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The Chemical Characterization of the Aroma of Dessert and Sparkling White Wines (Pedro Ximénez, Fino, Sauternes, and Cava) by Gas Chromatography−Olfactometry and Chemical Quantitative Analysis

EVA CAMPO, JUAN CACHO, AND VICENTE FERREIRA*

Laboratory for Flavor Analysis and Enology, Department of Analytical Chemistry, Faculty of Sciences, University of Zaragoza, 50009 Zaragoza, Spain

Wines from Pedro Ximénez (PX), Fino, botrytized Sauternes, and Cava were screened by gas chromatography−olfactometry (GC−O), and the most relevant aroma compounds were further quantified in six different wines of each group. The comparison of GC−O and quantitative data with similar data from white young wines has made it possible to identify the aroma compounds potentially responsible for the specific sensory characteristics of these wines. Results have shown that all these wines are relatively rich in 3-methylbutanal, phenylacetaldehyde, methional, sotolon, and the ethyl esters of 2-, 3-, and 4-methylpentanoic acids. While Cava has a less specific aroma profile halfway between these special wines and young white wines, PX is richest in 3-methylbutanal, furfural, β-damascenone, ethyl cyclohexanoate, and sotolon; Fino in acetaldehyde, diacetyl, ethyl esters of branched aliphatic acids with four, five, or six carbon atoms, and 4-ethylguaiacol; and Sauternes in phenylacetaldehyde, 3-mercaptohexanol, and 4-methyl-4-mercaptopentanone.

KEYWORDS: Aroma; flavor; aldehydes; Sherry; botrytized wines; oxidative aging; GC−O

INTRODUCTION

Dessert and sparkling wines are produced in limited geographical areas according to traditional wine-making procedures, which can include the use of grapes with special features as raw material. For example, sweet wines of great quality are obtained from overripe berries affected by *Botrytis cinerea* in regions of Sauternes (France) and Tokaji (Hungary). The development of *B. cinerea* fungus in the berries leads to significant transformations including skin-cell degradation, loss of water, and release of aroma compounds and precursors present in the skin (*1*). In other cases, such as Fino, the recently fermented wine is further transformed by the action of "flor yeasts", which grow aerobically on the surface of wines containing 15–15.5% ethanol. A third possibility is the transformation of the original wine by the action of oxygen and redox processes during barrel aging (oxidative aging of Port, Madeira, Pedro Ximénez (PX) or Vins Doux Naturels (VDN) wines). PX wines, in particular, derive from sun-dehydrated berries and, contrary to Fino wines, are fortified up to 15–18% ethanol content to prevent the development of flor yeasts and then submitted to oxidative aging (*1*). Both types of wines are finally matured in the traditional Sherry "solera" system, which involves blending less aged wines with more aged ones several times in a year. Finally, sparkling wines, such as the Spanish Cava, are produced following the traditional French "champenoise" method, which consists of a second fermentation in closed bottles and aging in contact with lees for at least nine months, the minimum time legally established (*2*). Obviously, all those chemical and biochemical processes imply a large change in the composition of the final product, including the appearance of new odorants, which may impact the aroma of that wine.

There is a clear interest in the knowledge of such odorants, not only for the purpose of product characterization but also because all the processes involved in the production of those particular wines may also be active, albeit at a minor scale, in the production and aging of some table wines. It is expected, therefore, that knowledge of the aroma composition of dessert or sparkling wines could bring about new insights into the chemistry of wine aroma, expanding the list of odorants potentially important, and learning about the chemical and biochemical processes through which the odorants are formed or degraded.

Despite the relatively abundant literature published with regards to some of these wines, few papers deal with a comprehensive characterization of the aroma profile of such products by gas chromatography−olfactometry (GC−O). To the best of our knowledge, Champagne (*3*), VDN (*4*), Passito (*5*), Madeira (*6*), and, more recently, botrytized Sauternes and Fiano wines (*7–9*) have been the subject of this kind of study. Other

* To whom correspondence should be addressed. Phone: 34 976762067. Fax: 34 976761292. E-mail: vferre@unizar.es.

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Table 1. Sample Type, Brand, Origin, Vintage, Grape Variety, and Ethanol Content of the Samples Analyzed

