The Australian Wine Research Institute, Glen Osmond, South Australia

# Aroma composition of Chardonnay wine

by

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## Die Aromazusammensetzung von Chardonnay-Wein

Zusammenfassung. — Die Aromastoffe im Dampfraum von Chardonnay-Weinen aus 6 aufeinanderfolgenden Jahrgängen wurden mittels Kapillar-Gaschromatographie und Gaschromatographie-Massenspektrometrie analysiert; hierbei wurden ungefähr 150 Verbindungen identifiziert. Ihre Beteiligung am Aroma des im Dampfraum enthaltenen Substanzgemisches wurde durch "Erschnüffeln" der gaschromatographisch aufgetrennten Komponenten bestimmt. Die wichtigsten Gärungsalkohole und -ester, Essigsäure sowie Damascenon stellen wesentliche Aromastoffe der Chardonnay-Weine dar.

#### Introduction

The Vitis vinifera cultivar Chardonnay is renowned for the production of high quality French White Burgundy and Chablis wines, and Champagne (LICHINE 1979); extensive plantings of Chardonnay are found in several other countries including North America (California), where its potential for producing high quality wines is also recognised (AMERINE et al. 1980). Although the area of vineyard planted with Chardonnay in Australia is small, it has increased rapidly in recent years — from 624 ha in 1980 to 978 ha in 1981 and 1,238 ha in 1982 (AUSTRALIAN BUREAU OF STATISTICS 1981, 1982, 1983). Chardonnay now rivals Riesling as the premium grape for white winemaking in this country. The making of Chardonnay wine under local conditions, unlike Riesling, incorporates contact with oak wood in virtually all instances: the juice may be fermented in the presence of wood chips or in wood casks but, most frequently, the wine is matured in wood casks. Typically, these wines have little residual sugar, exhibit oak flavour and, when marketed, often possess considerable bottle age bouquet.

## Materials and methods

# 1. Wine and juice samples

Commercial white table wines were made during the 6 vintages, 1976—1981, from Chardonnay grapes grown in the Hunter Valley district of New South Wales. Fermentation by natural yeasts occurred at 15—18 °C; malolactic fermentation occurred near or soon after the completion of the yeast fermentation. The wines were held in new French oak casks for 2—3 months, placed in 750 ml bottles and subsequently stored at about 15 °C.

Analytical data for these wines, including the concentration of L-malic, D-lactic and L-lactic acids (determined enzymically, ANONYMOUS 1980), are shown in Table 1.

Chardonnay juice was obtained from grapes also grown in the Hunter Valley and harvested in February 1982. At picking, the grapes had a total soluble solids content of about 23 °Brix. The grapes were destemmed and crushed in a roller mill; the juice, to

			_		_
1976	1977	1978	1979	1980	1981
11.7	12.3	12.4	12.9	13.0	11.9
1.13	1.68	1.63	2.33	2.52	1.52
6.1	6.1	6.2	7.7	6.5	7.1
0.80	0.62	0.65	0.88	0.93	0.69
1.39	0.31	0.30	2.09	0.35	1.00
0.68	1.13	1.13	0.03	0.80	0.25
0.07	0.09	0.09	0.15	0.10	0.11
3.43	3.54	3.55	3.31	3.18	3.15
4	3	3	3	8	3
101	114	121	133	105	111
	11.7 1.13 6.1 0.80 1.39 0.68 0.07 3.43	11.7 12.3  1.13 1.68  6.1 6.1  0.80 0.62  1.39 0.31  0.68 1.13  0.07 0.09  3.43 3.54  4 3	11.7     12.3     12.4       1.13     1.68     1.63       6.1     6.1     6.2       0.80     0.62     0.65       1.39     0.31     0.30       0.68     1.13     1.13       0.07     0.09     0.09       3.43     3.54     3.55       4     3     3	11.7     12.3     12.4     12.9       1.13     1.68     1.63     2.33       6.1     6.1     6.2     7.7       0.80     0.62     0.65     0.88       1.39     0.31     0.30     2.09       0.68     1.13     1.13     0.03       0.07     0.09     0.09     0.15       3.43     3.54     3.55     3.31       4     3     3	11.7     12.3     12.4     12.9     13.0       1.13     1.68     1.63     2.33     2.52       6.1     6.1     6.2     7.7     6.5       0.80     0.62     0.65     0.88     0.93       1.39     0.31     0.30     2.09     0.35       0.68     1.13     1.13     0.03     0.80       0.07     0.09     0.09     0.15     0.10       3.43     3.54     3.55     3.31     3.18       4     3     3     8

Table 1

Analytical data for Chardonnay wines 1)

Analysenwerte von Chardonnay-Weinen

which pectic enzyme and 90 mg  $SO_2$ /l were added, was left in contact with the grape solids for 8 h, after which it was pad-filtered and stored at 10 °C. Values for titratable acid expressed as g tartaric acid/l and pH were 6.5 and 3.12, respectively.

