

Impact Odorants of Different Young White Wines from the Canary Islands

RICARDO LÓPEZ,[†] NATALIA ORTÍN,[†] JUAN PEDRO PÉREZ-TRUJILLO,[§]
 JUAN CACHO,[†] AND VICENTE FERREIRA^{*,†}

Department of Analytical Chemistry, Faculty of Sciences, University of Zaragoza,
 50009 Zaragoza, Spain, and Department of Analytical Chemistry, Nutrition and Bromatology,
 University of La Laguna, 38201 La Laguna, Tenerife, Spain

Five young monovarietal white wines from the Canary Islands made from Gual, Verdello, Marmajuelo, white Listán, and Malvasia grape cultivars were studied to determine the characteristics of their most important aromas and the differences among them. The study was carried out using gas chromatography–olfactometry (GC-O) to detect the potentially most important aroma compounds, which were then analyzed quantitatively by gas chromatography–flame ionization detection and gas chromatography–mass spectrometry. The strongest odorants in the GC-O experiments were similar in all cases, although significant differences in intensity between samples were noted. Calculation of the odor activity values (OAVs) showed that 3-mercaptohexyl acetate was the most active odorant in the Marmajuelo and Verdello wines, as were 3-methylbutyl acetate in the Gual wine, β -damascenone in the Malvasia wine, and ethyl octanoate in the white Listán wine. However, the most important differences between varieties were caused by the three mercaptans (3-mercaptohexyl acetate, 3-mercaptohexanol, and 4-methyl-4-mercapto-2-pentanone) and the vinylphenols (4-vinylphenol and 2-methoxy-4-vinylphenol). The correlation between the olfactometric values and the OAVs was satisfactory in the cases when the compound eluted in the GC-O system was well isolated from other odorants and had aromatic importance and the OAVs for the different wines were sufficiently different.

KEYWORDS: Aroma; flavor; wine; OAV; GC-O; GC-MS; Verdello; Marmajuelo; Malvasia; Listán blanco; Gual

INTRODUCTION

The wine-making industry in the Canary Islands is currently in full growth and has two peculiarities. First, the climate is very different from the Mediterranean climate in which vines were first grown. Second, the fact that the Canaries are a group of islands has permitted the conservation of some grape varieties introduced from Europe prior to the phylloxera epidemic. Some of these varieties are still cultivated in Spain and Portugal (the Malvasia grape cultivar), but the cultivation of others ceased during the 20th century (Listán blanco) as they gave way to more productive or more commercial varieties (1). The application of modern enological techniques to the production of these wines has made it possible to obtain wines with interesting aromatic characteristics, which are studied in the present paper.

Previously published papers about the nature of wine odorants have used the olfactometric strategy known as aroma extract dilution analysis (AEDA) (2) for hierarchizing the odorants of wine (3, 4). Although this technique has proved to be highly efficient in providing a hierarchy of the odorants of a product,

it is not very sensitive to differences between different products, particularly if a small number of judges is used (5). This theoretical observation is confirmed by the results obtained in a recent study in which AEDA was combined with the measurement of the intensity of the odorants at different dilutions (6). It was found that intensity data provide much more information than the flavor dilution factors derived from an AEDA experiment, although it also revealed that dilution plays an all-important part in detecting the differences. Because of these observations, the gas chromatography–olfactometric (GC-O) technique used in the present work is based on the measurement of the intensity of the eluted odors by using a simple posterior rating scale. A basic study recently presented (7) showed that this technique is highly sensitive for discovering differences between odorant levels in different samples, which supports the interest shown by different authors in these techniques (8, 9).

Therefore, the work presented in this paper has two complementary objectives: first, to study the aroma composition of wines made with grapes from five different cultivars grown in the Canary Islands; and second, to explore the use of a GC-O technique based on the measurement of intensity to the study of such complex samples as these wines.

* Author to whom correspondence should be addressed (telephone 34 976762067; fax 34 976761292; e-mail vferre@unizar.es).

[†] University of Zaragoza.

[§] University of La Laguna.

MATERIALS AND METHODS

Reagents and Standards. Dichloromethane of HPLC quality was obtained from Fisher Scientific (Loughborough, U.K.), methanol of LiChrosolv quality was from Merck (Darmstadt, Germany), absolute ethanol (ACS quality) was purchased from Panreac (Barcelona, Spain), and pure water was obtained from a Milli-Q purification system (Millipore, Bedford, MA).

LiChrolut EN resins, prepacked in 200 mg cartridges (3 mL total volume) or in bulk, were obtained from Merck. The chemical standards were supplied by Aldrich (Gillingham, U.K.), Fluka (Buchs, Switzerland), Sigma (St. Louis, St. Louis, MO), Lancaster (Strasbourg, France), PolyScience (Niles, IL), Chemservice (West Chester, PA), Interchim (Modulon, France), International Express Service (Allauch, France), and Firmenich (Geneva, Switzerland), as in ref 10.

