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Comparison of Aroma Volatiles in Commercial Merlot and Cabernet Sauvignon Wines Using Gas Chromatography−Olfactometry and Gas Chromatography−Mass Spectrometry

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Seventy-four aroma active compounds were observed in Merlot and Cabernet Sauvignon wines produced in California and Australia. Volatiles were sampled using solid phase microextraction and analyzed using time-intensity gas chromatography−olfactometry and gas chromatography−mass spectrometry (GC-MS). The most intense odorants were 3-methyl-1-butanol, 3-hydroxy-2-butanone, octanal, ethyl hexanoate, ethyl 2-methylbutanoate, β-damascenone, 2-methoxyphenol, 4-ethenyl-2-methoxy-phenol, ethyl 3-methylbutanoate, acetic acid, and 2-phenylethanol. Aroma compounds were classified according to their aroma descriptor similarity and summed into nine distinct categories consisting of fruity, sulfury, caramel/cooked, spicy/peppery, floral, earthy, pungent/chemical, woody, and green/vegetative/fatty. Both Merlot and Cabernet Sauvignon wines were characterized by high fruity, caramel, green, and earthy aroma totals. Although there were distinct quantitative differences between Merlot and Cabernet wines, the relative aroma category profiles of the four wines were similar. Of the 66 volatiles identified by GC-MS, 28 were esters and 19 were minor alcohols. Between 81 and 88% of the total MS total ion chromatogram peak areas from each wine type were produced from only eight compounds: ethanol, ethyl octanoate, ethyl decanoate, ethyl acetate, 3-methyl-1-butanol, ethyl hexanoate, diethyl succinate, and 2-phenylethanol. Merlot wines from both Australia and California contained 4−5 times more ethyl octanoate than Cabernet Sauvignon wines from the same sources.

KEYWORDS: Wine; SPME; volatiles; aroma activity; GC-O; GC-MS

INTRODUCTION

Wine is a complex beverage containing over 800 identified volatiles (*1*). Most wine volatile identification and quantification studies have employed gas chromatography−mass spectrometry (GC-MS) (*2*−*7*). Wine odor activity values (OAV) have been determined using sensory thresholds to estimate the odor activity and relative strength (*8*, *9*). GC−olfactometry (GC-O) has been employed in the study of a wide variety of red (*10*−*14*) and white (*15*, *16*) wines. These studies have shown that the vast majority of wine volatiles have little to no aroma activity and that aroma activity is limited to relatively few volatiles.

As Merlot and Cabernet Sauvignon are commercially significant wines, their composition and aroma impact components have been examined using a variety of techniques. A recent GC-MS study of Cabernet Sauvignon and Merlot, among other red wines (*12*), reported that no aroma volatiles were characteristic of a single variety and only quantitative differences in volatiles were observed. Sensory studies (*17*) involving Cabernet Sauvignon and Merlot wines produced in France indicated that the aromas were similar. These same researchers later reported (*18*) that although the aromas were similar, the Merlot and Cabernet wines could be differentiated by the intensity of the caramel sensory descriptor, which was also mirrored in levels of 4-hydroxy-2,5-dimethylfuran-3(2*H*)-one (HDMF) and 4-hydroxy-2-ethyl-5-methylfuran-3(2*H*)-one (HEMF).

Two GC-O studies (*6*, *19*) have reported the most intense odorants observed in Cabernet Sauvignon and Merlot wines produced in Aragón, Spain, and Bordeaux, France. However, only three (β-damascenone, 2-phenylethanol, and 3-methylbutanol) of the 10−11 most potent odorants were the same in both studies. It was uncertain if the lack of agreement in aroma impact compounds was due to regional climatic or soil differences or seasonal differences between production years or if the differences were due to the manner in which the samples were prepared. It is known that wine aroma can be influenced by seasonal differences, viticulture practices, and wine-making

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practices (*20*−*23*). It has also been shown that different volatile extraction procedures can produce disparate results (*24*−*26*). Both GC-O studies (*6*, *19*) employed solvent extraction to separate the volatiles from the wine matrix and evaluated the volatiles using the identical GC-O procedure (aroma extract dilution analysis).

Therefore, the objective of this study was to compare the aroma composition in commercial Merlot and Cabernet Sauvignon wines from two disparate wine-growing regions from two different years using identical sample preparation and analytical procedures to determine if these wine types have aroma characteristics that can be observed from year to year and from different growing regions.