# 2. Analysis of juice and wine aroma volatiles

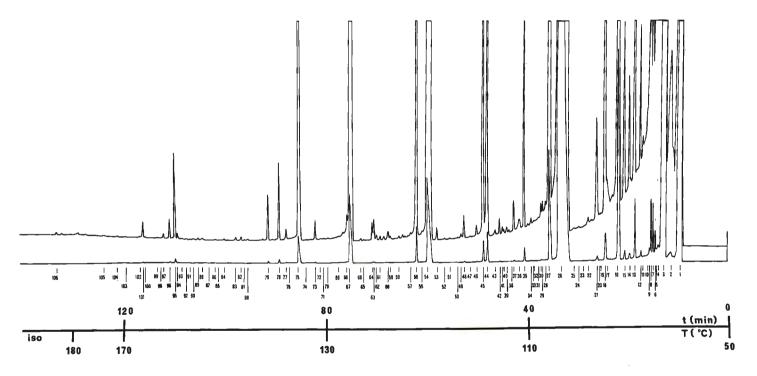
The concentration of dimethyl sulphide in wine was obtained by colorimetric assay (SIMPSON 1979 a).

Juice and wine headspace aroma components were isolated and analysed by GC and GC-MS, using 1-octanol as internal standard (SIMPSON and MILLER 1983). The concentration of 1,1,6-trimethyl-1,2-dihydronaphthalene, damascenone, cis- and trans- $\beta$ -methyl- $\gamma$ -octalactone, because of the small quantities present, was determined from GC-MS and key mass fragments. The assignment of relative quantities of compounds within a multi-component peak was also based on the analysis of key mass fragments within the peak envelope.

# 3. Sensory assessment and flavour threshold determination

The effluent from the SP1000 SCOT glass capillary column was split 1:1 to the FID and to a sniffing port via heated 0.3 mm ID glass-lined metal tube (DRAVNIEKS and O'DONNELL 1971). No internal standard was added to juice or wine used for sensory assessment. The flavour threshold of  $trans-\beta$ -methyl- $\gamma$ -octalactone and damascenone, purified by preparative GC, was obtained according to Meilgaard (1975) using a non-aromatic dry white wine made from *Vitis vinifera* cvs Doradillo, Palomino and Pedro Ximenez without wood contact and initially containing no measurable quantity of damascenone; free and total SO<sub>2</sub> contents were 20 and 173 mg/l, respectively.

<sup>1)</sup> Analysed June - July 1982.



Headspace chromatogram of the 1976 Chardonnay wine. Upper curve: recorder at highest sensitivity (attenuation = 40); lower trace: 20 times recorder decrease.

Dampfraum-Chromatogramm des 1976er Chardonnay-Weines. Obere Kurve: höchste Schreiberempfindlichkeit (Abschwächung = 40); unterer Verlauf: Schreiberempfindlichkeit auf 1/20 verringert.

 $\label{eq:Table 2} \mbox{Aroma composition of Chardonnay wines $^1$)} \\ \mbox{Aromazusammensetzung von Chardonnay-Weinen}$ 

Peak No. ²)		1976	1977	1978	1979	1980	1981	Aroma associated with peak(s) 3)
1	[Solvent]/dimethyl sulphide	(0.022)	(0.021)	(0.022)	(0.011)	(0.033)	(0.017)	
2	2-Methylpropanal 4)/methyl acetate							Sweet
3	Ethyl acetate/1,1-diethoxy- ethane 4)/2-methylbutanal 4)							Solvent-like, ethyl acetate
4	3-Methylbutanal							Acetic, harsh, green
5	Ethanol							
6	Benzene 4)/2,4,5-trimethyl- -1,3-dioxolane isomer	0.22	0.60	0.41	0.89	0.22	0.38	Sweet nutty
7	Ethyl n-propanoate	0.66	0.61	0.54	0.61	0.77	0.50	Sweet, estery
8	Ethyl 2-methylpropionate/ 1-ethoxy-1-propoxyethane 4)	0.80	0.93	0.96	0.56	0.63	0.35	Sweet, estery
9	1-Propyl acetate/3-pentanone 4)	0.12			0.02	0.13	0.10	Sweet, oily
0	2,4,5-Trimethyl-1,3- dioxolane isomer		-					
1	1-Ethoxy-1-(2-methyl- propoxy)ethane	0.01						
2 .	2-Methylpropyl acetate	0.15	0.17	0.06	0.03	0.34	0.46	Sweet, estery
3	1-Propanol 4)/ethyl n-butanoate/toluene 4)	1.14 (0.29)	0.93 (0.24)	0.96 (0.28)	2.32 (0.54)	2.12 (0.52)	1.53 (0.45)	Sweet, estery
.4	Ethyl 2-methylbutanoate	0.12 (0.012)	0.12 (0.014)	0.11 (0.013)	0.12 (0.014)	0.11 (0.014)	0.06 (0.006)	Estery