The 3-*tert*-butyl-4-hydroxyanisole (BHA) solution contained 10 mg of this compound per gram of ethanol, and it was used as an antioxidant. Sodium *p*-hydroxymercuribenzoate was purchased from Sigma, α,α,α -tris(hydroxymethyl)methylamine (TRIS) 99.9% from Aldrich, and cysteine 99% from Sigma.

Wine Samples. Young monovarietal white wines were made from Gual, Verdello, Marmajuelo, Malvasia, and Listán blanco cultivars. Wine samples were taken directly from the cellars to ensure that they consisted of a single grape variety. Wines were supplied by a winery in Tenerife (Spain) and were taken in December 2000.

Statistical Analysis. Two-way ANOVA was carried out with SPSS release 10.0 for Windows (Chicago, IL).

Wine Olfactometric Analysis. Polypropylene SPE tubes were packed with Lichrolut EN resins (Merck) to form a compact bed (1 g, 1 cm internal diameter). The beds were washed with 5 mL of dichloromethane, 10 mL of methanol, and 10 mL of a water/ethanol mixture (12% v/v). Sixty microliters of internal standard solution (2-ethyl-1-hexanol 600 mg/L in ethanol) and 70 μ L of BHA solution were added to 150 mL of wine. This volume of wine was passed through the SPE cartridge at \sim 2 mL/min. The SPE cartridge was then washed with 10 mL of water and dried by letting air pass through (negative pressure of 0.6 bar, 10 min). Analytes were recovered by elution with 10 mL of dichloromethane. The extract was concentrated first in a micro-Kuderna-Danish concentrator fitted to a three-ball Snyder column to a final volume of \sim 2 mL (48 °C) and then under a stream of pure N₂ up to 500 μ L.

These concentrated wine extracts were used in the GC-O study. Sniffings were carried out in a Thermo 8000 series GC equipped with a FID and a sniffing port (ODO-1 from SGE) connected by a flow splitter to the column exit. The column used was a DB-WAX from J&W (Folsom, CA), 30 m \times 0.32 mm with 0.5 μ m film thickness. The carrier was H₂ at 3 mL/min. One microliter was injected in splitless mode, 1 min being the splitless time. Injector and detector were both kept at 250 °C. The temperature program was the following: 40 °C for 5 min, raised at 4 °C/min to 200 °C. Six trained judges performed the olfactometric analysis of the extracts. Perceived intensity was measured according to a scale of five points: 5 = very intense odor; 4 = intense odor; 3 = clearly perceived odor; 2 = weak odor; 1 = very weak odor. The odorants were identified by comparison of their odors, chromatographic retention properties, and MS spectra with those of pure reference compounds.

Quantitative Analysis of Aroma Compounds. (a) *Major Compounds (Microextraction and GC-FID Analysis).* Quantitative analysis of major compounds was carried out using the method proposed and validated by Ortega et al. (11). In accordance with this method, 3 mL of wine and 7 mL of water were salted with 4.5 g of ammonium sulfate and extracted with 0.2 mL of dichloromethane. The extract was then analyzed by GC with FID detection. The GC was an HP5890 series II gas chromatograph with an HP76673A automatic sampler. The column was a DB-WAX 20 M from J&W, 60 m \times 0.32 mm with a 0.5 μ m film thickness. The carrier was H₂ at 3 mL/min, the split flow was 30 mL/min, and the injection was performed in split mode. Injector and detector were both kept at 250 °C. Three microliters was injected. The temperature program was as follows: 40 °C for 5 min, raised to 200 °C at 3 °C/min. Quantitative data were obtained by interpolation of relative peak areas in the calibration graphs built by the analysis of

synthetic wines containing known amounts of the analytes. 2-Butanol, 4-methyl-2-pentanol, 4-hydroxy-4-methyl-2-pentanone, and 2-octanol were used as internal standards.

(b) *Minor Compounds (SPE and GC-Ion Trap-MS Analysis).* This analysis was carried out using the method proposed and validated by López et al. (12). In accordance with the method, 50 mL of wine, containing 25 μ L of BHA solution and 75 μ L of a surrogated standards solution, was passed through a Lichrolut EN cartridge at \sim 2 mL/min. The sorbent was dried by letting air pass through (negative pressure of 0.6 bar, 10 min). Analytes were recovered by elution with 1.3 mL of dichloromethane. An internal standard solution was added to the eluted sample. The extract was then analyzed by GC with MS detection. The GC was a Star 3400CX fitted to a Saturn 4 electron impact ion trap mass spectrometer from Varian. The column was a DB-WAXetr from J&W, 60 m \times 0.25 mm with 0.5 μ m film thickness. The carrier was He at 1 mL/min. The temperature program was as follows: 40 °C for 5 min, raised to 230 °C at 2 °C/min. A 1093 septum-equipped programmable injector (SPI) from Varian was used. The program temperature of this injector was 30 °C for 0.6 min, raised to 230 °C at 200 °C/min. Three microliters of sample was injected. An *m/z* 35–220 mass range was recorded.

