Evaluation of Headspace Volatiles of Cabernet Sauvignon Wines Sampled by an On-Column Method

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An on-column method for direct headspace sampling was used to quantify volatiles of 20 1986 Cabernet Sauvignon wines from six regions in Napa Valley, CA. Most of the compounds were products of yeast fermentation, although 1-(1-methylethoxy)butane and 3-propylcyclopentene have not been reported in wine previously. The wines were classified correctly into region by stepwise discriminant analysis using six peaks, while principal component analysis (PCA) of the GC peaks showed some clustering by region. In contrast PCA of sensory ratings of these wines described elsewhere failed to cluster the wines on the basis of origin. Although the headspace method is reproducible and would be useful for analysis of major grape and fermentation volatiles, it cannot detect trace compounds, many of which are significant sensorially.

INTRODUCTION

Discrimination of wines on the basis of region of origin, maturity, or variety based on chemical analyses, volatile analyses, or sensory properties has been done previously, with statistical success at classification. In many of the studies, however, the data used to discriminate the wines utilized components which played little or no role in wine flavor. For example, trace elements have been used to classify wines according to type or region in several studies (Kwan et al., 1979; Maarse et al., 1987). Trace elements plus other wine components such as amino acids, organic acids, pigments, and flavonoids were used by other researchers (Etievant and Schlich, 1988a,b; Etievant, 1989; Forina et al., 1986; Moret et al., 1984a; Voet et al., 1984).

Several studies have analyzed volatiles to discriminate wines by variety, origin, or vintage (Kwan and Kowalski, 1980; Marais et al., 1981a,b; Moret et al., 1984b; Noble et al., 1980; Rapp et al., 1984; Schreier et al., 1976), but often the components that provided the best classification of wines by region or variety were ubiquitous fermentation products: 2-phenylethanol or hexanol (Kwan et al., 1980; Marais et al., 1981a).

The same approach has been used in examining the sensory properties of wines. The flavor of wines has been quantified by descriptive analysis, and these data have been examined by multivariate statistics to classify the wines by variety (Noble, 1988), location (Guinard and Cliff, 1987; Noble et al., 1984), or vintage (Noble and Shannon, 1987; Ohkubo et al., 1987). Descriptive analysis of wines has shown that it is sometimes possible to discriminate wines by geographic origin (Guinard and Cliff, 1987; Heymann and Noble, 1987).

In the present study, the headspace volatiles of 20 Cabernet Sauvignon wines from 6 different locations were examined by an on-column method.

EXPERIMENTAL PROCEDURES

Wines. Twenty sites were selected from six regions in Napa Valley, California, to provide locations which represented wide variation in soils, moderate variation in climate and rainfall, and

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Table I. Wines and Their Regions of Origin

region of origin	wine code	winery
1 Stags Leap District	1	Chimney Rock
	2	Clos Du Val
	3	Pine Ridge
	4	Shafer
	5	Silverado
	5	Stags Leap Wine Cellar (SLV)
	7	Stags Leap Wine Cellar (cask 23)
	8	Vichon Ilsley
	9	Steltzner
2 Rutherford-Oakville	10	Inglenock
	11	Mondavi (Tokolon vineyard)
3 Conn Creek	12	Joseph Phelps (Backus vineyard)
	13	Caymus (block I)
	14	Caymus (block B)
4 Spring Mountain	14	Keenan, Robert
	16	Newton
5 Howell Mountain	17	Dunn
	18	La Jota
6 Calistoga	19	Chateau Montelena
	20	Joseph Phelps Vineyard (Eisele vineyard)

minimal variation in root stock, vine age, or trellis. As described elsewhere (Elliott-Fisk and Noble, 1992; Noble and Elliott-Fisk, 1990), the six regions included Calistoga, Howell Mountain, Spring Mountain, Rutherford-Oakville, Conn Creek, and Stags Leap District. Commercial 1986 Cabernet Sauvignon wines made from these sites were obtained from participating wineries as listed by region in Table I. The wines were held at 10 °C after bottling until analysis 23–24 months after fermentation.