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15	Ethyl 3-methylbutanoate	0.20 (0.020)	0.18 (0.021)	0.17 (0.021)	0.23 (0.028)	0.20 (0.027)	0.11 (0.014)	Estery
16	Hexanal 4)/2-methyl- 1-propanol/1-ethoxy- 1-(2-methylbutoxy)- ethane 4)	6.81 (55)	10.82 (104)	10.81 (109)	7.73 (79)	7.14 (76)	5.90 (60)	Harsh, solvent-like, fusel alcohol
17	1-Ethoxy-1-(3-methyl- butoxy)ethane/2,6,6- -trimethyl-2-vinyl- tetrahydropyran 4)				0.24			
18	2-Methylbutyl acetate/ 3-methylbutyl acetate/ ethyl benzene 4)	0.92 (0.14)	0.72 (0.13)	0.76 (0.14)	0.95 (0.18)	1.16 (0.23)	2.93 (0.55)	Banana-like, acetate ester
19	p-Xylene							Harsh, hydrocarbon
20	Ethyl n-pentanoate						0.04	
21	1-Butanol/m-xylene 4)	0.15 (1.0)	0.29 (1.8)	0.35 $(2.4)$	0.46 (3.7)	0.35 $(3.4)$	0.14 (0.7)	Harsh, alcoholic
<b>2</b> 2	Ethyl 2-butenoate		0.01	0.01	0.01			
23	Cumene							
24	2-Heptanone/o-xylene							Slightly sweet
25	Methyl n-hexanoate							
26	2,2-Dimethyl-5-(1-methyl- propenyl)tetrahydro- furan isomer 4)/trans- -anhydrolinalool oxide 4)/ 2-methyl-1-butanol/ 3-methyl-1-butanol	72.8 (197)	71.7 (233)	70.5 (245)	69.2 (248)	69.7 (257)	72.6 (257)	Fusel alcohol, amyl alcohol
27	Ethyl n-hexanoate	3.81 (0.43)	2.64 (0.35)	2.55 (0.35)	4.31 (0.61)	4.76 (0.71)	4.50 (0.63)	Estery, wine-like

Table 2 (continued)

Pea No.	<del></del>	1976	1977	1978	1979	1980	1981	Aroma associated with peak(s) 3)
28	2,2-Dimethyl-5-(1-methyl- propenyl)tetrahydrofuran isomer/ <i>cis</i> -anhydrolinalool oxide							
29	1-Pentanol	0.01	0.02	0.01	0.01	0.01		
30	Styrene	0.01 (0.001)	0.01 (0.001)	(0.001)	0.01 (0.001)	(0.001)	(0.002)	Harsh
31	1-Ethoxy-1-hexoxyethane							
32	2-Methylbutyl n-butanoate/ 3-methylbutyl n-butanoate	·						
33	p-Cymene							
84	1-Hexyl acetate	(0.002)	(0.002)	(0.002)	(0.003)	0.01 (0.005)	0.09 (0.038)	Sweet
5	2-Octanone 4)/2-ethoxy- methyl furan	0.26 (0.23)	0.54 (0.55)	0.55 $(0.54)$	0.39 (0.40)	0.18 (0.17)	0.12 (0.14)	Green, woody
6	3-Hydroxy-2-butanone 4)/ octanal	0.02				0.04	0.03	Earthy
37	Ethyl 4-methylhexanoate	0.03						Estery
8	cis-3-Hexen-1-yl acetate						0.01	
9	trans-3-Hexen-1-yl acetate 4)/ 4-methyl-1-pentanol	(0.011)	0.01 (0.021)	0.01 (0.020)	(0.015)	(0.016)	0.02 (0.042)	Fusel alcohol
ŀ0	1-Propyl n-hexanoate							
1 -	Methyl lactate			0.02	0.03			
12	3-Methyl-1-pentanol	0.02 (0.036)	0.02 (0.061)	0.02 (0.059)	0.02 (0.071)	0.03 (0.074)	0.05 (0.170)	Initially sweet and then harsh
3	Ethyl n-heptanoate							Sweet

