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## Wine Headspace Analysis. Reproducibility and Application to Varietal Classification

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Wine headspace (HS) volatiles were collected by displacement and analyzed by gas chromatography (GC), GC-MS, and sensory evaluation of the split GC effluent. Over 77% of the peak areas quantified in triplicate had coefficients of variation <0.10. Nineteen peaks were selected for principal component analysis (PCA) and stepwise discriminant analysis (SDA). The first principal component (PC 1), although accounting for only 38% of the variance, separated 10 of the 11 White Riesling wines (R) from the nine Chardonnays (C) and four French Colombards (F). Weighted >0.50 on PC 1 were eight components, some of which had fruity, floral descriptions, consistent with the aroma of R. Weighted <-0.50 on PC 1 were three "fruity" esters, also consistent with the characteristic aromas of C and F. Interestingly, linalool, often thought to be important in R, was not weighted heavily on PC 1. By SDA, the 24 wines were sorted successfully into three varietal categories by discriminant functions using five components.

To distinguish among grape varieties, multivariate statistical techniques, including discriminant and cluster analyses, have been successfully applied to volatile composition, obtained by solvent extraction (Schreier et al., 1976; Rapp and Hastrich, 1978; Rapp et al., 1978), to trace element composition (Siegmund and Bachmann, 1978), and to a combination of compositional data including elemental composition, alcohols, and total acidity (Kwan and Kowalski, 1978). However, to investigate the important differences in the aromas of wines from different grape varieties, it is more appropriate to analyze the volatiles in the headspace at equilibrium concentrations and, further, to concentrate upon those components which are of sensory significance.

To evaluate the quantitative differences in volatile composition among wines, the technique of headspace analysis by displacement has been used by several workers (Bertuccioli and Montedoro, 1974, 1975; Bertuccioli and Viani, 1976; Coope, 1977; Noble, 1978). Sensory analysis of gas chromatographic effluent (GC-sniff) has been used by several investigators to evaluate the "aroma significance" of separated components in coffee (Tassan and Russell, 1974), bilberries (Von Sydow et al., 1970), peaches (Spencer et al., 1978), and wine (Noble, 1978; Rapp et al., 1978).

Although the volatiles of White Riesling have been studied extensively by extraction procedures (Van Wyck et al., 1967a,b,c; Shreier and Drawert, 1974, 1976; Schreier et al., 1974, 1975, 1977), no volatile investigations of

Table I. Description of Wines Evaluated

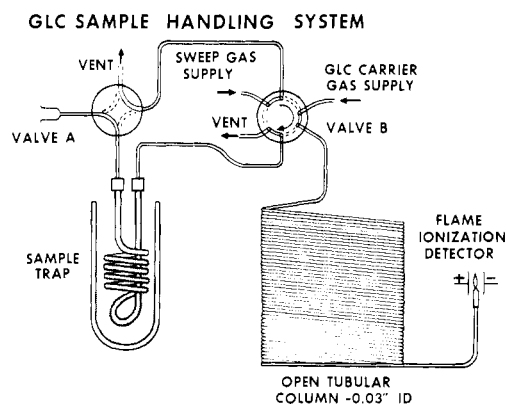
grape variety	code	vintage year	grape source <sup>a</sup> (county)	producer <sup>b</sup>
White Riesling	1	73	Santa Barbara	UC
	2	74	Butte	UC
	3	74	Napa <sup>c</sup>	UC
	4	74	Napa <sup>c</sup>	UC
	5	74	Sonoma <sup>d</sup>	UC
	6	74	Sonoma <sup>d</sup>	UC
	7	75	Napa <sup>e</sup>	UC
	8	75	Napa <sup>e</sup>	UC
	9	74	Napa	Comm
	10	74	Napa	Comm
	11	73	Napa	Comm
Chardonnay	12	73	Alameda	UC
	13	75	Alameda <sup>f</sup>	UC
	14	75	Alameda <sup>f</sup>	UC
	15	75	Napa	UC
	16	75	Napa <sup>g</sup>	UC
	17	75	Napa <sup>g</sup>	UC
	18	73	Salinas	UC
	19	73	Salinas	Comm
	20	75	Sonoma	UC
French Colombard	21	73	Mendocino	Comm
	22	74	Solano	UC
	23	nonvintage	Fresno	Comm
	24	75	Colusa	UC

<sup>a</sup> Wines made from the same vineyard have a common superscript. <sup>b</sup> UC = University of California, David Winery; Comm = commercial.

Chardonnay and French Colombard wines have been reported.

In this study, headspace volatiles of wine of three *Vitis vinifera* grape varieties, White Riesling, Chardonnay, and French Colombard, were analyzed by conventional gas chromatography [GC(FID)], by gas chromatography-mass

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**Figure 1.** System for direct transfer of volatiles to the GC column for splitless injection.

spectrometry (GC-MS), and by GC-sniff. The reproducibility of the technique and interpretation of the analysis of the volatiles will be discussed.

#### EXPERIMENTAL SECTION

**Wines.** Twenty-four California wines were analyzed in triplicate. Details about the 11 White Rieslings, nine chardonnays, and four French Colombards are shown in Table I.

