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ARTICLE

Modeling Quality of Premium Spanish Red Wines from Gas Chromatography−Olfactometry Data

Vicente Ferreira,*,† Felipe San Juan,† Ana Escudero,† Laura Culleré,† Purificación Fernández-Zurbano,§ M. Pilar Saenz-Navajas,§ and Juan Cacho†

†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, and §Department of Chemistry, Faculty of Sciences, University of La Rioja, 26006 Logroño, Spain

The aroma compositions of 25 premium Spanish red wines have been screened by quantitative gas chromatography−olfactometry and have been related to the quality scores of the wines. The study has shown that up to 65 odorants can be present in the aroma profiles of those wines, 32 of which have been detected in less than half of the samples. One new odorant is reported for the first time in wine [(*Z*)-2-nonenal], and only 11 odorants, most of them weak and infrequent, remain unknown. Quality was not positively correlated with any single compound or with any olfactometric vector built by the summation of odorants with similar odors. However, an olfactometric vector built by the summation of the olfactometric scores of defective odorants, such as 2-methoxy-3,5-dimethylpyrazine, 4-ethylphenol, 3-ethylphenol, 2,4,6-trichloroanisole, and *o*-cresol was significant and negatively related to quality. Quality could be satisfactorily explained by a simple partial least-squares model (79% explained variance in cross-validation) with just three *X*-variables: the aforementioned defective vector, a second vector grouping 9 other compounds with negative aroma nuances, and the fruity vector, grouping 15 compounds with fruit-sweet descriptors. This result shows that the quality of these red wines is primarily related to the presence of defective or negative odorants, and secondarily to the presence of a relatively large number of fruit-sweet odorants. Remarkably, only in a few low-quality samples could defective aroma nuances be detected, which suggests that defective and negative odorants exert a strong aroma suppression effect on fruity aroma.

KEYWORDS: Quality; aroma; wine; GC−olfactometry; odorants

INTRODUCTION

The quality of a food product is a multivariate and complex concept related primarily to questions such as its nutritional value and safety and, secondarily, to its organoleptic characteristics and perhaps functional value. In the case of a product such as wine, quality is complex and multidimensional (*1*, *2*). As wine consumption has mostly a hedonic objective, its quality is mainly related to its sensory characteristics, which determine the amount of pleasure that its consumption can deliver. Classically, the quality of a wine has been related first with the absence of defects, and a great deal of work has been invested in the identification and control of the molecules responsible for defects of different origin, such as the grape (*3*, *4*), microbial spoilage ((*5*), cork (*6*) or other closure (*7*, *8*), accidental contamination (*9*), oxidation (*10*−*12*), reduction (*13*, *14*), or wood-related problems (*15*). In a wine free from defects, quality should be related to the presence and intensity of positive odor and flavor nuances, such as fruity, woody, or toasty, and particularly to the number, intensity, harmony, and quality of all the taste, flavor, and chemosensory sensations perceived during the consumption of the wine (*16*). A great deal of work has also been invested in trying to understand the chemicals behind those perceptions, particularly woody character, fruity, green, toasted, and aging notes (*10*, *17*) and, more recently, about the taste-active and astringent compounds (*18*). On the whole, however, and despite all of this effort, it is not easy today to predict the overall quality of a wine from its chemical composition; partly because the effect on real market samples of the different molecules responsible for defects or positive flavor nuances is not well-known and partly because of the numerous studies showing the existence of strong interactions between the different taste- and flavor-active molecules. Because of this, the present research aims at assessing to what extent the odorant composition of wine is related to its general quality, and in that case, which odorants are really responsible for quality. To accomplish such goal, the aroma profiles of a relatively large number of standard market samples of Spanish extra-premium quality red wines have been screened by quantitative gas chromatography−olfactometry (GC-O), and such profiles have been related to the measured wine quality through simple statistical techniques.

*Author to whom correspondence should be addressed (telephone 34 976762076; fax 34 976761292; e-mail vferre@unizar.es).

MATERIALS AND METHODS

Wines. Twenty-five Spanish red aged wines from 11 different Spanish Denominations of Origin, Rioja (seven samples), Ribera de Duero (six samples), Toro (two samples), and one sample each from Cariñena,

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Table 1. Wines Analyzed in the Experiment Including Origin, Age, Varietal Composition, Oak Aging Time, and Some Basic Compositional Parameters

wine	Denomination of Origin	vintage year	grape variety	oak aging (months)	alcohol % (v/v)	pH	volatile acidity[a] (g/L)	residual sugar (g/L)	TPI[b]	CI[c]
Pago de Capellanes	Ribera de Duero	2003	Tempranillo (90%), Cabernet Sauvignon (10%)	18	13.5	3.75	0.56	1.55	48.3	13.3
Dominio de Atauta	Ribera de Duero	2004	Tempranillo	14	14.8	3.95	0.73	3.29	70.1	13.7
Avan Cepas centenarias	Ribera de Duero	2005	Tempranillo	15	14.5	3.66	0.63	3.32	62.0	19.9
La Montesa	Rioja	2001	Garnacha, Tempranillo, Mazuelo, Graciano	16	13.5	3.57	0.47	2.34	61.8	9.4
Albada	Calatayud	2005	Garnacha (94%), Merlot (6%)	13	14.5	3.37	0.43	2.90	62.8	16.2
Casa Castillo Pie Franco	Jumilla	2000	Monastrell	18	14.5	3.50	0.41	3.52	66.3	17.5
Enate	Somontano	2005	Shyrah	16	14.3	3.47	0.49	3.51	87.7	14.4
Muga	Rioja	2003	Tempranillo (70%), Garnacha (20%), others (10%)	24	13.5	3.54	0.61	3.62	57.2	13.4
Care Shyraz	Cariñena	2005	Shyrah	14	13.5	3.52	0.45	3.23	51.6	13.3
Luberri Cepas Viejas	Rioja	2003	Tempranillo	18	14.4	3.45	0.43	3.96	79.8	9.3
Allende Graciano	Rioja	2004	Graciano	24	13.2	3.61	0.68	2.97	93.1	11.5
Bembibre Dominio de Tares	Bierzo	2004	Mencía	15	14.0	3.70	0.54	1.65	61.0	12.4
San Vicente	Rioja	2004	Tempranillo	20	14.5	3.63	0.48	2.45	62.1	12.7
Ribas de Cabrera	Baleares	2000	Negra Mol	16	14.3	3.73	0.95	2.87	59.3	9.7
Chafandin Tempranillo	Ribera de Duero	2002	Tempranillo	15	14.2	3.86	0.39	2.76	62.3	10.9
Jean Leon	Penedés	2001	Cabernet Sauvignon (85%), Cabernet Franc (15%)	24	13.5	3.51	0.50	2.04	83.9	12.1
Venus La Universal	Montsant	2003	Shyrah (50%), Mazuelo (50%)	16	13.5	3.52	0.67	1.83	68.9	8.8
Roda	Rioja	2004	Tempranillo (81%), Graciano (15%), Garnacha (4%)	16	14.0	3.77	0.60	3.03	52.0	9.5
Neo	Ribera de Duero	2003	Tempranillo	14	13.5	3.93	0.51	2.43	70.1	14.5
Estancia Piedra Paredinas	Toro	2000	Tinta de Toro	18	14.1	3.48	0.60	2.24	70.0	11.4
San Roman	Toro	2002	Tinta de Toro	20	14.5	3.58	0.71	3.07	79.0	12.3
Fincas de ganuza	Rioja	2002	Tempranillo	20	14.1	3.65	0.51	3.14	76.7	13.3
Carmelo Rodero	Ribera de Duero	2000	Tempranillo (90%), Cabernet Sauvignon (10%)	15	13.5	3.57	0.52	2.14	48.4	7.9
Vallegarcia Cab Sauvignon-Merlot	Castilla	2002	Cabernet Sauvignon (80%), Merlot (20%)	16	14.5	3.46	0.41	1.36	51.5	10.2
Les Ones	Priorat	2002	Mazuelo (55%), Garnacha (35%), Shyrah (10%)	13	14.7	3.40	0.51	2.16	50.1	8.9