(c) *3-Mercaptohexyl Acetate, 3-Mercapto-1-hexanol, 4-Mercapto-4-methyl-2-pentanone, and 2-Methyl-3-furanthiol (SPE and GC-Ion Trap-MS Analysis).* One gram of Lichrolut EN resins was dry-packed in a 6 mL polypropylene cartridge. Resins were conditioned with 10 mL of methanol and then washed with 10 mL of a hydroalcoholic solution (13% ethanol v/v). Two hundred milliliters of wine containing 25 μ L of BHA solution was then passed through the bed of resins at a maximum speed of 4 mL/min. The bed was then washed with 200 mL of a solution of TRIS (2.42 g/100 mL, 40% methanol v/v, pH 7.2) and dried, and finally the odorants were eluted with 10 mL of dichloromethane.

This organic phase was extracted with four successive additions of 1 mL of a 1 mM *p*-hydroxymercuribenzoate solution in TRIS at pH 7.2. The four aqueous phases were combined and added with 600 μ L of a 200 mM cysteine solution in TRIS at pH 7.2. The aqueous solution was then extracted with three successive additions of 0.8, 0.4, and 0.4 mL of dichloromethane. The three organic phases were combined and dried over anhydrous sodium sulfate, and the extract was then concentrated under a stream of pure N₂ to 20 μ L.

This extract was analyzed by GC with MS detection. The GC was a CP3800 fitted to a Saturn 2200 electron impact ion trap mass spectrometer from Varian. The column was a DB-Waxetr from J&W, 60 m \times 0.25 mm \times 0.25 μ m film thickness. The carrier was He at 1 mL/min. The temperature program was the following: 40 °C for 5 min, then raised to 170 °C at 2 °C/min and, finally, to 230 °C at 20 °C/min. A 1079 PTV injector from Varian was used at 250 °C. Selected ion storage (SIS) from *m/z* 74 to 133 was used for 2-methyl-3-furanthiol, 4-mercapto-4-methyl-2-pentanone, 3-mercaptohexyl acetate, and 3-mercapto-1-hexanol with quantitative fragments *m/z* 120, 131, 87 + 88, and 82 + 83, respectively.

RESULTS AND DISCUSSION

Gas Chromatography—Olfactometry. The aroma of the monovarietal white wines of the Gual, Verdello, Marmajuelo, Listán blanco, and Malvasia varieties was first studied using GC-O, with a subsequent quantitative determination of some of the most important odorants. The results of the olfactometric experiments are given in **Table 1**. The data in this table are normalized olfactometric intensity values using a scale of 0–100 and, as each value has a defined confidence interval, the statistical significance of the observed differences can be estimated. An ANOVA (wine \times sniffer) was carried out on these data, which allowed the determination of those odorants for which olfactometric intensity differed significantly according to the corresponding grape variety (**Table 2**). **Table 3** completes the olfactometric experiments with the OAV of the quantified odorants.

Table 1. Odorants Found in Young White Wines from Several Varieties: Gas Chromatographic Retention Data, Olfactory Description, Chemical Identity, and Intensity Data Normalized to 100