44	2-Nonanone 4)/ethyl <i>trans</i> - -2-hexenoate 4)/ethyl lactate	0.71 (130)	1.11 (136)	1.14 (258)	0.10 (23)	1.10 (268)	0.28 (66)	Mild ester
45	1-Hexanol/2-methylpropyl n-hexanoate <sup>4</sup> )	0.45 (1.07)	0.41 (1.11)	0.41 (1.16)	0.49 (1.46)	0.35 $(1.10)$	0.54 (1.58)	Fusel alcohol
46	trans-3-Hexen-1-ol	0.01 (0.09)	$0.02 \\ (0.17)$	0.01 (0.17)	0.01 (0.12)	(0.09)	0.03 (0.42)	Harsh
47	3-Ethoxy-1-propanol							Harsh, unpleasant
48	cis-3-Hexen-1-ol	$0.02 \\ (0.21)$	$0.01 \\ (0.14)$	0.01 (0.16)	0.01 (0.14)	(0.11)	0.02 (0.20)	Harsh, alcoholic
. <b>49</b>	2-Decanone/methyl n-octanoate							Slightly sweet
50	3-Octanol							
51	trans-2-Hexen-1-ol							
52	cis-2-Hexen-1-ol							
53	Ethyl 2-hydroxy-3-methyl- butanoate 4)/1-propyl lactate	0.01	0.01	0.01	0.01	0.01	0.01	
54	Ethyl n-octanoate/trans- -furan linalool oxide 4)	5.09 (0.42)	3.75 (0.37)	3.52 (0.36)	5.22 (0.55)	6.26 $(0.67)$	5.52 (0.57)	Estery, wine-like
55	1-Octen-3-ol							
56	1-Heptanol 4)/2-furfural/ 2-methylpropyl lactate 4)/3-methylbutyl n-hexanoate 4)	0.83 (5.65)	1.00 (8.07)	0.99 (8.35)	0.15 (1.28)	0.13 (1.21)	0.04 (0.32)	Woody, furfural
57	Nerol oxide							
58	2-Ethyl-1-hexanol							
59	2-Acetyl furan							

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Table 2 (continued)

Peal No. <sup>2</sup>		1976	1977	1978	1979	1980	1981	Aroma associated with peak(s) 3)
	Ethyl 2,4-hexadien- oate <sup>4</sup> )/decanal	0.02						Harsh
61	Benzaldehyde							
	1-Propyl n-octanoate/ 2-methyl tetrahydro- thiophen-3-one	0.01	0.01				0.01	Initial estery and then harsh, raw vegetable-like
63	trans-Vitispirane	0.02 (0.004)	0.02 $(0.004)$	0.02 (0.003)	(0.002)	(0.002)	0.02 (0.004)	Floral, pleasant, mild
64	cis-Vitispirane	0.02 (0.003)	0.02 (0.004)	0.02 $(0.003)$	(0.001)	(0.002)	0.02 (0.003)	Floral, pleasant
65	Ethyl n-nonanoate							
	Ethyl 2-hydroxy-4-methyl- pentanoate 4)/linalool	(0.003)	(0.004)	(0.005)	(0.007)	(0.007)	(0.005)	Woody, floral
	2-Methylpropyl n-octan- oate 4)/1-octanol (internal standard)/ 5-methyl-2-furfural 4)	2.97	2.51	2.41	2.33	2.38	2.52	Woody, furfural-like
68	3-Methylbutyl lactate							
39	Diethyl malonate							
70	Methyl n-decanoate							
71	2,2'-Methylenebisfuran							Nutty
72	Ethyl laevulinate							
	Ethyl 2-furoate/γ-butyro- lactone ⁴)	0.02 (0.09)	0.02 (0.10)	0.02 (0.13)	0.01 (0.07)	(0.04)	0.01 (0.05)	Woody, oily
74	Ethyl methyl succinate							