[a] Expressed as sulfuric acid. [b] Total polyphenol index, expressed in absorbance × 100. [c] Color units, expressed as $(A_{420} + A_{520} + A_{620}) \times 5$.

Calatayud, Jumilla, Somontano, Priorat, Bierzo, Penedés, and Montsant, one "vi de taula de Balears", and one "Vino de la Tierra de Castilla", have been evaluated. All of the wines were extra-premium products with a price above 15 euros/bottle and were selected on the basis of sales criteria to obtain a sample representative of the Spanish high-quality red wine market. The detailed list of samples, including sample information and basic compositional data obtained following standard operating procedures, is shown in **Table 1**.

Reagents. *Solvents*. Dichloromethane and methanol were purchased from Merck (Darmstadt, Germany); water was purified in a Milli-Q system from Millipore (Bedford, MA).

Resins. Lichrolut EN resins (nonpolar resins) and polypropylene cartridges (0.8 cm internal diameter, 3 mL internal volume) were supplied by Merck (Darmstadt, Germany).

Standards. The standards used for identifications were supplied by Aldrich (Steinheim, Germany), Merck (Darmstadt, Germany), ChemService (West Chester, PA), Fluka (Buchs, Switzerland), Sigma (St. Louis, MO), PolyScience (Niles, IL), Lancaster (Strasbourg, France), Alfa Aesar (Karlsruhe, Germany), Panreac (Barcelona, Spain), SAFC (Steinheim, Germany), and Oxford Chemicals (Hartlepool, U.K.). β-Damascenone was a gift from Firmenich (Geneva, Switzerland), 3-methyl-2,4-nonanedione was a gift from Takasago International, and 3,5-dimethyl-2-methoxypyrazine was a gift from Mark Sefton (formerly Australia Wine Research Institute). Furfuryl ethyl ether was prepared by heating to 80 °C a mixture of the corresponding alcohol (100 mg), sodium hydride (100%, 100 mg), and iodoethane (1 mL) under a nitrogen atmosphere for 12 h. An alkane solution (C8−C28), 20 mg/L in dichloromethane, was employed to calculate the linear retention index (LRI) of each analyte. Bis(2-methyl-3-furyl) disulfide (98%) and (*E*)-2-nonenal were purchased from Aldrich (Madrid, Spain). (*Z*)-2-Nonenal was found in commercial (*E*)-2-nonenal at 5−10% level.

Wine Sensory Analysis. The sensory panel was composed of 8 females and 10 males, 30−60 years of age, all of them with long experience as wine tasters but with different backgrounds: 5 were aroma researchers, 4 were winemakers, 5 were sommeliers, and 4 were wine retailers. Each panelist participated individually in one session. First, the panelists were required to smell and taste each of the 25 wines, which were presented randomly in coded wine glasses, once in the proposed order, to minimize any bias introduced by the order of presentation. Afterward, they could smell and taste the samples as many times as they wanted and in any order. The panelists were asked to sort the wines into groups on the basis of quality (odor and taste). They were asked to form five groups and to put as many wines as they wished in each group. The groups were as follows: exceptional (scored as 5 during data recoding), good or very good (scored as 4), right or approved (scored as 3), poor or disappointing (scored as 2), and defective or rejectable (scored as 1). The panelists were informed about the general price of the samples before the tasting session, but no more data were disclosed. The panelists were also asked to provide a few words to describe each wine. The quality index of each wine was obtained by averaging all of the individual scores obtained by each wine after recoding. In case a bottle had a clear bottle-related sensory problem, a second bottle was provided. In those cases in which the problem affected only the first sample, this one was discarded and the sensory analysis and further studies were carried out on defect-free samples. If, however, all of the samples were defective, the samples were not discarded.

Gas Chromatography−Olfactometry. *Preparation of Extracts*. The volatiles of the wine were collected using a purge and trap system (*17*). The Lichrolut EN cartridge was placed on the top of a bubbler flask containing 80 mL of wine. Volatile wine constituents released in the headspace were trapped in the cartridge containing the sorbent and were further eluted with 3.2 mL of dichloromethane containing 5% methanol. The extract was concentrated to a final volume of 200 μL.

Sniffings were carried out by a panel composed of six expert sniffers. Each wine extract was smelled once by each panelist. Sniffing time was approximately 30 min, and each judge carried out one session per day. The experiments were carried out in a Thermo 8000 series GC equipped with a flame ionization detector (FID) and a sniffing port (ODO-1 from SGE) connected by a flow splitter to the column exit. The chromatographic conditions were the same as described in ref *17*. Panelists were asked to score the intensity of each aromatic stimulus using a 4-point scale (0 = not detected, 1 = weak, 2 = clear but not intense note, 3 = intense note). The signal obtained was modified frequency [MF (%)], which was calculated with the formula proposed by Dravnieks (*19*)

$$\mathrm{MF}\ (\%) = \sqrt{F(\%) \times I(\%)}$$

where $F(\%)$ is the detection frequency of an aromatic stimulus expressed as a percentage and $I(\%)$ is the average intensity expressed as percentage of the maximum intensity .