Headspace Sampling. Fifty milliliters of wine was placed into a 300-mL Erlenmeyer flask. To serve as an internal standard for quantitation, 500-μL of an aqueous 3-heptanol solution (100 μg/mL) was added to the wine sample. After the headspace of the sample flask was purged with nitrogen gas for 10 s to remove oxygen, the flask was sealed with a Teflon plug equipped with a Teflon stopcock.

A wine sample was heated in a water bath for 20 min at 25 °C. A sample of headspace gas (4 mL) was drawn into a 20-mL gastight syringe equipped with a fused silica capillary column needle (J&W Scientific, Folsom, CA) and then injected into a fused silica capillary column using an on-column injector (J&W Scientific) as described previously (Shimoda and Shibamoto, 1990).

It required 5 min to inject 4 mL of headspace gas through a capillary needle. After injection, the needle was withdrawn from
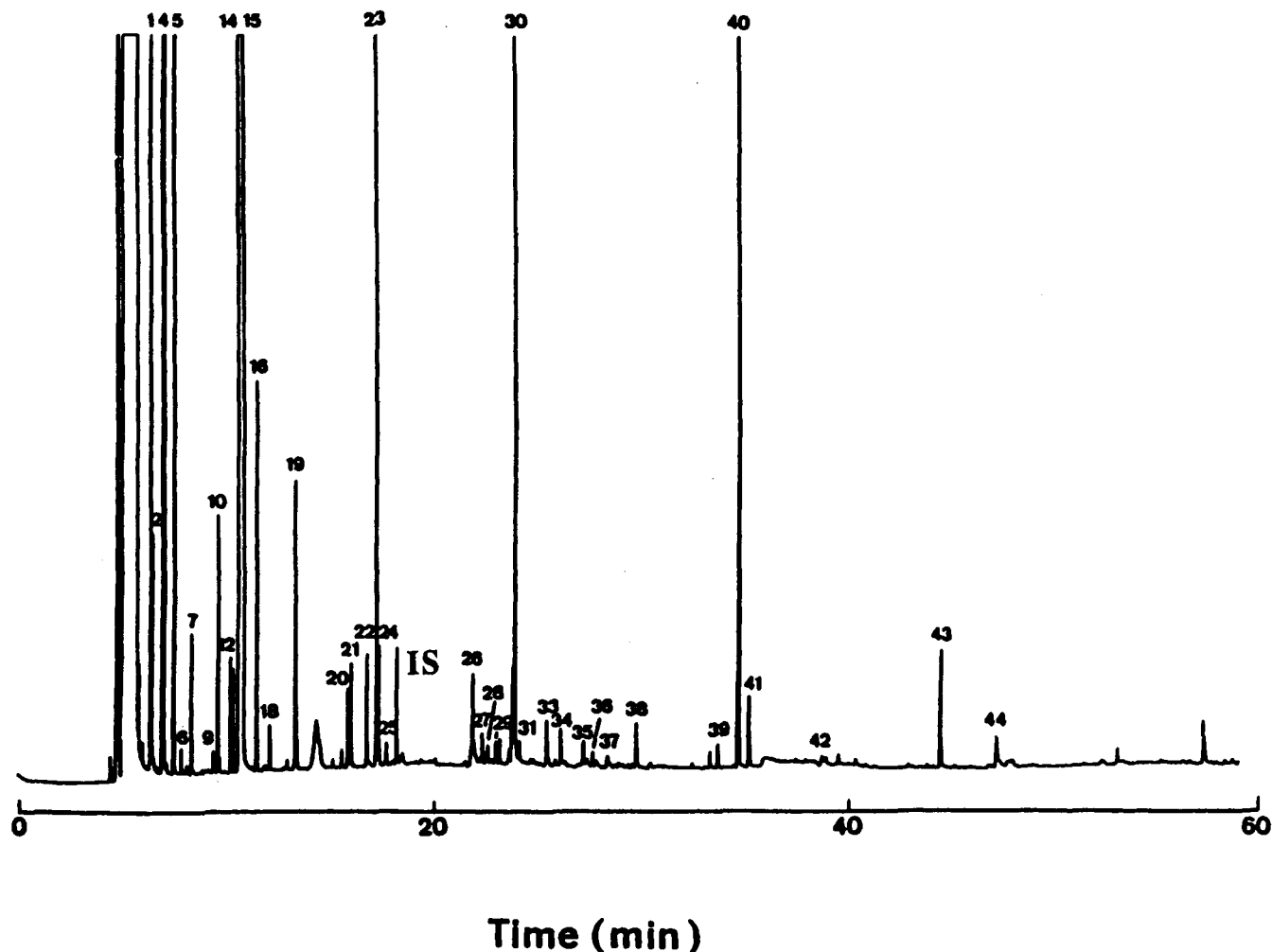
Time (min)