75	Acetophenone 4)/ethyl	0.94	0.89	0.74	1.16	1.76	1.19	Estery
	n-decanoate	(80.0)	(0.09)	(80.0)	(0.13)	(0.20)	(0.13)	
76	Furfuryl alcohol							Oily, olive oil
77	1-Nonanol/ethyl benzoate/ 2-methylbutyl n-octanoate/ 3-methylbutyl n-octanoate	0.01			0.01	0.01	0.01	Woody, aromatic
78	Diethyl succinate	0.07 (0.73)	0.09 (1.08)	0.09 (1.03)	0.07 (0.89)	0.11 (1.48)	0.05 (0.56)	Mild ester
79	α-Terpineol 4)/ethyl 9-decenoate	0.05 (0.004)	0.01 (0.001)	0.01 (0.002)	0.05 (0.005)	0.06 (0.006)	0.10 (0.011)	Harsh
80	1-Propyl n-decanoate							
· 81	Naphthalene							Fatty
82	1,1,6-Trimethyl-1,2- -dihydronaphthalene	(0.001)	(0.002)	(0.001)	(0.002)	(0.002)	(0.003)	Burnt, smokey
83	Unknown A/ethyl n-undecanoate 4)							Sweet
84	2-Methylpropyl n-decanoate/1-decanol							Coconut, fatty
85	Diethyl glutarate							
86	Ethyl phenylacetate							
87	Ethyl 2-methylpropyl succinate							
88	Unknown B							
89	2-Phenethyl acetate						0.01	
90	Damascenone							Geranium, raisin-like
		(0.066)	(0.066)	(0.130)	(0.130)	(0.130)	(0.170)	
91	Unknown C							
92	Unknown D							
						-		

Table 2 (continued)

Peak No. ²)	Component(s)	1976	1977	1978	1979	1980	1981	Aroma associated with peak(s) 3)
93	2-Methyl naphthalene				•			
94	Unknown E							
95	Ethyl n-dodecanoate	0.09 (0.009)	0.08 (0.00 <b>9</b> )	0.05 (0.006)	0.07 (0.007)	0.09 (0.012)	0.05 (0.007)	Fatty
96	Unknown F	0.02	0.01	0.02				
	Benzyl alcohol/2-methyl- butyl n-decanoate/ 3-methylbutyl n-decanoate						0.01	Woody
98	1-Methyl naphthalene							
99	cis-β-Methyl-γ-octalactone	(0.035)	(0.033)	(0.035)	(0.012)	(0.045)	(0.046)	Woody, coconut-like, fatty
00	Ethyl 3-methylbutyl succinate							
)1	2-Phenethanol	0.02 (1.77)	0.02 (3.08)	0.02 (3.22)	0.01 (1.86)	0.03 (3.66)	0.04 (4.91)	Coarse, harsh, fusel
02	5-Ethoxymethyl-2-furfural						0.01	
03	β-Ionone							Rose-like, pleasant
	<i>trans</i> -β-Methyl- γ-octalactone	(0.024)	(0.037)	(0.033)	(0.015)	(0.022)	(0.035)	Woody, fatty
05	1-Dodecanol							
)6	Ethyl n-tetradecanoate							

<sup>1)</sup> Expressed as % peak area of compounds eluting after 15.0 min; where no values are shown the peak area was less than 0.01 %; values shown in parenthesis are concentrations in wine of the main component(s) within the peak envelope (in mg/l); analysed June-July 1982.

 <sup>2)</sup> Refer to figure.
 3) See experimental section.
 4) Minor component(s) within the peak envelope.

# 4. Synthesis of ethyl 4-methylhexanoate

2,6-Dimethyl-2-octene, prepared from citronellal according to ESHINAZI (1961), was oxidised with periodate-permanganate to 4-methylhexanoic acid (VON RUDLOFF 1956). The corresponding ethyl ester was obtained by heating this compound together with redistilled absolute ethanol in the presence of a small quantity of sulphuric acid. The mass spectrum of ethyl 4-methylhexanoate recorded at 70 eV showed prominent ions above m/e 35 (%):

88 (100), 101 (98), 43 (79), 41 (68), 55 (60), 73 (42), 60 (38), 70 (34), 57 (33), 95 (31), 69 (27), 45 (25), 83 (25), 113 (25); also 129 (9). The van den Dool retention index (VAN DEN DOOL and Kratz 1963) on the SP1000 SCOT capillary column was  $I_E=664$ .

