Analytical Characterization of the Aroma of Five Premium Red Wines. Insights into the Role of Odor Families and the Concept of Fruitiness of Wines

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The aroma profile of five premium red wines has been studied by sensory descriptive analysis, quantitative gas chromatography−olfactometry (GC-O), and chemical quantitative analysis. The most relevant findings have been confirmed by sensory analysis. Forty-five odorants, including the most intense, were identified. At least 37 odorants can be found at concentrations above their odor threshold. A satisfactory agreement between GC-O and quantitative data was obtained in most cases. Isobutyl-2-methoxypyrazine, (*E*)-whiskey lactone, and guaiacol were responsible for the veggie, woody, and toasted characters of the wines, respectively. The sweet-caramel notes are related to the presence of at least five compounds with flowery and sweet notes. The phenolic character can be similarly related to the presence of 12 volatile phenols. The berry fruit note of these wines is related to the additive effect of nine fruity esters. Ethanol exerts a strong suppression effect on fruitiness, whereas norisoprenoids and dimethyl sulfide enhance fruity notes.

INTRODUCTION

In the past decade, different works concerning the overall identification of impact odorants in a variety of young and aged red wines by gas chromatography−olfactometry (GC-O) have been published. Most of these studies have focused on red varieties such as Cabernet Sauvignon, Merlot, Grenache, Tempranillo, and Pinot Noir and have shown that the vast majority of wine volatiles have little to no aroma activity and that specific aromatic profiles can be explained by relatively few odor compounds. In such works, the most common procedures for the preparation of wine extracts were liquid−liquid extraction (*1−3*), solid-phase extraction (SPE) (*4, 5*), or solid-phase microextraction (SPME) (*6, 7*). Although the quantitative GC-O technique employed in some of the studies above-mentioned showed a great potential, its success as a tool to identify consistent differences between samples was seriously limited by excessively complex olfactograms, particularly in those wines of highest quality and complexity. This fact was a direct consequence of the extraction procedure employed, as in such extracts a high number of odorants were extremely concentrated, reaching intensities near saturation in the sniffing port (*4, 5*).

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Table 1. Aroma References Used by the Sensory Panel

attribute	reference standard[a]
raisin	8–10 cut up raisins soaked for 15 min
berry fruit	6 mL each of strawberry, raspberry, and blackberry jam
veggie	5 g of sliced bell pepper soaked for 15 min + 5 mL of brine-canned green beans
woody	5 mL of oak essence
toasted	1 drop each of samples 48 (toast) and 49 (roasted almonds) of "Le Nez du Vin" Jean Lenoir
alcohol	2 mL of 95% ethanol
reduction	1 drop each of samples 6 (sulfur) and 9 (cabbage) of "Le Nez du Vin" Jean Lenoir
sweet	1 mL of prune juice + 5 mL of brine from canned figs
phenolic	100 mg of shoe polish + 2 cm × 2 cm of leather soaked for 30 h

[a] Quantities specified are those added to 40 mL of neutral red wine.

On the other hand, recent research carried out in our laboratory has evidenced that, by using a dynamic headspace technique in the preparation of wine extracts, it is possible to obtain relatively simple and clean olfactograms and to establish a hierarchy of the most important odorants according to their potential sensory impact. This technique has been successfully applied to characterize the aroma profile of young white wines from different varietals (*8, 9*).

One of the main aims of the present work is to determine, by using this novel dynamic headspace sampling technique and

Table 2. Odorants Found by GC-O in the Five Studied Wines[a]

DB-Wax (LRI)	DB-5 (LRI)	group code[b]	odor description	chemical identity[c]	ABA	MUR	POR	AMA	BOU	max−min
974		F	fruity	isopropyl acetate[d,5]	43	36	44	0	0	44
999	<800	F	fruity	ethyl propanoate[d,3]	37	10	33	0	0	37
1007	<800	F	fruity	ethyl 2-methylpropanoate[d]	73	74	80	0	0	80
1012	<800		butter, cream	2,3-butanedione[d]	82	70	64	75	87	23
1034	<800	F	solvent	isobutyl acetate[d]	37	53	63	50	40	26
1055	802	F	fruity	ethyl butyrate[d]	68	64	76	84	79	20
1060			garlic, sweaty	dimethyl disulfide[d,1]	46	5	55	0	0	55
1069	850	F	fruity	ethyl 2-methylbutyrate[d]	74	74	82	79	84	10
1079	<800		butter, cream	2,3-pentanedione[d,1]	38	48	0	0	56	56
1083	854	F	fruity, anise	ethyl 3-methylbutyrate[d]	65	79	72	38	71	41
1116	<800		fusel	isobutanol[d]	51	43	52	10	29	42
1128			fish	ni	23	0	40	0	0	40
1137	<800	F	banana	isoamyl acetate[d]	75	69	76	25	32	51
1152	941	F	fruity, anise	ethyl 2-methylpentanoate[d]	7	43	16	32	31	36
1206	969	F	fruity, anise	ethyl 4-methylpentanoate[d]	21	14	31	43	0	43
1224	<800		fusel	isoamyl alcohol[d]	83	82	88	79	79	9
1240			mushroom, grass	ni	0	0	0	0	35	35
1251	996	F	fruity, anise	ethyl hexanoate[d]	74	75	79	50	56	29
1282			synthetic, leather	ni	27	10	37	0	10	37
1297			lemon, ethanol	octanal[d,1] + furfuryl ethyl ether[d,6]	63	63	63	41	29	34
1308	975		mushroom	1-octen-3-one[e,2]	5	7	34	0	14	34
1315	860		meaty, onion	2-methyl-3-furanthiol[e,1]	79	62	59	0	14	79
1372	872		grass	1-hexanol[d]	16	41	25	10	29	31
1398	848		grass	(Z)-3-hexenol[d]	59	34	32	25	0	59
1408			fruity, licorice	ni	0	0	37	40	43	43
1422			solvent, rubber	ni	29	11	37	0	41	41
1429		F	licorice, anise	ethyl cyclohexanoate[d]	29	22	57	10	0	57
1439	907		coffee, toasted	2-furanmethanethiol[e,3]	56	22	46	18	0	56
1443	1094	V	pepper, earthy	3-isopropyl-2-methoxypyrazine[d,1]	66	48	53	0	0	66
1460	<800		vinegar	acetic acid[d,4]	56	63	76	84	87	31
1484			burned rubber, toasted	ni	14	18	7	43	0	43
1509	1172	V	pepper, earthy	3-sec-butyl-2-methoxypyrazine[d,1]	50	18	31	0	0	50
1535	1181	V	pepper, earthy	3-isobutyl-2-methoxypyrazine[d]	76	53	57	0	0	76
1560	1100	S	floral, muscat	linalool[d]	61	16	42	0	14	61
1632	1021		burnt bread	2-acetylpyrazine[e,2]	83	72	82	0	0	83
1641	822		cheese	butyric acid[d]	20	9	44	50	40	41
1660	1050	S	floral, honey	phenylacetaldehyde[d]	15	8	32	10	14	24
1682	878		cheese	2/3-methylbutyric acids[d]	78	69	86	74	79	17
1738	1181	S	honey, liqueur	ni	12	22	43	0	10	43
1833	1254	S	roses	2-phenylethyl acetate[d]	35	24	16	0	20	35
1838	1388		baked apple	β-damascenone[d]	62	71	66	82	79	20
1882	1089	P	smoky, hospital	guaiacol[d]	50	47	68	74	32	42
1907	1370	S	floral, pollen	ethyl dihydrocinnamate[d]	39	12	20	35	29	27
1939	1116		roses	β-phenylethyl alcohol[d]	72	65	84	89	53	36
1989	1134		coconut	(Z)-whiskey lactone[d]	78	67	67	71	43	35
2091		P	leather, phenolic	4-ethylguaiacol[d]	7	12	8	32	20	25
2113		P	wood, phenolic	ni	5	0	0	38	10	38
2129	1070	P	leather, spicy	m-cresol[d]	17	27	44	38	14	30
2179	1470		spicy, wood, phenolic	γ-decalactone[d] + ni	0	0	0	20	40	40
2226	1329	P	bitumen, leather	4-ethylphenol[d]	42	15	50	35	14	36
2237	1110		spicy	sotolon[d,1]	10	5	37	0	0	37
2612			honey, floral	phenylacetic acid[d]	6	5	0	20	32	32
2653	1560		vanilla, honey	ethyl vanillate[d]	6	6	42	18	14	36

