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Gas Chromatography−Olfactometry and Chemical Quantitative Study of the Aroma of Six Premium Quality Spanish Aged Red Wines

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The aroma of six premium quality Spanish red wines has been studied by quantitative gas chromatography−olfactometry (GC-O) and techniques of quantitative chemical analysis. The GC-O study revealed the presence of 85 aromatic notes in which 78 odorants were identified, two of which—1-nonen-3-one (temptatively) and 2-acetylpyrazine—are reported in wine for the first time. Forty out of the 82 quantified odorants may be present at concentrations above their odor threshold. The components with the greatest capacity to introduce differences between these wines are ethyl phenols produced by *Brettanomyces* yeasts (4-ethylphenol, 4-ethyl-2-methoxyphenol, and 4-propyl-2-methoxyphenol), 2,5-dimethyl-4-hydroxy-3(2H)-furanone (furaneol), (*Z*)-3-hexenol, thiols derived from cysteinic precursors (4-methyl-4-mercaptopentan-2-one, 3-mercaptohexyl acetate, and 3-mercaptohexanol), some components yielded by the wood [(*E*)-isoeugenol, 4-allyl-2-methoxyphenol, vanillin, 2-methoxyphenol (guaiacol), and (*Z*)-whiskylactone], and compounds related to the metabolism (2-phenylethanol, ethyl esters of isoacids, 3-methylbutyl acetate) or oxidative degradation of amino acids [phenylacetaldehyde and 4,5-dimethyl-3-hydroxy-2(5H)-furanone (sotolon)]. The correlation between the olfactometric intensities and the quantitative data is, in general, satisfactory if olfactometric differences between the samples are high. However, GC-O fails in detecting quantitative differences in those cases in which the olfactive intensity is very high or if odors elute in areas in which the odor chromatogram is too complex.

KEYWORDS: Wine; aroma; gas chromatography−olfactometry; quantitative analysis; GC-iontrap MS

INTRODUCTION

The aroma of wine has been the object of numerous studies in the past few years, despite which there remain numerous unanswered questions about the role that certain components play in its aromatic notes. This is particularly true in the case of wines of complex aroma and mainly in those of highest quality and complexity. For these wines and despite the extensive work published about their aromatic composition (*1*−*6*), it has not been possible to date to obtain a satisfactory reconstruction of their aroma, unlike the case of some white and rosé wines of simpler aromas (*7*, *8*).

This difficulty has entailed the necessity to look for alternative ways, such as the reconstruction of aromatic fractions extracted from the wine (*5*), the chemometric treatment of the olfactometric data (*4*), or the construction of chemometric models relating the aromatic composition to the sensory characteristics of wine (*6*). This last investigation showed that quantitative data from "easily analyzed" odorants carry out enough information to explain and predict some red wine aroma nuances. However, it also became evident that some other aroma nuances, such as fruit, licorice, spicy, or ripe fruit lactone, cannot be satisfactorily explained with such sets of chemical data. All of this suggests that the chemical interpretation of red wine aroma will require quantitative data on some more flavor chemicals, some of which are not easily analyzed and require specific isolation strategies. This fact has promoted the present research, in which novel analytical methods, including quantitative gas chromatography−olfactometry (GC-O), have been applied to determine a broad spectrum of wine flavor chemicals from six premium quality Spanish aged red wines. The main aims of this research are, first, to evaluate the amount of odorants potentially important to wine aroma that still are not known; second, to establish which odorants can be found at concentrations above or near the threshold; third, to determine which odorants can be responsible for the sensory differences between wines; and four, to evaluate the strengths and drawbacks of quantitative GC-O.

MATERIALS AND METHODS

Wines, Reagents, and Standards. Six aged Spanish red wines were studied; three were from Ribera Duero (RD1, RD2, and RD3), one was from Rioja (RJ), one was from Tierra de Castilla-León (C-L), and one was from Somontano (SM). All of the wines were premium quality wines that scored very high in different wine guides. A sensorial analysis

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was carried out by a panel of experts to verify the quality of the samples and to define their most important aromatic descriptors.

The chemical standards were supplied by Aldrich (Gillingham, U.K.), Fluka (Buchs, Switzerland), Sigma (St. Louis, MO), Lancaster (Strasbourg, France), PolyScience (Niles, U.S.A.), Chemservice (West Chester, U.S.A.), Interchim (Monlucon, France), International Express Service (Allauch, France), and Firmenich (Geneva, Switzerland).

LiChrolut EN resins, prepacked in 200 mg cartridges (3 mL total volume) or in bulk, were obtained from Merck (Darmstadt, Germany). Dichloromethane, high-performance liquid chromatography (HPLC) quality, was obtained from Fisher Scientific (Loughborough, U.K.); methanol, LiChrosolv quality, was from Merck; absolute ethanol, pentane, potassium hydrogen phthalate, sodium hydrogen carbonate, and ammonium sulfate were from Panreac (Barcelona, Spain), and all of them are were ARG quality; pure water was obtained from a Milli-Q purification system (Millipore, U.S.A.).

The BHA (3-*tert*-butyl-4-hydroxyanisole) solution contained 10 mg of this compound per g of ethanol. Sodium *p*-hydroxymercuribenzoate and cysteine 99% were purchased from Sigma, and α,α,α-tris-(hydroxymethyl)methylamine (TRIS) 99.9% was purchased from Aldrich-España (Madrid). O-(2,3,4,5,6-Pentafluorobenzyl)hydroxylamine hydrochloride (99% PFBHA), used as a derivatization reagent for carbonyl compounds, was purchased from Fluka-España (Madrid). Semiautomated solid phase extraction was carried out with a VAC ELUT 20 station from Varian (Walnut Creek, U.S.A.).

GC-O Analysis. Standard polypropylene SPE tubes (6 mL) were packed with LiChrolut EN resins (Merck) to form a compact bed (1 g, 1 cm internal diameter, 2 cm long). The beds were washed with 5 mL of dichloromethane, 10 mL of methanol, and 10 mL of water/ethanol mixture (12% v/v). Sixty microliters of internal standard solution (2-ethyl-1-hexanol 600 mg/L in ethanol) and 70 μL of BHA solution were added to 150 mL of wine. This volume of wine was passed through the SPE cartridge at 2 mL/min. The SPE cartridge was then washed with 10 mL of water and dried by letting air pass through (−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 about 2 mL (48 °C) and then under a stream of pure N_2 up to 500 μL. Extracts from the wines RD1 and RJ were selected for the representativity study, carried out as described in ref *5*.