**Isolation of Volatiles.** Headspace volatiles were sampled by displacement using a glass and Teflon 1-L syringe with a mechanized variable speed drive. One-hundred and thirty-five milliliters was placed in the syringe and air expelled, and nitrogen was used to back flush the syringe. After 20 min of equilibration, an adsorbent trap containing 240 mg of Tenax GC (2,6-diphenyl-*p*-phenylene oxide) was attached to the syringe exit port and 500 mL of headspace collected at a rate of 21 mL/min at room temperature ( $23 \pm 2^\circ\text{C}$ ). The Tenax GC trap was then removed from the syringe, and purified helium passed through at 50 mL/min for 25 min to remove ethanol and water. The trap was then attached to the heated switching box outlined in Figure 1, which was similar to that described by Flath et al. (1972). The Tenax GC trap was heated to  $115^\circ\text{C}$  with an aluminum heating block and the wine volatiles flushed from the trap for 30 min with helium at 50 mL/min into and 0.04 in i.d. stainless steel concentrator coil, chilled in dry ice/ethanol. The sample was then flashed onto the gas chromatograph column by appropriately switching the valves and heating the concentrator coil with a heat gun at  $250^\circ\text{C}$  for 45 s.

**Gas Chromatography.** A Hewlett/Packard 5831A GC was used. The flow controllers and the molecular sieve traps on the instrument were bypassed and the flow control achieved using a restrictor system. The carrier gas was saturated with water vapor. The column was a 213.5 m  $\times$  0.75 mm i.d. stainless steel open tubular column coated with methyl silicone oil (SF-96-50) with 5% by weight Igepal CO-880. Column temperature was programmed from 25 to  $50^\circ\text{C}$  at  $5^\circ\text{C}/\text{min}$ , then at  $1^\circ\text{C}/\text{min}$  to  $175^\circ\text{C}$ , and held isothermally for 50 min. The Hewlett/Packard 18850A GC terminal provided a tracing of the chromatograph, retention times, and peak areas.

**Gas Chromatography-Mass Spectrometry (GC-MS).** Volatiles were collected in the manner described previously, with the exception that 270 mL of wine was used. After 700 mL of headspace were collected, the syringe was filled with nitrogen and 700 mL more of headspace collected. The procedure was repeated until 4200 mL was collected. Volatiles were transferred to the concentrator as previously described. A 305 m  $\times$  0.75 mm i.d. stainless steel column with the same liquid phase

coating as that described previously was used for the GC-MS analysis. The GC was programmed isothermally at  $50^\circ\text{C}$  for 20 min, then at  $1^\circ\text{C}/\text{min}$  to  $175^\circ\text{C}$ , and held isothermally for the rest of the run.

A unit resolution quadrupole mass spectrometer (MS), consisting of a modified Beckman Thermotrac temperature programming oven with the vapor analysis valving system attached, was used for the GC-MS. The MS was an Electronic Associates mass filter with Finnigan Corporation electronics. The separator interface was a methyl silicone membrane, similar to that described by Forrey and Flath (1974). An ion energy of 70 eV and scan time of 1 s were used.

**Identification and Quantification.** Tentative identification of compounds was made by comparing mass spectral patterns of the unknowns (determined for each varietal) with those of authentic components. Confirmed identification was made by co-injection of known compounds with the wine vapor for retention time comparison. Approximate concentration of the compounds was calculated from the detector response to liquid injections of ethyl hexanoate. A linear response to different classes of compounds was assumed in calculating results.

**Sensory Analysis of GC Effluent (GC-Sniff).** Volatiles from 1400 mL of headspace were collected as described for GC-MS. The volatiles were transferred to the Hewlett/Packard 5831A and separated as described previously. The effluent was split 1:1 and the aromas of the eluting components sniffed by two individuals. Descriptions and relative intensity ratings on a 0 (no odor) to 9 (intense odor) scale were recorded on the GC trace. Three White Rieslings and two Chardonnays were analyzed by this procedure. Sensorially significant components were selected by retaining only those peaks which had intensity ratings of 2 or higher and which were described in at least two wines.

**Statistical Analyses.** To evaluate the reproducibility of the technique, coefficients of variation were calculated for retention times and peak areas across the triplicate analyses of each wine. For further analysis, the number of peaks selected as sensorially significant was reduced to 27 (Data Set I) by eliminating peaks which were not reproducibly resolved or detected. From these 27 peaks, eight were removed which either highly correlated with other components ( $r > 0.90$ ) or were present at concentrations 50-100 times the remaining 19 peaks (Data Set II).

Principal component analysis (PCA) was performed using the correlation matrix of the sensorially significant GC peaks to derive relationships among the compounds and make preliminary deductions regarding the importance of the different compounds. BMD-P4M (Dixon and Brown, 1977) was used with no rotation.

Stepwise discriminant analysis (SDA) was performed to classify the wines into the three varietal categories, using the discriminant analysis program BMD-07M (Dixon, 1973). Mean concentrations (ppb) of the sensorially significant GC peaks were used as variables without standardization for both SDA and PCA. Further descriptions of PCA and SDA are provided by Thorndike (1978) and Broschat (1979).