[a] Gas chromatographic retention data (LRI in both DB-Wax and DB-5 columns), aromatic group codes, olfactory descriptor, chemical identity, modified frequency percentage (% MF), and differences between maximum and minimum % MF values of an odorant among the five wines. Abbreviations: ABA, Abadía de Retuerta; MUR, Grans Muralles; POR, Cims de Porrera; AMA, Amat; BOU, Bouza; ni, not identified. [b] Group codes: F, fruity; V, veggie; S, sweet-caramel; P, phenolic. [c] Source: 1, Aldrich; 2, Lancaster; 3, Fluka; 4, Panreac; 5, Sugelabor; 6, standard synthesized (see Materials and Methods). [d] Identification based on coincidence of gas chromatographic retention and mass spectrometric data with those of the pure compounds available in the laboratory. [e] Identification based on coincidence of chromatographic retention data and on the similarity of odor with pure reference standards. The compound did not produce any clear signal in the mass spectrometer because of its low concentration.

further quantitative GC-O, the odorants most likely involved in the aroma profile of different premium quality barrel-aged red wines, including two high-quality wines from Uruguay made with *Vitis vinifera* L. cv. Tannat. This variety is the major variety in Uruguay for the production of red premium wines (*10*); however, because of its small cultivation in the world, it has not been thoroughly studied. The volatile composition of young Tannat wine has been previously characterized by GC-MS analysis (*11*), and preliminary results for the sensory evaluation

of this variety have been recently reported (*12*, *13*). However, there are no published studies dealing with the odor active compounds of Tannat wines, which means that the number and nature of the odorants responsible for the characteristic bouquet of these wines are not known.

The second major aim of the present work is to understand how the different odorants of the wines interact to form the most important odor nuances of the wines, particularly the berry fruit note. This question, for the most part, remains unanswered.

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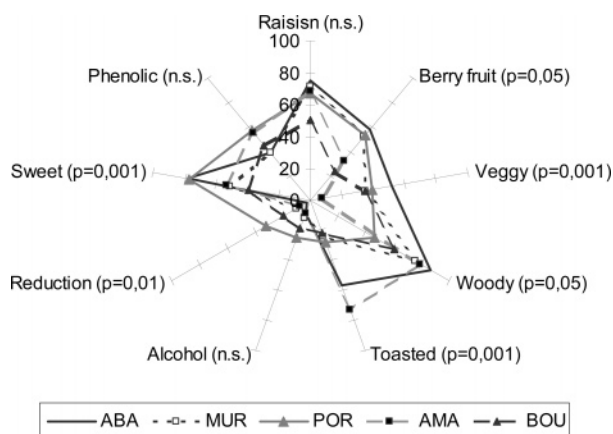
Figure 1. Diagram showing the aroma profile of the five studied wines. Abbreviations: ABA, Abadía de Retuerta; MUR, Grans Muralles; POR, Cims de Porrera; AMA, Amat; BOU, Bouza.

Previous research failed in finding any clear relationship between fruity esters and fruity notes in red wines (*14*), in other papers the models built for the fruity notes of red wines were not very satisfactory (*15*), and previous research based on classical reconstitution and omission tests failed in the identification of key odorants related to the fruity notes of red wines (unpublished results). The reasons for such failure may be diverse, namely, the aforementioned difficulty in establishing a clear hierarchy of odorants and the difficulty in determining all of the potentially relevant aroma compounds, and include also the fact that the aroma of these wines is particularly complex in terms of both the numbers of aroma compounds involved and the existence of complex interactions between odorants. Some examples of this complex picture have been recently presented by Atanasova et al. (*16–18*) and Segurel et al. (*19*). The first group of authors has demonstrated the existence of strong perceptual interactions between the fruity and woody characters of the wine, whereas the latter work has revealed an unexpected enhancing role played by dimethyl sulfide in the fruity notes of some red wines. Attending to all this, the present work seeks to combine the advantages of the new GC-O strategy, with comprehensive aroma chemical analysis and with sensory tests specifically designed to improve our understanding of the role of groups of odorants in the odor nuances of these red wines.

MATERIALS AND METHODS

Reagents and Standards. The chemical standards were supplied by Sigma (St. Louis, MO), Aldrich (Gillingham, U.K.), Fluka (Buchs, Switzerland), Lancaster (Strasbourg, France), PolyScience (Niles, IL), Interchim (Monlucon, France), Chem Service (West Chester, PA), and Firmenich (Geneva, Switzerland), as indicated in **Table 3**. Furfuryl ethyl ether was prepared by heating to 80 °C a mixture of the corresponding alcohol (100 mg), sodium hydride (100%, 100 mg), and iodoethane (1 mL) under a nitrogen atmosphere for 12 h. LiChrolut EN resins and prolypropylene cartridges were obtained from Merck (Darmstadt, Germany). Dichloromethane and methanol of LiChrosolv quality were from Merck; absolute ethanol and ammonium sulfate were from Panreac (Barcelona, Spain), and all of them were of ARG quality; pure water was obtained from a Milli-Q purification system (Millipore, Bedford, MA). Semiautomated solid-phase extraction was carried out with a VAC ELUT 20 station from Varian (Walnut Creek, CA). An alkane solution (C_8–C_{28}), 20 mg/L in hexane, was employed to calculate the linear retention index (LRI) of each analyte.