The identification of the odorants was carried out by comparison of their odors, chromatographic retention index in both DB-Wax and DB-5 (30 m × 0.32 mm × 1 μm film thickness) columns, and MS spectra with those of pure reference compounds.

Identification of Novel Compounds. *Preparation of Extracts.* Wines with high MF olfactometric scores in the evaluated odorants were selected. Extraction of 100 mL of wine was carried out on 50 mg LiChrolut EN resins. Before elution, the cartridge was washed with 20 mL of a mixture of water/methanol (60:40, v/v) containing 1% $NaHCO_3$ to remove fatty acids and some polar compounds. The cartridge was dried with N_2, and elution was finally carried out with 1.5 mL of dichloromethane. Fifty microliters of this extract was injected in a multidimensional GC-GC-MS system from Varian (Walnut Creek, CA). The system consisted of two independent gas chromatographs interconnected by a thermoregulated transfer line kept at 200 °C equipped with a Deans valve switching system (Valco Instruments, Houston, TX), two olfactory ports, and FID and MS detectors, as described in ref *20*. Chromatograph 1 was equipped with a DB-Wax column (polyethylene glycol) from J&W (Folsom, CA), 30 m × 0.32 i.d. with 0.5 μm film thickness. The oven temperature program was 40 °C during 5 min, then raised by 4 °C min^{-1} to 100 °C, followed by 6 °C min^{-1} to 220 °C, and finally held at this temperature for 40 min. Initially, the GC-O extract (50 μL) was monitored by olfactometry in the first chromatograph to select the fraction containing the target odorant. In further chromatographic runs, selective heart-cuttings were made to isolate the unknown odorant, which was transferred to the second chromatograph equipped with a FactorFour-VF-5MS column (polymethylsiloxane−5% diphenyl) from Varian (30 m × 0.32 mm × 1 μm film thickness). In this second oven, isolated odorant was trapped in a CO_2 cryotrapping unit and monitored by olfactometry with simultaneous MS detection. Two minutes after the heart-cutting, CO_2 flow was removed at the same time that the temperature program (4 °C min^{-1} to 200 °C and then 50 °C min^{-1} to 300 °C) of the second oven was activated. MS parameters were as follows: transfer line at 170 °C; ion trap at 150 °C; and trap emission current of 30 μA. The global run time was recorded in full-scan mode (m/z 45−250 mass range). Programmable injector conditions and delay time and heart-cutting interval were the same as those of ref *20*. The identity of the odorants was determined from the mass spectrum and linear retention indexes in both columns (DB-Wax and VF-5MS) and confirmed by injection of the pure reference standard.

Modeling Quality from Olfactometric Data. Simple correlation studies between the different MF olfactometric scores and the quality scores were first carried out using Excel. Odorants were further classified in different categories on the basis of the quality of its odor, as described in ref *21*. Olfactometric scores were then merged into olfactometric vectors by summation of the scores of odorants included in the same category. Additional categories were built by merging together odorants clearly related to defects or those others with unpleasant odors. Partial least-squares (PLS) regression models to explain quality scores as a function of olfactometric scores or vectors were then carried out using (PLSR) 1 with Unscrambler 9.7 (CAMO, Trondheim, Norway). The quality parameters studied to evaluate the prediction ability of the models were the slope of the regression curve between real and predicted Y variables (m), the root-mean-square error for the prediction (RMSEP), and the percentage of variance explained by the model (%EV).

RESULTS AND DISCUSSION

Gas Chromatography−Olfactometry. A summary of the results from the GC-O analysis of the 25 wines can be seen in **Table 2**. For the sake of simplicity, those odorants not reaching a maximum GC-O score of 24% MF in any of the 25 studied wines were eliminated and considered as noise. After this operation, the number of odorants was reduced to 65. There are some points that should be commented on.

Some of the listed components have been just recently identified, such as 2-methyl-3-(methyldithio)furan (*22*), ethyl 2-, 3-, and 4-methylpentanoate (*23*), and furfuryl ethyl ether (*20*); 3-methyl-2,4-nonanedione [tentatively identified (*24*)], 3,5-dimethyl-methoxypyrazine (*25*), and two of the odorants in the list, (*Z*)-2-nonenal and bis(2-methyl-3-furyl) disulfide, are identified in wine for the first time (the latter just tentatively). A third compound, 3-ethylphenol, has been reported only in German white wines (*26*). Remarkably, this last compound has an odor description very similar to that of 4-ethylphenol, and its odor threshold in a synthetic wine [12% (v/v) ethanol, 5 g L^{-1} tartaric acid, pH 3.2] has been estimated in our laboratory to be 0.5 μg L^{-1}, that is, 70 times lower than that of the para isomer (estimated as 35 μg L^{-1}). Only 11 odorants remain unknown. Most of them are very weak, although unknowns with $LRI_{DB\text{-}Wax}$ 1719 and 1789 reach olfactometric scores of up to 50% FM in some wines.

The list includes some compounds, such as TCA or 3,5-dimethylmethoxypyrazine, that have been clearly identified as sources off-odors, which is not surprising because wines for this study were selected randomly. The list also suggests that cysteinyl-related mercaptans and alkyl-2-methoxypyrazines are not very important aroma compounds in this kind of wine, at least in comparison with previous results from white wines (*21*). The low incidence or even absence of some oxidation-related aldehydes such as phenylacetaldehyde, 2-methylbutanal, or (*E*)-2-alkenals is also remarkable.

It should be observed that there is a relatively high variability on the GC-O profiles among wines. In fact, only 16 odorants have been detected in all of the samples, and only 20 of the 65 were detected in at least 90% of the samples. Similar conclusions are reached when considering the median of the olfactometric scores given in **Table 2**. This parameter represents the GC-O profile of an "average" wine that, as can be seen, only contains 33 odor zones. As expected, the group of "most frequent compounds" comprises some well-known fermentation, wood-related, or grape-derived compounds, although some lesser known compounds, such as ethyl 4-methylpentanoate, ethyl cyclohexanoate, octanal, 2-acetylpyrazine, 1-octen-3-one, 3-methyl-2,4-nonadione, 2-methyl-3-(methyldithio)furan, or (*Z*)-2-nonenal, are also present. All of these odorants have been reported previously, but there is nearly no information available about its precise origin, concentration, and role in the aroma of red wines. The possibility that these compounds were artifacts formed during sample preparation was considered and can be ruled out, because it was proved that their presence is not linked to the use of high temperatures in the detector, nor could they be detected in blank samples.

