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Aroma composition of aged Riesling wine

by

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Die Aromazusammensetzung von gealtertem Rieslingwein

Zusammenfassung. — Die Aromazusammensetzung von Rieslingweinen der Jahrgänge 1967, 1969, 1971, 1973 und 1975, die unter ähnlichen Bedingungen hergestellt worden waren, wurde mit Hilfe der Dampfraum-Gaschromatographie bzw. auf gaschromatographisch-massenspektrometrischem Wege analysiert. Es wurden über 140 Verbindungen identifiziert, von denen sich viele aus abgebauten Kohlenhydraten und Carotinoiden oder aus umgewandelten Terpenoiden herleiten ließen. Bei Wärmebehandlung des Traubensaftes von 9 Rebsorten wurden die beiden isomeren Vitispirane und 1,1,6-Trimethyl-1,2-dihydronaphthalin (TDN) gebildet; die entstandenen Mengen waren von Rebsorte und pH abhängig. Rieslingmost erbrachte die höchsten TDN-Konzentrationen. Dies weist darauf hin, daß im Wein dieser Rebsorte bei langer Kellerlagerung am sichersten aromawirksame Mengen von TDN zu erwarten sind.

Introduction

The *Vitis vinifera* variety Riesling is highly esteemed for white winemaking in Germany and extensive plantings are now found in Australia, North America (California) and South Africa. Young Riesling wines, made from sound grapes grown in the cooler viticultural regions of Australia, are typically light straw-coloured and have distinctive fruit flavour. Some of these wines are capable of developing deep yellow to amber colour and intense bottle bouquet with storage at normal cellar temperatures over 5—10 years (SIMPSON 1978, 1979 a); individual wines usually attain a maximum quality rating as bottle aged wines during this time, although some benefit from even longer storage.

The aroma compositions of the wines change during storage with the formation of volatile compounds considered to be derived from carbohydrate and carotenoid degradation. The monoterpene alcohols — important to the aroma of young wine — decrease in quantity whilst monoterpene oxides are formed. The ester composition changes due to shifts toward chemical equilibria: these changes are influenced by wine pH and storage temperatures (see also, MARAIS 1978, MARAIS and POOL 1980); the formation and hydrolysis of esters in model solutions and wines, and the kinetic factors involved, have been considered in more detail by RAMEY and OUGH (1980).

Previous investigations (SIMPSON 1978, and references cited therein) had demonstrated that, when young wine was heated under anaerobic conditions, it underwent compositional changes which simulated long-term storage. Some of these changes can occur with the heating of juice and may provide a means of examining the potential of wine made from that juice to develop bottle age aroma.

In this article, the aroma compositions of 6—14 year Riesling wines are presented and the factors responsible for the changes in composition during storage are discussed. Also, the effects of heating juice from 9 different grape varieties, including those most frequently used for white winemaking in Australia, are reported.

Materials and methods

1. Wines and juice samples

Commercial white table wines were made in 1967—1975 from Riesling grapes grown in the Eden Valley district of South Australia. 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.

Also, fruit from 9 different *Vitis vinifera* varieties was harvested during February—March 1981 from the Waite Agricultural Research Institute vineyard, Glen Osmond, South Australia. At picking, the grapes had a total soluble solids content (T.S.S.) of ca. 22 °Brix. The grapes were crushed in an air-bag press under nitrogen and treated overnight with pectic enzyme. The clarified juice was filtered and, after the addition of 100 mg SO₂/l, was placed in 750 ml bottles.