Wine Samples. *Spanish Wines.* Three premium Spanish aged red wines from different traditional Spanish Denominations of Origin (DO) were selected: Abadía de Retuerta Special Selection vintage 1998 (Tempranillo 75%, Cabernet Sauvignon 20%, and Merlot 5%), from

DO Ribera del Duero, aged for 18 months in barrels; Torres Grans Muralles vintage 1998 (Garnacha Tinta, Garnó, Sausó, and Mazuelo) from DO Conca de Barberá, aged for 12 months in barrels; and Cims de Porrera Classic vintage 1999 (70% Cariñena and 30% Grenache) from DO Priorat, aged for 17 month in barrels. The wines were chosen by five experts of the laboratory staff attending to their aroma quality. All of them were premium-quality wines that scored very high in different wine guides.

Uruguayan Wines. Two monovarietal red Tannat wines from 2000 and 2004 vintages were selected for this study. The Tannat Amat wine from the 2000 vintage was elaborated by Bodega Vinos Finos Juan Carrau in Cerro Chapeau (Rivera Province in northern Uruguay) and was aged in French oak barrels for 20 months. The second one, Tannat Bouza wine from vintage 2004, was elaborated by Bodega Bouza in Montevideo Province (southern Uruguay), and it was aged in French oak barrels for 8 months.

The sensory study, the GC-O analysis, and the quantitative determination were carried out in the 2 months after the selection of the wines. During this period, the bottles were stored at 4 °C in the dark.

Neutral and Dearomatized Wine for Model Sensory Tests. Two wine samples were used as the matrix for preparing synthetic mixtures of aromas: a red wine from Grenache (Monte Ducay, DO Cariñena, from the 2004 vintage) with a neutral aroma (score in berry fruit note <20% of the full scale), and this same wine previously dearomatized by adding 4 g of Licholut EN resins to 750 mL of wine and stirring during 12 h (*8*). The aroma of this dearomatized wine was of very low intensity and of neutral character. Its score in the berry fruit note was not significantly different from 0.

Sensory Descriptive Analysis of Selected Wines. The sensory panel was composed of six females and three males, 23–40 years of age, all of them belonging to the laboratory staff. All of them had extensive wine-tasting experience. Panelists attended five specific 1 h training sessions. In the first one, the panelists generated descriptive terms to define the wines. In sessions two and three, different aroma standards were presented and discussed by the panel. From these discussions, nine aroma terms (raisin, berry fruit, veggie, phenolic, toasted, woody, alcohol, sweet, and reduction) were selected for further descriptive analysis. The aroma reference standards employed to define each of these terms are listed in **Table 1**. In training sessions four and five, panelists scored the intensity of each attribute in three wines using a 7-point scale (0 = nondetected, 1 = weak, hardly recognizable note, 2 = clear but not intense note, 3 = intense note), half values being allowed. After the training period, wine samples were evaluated in duplicate during three formal sessions (three or four samples per session). In all cases, wines (20 mL at 20 °C) were served in coded, tulip-shaped wine glasses covered by glass Petri dishes. Samples were presented in a random order. Reference standards were smelled as necessary by the judges during each session. Data were processed by two-way analysis of variance with SPSS v. 11.5.

Sensory Experiments with Aroma Compounds. The test panel that carried out the sensory evaluation of different samples spiked with aroma compounds was composed of 12 subjects (8 women and 4 men, ranging from 23 to 45 years of age) belonging to the laboratory staff. All of them participated regularly in sensory tests. In all cases, samples (20 mL, 20 °C) were presented in a random order in coded tulip-shaped wine glasses covered with a Petri dish. The compounds for these assays were selected attending to the results of the GC-O and quantitative studies (maximum concentration was selected).

The first tests carried out were triangle tests in which the neutral wine, the dearomatized wine, or synthetic wines (mixtures of water/ ethanol at different levels containing 5 g/L tartaric acid, pH 3.5) were confronted with the corresponding spiked sample. When a significant difference was detected, the judges were asked to freely note the descriptors that had changed. In two cases ranking tests were also carried out.

GC-O Analysis. *Preparation of Wine Extracts.* Wine extracts were obtained by a dynamic headspace sampling technique (*8*). A standard SPE cartridge (0.8 cm internal diameter, 3 mL internal volume) filled with 400 mg of LiChrolut EN resins was first washed with 20 mL of dichloromethane and then dried by letting air pass through (negative pressure of 0.6 bar, 10 min). Such resins were selected because of their

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Table 3. Volatile and Aroma Compound Composition of the Five Studied Wines, Aromatic Group Codes, and Odor Thresholds (All Data Are Expressed as Micrograms per Liter)