RI	edor description	identity	Gual	Verdello	Marmajuelo	Listan	Malvas
<1000	fruity	ni ^d		14			36
<1000	green, anise, glue	ni					33
<1000	fruity, strawberry	ethyl isobutyrate ^a	67	53	67	53	33
<1000	butter, cream	2,3-butanedione ^a	44	28	39	33	42
1044	fruity	ethyl butyrate ^a	69	69	64	50	56
1063	gas, solvent	ni					30
1063	fruity	ethyl 2-methylbutyrate ^a	36	47	6	50	
1078	fruity, anise	ethyl 3-methylbutyrate ^a	58	50	50	61	25
1110	bitter, green	2-methylpropanol ^a	25	31	42	42	47
1121	gas, sunflower seed	ni	8	33		8	
1134	banana	3-methylbutyl acetate ^a	47	42	61	53	28
1158	grass	(Z)-3-hexenal ^b	53	28	33		36
1174	humid	ni	6		22	17	
1230	fusel	3-methylbutanol ^a	92	94	92	86	92
1258	fruity, anise	ethyl hexanoate ^a	75	75	81	75	61
1284	plastic, shoe store	ni	31	42	47	31	6
1291	plastic, shoe store	ni	28	17	19	22	19
1301	lemon	octanal ^c	6	8	6	11	6
1313	mushroom	1-octen-3-one ^a		42	14	19	47
1317	onion, meaty	2-methyl-3-furanthiol ^a	64	61	89	67	80
1364	rotten food	dimethyl trisulfide ^c			8	6	
1368	meaty	ni		11		14	6
1380	lemon, white flowers	ni	28	8	22		
1391	box tree	4-mercapto-4-methyl-2-pentanone ^a	53	56	53	8	47
1405	grass	(Z)-3-hexenal ^a	44	11	28	33	28
1415	gas, chlorine	ni	53	44	22	42	36
1431	fruity	ethyl octanoate ^a		25		17	3
1445	coffee, toasty	2-furfurylthiol ^a	58	75	54	53	58
1467	vinegar	acetic acid ^a	17	44	36	25	11
1469	baked potato	3-(methylthio)propanal ^a	64	39	61	31	42
1481	lemon, flowery	4-mercapto-4-methyl-2-pentanol ^c	6	31			31
1496	plastic	ni	39	33	19	44	36
1521	chlorine	ni	83	67	72	28	81
1545	green pepper	3-isobutyl-2-methoxypyrazine ^c			8		
1571	flowery, muscat	linalool ^a	44	69	53	67	69
1588	cheese	2-methylpropanoic acid ^a	36	50	44	42	39
1635	toasty, bitter almond	ni	69	47	61	64	64
1646	cheese	butyric acid ^a	89	72	69	72	86
1661	flowery, rose	phenyletanal ^a		17	22	6	11
1688	cheese	2-/3-methylbutyric acid ^a	81	94	81	75	83
1725	sweet, anise	ni	14	19		6	44
1739	box tree	3-mercaptohexyl acetate ^a	31	58	67	44	22
1744	cooked vegetable	3-(methylthio)propanol ^a	56	64	58	42	56
1837	flowery	2-phenylethyl acetate ^a	8	39	19		25
1841	baked apple	β -damascenone ^a	67	64	61	58	50
1869	cheese	hexanoic acid ^a	75	72	75	72	94
1875	sulfur	3-mercapto-1-hexanol ^a	25	33	44	28	
1884	phenolic	2-methoxyphenol ^a	17	28	25	33	25
1906	flowery	ethyl dihydrocinnamate ^a	19	14		6	14
1938	roses	2-phenylethanol ^a	75	67	67	67	61
2009	coconut	ni	17	39	14	22	
2023	curry	ni	22		19	14	
2024	bitumen, phenolic	ni		28		6	
2030	apricot	ni		19	8	31	39
2063	peach	γ -nonalactone ^a	42	42	17		56
2072	cotton candy	4-hydroxy-2,5-dimethyl-3(2H)-furanone ^a	72	83	78	58	81
2097	fatty acid	octanoic acid ^a	75	78	58	72	67
2111	cotton candy	5-ethyl-4-hydroxy-2-methyl-3(2H)-furanone ^a	44	25	25	19	47
2121	bitumen, animal	<i>p</i> -cresol ^c	19	33		17	19
2146	phenolic	2-methoxy-4-propylphenol ^c	17	6	11	22	8
2163	flowery	ethyl cinnamate ^a	8	36	6	17	11
2185	peach	γ -decalactone ^a	22	19	22	28	36
2198	clove	4-allyl-2-methoxyphenol ^a	56	58	44	39	25
2214	phenolic, spicy	4-ethylphenol ^a	33	44	22	36	
2230	smokey	2-methoxy-4-vinylphenol ^a	44	44	72	14	64
2230	lactone	ni	22	39		11	
2243	celery	3-hydroxy-4,5-dimethyl-2(5H)-furanone ^a	69	64	89	81	50
2270	honey	methyl anthranilate ^c	14				
2270	apricot	γ -undecalactone ^c		25	14	6	28
2320	fatty acid	decanoic acid ^a	86	78	86	78	64
2383	flowery	ni	25	39			
2396	dry fruit	ni		11	33	47	33
2427	almond shell	4-vinylphenol ^a	33	56	42	31	39
2510	smokey, phenolic	ni		25			

Table 1. (Continued)

RI	odor description	identity	Gual	Verdello	Marmajuelo	Listán	Malvas
2597	honey, pollen, roses	phenylacetic acid ^a	69	64	64	53	58
2612	vanilla	vanillin ^a	50	33	44	50	47
2654	vanilla	ni	14	22	14	8	17
2679	animal	ni	19	25	22		25
2699	flowery, clove, cinnamon	ni	17	31	8	11	28

^a Identification based on coincidence of GC retention and MS data with those of the pure compounds available in the laboratory. ^b Pure compound was not available, but GC retention and MS data were coincident with those reported in the literature. ^c Identification based on coincidence of chromatographic retention data and on the similarity of odors. The compound did not produce any clear signal in the mass spectrometer because of its low concentration. ^d Not identified.