MATERIALS AND METHODS

Single variety Cabernet Sauvignon and Merlot dry wines (750 mL bottles) were purchased locally in early 2005. The specific brands and notations used in this study were Cabernet #1 Black Swan, Australia, 2000; Cabernet #2 Napa Valley, CA, 2002; Merlot #1, Jacob's Creek, Australia, 2000; and Merlot #2 Harbinger Napa, CA, 2002. The Australian wines were from the Barossa Valley in the southeastern portion of the state of South Australia. The wines were stored at 4 °C until analyzed. All reagents and pure compounds used in this study were purchased from Acros (Geel, Belgium), Fischer Scientific (Pittsburgh, PA), Fluka (Milwaukee, WI), Givaundan Roure (Lakeland, FL), Lancaster (Ward Hill, MA), Sigma-Aldrich (St. Louis, MO), Sun Pure (Avon Park, FL), and Ultra Scientific (North Kingstown, RI) and are shown as superscript letters in the tables.

Solid Phase Microextraction (SPME) Procedures. Static headspace sampling was employed after the fiber was cleaned and conditioned. SPME parameters were optimized for extraction and desorption for wine volatiles. Ten milliliters of wine was added to a 40 mL glass vial containing a small Teflon-coated stirring bar with a screw top and Teflon-lined septum. After the equilibration time of 20 min, volatiles from the wine headspace were extracted for 30 min at 40 °C using a 100 mm 50/30 μm DVB/Carboxen/PDMS SPME fiber (Supelco, Bellefonte, PA). Before each exposure, the fiber was cleaned in a 260 °C injection port for 5 min.

GC-O. GC-O was carried out using a HP-5890 GC with a high volume (1.2 L/min) sniffing port (DATU, Geneva, NY) plus a flame ionization detector (FID). The column effluent was split 3:1 in favor of the sniffing port allowing simultaneous FID detection and sniffing of GC effluents. A SPME injector liner was employed. The injector temperature was 200 °C, and the detector temperature was 250 °C. The columns used were 30 μm × 0.32 μm × 0.5 μm DB-Wax column and a 30 μm × 0.32 μm × 0.5 μm DB-5 column, both from J&W Science (Folsom, CA). Helium was used as the carrier gas at 1.5 mL/min. The oven temperature program was 40 °C, ramped at 7 °C/min to 265 °C and then held for 5 min at the maximum temperature. All samples were analyzed by GC-O on both DB-5 and DB-Wax columns. Heated and humidified air was added in the sniffing port at 100 mL/min. Two experienced olfactory assessors were employed. Samples were sniffed at least three times by each assessor. Aroma descriptions and approximate times were recorded for every sample. Assessors indicated the intensity of each aroma peak using a linear potentiometer with a 0−1 V signal and also recorded the sensory description of the aroma as previously described by Bazemore and co-workers (*27*). Sensory descriptors were then transcribed into bound data files that contained the time-intensity values as well as sensory descriptors, which were defined as aromagrams. Average aromagram values were determined using Excel spread sheets. A peak was considered aroma active only if at least half the panel found it at the same time with similar description. Retention times, retention indices, and peak areas were averaged, with zero values used if no peak was detected. Panelists' time-intensity responses and the FID data were simultaneously collected using Chrom Perfect 5.00 software (Justin Innovations, Inc., Palo Alto, CA). A compound was deemed aroma active if it was detected in at least half of all sniffs. The intensity of each compound detected through GC-O was averaged. When a compound was not detected, its value was treated as missing, not zero. Alkane linear retention index values were determined for both columns (*28*).

GC-MS. GC-MS analyses were conducted using Perkin/Elmer Clarus 500 quadruple GC-MS, equipped with Turbo Mass software (Perkin/Elmer, Shelton, CT). Conditions were as follows: Helium was used as the carrier gas with a constant flow mode of 2 mL min^{-1}. The source was kept at 200 °C, and the transfer line and injector were kept at 220 °C. Compounds were separated on a 60 m, 0.25 mm i.d., 0.5 μm DB-Wax column (J&W Scientific). The mass spectrometer was operated in the total ion chromatogram (TIC) at 70 eV. Data were collected from 40 to 300 *m*/*z*. Mass spectral matches were made by comparison of NIST 2002 standard spectra (NIST, Gaithersburg, MD).

Identification Procedures. Initial identifications were based upon the matches made from spectra in the NIST library, aroma descriptors, and linear retention index matches from literature or from standards. The final confirmation was based upon the combined matching of retention indices (LRI values), full scan mass spectra values, and aroma descriptions from standards with those observed in the sample.