compound	ABA	MUR	POR	AMA	BOU	group code[a]	source	odor threshold[b]
carbonyl compounds								
acetoine	30259	11304	16555	55900	18300		Aldrich	150000 (39)
2,3-butanedione	1649	2501	237	690	1000		Aldrich	100 (40)
furfural	29	8.8	30	28	31		Fluka	14100 (41)
5-hydroxymethylfurfural	nd[c]	5.8	11	3.4	3.4		Aldrich	100000 (42)
5-methylfurfural	6.5	7.9	34	14	33		Fluka	20000 (39)
phenylacetaldehyde	1.5	nd	9.9	nd	nd	S	Aldrich	1[d]
β-damascenone	0.84	0.23	0.98	3.5	3.0		Firmenich	0.05 (40)
α-ionone	0.33	nd	0.17	nd	0.67		Sigma	2.6 (41)
β-ionone	0.14	0.18	0.14	0.23	0.09		Sigma	0.09 (41)
syringaldehyde	28	18	62	109	69		Aldrich	50000 (42)
esters								
ethyl 2-methylpropanoate	254	168	315	98	30	F	Aldrich	15 (41)
ethyl 2-methylbutyrate	13	17	21	32	9.2	F	Fluka	18 (41)
ethyl 3-methylbutyrate	20	25	25	20	22	F	Fluka	3 (41)
ethyl cyclohexanoate	0.01	0.008	0.012	nd	nd	F	Alfa Aesar	0.001 (42)
ethyl 2-methylpentanoate	0.012	0.050	0.016	0.018	0.020	F	Alfa Aesar	0.003 (42)
ethyl 4-methylpentanoate	0.15	0.10	0.13	0.18	0.06	F	Aldrich	0.010 (42)
ethyl butyrate	170	75	94	69	70	F	Aldrich	20 (41)
ethyl hexanoate	227	76	100	29	31	F	PolyScience	14 (41)
ethyl octanoate	102	40	69	24	33	F	PolyScience	580 (39)
ethyl decanoate	15.0	4.1	8.2	6.6	6.2	F	PolyScience	200 (41)
ethyl 3-hydroxybutyrate	521	340	401	380	48	F	Aldrich	20000[d]
ethyl furoate	6.4	11	12	17	7.8	F	Fluka	16000 (41)
ethyl lactate	652152	169470	146478	462500	94000		Aldrich	154000 (39)
diethyl succinate	18945	17525	25192	31500	6240		Fluka	200000 (39)
ethyl cinnamate	0.75	0.43	nd	1.22	nd	S	Aldrich	1.1 (41)
ethyl dihydrocinnamate	0.54	0.28	0.23	nd	nd	S	Fluka	1.6 (41)
methyl vanillate	14	14	19	5.2	nd		Lancaster	990 (43)
ethyl vanillate	161	175	349	109	58		Lancaster	3000 (43)
ethyl acetate	22803	31500	37267	66600	10440		PolyScience	12270 (42)
butyl acetate	13	14	13	18	16	F	Probus	1800 (39)
isobutyl acetate	38	43	57	40	10	F	Chem Service	1600[d]
isoamyl acetate	141	156	221	120	132	F	Chem Service	30 (41)
phenylethyl acetate	16.0	36	41	29	21	S	Chem Service	250 (40)
alcohols								
1-butanol	2396	2002	2502	1999	1900		Aldrich	150000 (39)
isobutanol	57893	47966	89670	28700	33300		Merck	40000 (41)
isoamyl alcohol	235696	257993	277139	112800	118800		Aldrich	30000 (40)
benzyl alcohol	449	1859	126	70	80		Aldrich	200000[d]
1-hexanol	1478	1463	1180	780	1190		Sigma	8000 (41)
(Z)-3-hexenol	234	87	48	66	91		Aldrich	400 (41)
$h\iota\nu\delta$;1gβ-phenyl ethanol	46207	96292	79220	60300	58900		Fluka	14000 (41)
furfuryl alcohol	625	nd	101	nd	nd		Fluka	2000 (42)
methionol	1905	2468	1624	3750	3410		Aldrich	1000 (41)
volatile phenols								
guaiacol	18.2	9.24	15.1	47.3	9.24	P	Aldrich	9.5 (41)
eugenol	27	17	26	60	26	P	Aldrich	6[d]
(E)-isoeugenol	5.5	2.9	3.2	2.7	1.6	P	Lancaster	6[d]
4-vinylphenol	27	5.9	21	nd	nd	P	Lancaster	180 (44)
4-vinylguaiacol	57	95	334	30	19	P	Lancaster	40 (40)
4-ethylphenol	nd	174	12	133	39.0	P	Aldrich	440 (43)
4-ethylguaiacol	1.2	32	3.4	39	7.2	P	Aldrich	33 (41)
4-propylguaiacol	0.61	3.9	1.1	nd	nd	P	Lancaster	
2,6-dimethoxyphenol	91	64	73	198	46	P	Aldrich	570 (43)
4-allyl-2,6-dimethoxyphenol	35	26	33	73	8.6	P	Aldrich	1200 (42)
m-cresol	2.3	nd	2.5	4.8	2.5	P	Fluka	68 (41)
o-cresol	4.6	2.3	1.4	nd	6.5	P	Aldrich	31 (43)
vanillin	50	31	75	24	16		Aldrich	995[d]
acetovanillone	72	91	104	97	62		Aldrich	1000[d]
terpenes								
α-terpineol	24	13	13	17	14		Fluka	250 (41)
β-citronellol	2.9	1.4	2.6	1.2	6.6		Aldrich	100 (39)
linalool	10	2.0	3.9	nd	nd	S	Aldrich	25 (41)
geraniol	nd	nd	nd	3.2	0.72		Fluka	20[d]
lactones								
(Z)-whiskey lactone	164	149	135	151	141		Aldrich	67 (43)
δ-octalactone	8.3	13	4.6	5.	13		Lancaster	400 (42)
δ-decalactone	22	7.7	34	14	9.8		Lancaster	
γ-butyrolactone	33339	17347	34863	30200	22900		Aldrich	35000[d]
γ-nonalactone	3.1	15	5.1	8.9	12		Aldrich	30 (41)
γ-decalactone	3.6	2.2	4.9	73	45		Fluka	400 (41)
(E)-whiskey lactone	20	23	28	nd	3.8		Aldrich	790 (41)

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Table 3. (Continued)

compound	ABA	MUR	POR	AMA	BOU	group code[a]	source	odor threshold[b]
acids								
propanoic acid	2793	3020	3112	8450	5970		PolyScience	8100 (*39*)
butyric acid	nd	440	nd	nd	1360		PolyScience	173 (*41*)
2-methylpropanoic acid	2082	670	2037	3140	4260		Aldrich	50 (*42*)
2-methylbutyric acid	265	89.0	234	225	198		Aldrich	33 (*41*)
3-methylbutyric acid	1651	1860	1770	1670	2180		Aldrich	33 (*41*)
hexanoic acid	3328	2557	1031	2730	2730		PolyScience	420 (*41*)
octanoic acid	2135	1035	546	1910	1700		Fluka	500 (*41*)
decanoic acid	1355	92.8	359	2430	3010		PolyScience	1000 (*41*)
phenylacetic acid	25.0	55.3	114	108	63.0		Aldrich	1000 (*45*)
benzoic acid	nd	71	14	17.8	1.28		Aldrich	1000[d]
miscellaneous								
isobutyl-2-methoxypyrazine	0.015	0.006	0.004	nd	nd	V	Aldrich	0.002 (*46*)
dimethyl sulfide (DMS)	60	44	104	19	18		Sigma-Aldrich	10–160 (*47*)