sample type	brand[a]	appellation	vintage	grape varieties	ethanol, % (v/v)
Pedro Ximenez (PX)	**Don PX Toro Albalá**	Montilla-Moriles	1975	Pedro Ximénez	16
	Alvear 1927	Montilla-Moriles	5[b]	Pedro Ximénez	16
	Leyenda	Sherry	10[b]	Pedro Ximénez	18
	Duquesa	Sherry	8[b]	Pedro Ximénez	18
	Fernando de Castilla Antique	Sherry	30[b]	Pedro Ximenez	15
	Garvey	Sherry	10[b]	Pedro Ximénez	16
Fino	**Tío Pepe**	Sherry	5[b]	Palomino Fino	15
	Jarana Lustau	Sherry	3[b]	Palomino Fino	15.5
	Cobos	Montilla-Moriles	3[b]	Pedro Ximénez	15
	Hnos. Sanchez Romate	Sherry	3[b]	Palomino Fino	16
	Quinta	Sherry	5[b]	Palomino Fino	15.5
	La Ina	Sherry	3[b]	Palomino Fino	15
botrytized	**Baron Philippe de Rotschild**	Sauternes	2002	Semillon, Sauvignon blanc, Muscadelle	14.5
	Aureus	Sauternes	2003	Semillon (85%), Sauvignon blanc (10%), Muscadelle (5%)	14
	Château Lamothe	Sauternes	2002	Semillon (85%), Sauvignon blanc (10%), Muscadelle (5%)	13.5
	Château Laribotte	Sauternes	2002	Semillon (90%), Sauvignon blanc (8%), Muscadelle (2%)	14
	Château Raymond Lafon	Sauternes	2000	Semillon (80%), Sauvignon blanc (20%)	13.5
	Château Doisy Daëne	Sauternes	2000	Semillon, Sauvignon blanc, Muscadelle	14
Cava	**Gramona, Brut Imperial**	Penedès	2002	Xarello (50%), Macabeo (40%), Chardonnay (10%)	11.5
	Segura Viudas, Brut Reserva	Penedès	3[b]	Macabeo (60%), Parellada (40%)	11.5
	Mestres, Brut nature Reserva especial	Penedès	2002	Macabeo, Xarello, Parellada	12
	Gramona Celler Batlle, Gran Reserva	Penedès	1998	Xarello (70%), Macabeo (30%)	11.5
	Torelló, Brut nature Gran Reserva	Penedès	2001	Macabeo (50%), Parellada (30%), Xarello (20%)	11.5
	Jaime Serra, Brut nature Vintage	Penedès	3[b]	Xarello, Parellada, Macabeo	11.5

[a] Samples in bold letters were submitted to GC−O analysis. [b] Samples with no attributable vintage date on the bottle. Instead, the aging period (years) is indicated.

research works have used GC−O techniques not to profile the aroma of the wine but to look for specific odorants that may have some similarity to a target aroma nuance (*10, 11*). This strategy is a kind of shortcut that may be successful if, effectively, there is a single aroma compound responsible for a target odor nuance. An example of such success was the identification of sotolon as responsible for nutty, spicy, curry notes of flor-Sherry (*12, 13*), VDN (*11*), Porto (*14*), or botrytized wines (*15*). However, such strategy is not exempt from risks derived from the multivariate character of wine aroma and from its complexity. There are also some other studies dealing with the characterization by means of gas chromatography−mass spectrometry (GC-MS) of the volatile fraction of Madeira (*16*), Fino (*17–20*), or Cava (*21–23*) wines. Such works have succeeded in the identification of different compounds as markers of age and of the winemaking process.

During the last years, semiquantitative GC−O performed on dynamic headspace (HS) extracts has been widely used in our laboratory to characterize the aroma profiles of different wine families (*6, 24, 25*). The major advantage of this procedure is that it makes it possible to obtain simpler and cleaner olfactograms than those obtained by traditional techniques such as liquid–liquid (L−L) or solid-phase extraction (SPE), usually affected by coelution and saturation problems in the sniffing port and that the extract is enriched in the odorants that really have the ability to reach the olfactory epithelium. As a result, it is possible to establish a clear hierarchy of the odorants and select, from all the odorants present in wine, only those that are potentially odor-active and, therefore, may deserve further attention in terms of chemical quantitative analysis. In addition, during the last years a large effort has been devoted to develop reliable analytical methods for the quantitative determination of the different odorants of wine (*26–32*), which makes it possible to get reliable data from nearly all the relevant aromas of wine.

Therefore, the main aim of the present work is the preliminary characterization, by using semiquantitative GC−O and further chemical quantitative analysis of four different wine types elaborated by some of the above-mentioned wine-making procedures. Of particular interest in the present research is to identify the odorants that are specific to these types of wines. In order to reach such goal, a comparison of the odorant profile of wines from the four categories and of a set of young dry white wines, just submitted to alcoholic fermentation, will be presented and discussed in the paper.

MATERIALS AND METHODS

Wines. A total of 24 samples classified in the categories detailed in **Table 1** were studied. This set included wines submitted to biological or oxidative aging; noble rot wines, and sparkling wines. Wines were chosen and evaluated by four experts belonging to the laboratory staff in order to verify the quality and the representativeness of the aroma of the wines. All the wines were studied by chemical quantitative analysis. A subset of four wines (bold letters in **Table 1**) was also studied by GC−O. The sensory evaluation, the GC−O analysis, and the quantitative determination were carried out during a period of 5 months. During this time, the bottles were stored at 4 °C in the dark.

Reagents and Standards. The chemical standards were supplied by Aldrich (Gillingham, U.K.), Fluka (Buchs, Switzerland), Sigma (St. Louis, MO), Lancaster (Strasbourg, France), PolyScience (Niles, IL), Chem Service (West Chester, PA), Interchim (Monluçon, France), International Express Service (Allauch, France), and Firmenich (Geneva, Switzerland). LiChrolut EN resins and polypropylene cartridges were obtained from Merck (Darmstadt, Germany). Dichloromethane and methanol of LiChrosolv quality were from Merck (Darmstadt, Germany), absolute ethanol, pentane, and ammonium sulfate were from Panreac (Barcelona, Spain), and all of them were 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).