#### RESULTS AND DISCUSSION

Representative chromatograms of White Riesling (R), Chardonnay (C), and French Colombard (F) wines are shown in Figure 2. The numbers of the peaks refer to the peak codes used throughout this paper. Sixty compounds were identified, as listed in Table II. With the exception of peak 61, tentatively identified as 2,2-dimethyl-6-

Table II. Identification of Compounds in Headspace of White Riesling, Chardonnay, and French Colombard Wines

peak no.	compound	wine variety in which identity confirmed <sup>a</sup>		
		White Riesling	Chardonnay	French Colombard
1	acetaldehyde		x	
3	ethanol	x	x	x
6	vinyl acetate	x		
7	1-propanol	x		
8	ethyl acetate	x	x	x
10	3-methyl-1-butanol	x		
11	2-methyl-1-propanol	x	x	x
13	1-butanol	x		
14	ethyl propanoate	x	x	x
15	1-propyl acetate	x	x	x
16	2,4,5-trimethyl-1,3-dioxolane	x		x
18	1,1-diethoxyethane	x	x	x
20	ethyl 2-methylpropanoate	x	x	x
21	3-methyl-1-butanol	x	x	x
22	2-methyl-1-butanol	x	x	x
23	2-methyl-1-propyl acetate	x	x	x
24	diethyl carbonate	x	x	
25	1-pentanol	x	x	
26	hexanal	x		
27	ethyl butyrate	x	x	x
29	butyl acetate	x		x
33	ethyl crotonate	x	x	x
34	ethyl lactate	x	x	x
35	ethyl 2-methylbutyrate	x	x	x
36	ethyl-3-methylbutyrate	x	x	x
37	ethylbenzene	x	x	
39	furfural	x	x	
40	3-methylbutyl acetate	x	x	x
41	2-methylbutyl acetate	x	x	x
42	cyclooctatetraene	x	x	x
45	hexanol	x	x	
46	ethyl pentanoate	x	x	
49	pentyl acetate	x		x
50	methyl hexanoate	x	x	
53	$\gamma$ -butyrolactone	x		
56	5-methyl-2-furfural	x	x	
57	benzaldehyde	x		
61	2,2-dimethyl-6-methyl-6-vinyl tetrahydropyran	x <sup>b</sup>		
65	ethyl hexanoate	x	x	x
66	hexyl acetate	x	x	x
68	$\Delta^3$ -carene	x	x	
71	<i>p</i> -cymene	x		
72	limonene	x	x	
77	$\gamma$ -terpinene	x	x	
83	ethyl heptanoate	x	x	x
84	nonanal	x		
85A	linalool	x		
87	methyl octanoate	x	x	x
92	2-phenylethanol	x	x	
93	diethyl succinate	x	x	x
94	naphthalene		x	
95	butyl hexanoate	x	x	
96	ethyl octanoate	x	x	x
101	$\beta$ -phenylethyl acetate	x	x	
102	3-methylbutyl hexanoate	x		
107	vitaspirane	x <sup>b</sup>	x <sup>b</sup>	
111	methyl dodecanoate	x	x	
113	trimethyldihydronaphthalene	x <sup>b</sup>	x <sup>b</sup>	
116	ethyl decanoate	x	x	x
120	ethyl dodecanoate	x	x	

<sup>a</sup> Compounds were identified by correspondence of GC retention times and MS pattern with those of authentic compounds, except where noted. <sup>b</sup> Tentative identification by comparison of MS only.

methyl-6-vinyltetrahydropyran, most of the compounds have been previously reported in wines.

Reproducibility of retention times across triplicate analyses was excellent as shown by the small coefficients of variation (CV) for White Riesling 1 in Table III. These CV are representative of the reproducibility among and within the rest of the wines. Despite the highly reproducible retention time data, peaks in the region 59–62 in

Chardonnay headspaces did not correspond to those in the French Colombard and White Riesling wines. Of these small peaks, none were identified with the exception of peak 61 in White Riesling.

Reproducibility of peak area determinations was similar in all wines as well and is illustrated again by the results for White Riesling 1 (Table III). Peak area CV's were less than 0.10 for 77% of the peaks reported, which is better

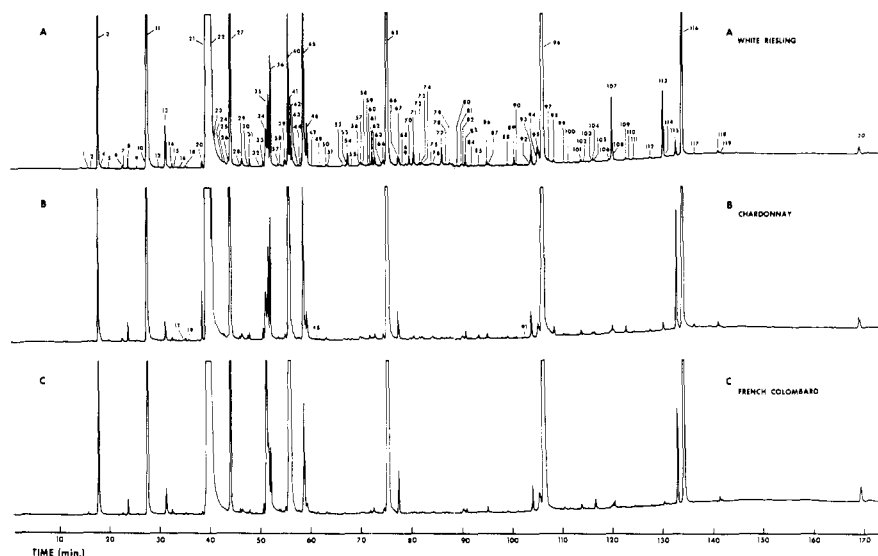


Figure 2. Representative varietal wine headspace profiles of White Riesling (A), Chardonnay (B), and French Colombard (C).