[a] Aromatic group codes: F, fruity; V, veggie; S, sweet-caramel; P, phenolic. [b] Reference from which the value has been taken is given in parentheses. In refs *28* and *43* the matrix was a 10% water/ethanol solution at pH 3.2; in ref *41* the matrix was an 11% water/ethanol solution containing 7 g/L glycerol and 5 g/L tartaric acid, pH adjusted to 3.4 with 1 M NaOH; in ref *39* thresholds were calculated in wine. In ref *40* the mixture was 10% in ethanol, in ref *44* the matrix was a synthetic wine containing 12% ethanol, 8 g/L glycerol, and different salts. In ref *42* the matrix was water. [c] Nondetected compound. [d] Calculated in our laboratory (*15*); orthonasal thresholds were calculated in a 10% water/ethanol mixture containing 5 g/L of tartaric acid at pH 3.2.

excellent ability to extract aroma compounds (*20*). The cartridge was placed on the top of a bubbler flask containing 80 mL of wine, and 20 mL of "synthetic saliva" solution (containing 0.168 g of NaHCO₃, 0.048 g of K₂HPO₄, 0.166 g of KH₂PO₄, and 0.088 g of NaCl per 100 mL) (*21*). The mixture was continuously stirred with a magnetic stir bar and kept at a constant temperature of 37 °C by immersion in a water bath. A controlled stream of nitrogen (100 mL/min) was passed through the sample during 200 min. This system represents an "artificial mouth" the purging conditions of which share features characteristic of both orthonasal and retronasal perception. Volatile wine constituents released in the headspace were trapped in the cartridge containing the sorbent and were further eluted with 3.2 mL of dichloromethane. The extract was kept at −30 °C for 2 h to eliminate any water content by freezing and further decantation. After this, the extract was concentrated under a stream of pure N₂ to a final volume of 200 µL. These concentrated wine extracts were used in the olfactometry assay.

Olfactometry. Sniffings were carried out in a Thermo 8000 series GC equipped with a flame ionization detection (FID) system and a sniffing port (ODO-1 from SGE, Ringwood, Australia) connected by a flow splitter to the column exit. The column used was a DB-Wax from J&W (Folsom, CA), 30 m × 0.32 mm i.d., with 0.5 µm film thickness. The carrier was H₂ at 3 mL/min. One microliter of the wine extract was injected in splitless mode, the splitless time being 1 min. Injector and detector were both kept at 250 °C. The temperature program was as follows: 40 °C for 5 min, then raised at 4 °C/min to 100 °C, at 6 °C min⁻¹ to 136 °C, and at 3 °C/min to 220 °C, and finally was held at 220 °C for 10 min. To prevent condensation of high-boiling compounds on the sniffing port, this was heated sequentially using a laboratory-made rheostat. A panel of eight subjects, four women and four men, carried out the sniffings of the extracts. All of them had extensive experience in GC-O analysis. Each judge evaluated the wine extract once in two time segments of 30 min to avoid fatigue (one session per day). The panelists were asked to measure the overall intensity of each odor using a 7-point category scale (0 = not detected; 1 = weak, hardly recognizable odor; 2 = clear but no intense odor, 3 = intense odor), half values being allowed. The quantitative ability of this technique has been already proved (*22*). The data processed were a mixture of intensity and frequency of detection (labeled as "modified frecuency", MF), which was calculated with the formula proposed by Dravnieks (*23*): MF (%) = $\sqrt{F(\%) \times I(\%)}$, where F (%) is the detection frequency of an aromatic attribute expressed as percentage and I (%) is the average intensity expressed as percentage of the maximum intensity.

The odorants were identified by comparison of their odors, chromatographic retention index in both DB-Wax and DB-5 columns, and MS spectra with those of pure reference compounds.

Chemical Quantitative Analysis. *Major Compounds (Liquid−Liquid Microextraction and GC-FID Analysis).* Quantitative analysis of major compounds was carried out using the method proposed and validated by Ortega et al. (*24*). 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 using the conditions described elsewhere (*24*). 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.

Minor Compounds (SPE and GC−Ion Trap−MS Analysis). This analysis was carried out using the method proposed and validated by López et al. (*20*). In accordance with the method, 50 mL of wine, containing 25 µL of BHA solution and 75 µL of a surrogate standards solution (3-octanone, β-damascone, heptanoic acid, and isopropyl propanoate), was passed through a LiChrolut EN cartridge at about 2 mL/min. The sorbent was dried by letting air pass through (−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 ion trap MS detection under the conditions described in ref *20*.

Minor Esters and Methoxypyrazines (SPE and GC-GC−Ion Trap−MS Analysis). This analysis was carried out using the method proposed and validated by Campo et al. (*25*). In accordance with the method, 100 mL of wine were passed through a 200 mg LiChrolut EN cartridge at about 3 mL/min. Major interferences were removed by rinsing with 25 mL of an aqueous solution 50% in methanol and 1% in NaHCO₃. Analytes were eluted with 1.5 mL of dichloromethane. Fifty microliters of this extract was injected in the solvent split mode and analyzed by GC-GC-MS under the conditions described in ref *25*.

Dimethyl Sulfide. This compound was determined by automated headspace SPME and further gas chromatography with pulsed flame photometric detection (GC-PFPD). The instrument was a Varian CP-3800 gas chromatograph fitted with a PFPD detector (Walnut Creek, CA) and a Combi Pal autosampler (CTC Analytics, Zwingen, Switzerland). Saturated NaCl brine (4.9 mL) was placed in a 20 mL standard headspace vial and sealed. After this, the vial was purged with a nitrogen stream of 2 bar for 1 min. Immediately after this operation, 100 µL of the wine sample, 5 µL of glyoxal (ethanedial; added to bind SO₂) solution (8% w/v), and 20 µL of the IS solution (ethyl methyl sulfide, 200 µg/L in methanol) were injected through the septum with a syringe. The samples were extracted at 35 °C for 20 min with a 85 µm Carboxen-PDMS SPME fiber (Supelco, Bellefonte, PA) and injected in the injection port set at 300 °C for 7 min (desorption + fiber

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reconditioning). The temperature program was as follows: 35 °C for 3 min, raised at 10 °C/min to 100 °C, and then raised at 20 °C/min to 220 °C. The detector temperature was 300 °C. Carrier gas was hydrogen at a constant flow rate of 2 mL/min.

RESULTS AND DISCUSSION

Sensory Descriptive Analysis of Wines. The aromatic characteristics of the five wines considered in this study were described by a sensory panel using the nine sensory descriptors listed in **Table 1**. The results of the sensory analysis can be seen in **Figure 1**. As shown in the figure, the aroma of these wines is described mainly as woody, sweet-caramel, raisin-dried fruit, toasted, berry fruit, veggie, and phenolic. All of the wines had relatively high scores in the raisin note, which seems to be a generic descriptor of this set of aged red wines. On the contrary, the scores given to the terms sweet-caramel, woody, toasted, berry fruit, and veggie were significantly different (according to the *p* value obtained for the wine factor in the two-way ANOVA), particularly the terms sweet-caramel, toasted, and veggie. The three Spanish wines were richest in berry fruit notes. The woody odor nuance is correlated with the time the wine spent in wood, except in the case of the wine from Priorat. This wine showed a small level of the reduction odor nuance.

