JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Aroma Chemical Composition of Red Wines from Different Price Categories and Its Relationship to Quality

Felipe San Juan, Juan Cacho, Vicente Ferreira, and Ana Escudero*

Laboratory for Aroma Analysis and Enology, Aragón Institute of Engineering Research (I3A), Department of Analytical Chemistry, Faculty of Sciences, University of Zaragoza, 50009 Zaragoza, Spain

Supporting Information

ABSTRACT: The aroma chemical composition of three sets of Spanish red wines belonging to three different price categories was studied by using an array of gas chromatographic methods. Significant differences were found in the levels of 72 aroma compounds. Expensive wines are richest in wood-related compounds, ethyl phenols, cysteinil-derived mercaptans, volatile sulfur compounds, ethyl esters of branched acids, methional, and phenylacetaldehyde and are poorest in linear and branched fatty acids, fusel alcohols, terpenols, norisoprenoids, fusel alcohol acetates, and ethyl esters of the linear fatty acids; inexpensive wines show exactly the opposite profile, being richest in *E*-2-nonenal, *E*-2-hexenal, *Z*-3-hexenol, acetoin, and ethyl lactate. Satisfactory models relating quality to odorant composition could be built exclusively for expensive and medium-price wines but not for the lower-price sample set in which in-mouth attributes had to be included. The models for quality reveal a common structure, but they are characteristic of a given sample set.

KEYWORDS: *red wine, aroma, price category, quality, aroma formation, aroma vectors*

INTRODUCTION

Analytical information about volatile compounds present in wine is crucial to understand the nature of its aroma. More than 800 odorants have been found, but only some play noticeable roles in the sensory perception of each wine.[1,2] Techniques such as olfactometry, or reconstitution, addition or omission tests,[3,4] have made it possible to determine which molecules can really contribute to the aroma properties of the wines. The need to determine the concentration of these molecules has prompted the development of analytical methods. Procedures exist which allow the quantification of a great number of compounds, and other more specific procedures are available for quantifying molecules that present significant problems due to low concentration or weak chemical stability.

The concentration of volatiles that can contribute to the aroma properties can be very different from one wine to another and is determined by many factors. The grape variety, vineyard management, and vitivinicultural practices determine which volatile molecules ultimately are present in the wine, therefore defining its aroma. Studies have been carried out showing differences in the aromatic potential of different grape varieties.[5] Besides this, the geographic situation,[6] climate,[7] and vineyard cultivation practices[8−10] greatly determine the composition of the grapes and, therefore, the resulting wine. Numerous studies have previously observed that the yeast strains used in the fermentation processes may affect in large measure the final aroma.[11,12] Furthermore, different enological techniques, as well as the aging process and its conditions, can stimulate the presence of different volatile molecules that can be responsible for very distinct aromatic notes. Not all but some of the previously named factors, while influencing the composition of the volatile fraction, also influence the wine's final price. Therefore, it is to be expected that wines of the same type, belonging to the same market segment, should share some aromatic characteristics but differ in some others that are most typical of a region or a specific type of grape. Wines awarded higher prices are logically produced following a more careful process that allows for greater aromatic quality. Nevertheless, the market value of a wine is also affected by aspects not so closely related to the production process. Previous research has demonstrated that factors such as fashion, harvest year, points awarded by experts, or the reputation of the winery and production zone can have a significant influence on price.[13−15] No consensus exists about the actual weight of these factors intrinsic to the production process, as they have high importance in some studies, whereas in others it seems that the viticulture and enology are the major factors determining the final price.[16,17]

The principal objective of the present work is to compare the aroma composition of wines from different market segments and to study whether the price difference is reflected in the aroma chemical composition. Further objectives are to assess the potential existence of similar formation pathways of aroma compounds and to build models relating wine quality within each group to the aroma chemical composition, to evaluate the existence of different or similar quality patterns linked to the market segment.

MATERIALS AND METHODS

Reagents and Standards. *Solvents.* Dichloromethane and methanol of SupraSolv quality, pentane of UniSolv quality, and ethanol of LiChrosolv quality were purchased from Merck (Darmstadt, Germany). Water was purified in a Milli-Q system from Millipore (Bedford, MA).

Received: December 9, 2011
Revised: March 23, 2012
Accepted: April 5, 2012
Published: April 5, 2012

dx.doi.org/10.1021/jf2050685 | J. Agric. Food Chem. 2012, 60, 5045−5056

Resins. Lichrolut EN resins and polypropylene cartridges were supplied by Merck (Darmstadt, Germany).

Standards. The chemical standards were supplied by Sigma (St. Louis, MO), Aldrich (Gillingham, U.K.), Fluka (Buchs, Switzerland), Lancaster (Strasbourg, France), PolyScience (Niles, IL), Alfa Aesar (Ward Hill, MA), Chem Service (West Chester, PA), Merck (Darmstadt, Germany), and Firmenich (Geneva, Switzerland), as indicated in Supporting Information.

Reagents. Sodium chloride, *l*-tartaric acid, ammonium sulfate, and $NaHCO_3$ were supplied by Panreac (Barcelona, Spain).

In some analysis methods, a semiautomated solid-phase extraction was carried out with a VAC ELUT 20 station from Varian (Walnut Creek, CA).

Wine Samples. Ninety six Spanish red wines from 32 different production zones were analyzed. Samples were distributed in three sets on the basis of sales criteria: a group of 25 wines with a price between 18 and 25 € per bottle (median age 2003), 35 wines with a price between 15 and 6 € per bottle (median age 2004), and a third group of 36 samples with a price under 6 € per bottle (median age 2008). Samples were stored at 5 °C. Sample details are shown in Supporting Information.

Wine Sensory Analysis. *Sensory Quality Determination.* The procedure of this sensory analysis is described by Ferreira et al.[1] The three sets of wines were analyzed by the same sensory panel but on different days. Panelists were informed about the range of prices of the samples in each case. The panelists were asked to sort the wines into five groups (exceptional, good, right, poor, and rejectable) on the basis of quality (odor and taste).

Sensory Descriptive Analysis. The procedure (according to the citation frequency method[18]of this sensory analysis is described by Saénz-Navajas et al.[19]

Quantitative Analysis of Major Compounds (Supporting Information). The analysis was carried out using the method published by Ortega et al.[20]

Quantitative Analysis of Minor and Trace Compounds (Supporting Information). The method is described by Lopez et al.[21]

Quantitative Analysis of Minor Esters (Supporting Information). This analysis was carried out using the method proposed and validated by Campo et al.[22]

Quantitative Analysis of Aldehydes (Supporting Information). Aldehydes were extracted following a solid-phase extraction (SPE) method and analyzed in a gas chromatography−mass spectrometry (GC-MS) system with negative chemical ionization (NCI), both described by Zapata et al.[23]

Quantitative Analysis of Sotolon, Furaneol, Maltol, and Homofuraneol (Supporting Information). These analytes were quantified by using an SPE extraction coupled with a GC-MS analysis. In this method, 3 mL of wine with 0.9 g of ammonium sulfate was diluted to 6 mL with milli-Q water. This solution was loaded in a 200 mg LiChrolut EN solid-phase extraction cartridge previously conditioned with 6 mL of methanol and another 6 mL of an aqueous solution containing 12% (v/v) ethanol. After this, the bed was washed with 1.5 mL of water and dried by applying vacuum for 30 min. Then interferences were removed with 6 mL of a mixture of pentane−dichloromethane (20:1). The analytes were eluted with 1.5 mL of dichloromethane with 5% of methanol added drop by drop. The recovered solution was spiked with 50 μL of the internal standard solution (2-octanol 65 mg L^{-1}) and concentrated to 0.5 mL under a nitrogen stream. Five microliters was injected into a Varian CP-3800 gas chromatograph with a Saturn 2000 ion trap mass spectrometric detector. The instrumental conditions are described by Ferreira et al.[24] The area of the corresponding ionic peaks was normalized by the area of the internal standard and was converted into a concentration value by means of a response factor. This was obtained by the analysis of a spiked wine with a known quantity of analytes.

Quantitative Analysis of Volatile Mercaptans (Supporting Information). A solid-phase microextraction (SPME) method was used to extract these compounds. The analyses were carried out in a GC-MS system. Both are described by López et al.[25]

Quantitative Analysis of 2,4,6-Trichloroanisole (TCA) and γ-Lactones (Supporting Information). The extraction procedure was the same as that used for the analysis of minority esters.[22] Fifty microliters of the obtained extract was injected into a GC-GC-MS system by using a solvent split-mode injection. The instrumental conditions were similar to those used for the analysis of minority esters although some changes, described next, were introduced. The oven temperature program of the first chromatograph was 40 °C during 5 min and then raised at 10 °C min^{-1} to 220 °C, and this temperature was maintained during 10 min. For the second chromatograph, a different oven temperature program was also applied. The initial temperature, 40 °C, was maintained during 23 min, and then a 4 °C min^{-1} ramp was applied to 200 °C followed by a second ramp of 50 °C min^{-1} to 300 °C. The selected heart-cutting windows were optimized to ensure a complete transfer of TCA and γ-lactones between the two columns. The m/z fragments chosen for quantitative purposes were 210 and 212 for TCA and 85 for lactones. Calibration was carried out by means of a response factor obtained by analyzing a wine spiked with known amounts of the analyte.