These concentrated wine extracts were used in the GC-O study. Sniffings were carried out in a Thermo 8000 series GC equipped with a flame ionization detector (FID) and a sniffing port (ODO-1 from SGE, Ringbow, Australia) connected by a flow splitter to the column exit. The column was a DB-WAX from J&W (Folsom, CA), 30 m × 0.32 mm with 0.5 μm film thickness. The carrier gas was H_2 at 3 mL/min. One microliter of extract was injected in the 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 at 4 °C/min up to 200 °C. Eight trained judges carried out the GC-O study. Judges were asked to measure the overall intensity of each odor using a 0−3 scale with seven possible scores (half values allowed). Each judge evaluated the six wine extracts once, and the eight intensity scores obtained for each odorant in each wine sample were averaged to give the mean intensity score for that odorant in that wine. A two way analysis of variance (ANOVA) (factor wine and judge) was carried out to determine the existence of significant differences in intensity scores between wines for each odorant. Analytical characteristics of these signals are described and discussed in ref *9*. The odorants were identified by comparison of their odors, chromatographic retention properties, and MS spectra with those of pure reference compounds.

Quantitative Analysis. *(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. (*10*). 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 (*10*). 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. (*11*). In accordance with the method, 50 mL of wine, containing 25 μL of BHA solution and 75 μL of a surrogated standards solution, 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 *11*.

(C) Furaneol [2,5-Dimethyl-4-hydroxy-3(2H)-furanone], Homofuraneol [2-Ethyl-4-hydroxy-5-methyl-3(2H)-furanone], and Sotolon [4,5-Dimethyl-3-hydroxy-2(5H)-furanone] (SPE and GC-Ion Trap MS Analysis). This analysis was carried out using the method proposed and validated in ref *12*. In accordance with the method, 50 mL of wine (to which 7.5 g of ammonium sulfate have been previously added) was loaded into a SPE bed formed by 800 mg of LiChrolut EN resins packed in a 6 mL filtration tube from Supelco (Madrid, Spain). The bed was washed with 5 mL of water first, then dried, and finally washed with 15 mL of a mixture pentane/dichloromethane (20/1). Analytes were eluted with 6 mL of dichloromethane. This volume was concentrated to 100 μL by evaporation in a centrifuge tube heated at 45 °C and analyzed by GC-ion trap MS under the conditions described in ref *12*.

(D) Octanal, Nonanal, Decanal, 1-Octen-3-one, (E,Z)-2,6-Nonadienal, and (E)-2-Nonenal (SPE and GC-Ion Trap MS Analysis). This analysis was carried out using the method proposed and validated in ref *13*. According to this method, 200 mL of wine was loaded into a 200 mg LiChrolut-EN solid phase extraction cartridge [previously conditioned with 4 mL of dichloromethane, 4 mL of methanol, and 4 mL of a 13% ethanol (v/v) aqueous solution]. Low molecular weight carbonyls, together with the majority of wine volatiles, were removed by cleanup with 60 mL of a 40% methanol (v/v) aqueous solution containing 1% $NaHCO_3$. Carbonyls retained in the cartridge were directly derivatized by passing through 2 mL of an aqueous solution of PFBHA (5 mg mL^{-1}) and letting the cartridge imbibed with the reagent 15 min at room temperature. Excess of reagent was removed with 10 mL of a 0.05 M sulfuric acid solution. Analytes were finally eluted with 2 mL of dichloromethane. Thirty microliters of internal standard solution (2-octanol 60 mg L^{-1} in dichloromethane) was added to the extract, which was then concentrated to 100 μL by evaporation in a centrifuge tube heated at 45 °C and analyzed by GC-ion trap MS under the conditions given in ref *13*.

(E) 3-Mercaptohexyl Acetate, 2-Furfurylthiol, 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 hydro alcoholic solution (13% ethanol v/v). A 200 mL amount of wine containing 25 μL 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 μL 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 N_2 to 100 μL. This extract (20 μL) was analyzed by GC with MS detection. The GC was a CP3800 fitted to a Saturn 2200 electronic impact ion trap mass spectrometer from Varian. The column was a DB-WAXetr from J&W (Folsom, CA), 60 m × 0.25 mm × 0.25 μm film thickness. The carrier was He at 1 mL/min. The temperature program was as follows: 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 under

Table 1. Sensory Descriptors Given by the Expert Panel to the Wines Considered in the Study

RD1	RJ	RD2	RD3	C-L	SM
toasted	leather	toasted wood	blackberry	toasted wood	phenolic
liquorices	tobacco	woody	woody	cacao	toasted wood
coffee	fruit jam	fruity		well-matured fruit	kirsch
spicy				plum	cherry
					woody

the following injection program: initial 40 °C for 0.60 min and then raised to 250 °C at 100 °C min^{-1}. The purge valve was opened the first 0.4 min and then closed until min 4.8. MS acquisition was carried out in selected ion storage (SIS) mode of an ionic range from 73 to 134 *m*/*z* for 2-methyl-3-furanthiol and 4-mercapto-4-methyl-2-pentanone and from 70 to 135 for 3-mercaptohexyl acetate, 2-furfurylthiol, and 3-mercapto-1-hexanol. The *m*/*z* quantitative fragments were 114, 75, 88, 81, and 82 *m*/*z*, respectively.

RESULTS AND DISCUSSION

Odorants Present in the Six Wines under Study. The aroma of six premium quality Spanish aged red wines has been studied by quantitative GC-O and subsequent chemical analysis. Relevant aroma sensory descriptors given by the expert panel are given in **Table 1**, and the results from the GC-O study are summarized in **Table 2**. The olfactometric experiment was carried out on extracts obtained by SPE of wine on LiChrolut-EN resins. In the conditions used (150 mL of wine percolated through a 1 g resin bed), the extraction of nearly all odorants is complete as it has been demonstrated in different analytical studies (*11*−*14*). Customary sensory tests performed on two of those extracts to evaluate their representativity yielded satisfactory results (22 out of 25 correct responses in a triangular test to compare between extracts and 18 out of 24 correct responses to group each extract with the wine it comes from). On the other hand, the olfactometric evaluation was carried out by a panel of eight trained tasters using a seven point quantitative scale. This strategy has been demonstrated to provide data of semi-quantitative value (*9*). The mean intensities given by the panel for a given odorant in two different samples will differ if the concentration of such odorant in both samples differs by a factor related to the particular sensory properties of the odorant (ranging from 1.2 to more than 10). It is expected, therefore, that all important odorants will have relatively high scores in **Table 2** and that those odorants responsible for a sensory difference between the samples will have different intensity scores in the table. The opposite, however, is not true, since the importance of polar compounds with low volatility in wine is overestimated by the extraction method used.

Table 2 lists the 85 different odor notes detected in the GC-O experiment, the identity of 78 of which could be identified, and the mean odor intensity scores given for the panel. Two of the odorants in the list are reported in wine for the first time: 1-nonen-3-one (just a temptative) and 2-acetylpyrazine, a well-known component of products that have undergone thermal processing (*15*). Another new finding is the confirmation of the occurrence of γ-undecalactone, whose presence had been postulated in a previous work (*16*). Quantitative data in **Table 4** show, however, that it is present at concentrations well below its threshold. On the basis of the intensity scores, only unknowns 1460 (max $I = 1.63$) and 1520 (max $I = 2.69$) could be important odorants, and on the basis of the differences in intensity between samples (**Table 3**), only unknowns 2085 and 1520 may be responsible for some sensory difference between the six wines. It seems, therefore, that the qualitative composition of this kind of wines is mostly well-known.