GC-O. The GC-O experiments were carried out on extracts obtained in a dynamic headspace system. The proposed head-space strategy has been successfully employed in previously published works (*8, 9*). The major advantage of this strategy is that it is possible to obtain simpler and cleaner olfactograms than those obtained in other studies, in which the extracts were obtained by solid-phase extraction of wine (*4*). The results derived from the olfactometric study carried out in the five wines are summarized in **Table 2**. Approximately 100 odorants were detected during the GC-O experiments, but, for the sake of simplicity, those not reaching a maximum GC-O score of 30% in any of the five studied wines were considered as noise. After this operation, the number of odorants was reduced to 53, as shown in **Table 2**. Most of the odorants reported in the table have been positively identified (retention index in two phases, odor quality, and MS similar to those of pure reference standards); among them are all of those reaching a GC-O score of >50. The odor zone with LRI 1297 is composed of two odorants: octanal and furfuryl ethyl ether, which was recently reported, albeit not identified, in Sherry and Madeira wines (*26*). Most of the compounds reported in the table have been previously identified as constituents of table wines. The single novelty is, perhaps, the presence of a group of compounds that have been recently identified in Sherry wines (*26, 27*). These compounds are ethyl 2-methylpentanoate, ethyl 4-methylpen-tanoate, and ethyl cyclohexanoate. Some other remarkable observations are as follows: the absence in the list of any of the cysteinyl-related mercaptans, which were found to play outstanding roles in the aroma of some white, rosé, and red wines (*4, 8, 28, 29*); the presence of different pyrazines, detected exclusively in the Spanish red wines; the presence in the GC-O profiles of Uruguayan wines (both made with Tannat) of γ-decalactone; and the virtual absence in these wines of ethyl 2-methylpropanoate and linalool. A final remark is the absence in the GC-O profiles of Tannat wines of 1,8-cineole, which was previously reported as an odorant potentially responsible for a eucalyptus-like note of some wines of this variety (*30*).

Quantitative Composition. The quantitative composition of the five wines is given in **Table 3**. Although not all of the

potentially relevant compounds could be quantified, the table reveals that there are at least 37 compounds at concentrations higher than the threshold and another 20 at concentrations at least higher than 0.1 times the threshold. There is an acceptable agreement between olfactometric and quantitative results, and some of the findings made in **Table 2** are also found here. For instance, data confirm the presence and potential importance of the ethyl esters of C6 and C7 branched and cyclic acids and the presence of small levels of isobutyl 2-methoxypyrazine in some of the Spanish wines. This last compound was not even detected in the wines from Tannat, which is in accordance with GC-O data. The relatively high amounts of γ-decalactone in the wines made with Tannat and the low levels of linalool, ethyl 2-methylpropanoate, and ethyl hexanoate in the wines of this variety are also confirmed by data in **Table 3**. Data in this table also indicate that wines from Tannat variety are richer in β-damascenone than the Spanish wines. This does not coincide with the GC-O scores in **Table 2** and must be attributed to the high imprecision associated with the olfactometric measurements of this compound, as has been demonstrated in previous studies (*22*).

Correlation between Olfactometric and Quantitative Data and Sensory Oroperties. At a first approximation, it should be expected that the odorants responsible for effective sensory differences in the studied samples show remarkable differences in their olfactometric scores and odor activity values (OAVs) in the different wines. The existence of such differences does not guarantee, however, an effective sensory importance, because this importance will ultimately depend on unknown factors, such as the ability of the odorant to create a sensory difference in the particular aroma mixture (*31*). This aspect, at present, cannot be predicted beforehand. In fact, not many compounds seem to be able to play individually a distinctive role in this set of complex wines. For instance, the three odorants showing the greatest olfactometric differences, measured as the parameter $MF_{max} - MF_{min}$ in the last column of **Table 2**, are acetylpyrazine, ethyl 2-methylpropanoate, and 2-methyl-3-furanthiol. Leaving aside ethyl 2-methylpropanoate, which shares aroma properties with many other ethyl esters, neither the distinctive "burnt bread" aroma of acetylpyrazine nor the empyreumatic "meaty and onion" aroma of 2-methyl-3-furanthiol is clearly identified in the aromas of this group of wines. This situation is clearly very different from that found in young white wines, the main aroma nuances of which were demonstrated to be determined by a small number of powerful odorants easily detected in the GC-O profiles (*8*). Similarly, the most discriminant odorants, on the basis of the quotient OAV_{max}/OAV_{min}, are ethyl 2-methylpropanoate and 2,3-butane-dione. However, the addition of these compounds at the concentration level at which they were found in these wines to a neutral wine did not bring about any significant change in the aroma (data not shown).

So far, the single compounds that seem to be related to a single aroma nuance are guaiacol and (Z)-whiskey lactone. The former is correlated with the toasted odor nuance and the latter with the woody character of the wine (see **Table 4**). In both cases the correlation obtained is better with the instrumental quantitative data, which should be related to the higher imprecision of the olfactometric measurement.

If the aroma of these wines cannot be directly or easily related to the individual compounds, it is because our brain has a limited ability to recognize different odors in complex mixtures (*32–34*). In such mixtures the brain does not always recognize the individual specific characteristics of an odorant, but a generic

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Table 4. Some Correlations between GC-O, Quantitative Data, and Sensory Notes

sensory note	olfactometric analysis		quantitative analysis	
	aromatic group	*r, p*	aromatic group	*r, p*
berry fruit	group F	0.906; 0.03	group F	0.908; 0.03
veggie	1-hexanol + (*Z*)-3-hexenol	0.630; ns	1-hexanol + (*Z*) -3-hexenol	0.704; ns
	group V	0.782; ns	IBMP	0.755; ns
	1-hexanol + (*Z*)-3-hexenol + V	0.762; ns	IBMP + 1-hexanol+ (*Z*)-3-hexenol	0.760; ns
sweet-caramel	group S	0.827; 0.08	group S	0.742; ns
toasty	guaiacol	0.602; ns	guaiacol	0.891; 0.04
phenolic	group P	0.849; 0.07	group P	0.813; 0.09
wood	(*Z*)-whiskey lactone	0.529; ns	(*Z*)-whiskey lactone	0.939; 0.02