2. Instrumental analyses

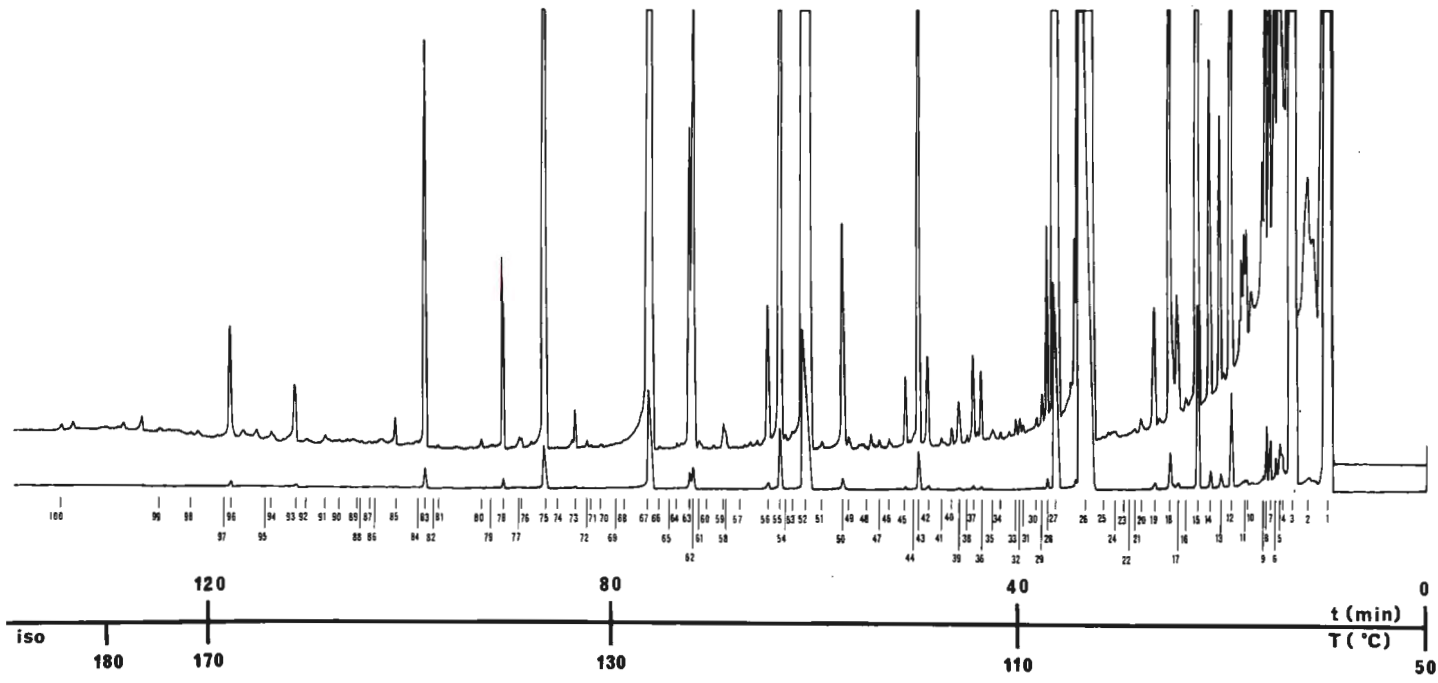
Wine headspace aroma components were isolated by methods similar to those described by RAPP and KNIPSER (1980). 1-Octanol as internal standard was added at a concentration of 3 mg/l to the wine prior to headspace collection. The Freon 11 solution containing the aroma components was concentrated to ca. 2 ml using a 200 mm × 10 mm ID Vigreux column packed with Fenske's helices and further reduced to ca. 50 µl using a 150 mm × 4 mm ID column packed with 3 mm glass spheres; both columns were water jacketed and maintained at 20 °C using a thermostated water bath-circulator. The aroma materials were analysed using SP1000 (modified Carbowax 20M) and SP2100 (silicone oil) SCOT glass capillary columns purchased from S.G.E., Melbourne, in a Perkin-Elmer Sigma 3B gas chromatograph with FID, injector and detector temperatures 250 °C, temperature programmed at 1 °/min from 50 to 180 °C, with 2.5 ml/min helium carrier gas and 27.5 ml/min nitrogen make-up gas. Peak areas were

Table 1
Analytical data for 1967—1975 Riesling wines¹⁾
Analysenwerte von Rieslingweinen, Jahrgänge 1967—1975¹⁾

	Vintage year				
	1967	1969	1971	1973	1975
Specific gravity (20/20 °C)	0.993	0.992	0.994	0.993	0.992
Ethanol (% v/v)	11.4	12.2	11.6	12.4	11.6
Reducing sugar (g glucose/l)	1.5	1.4	6.4	4.1	3.0
Titrateable acidity (g tartaric acid/l)	7.1	6.9	6.5	6.3	7.8
pH	3.10	3.08	3.00	3.09	3.08
Free SO ₂ (mg/l)	22	11	22	20	23
Total SO ₂ (mg/l)	108	101	140	133	120
Added ascorbic acid (mg/l) ²⁾	200	175	175	150	175

¹⁾ Determined at bottling (July—October in the year of vintage).

²⁾ Total addition made during post-fermentation processing.