Figure 1. Representative gas chromatogram of 4-mL headspace sample of wine. Peak numbers correspond to tentative identifications in Table II. IS denotes internal standard (Kovats index = 900).

the capillary column and then approximately 4 mL of helium carrier gas was drawn into the syringe. The needle was inserted into the column again, and the helium gas was injected into the column to clean the remaining headspace sample in the syringe. This cleaning procedure was repeated four times.

The headspace gas sample was cryofocused at about 20 cm from the beginning of the column with a Dewar containing liquid nitrogen for 5 min.

Gas Chromatography. A Hewlett-Packard 5890A gas chromatograph equipped with a 60 m × 0.25 mm i.d. fused silica capillary column with bonded phase DB-5, 0.25-μm film thickness (J&W Scientific), flame ionization detector (FID), and on-column injector (J&W Scientific) was used for analysis of headspace wine constituents.

After removal of the Dewar flask, the column temperature was held at 40 °C for 2 min and then programmed to 200 °C at 3 °C/min. The linear flow rate of the helium carrier gas was 20 cm/s. The detector temperature was 230 °C. The gas flow rates for the FID were as follows: hydrogen, 20 mL/min; air, 200 mL/min; makeup nitrogen, 30 mL/min. The GC peak areas were calculated with a Spectra-Physics Chrom Jet integrator and expressed relative to the peak area of the internal standard. Each wine was analyzed in duplicate.

Gas Chromatography/Mass Spectrometry (GC/MS). A gas chromatograph (HP 5890A) with on-column injector interfaced to a VG Trio 2 mass spectrometer was used to obtain mass spectra of gas chromatographic components of the headspace. The sampling procedure for GC/MS was the same as that described above. The ionization voltage was set at 70 eV, and the ion source temperature was 140 °C.

Identification of the wine headspace constituents was made by comparison of their GC Kovats indices (Kovats, 1965) and mass spectral patterns with published values.

Statistical Analysis. Reproducibility was assessed by calculation of the coefficient of variation for the duplicate GC analyses of each sample for each peak using Microsoft Excel (Microsoft Corp., Redmond, WA). In addition, a two-way analysis of variance (wines, reps) was performed on each peak. Stepwise discriminant analysis was performed on the 44 peaks for which quantitative data were obtained, using PROC STEPDISC on SAS (SAS, 1985). This analysis, in addition to indicating which components discriminate among the groups (the six regions), performs a one-way analysis of variance for each compound to determine which peaks differ significantly among regions. The peaks selected for the first four to six steps were then used to run discriminant analyses using PROC DISCRIM on SAS.

To see the relationships among the peaks and the wines, principal component analysis was run using PROC FACTOR on SAS on the quantified data for 44 peaks for the 20 wines.

RESULTS AND DISCUSSION

A typical gas chromatogram of the headspace of Cabernet Sauvignon wine is shown in Figure 1. The identities of the 44 peaks are provided in Table II with the reproducibility of the method illustrated by coefficients of variation for duplicate analyses of three wines. With the exception of very small peaks, the coefficient of variation of the duplicate analyses varied from less than 0.05 to 0.10. All of the peaks varied significantly across the 20 wines, while 14 peaks varied signficantly between replications (Table II). Only highly volatile and abundant compounds are detected in the headspace. Most of the peaks are products of yeast fermentation (Suomalainen and Lehtonen, 1979), as were the 21 components previously