Table 5. Addition Tests To Explain the Different Sensory Notes

addition	dearomatized wine		neutral wine	
	p	effect	*p*	effect
veggie note				
isobutyl 2-methoxypyrazine (IBMP) (5 ng/L)	>95%	ash, earthy	ns	
IBMP (15 ng/L)			>95%	green, earthy
1-hexanol (1.48 mg/L) + (*Z*)-3-hexenol (234 μg/L)	ns		ns	
IBMP (15 ng/L) + 1-hexanol (1.48 mg/L) + (*Z*)-3-hexenol (234 μg/L)			>99%	pepper, herbaceous
IBMP (5 ng/L) + 1-hexanol (1.48 mg/L) + (Z)-3-hexenol (234 μg/L)	>95%	pepper, herbaceous	ns	
sweet-caramel note				
phenylacetaldehyde (9.85 μg/L) + ethyl cinnamate (1.22 μg/L) + ethyl dihydrocinnamate (0.54 μg/L) + 2-phenylethyl acetate (40.91 μg/L) + linalool (10.26 μg/L)			>95%	ripe fruit, honey, sweet
toasty				
guaiacol 47.3 μg/L	>95%	phenolic, toasty	>99.9%	less sweet
phenolic				
guaiacol (47.3 μg/L) + eugenol (60 μg/L) + (*E*)-isoeugenol (5.5 μg/L) + 4-vinylphenol (27 μg/L) + 4-vinylguaiacol (334 μg/L) + 4-ethylphenol (174 μg/L) + 4-ethylguaiacol (39 μg/L) + 4-propylguaiacol (3.9 μg/L) + 2,6-dimethoxyphenol (198 μg/L) + 4-allyl-2,6-dimethoxyphenol (73 μg/L) + *m*-cresol (4.8 μg/L) + *o*-cresol (6.5 μg/L)	>99%	phenolic, leather	>99.9%	phenolic, leather
woody				
(*Z*)-whiskey lactone (164 μg/L)			>95%	woody
berry fruit note				
ethyl butyrate (170 μg/L) + ethyl hexanoate (227 μg/L) + isoamyl acetate (221 μg/L)	ns		ns	
ethyl 2-methylpropanoate (315 μg/L) + ethyl 2-methylbutyrate (32 μg/L) + ethyl 3-methylbutyrate (25 μg/L)	ns		ns	
ethyl cyclohexanoate (12 ng/L) + ethyl 2-methylpentanoate (50 ng/L) + ethyl 4-methylpentanoate (180 ng/L)	ns		ns	
nine fruity esters all together	ns		ns	

attribute shared by groups of them, for instance, "fruity" or "sweet". Accordingly, and attending also to previous experience, the odorants in both lists were grouped according to the nature of their aroma in the following groups: F, compounds with fruity (estery) character; V, compounds with vegetal character; S, compounds with sweet-flowery notes; and P, compounds with phenolic character.

As the data in **Table 4** show, the summation of the scores of all odorants with fruity descriptors correlates well with the intensity of the berry fruit note of these wines. Similarly, the summation of the scores of all the compounds with sweet-floral aroma is correlated with the sweet-caramel character of the wines; the summation of odorants with phenolic character is related to the phenolic character of the wine, and the summation of the odorants with vegetal (pepper and herbaceous) character may be correlated, although the significance level is not reached, with the veggie character of the wines. Most of these correlations between GC-O data and sensory data are also found with quantitative data. In this case, quantitative data have been previously normalized to odor activity values so that comparable units could be summed. These observations were further checked by different sensory experiments, as indicated in **Table 5**.

Sensory Tests To Confirm the Role of the Different Groups of Odorants. The veggie character of the wine should be primarily attributed to the presence of isobutyl 2-methoxy-pyrazine (IBMP) as the addition tests shown in **Table 5** reveal, and in accordance with data reported by other authors (*35*). The addition of just 5 or 15 ng/L of this compound to dearomatized wine or to wine, respectively, was significantly detected by the panel. In both cases an earthy aroma was noted. If together with this methoxypyrazine, (*Z*)-3-hexenol, and 1-hexanol are added, then the sensory effect is more easily perceived and a pepper odor nuance can be recognized, which suggests that the three components may interact synergistically.

The addition of five compounds with floral and very sweet notes to a neutral red wine at the maximum concentrations at which they were found in the studied wines was significantly detected. The aroma of the spiked sample was sweeter than that of neutral wine. These results confirm the sensory importance of this pool of compounds and suggest that they are active contributors to the sweet-caramel nuance of the studied wines. Similarly, the toasty note was found to be correlated to the level of guaiacol. The importance of this compound and its role in wine aroma was confirmed by the addition tests carried out on