Headspace chromatogram of the 1971 Riesling wine. Upper curve: recorder at highest sensitivity (attenuation = 40); lower trace: 20 times recorder decrease.
 Dampfraum-Chromatogramm des 1971er Rieslingweines. Obere Kurve: höchste Schreiberempfindlichkeit (Abschwächung = 40); unterer Verlauf: Schreiberempfindlichkeit auf 1/20 verringert.

obtained using a Hewlett-Packard model 3390A integrator. Identifications were made from retention data and peak enhancement with authentic materials, and with GC-MS using a Finnigan 4021 gas chromatograph-mass spectrometer-data system. Mass spectra were recorded at 70 eV.

3. Flavour threshold determination

The flavour threshold of nerol oxide, purified by preparative GC, was obtained by the method described by MEILGAARD (1975) using a white table wine initially containing negligible quantities of this compound.

4. Heat induction of bottle-age components in juice

The quantities of 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) and the isomeric vitispiranes in varietal grape juices (see Part 1) and juice samples heated at 50 °C for 28 d under nitrogen were determined by headspace analysis as earlier described, based on calibrations made by adding known amounts of purified reference materials to the Sultana juice. Additions of 5 M HCl and 5 M NaOH were made to provide Riesling and Sultana juice samples having pH values of 1.00, 2.80, 3.30 and 3.80; on heating, these values were altered by less than 0.02 units.

Results and discussion

1. Compositional analysis of aged Riesling wine

Compositions of the headspace volatiles of 1967, 1969, 1971, 1973 and 1975 Riesling wines are shown in Table 2; percent peak areas are given for components eluting after 17.5 min and added 1-octanol (internal standard). This alcohol occurs naturally in the wines but in trace quantities. The concentrations of the major components are also shown: these values were determined from calibrations made by adding known amounts of pure reference materials to a model wine solution containing potassium hydrogen tartrate and tartaric acid in ethanol-water (WILDENRADT and SINGLETON 1974). Where more than one compound was identified within a peak envelope the minor components are indicated in the table: these assignments were made by monitoring the key mass fragments of each compound throughout the peak envelope.

Over 140 compounds were identified in the aroma volatiles of aged Riesling wines, the majority being esters, alcohols and acetals previously reported in grapes and wine (SCHREIER 1979). Amongst the other components present were 5 C₁₃ compounds, 6 furan derivatives and 17 monoterpenes of which 13 were oxides. Only 3 sulphur-containing compounds, present in minor quantities, were identified: dimethyl sulphide, 2-methyl-tetrahydrothiophen-3-one and benzothiazole. These 3 compounds have also previously been reported in wines.

The component corresponding with peak 36 (see Table 2), on the basis of gas chromatographic behaviour and mass spectral data, is the ethyl ester of a branched chain heptanoic acid: I_R = 664 (van den Dool retention index on the SP1000 SCOT column, VAN DEN DOOL and KRATZ 1963); the mass spectrum showed prominent ions above m/e 35 (%): 88 (100), 43 (92), 101 (84), 41 (68), 55 (61), 73 (40), 57 (39), 70 (38), 60 (34), 45 (31), 69 (29), 95 (28), 61 (27), 113 (25); also 129 (9). The strong ion at m/e 101 indicates that the branching must be at C₄ or C₅, i.e. the compound is tentatively identified as ethyl 4-methylhexanoate or ethyl 5-methylhexanoate. This component was present in all wines in appreciably larger quantities than ethyl n-heptanoate (peak 41) and occurred at highest concentration in the 1969 wine.

Many of the aged wine components identified were aromatic hydrocarbons: benzene, toluene, *m*-xylene, cumene, styrene, *p*-cymene, naphthalene, 1-methyl naphthalene and 2-methyl naphthalene. Some of these compounds and the C₁₃ components identified, i.e. the spirane, the isomeric vitispiranes, ionene (a 1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene isomer) and TDN, are probably formed from carotenoid materials initially present in the grapes. EDMUNDS and JOHNSTONE (1965) and SCHREIER *et al.* (1979) identified toluene, *m*-xylene, TDN and ionene as thermal degradation products of β -carotene and related isoprenoids. The vitispiranes, identified in grape juice and wine (SIMPSON *et al.* 1977) and the volatiles from vanilla (SCHULTE-ELTE *et al.* 1978), are structurally related to several 2,6,10,10-tetramethyl-1-oxaspiro[4.5]decane derivatives isolated from tobacco; these and many of the diverse range of compounds obtained from this source are considered to be formed from carotenoid degradation and subsequent conversions brought about by oxidation, reduction, deamination, dehydration and cyclisation (ENZELL 1981). Trace quantities of isophorone, also identified in tobacco leaf, were found in the Riesling wines.