Table III. Representative Reproducibility of Retention Times and Peak Areas. Means ( $\bar{X}$ ) and Coefficients of Variation (CV) for White Riesling 1 ( $n = 3$ )

peak no. <sup>a</sup>	retention time, min		peak areas		peak no. <sup>a</sup>	retention time, min		peak areas	
	$\bar{X}$	CV	$\bar{X}^b$	CV <sup>c</sup>		$\bar{X}$	CV	$\bar{X}^b$	CV <sup>c</sup>
2	16.44	0.005	292		65	75.39	0.010	1254666	0.021
3/4	17.84	0.004	154467	0.078	66/67	77.61	0.009	10152	0.070
6/7	22.79	0.003	2073	0.300	68	78.27	0.009	220	
8	23.88	0.003	17318	0.508	69	79.11	0.009	1297	0.054
9	25.63	0.003	732	0.021	70	79.83	0.001	7269	0.043
11	27.63	0.003	961800	0.082	71	80.74	0.011	14430	0.033
12	30.03	0.003	955	0.516	72	81.81	0.009	1816	0.058
13	31.41	0.002	34333	0.060	73/74	82.26	0.001	3576	0.114
14	32.71	0.003	5199	0.376	76	84.26	0.009	1805	0.653
18	35.40	0.009	2088	0.195	77	86.24	0.009	14140	0.048
20	38.65	0.003	16073	0.590	78	87.14	0.009	992	0.682
21/22	39.99	0.002	12830000	0.029	79	87.89	0.001	620	0.036
25	43.15	0.012			81	90.22	0.001	1326	0.385
26/27	44.26	0.012	440833	0.058	83	91.01	0.008	8769	0.057
28	46.20	0.012	575	0.137	84	92.08	0.008	740	0.206
29	46.62	0.012	8185	0.059	85	93.54	0.001	265	
30	47.79	0.012	597	0.039	86	95.28	0.008	4266	0.009
31	48.15	0.012	5195	0.028	87	95.59	0.001	1509	0.056
32	50.20	0.012	318	0.146	88	99.32	0.008	772	0.045
33	50.81	0.012	4339	0.054	89	100.69	0.001	6469	0.029
34	51.38	0.011	40260	0.038	90	101.13	0.008	1615	0.027
35	51.80	0.012	57370	0.037	92/93	104.11	0.001	18470	0.105
36	52.24	0.012	78387	0.025	94/95	105.43	0.008	40680	0.394
37	53.82	0.011	2987	0.052	96	106.35	0.008	2154667	0.010
39	55.18	0.012	6442	0.051	101	114.02	0.001	2166	0.015
40	55.80	0.011	148333	0.031	102	114.52	0.001	257	
41	56.18	0.011	22380	0.021	103	116.16	0.008	1477	0.012
42	56.54	0.011	14767	0.290	104	116.44	0.001	5225	0.140
43	57.76	0.011	1216	0.060	105	116.70	0.001		
45	58.78	0.002	190600	0.040	106	119.68	0.008	871	0.274
46	59.53	0.002	36360	0.017	107/108	120.24	0.001	53380	0.009
49	61.98	0.010			109	123.02	0.007	1675	0.045
50	63.37	0.002	1842	0.040	110	123.55	0.007	582	0.166
54	67.66	0.010	9163	0.032	111	124.58	0.007	756	0.019
56/57	70.18	0.010	4310	0.228	112	127.83	0.007	1127	0.053
59	71.58	0.010	498	0.014	113/114	130.41	0.007	49217	0.034
60	72.00	0.001	766	0.200	115	133.00	0.007	11823	0.033
61	72.43	0.002	9975	0.022	116	134.21	0.007	424633	0.027
62	72.99	0.010	8265	0.030	118	141.38	0.007	2850	0.034
63/64	74.64	0.010	4872	0.061	120	169.25	0.001	10752	0.058

<sup>a</sup> Peaks not listed were absent. <sup>b</sup> Blanks indicate retention time noted, but no peak area printed. <sup>c</sup> Blank indicates peak quantified in only one wine.

than that reported for wine HS analysis (Noble et al., 1979) in which triplicate analyses were performed on three different bottles. The apparently greater precision of this analysis is attributable primarily to elimination of bottle

to bottle variability. CV's of large peaks, such as peak 65, ethyl hexanoate, and peak 96, ethyl octanoate, ranged between 0.019 and 0.090, which is comparable to the level of reproducibility reported by Stenroos et al. (1976) for