#### Results

# 1. Composition of Chardonnay wine

The Chardonnay wines from 6 successive vintages contained concentrations of ethanol indicative of fully ripe grape material (11.7—13.0 % v/v; Table 1); the younger wines had lower pH values, reflecting a slight change in winemaking technique. All wines contained little free SO<sub>2</sub> (3—8 mg/l) when analysed in June—July 1982. The concentration of L-malic, D-lactic and L-lactic acids (Table 1) indicated that a malolactic fermentation occurred strongly in the 1977, 1978 and 1980 wines, partially in the 1976 and 1981 wines and weakly, if at all, in the 1979 wine.

More than 140 compounds were identified in the Chardonnay wines (Table 2), most having previously been reported in grapes and wine (SCHREIER 1979, ETIEVANT and BAYONOVE 1983, SIMPSON and MILLER 1983). The differences between the Chardonnay wines were quantitative rather than qualitative.

The ethyl ester of a branched chain heptanoic acid found in relatively high concentrations in aged Riesling wine (SIMPSON and MILLER 1983) and also in Chardonnay wine (peak 37; Table 2) was shown on the basis of GC retention data and mass spectra recorded under similar conditions to be identical with ethyl 4-methylhexanoate obtained by synthesis. This compound had not been reported previously in wine.

# 2. Aroma assessment of Chardonnay juice and wine and flavour threshold determination

The components contributing most to the aroma of the 1982 Chardonnay juice as determined by sniff assessment of materials eluting from the SP1000 SCOT capillary column were linalool (floral aroma), damascenone (sweet, raisin-like),  $\beta$ -ionone (pleasant, rose-like) and  $\alpha$ -terpineol (apricot-like). These compounds were present at much higher concentrations (ca. 20—30  $\times$ ) in the juice than in the wines examined.

The aroma associated with each peak in the headspace chromatograms of the Chardonnay wines is described in Table 2. The more intense aromas throughout the chromatogram were assigned to specific peaks, however, sections of the chromatogram after the elution of ethyl n-decanoate (peak 75) and lacking definable peaks under the conditions employed, contained several very minor components having moderately intense "raisin-like" or "woody" aromas.

The flavour thresholds of damascenone and  $trans-\beta$ -methyl- $\gamma$ -octalactone in a non-aromatic dry white wine were found to be 0.05 and 0.10 mg/l, respectively.

#### Discussion

# 1. Composition of Chardonnay wine

Over 90 of the 140 components identified in the 1976—1981 Chardonnay wines are alcohols, acetals and esters; other major chemical groups include aldehydes and ketones (20 compounds), aromatic hydrocarbons (13), and monoterpene alcohols and oxides (9).

Many of the wine components are identifiable as juice components, as yeast and bacterial metabolites, and as products from oxidation reactions, wood extraction, carotenoid and carbohydrate degradation, esterification and acetalisation (Schreier 1979, Simpson and Miller 1983, P. J. Williams *et al.* 1980). The origin of components having special significance for the Chardonnay wine, i.e. those capable of influencing wine flavour or indicating grape cultivar or processing treatment, are now considered in more detail.

Wood maturation of the Chardonnay wine accounts for the presence of the oak lactones (*cis*- and *trans*-β-methyl-γ-octalactone, peaks 99 and 104, respectively; Table 2) which have been found in brandy, sherry, whisky (Οτsuka *et al.* 1974, Onishi *et al.* 1977) and port wine (Simpson 1980), all of which received wood treatment during processing.

Appreciable concentrations of hexanal (contained in peak 16), octanal (peak 36) and decanal (peak 60) were found, their formation by oxidation of the corresponding alcohol having been promoted during storage of the Chardonnay wine in new oak casks which are especially permeable to air (AMERINE et al. 1980).

Unknowns A, C-F (peaks 83, 91, 92, 94 and 96, respectively) are chemically similar as shown by their mass spectra: base peak at m/e 97 and major ions at m/e 41, 43, 55, 57, 71 and 167. The strong m/e 97 fragment suggests the presence of a furfuroxy grouping, implying that these compounds may be, or may be formed from, wood extractives. Further investigation of the nature of these compounds was not attempted because of the low concentration present and the negligible contribution to wine aroma.

Moderate to high levels of ethyl lactate were found in the Chardonnay wines due to esterification of lactic acid during storage and the influence of malolactic fermentation (Meunier and Bott 1979, Shinohara *et al.* 1979). Malolactic fermentation was encouraged in the wines, contrary to most white winemaking practice in Australia; the dominant bacteria were strains of *Leuconostoc oenos* (T. H. Lee, personal communication).