GC−O Study. *Preparation of Wine Extracts.* The volatiles of the wine were collected using a purge-and-trap system (*24*). The trap was formed by a standard polypropylene solid-phase extraction tube (0.8 cm internal diameter, 3 mL internal volume) packed with 400 mg of LiChrolut EN resins. Such resins were selected because of their excellent ability to extract aroma compounds (*33*). The bed was washed with 20 mL of dichloromethane and dried by letting air pass through (negative pressure of 0.6 bar, 10 min). The tube was placed on the top of a bubbler flask containing a mixture of 80 mL of wine and 20 mL

of "synthetic saliva" solution (containing 0.168 g $NaHCO_3$, 0.048 g K_2HPO_4, 0.166 KH_2PO_4, and 0.088 g NaCl per 100 mL) (*34*). 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^{-1}) 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 (*34*). 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 N_2 to a final volume of 200 μL.

Sniffing. The concentrated extract of the wine was used in the GC−O analyses. These were carried out in a Thermo 8000 series GC (Waltham, MA) 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 (poly(ethylene glycol)) from J&W (Folsom, CA), 30 m × 0.32 mm with 0.5 μm film thickness. The carrier was H_2 at 3 mL min^{-1}. One microliter of the wine extract was injected in splitless mode, with 1 min splitless time. Injector and detector were both kept at 250 °C. The temperature program was the following: 40 °C for 5 min, then raised at 4 °C min^{-1} up to 100 °C and at 6 °C min^{-1} up to 200 °C. To prevent condensation of high-boiling compounds on the sniffing port, this was heated sequentially using a laboratory-made rheostat. A panel of eight judges (six women and two men, ranging from 23 to 45 years of age), carried out the sniffing of the extracts. Prior to GC−O analysis, panelists followed a training period as described in ref *35*. Sniffing time was approximately 30 min, and each judge carried out one session per day. The panelists were asked to provide a descriptor to characterize the eluted odor and to rate its intensity using a 7-point category scale (0 = not detected; 1 = weak, hardly recognizable odor; 2 = clear but not intense odor, 3 = intense odor), half-values being allowed. Because a large number of odorants are at concentrations near the threshold in the headspace extracts, the data processed was a mixture of the intensity and the frequency of detection of an odorant. This parameter is labeled as "modified frequency". MF and is calculated with the formula proposed by Dravnieks (*36*): MF (%) = $(F(\%)I(\%))^{1/2}$ where $F(\%)$ is the detection frequency of an aromatic attribute expressed as percentage of total number of judges and $I(\%)$ is the average intensity expressed as percentage of the maximum intensity. For the sake of simplicity, those odorants not reaching a maximum GC−O score (MF) of 30% in any of the studied wines were considered as noise. Odorant identification was carried out by comparing GC retention data of the different odorants on two different columns (the DB-Wax detailed in the sniffing procedure and a Factor Four 5 ms from Varian, 30 m × 0.32 mm × 1.0 μm film thickness) and the mass spectrum with those of a pure reference compound. Such operation was carried out using a dual GC−GC−MS system composed of two independent chromatographs interconnected by means of a Deans valve and a heated interface. The first chromatograph was equipped with a FID and an olfactometric port, and the second one with a MS and a second olfactometric port. The complete description of the system is given in ref *30*. As explained in that reference, extracts of different complexity and concentration were injected on such dual system until a satisfactory mass spectrum for the odorant could be obtained. The identity in each individual sample was further confirmed by the different GC−MS analysis carried out as described below.

Statistical Analysis. One-way analysis of variance (ANOVA) was carried out to determine the influence of the factor "wine type" on the levels of each of the compounds chemically quantified. This analysis was run with SPSS vs 11.5 from SPSS Inc. (Chicago, IL).

Quantitative Analysis. Different analytical methods were employed in the quantification of the odorants detected by olfactometry.

Major compounds were analyzed by liquid–liquid extraction followed by gas chromatography with flame ionization detection (FID) as proposed by Ortega et al. (*26*). The quantification of most minor compounds and sotolon (4,5-dimethyl-3-hydroxy-2(5*H*)-furanone) was carried out by solid- phase extraction (SPE) and gas chromatography−ion trap mass spectrum analysis (GC−ion trap-MS) as described, respectively, in refs *33* and *27*. The analysis of ethyl cyclohexanoate, ethyl 2-, 3-, and 4-methylpentanoate, and methoxypyrazines was carried out by SPE and multidimensional gas chromatography with mass spectrum detection (GC−GC−MS) using the method optimized by Campo et al. (*30*). As described by Cullere et al. (*28*), methional, phenylacetaldehyde, and 3-methylbutanal were analyzed by SPE extraction and in-sorbent derivatization with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA). Derivatized analytes were quantified by GC−ion trap-MS analysis. Dimethyl disulphide (DMDS) was determined by automated headspace solid-phase microextraction (SPME) and further gas chromatography with pulsed flame photometric detection (GC-PFPD) (*31*). Finally, polyfunctional mercaptans were determined by liquid−liquid (L−L) microextraction and GC−negative ion-MS analysis as described in ref *29* but using deuterated analogues for the quantification of 3-mercaptohexanol and 4-mercaptopentanone.