Two unidentified components (unknowns B, C; peaks 67 and 88, resp.), which were present in the aged wines, gave mass spectra indicating close chemical relationships with the vitispirane isomers. Van den Dool retention indices on the SP1000 SCOT column and mass spectra showing prominent ions above *m/e* 35 were: (B) $I_E=929$; *m/e* (%): 43 (100), 175 (99), 190 (92), 77 (92), 105 (88), 79 (72), 91 (71), 41 (66), 93 (63), 65 (61), 82 (57), 109 (53), 119 (47), 147 (45); (C) $I_E=1144$; *m/e* (%): 107 (100), 190 (97), 105 (83), 93 (67), 77 (61), 55 (54), 79 (48), 53 (46), 41 (46), 91 (45), 175 (38), 95 (39), 119 (28). The mass spectrum of compound B showed a major ion at *m/e* 190 and a series of ions above *m/e* 100 which are 2 amu less than those present in the spectra of the vitispiranes (see SIMPSON *et al.* 1977). This compound eluted shortly after the vitispirane isomers on the SP1000 column, cf. *trans*-vitispirane: $I_E=882$; *cis*-vitispirane: $I_E=891$, and is likely to be a dehydrovitispirane with a molecular formula of C₁₃H₁₈O. Compound C, with a similar mass fragmentation to that of compound B but larger retention index, may be the corresponding alcohol with a molecular formula of C₁₃H₂₀O₂. Neither compound B nor C was present in sufficient quantity to attempt isolation and further characterisation.

Numerous furan derivatives, other than the monoterpenes, were identified in aged wine volatiles and were shown to increase in concentration with time (SIMPSON 1978, 1979 a). The major components in this group were 2-ethoxyfuran, ethyl 2-furoate and 2-furfural. Minor quantities of 2-acetyl furan, 5-ethoxymethyl-2-furfural, 5-methyl-2-furfural and 2,2'-methylenebisfuran were also found in the present studies (see Table 2). Nearly all these compounds are formed from the carbohydrates although ascorbic acid, added to the wines prior to bottling at concentrations of 150–200 mg/l (see Table 1), is an additional source of some of these components: TATUM *et al.* (1969) had shown that ascorbic acid on heating gave 2-furfural and 2-furoic acid amongst the major products and lesser amounts of 2,2'-methylenebisfuran and γ -butyrolactone. 5-Ethoxymethyl-2-furfural, which was found in port wines (SIMPSON 1980), can be formed readily in aqueous ethanolic solution from 5-hydroxymethyl-2-furfural. This latter compound is a major product of the degradation of hexoses.

As reported earlier (SIMPSON 1979 b), aged Riesling wines contain two monoterpene oxides in relatively high concentrations, viz. *trans*-furan linalool oxide and nerol oxide. Minor quantities of 2,6,6-trimethyl-2-vinyltetrahydropyran, *cis*- and *trans*-anhydrolinalool oxide, *cis*- and *trans*-2,2-dimethyl-5-(1-methyl-propenyl)tetrahydrofuran, *cis*- and *trans*-rose oxide, *cis*-furan linalool oxide, *trans*-pyran linalool oxide, 1,4-cineole and 1,8-cineole were identified in this investigation. The furan and pyran linalool oxides, nerol oxide and the rose oxides have been identified in the juice and young wine from several white grape varieties (SCHREIER *et al.* 1976, 1979, DRAWERT and SCHREIER 1978)

Table 2
 Aroma compositions of 1967—1975 Riesling wines¹⁾
 Aromazusammensetzung von Rieslingweinen, Jahrgänge 1967—1975¹⁾