RESULTS AND DISCUSSION

SPME Headspace Volatile Extraction. The most crucial step in any aroma analysis is the manner in which volatiles are sampled. In the case of wine, liquid−liquid extraction has been extensively employed (*16*, *26*, *29*, *30*). Although liquid−liquid extraction is the classical method of collecting and concentrating wine volatiles, the procedure has several disadvantages including inability to detecting early eluting (highly volatile) components, variable extraction efficiencies, and extraction of unwanted nonvolatiles such as carotenoids and lipids. In addition, liquid−liquid extraction is time-consuming and the excessive manipulation of the samples may lead to serious errors (*31*). The SPME static headspace sampling technique also has selectivity issues. However, SPME sampling is increasingly employed to collect and concentrate wine volatiles because it is solventless, allows the evaluation of low boiling volatiles, and is relatively easy to use (*32*−*34*).

In this study, it was found that warming the wines to 40 °C with 30 min of fiber exposure was sufficient to detect over 70 peaks, which could be integrated with area counts >40000 and provide reasonable fragmentation spectra for identification. Fiber exposure times less than 30 min reduced the amount of volatiles collected, making MS identification more difficult. As noted in earlier SPME studies (*27*, *33*), a longer exposure time increased the total amount of volatiles collected but reduced the relative amounts of the highly volatile compounds such as acetaldehyde. Low boiling components are apparently displaced from the SPME fiber by volatiles, which have a greater affinity for the fiber.

MS Analyses of Major Volatiles. The identity and relative peak areas of volatiles from Merlot and Cabernet wines are compared in **Table 1**. Over 100 peaks were initially detected but only 66 are included in the table as many of the smaller peaks did not produce a clean MS fragmentation spectrum even with background correction. The objective for this part of the study was to obtain component identification and relative peak areas in order to make comparisons between the samples. As shown in **Table 1**, all four wines were of similar composition; the major differences were quantitative rather than qualitative. Merlot wines exhibited approximately twice as much total MS TIC peak areas (excluding ethanol) as the Cabernet wines. The two Merlot wines had total normalized peak areas of 244 and 239, whereas the corresponding values for the Cabernet wines were 129 and 119.

To compare the volatiles in the four wines, peak areas were normalized on the single largest peak found in all samples (excluding ethanol). This peak was the ethyl octanoate peak in

Table 1. MS Identification, Occurrence, and Relative TIC Peak Areas of Wine Aroma Components[a]