RESULTS AND DISCUSSION

The main goal of this paper is to provide a comprehensive characterization, by means of semiquantitative GC−O and chemical quantitative analysis, of the aroma profile of white wines elaborated by some specific wine-making procedures: (a) sweet fortified wines made with Pedro Ximénez sun dried grapes, (b) flor-Sherry (Fino) wines produced under biological aging, (c) sweet wines made with grapes affected by *Botrytis cinerea* (noble rot), and (d) bottle-fermented sparkling wines. The elaboration of these products involves the action of other micro-organisms in addition to those carrying the main alcoholic fermentation and also a more or less complex aging process The different wines selected for the study are listed in **Table 1**.

The GC−O study was carried out in a subset of four wines, one from each wine type. The specimens selected for the GC−O study are highlighted in bold letters in **Table 1**. The results of the GC−O study are presented in **Table 2**. This table includes as well reference data on the GC−O profile of young dry table wines evaluated in a previous work carried out following the same research strategy as the one used in this paper (*24*). This makes possible a direct comparison between the GC−O profiles of PX, Fino, Sauternes, and Cava with the median profile of six different young dry wines. Such comparison should provide some clues about the chemical differences introduced by the processes involved in the production of the four wine types here studied. Data in the table have been arranged in two main categories: odorants exclusively detected in the special wines and, odorants detected in both table and special wines. **Table 3** shows chemical quantitative data from most of the odorants detected in the GC−O study, as these odorants are supposed to be potentially important in the aroma profile of the four wine types. The single odorant quantified not appearing in the GC−O list is acetaldehyde, which is too volatile to be retained in the trapping process. **Table 3** also includes an evaluation of the statistical significance of the differences between the group means for each one of the quantified compounds. The subsequent discussion of the results will mainly focus on those odorants for which significant differences between group types were found.

GC−O Study. As can be seen in **Table 2**, the major differences between the special and table wines are caused by the presence in the special wines of 19 odorants that were not even detected in the GC−O profiles of table wines. From these 19 odorants, 8 were detected in the Cava, 15 were detected in the Sauternes and Fino, and 16 were detected in the PX sample, which can provide a first estimation of the complexity of these wines. Four odorants, of which only two reach a GC−O score above 50, remain unidentified (odorants with LRI 1106, 1416, 1504, and 1717). A fifth unidentified odorant was also detected

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Table 2. Comparison of Odorants Found by GC−O in the Four Special Wines Studied with Young Dry Varietal Wine Data Extracted from Ref *24*[a]