The difference between the maximum MF and the median can be taken as a criterion for differentiability. Compounds reaching values above 50% in this parameter are marked in bold letters in the corresponding column of **Table 2**. As can be seen, these compounds are three phenols (3-ethylphenol, 4-ethylphenol, and 4-ethylguaiacol), Furaneol, 3,5-dimethyl-2-methoxypyrazine, and four sulfur compounds [methionol, methional, 4-mercapto-4-methyl-2-pentanone, and bis (2-methyl-3-furyl) disulfide]. Another criterion for differentiability is the difference between the max and the min. In this case, also isovaleric acid, acetic acid,

Table 2. GC-O Study: Gas Chromatographic Retention Data, Olfactory Description, Chemical Identity, Frequency of Occurrence (F), and Maxima, Median, and Minima Scores of Modified Frequency for Each Compound

LRI DB-5	LRI DB-Wax	odor descriptor	identity	supplier[f]	F (%)	max	median	min	max − min	max − median
663	908	mushroom	2-methylbutanal[a]	1	32	27	0	0	27	27
713	935	fruity, alcoholic	propyl acetate[a]	11	68	45	27	0	45	18
600	957	lactic, strawberry	2,3-butanedione (diacetyl)[a]	1	100	94	80	41	53	14
	984	plastic, solvent	ni[d]		16	33	0	0	33	33
771	1012	sweet	isobutyl acetate[a] + ni	9	100	67	47	29	38	20
800	1033	strawberry, lactic	ethyl butyrate[a]	1	100	83	73	45	38	10
846	1050	fruity, anise, strawberry	ethyl 2-methylbutyrate[a]	2	100	88	80	71	17	8
695	1054	lactic	2,3-pentanedione[a]	1	8	41	0	0	41	41
856	1068	fruity, anise	ethyl 3-methylbutyrate[a]	2	100	90	80	42	48	10
621	1099	bitter, green	isobutanol[a]	8	100	59	43	22	37	16
860	1124	banana	isoamyl acetate[a]	9	100	85	66	49	36	19
941	1141	sweet, floral	ethyl 2-methylpentanoate[a]	5	28	38	0	0	38	38
960	1185	sweet	ethyl 3-methylpentanoate[a]	5	28	33	0	0	33	33
969	1193	lactic, fruity	ethyl 4-methylpentanoate[a]	1	92	67	38	0	**67**	29
719	1217	fusel	isoamyl alcohol [a]	1	100	93	88	83	10	5
999	1242	fruity, anise	ethyl hexanoate [a]	6	100	85	71	59	26	14
	1284	toasted	ni		4	29	0	0	29	29
952/1004	1291	lemon, orange, solvent	furfuryl ethyl ether[a]/ octanal[a]	1/14	100	69	55	19	50	14
975	1303	mushroom	1-octen-3-one[a]	7	80	62	22	0	**62**	40
	1310	grass	ni		4	31	0	0	31	31
890	1315	fried, barbecue, toasted	2-methyl-3-furanthiol[a]	1	60	63	24	0	**63**	39
872	1366	green, grass	1-hexanol[a]	3	48	36	0	0	36	36
942	1383	box tree	4-mercapto-4-methyl-2-pentanone[a]	12	44	67	0	0	**67**	**67**
852	1394	grass	(*Z*)-3-hexenol[a]	1	56	53	19	0	53	34
1130	1424	fruity	ethyl cyclohexanoate[a]	5	92	55	31	0	55	24
1040	1433	wet cardboard	3,5-dimethyl-2-methoxypyrazine[a]	15	4	83	0	0	**83**	**83**
907	1436	toasted, coffe	2-furfurylthiol[a]	2	32	50	0	0	50	50
1093	1445	pepper, earthy	3-isopropyl-2-methoxypyrazine[a]	1	8	26	0	0	26	26
905	1452	green beans, cooked potatoes	methional[a]	1	36	55	0	0	55	**55**
600	1452	vinegar	acetic acid[a]	10	88	71	29	0	**71**	42
829	1467	sweet wood	2-furaldehyde (furfural)[a]	2	8	31	0	0	31	31
	1475	rubbery, burnt	ni		4	31	0	0	31	31
	1487	rubbery	ni		4	31	0	0	31	31
1147	1506	green, metallic	**(*Z*)-2-nonenal[a]**	1[e]	100	69	45	22	47	24
	1541	sweet, medicine	ni		16	31	0	0	31	31
1099	1561	floral	linalool[a]	1	60	45	19	0	45	26
1158	1592	bleach, unpleasant	2-methylisoborneol[c]	1	4	24	0	0	24	24
1022	1621	toasty, burnt	2-acetylpyrazine[a]	1	100	82	59	35	47	23
821	1641	cheese	butyric acid[a]	6	32	29	0	0	29	29
1170	1668	fried, barbecue, toasted	2-methyl-3-(methyldithio)furan[c]	3	52	65	19	0	**65**	46
898	1675	cheese	2-/3-methylbutyric acid[a]	1/1	84	80	51	0	**80**	29
977	1707	plastic, green, thiol, meat	methionol[a]	1	40	76	0	0	**76**	**76**
	1719	sweet, tea	ni		52	50	10	0	50	40
1181	1734	floral, honey	3-methyl-2,4-nonanedione[c]	16	56	43	14	0	43	29
	1766	sweet, ripe fruit	ni		4	26	0	0	26	26
	1789	earthy	ni		32	49	0	0	49	49
1087	1806	cork	2,4,6-trichloroanisole (TCA)[a]	1	4	45	0	0	45	45
1318	1811	rancid chip	(*E*,*E*)-2,4-decadienal[c]	1	16	31	0	0	31	31
1392	1818	sweet, apple	β-damascenone[a]	4	100	68	55	24	44	13
1086	1864	phenolic, chemical	2-methoxyphenol (guaiacol)[a]	1	100	82	57	14	**68**	25
1353	1886	sweet, pleasant	ethyl dihydrocinnamate[a]	2	92	51	29	0	51	22
1108	1916	roses	β-phenethyl alcohol[a]	2	100	83	61	35	48	22
1134	1957	sweet wood	(*Z*)-whiskey lactone[a]	1	100	70	49	24	46	21
	2010	musty, sweat	*o*-cresol[b]	1	16	29	0	0	29	29
1285	2034	clove	4-ethylguaiacol[a]	1	28	63	0	0	**63**	**63**
1096	2045	candy cotton	2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (Furaneol)[a]	1	36	57	0	0	57	**57**
	2077	rose, sweet,good phenolic	ni		4	31	0	0	31	31
1103	2091	animal, leather, phenolic	*p*-cresol (*m*-cresol)[a]	2/2	96	59	35	0	59	24
1404	2115	tea, clove	4-propylguaiacol[a]	7	44	50	0	0	50	50
1460	2131	floral, sweet	ethyl cinnamate[a]	1	56	39	12	0	39	27
1540	2155	meal, popcorn, toasted, fried	**bis(2-methyl-3-furyl) disulfide[c]**	13	8	51	0	0	51	**51**
1365	2176	clove	4-allyl-2-methoxyphenol (eugenol)[a]	1	68	46	22	0	46	24
1168	2185	leather, animal	4-ethylphenol[a]	1	16	57	0	0	57	**57**