Quantitative Analysis of Polyfunctional Mercaptans (Supporting Information). An SPE extraction method was used to separate these volatile compounds. The analysis was carried out by GC with MS detection in NCI mode. The method is described by Mateo-Vivaracho et al.[26]

Quantitative Analysis of Methoxypyrazines (Supporting Information). The extraction was carried out by using an SPE method with cation-exchange mixed-mode sorbent. The extract was injected into a GC-MS system. Method details are described by Lopez et al.[27]

Data Treatment. Comparison of average concentrations in the three groups of wines was performed by means of a one-way ANOVA analysis (Table 1). It was carried out with the SPSS (SPSS Inc., Chicago, IL) statistical package for Windows, release 16.0. In those cases in which the distribution followed a marked log-normal pattern, the geometric mean was compared. Least significant difference (95%) was calculated to establish which means were different. Furthermore, a principal components analysis (PCA) was carried out by using the Unscrambler 9.7 (CAMO A/S, Trondheim, Norway). Correlation coefficients between concentrations of different compounds were worked out by using Excel 2003.

To compare families of compounds (similar sensory properties and/or biochemical origin), quantitative data of 96 analyzed wines were transformed into odor activity values (OAVs) by dividing by odor thresholds (tabulated in Table 1). In the case of concentrations under the detection and quantification limits, these values were taken to calculate the OAV. OAVs of compounds in the same family were summed to obtain the OAV of the family.

To rank compounds or families of compounds in accordance to the discriminatory ability, the quotient between the maximum OAV and minimum OAV was worked out for each compound or family (in the case of an OAV minimum <0.2, this value was used). To explore the relationship between the quantitative data and the quality of wine, partial least-squares regression (PLSR) 1 was carried out by using the Unscrambler 9.7 (CAMO A/S, Trondheim, Norway). With this purpose, some compounds were grouped into families, attending to their sensory properties and biochemical origin. A first initial model was built by using X variables (quantitative data) which have the best individual correlation with Y variables (in accordance to the correlation coefficient). After that, different iterations excluding the least important variables were further run to look for the simplest model with the best prediction ability measured by cross-validation. The quality parameters studied to evaluate the prediction ability of the models were the root-mean-square error for the prediction (RMSEP) and the percentage of variance explained by the model (%EV).

RESULTS AND DISCUSSION

The study of the aroma chemical composition of 96 Spanish red wines, categorized into three different price groups, has provided quantitative data for 110 volatile compounds belonging to all main families of wine aroma, as shown in Table 1. Not all the volatile compounds could be analyzed in all the sample sets because of logistic difficulties in coordinating chemical analysis with sensory analysis and with the use of up to nine different

Table 1. Concentration Ranges and Mean Concentrations of Three Sets of Spanish Red Wines from Different Price Segments[a]

	concentration ranges			averages and significant differences[b]			
compounds	high-price wines	medium-price wines	low-price wines	high-price wines	medium-price wines	low-price Wines	odor threshold[c]
Carbonyl Compounds							
fermentative origin							
acetoin	<99.2−17600	<99.2−29000	321−62301	6025 c	9860 b	12886 a	150000[43]
aging-related							
furfural	10.6−51.0	4.03−79.7	−	26.3	21.1	−	14100[43]
5-methylfurfural	<0.059−17.9	<0.059−92.3	−	0.090 b	0.410 a	−	20000[44]
5-hydroxymethylfurfural	<0.114−10.9	<0.114−12.7	−	0.648 a	0.225 b	−	100000[45]
syringaldehyde	2.91−76.2	<0.385−65.2	0.950−673	14.9 a	0.887 b	17.2 a	50000[45]
norisoprenoids							
β-damascenone	<0.200−10.5	<0.200−2.10	<0.200−5.50	0.569 b	0.872 b	1.62 a	0.05[46]
α-ionone	<0.008−1.57	<0.008	<0.008	0.016 a	<0.008 b	<0.008 b	2.6[44]
β-ionone	<0.089−0.550	<0.089−1.17	<0.089−0.621	0.214	0.186	0.193	0.09[43]
oxidation-related							
E-2-hexenal	<0.06−0.558	<0.06−0.210	<0.06−0.388	<0.06 c	0.062 b	0.206 a	4[47]
E-2-heptenal	0.370−0.858	<0.070−0.158	<0.070−1.095	0.514 a	0.080 c	0.110 b	4.6[47]
E-2-octenal	0.436−1.13	0.170−0.282	0.170−0.720	0.599 a	0.187 c	0.267 b	3[47]
E-2-nonenal	0.820−2.00	<0.110−0.212	1.10−8.84	1.06 b	0.119 c	2.67 a	0.6[47]
methional	2.12−21.6	<0.030−2.61	<0.030−16.3	8.62 a	1.22 c	1.91 b	0.5[48]
benzaldehyde	−	−	<0.200−44.6	−	−	10.1	2000[49]
phenylacetaldehyde	20.4−126	<0.890−21.8	3.72−24.9	53.5 a	6.81 c	9.79 b	1[47]
rot in grape							
1-octen-3-one	<0.011−0.087	0.041−0.100	<0.011−0.075	0.018 c	0.060 a	0.044 b	0.015[2]
Esters							
linear fatty acid derivatives							
ethyl propanoate	<80.0−260	<80.0−320	84.9−1966	**142 b**	**186 a**	**260 a**	5500[d]
ethyl butyrate	70.0−270	90.0−320	87.0−252	**135**	**154**	**152**	125[d]
ethyl hexanoate	70.0−210	100−350	78.0−337	121 b	154 a	169 a	62[d]
ethyl octanoate	50.0−210	60.0−230	26.4−225	92.5	119	103	580[44]
ethyl decanoate	<4.03−81.1	<4.03−86.6	29.4−163	36.7 b	58.0 a	72.2 a	200[43]
branched acid derivatives							
ethyl 2-methylpropanoate	48.7−536	68.7−361	<4.03−419	153	146	114	15[43]
ethyl 3-hydroxybutyrate	90.0−600	100−370	−	210	221	−	20000[3]
ethyl 2-methylbutyrate	6.50−82.6	4.41−70.4	6.45−58.9	25.4 a	20.8 a	13.7 b	18[43]
ethyl 3-methylbutyrate	10.9−131	11.3−119	11.3−89.4	41.9 a	37.5 a	25.6 b	3[43]
ethyl 2-methylpentanoate	<0.0007−0.0910	<0.0007−0.0090	<0.0007	0.0020 a	0.0008 b	<0.0007 b	10[d]
ethyl 3-methylpentanoate	<0.0006−0.1110	<0.0006−0.0390	<0.0006	0.0030 a	0.0009 b	<0.0006 b	0.5[d]
ethyl 4-methylpentanoate	<0.0005−0.8820	0.0840−0.9340	<0.0005−0.533	0.150 b	0.305 a	0.110 b	0.75[d]
ethyl cyclohexanoate	<0.0008−0.0150	<0.0008−0.050	<0.0008	0.0036 a	0.0034 a	<0.0008 b	0.03[d]
varietal origin							
ethyl furoate	3.22−12.6	<0.004−18.1	2.99−18.8	7.12 a	4.59 b	7.42 a	16000[43]
ethyl cinnamate	<0.032−1.86	<0.032−1.14	<0.032−1.31	**0.727**	**0.398**	**0.428**	1.1[43]
ethyl dihydrocinnamate	<0.210−1.03	<0.210−0.91	<0.210−2.35	0.295 b	0.279 b	0.688 a	1.6[43]
ethyl vanillate	52.9−257	31.4−363	24.0−1287	108 b	91 b	233 a	3000[21]
methyl vanillate	<0.490−26.4	<0.490−22.9	<0.490−61.6	7.01 b	8.80 b	14.3 a	990[21]
fermentative origin							
diethyl succinate	7800−24200	4990−18400	6076−18562	**13308**	**11760**	**12150**	200000[44]
ethyl acetate	−	−	45134−127801	−	−	67182	12300[4]
ethyl lactate	44800−369000	32500−265000	22262−226827	117558 ab	94741 b	139359 a	154000[44]
butyl acetate	<0.640−2.76	<0.640−3.35	<0.640−23.5	1.12	1.27	1.81	1800[44]
isobutyl acetate	<0.542−83.1	16.9−89.3	33.3−102	**44.6 b**	**36.1 c**	**64.0 a**	1600[50]
isoamyl acetate	110−370	130−370	111−906	**200 b**	**215 b**	**290 a**	30[46]
hexyl acetate	<3.00	<3.00−120	−	<3.00 b	49.6 a	−	1500[44]
phenylethyl acetate	20.6−62.1	20.2−50	142−1008	32.3 b	28.0 b	475 a	250[46]
Alcohols							
1-butanol	530−960	630−1110	465−3058	**755 b**	**862 b**	**1243 a**	150000[44]
2-methylpropanol	21400−61400	23700−55100	28529−71473	**39136 b**	**41011 b**	**51279 a**	40000[46]
isoamyl alcohol	111000−305000	112000−283000	143276−353379	169545 b	173274 b	244047 a	30000[46]
1-hexanol	520−1560	250−1460	1147−3404	**1012 b**	**1036 b**	**1940 a**	8000[46]