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Table II. Tentative Identification and Reproducibility Estimated as Coefficient of Variation (CV)[a] for Duplicate Analyses of Wine Headspace Volatiles of Three Conn Creek Wines[b] and by Analysis of Variance for Replications and Wines

| peak[c] | Kovats index | tentative identification | ID method | | CV | | | sig of F statistics[d] | |
			GC	MS	no. 12[b]	no. 13[b]	no. 14[b]	reps	wines
1	515	methyl acetate	e	i	0.08	0.14	0.10	NS	***
2	521	1-propanol		i	0.11	0.12	0.18	NS	***
3	532	3-methyl-2-butanone		i	0.28	0.07	0.04	NS	***
4	568	ethyl acetate		i	0.01	0.11	0.13	*	***
5	609	2-methyl-1-propanol	e	i	0.00	0.13	0.12	**	***
6	628	unknown			0.25	0.00	0.10	NS	***
7	653	1-butanol	e	i	0.07	0.17	0.09	NS	***
8	693	unknown			0.13	0.22	0.00	NS	***
9	703	unknown			0.43	0.00	0.03	NS	***
10	709	ethyl propanoate	e	i	0.03	0.13	0.10	NS	***
11	712	unknown			0.00	0.07	0.10	NS	***
12	725	1-(1-methylethoxy)butane		j	0.02	0.12	0.11	NS	***
13	729	ethyl 2-methylpropanoate		i	0.00	0.18	0.10	NS	***
14	739	3-methyl-1-butanol		i	0.00	0.17	0.11	NS	***
15	742	2-methyl-1-butanol	h	i	0.02	0.01	0.11	*	***
16	758	2-methyl-1-propyl acetate	e	i	0.00	0.11	0.11	NS	***
17	765	diethyl carbonate	e	i	0.22	0.09	0.10	NS	***
18	772	1-pentanol	e	i	0.01	0.07	0.11	NS	***
19	799	ethyl butyrate	e	i	0.09	0.09	0.08	NS	***
20	845	ethyl 2-methylbutyrate		i	0.01	0.03	0.13	NS	***
21	851	ethyl 3-methylbutyrate	e	i	0.00	0.04	0.13	NS	***
22	868	furfural	f	i	0.01	0.17	0.11	NS	***
23	876	3-methyl-1-butyl acetate	g	i	0.02	0.09	0.09	NS	***
24	879	unknown			0.01	0.07	0.09	NS	***
25	885	3-propylcyclopentene		j	0.22	0.51	0.67	NS	***
26	962	benzaldehyde	g	i	0.52	0.02	0.39	***	***
27	970	unknown			0.04	0.21	0.07	NS	***
28	975	unknown			0.24	0.30	0.45	**	***
29	982	unknown			0.15	0.05	0.12	**	***
30	996	ethyl hexanoate	e	i	0.00	0.06	0.07	NS	***
31	1000	hexyl acetate	e	i	0.32	0.19	0.22	*	***
32	1010	unknown			0.32	0.16	0.00	NS	***
33	1025	unknown			0.08	0.13	0.07	*	***
34	1038	p-cymene	f		0.13	0.24	0.15	NS	***
35	1057	limonene	f		0.16	0.03	0.18	NS	***
36	1065	α-terpinene	f		0.16	0.07	0.04	NS	***
37	1078	unknown			0.04	0.25	0.06	*	***
38	1114	unknown			0.15	1.24	0.00	*	***
39	1176	unknown			0.26	0.30	0.00	•	***
40	1193	ethyl octanoate	e	i	0.15	0.14	0.12	*	***
41	1202	unknown			0.09	0.20	0.12	*	***
42	1273	unknown			0.10	0.04	0.00	NS	***
43	1391	ethyl decanoate	e	i	0.01	0.12	0.15	**	***
44	1453	unknown			0.00	0.07	0.08	NS	***

[a] CV = standard deviation/mean concentration; concentrations determined relative to internal standard peak area. [b] Wine codes defined in Table I. [c] Peak numbers correspond to those in Figure 1. [d] Significance level for F statistics for replications (reps) and wines; NS, *, **, *** denote $p > 0.05$ and $p < 0.05, 0.01,$ and 0.001, respectively. [e] Sadtler (1985). [f] Georgilopoulos and Gallois (1987). [g] Guichard and Souty (1988). [h] Schwab and Schreier (1988). [i] Stenhagen et al. (1974). [j] Heller and Milne (1978).