Odor Active Odorants. Table 4 shows the concentrations, normalized by their corresponding threshold values, of 82 odorants from these wines. Another four odorants could not be determined, since their concentrations are below the detection limit of the analytical method. These are 2-methyl-3-furanthiol (LD = 10 ng L^{-1}), 2-furfurylthiol (LD = 10 ng L^{-1}), 1-octen-3-one (LD = 60 ng L^{-1}), and (*E*,*Z*)-2,6-nonadienal (LD = 20 ng L^{-1}). Data in the table indicate that each of these wines contains between 33 and 38 odorants at concentrations above their threshold, a number much greater than that found in white and rosé wines (*7*, *8*, *16*). Altogether, there are 40 odorants that can reach concentrations above their threshold in this set of wines. As odor thresholds are affected by high imprecision and additive, synergic, and antagonistic effects can take place, these values should not be taken as close boundaries but as an approximation to the number of odorants that constitute the odor of such wines. It is remarkable that components not quantified in a previous investigation (*6*), such as 2,5-dimethyl-4-hydroxy-3(2H)-furanone (furaneol), 4,5-dimethyl-3-hydroxy-2(5H)-furanone (sotolon), 3-mercaptohexyl acetate, 4-mercapto-4-methylpentanone, 3-mercaptohexanol, and (*E*)-2-nonenal, are present at concentrations above their odor thresholds. The absence of these components may explain the limitations found in that study when explaining some aromatic notes.

Potentially Differencing Compounds. Differencing components are those that have a more acute role in the perception of sensory differences between samples. At the present time, this property can only be verified by means of sensory tests, although an approximation can be obtained by considering the variability in geometric terms (nonarithmetic) of concentrations or of concentrations normalized by their thresholds (OAV) (*16*). This approach is shown in **Table 5**. In agreement with data shown in the table, the components with greater potentiality to introduce variability are ethyl phenols. In addition to 4-ethylphenol and 4-ethyl-2-methoxyphenol, two components well-known and acknowledged as responsible for the aromatic deviations introduced by *Brettanomyces* yeasts (*17*), our study indicates that 4-propyl-2-methoxyphenol, a component hardly considered in the past, can also exert an important role. The aromatic and biogenetic similarity of these three components suggests an additive effect, which would increase its importance as a set responsible for aromatic differences. Other components or groups of components that according to data in this table, would also be responsible for the sensory differences are 2,5-dimethyl-4-hydroxy-3(2H)-furanone (furaneol), (*Z*)-3-hexenol, thiols derived from cysteinic precursors (*18*) (3-mercaptohexyl acetate, 4-methyl-4-mercaptopentan-2-one, and 3-mercaptohexanol), some wood-related compounds [(*E*)-isoeugenol, 4-allyl-2-methoxyphenol (eugenol), vanillin, (*Z*)-whiskylactone, 2-methoxyphenol (guaiacol)], and some compounds related either to the metabolism (2-phenylethanol, 3-methylbutyl acetate, ethyl esters of isoacids) or to the oxidative degradation of the amino acids [phenylacetaldehyde and to a lesser extent 4,5-dimethyl-3-hydroxy-2(5H)-furanone (sotolon)]. Some of these differences have an obvious effect on the sensory properties of wines. For instance, wines RJ and SM are described as leather, tobacco, and phenolic, in accordance to their high content in ethylphenols. The toasted wood character seems to be associated with the presence of furaneol, vanillin, and (*Z*)-whiskylactone.

Relation between Olfactometric and Quantitative Data. Tables 3 and **5** bring together those odorants with more variability in the set of six wines, according to the results of

Table 2. Odorants Found in Six Spanish Aged Red Wines: Gas Chromatographic Retention Data, Olfactory Description, Chemical Identity, and Mean Olfactometric Intensities (0–3 Scale, Eight Judges)

