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Quality and Aromatic Sensory Descriptors (Mainly Fresh and Dry Fruit Character) of Spanish Red Wines can be Predicted from their Aroma-Active Chemical Composition

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ABSTRACT: A satisfactory model explaining quality could be built in a set of 25 high quality Spanish red wines, by aroma-active chemical composition. The quality of the wines was positively correlated with the wine content in fruity esters, acids, enolones, and wood derived compounds, and negatively with phenylacetaldehyde, acetic acid, methional, and 4-ethylphenol. Wine fruitiness was demonstrated to be positively related not only to the wine content on fruity esters and enolones, but to wine volatile fatty acids. Fruitiness is strongly suppressed by 4-ethylphenol, acetic acid, phenylacetaldehyde, and methional, this involved in the perception of dry-fruit notes. Sensory effects were more intense in the presence of β-damascenone and β-ionone. A satisfactory model explaining animal notes could be built. Finally, the vegetal character of this set of wines could be related to the combined effect of dimethylsulfide (DMS), 1-hexanol, and methanethiol.

KEYWORDS: wine, aroma, model, quality, fruit, animal, vegetables, sensory, interaction

INTRODUCTION

Quality with reference to wine is a subjective term and difficult to define. The concept of wine quality has changed over time and varies from one viticultural region to another. Nevertheless, a number of studies have attempted to decode the different factors influencing quality.[1,2] One of the most important intrinsic elements is aroma. At present, one of the essential characteristics for a quality wine is to have an intense aroma. High value is also given to the complexity of the aroma, that is, to the perceived presence of diverse aromatic notes, with none being clearly dominant.

Many studies [3−5] have been carried out to determine the volatile compounds responsible for the most important aromatic nuances of each wine. In some cases, a single compound is capable of transmitting its own aroma, such as linalool in Moscatel wines or 4-ethylphenol in the Brett character of wine.[6] In others, the situation is more complex and various molecules influence and interact in the perception of a particular note, as has been observed with fruity aromas.[7] Different types of sensory interactions between different aromatic compounds have been described.[8−10]

Various methodological approaches have been used in the studies. Some work [11−14] used statistical tools such as PCA (Principal Components Analysis) or PLSR (Partial Least Squares Regression) to develop models and study relationships between the analytical data of specific volatile compounds and sensory perception. In other studies, that relationship was determined through sensory experiments.[7,15] Few cases have combined the two methods, that is, have demonstrated by sensory means what mathematical models obtained from quantitative data expressed. This has been done in the study of white wines,[16] which are less complex than red wines. Despite all of these studies, there is still much to be known about the role played by the different volatile compounds present in wine, and how their interactions stimulate the perception of the different notes.

The objective of the present work is to attempt to explain the overall quality and the principal aromatic notes perceived in extra-premium quality red wines by means of quantitative data. More specifically, the study endeavored to determine which volatile chemical compounds had a greater measure of influence, both negatively and positively, on the quality, and which ones were the causes of the different perceived aromatic notes. To this end, the mathematical models developed were tested by means of sensory experiments.

MATERIAL 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).

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), BDH Prolabo (Linars del Vallés, Spain), and Firmenich (Geneva, Switzerland), as indicated in Table 1. Purity of chemical standards is over 95% in all cases, most of them are over 99%.

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

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Table 1. Suppliers; Method of Analysis Used for Quantification of Each Compound; Odor Thresholds; Maximum, Minimum and Median Values of Concentration Found in Set of 25 Wines (All Data Are Expressed As Micrograms Per Liter); Quotient between Maximum Odor Activity Value (OAV) and Minimum OAV (Differentiation Ability); Correlation Coefficients (R) of Linear Regression between Odor Activity Values of Each Compound (OAV) and Quality[a]