Table 2. Continued

LRI DB-5	LRI DB-Wax	odor descriptor	identity	supplier[f]	F (%)	max	median	min	max − min	max − median
1170	2194	leather, animal	3-ethylphenol[a]	2	48	62	0	0	**62**	**62**
1114	2204	burnt, curry	4,5-dimethyl-3-hydroxy-2-(5*H*)-furanone (sotolon)[a]	13	72	49	19	0	49	30

[a] Identification based on coincidence of gas chromatographic retention in two different columns and mass spectrometric data with those of the pure compounds available in the laboratory. [b] As for footnote [a] but retention time in a single column. [c] Tentative identification: identification is based on coincidence of gas chromatographic retention in two different columns, but it has been not possible to get GC-MS signals. [d] ni, not identified. [e] Present in (*E*)-2-nonenal standard. [f] Suppliers: 1, Aldrich; 2, Fluka; 3, Sigma; 4, gift from Firmenich; 5, Alfa Aesar; 6, PolyScience; 7, Lancaster; 8, Merck; 9, Chem Service; 10, Panreac; 11, Sugelabor; 12, Oxford Chemicals; 13, SAFC; 14, standard synthesized in the laboratory (see Materials and Methods); 15, gift from Mark Sefton; 16, gift from Takasago Int.

guaiacol, 1-octen-3-one, ethyl 4-methylpentanoate, and 2-methylfuranthiol can be considered to be discriminating compounds (marked in bold in the corresponding column of the **Table 2**). Among these, 3,5-dimethyl-2-methoxypyrazine is particularly remarkable, because it was detected in a single wine. It should be noted that most of these compounds have rather negative odor descriptions and that, in fact, some of them have been described as the cause of some wine off-flavors (*6*, *27*).

Identification of New Odorants. (*Z*)-2-Nonenal is the odorant responsible for the odor zone with odor descriptors green and metallic detected at $LRI_{DB\text{-}Wax}$ 1506. It is a ubiquitous odorant detected in all wine samples at relatively high intensities and, in fact, the presence of such an odor zone in wine had been previously reported (*28*, *29*). The compound could be well isolated by GC-GC-O-MS from a wine extract obtained by direct solid phase extraction (SPE), as shown in **Figure 1**. The standard for its identification was obtained from (*E*)-2-nonenal, which contains 5−10% of (*Z*)-2-nonenal as a major impurity (*30*). (*Z*)-2-Nonenal has been recently reported as a constituent of cashew apple products (*30*), being grouped within the "green, metallic, mushroom, fatty" odorants.

Bis(2-methyl-3-furyl) disulfide is reported here tentatively as the odorant likely responsible for the odor zone eluting at $LRI_{DB\text{-}Wax}$ 2155 in two of the studied wines. The odor properties and chromatographic retention indices of such an odor zone correspond exactly to those of the pure standard; however, it was not possible to obtain a clear mass spectrometric signal from any wine extract. This molecule has odor descriptors very close to those of its monomer, 2-methyl-3-furanthiol, and has been reported previously in model orange juice (*31*), high-heat skim milk powder (*32*), and cashew apples (*30*) and has been also detected as a key odorant in a commercial meat flavoring (*33*). It is one of the most powerful odorants known. Its threshold in air is 0.0006−0.0024 ng L^{-1}, below even that of its monomer (*34*), whereas its reported threshold in water is 0.02 ng L^{-1} (*35*). Such odor potency could be in agreement with the difficulty in finding a mass spectrometric signal.

Sensory Analysis. In the present study, the quality of the wine samples was assessed by a group of experts formed by diverse wine professionals, such as aroma researchers, wine producers, sommeliers, and wine traders. Despite such diversity, a good correlation was obtained between the scores given by the different groups of professionals ($r^2 > 0.65$). Results of the sensory evaluation are given in **Figure 2**. Quality scores for the 25 wines range from 1.5 to 4.0, 1.0 and 5.0 being the minimum and maximum possible scores, respectively. The standard errors of the means ranged between 0.17 and 0.35 and tended to be larger for samples with low scores. Although the sensory evaluation was limited to the assessment of quality, the comments raised by the judges suggested that wines with very high or high quality scores ($Q > 3.5$) had strong positive odors and wines with low quality scores ($Q < 2.5$) had clear negative odors, such as dirty, reduced, oxidized, or animal, whereas wines with intermediate quality scores ($3.5 > Q > 2.5$) showed most often a very low aroma intensity and good taste and aftertaste. This observation has been further confirmed by specific descriptive sensory analysis (data not shown).