Table 2. Odorants with Significant Differences in Perceived Intensity According to White Wine Varieties

	I_{\max}	$I_{\max} - I_{\min}$	p
compounds with $I_{\max} > 70$			
3-hydroxy-4,5-dimethyl-2(5H)-furanone	89	39	0.016
RI 1521 (chlorine)	83	55	0.0001
2-methoxy-4-vinylphenol	72	58	0.012
compounds with $70 > I_{\max} > 50$			
3-mercaptohexyl acetate	67	45	0.035
3-(methylthio)propanal	64	33	0.036
ethyl 3-methylbutyrate	61	36	0.036
3-methylbutyl acetate	61	33	0.011
4-allyl-2-methoxyphenol	58	33	0.015
4-mercapto-4-methyl-2-pentanone	56	48	0.002
(Z)-3-hexenal	53	53	0.028
(Z)-3-hexenol	53	42	0.029
ethyl 2-methylbutyrate	50	50	0.0001
compounds with $I_{\max} < 50$			
RI 2396 (dry fruit)	47	47	0.010
1-octen-3-one	47	47	0.001
RI 1284 (plastic, shoe store)	47	41	0.025
4-ethylphenol	44	44	0.036
RI 1725 (sweet, anise)	44	44	0.003
3-mercapto-1-hexanol	44	44	0.005
phenylethyl acetate	39	39	0.002
RI 2030 (apricot)	39	39	0.024
RI 2228 (lactone)	39	39	0.019
RI <1000 (fruity)	36	36	0.001
RI <1000 (green, anise, glue)	33	33	0.008
RI 1121 (gas, sunflower seed)	33	33	0.019
4-mercapto-4-methyl-2-pentanol	31	31	0.0001
RI 1380 (lemon, white flowers)	28	28	0.038
RI 2024 (bitumen, phenolic)	28	28	0.012
RI 2510 (smoky, phenolic)	25	25	0.011
ethyl octanoate	25	25	0.043
RI 1174 (humid)	22	22	0.027
RI 2270 (honey)	14	14	0.088

^a p wine: ANOVA experiment wine \times sniffer.

A total of 78 odorants were detected in the GC-O experiment. These odorants can be divided into three large groups according to their olfactometric intensities. The first group is made up of odorants that reached 70% of the maximum olfactometric intensity in at least one sample. This group of most intense odorants is made up of 14 components, 13 of which were identified. The group includes two alcohols (isoamyl and 2-phenylethyl), an ester (ethyl hexanoate), five acids (butyric, hexanoic, octanoic, decanoic, and 2-/3-methylbutyric); two sulfur compounds (2-methyl-3-furanthiol and 2-furfurylthiol), an enolone and a lactone [4-hydroxy-2,5-dimethyl-3(2H)-furanone and 3-hydroxy-4,5-dimethyl-2(5H)-furanone], one phenol (2-methoxy-4-vinylphenol), and an unidentified odorant, RI 1521 (chlorine). The intensities of these odorants in the different wines were similar and, in fact, significant differences were observed in only three cases (Table 2). 3-Hydroxy-4,5-dimethyl-2(5H)-furanone was perceived with less intensity in the Malvasia wine,

whereas 2-methoxy-4-vinylphenol and RI 1521 were less intense in the Listán blanco wine.

The second important group of odorants consisted of 21 compounds with an intensity in the 50–70% range, 19 of which were identified. Significant differences were found in 9 components, 4 of which deserve special attention due to the intensity of the differences: 3-mercaptohexyl acetate, 4-mercapto-4-methyl-2-pentanone, ethyl 3-methylbutyrate, and (Z)-3-hexenal (Table 2).

Finally, another 43 odors were found (see Table 1) with intensity values lower than 50% in all five samples. Twenty-three of these compounds were identified. Nearly half of the components of this group displayed significant differences in the intensity, perceived by the judges from one wine to another (Table 2). RI 2396, 1-octen-3-one, 4-ethylphenol, RI 1725, and 3-mercaptohexanol are especially noteworthy because of the absolute and relative magnitudes of the differences.

The most notable olfactometric differences between the samples are summarized in Table 4. The Malvasia wine has a minimum content of 3-mercaptohexanol and its acetate, of 4-ethylphenol, and of ethyl-2-methyl butyrate and a maximum content of 1-octen-3-one, RI 1521, and RI 1725. The Listán wine is characterized by minimum contents of 2-methoxy-4-vinylphenol, RI 1521, (Z)-3-hexenal, and 4-mercapto-4-methyl-2-pentanone. The Marmajuelo wine has maximum contents of 3-mercaptohexanol and its acetate and of 2-methoxy-4-vinylphenol and a minimum content of RI 1725. The Verdello wine has a maximum content of 4-mercapto-4-methyl-2-pentanone and 4-ethylphenol and a high intensity of 3-mercaptohexyl acetate. Finally, the Gual wine has a maximum content of (Z)-3-hexenal and a minimum content of 1-octen-3-one.