	supplier	method of analysis[b]	max[c]	min[d]	med[e]	odor threshold[f]	OAV max/OAV min[f]	R[g]
			carbonyl compounds					
β-damascenone	Firmenich	20	10.5	<0.200	0.640	0.05[43]	18.8	0.04
β-ionone	Sigma	20	0.55	<0.089	0.320	0.09 [44]	4.58	0.32
acetaldehyde	Sigma-Aldrich	19	12609	718	10158	500 [43]	9.07	−0.03
methional	Aldrich	22	21.6	2.12	8.43	0.5 [45]	10.2	−0.51
phenylacetaldehyde	Aldrich	22	126	20.4	55.0	1 [46]	6.18	−0.44
			esters					
ethyl propanoate	Fluka	19	260	<80.0	140	5500[h]	3.25	−0.14
ethyl butyrate	Aldrich	19	270	70.0	140	125[h]	3.86	0.49
ethyl hexanoate	PolyScience	19	210	70.0	120	62[h]	3.00	0.58
ethyl octanoate	PolyScience	19	210	50.0	90.0	580 [47]	1.81	0.17
ethyl decanoate	PolyScience	20	81.1	<4.03	60.6	200 [44]	2.03	−0.18
ethyl 2-methylpropanoate	Aldrich	20	536	48.7	202	15 [44]	11.0	−0.11
ethyl 2-methylbutyrate	Fluka	20	82.6	6.50	28.1	18 [44]	12.7	−0.27
ethyl 3-methylbutyrate	Fluka	20	131	10.9	43.5	3 [44]	12.0	−0.07
ethyl 2-methylpentanoate	Alfa Aesar	21	0.091	<0.0007	<0.0007	10[h]	1.00	0.19
ethyl 3-methylpentanoate	Alfa Aesar	21	0.111	<0.0006	<0.0006	0.5[h]	1.11	0.11
ethyl 4-methylpentanoate	Aldrich	21	0.883	<0.0005	0.175	0.75[h]	5.88	−0.01
ethyl cyclohexanoate	Alfa Aesar	21	0.015	<0.0008	0.004	0.03[h]	20.0	0.41
isoamyl acetate	Chem Service	19	370	110	190	30 [43]	3.36	0.11
			alcohols					
1-hexanol	Sigma	19	1560	520	1000	8000 [43]	1.00	0.31
			volatile phenols					
4-ethylphenol	Aldrich	20	1214	<0.540	84.0	35[h]	173	−0.58
4-ethylguaicol	Aldrich	20	167	<0.035	8.57	33 [44]	25.3	−0.46
eugenol	Aldrich	20	56.9	<0.074	35.3	6 [44]	47.4	0.43
E-isoeugenol	Lancaster	20	8.27	<0.011	1.56	6 [32]	6.89	0.42
			lactones					
E-whiskylactone	Aldrich	20	346	34.7	229	790 [47]	2.19	0.42
Z-whiskylactone	Aldrich	20	668	<0.130	360	67 [47]	49.9	0.33
			acids					
acetic acid	BDH Prolabo	19	950000	512500	385000	300000 [48]	2.47	−0.50
butyric acid	PolyScience	19	1850	<54.8	580	173 [44]	6.61	0.49
2-methylpropanoic acid	Aldrich	19	2450	1240	1695	50 [49]	8.75	0.16
2-methylbutyric acid	Aldrich	20	365	88.4	208	33 [44]	4.12	−0.11
3-methylbutyric acid	Aldrich	20	430	55.4	139	33 [44]	7.76	−0.01
hexanoic acid	PolyScience	19	2120	390	1090	420 [44]	5.44	0.56
octanoic acid	Fluka	19	1020	180	440	500 [44]	5.67	0.27
decanoic acid	PolyScience	19	940	110	160	1000 [44]	4.70	−0.04
			enolones					
2,5-dimethyl-4-hydroxy-3(2H)-furanone (furaneol)	Aldrich	23	62.6	<10.0	16.5	5 [50]	6.26	−0.14
2-ethyl-4-hydroxy-5-methyl-3(2H)-furanone (homofuraneol)	Aldrich	[23]	725	<180	<180	125 [50]	4.03	0.26
			volatile sulfur compounds					
methanethiol	Sigma-Aldrich	[24]	18.0	<0.200	5.11	1.8−3.1[51]	90.1	0.21
dimethylsulfide	Sigma-Aldrich	[24]	208	30.1	57.4	25 [52]	6.92	−0.12

[a] Compounds with OAV maximum >5 are in bold letters. [b] Reference in which the method used to quantify the volatile compound is described. [c] Maximum concentration found in set of 25 wines. [d] Minimum concentration found in set of 25 wines. [e] Median concentration found in set of 25 wines. [f] Reference in which the odor threshold value has been calculated is given in parentheses. [f] For minimum OAV < 0.2, this value is taken to calculate the quotient. [g] Correlation coefficient of linear regression with quality. [h] Calculated in the laboratory: orthonasal thresholds were calculated in a 10% water/ethanol nixture containing 5 g/L of tartaric acid at pH 3.2.