Modeling Quality from Olfactometric Data. A correlation study showed that there is no single aroma component positively correlated with the quality scores. Compounds were then grouped on the basis of their aromatic character, such as floral, fruity, or phenolic as previously described (*21*) to build general olfactometric vectors with the summations of the GC-O scores of the individual odorants in the category. However, those parameters were not positively related to quality either, which suggests that the quality in the studied data set is not primarily determined by the presence of more or less compounds with positive aroma. A closer look at the data revealed that the most important difference between wines with low and high quality scores is that the former have high GC-O scores of one or several odorants usually related with quality problems. This is illustrated in **Table 3**, which shows major differences between the group of 11 wines with quality scores of > 3.5 and 5 with scores of < 2.5. As shown in the table, one of the wines in this last group contained the powerful odorant 3,5-dimethyl-2-methoxypyrazine; in the same wine 2,4,6-trichloroanisole was also detected. Two other wines of this category had relatively high GC-O scores of 4-ethylphenol, and nearly all of the five had relatively high scores in 4-ethylguaiacol, 3-ethylphenol, or *o*-cresol. The negative sensory effect exerted by some of these compounds is well documented in the scientific literature (*6*, *10*, *25*, *36*, *37*), particulary in the cases of TCA and ethylphenols. However, it should be noted that in an independent sensory descriptive analysis (data not shown), only two of these wines were classified as "animal-leather" and none was classified as corky. For the purpose of modeling, the olfactometric scores of these six odorants were summed to form a single olfactometric vector. Such a vector resulted was significantly and negatively correlated with the measured quality ($r^2 = 0.580$; $P < 0.0001$), which suggests that the presence of compounds in **Table 3** is a major cause of the low quality scores of these wines.

After this observation, a second olfactometric vector was formed by summing the GC-O scores of those other odorants in **Table 2** whose sensory description includes terms with negative connotations. The odorants in this second vector are listed in **Table 4** and are two sulfur compounds (methionol and methional) three unsaturated acid derivatives ((*Z*)-2-nonenal, 1-octen-3-one, (*E*,*E*)- 2, 4-decadienal), 2-methylbutanal, acetic acid, 3-isopropyl-2-methoxypyrazine and 2-methylisoborneol (tentatively identified). For many of these compounds a negative contribution to wine aroma has been suggested or reported (*12*, *36*, *38*), and in the case of 3-isopropyl-2-methoxypyrazine a report demonstrates that this component can make the perception of fruity notes to decrease (*17*). Data in **Table 4** indicate that some of those components, particularly the two sulfur compounds, can be found at higher levels in the subset of wines with quality scores between 3.5 and 2.5, in comparison with those with quality scores higher than 3.5. 2-methylisoborneol and 2-methylbutanal are at higher levels in the subset of samples with high quality scores, but

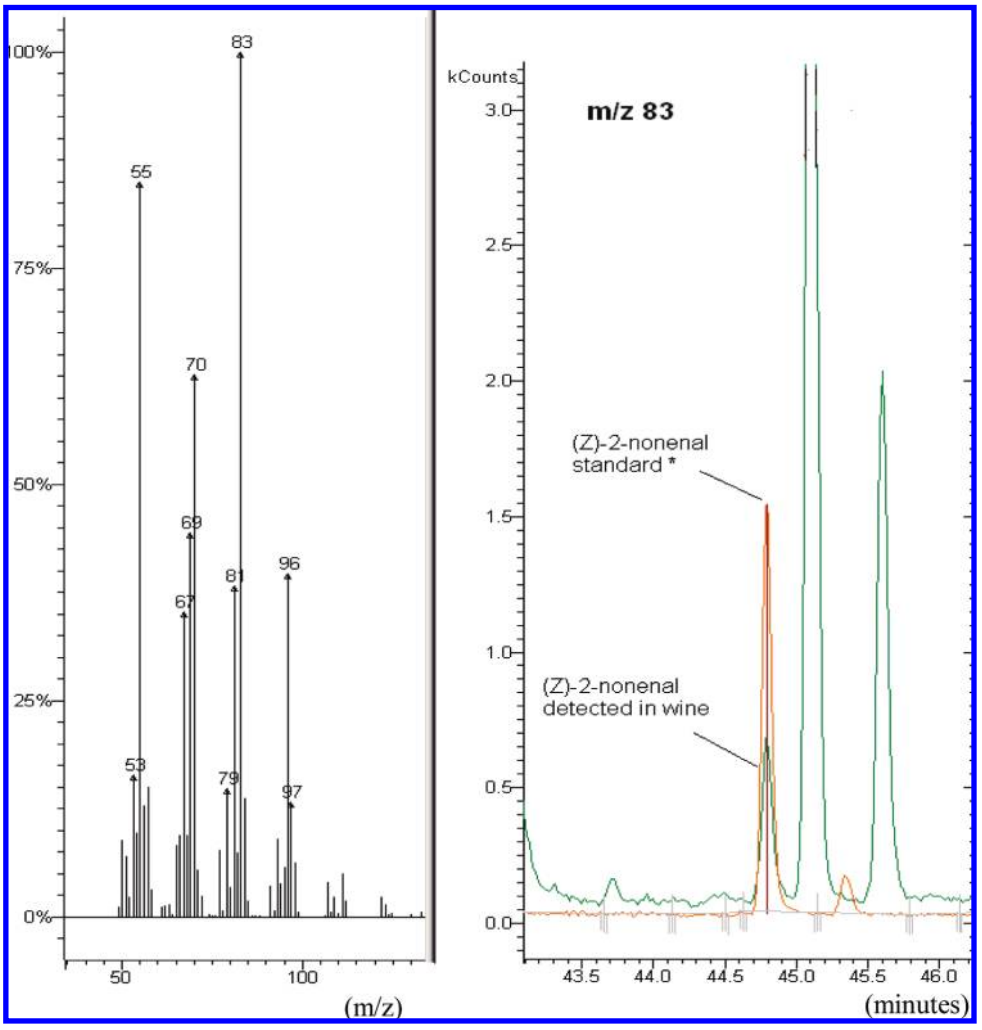

Figure 1. (*Z*)-2-Nonenal spectrum (isolated from wine). Expanded MS chromatograms corresponding to the fractions isolated in the first column of the dual GC-GC-MS system [50 μL of SPE extract and (*E*)-2-nonenal standard solution].

both have very low MF, which suggests that their importance in this set of samples is quite limited.

These two vectors grouping compounds in **Tables 3** and **4**, respectively, and the vectors with the summations of the general olfactometric descriptors (fruit-sweet, floral, and phenolic) were then used as *X*-variables to build a model to explain the quality scores. Among the general olfactometric descriptors the most relevant vector from the modeling point of view is that formed by the summation of the GC-O scores of compounds of fruity-sweet aroma. The 15 compounds forming this vector can be seen in **Table 5**, which also gives the average GC-O scores found in the subsets of high, low, and intermediate quality. It can be observed that wines with intermediate quality scores have usually lower average GC-O scores than wines with high quality but that wines with low quality have GC-O scores rather comparable, or even higher in the case of most C6-ethyl esters, to those of wines with high quality. This observation is quite interesting and explains why a positive correlation between quality and the fruity-sweet aroma vector was not observed.