RI	odor descriptor	identity	RD1	RJ	RD2	RD3	C-L	SM	average
972	fruity, strawberry	ethyl isobutyrate[a]	1.56	1.25	1.69	1.81	1.75	1.69	1.63
983	butter, cream	2,3-butanedione[a]	1.56	2.00	1.50	1.63	1.50	1.19	1.56
1005	flowery	isobutyl acetate[a]	0.63	0.5	0.19	0.94	0.94	0.44	0.60
1047	fruity	ethyl butyrate[a]	1.94	1.19	1.44	1.75	1.63	1.13	1.51
1060	fruity, green apple	ethyl 2-methylbutyrate[a]	1.00	1.25	1.63	1.50	1.13	1.50	1.33
1082	fruity, anise	ethyl 3-methylbutyrate[a]	1.56	1.75	1.69	1.25	1.44	1.13	1.47
1105	bitter, green	butyl acetate[a]	0.00	0.13	0.25	0.00	0.44	0.00	0.14
1125	bitter	2-methylpropanol[a]	0.44	0.50	0.38	0.5	0.38	1.00	0.53
1147	banana	3-methylbutyl acetate[a]	1.06	0.38	1.06	0.63	1.00	1.31	0.91
1170	grass	ethyl valerate[a]	1.13	0.75	0.63	1.13	1.06	1.44	1.02
1247	cheese	3-methyl-1-butanol[a]	1.69	2.38	2.44	2.50	2.13	2.63	2.29
1270	fruity, anise	ethyl hexanoate[a]	1.38	1.63	2.13	1.75	1.69	1.69	1.71
1295	fatty, wet	acetoin[a]	0.69	0.63	0.69	0.50	1.00	0.44	0.66
1300	lemon	octanal[a]	0.44	0.31	1.13	0.50	0.56	1.25	0.70
1317	mushroom	1-octen-3-one[a]	0.06	0.69	0.13	0.00	0.19	1.50	0.43
1322	onion, meaty	2-methyl-3-furanthiol[a]	2.50	1.88	1.81	2.25	2.19	2.13	2.13
1367	rotten food	dimethyl trisulfide[c]	0.63	0.00	0.00	0.00	0.00	0.81	0.24
1379	toasty, green, dry	1-hexanol[a]	0.94	1.19	1.69	1.44	1.13	0.88	1.21
1395	box tree	4-mercapto-4-methyl-2-pentanone[a]	0.44	0.25	0.50	0.70	1.00	0.70	0. 60
1407	grass	(*Z*)-3-hexenol[a]	0.88	1.06	1.31	1.19	1.19	1.44	1.18
1415	gas, chlorine,	nonanal[a] + NI[d]	1.31	1.38	0.75	1.06	1.19	1.31	1.17
1422	mushrooms	1-nonen-3-one[c]	0.00	0.06	0.00	0.00	0.00	0.31	0.06
1435	fruity, anise	ethyl octanoate[a]	0.13	0.56	0.38	0.81	0.25	0.88	0.50
1448	coffee, toasty	2-furfurylthiol[a]	1.50	1.44	1.69	1.44	2.00	1.38	1.57
1474	baked potato	3-(methylthio)propanal[a]	1.75	1.63	2.19	1.69	1.81	2.13	1.86
1477	vinegar	acetic acid[a]	0.00	0.50	0.25	0.50	0.38	0.38	0.33
1485	sweet	furfural[a]	0.88	1.06	0.88	0.69	1.56	0.94	1.00
1490	plastic	NI[d]	1.50	1.63	0.88	0.94	1.25	0.75	1.16
1520	chlorine	NI[d]	2.06	1.69	1.56	1.88	2.13	2.69	2.00
1540	green pepper	3-isobutyl-2-methoxypyrazine[a]	0.81	0.63	0.94	1.31	0.50	1.38	0.93
1555	wet, earth	(*E*)-2-nonenal[a]	0.81	0.81	1.06	0.50	1.00	0.88	0.84
1570	flowery, muscat	linalool[a]	1.18	0.63	1.31	1.31	1.06	1.31	1.13
1588	cheese	2-methylpropanoic acid[a]	0.81	1.88	1.5	0.94	0.56	1.13	1.14
1605	cucumber	(*E*,*Z*)-2,6-nonadienal[c]	0.00	0.38	0.19	0.13	1.38	0.00	0.34
1638	roasty	2-acetylpyrazine[a]	1.44	1.00	1.13	1.19	0.50	1.06	1.05
1650	cheese	butyric acid[a]	2.63	2.63	2.69	2.56	2.56	2.31	2.56
1671	flowery, rose	phenylacetaldehyde[a]	0.00	1.31	0.31	0.75	0.50	0.81	0.61
1691	cheese	3-methylbutyric acid[a]	2.69	2.88	2.88	2.75	2.44	2.69	2.72
1720	anise	α-terpineol[a]	0.81	1.25	0.50	1.38	0.63	0.81	0.90
1735	box tree	3-mercaptohexyl acetate[a]	0.00	0.00	0.38	0.00	0.38	0.94	0.28
1745	cooked vegetable	3-(methylthio)propanol[a]	1.94	2.19	1.56	1.25	1.88	2.31	1.85
1767	baked apple	NI[d]	0.75	0.63	0.38	0.75	0.75	0.56	0.64
1810	baked potato	NI[d]	0.38	0.88	0.63	0.56	0.47	0.38	0.55
1836	baked apple	β-damascenone[a]	1.44	1.63	1.38	1.13	1.50	1.44	1.42
1872	cheese	hexanoic acid[a]	2.44	2.69	2.63	2.44	2.38	2.00	2.43
1872	sulfur	3-mercapto-1-hexanol[a]	1.50	0.56	0.44	1.50	0.38	0.63	0.83
1883	phenolic, chemical	2-methoxyphenol[a]	1.94	1.50	1.88	1.25	2.19	1.44	1.70
1905	flowery	ethyl dihydrocinnamate[a]	0.63	0.75	0.81	0.31	0.44	1.31	0.71
1915	coconut	(*E*)-whiskylactone[a]	1.75	0.63	2.00	1.19	1.00	0.88	1.24
1940	roses	2-phenylethanol[a]	2.06	2.25	2.44	1.81	2.25	2.44	2.21
1947	violets	β-ionone[a]	0.25	1.06	0.50	0.63	0.75	0.63	0.64
1985	coconut	(*Z*)-whiskylactone[a]	1.88	2.56	2.25	2.06	2.44	2.56	2.29
2025	coconut, curry	NI[d]	0.69	1.13	0.63	0.81	0.75	0.31	0.72
2054	flowery, clove	4-ethyl-2-methoxyphenol[a]	0.88	1.50	1.25	1.94	0.94	1.75	1.38
2063	peach	γ-nonalactone[a]	1.69	1.81	0.75	0.75	1.94	0.81	1.29
2072	cotton candy	2,5-dimethyl-4-hydroxy-3(2H)-furnanone	1.44	1.31	1.75	1.81	1.81	2.06	1.70
2085	curry	NI[d]	0.38	0.63	1.38	0.50	0.00	0.00	0.48
2098	fatty acid	octanoic acid[a]	1.88	1.63	1.63	2.25	1.63	1.00	1.67
2105	cotton candy	2-ethyl-4-hydroxy-5-methyl-3(2H)-furanone	1.19	1.38	1.63	1.44	1.69	1.00	1.39
2115	bitumen, animal	*m*-cresol[a]	0.69	0.81	0.88	0.88	1.06	0.56	0.81
2123	cotton candy	4-hydroxy-5-methyl-3(2H)-furanone[c]	0.13	0.19	0.50	0.13	0.25	0.13	0.22
2142	phenolic	2-methoxy-4-propylphenol[a]	0.81	0.44	1.00	0.81	0.94	0.00	0.67
2160	flowery	ethyl cinnamate[a]	0.75	0.75	0.88	0.44	0.00	0.50	0.55
2175	peach, lactone-like	γ-decalactone[a]	1.00	1.06	0.88	0.56	1.00	0.44	0.82
2192	clove, balsamic	4-allyl-2-methoxyphenol[a]	0.94	1.38	1.81	0.88	0.94	2.30	1.37
2205	phenolic, leather	4-ethylphenol[a]	2.00	2.63	2.19	2.25	2.06	2.56	2.28
2223	phenolic, smokey	2-methoxy-4-vinylphenol[a]	1.19	0.63	0.50	0.63	0.81	0.00	0.63
2235	curry, burnt	4,5-dimethyl-3-hydroxy-2(5H)-furanone[a]	2.69	1.75	2.44	2.13	2.19	2.63	2.30
2252	honey, sweet	*o*-aminoacetophenone[c]	0.50	0.00	0.88	0.56	0.81	0.00	0.46
2260	honey, flowery	methyl anthranilate[c]	0.50	0.69	0.00	0.50	0.00	0.50	0.36
2270	apricot	γ-undecalactone[a]	1.19	1.25	1.00	0.81	1.06	0.00	0.89
2307	medicinal, phenolic	2,6-dimethoxyphenol[a]	1.00	1.19	1.19	1.19	1.44	1.69	1.28
2307	fatty acid	decanoic acid[a]	1.75	1.69	2.19	1.56	1.69	1.44	1.72