dx.doi.org/10.1021/jf2050685 | J. Agric. Food Chem. 2012, 60, 5045−5056

Table 1. continued

compounds	concentration ranges			averages and significant differences[b]			odor threshold[c]
	high-price wines	medium-price wines	low-price wines	high-price wines	medium-price wines	low-price Wines	
Alcohols							
Z-3-hexenol	<4.47−290	<4.47−220	11.4−690	51.9 b	40.0 b	147 a	400[46]
furfuryl alcohol	<0.067−1211	2.96−571	−	98.8 a	41.3 b	−	2000[45]
β-phenylethanol	18700−80500	19200−83100	24798−76511	38529 b	38987 b	48203 a	14000[43]
benzyl alcohol	70.0−5400	80.0−6050	196−3352	708	515	539	200000[3]
methionol	88.6−1348	142−647	568−2417	339 b	298 b	1200 a	1000[43]
Volatile Phenols							
o-cresol	0.610−1.96	0.560−2.01	0.894−2.49	**1.18 b**	**1.09 c**	**1.66 a**	31[44]
m-cresol	<0.017−1.59	<0.017−1.15	0.420−2.70	0.819 ab	0.698 b	0.942 a	68[1]
4-ethylphenol	<0.54−1214	<0.54−472	<0.54−406	31.4	14.1	12.5	35[d]
4-vinylphenol	<1.00−47.7	<1.00−272	<1.00−27.6	1.85 c	57.0 a	5.43 b	180[51]
guaiacol	7.83−22.7	2.28−38.1	<0.026−23.9	13.4 a	7.68 b	6.60 b	9.5[43]
4-ethylguaiacol	<0.035−167	<0.035−62.8	<0.035−26.3	4.53	2.10	1.61	33[43]
4-vinylguaiacol	<0.83−35.4	<0.83−10.4	<0.83−44.9	0.964 b	0.892 b	4.99 a	40[46]
4-propylguaiacol	<0.048−18.0	<0.048−18.0	<0.048−1.20	1.23 a	0.227 b	0.102 b	10[21]
2,6-dimethoxyphenol	1.61−82.1	9.71−188	9.82−61.8	5.48 b	28.9 a	28.4 a	570[21]
4-allyl-2,6-dimethoxyphenol	8.46−34.0	3.11−64.1	0.61−48.9	17.3 a	9.85 b	5.98 c	1200[45]
eugenol	<0.074−56.9	−	<0.074−10.84	14.9 a	−	3.29 b	6[43]
E-isoeugenol	<0.011−8.27	<0.011−33.2	<0.011	0.733 a	0.628 a	<0.011 b	6[3]
vanillin	<0.120−77.7	<0.120−81.2	<0.120−116	14.3 a	0.360 b	0.888 b	995[3]
acetovanillone	45.2−136	23.8−115	14.8−297	65.0 b	56.3 b	103 a	1000[4]
Terpenols							
linalool	<0.170−10.4	<0.170−16.4	1.07−13.4	**4.31 b**	**5.25 b**	**6.92 a**	25[43]
geraniol	<0.010−4.85	<0.010−9.10	<0.010−4.14	0.016 b	0.012 b	0.127 a	20[3]
α-terpineol	3.54−19.6	3.45−14.8	2.86−22.8	7.35	7.27	7.96	250[43]
β-citronellol	<0.440−6.53	<0.440−6.52	<0.440−8.64	1.22 b	1.41 b	3.45 a	100[44]
Lactones							
γ-butyrolactone	5750−31100	4860−22800	6805−25959	11571	11593	13400	35000[3]
E-whiskylactone	34.7−346	<0.021−308	<0.021−46.4	**198 a**	**117 b**	**5.60 c**	790[44]
Z-whiskylactone	<0.130−668	6.14−668	<0.130−99.1	**335 a**	**240 b**	**17.5 c**	67[44]
δ-octalactone	1.84−6.40	2.41−24.9	<0.810−6.62	**4.03 b**	**10.5 a**	**0.875 c**	400[45]
γ-octalactone	−	0.067−8.37	−	−	1.18	−	7[52]
γ-nonalactone	4.98−28.9	0.430−87.0	1.28−28.4	10.8 b	17.9 a	11.8 b	25[52]
δ-decalactone	−	−	2.5−52.1	−	−	25.5	386[53]
γ-decalactone	−	<0.01−5.89	<0.01−2.55	−	0.888	0.686	0.7[52]
γ-undecalactone	−	<0.020−0.220	−	−	0.038	−	60[52]
γ-dodecalactone	−	<0.030−0.443	−	−	0.045	−	7[52]
Acids							
acetic acid	285000−950000	−	164892−687086	451300	−	323038	300000[50]
butyric acid	<54.8−1850	340−2310	877−2207	**506 b**	**727 b**	**1542 a**	173[43]
2-methylpropanoic acid	620−1225	550−1750	733−1869	**870 c**	**1093 b**	**1325 a**	50[45]
2-methylbutyric acid	88.4−365	130−469	−	**219**	**247**	−	33[43]
3-methylbutyric acid	55.4−430	96.9−661	20.2−1104	142 c	240 b	495 a	33[43]
hexanoic acid	390−2120	540−2570	1232−4396	**1068 b**	**1172 b**	**2232 a**	420[43]
octanoic acid	180−1020	240−850	845−2720	429 b	445 b	1439 a	500[43]
decanoic acid	110−940	130−440	62.2−306	190 a	207 a	131 b	1000[43]
benzoic acid	3.31−79.3	10.2−96.5	−	22.8 b	31.5 a	−	1000[3]
phenylacetic acid	17.4−102	20.7−115	−	38.8	43.9	−	1000[54]
Enolones							
3-hydroxy-2-methyl-4-pyrone (maltol)	57.5−135	<7.61−79.7	<7.61−28.9	**92.3 a**	**27.2 b**	**8.71 c**	5000[55]
2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (Furaneol)	<10.0−62.6	<10.0−55.6	<10.0−103	18.3	19.2	24.2	5[50]
2-ethyl-4-hydroxy-5-methyl-3(2*H*)-furanone (homofuraneol)	<180−725	<180	<180	191	180	180	125[50]
4,5-dimethyl-3-hydroxy-2(5*H*)-furanone (sotolon)	<50.0	<50.0	<50.0	<50.0	<50.0	<50.0	15[56]
Volatile Sulfur Compounds (VSCs)							
dihydrogen sulfide	<2.00−141	7.80−136	8.01−39.8	**47.5 a**	**24.5 b**	**19.0 b**	1.1−1.6[57]
methanethiol	<0.200−18.0	<0.200−8.18	<0.200−5.71	4.42 a	2.48 b	2.83 b	1.8−3.1[58]