quantified in the headspace of fermenting Thompson Seedless musts by a purge and extraction method (Stashenko et al., 1992). Two compounds have not been reported in wine before: peak 12, 1-(1-methylethoxy)butane, and peak 25, 3-propyl cyclopentene. Also of note are the terpenes (peaks 34–36, which were tentatively identified on the basis of Kovats indices. These terpenes are not usually found in nonaromatic wine varieties, although trace amounts of linalool were detected in model fermentations (Hock et al., 1984).

The mean concentrations of the 23 peaks, which varied significantly among the regions, are provided for each wine region in Table III. Using six peaks (12, 19, 20, 22, 27, and 39), the wines were correctly classified by region by stepwise discriminant analysis. This particular peak combination may reflect some real trends, but more probably it is the result of the unique composition of GC peaks peculiar to these wines and the collinearity of the data set. For example, although peaks 19 and 20, which are, respectively, ethyl butyrate and ethyl 2-methylbutyrate, both have fruity aromas, the aroma significance of peak 12, 1-(1-

methylethoxy)butane, is unknown. This compound was high in two different wines from one winery in Conn Creek and may represent a contaminant rather than a grape or yeast metabolite. Although this unique component facilitates statistical separation into groups, it probably has no significance with respect to wine flavor. Further, this combination of six peaks is not the only one which will provide 100% classification. For example, peak 20, which was entered as a variable in the discriminant functions, is highly correlated with peak 21, ethyl 3-methylbutyrate ($r = 0.50$, df = 38, $p < 0.01$). Either compound provides perfect regional sorting in the six-compound solution. Despite this *caveat* for the use of this technique for classifying wine volatiles, many previous studies have reported the classification of wines by regions using solvent-extracted volatiles. For example, amyl acetate, hexyl acetate, and butanol grouped Colombar (French Colombard) wines by origin, whereas Chenin blanc wines were sorted using hexanol and 2-phenylethanol (Marais et al., 1981a). Venetian white wines were correctly classified by origin using cis-3-hexenol, ethyl 2-methyl-

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Table III. Mean Concentrations[a] (Milligrams per Liter) for Wine Headspace Volatiles Differing Significantly across Regions

peak[b]	tentative identification	region 1[c] (n = 9)	region 2 (n = 2)	region 3 (n = 3)	region 4 (n = 2)	region 5 (n = 2)	region 6 (n = 2)	sig[d]
2	1-propanol	0.553	0.475	0.778	0.083	0.263	0.001	***
3	3-methyl-2-butanone	0.225	0.085	0.123	0.018	0.016	0.001	*
6	unknown	0.048	0.040	0.122	0.250	0.120	0.140	**
9	unknown	0.107	0.138	0.160	0.078	0.100	0.158	**
11	unknown	0.174	0.175	0.132	0.245	0.113	0.208	*
12	1-(1-methylethoxy)butane	0.278	0.125	0.583	0.195	0.128	0.265	***
13	ethyl 2-methylpropanoate	0.226	0.118	0.555	0.158	0.113	0.250	***
17	diethyl carbonate	0.209	0.100	0.103	0.055	0.080	0.103	**
19	ethyl butyrate	2.027	1.760	2.462	2.325	1.802	3.128	**
20	ethyl 2-methylbutyrate	1.028	1.075	1.597	0.780	1.023	1.943	*
22	furfural	1.629	2.560	1.313	1.370	1.418	1.340	***
25	3-propylcyclopentene	0.344	0.243	0.283	0.188	0.263	0.273	*
27	unknown	0.202	0.125	0.333	0.051	0.145	0.133	***
28	unknown	0.304	0.170	0.275	0.225	0.183	0.120	*
29	unknown	0.279	0.190	0.347	0.170	0.173	0.113	**
31	hexyl acetate	0.236	0.125	0.197	0.188	0.200	0.133	**
32	unknown	0.114	0.113	0.082	0.043	0.195	0.100	**
33	unknown	0.240	0.190	0.512	0.198	0.163	0.135	**
37	unknown	0.264	0.215	0.170	0.213	0.313	0.140	*
38	unknown	0.880	0.680	0.350	0.360	0.595	0.295	*
39	unknown	0.363	0.183	0.184	0.170	0.168	0.255	**
42	unknown	0.513	0.268	0.250	0.265	0.595	0.313	*
43	ethyl decanoate	1.746	1.023	1.600	0.893	0.748	0.960	**