Odor Activity Value. Forty-three of the components identified in the olfactometric experiment were quantified, 31 of which were found at concentrations higher than their corresponding odor thresholds (Table 3). There was a great similarity among the samples. The 10 most potent aromas of each wine are practically the same, although the relative order varies considerably from one sample to another. The high OAVs of three of the thiols quantified (3-mercaptohexyl acetate, 4-mercapto-4-methyl-2-pentanone, and 3-mercapto-1-hexanol) in the Marmajuelo and Verdello samples are noteworthy if compared with data published by other authors (13). This helps to explain the aromatic descriptions normally assigned to these wines. The aromas of Verdello and Marmajuelo wines are usually described by wine tasters as being reminiscent of the box tree, citric fruits, or unripe fruit, which is in agreement with the high level of mercaptohexyl acetate in these wines. On the other hand, Malvasia wine is usually described as flowery, sweet, and fruity, which can be attributed to the high β -damascenone concentration and low concentration of thiols. The fruity aroma of Gual wine and Listán wine seems to be basically due to their relatively high content of ethyl esters and 3-methylbutyl acetate. Also noteworthy is the high concentration of β -damascenone in these

Table 3. Odor Activity Values^a of Odorants^b Found in Young White Wines from Several Varieties

	Gual	Verdello	Marmajuelo	Listán	Malvasía	av	odor threshold ^c (μg/L)
3-mercaptohexyl acetate	95	287	321	80	29	162	0.004 (23)
β-damascenone	67	115	113	103	188	117	0.05 (3)
ethyl octanoate	111	96	91	164	76	108	5 (20)
3-methylbutyl acetate	135	91	158	64	79	105	30 (3)
ethyl hexanoate	63	58	73	73	45	62	14 (20)
2-methoxy-4-vinylphenol	36	76	17	8.5	43	36	40 (3)
3-methylbutyric acid	36	54	27	33	28	36	33 (20)
4-mercapto-4-methyl-2-pentanone	41	41	48	<13	23	33	0.0008 (23)
ethyl butyrate	30	27	35	33	23	30	20 (3)
octanoic acid	20	16	24	26	13	20	500 (20)
butyric acid	13	15	18	23	16	17	173 (20)
hexanoic acid	17	13	19	22	12	17	420 (20)
3-mercapto-1-hexanol	17	7.0	44	4.3	1.8	15	0.06 (23)
ethyl acetate	16	16	17	13	11	14	12270 (24)
2-methyl-3-furanthiol	10	7.0	19	5.4	7.2	9.7	0.005 (4)
2-methylbutyric acid	8.4	14	6.0	7.1	8.2	8.7	33 (20)
propanoic acid	4.3	9.9	5.5	5.9	14	8.0	8100 (24)
3-methylbutanol	5.8	6.9	4.3	6.9	4.5	5.7	30000 (3)
4-vinylphenol	2.3	12	0.8	1.3	5.0	4.3	180 (25)
ethyl isobutyrate	2.6	7.3	3.0	4.7	2.7	4.1	15 (20)
ethyl 3-methylbutyrate	2.7	5.7	2.3	6.8	1.8	3.9	3 (20)
linalool	1.4	5.5	1.0	1.7	4.4	2.8	15 (20)
2-phenylethanol	1.4	6.2	1.1	2.5	2.8	2.8	14000 (20)
decanoic acid	1.7	1.3	2.1	1.8	1.5	1.7	1000 (20)
2,3-butanodione	2.4	1.0	1.0	1.0	2.6	1.6	100 (3)
2-phenylethyl acetate	1.3	1.8	1.3	0.8	1.9	1.4	250 (3)
ethyl cinnamate	0.6	2.7	<0.1	1.1	2.1	1.3	1.1 (20)
3-(methylthio)propanol	0.6	1.7	0.5	1.4	0.8	1.0	1000 (20)
2-methylpropanol	0.9	1.2	0.9	0.8	0.8	0.9	40000 (3)
4-allyl-2-methoxyphenol	1.4	1.1	<0.1	0.5	0.6	0.7	6 (20)
2-methylpropanoic acid	0.4	1.1	0.4	0.4	0.6	0.6	2300 (20)
acetic acid	0.8	0.6	0.6	0.3	0.5	0.6	200000 (3)
(Z)-3-hexenal	0.6	0.2	0.5	0.6	0.5	0.5	400 (3)
γ-nonalactone	0.5	0.6	0.4	0.4	0.5	0.5	30 (26)
phenyletanal	0.5	0.6	<0.1	0.3	0.5	0.4	5 (27)
ethyl dihydrocinnamate	0.3	0.7	0.2	0.2	0.5	0.4	1.6 (20)
ethyl 2-methylbutyrate	0.2	0.6	0.2	0.4	0.2	0.3	18 (20)
4-ethylphenol	<0.1	<0.1	<0.1	0.7	<0.1	0.1	140 (24)
2-methoxyphenol	0.1	<0.1	<0.1	<0.1	0.1	<0.1	10 (20)
γ-decalactone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	88 (24)
methyl anthranilate	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	3 (28)
phenylacetic acid	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1000 (29)
vanillin	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	200 (3)