dx.doi.org/10.1021/jf2050685 | *J. Agric. Food Chem.* 2012, 60, 5045−5056

Table 1. continued

compounds	concentration ranges			averages and significant differences[b]			odor threshold[c]
	high-price wines	medium-price wines	low-price wines	high-price wines	medium-price wines	low-price Wines	
Volatile Sulfur Compounds (VSCs)							
ethanethiol	<3.49	<3.49	<3.49	<3.49	<3.49	<3.49	1.1[59]
dimethyl sulfide	30.1−208	2.95−58.5	10.1−33.9	59.7 a	28.8 b	20.7 b	25[59]
diethyl sulfide	<1.63	<1.63	<1.63−1.66	<1.63	<1.63	<1.63	0.9[59]
dimethyl disulfide	<0.500−4.70	<0.500	<0.500−1.14	1.363 a	0.810 b	0.824 b	29[59]
diethyl disulfide	–	<3.19	<3.19	–	<3.19	<3.19	4.3[59]
Methoxypyrazines							
3-isopropyl-2-methoxypyrazine	–	<0.0005−0.0030	<0.0005−0.0004	–	0.0008	0.0009	0.015[60]
3-isobutyl-2-methoxypyrazine	–	<0.0005−0.0080	0.0005−0.0070	–	0.0020 a	0.0012 b	0.002[61]
3-secbutyl-2-methoxypyrazine	–	<0.0002−0.0006	<0.0002−0.0040	–	<0.0002	0.0006	na[e]
Polyfunctional Mercaptans							
2-methyl-3-furanthiol	0.126−0.613[f]	0.067−0.544	0.099−0.687	0.250	0.217	0.261	0.004[62]
4-methyl-4-mercapto-2-pentanone	<0.0006−0.0110[f]	<0.0006−0.023	<0.0006	0.0017 a	0.0013 a	<0.0006 b	0.0008[63]
3-mercaptohexyl acetate	0.0070−0.0125[f]	<0.0050−0.0470	<0.0050−0.0240	0.0096	0.0083	0.0077	0.004[63]
3-mercaptohexanol	0.161−0.671[f]	0.045−0.520	0.075−0.390	0.285	0.168	0.174	0.06[63]
2-furfurylthiol	0.0180−0.0660[f]	0.0070−0.1120	0.0090−0.0740	0.0270	0.0270	0.0220	0.0004[64]
benzylmercaptan	0.004−0.010[f]	0.003−0.045	0.003−0.028	0.0056	0.0084	0.0086	0.0003[65]
Miscellaneous							
2,4,6-trichloroanisole (TCA)	<0.0005−0.0080	<0.0005−0.0020	–	0.0006	<0.0005	–	0.004[66]

[a]Odor thresholds (calculated in red wine if available; otherwise threshold in synthetic wine is given) are also shown. Concentrations are expressed in micrograms per liter. ANOVA tests were carried out between groups of wines, and significant differences (95%) between mean concentrations for each compound are expressed with letters (a, b, and c). [b]In those cases in which the distribution followed a marked log-normal pattern, the geometric mean was compared. Arithmetic means are in bold and geometric means are in normal type. [c]Reference in which the odor threshold value has been calculated is given in parentheses. [d]Odor threshold 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. [e]Threshold is not available. [f]These compounds were analyzed in 5 out of 25 high-price wines.

analytical strategies. Despite that, data in the table provide a quite complete description of Spanish red wine aroma composition and the differences in composition linked to the price segment to which the wine belongs.

Compositional Differences Linked to Price Category. As in most cases (94 out of 110) the observed data distributions were not Gaussian, but log-normal, the ANOVA statistics were carried out on logarithms, and therefore geometric means are given. Significant differences were found in 72 cases, which just reflects the fact that the wines in the different price segments, even if such is a quite complex and rather heterogeneous concept, are chemically different as a consequence of differences in the whole winemaking process, wine origin, vintages, or grape varieties. As expected, major differences are found between inexpensive wines and those in the medium- and high-price categories. The principal component plot obtained from quantitative data (not shown) reveals that inexpensive wines are clearly separated from the two other categories. The medium-price segment can be seen to some extent as a subcategory of the most expensive wines, slightly sharing some compositional features of the most inexpensive wines. The following discussion will therefore focus on differences in chemical composition between wines in the most inexpensive and most expensive categories. The analysis of the compositional differences reveals that these have an origin in three major groups of factors: fermentation-related, contact with oak-related, and aging time-related.

(1) Fermentation-related differences. As the Table 1 shows, the levels of nearly all major volatiles formed during fermentation significantly depend on the price category. Inexpensive wines are the richest in fusel alcohols, in linear and branched fatty acids, in fusel alcohol acetates, and in the ethyl esters of the linear fatty acids. Acetoin, *Z*-3-hexenol, and ethyl lactate are also found at the highest levels in the most inexpensive wines. Conversely, the most expensive wines are the poorest in all these compounds.

(2) Oak-related differences. As the most expensive wines are characterized by long and careful aging on wood, they are the richest in compounds released from the wood such as whiskylactones, eugenol, *E*-isoeugenol, 4-allyl-2,6-dimethoxyphenol, 5-hydroxymethylfurfural, furfuryl alcohol, guaiacol, 4-propylguaiacol, maltol, and vanillin. All these compounds are found at the lowest levels in the most inexpensive wines.

(3) Aging time-related differences. These differences affect several groups of compounds whose formation/degradation is linked to some of the different subcomponents of the aging process: formation/degradation of varietal compounds; oxidation; reduction; esterification/hydrolysis processes.

   (a) Formation/degradation of varietal compounds. Data in Table 1 clearly show that the levels of nearly all aroma compounds derived from the grape and/or grape glycosidic precursors are found at highest levels in the most inexpensive wines: *β*-damascenone, ethyl dihydrocinnamate, ethyl and methyl vanillates, cresols, acetovanillone, linalool, geraniol, and *β*-citronellol. Dimethyl sulfide (DMS) and 4-methyl-4-mercapto-2-pentanone (4M4MP), which are formed from different kinds of precursor molecules, are however found at the highest levels in the most expensive wines.

   (b) Oxidation. An unexpected difference is found here because oxidation-related compounds seem to follow two opposite behaviors. *E*-2-heptenal, *E*-2-octenal,

dx.doi.org/10.1021/jf2050685 | J. Agric. Food Chem. 2012, 60, 5045−5056

methional, and phenylacetaldehyde are found, as expected, at maximal levels in the most expensive (and oldest) wines, but *E*-2-hexenal and *E*-2-nonenal are, on the contrary, found at the highest levels in the least expensive (and youngest) wines.

(c) Reduction. Dihydrogen sulfide, methanethiol, and dimethyl disulfide are found at maximal levels in expensive wines.

(d) Esterification/hydrolysis processes. The ethyl esters of branched acids are most concentrated in the most expensive wines, which on the contrary contain minimal levels of fusel alcohols acetates. Ethyl dihydrocinnamate, which is a grape-derived compound, is found also at the highest levels in the most expensive wines.

Some of the previous observations can be very easily explained, while others are more challenging. In the case of fermentation-related compounds, the highest levels of fatty acids and their ethyl esters and of fusel alcohol acetates observed in the most inexpensive wines were expected, because younger wines usually undergo a smaller maceration and most of the fermentation takes place in a purely liquid phase, while the fermentation of the wines to be aged is most of the time carried out in the presence of the grape solids. It is known that fermentations of liquid-phase-only tend to be more anaerobic, and hence the yeasts are forced to produce more fatty acid derivatives required to build stronger membranes.[28] However, the highest levels of fusel alcohols, of branched acids, and of acetoin indicate that yeast amino acid metabolism is absolutely different in both types of wines, but we do not have a clear explanation for this. The low-priced wines may be produced through a less-controlled and higher-rate fermentation, which may account for the excessive generation of these odorants.[29] It can be assumed that any nitrogen deficiency was carefully controlled in the most expensive wine set. The higher levels of *Z*-3-hexenol and of ethyl lactate may be due to the fact that the most expensive wines are most often made from well-ripened and selected grapes, while the most inexpensive are made with the bulk of the grapes reaching the cellar.

As for oak-related differences, they do not require any additional explanation, yet there are some observations worth mentioning. The first one is the relatively high levels of syringaldehyde, which is a wood-related compound in some inexpensive wines, which suggests that some of those wines were soaked with oak chips or a similar product and were enriched in this compound, which so far can be used as one of the markers for the chip aging process.[30] Surely the same observation can be applied to 2,6-dimethoxyphenol. In the cases of acetovanillone and ethyl and methyl vanillates, however, higher levels in inexpensive wines could be also explained by the evolution of grape glycosidic precursors.[31] Another interesting observation is related to the highest levels of 4-propylguaiacol, which was found to be a compound related to the simultaneous presence of *Brettanomyces* and exclusively new wood,[32] conditions that are found most likely in the aging of expensive wines.

The smaller levels of varietal compounds in premium wines (Table 1) should be attributed to the decline of these compounds during the longer aging process. The case of DMS is different, because it is known that this compound tends to increase with aging,[33] while in the case of 4M4MP the tiny but higher levels found in expensive samples may suggest that the best grapes could be richer in the precursors of this molecule, although it cannot be ruled out that differences may arise from fermentation or could be even related to the evolution of VSCs that, as was aforementioned, are also found at higher levels in the most expensive wines.

Differences in oxidation and reduction-related compounds are very interesting and challenging. The highest levels of *E*-2-hexenal and *E*-2-nonenal found in the most inexpensive and the youngest wines suggest that these compounds are formed from the oxidation of fatty acids, surely during the crushing of grapes. On the contrary, the two other alkenals, methional and phenylacetaldehyde, would be formed by the slow oxidation of the corresponding alcohols (methionol and β-phenylethanol) and from amino acids (methionine and phenylalanine) during wine aging. What is quite surprising is that the most expensive wines are simultaneously the richest in oxidation and in reduction-related compounds.

