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ARTICLE

Effects of the Nonvolatile Matrix on the Aroma Perception of Wine

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Eighteen reconstituted wine samples were prepared by mixing nonvolatile and volatile fractions obtained from six different wines, two whites and four reds, with different characteristics, in an approach that makes it possible to have the same aroma composition in different nonvolatile matrices and vice versa. The aroma elicited by those reconstituted samples was described by a specifically trained sensory panel. Additional gas chromatography−olfactometric and gas chromatography−mass spectrometric studies were carried out to measure differences in aroma release. Results have shown that the nonvolatile matrix of wine exerts a powerful effect on the perception of aroma, strong enough even to make a white wine aroma to smell as a red wine (increasing red, black, and dry fruit notes in detriment of white, yellow, citrus, and tropical) and vice versa and also to create differences in the aroma of reds. It has also been confirmed that the wine nonvolatile matrix exerts a powerful influence on the release of odorants. In particular, headspaces above a white wine matrix are richer in fruity esters and volatile fatty acids. Red wine nonvolatile matrices seem also to retain strongly 3-mercaptohexyl acetate, hence reducing its sensory impact. Comparison of red wine nonvolatile matrices reveals that differences in the retention power of the matrix can affect differentially the pattern of release of linear and branched esters and also of acids.

KEYWORDS: Sensory analysis; flavor−matrix interactions; aroma release; wine; fruity aroma

INTRODUCTION

The chemistry of grape and particularly of wine flavor has been the focus of much research due to the complexity of the volatile aromas that contribute to wine flavor and the nuanced variations arising from different grape varieties (*1*), growing regions (*2*), and vintage years (*3*). Much of the focus of wine flavor chemistry research has dealt with the identification and measurement of the major components that contribute to taste and aroma. However, knowledge of volatile and nonvolatile composition alone is not enough to completely understand the overall wine aroma and in general its flavor. Interactions among odorants, perceptual interactions between sense modalities, and interactions between the odorant and different elements of the wine nonvolatile matrix can all affect the odorant volatility, flavor release, and overall perceived flavor (or aroma) intensity and quality (*4*).

Recently, studies on physical−chemical aroma interactions in complex mixtures have been carried out. In addition to perceptual interactions of odorants with each other (*5*), studies on interactions of odorants with nonvolatile matrix components such as anthocyanins (*6*), polysaccharides (*7*), polyphenolic compounds (*8*−*10*), or sulfur dioxide and catechols (*11*) have been carried out. These works have demonstrated that different compounds present in wine matrices can change the odorant volatility and concentration in the headspace. Jones et al. (*12*) studied the influence of interactions between major white wine components on the sensory properties of a model wine, demonstrating the influence of protein, alcohol, and glycerol concentration on the aroma attributes.

Polyphenols and tannins make up a significant portion of the nonvolatile matrix composition of red wines and, hence, several recent studies have focused on the influence of the interactions between aroma molecules and polyphenols on the volatility and further release of the odorant in model solutions. Dufour and Bayone (*8*) investigated the influence of catechin and a highly condensed wine tannin fraction on the volatility of aroma substances in model solutions. This study suggested that hydrophobicity acts as a driving force for bimolecular aroma−phenolic compound interactions. Other studies (*9*, *10*, *13*) carried out on polyphenol−odorant interactions showed a structural dependence of the strength of the interaction and the presence of $\pi-\pi$ stacking, which were stabilized by hydrogen bonds between the galloyl ring of the phenolic compounds and the aromatic ring of the odorant. Moreover, advanced diffusion methods based on NMR have been used to investigate interactions of odorant

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mixtures with macromolecules such as proteins or polymeric epicatechin units of cacao bean extracts (*13*).

Although the understanding of the relationships between chemical composition and sensory perception has improved, especially by investigations aimed at gaining knowledge on how odorants and matrix components interact chemically, the investigations have seldom gone beyond that of model solutions with a reduced number of components. As a result, although there is clear evidence that interactions between aroma molecules and nonvolatile components of wine must have some relevant sensory effects, the magnitude, relative importance, and qualitative nature of such sensory effects in real wines are not known. In this context, the aims of this study are (1) by using a construction/deconstruction strategy, to assess by sensory analysis the influence of the nonvolatile matrix of the wine on its aroma properties; and (2) by using GC-O and instrumental quantitative analysis, to make a preliminary estimation of the odorants and phenomena more likely involved in the aroma sensory changes induced by the presence of the nonvolatile matrix.