LRI DB-WAX	LRI DB-5	odor description	identity	MF (%) scores YD (median, $n = 6$)	PXI	FIN	SAU	CAV
			Odorants Exclusively Detected in the Special Wines					
<1000	<800	solvent, rancid	3-methylbutanal[b]	[e]	71	84	19	52
1059	914	sweaty, garlic	dimethyl disulphide (DMDS)[b]	[e]	80	62	41	7
1106	–	solvent	[d]	[e]	45	[e]	[e]	[e]
1142	940	fruity, sweet	ethyl 2-methylpentanoate[b]	[e]	41	[e]	[e]	16
1189	960	fruity, anise	ethyl 3-methylpentanoate[b]	[e]	16	31	13	15
1297	<800	sweet, fresh	octanal[c] + furfuryl ethyl ether[c]	[e]	25	37	18	7
1307	976	mushroom	1-octen-3-one[c]	[e]	25	7	30	[e]
1416	1040	fruity, anise	[d]	[e]	14	47	[e]	[e]
1427	1130	liquorices, anise	ethyl cyclohexanoate[b]	[e]	68	57	50	66
1440	907	coffee	2-methyl-3-furanmetanothiol[b]	[e]	[e]	14	47	[e]
1463	904	baked potato	methional[b]	[e]	25	30	15	16
1476	830	sweet-fruity	furfural[b]	[e]	41	19	20	[e]
1504		fruity, anise	[d]	[e]	[e]	[e]	44	[e]
1541	1094	fruity, anise	2-hydroxy-3-methylpentanoate[b]	[e]	59	80	18	[e]
1717		peppermint	[d]	[e]	56	16	31	5
1906	1370	flowery, pollen	ethyl dihydrocinnamate[b]	[e]	43	37	41	[e]
1990	1333	coconut	(*Z*)-whiskylactone[b]	[e]	57	51	35	[e]
2063	1299	leather, spicy	4-ethylguaiacol[b]	[e]		59	[e]	[e]
2240	1109	spicy	4,5-dimethyl-3-hydroxy-2(5*H*)-furanone (sotolon)[b]	[e]	45	43	51	[e]
			Odorants Present in Both Table and Special Wines					
<1000	<800	fruity	ethyl 2-methylpropanoate[b]	45	76	75	55	40
1011	<800	butter, cream	2,3-butanedione[b]	75	80	55	40	65
1032	<800	solvent	isobutyl acetate[b]	46	60	65	63	57
1054	801	fruity	ethyl butyrate[b]	76	76	73	78	79
1067	849	fruity	ethyl 2-methylbutyrate[b]	63	85	82	78	78
1082	853	fruity, anise	ethyl 3-methylbutyrate[b]	69	80	80	74	76
1115	<800	fusel	isobutanol[b]	42	37	27	60	43
1137	870	banana	isoamyl acetate[b]	80	56	65	76	49
1204	969	fruity, anise	ethyl 4-methylpentanote[b]	3.5	45	53	18	38
1223	<800	fusel	isoamyl alcohol[b]	81	85	80	89	79
1246	996	fruity, anise	ethyl hexanoate[b]	82	57	75	82	81
1314	861	onion, meaty	2-methyl-3-furanthiol[b]	42	66	47	68	71
1386	952	box tree	4-mercapto-4-methyl-2-pentanone[b]	21	[e]	[e]	44	[e]
1396	849	grass	(*Z*)-3-hexenol[b]	43	0	19	75	39
1441	1094	pepper, earthy	3-isopropyl-2-methoxypyrazine[b]	55	10	10	65	52
1459	<800	vinegar	acetic acid[b]	51	25	5	65	43
1510	1173	pepper, earthy	3-*sec*-butyl-2-methoxypyrazine[b]	10	[e]	5	31	[e]
1535	1181	pepper, earthy	3-isobutyl-2-methoxypyrazine[b]	56	37	25	60	43
1560	1100	floral, muscat	linalool[b]	14	85	23	54	[e]
1631	1022	toasty, burnt	2-acetylpyrazine[c]	41	80	76	78	69
1640	820	cheese	butyric acid[b]	9	32	10	35	47
1660	1050	honey	phenylacetaldehyde[b]	14	76	66	83	51
1681	878	cheese	2-/3-methylbutyric acid[b]	50	76	76	80	56
1743	1180	honey, liqueur	[d]	23	44	22	21	23
1835	1254	roses	2-phenylethyl acetate[b]	28	10	22	38	23
1836	1388	baked apple	β-damascenone[b]	58	73	58	44	63
1874	1524	sulfury, citrus	3-mercaptohexanol[b]	5	[e]	[e]	31	[e]
1882	1089	smoky	guaiacol[b]	12	61	18	45	[e]
1938	1116	roses	β-phenylethyl alcohol[b]	46	47	78	84	64
2126	1070	leather, urine	*m*-cresol[b]	18	32	[e]	49	[e]
2227	1328	bitumen	4-vinylguaiacol[b]	19	45	9	53	25

[a] Gas chromatographic retention data (LRI), olfactory description, chemical identity, and modified frequency percentage (% MF) are reported. Abbreviations; YD (young dry), PXI (Pedro Ximénez), FIN (Fino), SAU (Sauternes), CAV (Cava). [b] Identification based on coincidence of chromatographic retention data and on the similarity of odor with those of pure compounds available in the laboratory. [c] 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. [d] Compound not identified. [e] Compound not detected.

in the table wines (LRI 1743). Except for the unknown with LRI 1416, for which a mass spectrum was provided in ref *37*, it was not possible to get a clear mass spectrum of any of the other compounds, despite the efforts made in their preconcentration and isolation. The identity of another odorant (2-hydroxy-3-methylpentanoate) could not be conclusively determined either (*37*).

It should be remarked that, leaving aside 4-ethylguaiacol, only two odorants (1106 in PX; and 1504 in Sauternes) seem to be specific to some of the studied samples. This indicates that, despite the differences in the wine-making procedures of these wines, the active chemical processes leading to the generation of aroma compounds are limited. It is worth noting the relatively high GC−O scores of some ethyl esters of aliphatic branched or cyclic acids, ethyl 2-methylpentanoate, ethyl 3-methylpentanoate, and ethyl cyclohexanoate. The latter compound presents the highest GC−O scores in Fino and PX wines. Although the origin of these esters is not clear, their structure suggests that they could be byproducts of the catabolism of amino acids by some micro-organisms. Ethyl dihydrocinnamate, an odorant related to the rock-rose nuance of some Port wines (*38*), was detected in all samples except Cava. On the basis of their GC−O

