra-decanoate	++++	----	++++	++	--	----	----	++++
76	Unknown								--
79	Unknown	+							
82	Unknown								-
83	Unknown		+						-
84	Unknown	-		+					-
85	Ethyl n-hexa-decanoate	++++	---	++				--	+++

[1] Based on the difference of peak heights (in mm) from the previous analysis or control wine, attenuation at 32×10^{-11} amp: +/−, increase/decrease >10; ++/−− increase/decrease >20; +++/−−− increase/decrease >50; ++++/−−−−, increase/decrease >100.

[2] Refer to figure.
[3] Changes relative to control wine.
[4] 1,1,6-Trimethyl-1,2-dihydronaphthalene.

2. Ethyl acetate content

Concentrations of ethyl acetate as determined by g.c. in the control wine and wine quick-aged for 14 and 28 d were 43, 47 and 55 mg/l, respectively (means of duplicate analyses), the standard deviation being 4 %. Oxidised wines were not analysed for ethyl acetate content.

3. Flavour evaluation

Riesling wine oxidised at 15 and 50 °C was scored lower than the control wine (Table 3). The decrease in score relative to the control correlated closely with extent

Table 2

Effects of oxidation and quick-ageing on the concentration of the major volatile components of wine (mg/l)

Einfluß der Oxidation und der künstlichen Alterung auf die Konzentration der wichtigsten Aromakomponenten von Wein (mg/l)

Component	0[1]	15 °C in the presence of air		50 °C in the presence of air					50 °C under nitrogen
				Duration (d)					
		28	56	1	3	7	14	28	28
Ethyl n-hexanoate	0.74	1.00	0.66	0.76	0.84	0.93	0.95	0.96	0.98
Hexyl acetate	0.58	0.69	0.66	0.55	0.53	0.48	0.34	0.15	0.19
1-Hexanol (+ Ethyl lactate)	1.83	2.73	2.66	2.07	2.27	2.41	2.56	2.65	2.39
Acetic acid	200	240	200	210	220	230	250	240	240
Ethyl n-octanoate	0.99	1.57	1.69	1.01	1.09	1.27	1.38	1.50	1.52
Benzaldehyde	0.01	0.26	0.28	0.02	0.04	0.05	0.07	0.18	0.00
Vitispirane	0.00	0.00	0.02	0.01	0.04	0.13	0.25	0.36	0.33
Ethyl furoate	0.04	0.05	0.25	0.05	0.06	0.09	0.11	0.16	0.15
Ethyl n-decanoate	0.22	0.30	0.58	0.14	0.17	0.21	0.25	0.32	0.58
Diethyl succinate	0.5	1.5	2.4	0.5	0.6	1.5	1.9	4.4	3.8
TDN[2]	0.000	0.001	0.004	0.001	0.003	0.013	0.034	0.090	0.066
2-Phenethanol	8.1	10.7	15.9	9.2	9.4	10.0	11.0	11.0	15.9

[1]) Control.
[2]) 1,1,6-Trimethyl-1,2-dihydronaphthalene.

Table 3

Quality assessment of wine subjected to oxidation

Qualitätsbeurteilung von Wein nach Oxidationsbehandlung

	Storage temperature					
	15 °C			50 °C		
				Duration (d)		
0[1]	28	56	1	3	7	
			Mean score[2]			
14.8	12.2	7.3	12.4	8.8	5.7	
			LSD (P = 0.01)	1.9		

[1]) Control.
[2]) 10 tasters; using a 20 point system: colour (3), aroma (7) and taste 10).

Table 4

Optical densities of wine subjected to oxidation and quick-ageing

Optische Dichte von Wein nach Oxidation und künstlicher Alterung

Wave-length (nm)	0[1]	15 °C in the presence of air		Storage conditions 50 °C in the presence of air Duration (d)					50 °C under nitrogen	
		28	56	1	3	7	14	28	14	28
400	0.133	0.135	0.192	0.137	0.163	0.203	0.279	0.009	0.002	0.221
420	0.090	0.091	0.134	0.092	0.105	0.132	0.190	0.097	0.005	0.149
500	0.017	0.037	0.076	0.019	0.038	0.046	0.067	0.024	0.029	0.046
600	0.004	0.014	0.034	0.005	0.014	0.014	0.019	0.277	0.133	0.011
700	0.002	0.003	0.010	0.003	0.005	0.005	0.008	0.402	0.192	0.004

[1]) Control.

of oxidation. Wine samples heated at 50 °C in the presence of air for longer than 7 d were not included in the assessments because maderization was sufficiently pronounced that the samples were no longer typical of white table wine.