		relative peak area			
		Merlot		Cabernet	
compound name	LRI (wax)	Aust.	CA	Aust.	CA
acetaldehyde[b]	692	ND	0.1	0.1	0.1
dimethyl sulfide	760	0.1	ND	ND	0.1
methyl acetate [g]	839	ND	ND	ND	ND
ethyl acetate[b]	891	31.8	19.4	23.6	28.3
ethanol [g]	933	NI	NI	NI	NI
ethyl propanoate[j]	951	0.9	ND	0.8	0.6
ethyl 2-methylpropanoate[c]	960	0.6	ND	0.6	ND
2,3-butanedione[d]	970	ND	10.5	ND	0.5
2-methylpropyl acetate[g]	1029	0.5	ND	0.4	0.4
ethyl butanoate	1041	0.7	0.7	0.5	0.5
ethyl 2-methylbutanoate[j]	1057	ND	2.2	0.4	ND
ethyl 3-methylbutanoate[e]	1072	0.6	ND	0.7	0.9
2-methyl-1-propanol[e]	1093	ND	1.1	ND	ND
3-methylbutyl acetate [g]	1126	1.8	1.4	1.6	1.6
3-methyl-1-butanol[e]	1209	15.6	22.4	21.2	19.8
ethyl hexanoate[d]	1239	12.3	12.6	9.1	7.2
hexyl acetate[j]	1279	ND	0.3	ND	ND
furfuryl formate[j]	1293	0.6	0.7	0.6	0.7
2-octanol[j]	1301	ND	0.3	ND	ND
3-methyl-1-pentanol[d]	1331	1.5	2.9	1.9	1.8
ethyl heptanoate[j]	1341	1.6	1.1	1.9	2.0
methyl octanoate[j]	1399	ND	0.3	ND	ND
nonanal[b]	1408	0.4	ND	0.4	0.3
ethyl octanoate[d]	1444	100.0	76.9	18.2	12.1
acetic acid	1461	0.9	2.6	0.9	1.3
isopentylhexanoate[j]	1469	0.4	0.5	ND	ND
furfural[d]	1480	0.8	0.8	1.0	0.6
mercaptoacetic acid[j]	1505	0.2	ND	ND	0.3
decanal[b]	1515	1.9	0.4	1.0	0.6
linalool	1546	0.5	3.5	0.4	0.2
benzaldehyde [g]	1555	ND	ND	0.2	1.1
octanol[b]	1563	0.3	0.3	0.3	0.3
ionene (1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene)	1565	1.4	1.2	0.4	0.5
2,3-butanediol[j]	1580	ND	1.2	ND	ND
3-methylbutyl lactate[j]	1583	0.3	ND	0.3	0.4
5-methylfurfural[j]	1597	0.3	0.4	0.3	0.0
undecanal[j]	1622	ND	0.3	ND	0.3
ethyl decanoate[d]	1648	34.2	16.9	3.0	1.8
nonanol[b]	1666	0.5	ND	ND	0.3
3-methylbutyl octanoate	1670	0.7	0.3	ND	ND
diethyl succinate[j]	1687	11.4	12.0	14.5	11.8
ethyl 9-decenoate[j]	1703	0.8	1.1	0.4	ND
α-terpineol[b]	1719	0.3	ND	ND	ND
dodecanal[b]	1729	0.3	0.3	0.2	ND
decanol[j]	1769	0.4	0.3	0.2	0.2
1-methyl-1-phenylethanol[j]	1776	ND	ND	0.3	0.3
naphthalene[f]	1791	0.3	0.4	0.3	ND
methyl salicylate[j]	1820	ND	0.5	0.5	0.5
2-phenylethyl acetate[j]	1847	0.3	ND	ND	ND
ethyl dodecanoate[j]	1856	1.0	0.3	ND	0.2
hexanoic acid[d]	1861	0.3	0.6	0.8	0.5
geranylacetone[j]	1877	0.4	ND	ND	0.2
2-methoxyphenol (guaiacol)[d]	1889	ND	ND	0.3	ND
benzyl alcohol [g]	1904	0.6	ND	0.3	0.4
2-phenylethanol[j]	1920	0.6	0.6	0.8	0.5
β-undecalactone[c]	1935	0.4	ND	ND	0.2
2-phenylethanol[j]	1946	8.3	13.4	15.6	11.1
1-dodecanol[j]	1981	0.5	ND	0.4	ND
γ-nonalactone[d]	2012	0.6	0.4	0.4	0.3
ethyl tetradecanoate[j]	2070	0.3	ND	0.3	0.4
octanoic acid[h]	2086	2.2	3.1	2.1	2.7
ethyl pentadecanoate[j]	2179	0.2	0.8	0.6	0.7
1-tetradecanol[j]	2200	0.3	0.6	0.2	0.2
4-ethylphenol[j]	2210	ND	0.4	ND	ND
ethyl hexadecanoate	2288	ND	1.3	0.3	0.5
decanoic acid[d]	2314	0.6	1.7	0.6	0.6

[a] Peak areas normalized (100) to the largest nonethanol peak. ND, not detected; NI, not included. Identifications were confirmed using standards from the following sources. [b] Sun Pure. [c] Lancaster. [d] Aldrich. [e] Fluka. [f] Acros. [g] Fischer. [h] Ultra Science. [i] Givaundan Roure. [j] Tentatively identified based upon library spectral matching and literature LRI values only.

the Australian Merlot. It was assigned a value of 100, and the remaining peaks in all four samples were normalized to it. High ethyl octanoate values were characteristic of both Merlot samples (100 and 77). The corresponding Cabernet values were 18 and 12. Ethyl acetate and 3-methyl-1-butanol had larger peak areas than ethyl octanoate in Cabernet wines. The eight largest peaks produced between 81 and 85% of the total volatile nonethanol peak area. These eight peaks consisted of ethyl octanoate, ethyl decanoate, ethyl acetate, 3-methyl-1-butanol, isopentyl hexanoate, diethyl succinate, and 2- phenylethanol. Five of these eight major volatiles were esters.

Previous studies reported wide ranges of ester values such as ethyl octanoate and ethyl decanoate in Cabernet and Merlot wines (*12*). In the current study, there were 29 esters among the 66 volatiles identified. Esters were responsible for the vast majority (60−83%) of the total nonethanol MS peak areas. The proportion of esters in three of the four wines ranged between 60 and 63% of the total nonethanol MS peak area. However, the proportion of esters in the Australian Merlot was 83%. Esters are the primary source of fruity aromas in wines, and ester content can vary considerably among cultivars. For example, in Baga red wine from Portugal, esters contributed to only 15% of the total volatiles (*35*).