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Table 3. Average Concentration of Compounds Detected by GC−O in the Four Different Wine Types and in the Group of Young Dry Wines[a]

compounds	CAS no.	Pedro Ximenez	Fino	Sauternes	Cava	young dry
			Carbonyl Compounds			
acetaldehyde**	75-07-0	13290 (2545) c	75578 (29315) d	3275 (835) a	8246 (1372) b	2520 (143) a
3-methylbutanal***	590-86-3	94 (16) d	50 (8.2) c	16 (1.8) b	36 (8.7) bc	2.1 (1.0) a
phenylacetaldehyde***	122-78-1	68 (6.4) c	39 (3.6) b	97 (17) d	30 (5.3) b	3.9 (1.3) a
methional*	3268-49-3	20 (3.8) c	14 (6.1) b	21 (6.9) bc	17 (2.9) c	0.99 (0.4) a
2,3-butanedione***	431-03-8	781 (229) a	9705 (1652) b	387 (217) a	462 (249) a	190 (49) a
furfural**	98-01-1	4438 (1573) b	365 (53) a	1339 (475) a	694 (221) a	48.5 (3.4) a
β-damascenone***	23726-93-4	10 (2.4) c	2.6 (0.4) a	0.81 (0.21) a	6.6 (0.64) b	3.2 (0.9) ab
			Branched Esters			
ethyl 2-methylpropanoate***	97-62-1	54 (27) a	1886 (296) b	98 (20) a	46 (15) a	51 (3.7) a
ethyl 2-methylbutyrate***	7452-79-1	4.1 (2.0) a	49 (5.2) b	3.4 (1.1) a	5.1 (1.1) a	9.8 (2.1) a
ethyl 3-methylbutyrate***	108-64-5	7.5 (3.0) ab	73 (6.2) c	3.6 (0.71) a	11 (1.3) ab	15 (3.2) b
ethyl 2-methylpentanoate**	39255-32-8	0.016 (0.008) cd	0.026 (0.003) d	0.010 (0.003) bc	0.011 (0.001) bc	<0.0007 a
ethyl 3-methylpentanoate***	5870-68-8	0.064 (0.024) b	0.319 (0.058) c	0.035 (0.003) b	0.032 (0.003) b	<0.0007 a
ethyl 4-methylpentanoate***	25415-67-2	0.74 (0.37) b	1.5 (0.14) c	0.092 (0.019) a	0.222 (0.0291) ab	0.073 (0.007) a
			Linear Esters			
ethyl butyrate***	105-54-4	90 (29) a	299 (32) c	62 (14) a	212 (6) b	343 (43) c
ethyl hexanoate***	123-66-0	66 (19) a	215 (26) a	148 (44) a	672 (61) b	785 (120) b
ethyl octanoate**	106-32-1	174 (142) a	82 (17) a	172 (47) a	620 (79) b	627 (141) b
			Other Esters			
ethyl cyclohexanoate*	3289-28-9	0.025 (0.009) c	0.003 (0.002) ab	0.009 (0.008) bc	<0.0008 a	<0.0008 a
ethyl dihydrocinnamate*	2021-28-5	0.39 (0.09) b	0.39 (0.09) b	0.22 (0.06) ab	0.13 (0.02) a	0.17 (0.04) a
3-methylpropyl acetate***	110-19-0	37 (12) a	50 (5.1) a	208 (32) c	23 (5.1) a	102 (19) b
isoamyl acetate***	123-92-2	39 (15) a	55 (11) a	85 (20) a	34 (10) a	1605 (347) b
2-phenylethyl acetate***	103-45-7	34 (13) a	183 (18) b	115 (13) ab	49 (12) ab	409 (68) c
			Alcohols			
isobutanol***	78-83-1	6578 (1781) a	30098 (4300) bc	38788 (4158) c	20690 (5737) b	25083 (3621) b
isoamyl alcohol***	123-51-3	38770 (14529) a	137253 (12596) b	77665 (11793) a	150995 (16684) bc	186650 (14627) c
(*Z*)-3-hexenol**	928-96-1	46 (8.1) a	123 (14) ab	86 (3.8) a	205 (24) b	193 (61) b
β-phenylethanol	60-12-8	25915 (8284)	45075 (3037)	52627 (16018)	21313 (3413)	31183 (6079)
			Volatile Phenols			
guaiacol	90-05-1	2.6 (1.8)	0.61 (0.06)	1.32 (0.39)	0.29 (0.05)	1.9 (0.3)
m-cresol***	108-39-4	6.7 (0.93) ab	8.9 (0.61) b	11 (2.3) b	2.38 (0.46) a	1.9 (0.72) a
4-vinylguaiacol*	7786-61-0	196 (33) a	156 (29) a	618 (131) ab	219 (37) a	1011 (434) b
4-ethylguaiacol***	2785-89-9	12 (3.7) a	96 (21) b	0.24 (0.08) a	3.3 (2.9) a	4.1 (1.9) a
			Terpenes			
linalool*	78-70-6	5.7 (4.6) a	0.24 (0.07) a	2.1 (0.47) a	0.10 (0.01) a	38 (19) b
			Lactones			
(*Z*)-whiskylactone**	39212-23-2	11 (5.9) bc	22 (5.1) c	11 (3.9) bc	<0.3 a	<0.3 a
4,5-dimethyl-3-hydroxy-2(5*H*)-furanone (sotolon)**	28664-35-9	176 (76) d	113 (26) cd	18 (1.9) bc	8.4 (2.1) bc	<0.8 a
			Acids			
butyric acid***	107-92-6	627 (147) a	1846 (224) c	564 (89) a	925 (150) ab	1460 (157) bc
3-methylbutyric acid***	503-74-2	27 (11) a	12 (7.4) a	22 (5.0) a	47 (6.1) a	522 (91) b
			Methoxypyrazines			
3-isopropyl-2-methoxypyrazine	25773-40-4	<0.0004	<0.0004	<0.0004	<0.0004	0.0005 (0.0001)
3-*sec*-butyl-2-methoxypyrazine	24168-70-5	<0.0004	<0.0004	<0.0004	<0.0004	0.0006 (0.0001)
3-isobutyl-2-methoxypyrazine	24683-00-9	<0.0003	<0.0003	<0.0003	<0.0003	0.003 (0.0005)
			Mercaptans			
dimethyl disulphide (DMDS)	624-92-0	9.8 (0.4)	8.6 (0.20)	9.4 (0.14)	8.5 (0.20)	[b]
4-mercapto-4-methyl-2-pentanone	19872-52-7	<0.0001 a	<0.0001 a	0.0033 (2.1) b	<0.0001 a	[b]
3-mercaptohexanol	51755-83-0	<0.007 a	<0.007 a	3.348 (1.4) c	0.210 (0.11) b	[b]
2-methyl-3-furanthiol	28588-74-1	35 (18)	37 (13)	45 (17)	48 (12)	[b]
2-methyl-3-furanmetanothiol	98-02-2	a[c]	a[c]	3 (1.5) b	1 (1) b	[b]