Flavour threshold values in wine were determined by the method described by MEILGAARD (1975 a): hexyl acetate (2.4), benzaldehyde (3.0), vitispirane (0.80) and TDN (0.020 mg/l).

4. Colour changes with oxidation and quick-ageing

Changes in optical densities of wine samples subjected to oxidation and quick-ageing (Table 4) were typical of those reported elsewhere (see SINGLETON and KRAMLING 1976, and references cited therein); oxidised wine turned a brown colour whereas quick-ageing produced a deep yellow colour.

5. Effect of oxidation and quick-ageing on the aldehyde content of wine

Accelerated oxidation of wine initially resulted in a slight reduction of free aldehyde content (i.e. aldehydes not bound as acetals). This was followed by a substantial increase after 7 d (Table 5). Oxidation at cellar temperature for 56 d produced a slight reduction in aldehyde content whereas quick-ageing resulted in a more marked decrease.

Table 5

Free aldehyde content of oxidised and quick-aged wine (mg/l)[1]

Gehalt an freiem Aldehyd in oxidiertem und künstlich gealtertem Wein (mg/l)[1]

Storage conditions	0[2]	1	3	Duration (d) 7	14	21	28	56
Control	46.8							
15 °C/air							46.8	45.7
50 °C/air		46.2	46.0	44.4	47.7	58.4	64.6	
50 °C/nitrogen					42.7		42.8	
						S.E. = 0.3		

[1]) Mean of 2 determinations.
[2]) Control.

Discussion

1. Compositional analysis

Headspace analysis of wine by g.c. clearly demonstrated that there were overall increases in quantities of aroma volatiles with oxidation and quick-ageing. New components formed, and, on the basis of peak heights, there was a greater frequency of increases in concentration of components initially present in the wine (Table 1).

A linear relationship between amount of compound added and increase in peak area in the headspace chromatogram was found for the major aroma volatiles. Concentrations of these components in oxidised and quick-aged wine (Table 2) were determined from the calibrations obtained. Because acetic acid (peak 29, see Figure) gave a broad peak and was only partially resolved from ethyl n-octanoate, the concentrations of acetic acid were estimated by peak height.

A rapid test for assessing the influence of non-enzymic oxidation in wine, especially browning capacity, is to heat the wine in the presence of air; for examples, see SINGLETON and KRAMLING (1976). Although reaction rates are generally increased with heating, specific reactions may be affected differently as was apparent from comparisons of the aroma compositions of wine oxidised at 15 and 50 °C. The hydrocarbon TDN, which has also been found in the headspace volatiles of red wine (BERTUCCIOLI and VIANI 1976), and vitispirane formed more readily at the higher temperature whereas the development of ethyl 9-decenoate was favoured at the lower temperature.

Relatively high concentrations of TDN and vitispirane in the quick-aged wine showed that these compounds formed readily with heating under both oxidative and non-oxidative conditions. Also, they are major components of bottle-aged Riesling wine (SIMPSON 1978).

A common precursor to both vitispirane and the hydrocarbon TDN is implied from the concomitant development of these components in wine (SIMPSON et al. 1977). Recent studies by LAROE and SHIPLEY (1970) have shown that α- and β-ionone and structurally related compounds can be derived from carotenoids. The possible biogenesis in tobacco of TDN from α-ionone by oxidation and acid-catalysed rearrangement has been described (DAVIS et al. 1976). Therefore, carotenoids or related materials are likely sources of vitispirane and TDN in wine. Since vitispirane and TDN were major components in the aroma volatiles of Riesling wine that had been freeze-dried, reconstituted and subjected to accelerated oxidation, the immediate precursors of these compounds have little volatility.