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. Twenty-five Spanish red aged wines from 11 different Spanish Denominations of Origin: Rioja (7 samples), Ribera de Duero (6 samples), Toro (2 samples), and one sample from Cariñena, Calatayud, Jumilla, Somontano, Priorat, Bierzo, Penedés, Montsant, one "vi de taula de Balears" and one "Vino de la Tierra de Castilla". 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. Samples were stored at 5 °C. The details of the samples are shown in Ferreira et al.[13]

Dearomatized Wine. For the sensory study, one young red wine with a neutral aroma from Cariñena was dearomatized. One gram of Lichrolut EN resin was added to 750 mL of wine and it was stirred for 12 h. This dearomatized wine was of very low intensity and neutral character.

Wine Sensory Analysis. *Sensory Quality Determination.* The procedure of this sensory analysis is described by Ferreira et al.[13] Classification of wine according measured quality is also expressed in that reference.

Sensory Descriptive Analysis. The procedure (according to the citation frequency method [17] of this sensory analysis is described by Saénz-Navajas et al.[18] Data of these analyses are also expressed in that reference.

Quantitative Analysis of Major Compounds. The analysis was carried out by the method published by Ortega et al. [19]

Quantitative Analysis of Minor and Trace Compounds. The method is described by Lopez et al.[20]

Quantitative Analysis of Minor Esters. This analysis was carried out using the method proposed and validated by Campo et al. [21]

Quantitative Analysis of Aldehydes. 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.[22]

Quantitative Analysis of Sotolon, Furaneol, Maltol, and Homofuraneol. 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 were 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 a hydro-alcoholic solution containing 12% (v/v) in 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 in a Varian CP-3800 gas chromatograph with a Saturn 2000 ion trap mass spectrometric detector. The instrumental conditions are described by Ferreira et al. 2003.[23] 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 Sulfur Compounds. A Solid phase Micro Extraction (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.[24]

Data Treatment. Quantitative data (Table 1) of 25 analyzed wines were transformed in Odor Activity Values (OAV) by dividing by odor thresholds (tabulated in Table 1). In case of concentrations under detection and quantification limits, these values were taken to calculate OAV. In order to rank compounds in accordance to the discriminatory ability, the quotient between the maximum OAV and minimum OAV was worked out for each compound (in case of OAV minimum <0.2, this value was used). Moreover, correlation coefficient of linear regression between OAVs of each compound and quality or an aromatic note (data not shown) was calculated using Excel.

To explore the relationship between the quantitative data and the quality of wine or a single sensory attribute, partial least-squares regression (PLSR) 1 was carried out using the Unscrambler 9.7 (CAMO A/S, Trondheim, Norway). With this purpose some compounds were grouped into families, in accordance with 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 variable (in accordance to 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 slope (m), the offset and the correlation coefficient of the regression curve between real and predicted Y variables, the root-mean-square error for the prediction (RMSEP), and the percentage of variance explained by the model (%EV).

Validation of the Models by Sensory Analysis. *Sensory Panel.* The test panel that carried out the different sensory experiments described in this work was composed of 11 subjects (seven women and four men, ranging from 23 to 45 years of age) belonging to the laboratory staff. All of them participated regularly in sensory tests. In all tests, samples (20 mL, 20 °C) were presented in a random order in coded black tulip shaped wine glasses covered with a Petri dish.

Triangular Tests. [25]. In order to prove if one or several odorants has a significant effect in the aroma of an initial sample, triangular tests were carried out. The samples confronted in the test were, on one hand, a dearomatized wine containing or not other odorants and, on the other hand, the same sample to which the targeted odorant or odorants were added. Three cups were presented to each judge, who had to decide which sample was different from the two others. Number of right answers was compared with tabulated values to decide if significant differences exist due to targeted odorant or odorants. When a difference was detected, the judges were asked to freely note the descriptors which caused the difference.