Table IV. Concentration Means and Ranges (ppb) of Volatiles for Each Variety

peak no.	White Riesling ( <i>n</i> = 11)		Chardonnay ( <i>n</i> = 9)		French Colombard ( <i>n</i> = 4)	
	range	mean	range	mean	range	mean
1	0-0.0025	0.0012	0-0.0028	0.0010	0.0012-0.011	0.0044
2	0-0.0010	0.00045	0-0.00082	0.00032	0.00024-0.0013	0.00074
3/4	0.27-0.79	0.44	0.28-0.57	0.43	0.37-0.40	0.38
5	0-0.0026	0.0013	0-0.0011	0.00033	0-0.0020	0.00051
6/7	0.00018-0.0067	0.0031	0.0022-0.0055	0.0037	0.0026-0.0062	0.0049
8	0.021-0.041	0.029	0.019-0.087	0.033	0.024-0.074	0.039
9	0.00018-0.0026	0.0014	0-0.0013	0.00053	0-0.0012	0.00082
10	0-0.0017	0.00026	0-0.0011	0.00030	0-0.0014	0.00034
11	0.60-2.30	0.19	0.82-2.03	1.26	0.72-1.46	1.03
12	0-0.0023	0.00021				
13	0.025-0.082	0.044	0.027-0.073	0.043	0.039-0.074	0.059
14	0.0037-0.018	0.010	0.0046-0.019	0.010	0.0075-0.012	0.0090
15	0-0.0012	0.00032	0.00084-0.0057	0.0031	0.00076-0.014	0.0062
17	0-0.00073	0.00018	0-0.0041	0.0016	0.00043-0.0027	0.0011
18	0.00047-0.016	0.0062	0.0030-0.021	0.012	0.00076-0.022	0.0075
19	0-0.0012	0.00015	0-0.0020	0.00066	0-0.0077	0.0047
20	0.0027-0.044	0.018	0-0.090	0.039	0-0.058	0.031
21/25	21.4-61.3	41.2	0.83-54.5	32.2	23.4-31.8	28.1
26/27	0.20-1.70	0.77	0.60-2.13	1.33	1.05-1.54	1.30
28	0.00016-0.013	0.0026	0.0014-0.028	0.011	0.0028-0.048	0.015
29	0.0037-0.020	0.0084	0.0043-0.022	0.0091	0.0034-0.0083	0.0054
30	0-0.0014	0.00021	0-0.0066	0.0028	0-0.0029	0.0015
31	0.0021-0.035	0.011	0.0014-0.0099	0.0043	0.0022-0.0098	0.0054
32	0-0.0012	0.00036				
33	0.0013-0.021	0.0054	0.0027-0.024	0.014	0.014-0.021	0.017
34	0.025-0.096	0.049	0.019-0.13	0.055	0-0.67	0.081
35	0.068-0.49	0.23	0.045-0.21	0.12	0.059-0.17	0.11
37	0.0028-0.019	0.010	0.0031-0.019	0.0094	0.0044-0.026	0.011
38	0.00061-0.016	0.0073	0-0.0054	0.0022	0.0012-0.033	0.013
39	0.0071-0.040	0.025	0-0.034	0.016	0-0.018	0.0078
40	0.35-8.81	2.40	1.00-27.8	14.8	2.94-40.09	14.12
41	0.011-0.29	0.16	0.11-1.37	0.79	0.20-0.48	0.32
42	0.0090-0.042	0.024	0.029-0.061	0.041	0-0.016	0.0052
43	0-0.0050	0.0024	0.0021-0.0074	0.0045	0.00045-0.0081	0.0042
44	0-0.0019	0.00050	0.0019-0.0078	0.0039	0-0.014	0.0053
45	0.24-0.64	0.38	0.29-0.83	0.45	0.060-0.139	0.26
46	0.022-0.087	0.040	0.030-0.078	0.052	0.020-0.045	0.031
47	0-0.0023	0.00038			0-0.0011	0.00035
48	0-0.0063	0.0011	0.00057-0.011	0.0049	0.0015-0.026	0.0081
49			0-0.00084	0.00013		
50	0.0016-0.0059	0.0033	0.0019-0.0047	0.0035	0.0026-0.0062	0.0038
51	0-0.0042	0.00040	0-0.00096	0.00011	0-0.0037	0.00092
52	0-0.00081	0.00020	0-0.00090	0.00026	0-0.00093	0.00023
53			0-0.0013	0.00015		
54	0-0.038	0.013	0-0.00042	0.000050	0-0.00034	0.000085
55	0-0.00067	0.00006	0-0.0018	0.00037	0-0.00081	0.00020
56/57	0.00080-0.011	0.0060	0.0041-0.015	0.0067	0.0017-0.011	0.0070
58	0.00080-0.0085	0.0032	0.0023-0.021	0.0070	0-0.0057	0.0032
59	0-0.014	0.0036			0-0.0064	0.0021
59A			0.0026-0.031	0.020		
60	0-0.0041	0.0030			0.0022-0.036	0.011
61	0.0033-0.064	0.025			0.0036-0.058	0.019
61A			0.0026-0.054	0.032		
62	0-0.020	0.0056			0-0.0082	0.0037
63/64	0.0052-0.015	0.010	0.0057-0.016	0.010	0-0.011	0.0059
65	1.98-4.16	3.39	2.19-6.39	4.83	3.30-6.20	5.24
66/67	0.024-0.50	0.15	0.020-2.72	0.97	0.072-1.57	0.59
68					0-0.00041	0.00010
69	0-0.0031	0.00061			0-0.00040	0.00010
70	0.0027-0.023	0.0093	0-0.0036	0.00050	0-0.0076	0.0024
71	0.0045-0.035	0.014	0-0.0068	0.0026	0-0.0038	0.0024
72	0.0029-0.030	0.011	0.00084-0.0054	0.0026	0.00043-0.021	0.0058
73/74	0.0048-0.018	0.010	0.016-0.010	0.0057	0.0019-0.0056	0.0035
75	0-0.018	0.0055	0-0.0032	0.0012		
76	0.0018-0.023	0.0069	0.0013-0.0047	0.0031	0.0016-0.0047	0.0031
77	0.0057-0.035	0.015	0-0.0057	0.0011	0-0.0049	0.0021
78	0-0.0072	0.0029	0-0.0012	0.00036	0-0.0019	0.00089
79	0-0.0024	0.00062	0-0.0017	0.00030	0-0.0012	0.00029
80	0-0.0020	0.00039	0-0.00068	0.000080	0-0.00035	0.000090
81/82	0.0031-0.012	0.0058	0.0034-0.013	0.0074	0.0030-0.014	0.010
83	0.0096-0.048	0.024	0.0036-0.016	0.0096	0.0043-0.0068	0.0053
84	0-0.037	0.00068	0-0.0013	0.00052	0-0.00051	0.00017
85	0-0.00077	0.00011	0-0.014	0.0048		
85A	0-0.029	0.0078	0-0.0056	0.0018		
86	0.0041-0.011	0.0075	0.0032-0.0094	0.0076	0.0057-0.0097	0.0077