MATERIALS AND METHODS

Chemicals and Reagents. The chemical standards 2,3-butanedione, isobutyl acetate, isobutanol, isoamyl acetate, isoamyl alcohol, ethyl hexanoate, ethyl butyrate, octanal, *E*-2-nonenal, butyric acid, 2-/3-methylbutyric acid, *Z*-whiskey lactone, ethyl 4-methylpentanoate, methional, methionol, linalool, 2-acetylpyrazine, 2-methoxyphenol, Furaneol, and sotolon were supplied by Aldrich (Gillingham, U.K.); ethyl 2-/3-methylbutyrate, ethyl dihydrocinnamate, β-phenylethyl alcohol, and *p*-cresol were from Fluka (Buchs, Switzerland); 1-octen-3-one was from Lancaster (Strasbourg, France); acetic acid was from Panreac (Barcelona, Spain); and homofuraneol was from SAFC (distributed by Sigma-Aldrich). β-Damascenone was a gift from Firmenich (Geneva, Switzerland); 3,5-dimethyl-2-methoxypyrazine was a gift from Mark Sefton (formerly Australia Wine Research Institute), and 3-mercaptohexyl acetate was supplied by Oxford Chemicals.

Dichloromethane, methanol, and ethanol of LiChrosolv quality were from Merck (Darmstadt, Germany). Pure water was obtained from a Milli-Q purification system (Millipore, Bedford, MA). Polypropylene cartridges (3 mL) prepacked with LiChrolut EN resins were also obtained from Merck, whereas tartaric acid and $NaHCO_3$ was supplied by Panreac .

Wines. A set of six wines with marked technological and sensory differences were selected. These were all commercially available Spanish wines. The wines were a 1-year-old monovarietal Chardonnay wine fermented in stainless steel vats and aromatically intense (W1); a 1-year-old monovarietal Chardonnay wine aged under its lees in oak barrels (W2); a 1-year-old monovarietal Tempranillo red wine with light body, little astringency and not intense aromatically (W3); a 4-year-old (18 months in oak barrels) 90% Tempranillo−10% Cabernet Sauvignon red wine with full body, well-balanced structure, and aromatically intense (W4); a 3-year-old (18 months in oak barrel) monovarietal Tempranillo red wine with marked astringency (W5),; and a 3-year-old (12 months in oak barrels) monovarietal Tempranillo red wine with marked woody aroma (W6). W1 was selected as model for fruity white wine, W2 as model for a protein-rich white wine, W3 as model for a neutral red, W4 as model for a highly structured polyphenol-rich red wine, and W5 as model for a very astringent wine; W6 was exclusively selected because of its typical woody aroma.

Sample Preparation. *Aroma Extracts*. SPE cartridges (in 6 mL reservoirs) filled with 2000 mg of LiChrolut EN resins were put in the extraction unit (VAC ELUT 20 Station from Varian) and conditioned by passing slowly 20 mL of ethanol and 30 mL of a 12.0% hydroalcoholic solution (v/v) with pH fixed at 3.0 with tartaric acid. After this, 600 mL of wine was loaded. The cartridge was then rinsed with 20 mL of the hydroalcoholic solution, and aroma compounds were finally eluted with 20 mL of ethanol using positive pressure to avoid air contact. The extract was spiked with butylated hydroxyanisole (BHA) at 10 mg L^{-1} and was stored in vials sealed with no headspace at −25 °C until sample preparation.

Table 1. Eighteen Reconstituted Wines: Nonvolatile Extract (M*i*), Wine Aromas (A*j*)[a]

	M1	M2	M3	M4	M5
A1	x	x	x	x	x
A2					x
A3	x	x	x	x	x
A4			x	x	x
A5			x	x	x
A6					x

[a] Samples are referred to in the text as M*i*A*j* (formed by the addition of the nonvolatile extracts of wine *i* and the aromas of wine *j*).