Ranking Tests.[25]. The effect of the addition of different odorants on an aromatic note was studied by means of ranking tests. Nine judges had to put in order 3 or 4 samples with different concentrations of studied compound or group of compounds (one of them was the initial sample without addition of the targeted compound) in accordance with the intensity of the considered note. The effect of the studied odorant was measured by the summation of the ranks established by each panellist: weakest odor (1), second least intense odor (2), second most intense odor (3), and most intense odor (4). Significance of the ranking was determined by a Friedman test.[25]

Table 2. Quality Parameters of PLSR Models

model	%EV[a]	RMSEP[b]	m[c]	offset[d]	CC[e]	no. X[f]	no. PC[g]
quality	58.9	0.56	0.61	1.16	0.78	10	2
global fruit	73.3	3.55	0.69	6.59	0.83	12	3
animal	60.0	2.91	0.52	2.75	0.72	6	2
vegetables	58.7	2.07	0.49	2.87	0.70	6	4

[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.

RESULTS AND DISCUSSION

The chemical aroma composition (101 compounds) of 25 high quality red wines from Spain was determined by using 8 different analytical methods. These data will be presented in a next paper. Table 1 shows the compounds that involve in the models.

Modeling the Quality of Red Wine. The first aim of this work was to relate quantitative data of odorants with the quality of wine as it was done in a previous report in which quality was related to GC-O data.[13] Experts belonging to diverse professions related to wine or sensory evaluation were selected for the evaluation of quality and a good correlation was obtained between the scores given by the different groups of professionals. Each expert had a personal idea about what quality is and there was no intention of making them reach a consensus. The high internal correlation between the individual scores for quality and the mean suggested, however, that the experts share a common vision about the quality of these wines.

To reach the purpose of modeling quality, the correlation between the different aroma compounds and quality was calculated (data shown in Table 1). Initially, only odorants with a potentially significant effect on aroma, as suggested by their OAV, were considered (compounds reaching a high maximum OAV, higher than 5, are marked in bold in Table 1). As additional criterion for building the model, the ratio between the maximum and minimum OAVs (limited the minimum to 0.2), which is related to the potential ability of the compound to cause sensory differences, was also considered (data shown in Table 1). Some of the aroma chemicals were grouped into families, in accordance with their sensory properties and biochemical origin. A good PLS model was obtained and it was able to explain a 59% of the Y variance (measured by cross-validation). Its composition and properties are summarized in Tables 2 and 3. As can be seen in Table 3, the model is composed of 10 variables, 6 of which are vectors comprising groups of aroma compounds.

Data in Table 3 are mostly consistent with previous reports, and quality appears to be significantly and positively related to wine contents in fruity esters (minor branched and major linear ethyl esters) and norisoprenoids, which is in accordance to results from a previous work;[13] to enolones; to cask aging derived compounds, in agreement with the role played by these compounds in some positive aroma nuances [12] and to acids, which has also been previously observed.[11] However, quality is significantly and negatively influenced by wine contents in 4-ethylphenol, methional, acetic acid, and phenylacetaldehyde, as has been previously suggested.[12,13,26] All of these compounds are aroma defects. The importance of absence of these has also been previously observed.[27]

Table 3. X Variables of Quality Model and Its Regression Coefficients

vector	regression coefficient	compounds
minor branched ethyl esters	0.083	ethyl 4-methylpentanoate
		ethyl 3-methylpentanoate
		ethyl 2-methylpentanoate
		ethyl ciclohexanoate
major ethyl esters	0.006	ethyl propanoate
		ethyl butyrate
		ethyl hexanoate
		ethyl octanoate
		ethyl decanate
		ethyl 2-methylpropanoate
		ethyl 2-methylbutyrate
		ethyl 3-methylbutyrate
norisoprenoids	0.038	β-damascenone
		β-ionone
acids	0.598	butyric acid
		hexanoic acid
		octanoic acid
		decanoic acid
		2-methylpropanoic acid
		2-methylbutyric acid
		3-methylbutyric acid
aging related compounds	0.222	eugenol
		E-isoeugenol
		E-whiskylactone
		Z-whiskylactone
enolones	0.088	furaneol
		homofuraneol
methional	−0.150	
phenylacetaldehyde	−0.201	
4-ethylphenol	−0.327	
acetic acid	−0.283	