The changes in composition of the esters with oxidation and quick-ageing can largely be explained by equilibrium reactions. Studies by NORDSTRÖM (1965) had shown that the major esters of fermented beverages were secondary products of yeast metabolism and resulted from alcoholysis of acyl-coenzyme A derivatives. As a consequence, the quantities of esters formed have little relation with equilibrium values and may be well below or in excess of these values. In wine, progression toward ester equilibrium (i.e. rate of esterification/hydrolysis) is exceedingly slow at normal temperatures and pH; equilibrium is not attained after years of storage (PEYNAUD 1937). This author also showed that rates of esterification of the major acids in wine varied considerably and that lactic and succinic acids more quickly approached equilibrium with their ethyl esters (compared with other organic acids

in wine). This is consistent with the observation that diethyl succinate content increased more rapidly than ethyl 9-decenoate with oxidation and quick-ageing despite both being major aroma components of bottle-aged Riesling wine (unpublished results). van Wyk et al. (1967) had found that succinic acid and 9-decenoic acid were major organic acids in Riesling wine.

The content of hexyl acetate increased slightly with oxidation at 15 °C but decreased markedly with accelerated oxidation and quick-ageing. A decrease is expected from calculations of equilibrium values.

Ethyl acetate is the major ester and largely accounts for the volatile ester content of wine; Ribéreau-Gayon et al. (1972, p. 378) recorded values of 0.5—1.2 meq/l (44-106 mg/l) and the concentrations in current vintage Australian white table wines were found to be 50—100 mg/l (unpublished data). With quick-ageing the ethyl acetate content increased and the value after 28 d (55 mg/l) was significantly different from that after 14 d (47 mg/l) or that of untreated wine (43 mg/l). Using the formula of Berthelot (see Ribéreau-Gayon et al. 1972, p. 377) it was found that ethyl acetate content remained below its equilibrium value during quick-ageing.

Increases in acetic acid content with accelerated oxidation may result from oxidation of ethanol, but a similar increase was found with quick-ageing (Table 2) despite the loss due to esterification. The formation of acetic acid under essentially anaerobic conditions warrants further investigation.

The content of 2-phenethanol also increased with oxidation and quick-ageing. Rodopoulo (1965) observed an increase of this component in wine on heating which he contributed to degradation of protein and "oxidative deamination" of the free amino acid (phenylalanine).

2. Flavour evaluation

Under oxidative conditions all treatments examined resulted in a significant loss of wine quality (Table 3). Quality assessment with quick-ageing was made difficult because of the different style of wine produced compared with untreated wine; however, Singleton et al. (1964) have shown that certain wines could benefit from such treatments.

Changes in concentrations of the major fatty acid (C_6—C_{10}) esters in wine with oxidation and quick-ageing did not individually exceed their flavour threshold values. However, the overall increase in quantity of this chemical group is likely to affect flavour. The only major component (see Table 2) showing sufficient change in concentration to exceed its flavour threshold was the hydrocarbon TDN. This compound was found to be a major contributor of bottle-aged bouquet in Riesling wine (Simpson 1978). Therefore, the flavour changes which occurred with oxidation and quick-ageing must have been due in part to changes in concentrations of classes of chemicals (Table 1) and of components which are not readily observable in the headspace chromatograms. Minor components are capable of influencing aroma as is evident from the range in flavour threshold values given for beer (Meilgaard 1975 b). These values provide a good indication of threshold values for most alcoholic beverages. Using the technique of Dravnieks and O'Donnell (1971) for aroma assessment of volatiles emerging from the g.c., the development of intense aromas described as "burnt", "cooked" and "aldehydic" were noted throughout the chromatography of

the more oxidised wine samples; with the exception of benzaldehyde, these aromas could not be assigned to discrete peaks. Aldehydes such as isobutyraldehyde and isovaleraldehyde are likely to be present; they form in maderized wine and contribute to the rancio aroma (CANTARELLI 1967). In addition, low molecular weight components eluting before *act-* and isoamyl alcohols and which are poorly retained by the porous resin used in the concentration of headspace volatiles, are absent or present in reduced quantities in the observed aroma volatiles i.e. their relative importance to wine aroma cannot be determined satisfactorily by these techniques.