[a] Concentrations determined relative to internal standard peak area. [b] Peak numbers correspond to those in Figure 1. [c] Region codes defined in Table I. [d] Significance level of F statistic for regions; *, **, *** denote $p < 0.05$, 0.01, and 0.001, respectively.
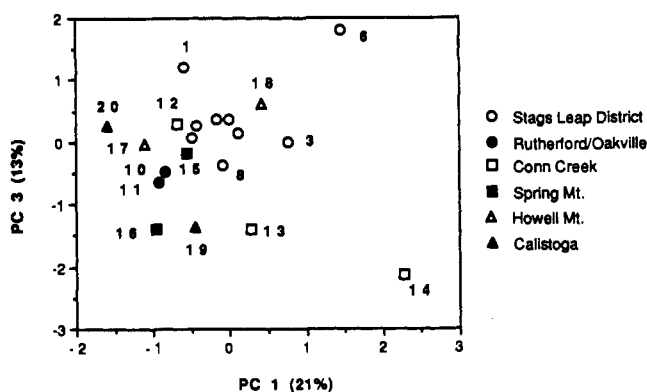

Figure 2. Wine factor scores from principal component analysis of 44 GC peaks for principal component (PC) I vs III. Codes for wines are defined in Table I.

propanoate, 1-hexanol, ethyl octanoate, and octanoic acids (Moret et al., 1984b). Kwan et al. (1980) were able to discriminate between French and American Pinot noir wines using hexanol and cyclohexane levels, whereas p-hydroxbenzaldehyde and 2-phenylethanol separated Californian from Oregon and Washington Pinot noir wines. In all of the examples above and in these data, classification of wines by origin using volatiles which are produced by yeasts during the primary or ethanolic fermentation is based on the unique distribution of volatiles in the wines sampled, not the unique and distinctive contribution to flavor which they afford. With discriminant analyses, a function is derived which maximizes the ratio of the between-group variability to the within-group variability; consequently, the selection of peaks is based solely on their ability to separate groups.

To give an overall picture of the distribution of the volatiles, a principal component analysis was performed. No grouping of the wines by origin was observed on the first two principal components, which together accounted for 37% of the total variation. However, some clustering of wines by regions is seen in Figure 2, in which the configurations of the wines on the first and third principal components are displayed. The two wines from Ruth-

erford-Oakville are located very close to each other, but the three Conn Creek area wines are widely separated. Similarly, the two Calistoga wines are not located closely. Seven of the Stags Leap District wines are clustered with two outliers (no. 1 and 6) widely separated from the rest. However, the configuration of these 1986 Cabernet Sauvignon wines provided by PCA of the headspace volatiles is very different from that arising from analysis of other variables measured at the same time for these same wines. No clustering by origin was seen in PCA of the intensity ratings of 13 sensory descriptive terms (Spears, 1990; Noble et al., 1990) or nonvolatile composition (Noble et al., 1990), whereas some clustering did occur in the PCA of the volatile data, which indicates that the gas chromatographic variables vary differently across the wines than do the specific sensory terms or selected nonvolatile components.

Over 600 compounds have been identified in wines, as summarized by Rapp (1988). Recently, concentrations of trace amounts of 2-methoxy-3-isobutylpyrazine have been correlated with the intensity of the "varietal", distinct vegetative aroma of Cabernet Sauvignon (Allen et al., 1989), which was first identified as the "impact compound" in bell peppers by Buttery et al. (1969). Detection of this or similar trace impact compounds is not possible with sampling of small volumes of headspace; however, this headspace method does lend itself to analysis of the more highly concentrated, highly volatile constituents such as the major esters produced during fermentation.

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