Modeling the General Fruity Note of Red Wine. The aroma sensory properties of the wine set were determined by a trained sensory panel using a previously defined profiling strategy [28] and were presented and analyzed in the reference.[29] Among all of the aroma terms used by the sensory panel, the aggregated term "fruity" which includes all the different fruity terms of the wine (red fruit, black fruit, white fruit, dry fruit, and exotic fruit) was the most important in terms of both frequency of citation and relationship with quality. This aromatic note has been previously related to quality [30] and its chemical interpretation was considered to be one of the most important aims of the present work. A PLS model was built considering mainly the aroma chemicals with potential major sensory relevance and grouping some of them into families, in accordance with their sensory properties and biochemical origin. The best model was able to explain a 73% of the Y variance (measured by cross-validation) and its composition and properties are summarized in Tables 2 and 4. As can be seen in Table 4, the model is composed of 12 variables, 7 of which are vectors comprising groups of aroma compounds. As shown in Table 2, the RMSEP of the model is 3.55, which for a variable which ranges from 14 to 30 can be considered satisfactory.

According to Table 4, the fruity note of the studied wines is caused primarily by 5 groups of compounds with fruity

Table 4. *X*-Vectors and Its Regression Coefficients in The PLS Model for Predicting Red Wine Fruitiness Aroma Chemical Composition

vector	regression coefficient	compounds
minor branched ethyl esters	0.060	ethyl 4-methylpentanoate
		ethyl 3-methylpentanoate
		ethyl 2-methylpentanoate
		ethyl cyclohexanoate
linear major ethyl esters	0.720	ethyl propanoate
		ethyl butyrate
		ethyl hexanoate
		ethyl octanoate
		ethyl decanoate
isoamyl acetate	0.876	
branched major ethyl esters	0.636	ethyl 2-methylpropanoate
		ethyl 2-methylbutyrate
		ethyl 3-methylbutyrate
enolones	1.740	furaneol
		homofuraneol
linear acids	1.593	butyric acid
		hexanoic acid
		octanoic acid
		decanoic acid
branched acids	2.758	2-methylpropanoic acid
		2-methylbutyric acid
		3-methylbutyric acid
C-13 norisoprenoids	−0.470	β-damascenone
		β-ionone
methional	−0.916	
phenylacetaldehyde	−2.280	
acetic acid	−2.400	
4-ethylphenol	−2.317	

characteristics (13 esters divided into 4 groups plus one group with two enolones). These findings are greatly in accordance with previous observations [31−34] as also are the negative role on wine fruitiness played by 4-ethylphenol, acetic acid, methional, and phenylacetaldehyde.[12] On the contrary, the model suggests that wine fruitiness is positively contributed by fatty acids and by isoacids, and negatively contributed by β-damascenone and β-ionone. These suggestions are very unexpected. In the first case, because compounds with odor descriptors such as cheese, rancid, sweat, or butter do not seem to be part of our concept of fruitiness. Furthermore, a negative relationship between branched acids and fruity note has been previously observed by Ugliano et al[35] and in the second case, because of the known enhancing effect exerted by β-damascenone on the wine fruity character.[32,36]

In order to confirm the role of the different chemical families in the perception of fruitiness and particularly in order to investigate the previous unexpected findings, a series of sensory tests were carried out on two basic aroma models. The first one (called fruity base 1) was made of a dearomatized red wine to which the 4 groups of fruity esters shown in Table 4 were added at their maximum concentrations found in the set of wines. The second one (fruity base 2) was similarly prepared but contained in addition 1.28 μg L^{-1} of β-damascenone and 0.32 μg L^{-1} of β-ionone.

The surprising apparent negative effect of these two last compounds on the perception of fruitiness was first investigated by adding to the "fruit base 1" model, increasing amounts of β-damascenone and β-ionone. The sensory panel was then asked to rank the samples according to their fruitiness. The results of this experiment are summarized in Table 5 and provide an interesting clue. As expected, the fruity character increased with the concentration of norisoprenoids, but the highest level of addition (equivalent to the maxima amounts found in the wine set) caused a decrease on wine fruitiness. This apparently bizarre result has a large conceptual and practical relevance. The result may be best interpreted in terms of aroma profiles, rather than of aroma intensities: wine fruitiness is a concept, and the odor concepts seem to be linked to the existence of well-defined ratios of odorants.[37] In fact, and on the basis of interviews with the judges, the aroma of that sample was not less intense, but different in quality, being categorized as too sweet and closer to dry fruit (raisin). From this point of view, the result suggests that the odor chemical profile defined by the fruity ester/norisoprenoid ratio of the level of addition 2 in Table 5 is closest to the concept for wine fruitiness of judges in the sensory panel and that profiles defined by smaller or higher levels of norisoprenoids are further away from that concept. Differences caused by smaller levels are mainly of a quantitative nature, but differences at higher levels are of a qualitative character, as will later be confirmed. From the practical point of view, this challenges our way of modeling, since it reveals that using linear models is just a naïve first approximation.