Table IV (Continued)

87	0-0.0052	0.0030				
88	0-0.0049	0.0012	0.00078-0.0079	0.0027	0.00074-0.0018	0.0011
89	0-0.023	0.0087				
90	0-0.0039	0.0013	0-0.0036	0.00064	0-0.00096	0.00069
92/93	0.022-0.084	0.052	0.020-0.069	0.035	0.0015-0.039	0.025
94/95	0.033-0.14	0.092	0.037-0.076	0.058	0-0.067	0.044
96	3.53-7.95	5.83	2.70-12.4	8.58	5.00-11.3	9.12
97	0-0.011	0.0022	0-0.0018	0.00039		
98	0-0.0049	0.0022	0-0.015	0.0042		
99	0-0.0073	0.0018	0-0.0038	0.0025	0-0.0050	0.0023
100	0.0011-0.0040	0.0024	0.00072-0.0039	0.0015	0-0.0051	0.0020
101	0.0052-0.014	0.0083	0.0065-0.015	0.010	0.0032-0.012	0.0088
102	0-0.0033	0.0019	0-0.0036	0.0021	0-0.0023	0.0017
103	0-0.015	0.0024	0-0.0032	0.0043		
104/105	0.013-0.039	0.024	0.0028-0.051	0.026	0-0.056	0.022
106	0.00069-0.017	0.0067	0.00025-0.0027	0.0013	0-0.0087	0.0032
107/108	0.006-0.32	0.11	0.0032-0.018	0.0081	0.0049-0.031	0.015
109	0-0.0040	0.00036	0-0.011	0.0016		
110	0-0.0025	0.0016				
111	0-0.0020	0.0013	0-0.0024	0.0018	0-0.0018	0.0010
112	0-0.0027	0.0014	0-0.0074	0.0027	0-0.0024	0.0016
113/114	0.0036-0.39	0.13	0-0.051	0.0093	0-0.018	0.0086
115	0.021-3.16	0.36	0.0021-0.058	0.17	0.0047-0.17	0.061
116	0.91-1.72	1.26	0.39-3.22	2.05	0.51-2.11	1.63
117	0-0.0015	0.00013	0-0.0054	0.00093		
118	0.0042-0.017	0.0097	0.0050-0.022	0.013	0.0012-0.015	0.0095
119	0-0.0033	0.0015	0-0.0046	0.0024	0-0.0027	0.0019
120	0.0093-0.067	0.034	0.015-0.10	0.071	0.010-0.037	0.027

beer volatile extract analysis. Small peaks, however, tended to have poorer reproducibility which most often could be attributed to variation in the point at which integrations begin and end.

The mean and range in concentration in ppb for each volatile within each variety are shown in Table IV. Peak means from triplicate analyses of each wine are described in supplementary material. In Table V, a summary of the description of the exit port evaluations is provided. Sensorially significant peaks used in Data Set I ( $n = 27$ ) and II ( $n = 19$ ) are noted. Of the total volatiles quantified, over 90% are produced by five volatiles: 3-methyl-1-butanol, 2-methyl-1-butanol, ethyl hexanoate, ethyl octanoate, and ethyl decanoate. All of these, with the exception of the last, were rated as producing an intense aroma. Not unexpectedly, several very small components elicited medium to high intensity ratings, with only three peaks described in wine related terms. Often, variations in component concentrations within a wine variety were as great as among variety, although exceptions are apparent. Five components were detected only in White Riesling, three were unique to Chardonnay, and one to French Colombard. Ethyl esters were consistently higher in Chardonnay and French Colombard than in White Riesling.

In principal component analyses of 27 GC peaks (Data Set I) or 19 peaks (Data Set II), the first principal component separated White Riesling from Chardonnay and French Colombard, although it only accounted for 37.5 and 38.0% of the variance, respectively. In Figure 3, the factor loadings are plotted for Data Set II; in Figure 4 the factor scores are shown for each wine for principal components I and II, which together account for 52.2% variation. With the exception of wine 2, White Riesling wines have higher factor I scores than the other two varieties. That this PCA has any relationship to the wine aromas can be verified by the proximity of wines made from the same vineyard (3, 4; 5, 6; 7, 8; 13, 14; and 16, 17; see Table I).