Peak No. ²⁾	Component(s)	Vintage year				
		1967	1969	1971	1973	1975
1	Solvent/dimethyl sulphide ³⁾					
2	Methyl acetate					
3	Ethyl acetate/ 1,1-diethoxyethane ³⁾					
4	3-Methylbutanal					
5	Ethanol					
6	Benzene ³⁾ /2,4,5-trimethyl- 1,3-dioxolane isomer					
7	Ethyl n-propanoate/ 1,1-diethoxypropane ³⁾					
8	Ethyl 2-methylpropionate					
9	1-Propyl acetate/ 1-ethoxy-1-propoxyethane					
10	2,4,5-Trimethyl- 1,3-dioxolane isomer		0.04	0.07	0.07	
11	2-Methylpropyl acetate	0.03	0.08	0.09	0.07	0.03
12	1-Propanol ³⁾ /ethyl n-butoanoate/toluene ³⁾	1.41	2.03	1.80	1.43	1.48
13	Ethyl 2-methylbutanoate	0.14 (0.01)	0.27 (0.02)	0.30 (0.02)	0.22 (0.02)	0.19 (0.02)
14	Ethyl 3-methylbutanoate	0.23 (0.02)	0.33 (0.03)	0.37 (0.06)	0.22 (0.02)	0.26 (0.02)
15	Hexanal ³⁾ /2-methyl- 1-propanol	4.92 (45.8)	4.50 (37.6)	4.33 (25.2)	4.31 (25.2)	3.72 (26.3)
16	Ethyl carbonate					
17	2,6,6-Trimethyl-2-vinyl- tetrahydropyran			0.21 (0.01)	0.11 (0.01)	
18	2-Methylbutyl acetate/ 3-methylbutyl acetate	0.62 (0.11)	0.95 (0.18)	1.04 (0.11)	0.76 (0.08)	0.80 (0.12)
19	Ethyl n-pentanoate ³⁾ / 1-butanol/m-xylene ³⁾	0.10	0.14	0.17	0.11	0.09
20	1-Butyl 2-methylpropanoate					
21	Ethyl 2-butenolate					
22	1,4-Cineole					
23	Cumene					
24	2-Heptanone					
25	Methyl n-hexanoate					
26	2,2-Dimethyl-5-(1-methyl- propenyl)tetrahydrofuran isomer ³⁾ /1,8-cineole ³⁾ / <i>trans</i> -anhydrolinalool oxide ³⁾ /2-methyl- 1-butanol/3-methyl- 1-butanol	76.4 (247)	70.7 (205)	61.8 (143)	68.1 (138)	68.0 (167)
27	Ethyl n-hexanoate	4.23 (0.54)	6.00 (0.69)	8.28 (0.66)	6.43 (0.52)	7.17 (0.70)

Table 2 (continued)

Peak No.	Component(s)	1967	1969	1971	1973	1975
28	2,2-Dimethyl-5-(1-methylpropenyl)-tetrahydrofuran isomer/ <i>cis</i> -anhydro-linalool oxide ³)	0.10 (0.04)	0.21 (0.02)	0.17 (0.01)	0.18 (0.03)	0.10 (0.04)
29	1-Pentanol	0.03	0.08	0.02	0.04	
30	1-Butyl 3-methylbutanoate/styrene					
31	2-Methylbutyl n-butanoate/3-methylbutyl n-butanoate		0.03			
32	p-Cymene					
33	1-Hexyl acetate	0.01			0.01	0.01
34	2-Ethoxymethyl furan					
35	3-Hydroxy-2-butanone/octanal					
36	Ethyl methylhexanoate isomer (A)	0.02	0.31	0.06	0.03	
37	<i>cis</i> -3-Hexen-1-yl acetate	0.03	0.04	0.10	0.05	
38	<i>trans</i> -3-Hexen-1-yl acetate ³ /4-methyl-1-pentanol	0.01				0.06
39	1-Propyl n-hexanoate ³ /methyl lactate	0.02	0.01		0.03	0.02
40	3-Methyl-1-pentanol	0.02	0.01			0.01
41	Ethyl n-heptanoate					
42	2-Nonanone ³ /ethyl <i>trans</i> -2-hexenoate ³ /ethyl lactate	0.14 (28.5)	0.07 (12.5)	0.11 (16.6)	0.08 (10.2)	0.05 (8.4)
43	1-Hexanol/ <i>cis</i> -rose oxide ³)	1.47 (3.95)	0.77 (1.86)	0.83 (1.40)	1.11 (1.87)	0.93 (1.91)
44	2-Methylpropyl n-hexanoate					
45	<i>trans</i> -3-Hexen-1-ol/ <i>trans</i> -rose oxide ³)	0.08	0.06	0.06	0.04	0.03
46	3-Ethoxy-1-propanol					
47	<i>cis</i> -3-Hexen-1-ol					
48	Methyl n-octanoate/3-octanol					
49	<i>trans</i> -2-Hexen-1-ol	0.01	0.01		0.01	0.01
50	<i>cis</i> -2-Hexen-1-ol ³ /acetic acid	0.14	0.17	0.32	0.22	0.20
51	1-Propyl lactate					
52	Ethyl n-octanoate/ <i>trans</i> -furan linalool oxide ³)	3.93 (0.37)	6.39 (0.54)	9.98 (0.59)	7.93 (0.47)	9.24 (0.66)
53	1-Octen-3-ol					
54	1-Heptanol	0.01				
55	2-Furfural/2-methylpropyl lactate ³ /3-methylbutyl n-hexanoate ³)	1.41 (10.7)	1.46 (9.95)	1.42 (7.69)	1.33 (7.25)	0.69 (4.56)