On the other hand, esterification processes introduce differences depending on the ratio at which the corresponding alcohol−acid pair have been produced during fermentation. Compounds produced at ratios close to the equilibrium (ethyl esters of fatty acids) remain with little change,[34−36] compounds produced at ratios above equilibrium (fusel alcohol acetates) have a strong decline,[34,37] and compounds produced at ratios below equilibrium (branched acid esters) increase with time.[36,38,39]

Finally, is worth mentioning that several relevant odorants are found at similar concentrations in all the wines, regardless of market category. In the cases of methoxypyrazines, sotolon, homofuraneol, diethyl sulfide, diethyl disulfide, or ethanethiol, all the wines seem to have very poor levels of these compounds. In other cases, such as 4-ethylphenol, the lack of significance must be attributed to the huge variabilities usually found in the level of this compound. The cases of Furaneol or of some polyfunctional mercaptans suggest that their levels depend on multiple factors.

Correlation Study. A correlation study was carried out within each one of the price categories to verify the existence of odorants that could be formed by the same or related pathways. Results of such study are given in Table 2. Some of these correlations are well-known, were expected, and are common to the three price categories; others were unexpected or seemed to follow a more complex pattern, suggesting the existence of several formation/degradation pathways. Some of those pathways would be more or less active in just one of the wine price categories, which would explain that the correlation is observed only within one or two categories. This is the case for the pairs methional/methionol and phenylacetaldehyde/β-phenylethanol, for which a significant correlation is found exclusively in the most expensive sample set. This suggests that the corresponding alcohol is the main source of the aldehyde but only in aged wine, while in younger wines the aldehyde would be formed effectively also from other precursors, such as the amino acid as suggested elsewhere.[40] The correlation between methional and phenylacetaldehyde observed only in inexpensive wines suggests a decoupling between the formation rates of these compounds in aged wines, surely because of the different availability of the corresponding alcohol precursors.

The high degree of correlation between ethyl 2-, 3-, and 4-methylpentanoate and ethyl 2- and 3-methylbutyrate and the nearly null correlation between these compounds and ethyl cyclohexanoate is also worth mentioning. The existence of these correlations suggests that the precursor acids are also fermentative compounds formed by yeast along a chemical pathway similar to

Table 2. Groups of Compounds Whose Concentration Values Are Correlated within a Wine Set[a]

compounds	high-price wines	medium-price wines	low-price wines
ethyl butyrate, butyric acid, ethyl hexanoate, hexanoic acid, ethyl octanoate, octanoic acid	**>0.65**	**>0.60**	**>0.50**
ethyl 2-methylpropanoate, ethyl 3-methylbutyrate, ethyl 2-methylbutyrate	**>0.50** (+ phenylethyl acetate, isobutyl acetate)	**>0.70**	**>0.60**
ethyl 2-, 3-, and 4-methylpentanoate, ethyl 2 and 3-methylbutyrate	**>0.70** (− ethyl 2-methylpentanotate)	**>0.55**	<0.01
2-methylpropanol, isoamyl alcohol, methionol, *β*-phenylethanol	**>0.70**	**>0.60** (− methionol)	**>0.50**
2-methylpropanol, isoamyl alcohol, *β*-phenylethanol, ethyl 2-methylpropanoate, ethyl 3-methylbutyrate, ethyl 2-methylbutyrate	**>0.50**	**>0.50**	**>0.50**
isoamyl alcohol, 2-methylpropanol, 2-methylpropanoic acid	>0.20	>0.39	**>0.60**
2- and 3-methylbutyric acid	**0.65**	**0.91**	na[b]
acetic acid, ethyl acetate, acetoin	**0.60** (− ethyl acetate)	na	**>0.60**
ethyl furoate, phenylethyl acetate	**0.50**	0.17	**0.63**
linalool, *β*-citronellol	**0.62**	**0.64**	**0.64**
linalool, *β*-damascenone	0.01	**0.59**	<0.01
4-ethylphenol, 4-ethylguaiacol	**>0.70** (+ 4-vinylphenol, 4-vinylguaiacol)	**0.64**	**>0.60** (+ 4-propylguaiacol)
Z/*E*-whiskylactones, eugenol, *δ*-octalactone, vanillin, 2,6-dimethoxyphenol, syringaldeyde, acetovanillone	**>0.50**	**>0.50** (+ guaiacol, furfural, 5-methylfurfural, 5-hydroxymethylfurfural, *o*-cresol, *E*-isoeugenol, maltol)	**>0.50**
methyl vanillate, *α*-terpineol	**0.85**	**0.64**	0.39
ethyl vanillate, methyl vanillate, acetovanillone, *γ*-nonalactone, *δ*-decalactone	>0.30	>0.10	**>0.50**
γ-nonalactone, *γ*-octalactone, *γ*-decalactone	na	**>0.75**	na
γ-nonalactone, *α*-terpineol	**0.73**	0.04	0.30
methional, phenylacetaldehyde	0.19	**0.50**	**0.73**
methional, methionol	**0.72**	0.01	0.01
E-2-hexenal, *E*-2-heptenal, *E*-2-octenal, *E*-2-nonenal	**>0.65**	>0.50	<0.01
β-phenylethanol, phenylacetaldehyde	**0.60**	**0.56**	0.10
2-methyl-3-furanthiol, 2-furfurylthiol	na	0.01	**0.50**
3-mercaptohexyl acetate, 3-mercaptohexanol	na	0.38	**0.67**
furfurylthiol, benzylmercaptan	na	**0.74**	<0.01

[a]Correlation coefficients higher than 0.5 are marked in bold. For cases in which a compound holds/does not hold the correlation in a single group, such a compound is indicated in parentheses after a ± sign. [b]Not available. In some cases correlation coefficients were not calculated because concentration data of some compounds were not available in that group of wines.

dx.doi.org/10.1021/jf2050685 |*J. Agric. Food Chem.* 2012, 60, 5045−5056

Table 3. Families of Odorants and Ranges of Odor Activity Values (sum of individual OAVs) Observed in the Three Different Price Categories of Spanish Red Wines[a]

			OAV interval			average OAV and significant differences[c]		
	family of odorants	compounds[b]	high-price wines	medium-price wines	low-price wines	high-price wines	medium-price wines	low-price wines
higher OAVs in expensive wines	volatile mercaptans	dihydrogen sulfide, methanethiol, ethanethiol, dimethyl sulfide, diethyl sulfide, dimethyl disulfide	16.3−80.4	10.5−47.9	10.7−27.5	32.4 a	20.0 b	19.1 b
	ethyl esters of branched acids	ethyl 2-methylpropanoate, ethyl 2-methylbutyrate, ethyl 3-methylbutyrate	7.24−70.1	9.60−58.3	5.91−60.4	26.3 a	23.4 ab	19.1 b
	oak-related compounds	eugenol, *E*-isoeugenol, *Z*-whiskylactone, *E*-whiskylactone, 2,6-dimethoxyphenol, 4-allyl-2,6-dimethoxyphenol, 4-vinylphenol, 4-vinylguiacol, 4-propylguaiacol, acetovanillone, guaiacol, vanillin, methyl vanillate, ethyl vanillate, δ-octalactone	4.05−24.5	1.28−16.9	0.45−5.12	12.0 a	5.13 b	2.09 c
	polyfunctional mercaptans (varietals)	4-methyl-4-mercapto-2-pentanone, 3-mercaptohexyl acetate, 3-mercaptohexanol	7.41−19.3	3.64−47.7	3.24−12.9	11.5 a	8.32 a	5.75 b
	ethyl phenols	4-ethylphenol, 4-ethylguaiacol	0.02−39.7	0.02−14.4	0.03−12.4	1.12 a	0.60 b	0.42 b
	ethyl cinnamates	ethyl cinnamate, ethyl dihydrocinnamate	0.16−1.95	0.16−1.34	0.16−1.73	**0.87 a**	**0.56 b**	**0.87 a**
higher OAVs in inexpensive wines	branched fatty acids	2-methylpropanoic acid, 3-methyl butyric acid	15.3−31.4	9.60−58.3	20.5−68.3	**22.3 b**	**26.3 b**	**45.3 a**
	norisoprenoids	β-damascenone, α-ionone, β-ionone	4.99−214	4.99−49.5	4.99−111	15.3 b	20.6 b	34.8 a
	linear fatty acids	butyric acid, hexanoic acid, octanoic acid, decanoic acid	2.17−18.0	5.31−18.0	9.83−26.2	6.61 c	8.13 b	17.4 a
	fusel alcohols	2-methylpropanol, 1-butanol, isoamyl alcohol, 1-hexanol, *Z*-3-hexenol, β-phenylethanol, methionol	6.40−18.5	6.10−16.9	8.47−19.7	**10.2 b**	**10.2 b**	**14.6 a**
	fusel alcohol acetates	butyl acetate, isobutyl acetate, isoamyl acetate, hexyl acetate, phenylethyl acetate	3.84−12.5	4.50−12.5	5.30−32.2	**6.84 b**	**7.36 b**	**11.8 a**
	ethyl esters of the linear fatty acids	ethyl propanoate, ethyl butyrate, ethyl hexanoate, ethyl octanoate, ethyl decanoate	1.90−6.23	2.82−8.46	2.49−7.69	**3.56 b**	**4.38 a**	**4.73 a**
	E-2-alkenals	*E*-2-hexenal, *E*-2-heptenal, *E*-2-octenal, *E*-2-nonenal	1.63−4.03	0.27−0.52	2.07−14.9	2.09 b	0.30 c	4.68 a
	terpenols	linalool, geraniol, β-citronellol, α-terpineol	0.03−0.61	0.02−1.15	0.07−0.79	0.18 b	0.20 b	0.32 a