The second unexpected result was the apparent positive contribution of some acids to wine fruitiness, which was equally assayed by means of ranking tests similar to those previously described. As shown in Table 5, the fruity character of the wines increased with the presence of linear acids, although differences were only significant when the addition was carried out on the "fruity base 2" model, i.e.; when norisoprenoids were also present. In the case of branched fatty acids, results given in Table 5 show a quite similar trend, although in this case the level of statistical significance was not even reached. On the whole, however, results confirm that compounds of nonfruity aroma, some even of rather unpleasant aroma, are effective and positive contributors to the perception of red wine fruitiness. However, it should be noted that the relative weak significance of the effects noticed in the tests do not seem to be consistent with the highest weight that these compounds play in the model according to their regression coefficients (see Table 4). In other words, even if the positive contribution of these compounds to fruitiness has been shown to be true, the experimental results do not support a principal contribution to fruitiness, as suggested by the model. The answer, or at least one answer to this apparent contradiction, was found when investigating the effects of 4-ethylphenol on fruitiness.

The negative role played by 4-ethylphenol on red wine fruitiness was also confirmed by ranking tests. Now a third fruit base including esters, norisoprenoids, and acids, was included in the experiments. Results are given in Table 6 and clearly confirm that the fruity character is completely suppressed by the presence of 4-ethylphenol. It is remarkable that in the three experiments, the sample containing 700 μg L^{-1} of this compound was selected as the least fruity by all the judges. But results in the table also reveal a very interesting trend. As can be seen, the impact of small amounts of 4-ethylphenol decreases with the fruity character of the original model (fruit base 1 < fruit base 2 < fruit base 3). In

Table 5. Results of Different Ranking Tests Carried out to Check the Sensory Effect of Different Odorants on the Fruity Notes of Red Wine[a]

	fruit base 1 (without norisoprenoids)					fruit base 2 (with norisoprenoids)				
	level of addition[(1)]				s[(2)]	level of addition				s
	0	1	2	3		0	1	2	3	
norisoprenoids	15[a]	23[ab]	31[b]	21[a]	>95%					
linear acids	18.5	25.5	21	25	ns[(3)]	12 [a]	24 [b]	26 [b]	28 [b]	>95%
branched acids	22	23	19.5	25.5	ns	18.5	22	21	28.5	ns
acetic acid	31.5[a]	23.5 [ab]	16 [b]	19 [b]	>95%	28.5[a]	20.5[ab]	25.5[a]	15.5[b]	>90%
phenylacetaldehyde	21.5	24	27	17.5	ns	22.5 [ab]	28.5 [a]	24.5 [a]	14.5 [b]	>95%
methional	20	18.5	15.5		ns	19.5	19	15.5		ns
methional (dry fruit)	12 [a]	18 [ab]	24 [b]		>95%	10.5 [a]	22.5 [b]	21[b]		>99%
methional (fresh fruit)	20	18.5	15.5		ns	25.5[a]	14[b]	14.5 [b]		>99%
norisoprenoids (dry fruit)	12[a]	20[ab]	24[b]	34[c]	>99%					
norisoprenoids (fresh fruit)	18	20	29	23	ns					
phenylacetaldehyde (dry fruit)	22.5	24	21.5	22	ns	31[a]	23[ab]	20[b]	16[b]	>95%
phenylacetaldehyde (fresh fruit)	30	21.5	17.5	21	ns	19.5	22.5	23	25	ns

[a] 1, Four levels of addition (0, minimum, median, and maximum concentration of 25 wines set); 2, Significance; 3, Not significant; different superscripts indicate significant differences.