Peaks 36, 73, 78, 87, 89, 92, 107, and 113 had factor loadings  $>0.50$  on factor I and are found in higher amounts in White Riesling than Chardonnay or French Colombard. Some exhibited spicy, floral characteristics which are

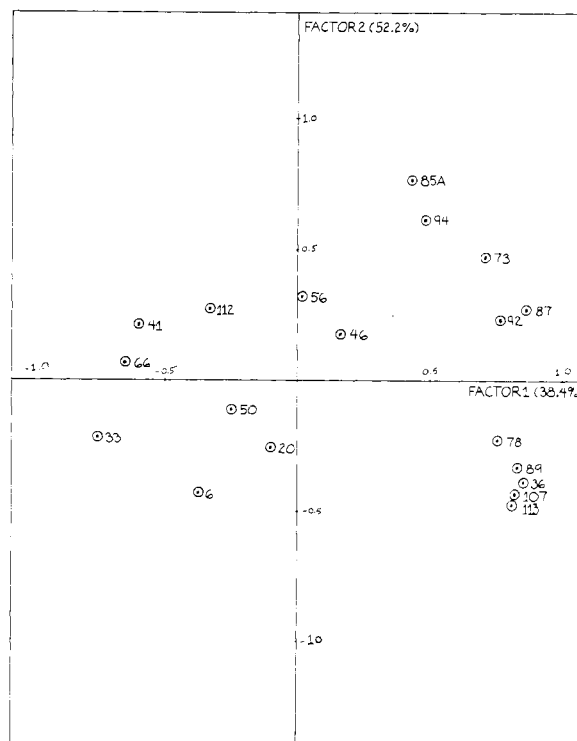


Figure 3. Principal component analysis of 19 wine volatiles. Factor loadings for GC peaks for principal components I and II.

consistent with the aroma of Riesling. Peaks 107 and 113, tentatively identified as Vitaspirane and trimethyl-dihydronaphthalene, have been suggested to contribute to the aromas of "older" Riesling wines (Simpson, 1977, 1978; Simpson et al., 1977). Although linalool is very often thought to be an important component in White Riesling aroma, it does not contribute heavily to the first axis, but is highly loaded on the second factor, which partitions the wines in an uninterpretable dimension. Further, two wines, which had distinct floral "Riesling" aromas (2 and 11), had no detectable linalool.

Strongly negatively loaded ( $<-0.50$ ) on the first principal component are peaks 33, 41, and 66, all of which are de-

Table V. Summary of Descriptors Used in Sensory Evaluation of GC Effluents of Wines 1, 4, 11, 12, 13<sup>a</sup>

peak no. <sup>b</sup>	descriptor	intensity rating <sup>c</sup>
6*	butterscotch	3-6
13	chemical, alcohol	2-3
20*	fruity, ester	2-3
21-25	fusel oil, organic lab	9
26/27**	cherry, ester	4-6
29	faint kool-aid	1
33*	citrus, pungent	2-3
34**	fruity	1
35**	apple, fruity	2-3
36*	apple, fruity	6-7
40**	banana, fruity	7-9
41*	banana, fruity	2-3
44	damp cellar, fruity	1
45**	grassy, chemical	1
46*	fruity	2-3
50*	fruity, cooked	2
51	hash brown potatoes	3-5
56/57*	piney	1
	fruity	3
59	mercaptan	1
61	baked bread	2
62	onion, garlic, sulfur	2-3
63/64	mushrooms	1-2
65**	fruity, ester, "heavy"	7-8
66*	fruity, grassy	3
72	terpene, pine, floral	1-2
73/74*	spicy, floral	2-3
75	potato chips	2
76	potato chips, dried vegetables	2
77	popcorn, mushroom	1
78*	fruity, ester	2
85	floral	1
85A*	floral, linalool	1-3
86	fruity	1
87*	fruity	2-3
89*	baked bread, dried vegetables	1-3
92/93*	fruity, floral, grassy	2-4
94/95*	floral, pine, terpene	2-4
96**	fruity, "green"	7-9
100	floral	1
101	chemical, floral	1
102	manure	2-3
107/108*	fried, terpene, spicy	1-3
109	floral, melon	1
112*	wine cellar, iris	2-4
113/114*	chemical, acrid, petroleum	6-7
115	spicy, fruity	1
	winery	3
116**	fruity	2-4
118	winery	3

<sup>a</sup> Descriptors listed were reported in two or more wines.

<sup>b</sup> Peaks labeled \* were used in both Data Sets I and II, peaks labeled with \*\* were used only in Data Set II ( $n = 19$ ). <sup>c</sup> Intensity was rated on a 10 point scale, from 0 = no aroma to 9 = intense aroma.

scribed as fruity, and found in higher concentrations in Chardonnay and French Colombard. When PCA of Data Set I was performed, factor loadings of the 19 variables also present in Data Set II and wines factor scores were similar to the pattern shown in Figure 3. However, of the added eight "fruity" ester peaks (26, 34, 35, 40, 45, 65, 96, 116), all but 34, 35, and 45 were strongly negatively loaded on factor I, which is consistent with the fruity, apple-like aroma of Chardonnay and to a lesser extent of French Colombard. The only "fruity" apple-like compounds weighted positively on factor I were peaks 35 and 36, ethylmethyl butyrate isomers.