Table 2. Continued

RI	odor descriptor	identity	RD1	RJ	RD2	RD3	C-L	SM	average
2345	lemon, anise	farnesol-a[b]	0.50	0.56	1.25	0.69	1.38	0.00	0.73
2372	floral	(*E*)-isoeugenol[a]	0.44	1.00	1.19	0.75	0.50	0.50	0.73
2387	floral, honey, pollen	farnesol-c[b]	0.00	0.00	0.44	0.00	0.00	0.00	0.07
2427	almond shell	4-vinylphenol[a]	0.50	1.06	0.75	0.63	0.56	0.81	0.72
2457	rancid, dry	NI[d]	1.06	1.06	0.63	0.81	0.75	0.69	0.83
2517	dry, metallic	dodecanoic acid[a]	0.50	1.00	0.44	1.25	0.56	0.75	0.75
2570	sweet, pollen, floral	4-allyl-2,6-dimetoxyphenol[a]	0.38	0.38	0.38	0.63	1.00	0.25	0.50
2585	honey, pollen, roses	phenylacetic acid[a]	2.69	2.44	2.44	2.25	2.50	2.44	2.46
2595	vanillin	vanillin[a]	2.38	2.00	1.00	2.00	2.63	1.81	1.97
2607	vanillin	methyl vanillate[a]	0.00	0.94	0.25	0.94	1.13	0.38	0.56
2665	pollen, flowery	ethyl vanillate[a]	1.06	1.00	0.45	0.94	1.44	0.44	0.89
2685	flowery, clove, vanilla	acetovanillone[a]	0.19	0.00	0.00	0.69	0.00	0.88	0.29

[a] Identification based on coincidence of gas chromatographic retention and mass spectrometric data with those of the pure compounds available in the lab. [b] Pure compounds were not available, but gas chromatographic retention and mass spectrometric 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] NI, not identified compounds.

Table 3. Odorants for Which Maximum Differences between the Six Studied Wines Were Observed in the GC-O Experiment

identity	mean intensity	max *I* – min *I*	P*[a]	*r* (OAV)	*r* (logOAV)
vanillin	1.97	1.63	0.080	**0.81**	**0.86**
1-octen-3-one	0.43	1.50	0.003		
4-allyl-2-methoxyphenol	1.37	1.42	0.002	**0.81**	**0.76**
farnesol-a	0.73	1.38	0.001		
Ni (RI 2085)	0.48	1.38	0.002		
(*E*,*Z*)-2,6-nonadienal	0.34	1.38	0.000		
(*E*)-whiskylactone	1.24	1.37	0.290	**0.76**	**0.74**
2-methylpropanoic acid	1.14	1.32	0.036	**0.79**	**0.82**
phenylacetaldehyde	0.61	1.31	0.023	**0.93**	**0.94**
octanoic acid	1.67	1.25	0.104	**0.88**	**0.83**
γ-undecalactone	0.89	1.25	0.053		
γ-nonalactone	1.29	1.19	0.103	**0.94**	**0.96**
2-methoxy-4-vinylphenol	0.63	1.19	0.101	**0.77**	**0.71**
Ni (RI 1520)	2.00	1.13	0.057		
methyl vanillate	0.56	1.13	0.007	0.02	0.02
3-mercapto-1-hexanol	0.83	1.12	0.144	**0.88**	**0.82**
3-(methylthio)propanol	1.85	1.06	0.236	**0.97**	**0.99**
4-ethyl-2-methoxyphenol	1.38	1.06	0.179	**0.86**	**0.78**
ethyl vanillate	0.89	1.00	0.124	0.48	0.52
ethyl dihydrocinnamate	0.71	1.00	0.269	0.55	0.60
2-methoxy-4-propylphenol	0.67	1.00	0.059	**0.73**	**0.85**
4,5-dimethyl-3-hydroxy-2(5H)-furanone	2.30	0.94	0.065	0.60	0.60
3-methyl-1-butanol	2.29	0.94	0.369	0.11	0.08
2-methoxyphenol	1.70	0.94	0.313	**0.81**	**0.76**
2-acetylpyrazine	1.05	0.94	0.306		
octanal	0.70	0.94	0.020	0.25	0.25
3-mercaptohexyl acetate	0.28	0.94	0.000	**0.81**	**0.78**
3-methylbutyl acetate	0.91	0.93	0.325	**0.81**	**0.88**

[a] P* wine: ANOVA experiment wine × sniffer.

the olfactometric (**Table 3**) or quantitative study (**Table 5**). **Table 3** also includes the correlation coefficient between the olfactometric scores and the OAV or log(OAV). Correlation between these values is in general satisfactory, at least if the olfactometric difference is high. Data in the table show that if the difference $I_{max} - I_{min}$ is higher than 1, the correlation coefficient ranges from 0.71 to 0.99 except for methyl vanillate. In this case, the olfactometric signal may be distorted by the previous elution of the powerful vanillin. When $I_{max} - I_{min}$ is equal to or below 1, the correlation between olfactometric and instrumental quantitative data is, in general, poorer, particularly if the olfactometric difference is not significant from a statistical point of view (cases of ethyl vanillate, ethyl dihydrocinnamate, or 3-methyl-1-butanol). In the case of octanal, for which the panel found a significant difference between samples, the causes of the poor correlation are less clear, but the coelution of some other unknown odorant should not be discarded. Something similar happens to 4,5-dimethyl-3-hydroxy-2(5H)-furanone, whose olfactometric signal appears in an area with a large number of odors. In the case of 3-methyl-1-butanol, the olfactometric signal is simply saturated.

Leaving aside these cases, it can be seen that most of the compounds present in **Table 3** also can be found in **Table 5**. The absence from **Table 5** of compounds such as (*E*)-whiskylactone, γ-nonalactone, or 2-methoxy-4-vinylphenol is due to their low OAV. In all of these cases, the ratio OAV_{max}/OAV_{min} is higher than 2, but OAV_{min} is below 0.2 (the limit used in **Table 5**). In these cases, olfactometric data overestimate the importance of the component as a result of the technique used in the preparation of the extract. In the case of 3-(methylthio)propanol, the cause must be different. A possible cause is that for this component, the olfactory intensity changes greatly with its concentration (the signal becomes saturated at 10 times the threshold, while in the rest of cases at least a 100-fold

Table 4. Odor Activity Values (OAVs) of Odorants Found in the Six Spanish Aged Red Wines Studied[a]