The final model was built by using partial least square regression type 1. A satisfactory model could be built by introducing only the three vectors described in **Tables 3**−**5**. The model is

$$Q = 2.984 + 0.225 \times \Sigma F - 0.538 \times \Sigma D - 0.163 \times \Sigma N$$

where ΣF is the olfactometric vector composed by the summations of GC-O scores of odorants with fruity character (**Table 5**), ΣD is the olfactometric vector composed by the summations of GC-O scores of odorants related to defects (**Table 3**), and ΣN is the one composed by the summations of GC-O scores of odorants with negative character (**Table 4**). This regression model is highly significant ($P < 0.0001$), the total explained variance is 78% (68% by cross-validation), and the root-mean-square prediction error (RMSEP) is 0.348. The model could be improved just by eliminating 4-ethylguaiacol from the ΣD vector, which suggests that this compound may play a role not as negative as the other ethylphenols. The parameters for this model are

$$Q = 2.984 + 0.260 \times \Sigma F - 0.588 \times \Sigma D - 0.111 \times \Sigma N$$

In this case, the explained variance rose to 83.5% (79% by cross-validation), the slope improved to 0.83, and the RSME decreased to 0.29. The plot relating predicted versus measured quality values is given in **Figure 3**. As can be seen, the model is not able to provide clear-cut boundaries for all quality categories, particularly between some wines with high and intermediate quality scores, but provides a reasonably good predictor of the quality in most cases. Prediction errors are higher for low-quality samples, but in those cases a higher variability in the measurement of quality was also observed.

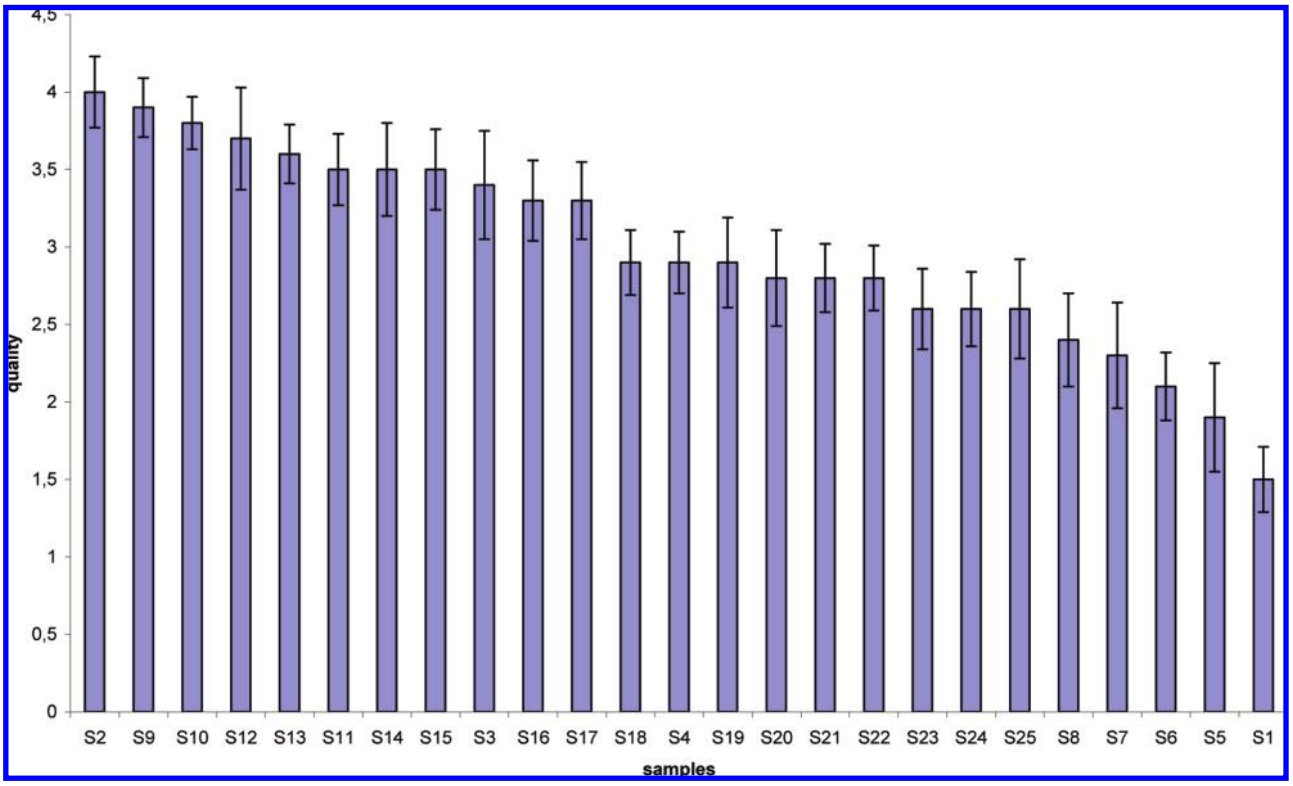

Figure 2. Mean quality scores obtained for the 25 wines in the study. Error bars are the standard mean error.

Table 3. Maximum GC-O Scores (MF) of Some Defect-Related Odorants in Three Different Sample Subsets [Wines with Quality Scores (*Q*) below 2.5, *Q* between 2.5 and 3.5, and *Q* above 3.5] and Frequencies of Occurrence (*F*) in the Low-Quality Subset (*Q* < 2.5)

	below 2.5	2.5 < *Q* < 3.5	above 3.5	difference	% *F*
3,5-dimethyl-2-methoxypyrazine	83	0	0	83	20
4-ethylphenol	57	19	7	50	40
2,4,6-trichloroanisole (TCA)	45	0	0	45	20
3-ethylphenol	62	43	19	43	100
4-ethylguaiacol	63	48	26	37	80
o-cresol	29	0	0	29	80

Table 4. Mean GC-O Scores (MF%) of Some Odorants with Negative Odor Nuances in Two Different Sample Subsets [Wines with Quality Scores (*Q*) between 2.5 and 3.5 and with *Q* above 3.5] and Frequencies of Ocurrence (F) in the Whole Data Set