Few of the monoterpene alcohols and oxides, considered to be major contributors to the grape varietal bouquet of Riesling wine (RIBÉREAU-GAYON *et al.* 1975, SCHREIER *et al.* 1977), are distinguishable as peaks in g.c. analyses of the headspace volatiles. However, linalool, which co-eluted with minor quantities of ethyl n-nonanoate, appeared to increase in concentration with oxidation at lower temperature and (after an initial increase) decreased with accelerated oxidation and quick-ageing whereas nerol (peak 61, see figure) showed little change. The treatments are likely to favour interconversion of the acyclic monoterpenoids (linalool, nerol and geraniol) and subsequent acid-catalysed cyclisation to α-terpineol (WHITTAKER 1967); since this monoterpene has a higher flavour threshold (RIBÉREAU-GAYON *et al.* 1975) its accumulation will be concurrent with a loss of fruit bouquet, which is known to occur with wine oxidation and ageing (AMERINE *et al.* 1967, p. 284). Also, the relative contribution to aroma by the monoterpenoids can be decreased by an overall increase in other aroma volatiles and by production of highly odoriferous compounds; this would effectively result in a loss of fruit bouquet even in the absence of changes in composition of the monoterpenoids.

3. Colour changes with oxidation and quick-ageing

There were progressive increases in optical densities at all wavelengths in the visible region (400—700 nm) with oxidation and quick-ageing (Table 4). Greater change occurred under oxidative conditions at the same storage temperature as expected from earlier studies (SINGLETON and KRAMLING 1976, and references cited therein).

By comparing the changes in optical densities with the changes in composition of the aroma volatiles, especially with the untreated wine and wine oxidised at 50 °C for 1 d it is apparent that headspace analysis provides a very sensitive measure of wine condition and alteration during storage.

4. Effects of oxidation and quick-ageing on the aldehyde content of wine

The formation of aldehydes with wine oxidation is well documented (CANTARELLI 1967, WILDENRADT and SINGLETON 1974). These compounds have low flavour thresholds (MEILGAARD 1975 b) and, therefore, can have a strong influence on aroma even at relatively low concentrations.

The aldehyde content of oxidised and quick-aged Riesling wine (Table 5), determined by the method of GUYMON and CROWELL (1963), does not include aldehydes bound as acetals. The equilibrium between free and bound aldehydes in wine is rapidly attained (GUYMON and CROWELL 1963) and assay conditions should have allowed equilibrium at room temperature to have been reached. In addition, the pro-

portion in the bound form (at equilibrium) is low since acetal formation in wine solution is not favoured MISSELHORN (1975). This value can be calculated (PEYNAUD and MAURIÉ 1938).

Increased aldehyde content with oxidation is due largely to the production of acetaldehyde from ethanol. WILDENRADT and SINGLETON (1974) have postulated that this oxidation is brought about by hydrogen peroxide produced from dissolved oxygen reacting with polyphenolics in the wine. Losses of aldehydes through reaction with polyphenolics, acetal formation and oxidation to carboxylic acids can account for the decreases in aldehyde content which occurs with quick-ageing and, in certain instances, with oxidation.

Summary

Compositional changes in the aroma volatiles of Riesling wine with oxidation and quick-ageing have been examined using gas chromatographic (g.c.) headspace analysis. Changes in the concentrations of ethyl esters of the C_6—C_{10} fatty acids, hexyl acetate, ethyl furoate, diethyl succinate, 1-hexanol/ethyl lactate and 2-phenethanol were observed with all treatments. Vitispirane and 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) readily formed at elevated temperatures with both oxidative and non-oxidative storage, whereas, appreciable amounts of aldehydes including benzaldehyde and furfural were produced under oxidative conditions.

Changes in concentrations of the major components present in the collected aroma volatiles, except for the hydrocarbon TDN, did not exceed flavour threshold values. However, changes in the amounts of compounds in the same chemical classes and the formation of minor aroma-intense components are considered to be responsible for much of the observed flavour alterations. Loss of the more aroma-significant monoterpene alcohols and an overall increase in aroma components with oxidation and quick-ageing can account for loss of fruit bouquet in Riesling wine.

The aldehyde content of wine heated under nitrogen decreased whereas oxidative storage could lead to increased or decreased amounts. This demonstrated that monitoring total free aldehyde content (as distinct from concentrations of individual aldehydes) would give little indication of previous storage or present conditions of the wine.

Headspace analysis by g.c. has been shown to provide a sensitive measure of the extent of oxidation and ageing in wine.

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