	RD1	RJ	RD2	RD3	C-L	SM	average	odor threshold[b] (μg/L)
acetaldehyde	84.9	91.3	97.2	90.2	88.7	85.5	89.6	500 (7)
3-methylbutyric acid	42.9	60.0	35.7	32.2	49.1	77.5	49.5	33 (2)
ethyl octanoate	57.4	38.8	70.1	42.3	46.1	32.4	47.9	5 (2)
β-damascenone	20.8	48.8	39.8	18.2	55.5	50.5	38.9	0.05 (7)
ethyl hexanoate	45.8	24.81	31.6	36.0	26.7	18.2	30.5	14 (2)
2,5-dimethyl-4-hydroxy-3(2H)-furanone	28.8	6.06	29.8	27.4	41.2	34.9	28.0	5 (1)
ethyl isobutyrate	15.2	36.9	15.0	14.5	19.9	37.9	23.2	15 (2)
ethyl isovalerate	18.9	33.4	13.2	10.0	20.4	30.6	21.1	3 (2)
ethyl butyrate	25.9	15.3	18.3	19.3	15.9	17.3	18.7	20 (2)
3-methylbutyl acetate	13.4	13.6	16.1	8.31	12.0	27.6	15.2	30 (2)
3-mercaptohexyl acetate	6.19	9.52	8.57	15.9	16.4	22.5	13.2	0.0042 (19)
butyric acid	17.0	8.46	15.0	13.1	13.8	10.5	13.0	173 (2)
4-allyl-2-methoxyphenol	4.57	11.16	9.03	6.9	9.26	14.6	9.24	6 (2)
4-mercapto-4-methyl-2-pentanone	5.00	6.25	8.75	13.7	6.25	13.1	8.85	0.0008 (19)
4,5-dimethyl-3-hydroxy-2(5H)-furanone	4.00	10.0	7.54	7.67	8.07	11.83	8.20	0.7 (20)
3-methyl-1-butanol	8.31	8.78	6.32	5.53	8.04	9.69	7.80	30000 (7)
2,3-butanedione	3.40	9.80	ND	7.28	6.90	10.2	7.52	100 (2)
hexanoic acid	9.92	4.66	7.11	8.05	6.74	3.43	6.65	420 (2)
2-methylbutyric acid	4.43	7.79	4.07	4.60	5.82	8.56	5.88	50 (21)
(*Z*)-whiskylactone	3.01	4.57	5.16	4.31	6.58	8.79	5.40	67 (22)
octanoic acid	6.61	4.16	5.36	6.56	5.51	2.19	5.06	500 (2)
3-mercaptohexanol	4.68	3.42	2.72	5.12	3.30	5.47	4.12	0.06 (19)
4-ethyl-2-methoxyphenol	0.57	10.64	0.67	4.75	1.13	6.83	4.10	33 (2)
2-phenyletanol	2.63	5.94	2.15	1.71	3.50	4.15	3.35	14000 (2)
β-ionone	3.47	3.41	3.00	4.28	2.45	3.43	3.34	0.09 (2)
3-(methylthio)propanol	2.40	3.41	2.60	2.25	3.30	3.88	2.97	1000 (2)
ethyl lactate	2.58	1.99	3.90	2.37	4.37	1.62	2.80	154636 (23)
(*E*)-2-nonenal		2.23	2.25	1.18	2.76	1.61	2.01	0.17 (24)
4-ethylphenol	0.33	6.00	0.27	1.74	0.78	3.09	2.00	440 (22)
ethyl 2-methylbutyrate	1.20	3.40	1.04	1.03	1.69	2.91	1.88	18 (2)
2-methylpropanol	1.55	2.07	1.67	1.43	1.75	2.47	1.82	40000 (2)
phenylacetaldehyde	1.38	3.60	0.77	1.32	1.09	2.18	1.72	1 (*)[c]
ethyl cinnamate	2.14	1.13	1.55	1.26	1.83	1.08	1.50	1.1 (2)
2-methoxyphenol	1.35	0.96	1.62	0.79	2.21	1.53	1.41	9.5 (2)
vanillin	0.80	0.66	1.47	0.68	1.42	2.09	1.19	60 (*)
(*Z*)-3-hexenol	0.76	0.69	1.99	1.61	0.99	0.51	1.09	400 (2)
2-methylpropanoic acid	0.62	1.15	0.75	0.72	0.89	1.68	0.97	2300 (2)
γ-butyrolactone	0.60	0.69	0.86	0.70	1.11	1.38	0.89	35 (*)
2-methoxy-4-vinylphenol	0.71	0.57	0.35	0.44	0.62	0.70	0.60	40 (7)
ethyl dihydrocinnamate	0.53	0.47	0.69	0.41	0.71	0.50	0.55	1.6 (2)
2-methoxy-4-propylphenol	0.06	0.20	0.09	0.33	0.69	1.65	0.50	10 (*)
decanoic acid	0.47	0.43	0.50	0.46	0.57	0.29	0.45	1000 (2)
1-hexanol	0.44	0.33	0.62	0.54	0.40	0.25	0.43	8000 (2)
linalool	0.49	0.26	0.61	0.38	0.48	0.31	0.42	25 (2)
(*E*)-isoeugenol	0.24	0.10	1.20	0.13	0.75	0.10	0.42	6 (*)
2-ethyl-5-methyl-4-hydroxy-3(2*H*)-furanone	0.37	0.13	0.30	0.43	0.35	0.41	0.33	55 (20)
γ-nonalactone	0.25	0.21	0.38	0.44	0.17	0.38	0.30	30 (2)
ethyl vanillate	0.22	0.37	0.15	0.17	0.29	0.24	0.24	990 (11)
ethyl decanoate	0.28	0.18	0.20	0.40	0.24	0.10	0.23	200 (2)
(*E*)-whiskylactone	0.23	0.07	0.27	0.06	0.22	0.18	0.17	790 (22)
furfuryl alcohol	0.03	0.02	0.44	0.09	0.23	0.20	0.17	2000 (21)
4-vinylphenol	0.14	0.27	0.06	0.05	0.08	0.25	0.14	180 (22)
phenylethyl acetate	0.09	0.21	0.11	0.05	0.16	0.19	0.13	250 (7)
acetoin	0.21	0.19	0.18	0.04	0.03	0.10	0.13	150000 (23)
2,6-dimethoxyphenol	0.11	0.09	0.13	0.05	0.15	0.11	0.11	570 (11)
diethyl succinate	0.11	0.13	0.09	0.08	0.12	0.09	0.10	200000 (23)
acetovanillone	0.07	0.07	0.08	0.07	0.09	0.08	0.08	1000 (*)
γ-decalactone	0.06	0.09	0.09	0.07	0.05	0.08	0.07	88 (2)
o-cresol	0.06	0.06	0.06	0.05	0.08	0.07	0.06	31 (11)
phenylacetic acid	0.02	0.09	0.02	0.02	0.04	0.09	0.05	1000 (25)
decanal		0.04	0.06	0.07	0.04	0.05	0.05	10 (*)
nonanal		0.05	0.05	0.05	0.04	0.05	0.05	15 (*)
α-terpineol	0.06	0.03	0.05	0.02	0.06	0.04	0.04	250 (2)
isobutyl acetate	0.02	0.03	0.04	0.02	0.03	0.05	0.03	1600 (8)
ethyl 3-hidroxybutyrate	0.03	0.02	0.03	0.02	0.03	0.02	0.03	20000 (*)
β-citronelol	0.03	0.01	0.02	0.03	0.03	0.03	0.03	100 (23)
δ-decalactone	0.02	0.04	0.02	0.02	0.03	0.03	0.02	386 (2)
hexyl acetate	0.02	0.03	0.01	0.03	0.02	0.03	0.02	1500 (23)
δ-octalactone	0.03	0.02	0.02	0.02	0.03	0.02	0.02	400 (21)
m-cresol	0.01	0.04	0.02	0.02	0.03	0.02	0.02	68 (2)
3-hydroxy-2-methyl-4-pyrone	0.02	0.01	0.02	0.01	0.03	0.02	0.02	5000 (*)
4-allyl-2,6-dimethoxyphenol	0.01	0.01	0.03	0.01	0.03	0.04	0.02	1200 (21)
benzoic acid	0.01	0.03	0.02	0.00	0.02	0.02	0.02	1000 (*)
octanal		0.02	0.01	0.02	0.02	0.02	0.02	15 (*)