(Table continued on page 58—59)

Table 2 (continued)

Peak No.	Component(s)	1967	1969	1971	1973	1975
56	Nerol oxide/ <i>cis</i> -furan linalool oxide ³)	0.11 (0.06)	0.15 (0.07)	0.15 (0.05)	0.13 (0.04)	0.14 (0.05)
57	2-Ethyl-1-hexanol					
58	Theaspirane/2-acetyl furan	0.02	0.17	0.05	0.07	0.02
59	Ethyl 2,4-hexadienoate					
60	Benzaldehyde					
61	2-Methyltetrahydrothiophen-3-one/ 1-propyl n-octanoate					
62	<i>trans</i> -Vitispirane	0.33 (0.058)	0.45 (0.057)	0.62 (0.071)	0.42 (0.048)	0.34 (0.053)
63	<i>cis</i> -Vitispirane	0.18 (0.032)	0.20 (0.046)	0.36 (0.054)	0.34 (0.038)	0.15 (0.024)
64	Ethyl n-nonanoate					
65	Linalool					
66	2-Methylpropyl n-octanoate					
67	1-Octanol (internal standard)/5-methyl-2-furfural ³ /unknown B ³ /3-methylbutyl lactate ³)	2.68	2.98	3.73	3.71	3.07
68	Diethyl malonate					
69	Isophorone					
70	Methyl n-decanoate					
71	2,2'-Methylenebisfuran					
72	Ethyl laevulinate/hotrienol					0.01
73	Ethyl 2-furoate/ γ -butyrolactone ³)	0.04 (0.18)	0.06 (0.27)	0.04 (0.13)	0.04 (0.13)	0.04 (0.17)
74	Ethyl methyl succinate					
75	Acetophenone ³ /ethyl n-decanoate	0.36 (0.04)	0.66 (0.06)	1.40 (0.09)	1.12 (0.07)	1.48 (0.11)
76	1-Nonanol/ethyl benzoate					0.01
77	2-Methylbutyl n-octanoate/3-methylbutyl n-octanoate					
78	Diethyl succinate	0.20 (2.14)	0.16 (1.58)	0.19 (1.50)	0.22 (1.72)	0.20 (1.89)
79	1,1,6-Trimethyl-1,2,3,4-tetrahydronaphthalene (ionene)					
80	α -Terpineol ³ /ethyl 9-decenoate	0.04	0.09		0.02	0.01
81	1-Propyl n-decanoate					
82	Naphthalene					
83	<i>trans</i> -Pyran linalool oxide ³ /1,1,6-trimethyl-1,2-dihydronaphthalene	0.42 (0.054)	0.36 (0.045)	0.46 (0.043)	0.39 (0.038)	0.34 (0.039)
84	Ethyl n-undecanoate					
85	2-Methylpropyl n-decanoate/1-decanol	0.02	0.02	0.03	0.03	0.03
86	Diethyl glutarate					

Table 2 (continued)

Peak No.	Component(s)	1967	1969	1971	1973	1975
87	Ethyl phenylacetate					
88	Unknown C					
89	Ethyl 2-methylpropyl succinate					
90	2-Phenethyl acetate					
91	1-Decyl n-butanoate					
92	2-Methyl naphthalene					
93	Ethyl n-dodecanoate	0.04 (0.01)	0.03	0.07 (0.01)	0.02	0.03
94	1-Undecanol/benzyl alcohol/2-methylbutyl n-decanoate/3-methylbutyl n-decanoate					0.01
95	1-Methyl naphthalene					
96	Ethyl 3-methylbutyl succinate ³⁾ /2-phenethanol	0.10 (12.1)	0.09 (10.1)	0.15 (11.2)	0.12 (9.5)	0.12 (10.9)
97	5-Ethoxymethyl-2-furfural					0.01
98	Benzothiazole					
99	1-Dodecanol					
100	Ethyl n-tetradecanoate					
	Total	100.0	100.1	98.9	99.5	99.1

¹⁾ Expressed as % peak area of compounds eluting after 17.5 min; where no values are shown the peak area was less than 0.01 %; values shown in parenthesis are concentrations in wine (in mg/l); analysed in January 1982.