Nonvolatile Extracts. Fifty milliliters of wine was lyophilized in 250 mL rounded flasks, and after this, samples were extracted with 3 × 10 mL of dichloromethane to eliminate remaining volatile compounds. Afterward, dichloromethane was completely eliminated by forcing a stream of pure nitrogen (ca. 50 mL min^{-1}) to pass through the sample for 20 min. The total absence of dichloromethane was assessed by headspace solid phase microextraction (Carboxen/PDMS 75 μm at 30 °C × 10 min) and GC with electron capture detector (overall system detection limit = 1 ng/sample). The extract was then dissolved in mineral water (Evian, Evian-les Bains, France) and brought up to 10 mL (5 times concentrated). After this, samples were placed in vials with no headspace to avoid sample−oxygen contact and stored at 5 °C until sample preparation.

Sample Reconstitutions. Reconstituted wines were prepared by mixing 20 mL of aroma extract (corresponds to the aroma of 600 mL of wine), 120 mL of nonvolatile extract (corresponds to 600 mL of wine), and 52 mL of ethanol and bringing the mixture to 600 mL with bottled mineral water (final ethanol content of 12% (v/v)). Eighteen samples were prepared by combining different volatile and nonvolatile extracts from different wines as shown in **Table 1**. Samples were stored at 5 °C in bottles hermetically closed with no headspace to avoid contact with oxygen until sensory evaluation. As can be seen in the table, the aroma extracts from wines 1 and 3 (A1 and A3) were combined with all of the nonvolatile matrices (M1−M5, M6 was considered to be irrelevant) to have a clear picture of the effects of the nonvolatile matrix on two very different types of aroma, and the astringent nonvolatile matrix from W5 (M5) was combined with the six aroma extracts (A1−A6) to have a clear picture of the effect of aroma on its taste properties (*14*). Four more combinations (M3A4, M3A5, M4A4, and M4A5) were also included in an attempt to get information about the possible existence of interactions.

GC−Olfactometry. Aromatic extracts of samples were obtained by a dynamic headspace sampling technique (*1*). A standard SPE cartridge (0.8 cm internal diameter, 3 mL internal volume) filled with 400 mg of LiChrolut EN resins was first washed with 20 mL of dichloromethane and then dried by letting air pass through (negative pressure of 0.6 bar, 10 min). The tube was placed on top of a bubbler flask containing 80 mL of wine, which was continuously stirred with a magnetic stir bar and kept at a constant temperature of 37 °C by water bath immersion. A controlled stream of nitrogen (100 mL min^{-1}) was passed through the sample during 200 min. Volatile constituents released into the headspace were trapped in the cartridge containing the sorbent and were further eluted with 3.2 mL of a mixture of dichloromethane/methanol (95:5 (v/v)). The extract was kept at −30 °C for 2 h to eliminate any water content by freezing and further decantation. The extract then was concentrated under a stream of pure N_2 for a final volume of 200 μL.

Sniffings were carried out in a Thermo 8000 series GC equipped with a flame ionization detection (FID) system and a sniffing port (ODO-1 from SGE, Ringwood, Australia) connected by a flow splitter to the column exit. The column used was a DB-WAX from J&W (Folsom, CA), 30 m × 0.32 mm i.d., with 0.5 μm film thickness. The carrier was H_2 at 3 mL min^{-1}. One microliter of the sample extract was injected in splitless mode, the splitless time being 1 min. The injector and detector were both kept at 250 °C. The temperature program was as follows: 40 °C for 5 min, raised at 4 °C min^{-1} to 100 °C, at 6 °C min^{-1} to 136 °C, and at 3 °C min^{-1} to 220 °C, and finally held at 220 °C for 10 min. To prevent condensation of high-boiling compounds on the sniffing port, the port was heated sequentially using a laboratory-made rheostat. A panel of six subjects, four women and two men, carried out the sniffings of the extracts. All of

them had extensive experience in GC-O analysis. Each judge evaluated the sample extract once in two time segments of 30 min to avoid fatigue (one session per day). The panelists were asked to measure the overall intensity of each odor using a 7-point category scale (0 = not detected; 1 = weak, hardly recognizable odor; 2 = clear but no intense odor, 3 = intense odor), half-values being allowed. The quantitative ability of this technique has been already demonstrated (*15*). As shown in ref *15*, the precision of the signals is relatively constant (3.6−8% of full scale), although the ability to detect differences in concentration depends to a large extent on the individual intensity/log(concentration) plots. The data processed were a mixture of intensity and frequency of detection (labeled as "modified frecuency", MF), which was calculated with the formula proposed by Dravnieks (*16*)