[a] Values in parentheses correspond to the mean standard error of the group ($n = 6$). All data are expressed in μg L^{-1}. The significance of the factor "wine type" was determined according to one-way ANOVA: ∗, ∗∗, and ∗∗∗ indicate significance with $\alpha < 0.05$, 0.01, and 0.001, respectively. Different letters indicate the existence of a significant difference (Duncan test). [b] Compound not analyzed. [c] Compound not detected.

scores, the amino acid-derived compounds (3-methylbutanal, sotolon, and methional) seem to constitute a relevant pool of odorants of these kinds of wines. Furfural, a sugar or oak derived compound, was detected by the panel in all samples submitted to barrel aging and was found at higher levels in PX, in which this molecule can be also formed from the sugars. Furfuryl ethyl ether is the product of the reaction between furfurol and ethanol. There are some other wine components (volatile phenols and (*Z*)-whiskylactone) extracted by ethanol from wood cask or formed during barrel aging that can also be relevant in some of the studied wines. Finally, two sulfur compounds (DMDS and 2-furanmethanethiol) were also easily detected by GC−O in some of the studied wines.

Quantitative Analysis of Odor Compounds. Results of the quantitative analysis, shown in **Table 3**, confirm and expand most of the observations previously made about the chemical composition of these special wines. Generally speaking, the four wine types have in common higher levels of 3-methylbutanal, phenylacetaldehyde, methional, sotolon, and ethyl 2-, 3-, and 4-methylpentanoates than those found in young dry wines, as

can be seen in **Table 3**, and leaving aside the Cava wines, they also have higher levels of ethyl cyclohexanoate and (*Z*)-whiskylactone. All these wines also have lower levels of isoamyl and phenylethyl acetates, 4-vinylguaiacol, linalool, isovaleric acid, and methoxypyrazines, and leaving aside again the Cava wines, they also have smaller levels of ethyl esters of fatty acids. It can be stated, therefore, that the four wine types share a common aroma profile, even if important differences between them can be found, as will be discussed below.

Pedro Ximénez (PX). The aroma profile of PX wines is specifically characterized by having the highest concentrations of 3-methylbutanal, furfural, and β-damascenone. Similarly, PX wines presented high levels of sotolon and ethyl cyclohexanoate, although they did not differ significantly from those found in Fino and Sauternes, respectively. These wines also have important levels of phenylacetaldehyde and methional and the lowest levels of isobutanol. The simultaneous occurrence of sotolon and furfural suggests that the former is not formed following a strictly chemical degradation of threonine into 2-ketobutyric acid (*39*) but that its formation is related to sugar degradation, as has been suggested by Ferreira et al. and Camara et al. (*14, 40*). This highlights the existence of a certain similarity in the genesis of aroma compounds between Port, Madeira, and PX wines, all them having in common an oxidative aging in the presence of relatively high levels of sugars. PX wines, in particular, derive from grapes reaching sugar levels above 300 g L^{-1}, which helps explain their high levels of sotolon (up to 540 μg L^{-1}). The average levels of phenylacetaldehyde and methional in PX samples (68 and 20 μg L^{-1}) are also similar to those reported by Cullere et al. (*41*) in Port wines (78 and 17 μg L^{-1}), while the levels of 3-methylbutanal are higher than those found in Port (94 μg L^{-1} vs 28 μg L^{-1}, respectively). The development of phenylacetaldehyde, and surely also that of methional, is dependent on dissolved O_2 concentration in wines (*42*).