	2.5 < *Q* < 3.5	above 3.5	difference	% *F*
methionol	42	15	27	40
methional	25	6.5	18.5	36
(*Z*)-2-nonenal	52	43	9	100
1-octen-3-one	30	22	8	80
(*E*,*E*)-2,4-decadienal	6.2	4	2.2	16
3-isopropyl-2-methoxypyrazine	3.4	2.4	1	8
acetic acid	28	27	1	88
2-methylisoborneol	0	2	−2	4
2-methylbutanal	2	6	−4	32

Table 5. Mean GC-O Scores (MF) of Some Odorants with Fruity Odor Nuances in Three Different Sample Subsets [Wines with Quality Scores (*Q*) below 2.5; Those with *Q* between 2.5 and 3.5; and Those with *Q* above 3.5] and Frequencies of Occurrence (*F*) in the Whole Data Set

	below 2.5	2.5 < *Q* < 3.5	above 3.5	% *F*
propyl acetate	21	15	28	68
2,3-butanedione (diacetyl)	74	74	81	100
isobutyl acetate	43	49	45	100
ethyl butyrate	68	62	74	100
ethyl 2-methylbutyrate	76	76	81	100
2,3-pentanedione	0	0	7	8
ethyl 3-methylbutyrate	76	76	76	100
isoamyl acetate	75	65	68	100
ethyl 2-methylpentanoate	11	2	8	28
ethyl 3-methylpentanoate	14	3	7	28
ethyl 4-methylpentanoate	51	28	35	92
ethyl hexanoate	72	72	71	100
ethyl cyclohexanoate	43	20	36	92
β-damascenone	54	53	54	100
2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (Furaneol)	0	21	30	36
total	678	616	701	

In summary, the model indicates that a major part of the quality of this particular set of red wines depends primarily on its aroma composition and, particularly, on its contents on 3- and 4-ethylphenols, TCA, *o*-cresol, and 3,5-dimethyl-2-methoxypyrazine and also on the presence of some compounds with bad aroma. Secondarily, quality is also positively related to the presence of a number of chemicals with fruity and sweet descriptors. This result does not mean that polyphenols and some other components with influence on taste properties or aroma components derived for wood do not have influence on quality. In fact, quality was positively related to wine alcoholic degree ($r^2 = 0.19$, $P < 0.05$), residual sugar ($r^2 = 0.31$, $P < 0.01$), and color intensity ($r^2 = 0.33$, $P < 0.01$), although it was not related to wine age or the total polyphenolic content despite the existence of a large variability in these parameters. Rather, this result suggests that whereas winemakers can ensure a correct balance of taste properties of premium wines, there is still a large uncertainty in the resulting aroma composition. The

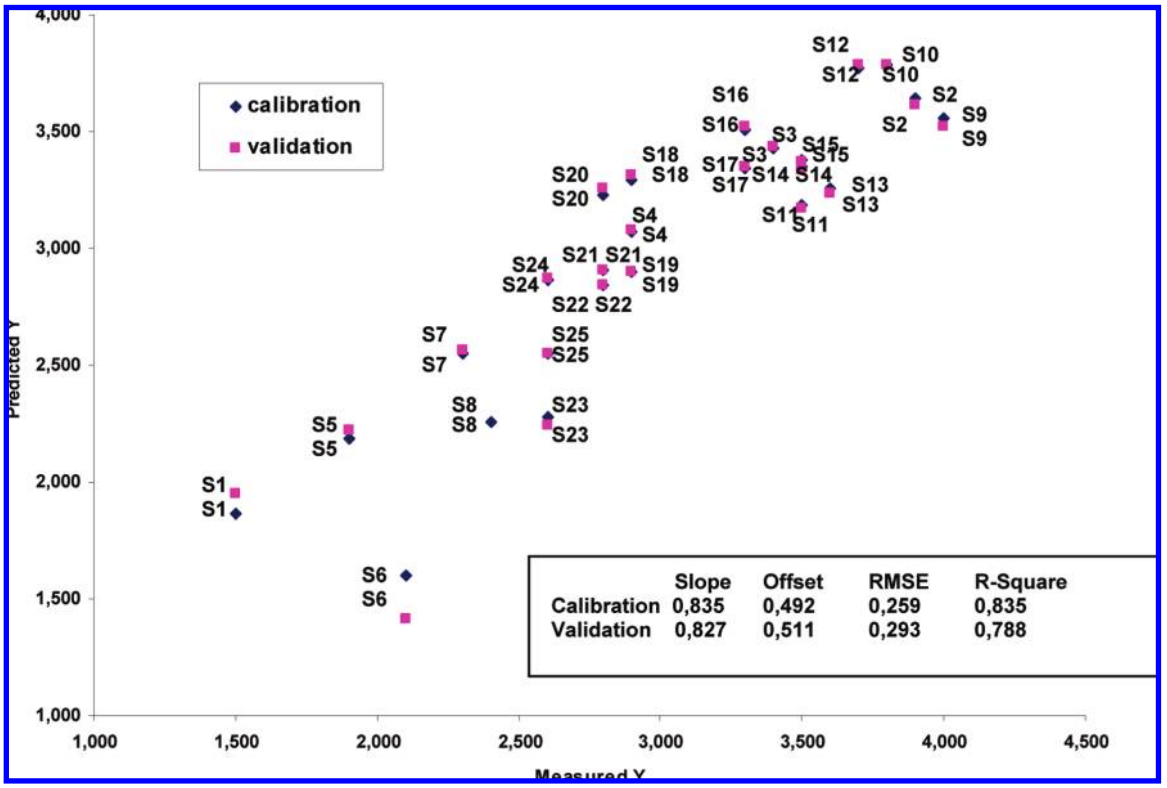

Figure 3. Plot of predicted versus measured quality scores obtained with the final model.

model, secondarily, also supports the relevance of some previous observations about the role of some compounds, such as alkyl-2-methoxypyrazines or acetic acid, as depreciators of the aroma intensity at levels before they are clearly perceived as defects (*17*). Similar depreciating roles played by ethylphenols and some aldehydes in the intensity of fruity notes in red wines have also been previously reported (*10*). These suppression effects may be the cause of the low or even null aroma intensity observed in wines with intermediate quality scores. Finally, the model should not be interpreted narrowly, in the sense that the exact roles played by some of the different odorants taking part in the model still have to be further explored; rather, it should be considered as a general outline about the structure of the quality vectors of red wine.

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