Despite the exclusive presence of peaks 87 and 89 in White Riesling wines, use of either peak alone in discriminant analysis did not permit correct classification of the varieties into three groups nor, using only R and C wines,

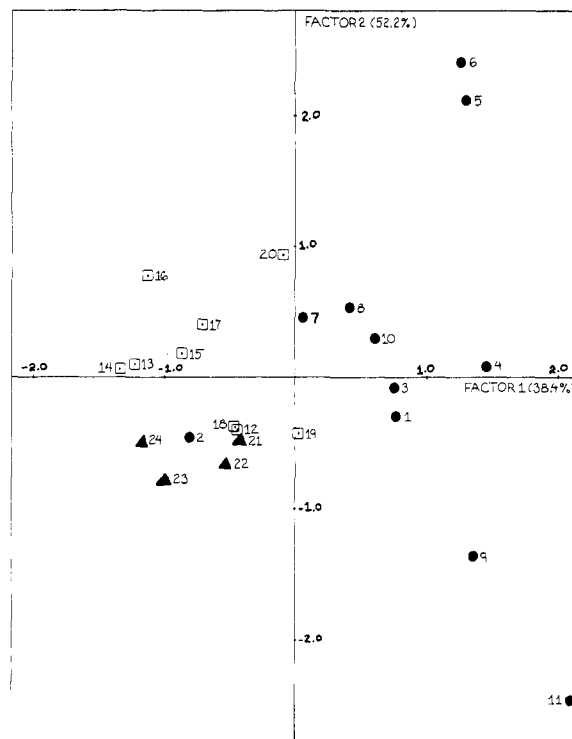


Figure 4. Principal component analysis of 19 wine volatiles. Wine factor scores for principal components I and II. (●) White Riesling, (□) Chardonnay, and (▲) French Colombard.

into two groups. To discriminate accurately between White Riesling and Chardonnay wines, four peaks were used: 87, 46, 41, and 56. To sort the 24 wines correctly into three varietal categories, five components were required: peaks 87, 41, 20, 56, and 92. However, upon deletion of Riesling 2 (which had no detectable concentration of either peak 87 or 89, and by PCA (Figure 3) was not grouped with Rieslings), either peak 87 or 89 successfully classified R and C wines. Without Riesling 2, the remaining 23 wines were assigned correctly to R, C, or F categories using peaks 87, 46, and 85A. With the exception of peaks 20, 46, and 56, variables selected in stepwise discriminant analysis were weighted heavily on principal components I or II. As expected, because of the correlation among GC peaks, the variables and coefficients used in the discriminant functions change considerably, both as the cases used to derive the functions and as the variables are changed. Although the functions had U statistics significant at the 99% level, testing the validity of the functions required use of data outside of that used for deriving the functions and will be discussed in another paper. Ideally, either multivariate analysis should be performed on a far larger number of samples to provide results which can be generalized to wines outside of the data set.

#### SUMMARY

Wine headspace (HS) volatiles were collected by displacement and analyzed by gas chromatography (GC), GC-MS, sensory evaluation of the split GC effluent (GC-sniff). Sixty compounds were identified, only one of which (2,2-dimethyl-6-methyl-6-vinyltetrahydropyran) not having been reported previously in wine. Twenty-seven (I) peaks were selected from the 120 peaks detected for principal component analysis (PCA) and stepwise discriminant analysis (SDA) by eliminating those with poor reproducibility or low intensity aroma rating by GC-sniff. Eight large or very highly correlated ester peaks were removed from I to provide a second data set (II,  $n = 19$ ). In PCA of both I and II, the first principal component (PC I),

although accounting for only 38% of the variance, separated 10 of the 11 White Riesling wines (R) from the nine Chardonnays (C) and four French Colombards (F). Weighted >0.50 on PC I (Data Set II) were eight components, found in higher concentrations in R than C or F, some of which had fruity, floral descriptions, consistent with the aroma of R. Weighted <-0.50 on PC I were three "fruity" esters, also consistent with the characteristic aromas of C and F. Interestingly, linalool, often thought to be important in R, was not weighted heavily on PC I. By SDA, the 24 wines were sorted successfully into three variety categories by discriminant functions using five components.

**Supplementary Material Available:** Peak means (ppb) of triplicate analyses of each of the 24 wines are listed (15 pages). Ordering information is given on a current masthead page.

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## Components of Almond Hulls: Possible Navel Orangeworm Attractants and Growth Inhibitors

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A total of 44 components of the vacuum steam volatile oil of almond hulls have been identified using capillary GLC-MS. Major components include nonanoic acid, eugenol, (*E*)-2-decenal, benzaldehyde, nonanal, nonanol, and an unidentified lactone (mol wt 168). Unusual components include 6-methyl-3,5-heptadien-2-one, geranylacetone, borneol,  $\gamma$ -nonalactone, and methyleugenol. Direct ether extraction of the hulls gave 1-1.5% of a nonvolatile triterpenoid.

The navel orangeworm *Amyelois transitella* is a serious pest to the almond (*Prunus amygdalus*) crop in California (cf. Curtis and Barnes, 1977). The moth lays its eggs on

the outside of the almond hull and the larva consumes some of the hull before finding its way into the kernel or completes its life cycle in the hull.

Previous work by one of the authors (Soderstrom, 1978) had indicated that there was some growth inhibition to the navel orangeworm with the Mission variety almond hulls relative to the Nonpareil variety. It seemed possible that this inhibition was due to the presence of some unknown chemical component in the Mission variety. The volatile chemical components are of interest also from another point of view in that they may be involved in the olfactory attraction of the navel orangeworm to the almond hulls.

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