²⁾ Refer to figure.

³⁾ Minor component(s) within the peak envelope.

and in recent times RAPP and coworkers (RAPP and KNIPSER 1980, RAPP *et al.* 1980) have found 2,6,6-trimethyl-2-vinyltetrahydropyran and *cis*- and *trans*-anhydrolinalool oxides in some muscat varieties. 2,2-Dimethyl-5-(1-methylpropenyl)tetrahydrofuran, 1,4-cineole and 1,8-cineole have previously only been detected in heated Muscat of Alexandria juice (WILLIAMS *et al.* 1980 a). Only trace quantities of linalool, hotrienol and α -terpineol were present in the 1967–1975 Riesling wines, whereas these are major terpenoids of young Riesling wine. The total quantity of volatile monoterpenes in young Riesling wine is ca. 0.5 mg/l based on the concentrations of individual components reported by SCHREIER *et al.* (1979). The total quantities of volatile monoterpenes present in the aged wines should be 1–2 mg/l, based on the values shown in Table 2 and the expected concentrations of *trans*-furan linalool oxide (see SIMPSON 1979 a); this indicates a significant overall increase. Whilst some of the monoterpenoid material in aged wine can be derived from the initial volatile components, other sources must also exist. It now seems likely that involatile monoterpene glycosides and hydroxylated linalool derivatives (RAPP and KNIPSER 1979, RAPP *et al.* 1980, WILLIAMS *et al.* 1980 a, 1980 b, 1982) account for the production of volatile terpenes during long-term storage. 3,7-Dimethylocta-1,5-dien-3,7-diol is a potential source of both hotrienol and nerol oxide. From observations made by WILLIAMS *et al.* (1980 a) it seems that hotrienol under acidic

conditions will rearrange to nerol oxide, thus consistent with the moderate quantities of nerol oxide and trace quantities of hotrienol found in aged Riesling wines. These workers also showed that 3,7-dimethyloct-1-en-3,6,7-triol, when heated in model solutions at wine pH, produced the furan linalool oxide isomers, with the *trans*-isomer predominating. Only minor amounts of the *cis*-isomer were present in aged wine volatiles. Many of the reaction products of 3,7-dimethyloct-1-en-3,6-diol and 3,7-dimethyloct-1-en-3,7-diol identified in the model studies were also identified in the aged Riesling wines, i.e. *cis*- and *trans*-anhydrolinalool oxides, the isomeric 2,2-dimethyl-5-(1-methylpropenyl)tetrahydrofurans and 2,6,6-trimethyl-2-vinyltetrahydropyran. STRICKLER and KOVÁTS (1966) had shown that the last-mentioned compounds could also be formed from linalool but strong acid and heating were required.

Whilst the major terpene alcohols virtually disappear from Riesling wine over 2—3 years at usual cellar temperatures, there is generally an initial increase in the concentration of α -terpineol (SIMPSON, unpublished data). This would be explained by the conversion of linalool and geraniol to α -terpineol, which occurs under mild conditions (STEVENS *et al.* 1972). The subsequent loss of α -terpineol could be explained by its conversion to terpin hydrate (see VERGHESE 1970, and references cited therein); the latter compound would not be present in appreciable quantities in the headspace volatiles due to its lower volatility. Hotrienol in the young wine may be converted to nerol oxide, as already outlined. The small quantities of 1,4-cineole and 1,8-cineole found in the aged Riesling wines can be formed from hydroxylated linalool derivatives as described, but can also be produced from linalool and geraniol (STEVENS *et al.* 1972). The cineoles were minor products of the acid-catalysed rearrangement of linalool, examined by STRICKLER and KOVÁTS (1966). Consequently, the terpenes present in the headspace volatiles from aged Riesling wine are the end products of acid-catalysed conversions of the volatile monoterpene alcohols initially present in the young wine and the reaction products from the less volatile hydroxylated linalool derivatives and glycosides recently identified in grapes and wine.

Despite the large number of compounds identified in the aged Riesling wines and the presence of components, which are derived from carbohydrate and carotenoid degradation and terpenoid rearrangements and which increase in concentration with storage in individual wines, little correlation between aroma composition and wine age is evident (see Table 2). Differences in the initial compositions of the wines and slower rates of reactions occurring after 5 years storage presumably account for the extent of correlation found.