Table 6. Results of the Ranking Tests Carried out to Check the Sensory Effect of 4-Ethylphenol on the Fruity Note of Red Wine[a]

	level of 4-ethyl phenol (μg/L)				s [(1)]
		50	120	700	
fruit base 1 (without norisoprenoids)	35 [a]	23.5 [b]	22.5 [b]	9 [c]	>99%
fruit base 2 (with norisoprenoids)	35 [a]	26[ab]	20 [b]	9 [c]	>99%
fruit base 3 (base 2 + acids)	30.5[a]	27 [a]	23.5 [a]	9 [b]	>99%

[a] 1, Significance; different superscripts indicate significant differences.

fact, the effect caused by 120 μg L^{-1} of 4-ethylphenol on the fruit base 3 is smaller than that caused by 50 μg L^{-1} in the two other bases. These results corroborate the recent observation made by Romano et al.[38] concerning the apparent "masking effect" of isobutyric and isovaleric acids on the perception of 4-ethylphenol and provide an explanation for the high weight that the two families of acids have on the model. Taken together, results suggest that this group of molecules may play a double role on the perception of wine fruitiness; as direct fruity contributors and as counteractants on the perception of 4-ethylphenol.

Acids, as direct fruity contributors, are responsible for the highest intensity of the fruity note (see Table 5). As it is know from our knowledge from binary mixtures,[9,39] the odor dominance in a simple mixture is primarily driven by the ratios of intensities between its components and, accordingly, a higher intensity of the fruity note will require a higher intensity (i.e., concentration) of 4-ethylphenol for becoming noticed, which would satisfactorily explain the observations in Table 6. According to classic psychophysics, this kind of effect is known as masking [40] and it is rather unspecific; norisoprenoids and acids mask the action of 4-ethylphenol simply because they add intensity to the fruity note making it more dominant in the mixture. Certainly a second possibility would be a direct action of acids on the signal elicited by 4-ethylphenol, as well as through antagonism at the receptor level,[41] and also at the bulbar/mitral cell or even at higher brain-processing levels. The existence of this effect, known as counteraction, cannot be unequivocally deduced from present data.

The effect exerted by acetic acid and phenylacetaldehyde on red wine fruitiness was also confirmed by means of ranking tests with fruit bases 1 and 2. Results are given in Table 5, and confirm in both cases the negative contribution of both chemicals to the perception of fruitiness. However, while the effect of acetic acid seems to be independent of the composition of the base, the effect of phenylacetaldehyde seems to be far more complex with some resemblances to what we observed for β-damascenone and β-ionone. As in that case, small amounts of this honey-smelling compound seem to exert a positive effect on the perception of fruitiness but the presence of higher amounts make the wine become less fruity. The case of methional is more difficult and in fact, the levels that we had to assay (50 and 100 μg L^{-1}) were above those found in the wine set. Even these high levels did not bring about any significant effect, as shown in Table 5, although in both bases the highest level of methional was ranked as the least fruity, as suggested by the model. However, some of the judges noticed a clear dry fruit-raisin note on the models containing methional, which lead us think that the instructions given to the sensory panel to evaluate wine fruitiness could be misleading in this case. If the addition of the odorant causes not only an increase/decrease on the fruitiness but a shift on quality

Table 7. *X* Variables of Animal Note Model and Its Regression Coefficients

vector	regression coefficient	compounds
4-ethylphenol	2.865	
4-ethylguaiacol	0.270	
ethyl esters	−0.179	ethyl 4-methylpentanoate
		ethyl 3-methylpentanoate
		ethyl 2-methylpentanoate
		ethyl cyclohexanoate
		ethyl propanoate
		ethyl butyrate
		ethyl hexanoate
		ethyl octanoate
		ethyl decanoate
		ethyl 2-methylpropanoate
		ethyl 2-methylbutyrate
		ethyl 3-methylbutyrate
isoamyl acetate	−0.219	
acids	−1.395	butyric acid
		hexanoic acid
		octanoic acid
		decanoic acid
		2-methylpropanoic acid
		2-methylbutyric acid
		3-methylbutyric acid
C-13 norisoprenoids	−1.342	β-damascenone
		β-ionone

Table 8. *X* Variables of Vegetables Note Model and Its Regression Coefficients

vector	regression coefficient	compounds
1-hexanol	0.102	
methanethiol	0.449	
dimethylsulfide	3.742	
acetaldehyde	−0.786	
linear acids	−2.857	butyric acid
		hexanoic acid
		octanoic acid
		decanoic acid
linear ethyl esters	−0.655	ethyl propanoate
		ethyl butyrate
		ethyl hexanoate
		ethyl octanoate
		ethyl decanate