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

where F (%) is the detection frequency of an aromatic attribute expressed as percentage and I (%) is the average intensity expressed as percentage of the maximum intensity. The odorants were identified by comparison of their odors, chromatographic retention index in DB-WAX column, and MS spectra with those of pure reference compounds. In the case of 3-mercaptohexyl acetate, the signal was too weak to get a clear MS, and hence the presence of the compound was verified by the analysis of this compound exclusively in the M1A1 sample by using the GC−negative ion mass spectrometric method described in ref *17*.

Instrumental Quantitative Analysis. Three types of samples were analyzed: the original wines, the dearomatized nonvolatile matrices (diluted with water and ethanol to make a 12% v/v wine), and extracts obtained in the dynamic headspace trapping system described above. The volatile components of wines and dearomatized wines were determined following the procedures described below. The volatile components of the headspace extracts were determined by direct GC−ion trap MS under the GC-MS conditions used in the analysis of minor compounds (see below) but using as internal standards hexyl butyrate, methyl benzoate, and methyl phenylacetate (all at 1 mg L^{-1}).

Major Compounds (*Liquid−Liquid Microextraction and GC-FID Analysis*). Quantitative analysis of major compounds of the original wines was carried out using the method proposed and validated by Ortega et al. (*18*). In accordance with this method, 3 mL of wine and 7 mL of water were salted with 4.5 g of ammonium sulfate and extracted with 0.2 mL of dichloromethane. The extract was then analyzed by GC with FID using the conditions described elsewhere (*18*). Quantitative data were obtained by interpolation of relative peak areas in the calibration graphs built by the analysis of synthetic wines containing known amounts of the analytes. 2-Butanol, 4-methyl-2-pentanol, 4-hydroxy-4-methyl-2-pentanone, and 2-octanol were used as internal standards.

Minor Compounds (*SPE and GC-Ion Trap-MS Analysis*). This analysis was carried out using the method proposed and validated by Lopez et al. (*19*). In accordance with the method, 50 mL of wine, containing 25 μL of BHA solution and 75 μL of a surrogate standards solution (3-octanone, β-damascone, heptanoic acid, and isopropyl propanoate), was passed through a LiChrolut EN cartridge at about 2 mL min^{-1}. The sorbent was dried by letting air pass through (−0.6 bar, 10 min). Analytes were recovered by elution with 1.3 mL of dichloromethane. An internal standard solution was added to the eluted sample. The extract was then analyzed by GC−ion trap MS detection under the conditions described by Lopez et al. (*19*).

Sensory Analysis. A total of 36 students or staff members from the University of Burgundy (France) were recruited on the basis of their interest and availability during 12 weeks (one 1 h session per week). They were not paid for their participation. Among these 36 panelists 30 were selected for the experiment (12 males and 18 females from 20 to 69 years of age).

Panel Training. Panelists attended eight descriptive sensory training sessions over a period of two months, during which panelists worked in subgroups. They were provided with a list of 110 terms obtained from the literature (*20*) but with some modifications, as presented in **Table 2** along with their corresponding odor reference standards.

During training, different reference standards representative of aroma, taste, and astringency terms were presented. Standards were either commercially available odorants taken from International Flavor and Fragances (Dijon, France), Sentosphère (Paris, France), "Le Nez du Vin" (Jean Lenoir, Provence, France), and Firmenich (Geneva, Switzerland) or natural products prepared at the beginning of each session. For taste and astringency, solutions containing different concentrations of table sugar (0−12 g L^{-1}) for sweetness, tartaric acid (0−1.5 g L^{-1}) for acidity, quinine sulfate (0−10 mg L^{-1}) for bitterness, and potassium and aluminum sulfate (0−5 g L^{-1}) for astringency stimuli were presented to the panel to aid with recognition and discrimination between the different oral sensations.