Saccharomyces cerevisiae and the associated enzyme, acyl-SCoA, are responsible for many of the ethyl esters as well as minor alcohols formed during the fermentation process (*36*). There are 17 minor alcohols identified in **Table 1**, with 3-methyl-1-butanol being the largest. Other alcohols in this group include fusel alcohols such as 3-methyl-1-butanol and 2-phenylethanol. Minor alcohols are released from the slow acid hydrolysis of the corresponding esters, and their MS peak areas are considerably smaller than the parent ester. The total ester MS peak area was about 2−7 times greater than the corresponding minor alcohols.

Phenols are products of the shikimic acid pathway and can be extracted from charred wood or released from grape glucosidal precursors (*1*). 2-Methoxy-4-(2-propenyl)phenol (eugenol), 2-methoxyphenol (guaiacol), 4-ethylphenol, and 2-phenylethanol are compounds typically extracted from wood.

GC-O Analyses. Seventy-four aroma volatiles detected in the four wines are listed in **Table 2** in terms of increasing elution times on a polar column (DB-Wax). Identification, aroma descriptors, odor group, LRI values, occurrence, and relative intensity are presented.

The four wines in this study had 24 aroma components in common. An additional 14 components were observed in three of the four wines. Aroma volatiles in California Cabernet were the most complex as compared to the other Cabernet or two Merlot wines. It contained 61 aroma volatiles as compared to 51 for the Australian Cabernet. The Merlot samples from California and Australia contained 50 and 49 aroma components, respectively. Ironically, the California Cabernet exhibited the smallest total MS peak area but the largest total aroma peak area suggesting that this wine contained several potent aroma compounds at very low concentrations.

GC-O Identification and Comparison. Relative intensities for each of 74 aroma active compounds are listed in **Table 2** along with the specific wine in which it was observed. The most intense odorants in both Merlot and Cabernet wines were 3-methyl-1-butanol, 3-hydroxy-2-butanone, octanal, ethyl hexanoate, ethyl 2-methylbutanoate, β-damascenone, 2-methoxyphenol (guaiacol), 4-ethenyl-2-methoxy-phenol, ethyl 3-methylbutanoate, acetic acid, and 2-phenylethanol.

Using calculated OAVs from MS quantitative data, Ferreira and co-workers (*12*) reported that ethyl octanoate, β-damascenone, ethyl hexanoate, 3-methyl-butanoic acid, and isoamyl acetate were the most important odorants in four young red

Table 2. Characterization and Identification of Wine Aroma Components[a]