The Chardonnay wines contained few monoterpenes compared with those found in Muscat or Riesling wine (ETIEVANT et al. 1983, SIMPSON and MILLER 1983). Minor quantities of linalool (peak 66) and  $\alpha$ -terpineol (peak 79) and trace quantities of 2,6,6-trimethyl-2-vinyltetrahydropyran (peak 17), the 2,2-dimethyl-5-(1-methylpropenyl)tetrahydrofuran isomers (peaks 26 and 28), trans-anhydrolinalool oxide (peak 26) and nerol oxide (peak 57) were found in Chardonnay wine.

Minor quantities only of *trans*-vitispirane (peak 63), *cis*-vitispirane (peak 64), 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN, peak 82), unknown B (peak 88) — a compound initially found in aged Riesling wines and considered likely to be a dehydrovitispirane (SIMPSON and MILLER 1983) — were present in Chardonnay wine. Damascenone (peak 90) and  $\beta$ -ionone (peak 103) were found at low concentrations but, because of their intense aroma, can affect wine flavour (see below).

In common with the vitispiranes and TDN, both damascenone and  $\beta$ -ionone are  $C_{13}$  compounds presumed to be derived from carotenoid degradation (OHLOFF 1978 a). Acree *et al.* (1981) found up to ca 0.005 mg/l of damascenone in juice and wine from several cultivars of *Vitis labruscana*, rotundifolia and vinifera; Schreier and Drawert (1974) first reported the presence of  $\beta$ -ionone in wine whilst Masuda and Nishimura

(1980) found 0.01 mg/l of damascenone in a wine and 0.03—0.11 mg/l in grape brandies, and demonstrated that the concentration of damascenone was increased by heating.

The origin of ethyl 4-methylhexanoate in wine has not been determined but, on the basis of chemical structure, is probably formed via the corresponding acid from a carotenoid or monoterpenoid precursor.

## 2. Flavour considerations

AMERINE and ROESSLER (1976) described Chardonnay wine as "fig-, apple- or melon-like": they also indicated that, unlike the wine, the juice seldom has a distinctive

 ${\bf Table~3}$  Concentration and flavour threshold of some aroma components of Chardonnay wines Konzentration und Wahrnehmungsschwelle einiger Aromakomponenten von Chardonnay-Weinen

	Concentration	(mg/l)	Fla	Flavour threshold (mg/l)				
Component	Range	Mean	In water	In ethanol- water	In beer ¹)	In wine		
Dimethyl sulphide	0.0110.033	0.021	0.00008 2)		0.05	0.03 <sup>2</sup> )		
Ethyl n-butanoate	0.24-0.54	0.39			0.4			
2-Methyl-1-propanol	55—109	81		75 ³)	200			
3-Methylbutyl acetate	0.13-0.55 4)	0.23		$0.20^{3}$ )	1.6	1.0 5)		
3-Methyl-1-butanol	197—257 <sup>6</sup> )	240		$7.0^{3}$ )	70			
Ethyl n-hexanoate	0.350.71	0.51		0.25 ³)	0.23	0.08 7)		
Ethyl lactate	23—268	147		14 ³)	250	ca. 150 <sup>8</sup> )		
1-Hexanol	1.07—1.58	1.25		$5.2^{3}$ )	4.0			
Ethyl n-octanoate	0.36 - 0.67	0.49			0.9	0.58 7)		
Linalool	0.003-0.007	0.005	0.1 9)					
Ethyl n-decanoate	0.08-0.20	0.12			1.5	0.51 7)		
1,1,6-Trimethyl-1,2- -dihydronaphthalene	0.001—0.003	0.002				0.02 5)		
Damascenone	0.066—0.170	0.115	0.000009 10)	0.01 11)		$\begin{array}{c} 0.05 \\ 1.6 \end{array}$		
<i>cis</i> -β-Methyl-γ-octa- lactone	0.012—0.146	0.034		0.79 13)				
$\textit{trans}\text{-}\beta\text{-}Methyl\text{-}\gamma\text{-}octalactone$	0.015—0.037	0.028		0.067 13)		0.10		
Acetic acid	620—930 14)	760 14)	24 15)	26 ³)	175			

<sup>1)</sup> MEILGAARD (1975).

<sup>2)</sup> Spedding and Raur (1982).

<sup>3)</sup> In 9.4 % ethanol-water (SALO 1970).

<sup>4)</sup> Includes 2-methylbutyl acetate.

<sup>5)</sup> SIMPSON (1979 b).

<sup>6)</sup> Includes 2-methyl-1-butanol.

<sup>7)</sup> In aroma stripped, reconstituted wine (DE WET 1978).