PX wines present relatively large concentrations of ethyl 2-, 3-, and 4-methylpentanonates and of ethyl cyclohexanoate. A recent work dealing with the occurrence of these compounds in different wine families revealed that they are specially important in products with high alcohol content and submitted to long aging periods (*30*). Remarkably, β-damascenone seems to be a quite specific aroma compound of PX wines, as the statistical study reveals. Recent works carried out by Pineau et al. (*43*) and Escudero et al. (*25*) have revealed that this compound plays mainly the role of aroma enhancer in table wines, in which it is most often found at levels below 4 μg L^{-1}. The relatively huge levels at which this compound is found in PX wines, an average concentration of 10 μg L^{-1} and an amazing 21.7 μg L^{-1} maximum, may suggest that it could be directly involved in the raisin-like notes generally evoked in these wines. Finally, the lowest levels of isobutanol and isoamyl alcohol are most surely because in PX the natural fermentation is interrupted when the ethanol reaches between 4% and 10% (v/v).

Fino. Fino presents a distinctive aroma chemical composition characterized by significantly high levels of acetaldehyde, diacetyl, ethyl esters of branched aliphatic acids with four, five, or six carbon atoms and 4-ethylguaiacol. It also has high levels of sotolon and 3-methylbutanal. Acetaldehyde is synthesized from ethanol by flor yeast during biological aging. This compound has been traditionally employed as an age marker of this process, and its level provides an easy way to differ Fino wines from other types of Sherry produced by oxidative aging (*18*). Similarly, the ethyl esters of branched aliphatic acids are the result of the slow esterification with ethanol of the acids formed by flor yeast by Strecker degradation from the corresponding amino acids or amino acid derivatives, such as ketoacids (*44*). In this type of sample, sotolon is formed by the aldol condensation between acetaldehyde and 2-ketobutyric acid derived from threonine via an enzymatic reaction, only possible in presence of flor yeasts (*39*). The levels of sotolon are similar to those recently reported by Moreno and co-workers (*17*) and range from 56 to 160 μg L^{-1}, well above the odor threshold (15 μg L^{-1}) estimated for this compound in Fino type wines (*13*). Finally, results in **Table 3**, in accordance with previous reports (*17, 19*), confirm that 4-ethylguaiacol is also a characteristic aroma compound of Fino wines. The formation of 4-ethylguaiacol from wine *p*-coumaric and ferulic acids by *Brettanomyces* or *Dekkera* yeast is well referenced in the literature (*45, 46*).

Sauternes. The most outstanding features of the aroma chemical profile of Sauternes are that is has the highest content of phenylacetaldehyde and 3-mercaptohexanol and a tiny but significant concentration of 4-methyl-4-mercaptopentanone. Sauternes wines also showed a minimum content of β-damascenone, although this did not differ significantly from those found in Fino and table wines. The average level of phenylacetaldehyde, a *Botrytis cinerea* metabolite (*47*), in Sauternes wines was 97 μg L^{-1}, in agreement with the values reported by Sarrazin et al. (*7*). This compound seems to be the result of the oxidation induced in berries by the secretion of oxidases by the noble rot (*1*). The role of phenylacetaldehyde on the honey-like odor typically found in Sauternes wines has been demonstrated by Ferreira et al. (*42*) who showed that the addition of 50 μg L^{-1} of this compound to a young white dry wine resulted in a clear perception of honey notes. Similarly, the levels of 3-mercaptohexanol and of 4-methyl-4-mercaptopentanone found in this type of wine were much higher than those found in the rest of the wine types, in agreement with previous reports (*7, 48*). Finally, even if it does not reach the levels found in PX and Fino wines, sotolon is an important constituent of Sauternes wines. Its concentration ranged from 13 to 23 μg L^{-1}. Masuda et al. (*15*) demonstrated that the contribution of sotolon to the distinctive sweet aroma of botrytized wines was effective at concentrations greater than 2.5 μg L^{-1}.

Cava. In light of both the GC−O study and the chemical data, it can be said that the aroma profile of Cava is something between the young dry wines and the rest of the special wines. The aroma chemical profile of this type of wine is not specifically characterized by the presence of any outstanding odorant. However, it contains relatively high levels of acetaldehyde and of the other three oxidation-related aldehydes (methional, phenylacetaldehyde, and 3-methylbutanal), as well as of β-damascenone and sotolon, as is shown in **Table 3**. At the same time, the contents of linear esters (ethyl hexanoate and ethyl octanoate) and branched ethyl esters (ethyl 2-methylpropanoate, ethyl 2-methylbutyrate, and ethyl 3-methylbutyrate) in Cava are comparable to those of young dry wines.

The present paper provides a better understanding of the aroma composition of Pedro Ximenez, Fino, botrytized Sauternes, and Cava wines, contributing to the information database of wine flavor chemistry. This research suggests that the most important sources of aroma compounds derived from the different winemaking processes of the studied wines are the esterification of some branched fatty acids derived from amino acids and the oxidation of different precursors. Consequently, all these wines are relatively rich in 3-methylbutanal, pheny-

lacetaldehyde, methional, sotolon, and the ethyl esters of 2-, 3-, and 4-methylpentanoic acids. PX, Fino, and Sauternes have, in addition, some specific odorants or particularly high levels of some of the aforementioned odorants, while Cava has a less specific aroma profile halfway between these special wines and young white wines. More research is needed to verify, from a sensory point of view, the actual role of some of the above-mentioned compounds in the aroma features of the studied wines.

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