					Merlot		Cabernet	
identification	descriptor	category	LRI	MS	CA	Aust.	CA	Aust.
acetaldehyde[C,F,b]	painty, pungent	7	<800	X	8	9	8	-
unidentified	sulfur, fruity	2	887		-	-	20	16
ethyl acetate[C,G,L,O,b]	ethereal-fruity	7	894	X	-	14	-	-
ethanol[A,C,L,g]	alcohol	7	941	X	30	23	23	20
ethyl propanoate[F,d]	sweet, fruity	1	946	X	-	-	23	20
ethyl 2-methylpropanoate[c]	sweet, fruity	1	965	X	30	45	34	26
2,3-butanedione[A,C,G,O,P,d]	buttery	3	977	X	-	9	-	-
2-methylpropyl acetate [A,C,G,O,T,g]	fruity, green	1	1005	X	32	19	43	38
ethyl butanoate[A,C,G,O,P,b]	fruity, sweet	1	1033	X	-	27	29	12
ethyl 2-methylbutanoate[F,J,G]	apple, sweet	1	1052	X	35	58	38	34
ethyl 3-methylbutanoate[A,C,J,e]	fruity, floral	1	1071	X	36	29	52	7
2-methyl-1-propanol[A,O,P]	nail polish	7	1098	X	-	-	33	10
1-butanol[J,j]	chemical, fruit	7	1116		11	15	-	-
3-methylbutyl acetate[F,T]	banana	1	1125	X	7	7	-	12
ethyl pentanoate[A,C,G,O,d]	ethereal-fruity	1	1139	X	-	27	26	6
myrcene[F,P,d]	musty, green	9	1166	X	-	-	-	32
1-pentan-3-ol[A,C,F,G,J,O,P,d]	green, parsley	9	1174	X	17	24	-	-
limonene[F,T,e]	citrus-like	1	1193	X	20	21	30	29
3-methyl-1-butanol[A,C,G,J,P,T]	malty	3	1217	X	51	21	97	62
ethyl hexanoate[C,P,T,d]	fruity	1	1237	X	24	41	46	44
hexyl acetate[A,P,T]	fruit, herb	1	1265	X	4	-	13	26
3-hydroxy-2-butanone (acetoine)[G,J]	dairy, over ripe fruit	3	1290		30	35	4	35
octanal[A,F,G,J,P,b]	fatty	9	1306	X	27	34	48	-
2-methyl-3-furanthiol[G,A,P]	onion, meaty	3	1323	X	-	-	31	15
3-methyl-1-pentanol[A,C,G,P,T,d]	fruity, floral	1	1334	X	17	20	21	-
n-hexanol[P,T,d]	cut grass, sweet	9	1363	X	9	23	21	-
2-formylthiophene	sulfury, onion	2	1382		-	24	21	16
4-mercapto-4-methyl-2- pentanone[A,C,F,G,J,P]	sulfury, fruity	2	1395	X	18	22	22	29
1-nonanal[A,C,F,G,P,b]	citrusy, floral	5	1409	X	5	-	34	6
1-hexanol[d]	green, sweet	9	1425		-	20	38	18
ethyl octanoate[A,I,T,d]	ripe fruit	1	1436	X	35	24	24	28
acetic acid[A,C,F,G,I,P,g]	pungent, sour	7	1452	X	11	40	40	22
3-methylbutyl hexanoate	sweet fruity	1	1464		17	-	47	-
methional[A,F,G]	cooked potato	3	1469	X	14	-	29	32
furfural[F,I,J,d]	sweet, bread like	3	1476	X	-	-	20	-
octyl acetate[d]	fruity, herbal	1	1490	X	12	-	29	-
decanal[b]	sweet waxy, orange	3	1507	X	22	-	9	24
benzaldehyde[F,I,J,T,g]	sweet, cherry	3	1530	X	29	31	8	17
2,3-butanediol	cream	3	1545	X	-	-	-	16
unidentified	fatty, sulfury	9	1586		-	-	35	-
5-methyl furfural[A,C,G,P]	warm, spicy	4	1607		-	10	18	16
undecanal[j]	waxy, floral	9	1625		12	-	-	-
ethyldecanoate[C,F,J,d]	fruity	1	1633		-	14	14	-
butyric acid[G,J,T,d]	spicy, sour	4	1644	X	-	17	-	-
1-nonanol[F,b]	fatty-floral	9	1656		11	15	35	18
3-methylbutyl octanoate[A,C,F,P,j]	oily	9	1673		44	50	10	26
diethyl succinate[T,j]	fermented, floral	9	1704	X	-	15	55	-
ethyl-9-decenoate[A,j]	rose	5	1707	X	-	15	9	-
α-terpineol[A,C,F,T,b]	weak floral, spicy	5	1718	X	27	22	13	5
dodecanal[b]	floral, waxy	5	1729	X	27	24	9	32
3-mercaptohexyl acetate[F,O,j]	candy, cooked fruit	3	1740		-	22	47	-
unidentified	sugary, burnt	3	1761	X	16	-	5	8
1-decanol[j]	sweet, fatty	3	1771	X	24	38	10	35
ethyl 2-phenylacetate[T,C,F,S,O,j]	rose, floral	5	1779	X	24	25	12	35
unidentified	spicy, cumin-like	4	1798		-	-	29	13
unidentified	walnut, fruity	6	1818	X	20	24	14	3
β-damascenone[A,C,G,J,O,P,i]	honey, sweet	3	1831	X	26	34	22	55
2-methoxyphenol (guaiacol)[C,P,d]	smokey, burnt	6	1865		21	24	41	47
(*E*)-whiskey lactone[A,P,j]	oily, rancid	9	1910		-	12	20	-
2-phenylethanol[A,C,G,T,j]	rose, spicy	5	1921	X	39	45	5	26
(*Z*)-whiskey lactone[A,C,F,G,j]	sweet, coconut	3	1971		33	53	49	38
γ-nonalactone[d]	rotten old fruit	6	2018	X	18	-	100	-
4-ethyl-2-methoxy-phenol[A,C,F,G,J,P,j]	earthy, spicy	6	2036		28	52	14	-
2,5-dimethyl-3(2*H*)furanone[d]	sugary, fruity	3	2044	X	-	-	39	20
p-cresol[A,G,J,O,d]	smokey	6	2076		27	-	-	10
octanoic acid[J,h]	rotten fruit	6	2089	X	-	11	14	-
unidentified	vitamin, medicine	6	2097		-	14	32	9
homofuraneol[A,C,G,O,P,d]	sulfury, smokey	6	2109		18	-	50	-
2-methoxy-4-propyl-phenol[j]	woody, medicine	8	2174		13	17	50	15
sotolon[A,C,J,P,d]	curry	4	2190		13	-	-	-
4-ethenyl-2-methoxy-phenol[J,j]	peppery, spicy	4	2207	X	27	39	-	44
decanoic acid[P,d]	sour, fatty	9	2270	X	-	9	-	11