<sup>8)</sup> Shinohara et al. (1979).

<sup>9)</sup> In sugar-water solution (RIBÉREAU-GAYON et al. 1975).

<sup>10)</sup> OHLOFF (1978 b).

<sup>11)</sup> In 40 % ethanol-water (Masuda and Nishimu-Ra 1980).

<sup>12)</sup> ETIEVANT et al. (1983).

<sup>&</sup>lt;sup>13</sup>) In 30 % ethanol-water (Otsuka *et al.* 1974).

<sup>14)</sup> Based on titratable acidity (Table 1).

<sup>15)</sup> Baker (1963).

aroma. The volatile components of fig (Jennings 1977, Buttery et al. 1981), apple (Schreier et al. 1978, A. A. Williams et al. 1980), muskmelon and watermelon (Kemp et al. 1971, 1972, 1973, 1974, Kemp 1975, Yabumoto and Jennings 1977) are complex and include many of the compounds found in wine; it is, however, likely that the balance of alcohols, esters, aldehydes and ketones in Chardonnay wine contributes to a likeness to specific fruits.

Despite the large number of components identified in the Chardonnay wines, few — mainly fermentation esters and alcohols — are important to aroma (Table 3).

The ethyl esters of the  $C_4$ — $C_{12}$  fatty acids, based on their concentration in the Chardonnay wines and their flavour thresholds (Table 3), are important contributors to aroma: the flavour threshold of ethyl n-hexanoate was exceeded in all wines and the quantities of ethyl n-butanoate, ethyl n-octanoate and ethyl n-decanoate can be expected to enhance the "estery" and "wine-like" aroma attributable to this chemical group (SIMPSON 1979 b).

The 1978 and 1980 wines contain concentrations of ethyl lactate slightly higher than the threshold value of 250 mg/l reported for beer (MEILGAARD 1975); SHINOHARA et al. (1979) estimated the threshold in wine to be about 150 mg/l and indicated that this compound was an important flavour component in some of the wines that they analysed. From our observations made during GC-sniff assessments, ethyl lactate has a low aroma intensity, and contributes little to the overall aroma of the Chardonnay wine.

The combined concentration of 2-methyl-1-butanol and 3-methyl-1-butanol exceeds the threshold for the latter compound in all wines. Other fusel alcohols including 2-methyl-1-propanol, and 1-hexanol, also make contributions to wine flavour. Although these compounds in isolation have harsh and unpleasant aromas, they are responsible for an integral part of wine flavour (AMERINE et al. 1980).

The concentration of acetic acid, based on volatile acidity (Table 1), exceeds its flavour threshold in all wines. Consequently, acetic acid is a contributor to the flavour of the wines.

The quantity of damascenone in all 6 Chardonnay wines exceeded the flavour threshold of 0.05 mg/l, determined in a non-aromatic white wine containing moderately low free SO<sub>2</sub> content. In the presence of SO<sub>2</sub>, damascenone should form a bisulphite addition compound, reducing its effective concentration and aroma intensity (SCHREIER and DRAWERT 1974). These factors and the wine medium may account for the difference in flavour threshold reported by ETIEVANT et al. (1983) and in the present work.

 $\beta$ -Ionone was present in the Chardonnay wines at a concentration much lower than that of damascenone; assuming a similar flavour threshold to that of damascenone (Ohloff 1978 b),  $\beta$ -ionone should be correspondingly less important to wine aroma.

The hydrocarbon TDN has negligible influence on the aroma of the Chardonnay wine; as indicated earlier (SIMPSON and MILLER 1983), wines made from many grape cultivars have little potential to produce TDN during long-term ageing.

The oak lactones and minor components found to have "woody" aromas during GC-sniff assessment, account at least in part for the "woody" flavour of the Chardonnay wines.

## Summary

The headspace aroma volatiles of Chardonnay wines from 6 consecutive vintages were analysed by capillary gas chromatography and gas chromatography-mass spec-

trometry, some 150 compounds were identified. The contribution to aroma of the components of the headspace collection was determined by sniffing the column effluent following gas chromatographic separation. The major fermentation alcohols and esters, acetic acid and damascenone were important aroma compounds of the Chardonnay wines.

# Acknowledgements

The authors appreciate the co-operation of Tyrrell's Vineyards Pty Ltd, Pokolbin, NSW 2321 for supplying the juice and wines for analysis and of Naarden (Australia) Ltd, Birrong, NSW 2143 for donating a generous sample of citronellal.

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Eingegangen am 11. 11. 1983

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