^a Mean data calculated with two samples of the same wine. Standard deviation below 10% for all cases with the exceptions of vanillin (16%) and 3-mercaptohexyl acetate, 3-mercapto-1-hexanol, 4-mercapto-4-methyl-2-pentanone, and 2-methyl-3-furanthiol (20–25%). ^b Compounds listed in **Table 1** and not quantified: (Z)-3-hexenal, octanal, 1-octen-3-one, dimethyl trisulfide, 2-furfurylthiol, 4-mercapto-4-methyl-2-pentanol, 3-isobutyl-2-methoxypyrazine, 4-hydroxy-2,5-dimethyl-3(2H)-furanone, 5-ethyl-4-hydroxy-2-methyl-3(2H)-furanone and 3-hydroxy-4,5-dimethyl-2(5H)-furanone. ^c Reference from which the value has been taken is given in parentheses. In refs 23 and 24 thresholds were calculated in a 12% water/ethanol mixture; in ref 3 the mixture was 10% in ethanol; in ref 20 the matrix was a 10% water/ethanol solution containing 7 g/L glycerol at pH 3.2; in ref 4 the matrix was a 10% water/ethanol solution at pH 3.2; in ref 25 the matrix was a synthetic wine containing 12% ethanol, 8 g/L glycerol, and different salts; in ref 27 the mixture was 11% in ethanol, 4 g/L tartaric acid, at pH 3.5; in refs 28 and 29 the matrix was water; in ref 26, a 10% water/ethanol solution containing a Chenin Blanc aroma extract was used.

Table 4. Components Showing the Greatest Differences in the Olfactometric Experiment

identity	Gual	Verdello	Marmajuelo	Listan	Malvasia
2-methoxy-4-vinylphenol	44	44	72	14	64
RI 1521	83	67	72	28	81
3-mercaptohexyl acetate	31	58	67	44	22
4-mercapto-4-methyl-2-pentanone	53	56	53	8	47
(Z)-3-hexenal	53	28	33	0	36
ethyl 2-methylbutyrate	36	47	6	50	0
RI 2396	0	11	33	47	33
1-octen-3-one	0	42	14	19	47
RI 1725	14	19	0	6	44
4-ethylphenol	33	44	22	36	0
3-mercapto-1-hexanol	25	33	44	28	0

samples, higher than that reported for other white or rosé wines (3, 4). The warm climate of the Canary Islands may have an

influence on the accumulation of the precursors of this component and their subsequent hydrolysis (14, 15).

The relationship between the intensity of an odor and the logarithm of the concentration of the odorant is in most cases a sigmoid (7, 16). The central part of such a sigmoid can be represented by a linear function ($I = n \log C + b$), which is the well-known Fechner law. After this law, differences in odor intensity observed between two solutions of an odorant present at different concentration (C_1 and C_2) are not related to the arithmetic difference of concentration ($C_1 - C_2$) but to the ratio of such concentrations (C_1/C_2). As the OAV is just a concentration normalized to the odor threshold, OAVs cannot be compared by subtraction. Rather, the parameters to be considered are the ratio between the OAVs of the different samples and the standard deviation of the logarithms of the OAVs. These values can be seen in **Table 5**, and some important conclusions can be drawn. The components with the greatest capacity to introduce modifications in the aromas are three thiols, 3-mercaptohexanol, its acetate, and 4-methyl-4-mercapto-2-pentanone,

Table 5. Compounds That Introduce the Greatest Differences in Aroma Measured by the Quotient between the Maximum/Minimum OAV and the Standard Deviation (in Logarithmic Scale) of the OAVs