Table 4. Continued

	RD1	RJ	RD2	RD3	C-L	SM	average	odor threshold[b] (μg/L)
1-butanol	0.01	0.01	0.01	0.01	0.01	0.01	0.01	150000 (23)
butyl acetate	0.00	0.00	0.00	0.00	0.01	0.00	0.00	1800 (23)
γ-undecalactone		0.01				0.01	0.01	60 (21)
methyl vanillate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3000 (11)
benzyl alcohol	0.00	0.00	0.00	0.00	0.00	0.01	0.00	200000 (*)
furfural	0.00	0.00	0.00	0.00	0.00	0.00	0.00	14100 (2)
siringaldehyde	0.00	0.00	0.00	0.00	0.00	0.00	0.00	50000 (21)
5-methylfurfural	0.00	0.00	0.00	0.00	0.00	0.00	0.00	20000 (23)

[a] Blank cells indicate missing data. [b] The reference from which the value has been taken is given in parentheses. In refs *8*, *11*, and *24*, the matrix was a 10% water/ethanol solution at pH 3.2; in ref *2*, the matrix was a 11% water/ethanol solution containing 7 g/L glycerol and 5 g/L tartaric acid, with the pH adjusted to 3.4 with 1 M NaOH; in refs *23* and *19*, thresholds were calculated in a 12% water/ethanol mixture. In ref *7*, the mixture was 10% in ethanol; in ref *22*, the matrix was a synthetic wine containing 12% ethanol, 8 g/L glycerol, and different salts. In ref *20*, the threshold was calculated in a synthetic solution at 18% of alcohol and 100 g/L of sugar at pH 3.5. In ref *21*, the matrix was water. [c] (*) Calculated in the laboratory; orthonasal thresholds were calculated in a 10% water/ethanol mixture containing 5 g/L of tartaric acid at pH 3.2.

Table 5. Compounds Introducing Potential Maximum Differences in Aroma, as Measured by the Quotient Maximum/Minimim OAV and the Standard Deviation (in Logarithmic Scale Since Odor Intensity Is Proportional to logC) of the OAVs from the Six Wine Samples Studied[a]

	OAV_{max}/OAV_{min}	$10^{SD(log(OAV)i)}$
4-ethylphenol	22.4	$10^{0.54}$
4-ethyl-2-methoxyphenol	18.6	$10^{0.55}$
2-methoxy-4-propylphenol	8.30	$10^{0.54}$
2,5-dimethyl-4-hydroxy-3(2H)-furanone	6.79	$10^{0.30}$
(*E*)-isoeugenol	6.00	$10^{0.46}$
phenylacetaldehyde	4.66	$10^{0.24}$
(*Z*)-3-hexenol	3.90	$10^{0.23}$
3-mercaptohexyl acetate	3.62	$10^{0.17}$
2-phenylethanol	3.48	$10^{0.20}$
ethyl isovalerate	3.33	$10^{0.20}$
3-methyl-1-butyl acetate	3.32	$10^{0.17}$
ethyl 2-methylbutyrate	3.30	$10^{0.23}$
4-allyl-2-methoxyphenol	3.19	$10^{0.17}$
vanillin	3.19	$10^{0.21}$
β-damascenone	3.06	$10^{0.21}$
octanoic acid	3.01	$10^{0.18}$
2,3-butanedione	3.01	$10^{0.19}$
4,5-dimethyl-3-hydroxy-2(5H)-furanone	3.00	$10^{0.16}$
(*Z*)-whiskylactone	2.90	$10^{0.16}$
hexanoic acid	2.90	$10^{0.17}$
2-methoxyphenol	2.81	$10^{0.16}$
4-mercapto-4-methyl-2-pentanone	2.75	$10^{0.18}$
ethyl lactate	2.70	$10^{0.17}$
2-methylpropanoic acid	2.70	$10^{0.16}$
ethyl isobutyrate	2.61	$10^{0.20}$
ethyl hexanoate	2.52	$10^{0.14}$
3-methylbutyric acid	2.40	$10^{0.14}$
(*E*)-2-nonenal	2.35	$10^{0.15}$
γ-butyrolactone	2.30	$10^{0.14}$
ethyl octanoate	2.16	$10^{0.12}$
2-methylbutyric acid	2.10	$10^{0.14}$
3-mercaptohexanol	2.01	$10^{0.12}$
butyric acid	2.01	$10^{0.11}$
ethyl cinnamate	2.00	$10^{0.12}$

[a] The minimum OAV considered was 0.2.

variation in C is required) (Pet'ka, J.; Cacho, J.; Ferreira, V. Manuscript in preparation).

The reverse comparison, that is, which components identified as discriminatory by the quantitative analysis (**Table 5**) are not recognized as such by the olfactometric analysis, shows the following: (i) The olfactometric analysis does not allow detecting differences if the olfactory intensity is very high. This is the case of 4-ethylphenol, 2-phenylethanol, (*Z*)-whiskylactone, and hexanoic, 2- and 3-methylbutyric, and butyric acids. (ii) Ethyl lactate and γ-butyrolactone were not even detected in the olfactometric analysis. This is probably due to their poor extraction. (iii) In the case of 2,5-dimethyl-4-hydroxy-3(2H)-furanone and β-damascenone, the most probable cause is the small slope observed in the variation of the olfactory intensity with the concentration (*9*). In this case, it would be the OAV data that overestimate the importance of the component. (iv) The absence from **Table 3** of components such as ethyl 2- and 3-methylbutyrates, ethyl isobutyrate, ethyl hexanoate, and 2,3-butanedione can be related to the difficulty to obtain good olfactometric measurements when there are many odorants that elute in short times.

We can conclude that quantitative GC-O has a strong potential, but its success as a tool to identify consistent differences between samples can be seriously limited by excessively complex olfactograms, in which a high number of odorants reach intensities near their saturation. As a corollary, it is clear the interest to simplify olfactograms as much as possible, by preferentially eliminating those components that do not have great importance and by limiting as much as possible the number of components whose intensity is near saturation. Both objectives could be achieved by the use of static or dynamic headspace techniques in the preparation of the extracts.