Table 9. Triangular Tests to Check the Effect of the Addition of Different Compounds in Vegetables Note

	p^a	effect[b]
dimethylsulfide (57 μg/L)	ns[c]	
dimethylsulfide (100 μg/L)	>99.9%	truffle
dimethylsulfide (100 μg/L) + 1-hexanol (1000 μg/L)	>99.9%	truffle, herbaceous
methanethiol (5.1 μg/L)	>99.9%	cabbage
dimethylsulfide (100 μg/L) + 1-hexanol (1000 μg/L) + methanethiol (5.1 μg/L)	>99.9%	vegetable, cabbage

[a] Significance of the effect. [b] Most common descriptors provided by judges. [c] Not significant.

toward a different kind of fruitiness the panel would be faced with a nearly impossible task. Because of this, in a new series of experiments the panel was specifically instructed to rank samples according to their dry-fruit character (raisin, dry plum, dry peach), as well as their fresh-fruit character (any other fruit at not very ripen state). The experiment was also carried out with phenylacetaldehyde and norisoprenoids, in order to get a better insight on the role played by these compounds.

Results of that series of experiments are all given at the bottom of Table 5. In the case of methional, results conclusively show that this potato-smelling compound transforms the fresh fruit note into dry fruit note, the effect being particularly strong in the presence of norisoprenoids. In this case, the mixture of odors has as a major consequence the creation of a new odor note, which is not a frequent outcome in the scientific literature, at least in the many studies carried out with simple mixtures. The implication of norisoprenoids in the dry fruit note is also supported by data presented in the table and it corroborates observations made in a previous study.[4] On the contrary, the concerted action of phenylacetaldehyde and norisoprenoids brings about the nearly complete disappearance of the dry fruit note, as the significant decrease observed when increasing the levels of phenylacetaldehyde in the fruit base 2 reveals. This result suggests that phenylacetaldehyde is not a component of the complex perception defined as dry fruit and that it, as discussed in the case of 4-ethylphenol, masks or counteract both the dry fruit and fresh fruit odors.

Modeling the Animal and Vegetables Note of Red Wine. Leaving aside the fruity note, two other aroma nuances were particularly important in the differentiation of the wine set: the animal/leather and vegetables notes. The first one was feasible to build a reliable multivariate model. The best model was able to explain a 60% of the *Y* variance (measured by cross-validation) and its composition and properties are summarized in Tables 2 and 7. As can be seen in Table 7, the model is composed of 6 variables, 3 of which are vectors comprising groups of aroma compounds. According to Table 7, the animal note of the studied wines is caused primarily by two compounds with animal characteristics (4-ethylphenol and 4-ethyl guaiacol). And the model suggests that animal note is negatively contributed by isoamyl acetate and 3 groups of compounds with positive loadings in fruity note: ethyl esters, acids, and norisoprenoids.

In the case of the vegetable, a model with a relatively high predictive ability could be found (60% explained variance by cross validation). The basic quality parameters of the model are given in Table 2, while its compositional structure is given in Table 8. In accordance with data in this table, this term can be explained by six variables, two of them formed by groups of compounds. According to the regression coefficients, the vegetables note of these wines, which have a low concentration in alkyl 2-methoxypyrazines [42] is primarily caused by dimethylsulfide, methanethiol and hexanol. A tentative validation of this hypothesis was carried out by a series of simple sensory tests as shown in Table 9. In this case, the experiment consisted of triangle tests carried out on a dearomatized red wine base followed by a description of the differences introduced by the different compounds spiked. As can be seen, according to most of

the judges, DMS on its own causes a truffle note which becomes slightly herbaceous in the presence of 1-hexanol and strongly vegetal and cabbage-like when methanethiol (which on its own causes a strong cabbage odor) is included in the model. The sensory effects were in all cases very intense and most of panellist gave similar descriptors.

The model also suggested that acetaldehyde, linear fatty acids, and their ethyl esters could suppress the perception of the vegetable note. This was assessed by means of a ranking test carried out on dearomatized wines containing dimethylsulfide, methanethiol, and hexanol and different levels of the linear fatty acids, linear ethyl esters, and acetaldehyde. Results of the tests (data not shown) did not support the relevant role that the model attributes to linear fatty acids, linear ethyl esters, and acetaldehyde.

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