2. Formation of TDN and the vitispiranes in juice

The production of TDN and the isomeric vitispiranes in varietal grape juices on heating is shown in Table 3; these juices were obtained from grapes of similar ripeness (see Table 3). The conditions used, i.e. heating at 50 °C for 28 d under nitrogen were identical with those for the "quick ageing" of wines (see SIMPSON 1978). From earlier observations (SIMPSON, unpublished results), similar quantities of these compounds were produced under the same conditions in both the wine and the juice from which it was made. Of the juices examined, that from Emerald Riesling (Riesling \times Muscadelle) gave the highest yield of vitispirane but Riesling juice gave most TDN. All varieties showed the potential to produce these materials but Riesling and closely related varieties may be the only varieties able to produce quantities of TDN capable of affecting wine aroma, even with long-term cellar storage. The formation of TDN and the isomeric vitispiranes is influenced by pH as shown with the Sultana and Riesling juice samples. Highest concentrations of TDN were produced at pH 2.80 and 3.30, which

Table 3

Content of vitispirane and TDN in fresh and heated grape juice¹⁾ (in mg/l)
 Vitispiran- und TDN-Gehalt (mg/l) in frischem und wärmebehandeltem Traubensaft¹⁾

Sample	T.S.S. (° Brix)	Vitispirane		TDN	
		Fresh	Heated ²⁾	Fresh	Heated ²⁾
Chenin blanc	21.4	0.00	0.05	0.000	0.003
Emerald Riesling	21.2	0.01	0.44	0.000	0.028
Muscat gordo blanco	22.1	0.01	0.10	0.000	0.008
Palomino	22.0	0.01	0.05	0.000	0.002
Riesling, pH 1.0	21.9	0.00	0.01	0.000	0.042
Riesling, pH 2.8	21.9	0.00	0.17	0.000	0.058
Riesling, pH 3.3	21.9	0.00	0.25	0.000	0.065
Riesling, pH 3.8	21.9	0.00	0.27	0.000	0.028
Semillon	22.0	0.00	0.03	0.000	0.002
Sultana, pH 2.8	20.6	0.00	0.11	0.000	0.032
Sultana, pH 3.3	20.6	0.00	0.14	0.000	0.030
Sultana, pH 3.8	20.6	0.00	0.13	0.000	0.013
Sylvaner	22.1	0.01	0.12	0.000	0.004
Traminer	22.5	0.00	0.02	0.000	0.002

¹⁾ Analysed March—April 1982.

²⁾ 50 °C under N₂ for 28 d.

correspond with the lower pH range for grape juice and wine. At artificially low pH (1.00) little vitispirane was formed or it was further degraded.

3. Flavour aspects

As previously reported (MARAIS 1979, SIMPSON 1979 a, 1979 b), dimethyl sulphide (DMS) and TDN are important contributors to the aroma of bottle aged Riesling wines. The concentrations of DMS were not determined in these studies but the concentrations of TDN exceeded its flavour threshold of 0.020 mg/l in all wines. Although present in minor quantities, the aromatic hydrocarbons: benzene, toluene, m-xylene, p-cymene, cumene, styrene, ionene, naphthalene, 1-methyl naphthalene and 2-methyl naphthalene can be expected to contribute to the hydrocarbon-like aroma evident in these wines.

Although many esters were identified, only the ethyl esters of the medium chain fatty acids were present at concentrations approaching or exceeding their flavour thresholds. These esters are responsible for the "fruity" and "wine-like" aroma of young wines; since their concentrations are not markedly different in aged wines their overall influence in these wines will be less significant.

Although the content of nerol oxide in the 1967 and 1969 Riesling wines approached the flavour threshold of 0.08 mg/l, all 5 wines contained sub-threshold concentrations. However, with the presence of minor quantities of other monoterpene oxides, in particular, 2,6,6-trimethyl-2-vinyltetrahydropyran and the 2,2-dimethyl-5-(1-methylpropenyl)tetrahydrofuran isomers, the flavour threshold for this group of compounds is likely to be exceeded and they may contribute a "cineole-like" aroma to aged Riesling wines.

Summary

The aroma compositions of 1967, 1969, 1971, 1973 and 1975 Riesling wines made under similar conditions were analysed by headspace GC and GC-MS. Over 140 compounds were identified, many of which were derivable from carbohydrate and carotenoid degradations and terpenoid rearrangements. The 2 isomeric vitispiranes and 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) were produced in 9 varietal grape juices with heating; the quantities formed were influenced by grape variety and pH. Riesling juice gave the highest concentrations of TDN, which indicated that wine from this grape variety has the most potential to produce aroma-significant quantities of TDN during long-term cellar storage.

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