[a]ANOVA tests were carried out between groups of wines and significant differences (95%) between average OAVs for each family are expressed with letters (a, b, and c). [b]Only compounds analyzed in the three groups of wines were considered. [c]In those cases in which the distribution followed a marked log-normal pattern, the geometric mean was compared. Arithmetic means are in bold, and geometric means are in normal type.

dx.doi.org/10.1021/jf2050685 |*J. Agric. Food Chem.* 2012, 60, 5045−5056

that of their five-atom counterparts, while ethyl cyclohexanoate and its likely precursor cyclohexanoic acid would follow a completely different genesis.

Potential Sensory Differences Derived from Compositional Differences. To handle such a complex set of compositional data and to look for potential aroma patterns, we will group odorants into odor-related categories and will consider them as "aroma families". An aroma family is therefore a group of compounds sharing aroma properties that has been processed together. The score from such a vector in a given wine is obtained by the summation of all the concentrations of the compounds in the family, normalized to the corresponding odor thresholds, i.e., the odor activity values (OAVs). Results of this treatment are summarized in Table 3. Results in the table should be interpreted with caution and taken just as an approximation of the odor profiles of the products because of the following: (1) OAV data are affected by the additional uncertainty linked to the measurements of the odor thresholds. (2) The relevant parameter in odor mixing is not the OAV but rather the odor intensity. While OAV assumes a linear dependence on concentration (C), the relationship between odor intensity and C is more complex and differs between compounds. Despite that, the table makes it possible to make a simple assessment about the families of odorants and odors that are most likely contributors to odor differences between the three sample sets. The table confirms most of the observations made in the previous paragraphs and most clearly illustrates that the average aroma compositions of expensive and inexpensive wines follow nearly an opposite pattern. Aroma chemical profiles of expensive wines are richest in wood-related odorants, ethyl phenols, cysteinil-derived mercaptans, volatile mercaptans, the ethyl esters of branched acids, and also methional and phenylacetaldehyde (see Table 1) and are poorest in linear fatty acids, fusel alcohols, branched fatty acids, terpenols, norisoprenoids, fusel alcohol acetates, and ethyl esters of the linear fatty acids. Inexpensive wines show exactly the opposite profile. The profile of medium-price wines is intermediate between those two extremes, albeit closer to the expensive group, and the most remarkable difference is the lowest levels of alkenals found in these wines. The study in summary confirms that the aroma chemical profiles of wines belonging to different price segments are completely different. It should be again remarked that some of the major differences were not clearly expected or at least are much clearer of what naively one had expected. In relation to the aroma chemical profile of expensive wines, these less expected differences are (1) the significantly lower levels of fermentation compounds with coarse aroma (fusel alcohols, branched fatty acids, linear fatty acids), (2) the highest levels of reduction compounds, even of varietal polyfunctional mercaptans, (3) the low levels of alkenals, and (4) the smaller levels of varietal compounds formed from glycosidic precursors (terpenols and norisoprenoids).

Models Relating Quality to Odorant Composition. Quality was measured by a panel of experts and was rated independently within each one of the three sample sets (see Materials and Methods). The modeling study has as a major aim to reveal whether wine quality follows similar or different patterns among the different categories. Models were built by using PLSR1 and are shown in Tables 4 and 5. The first remarkable observation is that good models could be built exclusively for expensive and medium-price wines but not for the lower-price sample set. In this case it was necessary to split the set into two subsets: wines with or without woody notes,

Table 4. Quality Parameters of PLSR1 Models Linking Quality with Aroma Chemical Composition in the Three Price Categories (inexpensive wines were split into two subcategories with/without wood)

model	%EV[a]	RMSEP[b]	m[c]	offset[d]	CC[e]	no. X[f]	no. PC[g]
high-price wines	58.9	0.56	0.61	1.16	0.78	10	2
medium-price wines	74.9	0.31	0.79	0.61	0.88	16	4
low-price wines (wooded)	68.7	0.33	0.52	1.32	0.87	6	2
low-price wines (unwooded)	52.7	0.45	0.52	1.29	0.78	4	3

[a]Percentage of variance explained by the model. [b]Root-mean-square prediction error. [c]Slope of the regression curve between real and predicted Y variables. [d]Offset of the regression curve between real and predicted Y variables. [e]Correlation coefficient between real and predicted Y variables. [f]Number of X variables in the model. [g]Number of principal components in the model.

which suggests that the wine experts use two different quality scales for assessing wine quality, one for unwoody and a second one for woody wines. Even after this operation, modeling the quality of the unwoody subset was very difficult, and only after the sensory attribute "sweetness in mouth" was included, could an acceptable model be obtained. The reasons for this are unclear and deserve further investigation. One possible explanation would be related to the potential existence of more unbalances in the aroma and gustative profiles of this sample set, but other explanations cannot be ruled out. For instance, within this sample set, a major interaction between aroma composition and in-mouth sensory properties is expected.[41]

In any case, the models given in Table 5 confirm that within each category (splitting the inexpensive into two) aroma compounds play more or less different roles as quality markers. Comparing the models for expensive and medium-price wines, it can be seen that they share a general common structure but that there are also some remarkable differences. The general structure shows that quality is, as previously reported,[1] positively related to the presence of aroma compounds with pleasant character, such as oak-related compounds, ethyl esters or norisoprenoids, while it is negatively related to the presence of aroma compounds with a relatively unpleasant character, such as 4-ethylphenol, methional, or phenylacetaldehyde. Major differences between these two models are found in the role played by branched acids, major alcohols, and γ-lactones. Branched acids form a positive aroma vector (together with linear acids) within the expensive wines, while they are negative contributors to the quality of medium-price wines. Fusel alcohols and γ-lactones do not seem to influence quality in the former set, but are major negative quality factors within the medium-price category. While the negative role of γ-lactones and branched acids may be attributed to the fact that these compounds are present at higher levels in the medium-price wine set, this is certainly not the case for major alcohols. The negative role for major alcohols may be well-linked to the differences in aroma balances within both categories and to the differences in volatility caused by the major retentive power of the matrix of the most expensive wines.[42] Finally, the models for the most inexpensive wines share again the general pattern of positive aroma compounds vs less pleasant aroma compounds, but the key compounds are different, which clearly illustrates that quality is characteristic of a given sample set.

dx.doi.org/10.1021/jf2050685 | J. Agric. Food Chem. 2012, 60, 5045−5056

Table 5. Variables of Quality Models for Each Group of Wines[a]

	high-price wines	medium-price wines	low-price wines (wooded)	low-price wines (unwooded)
positive contributors	linear and branched, fatty acids (0.598)	oak-related compounds (0.582)	*Z*-whiskylactone (0.151)	cinnamates (0.083)
	oak-related compounds (0.222)	isoamyl acetate (0.327)	3-mercaptohexanol (0.147)	
	Furaneol and homofuraneol (0.088)	ethyl cinnamate and ethyl dihydrocinnamate (0.118)	guaiacol (0.145)	
	minor branched ethyl esters (0.083)	norisoprenoids (0.098)	ethyl acetate (0.140)	
	norisoprenoids (0.038)	major branched ethyl esters (0.096)		
	major, linear and branched, ethyl esters (0.006)	major linear ethyl esters (0.057)		
		terpenols (0.028)		
		linear fatty acids (0.014)		
negative contributors	4-ethylphenol (−0.327)	fusel alcohols (−0.599)	acetoin (−0.130)	*E*-2-alkenals (−0.382)
	acetic acid (−0.283)	γ-lactones (−0.333)	volatile mercaptans (−0.074)	acetoin (−0.242)
	phenylacetaldehyde (−0.201)	4-ethylphenol (−0.283)		sweetness (−0.022)
	methional (−0.150)	phenylacetaldehyde (−0.121)		
		methional (−0.073)		
		methoxypyrazines (−0.037)		
		branched fatty acids (−0.033)		

[a]Regression coefficients are expressed in parentheses.