[a] Aroma intensities normalized to most intense peak in all four wine types. Average aroma intensities were normalized with most intense aroma = 100; the hyphen indicates a compound not detected. Identifications were confirmed using standards from the following sources. [b] Sun Pure. [c] Lancaster. [d] Aldrich. [e] Fluka. [f] Acros. [g] Fischer. [h] Ultra Science. [i] Givaundan Roure. [j] Tentatively identified based upon literature LRI values and similar aroma charactersitics. Identification notes: Superscripts indicate the named compound also reported in similar wines in the following sources: A, ref *40*; C, ref *6*; F, ref *14*; G, ref *1*; I, ref *13*; J, ref *41*; O, ref *42*; P, ref *43*; and T, ref *44*.

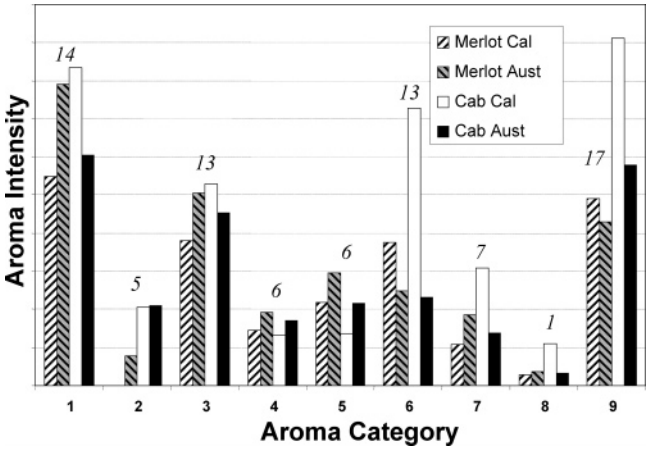

Figure 1. Aroma intensities grouped by sensory group. Aroma category: 1, fruity; 2, sulfury; 3, caramel, cooked; 4, spicy, peppery; 5, floral; 6, earthy; 7, pungent, chemical; 8, woody; and 9, green, vegetative, and fatty. The italicized numerals above the bars in each category indicate the number of aroma compounds in that aroma category.

wines including Merlot and Cabernet. All five of these compounds are also listed in **Table 2**.

All but 10 of the 74 aroma peaks reported in **Table 2** were initially identified by matching LRI values with aroma descriptors. Identifications were also based upon whether the compound had been previously reported in a red wine with a similar LRI (wax) value. **Table 2** contains a column indicating whether the identification could be confirmed by a full scan MS spectral match or from at least three selected ion chromatograms producing a peak at the same retention time as a standard. Compounds reported in previous wine studies are denoted by a superscript letter, which identifies the particular study. Most compounds have been reported in earlier studies, and no single study contained more than 40% of the aroma components reported in this study.

Wine Aroma Categories. With over 70 aroma components of wide-ranging intensities and no single character impact compound, it is difficult to predict the overall aroma impact of these wines from the sheer size of the data. To estimate overall wine aroma, the aroma active compounds were grouped into nine odor categories based on similar odor descriptors. The individual intensities were totaled to produce a group or category intensity, and the results were graphed in **Figure 1**. The nine categories were modeled from the widely employed wine aroma wheel (*37*).

Intensity patterns in the category data suggest that the major aroma characteristics of these wines would consist of fruity, green, and caramel aroma characteristics. Earlier sensory studies (*18*) using descriptive analysis on nonaged Merlot and Cabernet wines found that caramel, rose, and leather were the most important sensory descriptors for these wines. Fruity was the single most intense aroma category shown in **Figure 1**. This is consistent with the large number of esters, 29, identified in the MS portion of the study. Sensory flavor profile studies of Merlot and Cabernet wines (*38*) report fruity character as one of the most significant flavor characteristics. Categories 9 (green, vegetative, fatty) and 3 (caramel, cooked) were also major aroma categories in the current study. It should be kept in mind that these category intensity values were obtained from the sum of individual aroma compounds separated from others and the wine matrix. When combined, synergy, suppression, and matrix effects may alter the intensities of these descriptors. However, the favorable matching of these GC-O category summaries with published sensory studies suggests that the approach is valid.