CONCLUSIONS

The study presented here has shown that red wines of premium quality possess a large number of odorants detectable in the olfactometric studies, a fact that complicates olfactograms excessively and can cause difficulties in their interpretation. The number of components present in concentrations above their threshold value is quite substantial, which complicates the analytical control. The study of those components with greater potential capacity to introduce differences between these wines shows that the critical factors are the effect of yeasts of the *Brettanomyce* type, the variety of wood used in the aging, as well as factors related to the grape, such as its content in cysteinil precursors and (*Z*)-3-hexenol or its amino acid profile.

LITERATURE CITED

(1) López, R.; Ferreira, V.; Hernández, P.; Cacho, J. F. Identification of impact odorants of young red wines made with Merlot, Cabernet Sauvignon and Grenache grape varieties: a comparative study. *J. Sci. Food Agric.* **1999**, *79*, 1461−1467.

(2) Ferreira, V.; Lopez, R.; Cacho, J. F. Quantitative determination of the odorants of young red wines from different grape varieties. *J. Sci. Food Agric.* **2000**, *80*, 1659−1667.

(3) Kotseridis, Y.; Baumes, R. Identification of impact odorants in Bordeaux red grape juice, in the commercial yeast used for its fermentation, and in the produced wine. *J. Agric. Food Chem.* **2000**, *48*, 400−406.
(4) Ferreira, V.; Aznar, M.; López, R.; Cacho, J. Quantitative gas chromatography-Olfactometry carried out at different dilutions of an extract. Key differences in the odor profiles of four high-quality Spanish aged red wines. *J. Agric. Food Chem.* **2001**, *49*, 4818−4824.
(5) Aznar, M.; López, R.; Cacho, J. F.; Ferreira, V. Identification and quantification of impact odorants of aged red wines from Rioja. GC-olfactometry, quantitative GC-MS and odor evaluation of HPLC fractions. *J. Agric. Food Chem.* **2001**, *48*, 2924−2929.
(6) Aznar, M.; López, R.; Cacho, J.; Ferreira, V. Prediction of aged red aroma properties from aroma chemical composition. Partial least-squares regression models. *J. Agric. Food Chem.* **2003**, *51*, 2700−2707.
(7) Guth, H. Quantification and sensory studies of character impact odorants of different white wine varieties. *J. Agric. Food Chem.* **1997**, *45*, 3027−3032.
(8) Ferreira, V.; Ortín, N.; Escudero, A.; López, R.; Cacho, J. Chemical characterization of the aroma of grenache rosé wines. Aroma Extract Dilution Analysis, quantitative determination and sensory reconstitution studies. *J. Agric. Food Chem.* **2002**, *50*, 4048−4054.
(9) Ferreira, V.; Pet'ka, J.; Aznar, M.; Cacho, J. Quantitative gas chromatography-olfactometry. Analytical characteristics of a panel of judges using a simple quantitative scale as gas chromatography detector. *J. Chromatogr. A* **2003**, *1002*, 169−178.
(10) Ortega, C.; López, R.; Cacho, J.; Ferreira, V. Fast analysis of important wine volatile compounds. Development and validation of a new method based on gas chromatographic-flame ionisation detection analysis of dichloromethane microextracts. *J. Chromatogr. A* **2001**, *923*, 205−214.
(11) López, R.; Aznar, M.; Cacho, J.; Ferreira, V. Quantitative determination of minor and trace volatile compounds in wine by Solid-phase Extraction and Gas Chromatography with Mass Spectrometric detection. *J. Chromatogr. A* **2002**, *966*, 166−177.
(12) Ferreira, V.; Jarauta, I.; López, R.; Cacho, J. Quantitative determination of sotolon, maltol and free furaneol in wine by solid-phase extraction and gas chromatography-ion-trap mass sepectrometry. *J. Chromatogr. A* **2003**, *1010*, 95−103.
(13) Ferreira, V.; Culleré, L.; Lopez, R.; Cacho, J. Analysis of important odor-active aldehydes of wine through the Gas Chromatography−Mass Spectrometric determination of their O-(2,3,4,5,6-pentafluorobenzyl)oximes formed directly in the solid-phase extraction cartridge used for selective isolation. *J. Chromatogr. A* **2004**, *1028*, 339−345.
(14) Ferreira, V.; Jarauta, I.; Ortega, C.; Cacho, J. A simple strategy for the optimization of Solid-Phase-Extraction procedures through the use of solid−liquid distribution coefficients. Application to the determination of aliphatic lactones in wine. *J. Chromatogr. A* **2004**, *1025*, 147−156.
(15) Fenaroli, G.; Burdock, G. A. *Fenaroli's Handbook of Flavor Ingredients*, 3rd ed.; CRC Press: Boca Raton, FL, 1995.
(16) López, R.; Ortín, N.; Pérez-Trujillo, J. P.; Cacho, J.; Ferreira, V. Impact odorants of different young white wines from the Canary islands. *J. Agric. Food Chem.* **2003**, *51*, 3419−3425.
(17) Chatonnet, P.; Dubourdieu, D.; Boidron, J. N.; Pons, M. The origin of ethylphenols in wines. *J. Sci. Food Agric.* **1992**, *60*, 165−178.
(18) Tominaga, T.; Peyrot des Gachons, C.; Dubourdieu, D. A new type of flavor precursors in Vitis vinifera L. cv. Sauvignon blanc: S-cysteine conjugates. *J. Agric. Food Chem.* **1998**, *46*, 5215−5219.
(19) Tominaga, T.; Murat, M. L.; Dubourdieu, D. Development of a method for analyzing the volatile thiols invoved in the characteristic aroma of wines made from Vits vinifera L. Cv Sauvignon Blanc. *J. Agric. Food Chem.* **1998**, *46*, 1044−1048.
(20) Cutzach, I.; Chatonnet, P.; Henry, R.; Pons, M.; Dubourdieu, D. Etude sur l'arôme des vins doux naturels non muscatés. 2e partie: Dosages de certains composés volatils intervenant dans l'arôme des vins doux naturels au cours de leur élevage et de leur vieillissement. *J. Int. Sci. Vigne Vin* **1998**, *32*, 211−221.
(21) *Compilation of Odour Threshold Values in Air and Water*; van Gemert, L. J., Nettenbreijer, A. H., Eds.; TNO: Zeist, 1977.
(22) Boidron, J. N.; Chatonnet, P.; Pons, M. Influence du bois sur certaines substances odorantes des vins. *Connaissance Vigne Vin* **1988**, *22*, 275−293.
(23) Etievant, P. X. Wine. In *Volatile Compounds in Foods and Beverages*; Maarse, H., Ed.; Marcel Dekker: New York, NY, 1991; pp 483−546.
(24) Chatonnet, P.; Dubourdieu, D. Identification of substances responsible for the "sawdust" aroma in oak wood. *J. Sci. Food Agric.* **1998**, *76*, 179−188.
(25) Maga, J. A. Taste thresholds values for phenolic acids which can influence flavor properties of certain flours, grains and oilseeds. *Cereal Sci. Today* **1973**, *18*, 326−330.

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