Table 6. Specific Sensory Tests Carried out To Explain the Berry Fruit Note

test	type of test/matrix	mixtures essayed[a]	significance	observations[b]
		(**A**) Effect of Alcohol		
1	triangle test/water	matrix vs matrix + fruity esters	>99.99%	very intense green apple aroma
2	triangle test/synthetic wine 10% ethanol	matrix vs matrix + fruity esters	>99.9%	mild fruity, estery-like aroma
3	triangle test/synthetic wine 12% ethanol	matrix vs matrix + fruity esters	>95%	slightly sweet aroma
4	triangle test/synthetic wine 14.5% ethanol	matrix vs matrix + fruity esters	ns	ethanol
5	ranking test for fruitiness/synthetic wines with different alcohol levels	fruity esters in water and in synthetic wines with 10, 12, and 14.5% ethanol	>99.9% Friedman test >99.9% Page test	fruitiness inversely correlates with ethanol level
		(**B**) Effect of Norisoprenoids		
6	triangle test/synthetic wine 10% ethanol	matrix vs matrix + fruity esters + norisoprenoids (low level)	>99.99%	berry fruit
7	triangle test/synthetic wine 10% ethanol	matrix vs matrix + fruity esters + norisoprenoids (high level)	>99.99%	raisin, dried plum
8	triangle test/synthetic wine 10% ethanol	matrix + norisoprenoids vs matrix + norisoprenoids (low level) + fruity esters	>99%	berry fruit
9	triangle test/synthetic wine 10% ethanol	matrix + fruity esters vs matrix + norisoprenoids (low level) + fruity esters	>95%	sweeter aroma
10	ranking test for fruitiness/synthetic wine 10% ethanol	matrix vs matrix + fruity esters vs matrix + fruity esters + norisoprenoids (low level)	>99% Friedman test >99% Page test	fruitiness increases following the expected order
11	triangle test/dearomatized wine	matrix vs matrix + fruity esters + norisoprenoids (low level)	ns	
		(**C**) Effect of DMS		
12	triangle test/dearomatized wine	matrix vs matrix + 10 μg/L DMS	ns	
13	triangle test/dearomatized wine	matrix vs matrix + fruity esters + norisoprenoids (low level) + 10 μg/L DMS	>99%	sweet tobacco, fruity, strawberry
14	triangle test/dearomatized wine	matrix + 10 μg/L DMS vs matrix + fruity esters + norisoprenoids (low level) + 10 μg/L DMS	>99%	sweet tobacco, fruity, strawberry
15	triangle test/dearomatized wine	matrix + 10 μg/L DMS vs matrix + fruity esters + norisoprenoids (high level)+ 10 μg/L DMS	>99%	sweet tobacco, green olives
16	triangle test/dearomatized wine	matrix vs matrix + fruity esters + norisoprenoids (low level) + 50 μg/L DMS	>99%	olives, fruity, sulfury
17	triangle test/dearomatized wine	matrix vs matrix + fruity esters + norisoprenoids (high level) + 50 μg/L DMS	>99.9%	olives, martini type, sulfury
18	triangle test/dearomatized wine	matrix vs matrix + fruity esters + 100 μg/L DMS	>99.9%	olives, martini type, sulfury
19	triangle test/dearomatized wine	matrix + 100 μg/L DMS vs matrix + fruity esters + 100 μg/L DMS	>95%	less sulfury
20	triangle test/dearomatized wine	matrix vs matrix + fruity esters + norisoprenoids (low level) + 100 μg/L DMS	>99.9%	olives, martini type, sulfury, fruity
21	triangle test/ dearomatized wine	matrix + 100 μg/L DMS vs matrix + fruity esters + norisoprenoids (low level) + 100 μg/L DMS	>95%	olives, sweet
22	triangle test/dearomatized wine	matrix vs matrix + fruity esters + norisoprenoids (high level) + 100 μg/L DMS	>99.9%	olives, martini type, sulfury
23	triangle test/neutral wine	matrix vs matrix + 100 μg/L DMS	ns	
24	triangle test/neutral wine	matrix vs matrix + fruity esters + norisoprenoids (low level) + 100 μg/L DMS	>95%	berry fruit, sweet
25	triangle test/neutral wine	matrix + 100 μg/L DMS vs matrix + fruity esters + norisoprenoids (low level) + 100 μ/L DMS	>95%	berry fruit, sweet

[a] The mixture named fruity esters had the nine most powerful fruity esters at the concentrations indicated in **Table 4**. [b] Sensory changes caused by the specific addition tested (second sample of the test).

dearomatized and neutral wine, as shown in **Table 5**. In both cases the additions were detected and the dearomatized wine spiked with guaiacol developed phenolic and toasted odor nuances. This did not happen, however, when the addition was carried out on neutral wine, which suggests that the toasty note is the result of the interaction of several odorants, apart from guaiacol. The role of the group of compounds with phenolic character and of (*Z*)-whiskey lactone on the phenolic leather

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and woody notes of the wines was also confirmed by addition tests, as shown in **Table 5**.

Investigations into the Fruity Aroma of Wines. The berry fruit note was the most complicated and interesting from the chemical point of view. In this case, the addition of different groups of compounds with fruity character to either a dearomatized red wine or a neutral red wine did not bring about any clear change in the sensory properties of the sample, as can be seen in **Table 5**. Even the mixture of nine different chemicals (the fruity compounds of higher OAVs), all of them at concentrations well above their thresholds, was not able to induce any clear change in the aroma. This result was not expected, and additional experiments were carried out to find an explanation.

The first group of experiments evaluated the effect of ethanol on the perception of fruitiness from mixtures of the nine fruity compounds at the maximum concentrations found in the wines. The results of these experiments are found in **Table 6A**. When there is no ethanol in the mixture, the smell is strong and apple-like, reminiscent of an apple drink (test 1). However, the intensity of the smell decreases with the amount of ethanol present in the mixture, so that at 10% the intensity of the fruity odor is much less intense (test 2), at 12% it is just barely perceptible (test 3), and at 14.5% ethanol it is no longer perceived (test 4). In addition, the nature of the odor is also dramatically changed, because when ethanol is present in the mixture, the odor is described just as sweet and fruity. A ranking test confirmed these results (test 5). These results are in agreement with those reported by Guth (*36*) and LeBerre et al. (*37*) and are in apparent disagreement with the sensory descriptors of dealcoholized wines (*38*), which suggests that the lower fruitiness of dealcoholized wines may be attributed to the loss of fruity esters during the dealcoholization. In any case, this set of results indicates that the perception of fruitiness in these wines should be related to something apart from the fruity esters.

In a second set of experiments, the different wine odorants or groups of odorants were checked as aroma enhancers for this sensory note. This screening (based on informal tasting sessions) suggested that norisoprenoids (β-damascenone and β-ionone) and to a minor extent also vanillin-related compounds (methyl vanillate, vanillin, ethyl vanillate, and acetovanillone) and dimethyl sulfide (DMS) could play such role. The role of these compounds was further studied by different sensory tests. In the case of vanillin-related compounds, such interaction was not statistically significant (data not shown). On the contrary, the enhancing role played by norisoprenoids in hydroethanolic solutions was amazing, as can be seen in **Table 6B**. The addition of low levels of β-damascenone (0.85 μg/L) and β-ionone (0.14 μg/L) to the mixture of the esters brought about a clear increase of the fruity note (tests 6, 8, and 9), and the addition of high levels (3.5 and 0.23 μg/L, respectively) had as consequence the development of a strong raisin−dry plum note (test 7). A ranking test confirmed these results (test 10). Surprisingly, such an enhancing role was not evident when the experiment was carried out on dearomatized wine (test 11).

The situation changes if a small amount of DMS is present in the mixture, as shown in **Table 6C**. Although 10 μg/L of this compound could not be perceived in dearomatized wine (test 12), its presence in the mixture makes it possible to perceive complex sweet-fruity (tests 13 and 14) or green olive notes (test 15). The presence of higher amounts of DMS makes the aroma of the mixture more intense, albeit in these cases the sulfury notes of this compound are more evident (tests 16−22).

However, when the addition of the mixture is carried out on a neutral wine, the sulfury nuance of DMS is not perceived at the concentration added, and the simultaneous addition of DMS, the fruity esters, and the norisoprenoids brings about an increase of the berry fruit note (tests 23−25). These results are in accordance with the results recently presented by Segurel et al. (*19*) and confirm that fruity notes of red wines are the result of a complex interaction between fruity esters, ethanol, norisoprenoids, DMS, and, probably, some other wine volatiles.

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