	OAV_{max}/OAV_{min}^a	$10^{SD(\log(OAV))}$
3-mercapto-1-hexanol	22.0	3.4
3-mercaptohexyl acetate	11.1	2.7
2-methoxy-4-vinylphenol	8.9	2.3
4-mercapto-4-methyl-2-pentanone	8.0	2.4
4-vinylphenol	6.0	2.8
2-methyl-3-furanthiol	3.5	1.6
ethyl 3-methylbutyrate	3.4	1.8
propanoic acid	3.3	1.6
2-phenylethanol	3.1	2.0
ethyl isobutyrate	2.8	1.6
β -damascenone	2.8	1.4
linalool	2.8	2.1
3-methylbutyl acetate	2.5	1.5
2-methylbutyric acid	2.3	1.4
ethyl octanoate	2.2	1.3
octanoic acid	2.0	1.3
3-methylbutyric acid	2.0	1.3
hexanoic acid	1.8	1.3
butyric acid	1.8	1.2
ethyl hexanoate	1.6	1.2
3-methylbutanol	1.6	1.3
ethyl acetate	1.5	1.2
ethyl butyrate	1.5	1.2
ethyl cinnamate	1.4	1.6
2,3-butanedione	1.3	1.7
decanoic acid	1.1	1.2
2-phenylethyl acetate	1.0	1.3

^a If $OAV_{min} < 2$, then $(OAV_{max})/2$.

and the two quantified vinylphenols. The ratio between the maximum and the minimum OAVs was >6 in all cases. Whereas the dependence of thiols on the grape variety has been clearly demonstrated (13, 17), the differences in the levels of phenols may be due to occasional contamination (18, 19). A second group is made up of the components with a maximum/minimum OAV ratio between 2.5 and 6. This group includes β -damascenone, linalool, and most of the fermentation components associated with the metabolism of amino acids. The moderate dependence of all these components on the grape variety is in agreement with recently reported observations (20, 21). The last group is composed of the aromas generated in the metabolism of fatty acids by yeasts, such as fatty acids and their ethyl esters. Some of these compounds have high OAVs, but the maximum/minimum OAV ratio is well below 2.5, which confirms that the influence of grape variety on the synthesis of these components is of secondary importance.

Comparison between Gas Chromatography—Olfactometry and Odor Activity Value. As the olfactometric data given in Table 1 were obtained by studying an extract rather than a fraction of the headspace, no clear correlation can be established between the data in Tables 1 and 3. In fact, the importance of the most soluble and least volatile components in Table 1 is clearly overestimated. For instance, 3-methylbutanol and numerous fatty acids are the most intense odorants in Table 1, which is not in agreement with the OAV data reported in Table 3. This effect has been reported previously (22) and has as a consequence that the actual importance of unidentified odorants cannot be estimated from GC-O data.

However, a comparison between Tables 2 and 5 shows that the olfactometric and concentration values are in good agreement, at least for components for which significant differences were detected from one sample to another. The study of the correlation between the olfactometric value of a component and

Table 6. Correlation Coefficients between the Olfactometric Intensity (Table 1) and the OAV or Its Logarithm (Table 3) for Components with Significant Differences in the OAV

	r	$r(\log)$
3-mercapto-1-hexanol	0.70	0.83
3-mercaptohexyl acetate	0.94	0.94
2-methoxy-4-vinylphenol	0.18	0.40
4-mercapto-4-methyl-2-pentanone	0.90	0.98
4-vinylphenol	0.86	0.67
2-methyl-3-furanthiol	0.72	0.67
ethyl 3-methylbutyrate	0.59	0.66
2-phenylethanol	0.26	0.12
ethyl isobutyrate	0.07	0.07
β -damascenone	0.91	0.89
linalool	0.72	0.75
3-methylbutyl acetate	0.54	0.47
2-methylbutyric acid	0.90	0.87

its instrumentally determined OAV is examined and makes it possible to extract some noteworthy observations (Table 6).

(1) The correlation between the two values is very satisfactory if the odor is clearly separated from others in the GC-O and if the difference between the concentrations is high, as occurs with 3-mercapto-1-hexanol, mercaptohexyl acetate, and 4-methyl-4-mercapto-2-pentanone. In these cases the correlation coefficients between GC-O and instrumental data ranged from 0.83 to 0.95 (Table 6).

(2) When the odor appears in a complex area of the chromatogram, the correlation is rather poor due to the difficulty of measuring the intensity of the odor correctly. This is the case for 2-methoxy-4-vinylphenol, which coeluted with a substance that smells of lactone (Table 1). Another case is ethyl 2-methylbutyrate, which could not be detected in Malvasia wine because of the coelution of an unknown odor (Table 1). This lack of detection made us include the compound in Table 2 when the data in Table 3 indicate that the levels of this component vary very little from one sample to another. Another similar case is ethyl isobutyrate, the poor correlation being due to coelution with diacetyl.

(3) The interference has less effect when the characteristics of the coeluted odors are very different, as with 2-methyl-furanthiol. Although this compound virtually coeluted with 1-octen-3-one, the judges were able to measure its intensity correctly.

In conclusion it can be said that the most important odorants of the five studied wines have been identified and most of them quantified. In addition, the study has revealed that the posterior intensity rating GC-O technique used is a powerful method to detect differences between different samples or products.

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