In this case, acetoin and *E*-2-alkenals (only in unwoody samples) arise as key quality-related compounds. Acetoin does not reach its threshold; however, data in Table 2 show that it is highly correlated to acetic acid.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Compounds quantified in each one of the analytical methods, including supplier. Wines analyzed in the experiment including production zone and vintage year. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 34 976 762503. Fax: 34 976761292 Email: escudero@unizar.es.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Ferreira, V.; San Juan, F.; Escudero, A.; Cullere, L.; Fernandez-Zurbano, P.; Saenz-Navajas, M. P.; Cacho, J. Modeling quality of premium Spanish red wines from gas chromatography-olfactometry data. *J. Agric. Food Chem.* **2009**, *57* (16), 7490−7498.

(2) Cullere, L.; Cacho, J.; Ferreira, V. Validation of an analytical method for the solid phase extraction, in cartridge derivatization and subsequent gas chromatographic-ion trap tandem mass spectrometric determination of 1-octen-3-one in wines at ngL(−1) level. *Anal. Chim. Acta* **2006**, *563* (1−2), 51−57.

(3) Escudero, A.; Campo, E.; Fariña, L.; Cacho, J.; Ferreira, V. Analytical characterization of the aroma of five premium red wines. Insights into the role of odor families and the concept of fruitiness of wines. *J. Agric. Food Chem.* **2007**, *55* (11), 4501−4510.

(4) Escudero, A.; Gogorza, B.; Melus, M. A.; Ortin, N.; Cacho, J.; Ferreira, V. Characterization of the aroma of a wine from Maccabeo. Key role played by compounds with low odor activity values. *J. Agric. Food Chem.* **2004**, *52* (11), 3516−3524.

(5) LopezTamames, E.; CarroMarino, N.; Gunata, Y. Z.; Sapis, C.; Baumes, R.; Bayonove, C. Potential aroma in several varieties of Spanish grapes. *J. Agric. Food Chem.* **1997**, *45* (5), 1729−1735.

(6) Robinson, A. L.; Boss, P. K.; Heymann, H.; Solomon, P. S.; Trengove, R. D. Influence of yeast strain, canopy management, and site on the volatile composition and sensory attributes of Cabernet Sauvignon wines from western Australia. *J. Agric. Food Chem.* **2011**, *59* (7), 3273−3284.

(7) Jones, G. V.; Duff, A. A.; Hall, A.; Myers, J. W. Spatial analysis of climate in winegrape growing regions in the western United States. *Am. J. Enol. Viticult.* **2010**, *61* (3), 313−326.

(8) Ou, C. R.; Du, X. F.; Shellie, K.; Ross, C.; Qian, M. C. Volatile compounds and sensory attributes of wine from Cv. Merlot (Vitis vinifera L.) grown under differential levels of water deficit with or without a kaolin-based, foliar reflectant particle film. *J. Agric. Food Chem.* **2010**, *58* (24), 12890−12898.

(9) Kok, D. Influences of pre- and post-veraison cluster thinning treatments on grape composition variables and monoterpene levels of Vitis vinifera L. cv. Sauvignon Blanc. *J. Food Agric. Environ.* **2011**, *9* (1), 22−26.

(10) Kliewer, W. M.; Dokoozlian, N. K. Leaf area/crop weight ratios of grapevines: Influence on fruit composition and wine quality. *Am. J. Enol. Viticult.* **2005**, *56* (2), 170−181.

(11) Callejon, R. M.; Clavijo, A.; Ortigueira, P.; Troncoso, A. M.; Paneque, P.; Morales, M. L. Volatile and sensory profile of organic red wines produced by different selected autochthonous and commercial Saccharomyces cerevisiae strains. *Anal. Chim. Acta* **2010**, *660* (1−2), 68−75.

(12) Antonelli, A.; Castellari, L.; Zambonelli, C.; Carnacini, A. Yeast influence on volatile composition of wines. *J. Agric. Food Chem.* **1999**, *47* (3), 1139−1144.

(13) Hay, C. The political economy of price and status formation in the Bordeaux en primeur market: the role of wine critics as rating agencies. *Socio-Econ. Rev.* **2010**, *8* (4), 685−707.

(14) Ali, H. H.; Lecocq, S.; Visser, M. The impact of gurus: Parker grades and En primeur wine prices. *Econ. J.* **2008**, *118* (529), 158−173.

(15) Ali, H. H.; Nauges, C. The pricing of experience goods: The example of en primeur wine. *Am. J. Agric. Econ.* **2007**, *89* (1), 91−103.

(16) Haeger, J. W.; Storchmann, K. Prices of American Pinot Noir wines: Climate, craftsmanship, critics. *Agric. Econ.* **2006**, *35* (1), 67−78.