The aroma category assigned to each of the 74 aroma active compounds is listed in **Table 2**. Most of the aroma compounds were easily assigned one of the nine aroma categories as their sensory descriptions directly fit one category. However, a few aroma components were difficult to assign a single category in that their descriptors sometimes fit two categories or were not obvious candidates for any category. An example of the first type can be found for the unidentified compound (LRI 887), which was described as both fruit and sulfury. Because each sample was sniffed at least six times, the category assignment was based upon the descriptor observed most often. In this case, sulfur was used more than fruity, and thus, the compound was assigned to the sulfur category. In situations where none of the nine categories names were employed as descriptors, the category assignment was based on the similarity or association of the descriptor. For example, five aroma compounds were described as rancid (see **Table 1**) and were assigned to category 9, as rancid is often associated with fatty.

Comparison of Merlot and Cabernet Aromas. Although the general patterns of aroma category intensities were similar for all four wines, there were subtle differences between the wines. In terms of MS data, the Merlot total nonethanol TIC peak areas were almost twice as large as the Cabernet totals. As previously mentioned, the California Cabernet was the most dissimilar of the four wines. Although the relative pattern of the aroma category intensities was similar to the other wines, the total odor intensity was 40−65% higher. Ironically, this wine had the lowest total TIC peak area. The California Sauvignon had a greater number of aroma components than the other three wines, which also contributed to the greater overall category intensity scores. The uniquely high values for earthy (category 6) and green/fatty (category 9) suggest that the California Cabernet wine was subjected to either more oak contact time or greater skin contact time. Of these two possibilities, the latter seems most probable.

Kotseridis and co-workers reported (*18*) that the aroma of Merlot and Cabernet wines could be differentiated by the intensity of the caramel descriptor and specifically HDMF plus HEMF. The results from this study would also support the contention that these are differentiating compounds. As shown in GC-O **Table 2**, HDMF was not observed in either Merlot wine but was observed in both Cabernet wines.

Comparison of Most Intense Odorants. One of the primary reasons for this study was to determine why there was so little agreement in the earlier studies (*6*, *19*) with respect to the major aroma impact compounds in wines of such commercial importance. Furthermore, the classes of compounds listed were very dissimilar. Four ethyl esters were listed among the 11 most intense odorants in the Spanish study (*6*). No esters were included in the corresponding French study. The most intense odorants in the French study (*19*) consisted primarily of alcohols, acids, furans, and a single ketone.

The three intense aromas common to the two earlier GC-O studies, 2-phenylethanol, 3-methyl-1-butanol, and β-damascenone, were also found to be among the most intense aromas in this study as well. There were other similarities with earlier reports. The current study and the French study (*19*) both list 3-methylbutanol and acetic acid among the most intense odorants. Acetic acid is only listed in the Spanish study with no indication of intensity.

The differences between the earlier studies and the current study extend beyond the most intense odorants. There are

significant differences in total number and types of aroma active compounds observed. Lopez and co-workers (*6*) observed 85 aroma components and identified 63 in their GC-O study of Spanish Merlot and Cabernet wines. Their total number of aroma components was similar to the 74 volatiles observed in this study. However, only 33 of their identified aroma components were also found in the current study. Of the 48 aroma compounds reported by Kotseridis and co-workers in their GC-O study of French Merlot and Cabernet wines (*19*), 18 were also observed in this study. The most likely explanation for this limited agreement is probably due to the different procedures used to extract volatiles from the wines. Both of the previous studies employed solvent extraction to remove aroma volatiles from the wine whereas this study employed static headspace using SPME.

Furthermore, previous studies employed different extracting solvents, extracting times, and extraction temperatures. Volatiles from the Spanish wines were extracted with freon 11 in a continuous mode for 24 h at 28 °C. Volatiles from the French wines were extracted with dichloromethane at 1 °C under nitrogen for 30 min with stirring in a batch process. Freon 11 is fairly nonpolar as compared to dichloromethane. The polarity, contact time, and extraction temperature differences are large enough to suggest that there would be major differences in the kinds and amounts of volatiles extracted from the wines.

It has been reported (*25*) that extracts prepared according to classic solvent extraction lack several characteristic wine odors and have additional unpleasant and nauseous odors absent in the original wine. Lopez and Gomez (*26*) compared the extraction efficiencies of freon 11 and dichloromethane and found significant differences in the extraction efficiencies of the two solvents for wine volatiles. Castro and co-workers (*39*) found similar volatile recoveries from continuous liquid−liquid extraction (pentane and diethyl ether) and SPME.

The results from this study suggest that Merlot and Cabernet wines share many aroma impact compounds in common even when produced in different years from disparate geographic regions.

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