(17) Troncoso, J. L.; Aguirre, M. Short communication. Price determinants of Chilean wines in the US market: a hedonic approach. *Span. J. Agric. Res.* **2006**, *4* (2), 124−129.
(18) Campo, E.; Ballester, J.; Langlois, J.; Dacremont, C.; Valentin, D. Comparison of conventional descriptive analysis and a citation frequency-based descriptive method for odor profiling: a case of Burgundy Pinot noir wines. *Food Qual. Pref.* **2010**, *21* (1), 44−55.
(19) Saenz-Navajas, M. P.; Martin-Lopez, C.; Ferreira, V.; Fernandez-Zurbano, P. Sensory properties of premium Spanish red wines and their implication in wine quality perception. *Aust. J. Grape Wine Res.* **2011**, *17* (1), 9−19.
(20) Ortega, C.; Lopez, R.; Cacho, J.; Ferreira, V. Fast analysis of important wine volatile compounds. Development and validation of a new method base don gas chromatographic-flame ionisation detection analysis of dichloromethane microextracts. *J. Chromatogr., A.* **2001**, *923* (1-2), 205−214.
(21) Lopez, R.; Aznar, M.; Cacho, J.; Ferreira, V. 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* (1−2), 167−177.
(22) Campo, E.; Cacho, J.; Ferreira, V. Solid phase extraction, multidimensional gas chromatography mass spectrometry determination of four novel aroma powerful ethyl esters - Assessment of their occurrence and importance in wine and other alcoholic beverages. *J. Chromatogr., A* **2007**, *1140* (1−2), 180−188.
(23) Zapata, J.; Mateo-Vivaracho, L.; Cacho, J.; Ferreira, V. Comparison of extraction techniques and mass spectrometric ionization modes in the analysis of wine volatile carbonyls. *Anal. Chim. Acta* **2010**, *660* (1−2), 197−205.
(24) Ferreira, V.; Jarauta, I.; Lopez, R.; Cacho, J. Quantitative determination of sotolon, maltol and free Furaneol in wine by solid-phase extraction and gas chromatography-ion-trap mass spectrometry. *J. Agric. Food Chem.* **2003**, *1010* (1), 95−103.
(25) Lopez, R.; Lapena, A. C.; Cacho, J.; Ferreira, V. Quantitative determination of wine highly volatile sulfur compounds by using automated headspace solid-phase microextraction and gas chromatography-pulsed flame photometric detection - Critical study and optimization of a new procedure. *J. Chromatogr., A* **2007**, *1143* (1−2), 8−15.
(26) Mateo-Vivaracho, L.; Cacho, J.; Ferreira, V. Improved solid-phase extraction procedure for the isolation and in-sorbent pentafluorobenzyl alkylation of polyfunctional mercaptans. Optimized procedure and analytical applications. *J. Chromatogr., A* **2008**, *1185* (1), 9−18.
(27) López, R.; Gracia-Moreno, E.; Cacho, J.; Ferrreira, V. Development of a mixed-mode solid phase extraction method and further gas chromatography mass spectrometry for the analysis of 3-alkyl-2-methoxypyrazines in wine. *J. Chromatogr., A* **2011**, *1218* (6), 842−848.
(28) Ferreira, V.; Fernandez, P.; Cacho, J. F. A study of factors affecting wine volatile composition and its application in discriminant analysis. *Food Sci. Technol.-Leb. and Tech.* **1996**, *29* (3), 251−259.
(29) Mauricio, J. C.; Moreno, J.; Zea, L.; Ortega, J. M.; Medina, M. The effects of grape must fermentation conditions on volatile alcohols and esters formed by Saccharomyces cerevisiae. *J. Sci. Food Agric.* **1997**, *75* (2), 155−160.
(30) Arapitsas, P.; Antonopoulos, A.; Stefanou, E.; Dourtoglou, V. G. Artificial aging of wines using oak chips. *Food Chem.* **2004**, *86* (4), 563−570.
(31) Jarauta, I.; Cacho, J.; Ferreira, V. Concurrent phenomena contributing to the formation of the aroma of wine during aging in oak wood: An analytical study. *J. Agric. Food Chem.* **2005**, *53* (10), 4166−4177.
(32) Ferreira, V.; Jarauta, I.; Cacho, J. Physicochemical model to interpret the kinetics of aroma extraction during wine aging in wood. Model limitations suggest the necessary existence of biochemical processes. *J. Agric. Food Chem.* **2006**, *54* (8), 3047−3054.
(33) Segurel, M. A.; Razungles, A. J.; Riou, C.; Trigueiro, M. G. L.; Baumes, R. L. Ability of possible DMS precursors to release DMS during wine aging and in the conditions of heat-alkaline treatment. *J. Agric. Food Chem.* **2005**, *53* (7), 2637−2645.
(34) Ramey, D. D.; Ough, C. S. Volatile ester hydrolysis or formation during storage of model solutions and wines. *J. Agric. Food Chem.* **1980**, *28* (5), 928−934.
(35) Shinohara, T.; Watanabe, M. Effects of fermentation conditions and aging temperature on volatile ester contents in wine. *Agric. Biol. Chem.* **1981**, *45* (11), 2645−2651.
(36) Oliveira, J. M.; Oliveira, P.; Baumes, R. L.; Maia, O. Changes in aromatic characteristics of Loureiro and Alvarinho wines during maturation. *J. Food Comp. Anal.* **2008**, *21* (8), 695−707.
(37) Lambropoulos, I.; Roussis, I. G. Inhibition of the decrease of volatile esters and terpenes during storage of wines and a model wine medium by wine phenolic extracts. *Food Technol. Biotechnol.* **2007**, *45* (2), 147−155.
(38) Diaz-Maroto, M. C.; Schneider, R.; Baumes, R. Formation pathways of ethyl esters of branched short-chain fatty acids during wine aging. *J. Agric. Food Chem.* **2005**, *53* (9), 3503−3509.
(39) Ugliano, M.; Siebert, T.; Mercurio, M.; Capone, D.; Henschke, P. A. Volatile and color composition of young and model-aged Shiraz wines as affected by diammonium phosphate supplementation before alcoholic fermentation. *J. Agric. Food Chem.* **2008**, *56* (19), 9175−9182.
(40) Vallet, A.; Lucas, P.; Lonvaud-Funel, A.; de Revel, G. Pathways that produce volatile sulphur compounds from methionine in Oenococcus oeni. *J. Appl. Microbiol.* **2008**, *104* (6), 1833−1840.
(41) Sáenz-Navajas, M. P.; Campo, E.; Fernández-Zurbano, P.; Valentin, D.; Ferreira, V. An assessment of the effects of wine volatiles on the perception of taste and astringency in wine. *Food Chem.* **2010**, *121* (4), 1139−1149.
(42) Saenz-Navajas, M. P.; Campo, E.; Cullere, L.; Fernandez-Zurbano, P.; Valentin, D.; Ferreira, V. Effects of the nonvolatile matrix on the aroma perception of wine. *J. Agric. Food Chem.* **2010**, *58* (9), 5574−5585.
(43) 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* (11), 1659−1667.
(44) Etievant, P. X. *Wine. Volatile compounds of food and beverages*; Marcel Dekker: New York, 1991.
(45) Gemert, L. J.; Nettenbreijer, A. H. *Compilation of odour threshold values in air and water*; National Institute for Water Supply: Zeist, 1977.
(46) Guth, H. Quantitation and sensory studies of character impact odorants of different white wine varieties. *J. Agric. Food Chem.* **1997**, *45* (8), 3027−3032.
(47) Cullere, L.; Cacho, J.; Ferreira, V. An assessment of the role played by some oxidation-related aldehydes in wine aroma. *J. Agric. Food Chem.* **2007**, *55* (3), 876−881.
(48) Escudero, A.; Hernandez-Orte, P.; Cacho, J.; Ferreira, V. Clues about the role of methional as character impact odorant of some oxidized wines. *J. Agric. Food Chem.* **2000**, *48* (9), 4268−4272.
(49) Peinado, R. A.; Moreno, J.; Bueno, J. E.; Moreno, J. A.; Mauricio, J. C. Comparative study of aromatic compounds in two young white wines subjected to pre-fermentative cryomaceration. *Food Chem.* **2004**, *84* (4), 585−590.
(50) Ferreira, V.; Ortin, N.; Escudero, A.; Lopez, R.; Cacho, J. Chemical characterization of the aroma of Grenache rose wines: Aroma extract dilution analysis, quantitative determination, and sensory reconstitution studies. *J. Agric. Food Chem.* **2002**, *50* (14), 4048−4054.
(51) Boidron, J. N.; Chatonnet, P.; Pons, M. Influence of wood on some aromatic substances in wines. *Connaiss. Vigne Vin* **1988**, *22* (4), 275−294.
(52) Gemert, V. *Compilation of odor thresholds*; Boelens Aroma chemical Information Services: Zeist, The Netherlands, 2003.
(53) Ferreira, V.; Aznar, M.; Lopez, R. Olfactometry and aroma extract dilution analysis of wines. In *Molecular Methods of Plants Analysis*; Jackson, J., Linskens, H., Inman, R., Eds.; Springer: New York, 2001; pp 89−122.

(54) Maga, J. A. Taste threshold values for phenolic acids which can influence flavor properties of certain flours, grains and oilseeds. *Cereal Sci. Today* **1973**, *18*, 326−330.
(55) Cutzach, I.; Chatonnet, P.; Dubourdieu, D. Study of the formation mechanisms of some volatile compounds during the aging of sweet fortified wines. *J. Agric. Food Chem.* **1999**, *47* (7), 2837−2846.
(56) Martin, B.; Etievant, P. X.; Lequere, J. L.; Schlich, P. More clues about sensory impact of sotolon in some flor Sherry wines. *J. Agric. Food Chem.* **1992**, *40* (3), 475−478.
(57) Siebert, T. E.; Bramley, B.; Solomon, M. R. Hydrogen sulfide: aroma detection threshold study in red and white wine. *AWRI Tech. Rev.* **2009**, 183.
(58) Solomon, M. R.; Geue, J.; Osidazc, P.; Siebert, T. Aroma detection threshold study of methanethiol in white and red wine. *AWRI Tech. Rev.* **2010**, *186*, 8−10.
(59) Goniak, O. J.; Noble, A. C. Sensory study of selected volatile sulfur compounds in white wine. *Am. J. Enol. Viticult.* **1987**, *38*, 223−227.
(60) Pickering, G. J.; Karthik, A.; Inglis, D.; Sears, M.; Ker, K. Determination of ortho- and retronasal detection thresholds for 2-isopropyl-3-methoxypyrazine in wine. *J. Food Sci.* **2007**, *72* (7), S468−S472.
(61) de Boubee, D. R.; Van Leeuwen, C.; Dubourdieu, D. Organoleptic impact of 2-methoxy-3-isobutylpyrazine on red Bordeaux and Loire wines. Effect of environmental conditions on concentrations in grapes during ripening. *J. Agric. Food Chem.* **2000**, *48* (10), 4830−4834.
(62) Tominaga, T.; Dubourdieu, D. A novel method for quantification of 2-methyl-3-furanthiol and 2-furanmethanethiol in wines made from Vitis vinifera grape varieties. *J. Agric. Food Chem.* **2006**, *54* (1), 29−33.
(63) Tominaga, T.; Murat, M. L.; Dubourdieu, D. Development of a method for analyzing the volatile thiols involved in the characteristic aroma of wines made from Vitis vinifera L. cv. Sauvignon Blanc. *J. Agric. Food Chem.* **1998**, *46* (3), 1044−1048.
(64) Tominaga, T.; Blanchard, L.; Darriet, P.; Dubourdieu, D. A powerful aromatic volatile thiol, 2-furanmethanethiol, exhibiting roast coffee aroma in wines made from several Vitis vinifera grape varieties. *J. Agric. Food Chem.* **2000**, *48* (5), 1799−1802.
(65) Tominaga, T.; Guimbertau, G.; Dubourdieu, D. Contribution of benzenemethanethiol to smoky aroma of certain Vitis vinifera L. wines. *J. Agric. Food Chem.* **2003**, *51* (5), 1373−1376.
(66) Soleas, G. J.; Yan, J.; Seaver, T.; Goldberg, D. M. Method for the gas chromatographic assay with mass selective detection of trichloro compounds in corks and wines applied to elucidate the potential cause of cork taint. *J. Agric. Food Chem.* **2002**, *50* (5), 1032−1039.