The training period included two phases: a general and a product-specific training phase. During the general training phase (four sessions), panelists became familiar with aroma attributes and with intensity rating of sweetness, acidity, bitterness, astringency, aromatic, and global intensity as well as persistence. During a typical session panelists had to evaluate two to four different wines by describing their odor properties by choosing up to five descriptors in the aroma list and by rating sweetness, acidity, bitterness, and astringency on a 10-point scale (0 = "absence", 1 = "very low", and 9 = "very high"), aromatic and global intensity on a 9-point scale (1 = "very low" and 9 = "very high"), and global persistence on a 9-point scale (1 = "very short" and 9 = "very long"). The wines selected for this training phase presented intense and easily recognizable odor properties and included red, white, and rosé wines of diverse grape varieties and origins. The session ended with a discussion during which the panel leader compared the intensity scores given by panelists and highlighted the terms most frequently cited to describe each wine.

The specific training phase consisted of four sessions during which panelists became familiar with the type of samples of the study. During this phase, panelists described odor properties and rated the intensity of sweetness, acidity, bitterness, astringency, and aromatic and global intensity, as well as global persistence of 10 Spanish commercially available wines and of 5 (in duplicate) reconstituted wines different from those used for the study (formed by the nonvolatile extract of W6 and the aroma of W1, W2, W3, W4, or W5).

Sample Evaluation. The 18 reconstituted samples and original wines were aromatically evaluated and rated in terms of sweetness, acidity, bitterness, astringency, and aromatic and global intensity as well as global persistence.

Trained panelists described samples in duplicate. Ten-milliliter samples were presented in dark ISO (*21*) approved wine glasses labeled with three-digit random codes and covered by plastic Petri dishes according to a random arrangement. Panelists were asked to smell each sample and to describe their odor by choosing a maximum of 5 attributes from the list of 110 according to a citation frequency method (scores were computed from the number of panelists that selected a term) (*20*, *22*, *23*). Once the aroma attributes were noted, panelists were asked to introduce the sample into his/her mouth and rate sweetness, acidity, bitterness, astringency, and aromatic and global intensity as well as global persistence on the above-mentioned point scales for each wine. Panelists were imposed a 7-min interval between each sample evaluation. They were asked to rinse their mouths with water, to have some plain crackers, and finally to rinse their mouths again with water.

All samples and wines were served at room temperature and were evaluated in individual booths. Samples were stored at 5 °C. Panelists were not informed about the nature of the samples to evaluate.

Data Analysis

(**a**) **Analysis of Panel Performance.** To assess the individual performance, an average reproducibility index (Ri) was calculated for each of the panelists as proposed by Campo et al. (*20*)

$$R_\mathrm{i} = \sum [2 \times \mathrm{des_{com}}(\mathrm{des_{rep1}} + \mathrm{des_{rep2}})]/n$$

where $\mathrm{des_{com}}$ is the number of common terms given by the panelist in the two replicates of a wine, $\mathrm{des_{rep1}}$ and $\mathrm{des_{rep2}}$ are the numbers of terms given by the panelist in the first and second repetitions, respectively, and n is the number of wines. The responses from the subjects showing an $R_\mathrm{i} < 0.2$ were left out from the study. According to this, 30 panelists were selected and with them a three-way ANOVA for the in-mouth attributes involving samples (S), judge (J), and replicate (R) as fixed factors and all first-order interactions was calculated, and panel performance was confirmed.

(**b**) **Reconstituted Wine Characterization.** Only aromatic descriptors cited by a minimum of five subjects (15% of the panel) in, at least, one wine/repetition were considered for subsequent statistical analysis.

Table 2. Final List of Descriptors Used for Descriptive Analysis by Frequency of Citation, with the Corresponding Odor Reference Standards Presented during the Training Period and the Employed Quantities

descriptor	odor reference	quantity or concentration
fruit		
white fruits		
quince	quince jelly, Bonne Maman	2 teaspoons[a]
pear	pear nectar, Carrefour	30 mL[a]
apple	apple juice, Carrefour kids	30 mL[a]
yellow fruits		
apricot/peach	apricot nectar, Carrefour + peach syrup, William	15 mL of each[a]
melon	dry melon, Royal Orchid	10 g cut and in 30 mL of water[a]
citrus fruits		
bergamot	bergamot candies, Confiserie Stanislas	2 units in 10 mL of hot water[a]
lemon	lemon extract, Vahiné	20 drops in 30 mL of water[a]
orange	orange extract, Vahiné	20 drops in 30 mL of water[a]
grapefruit	grapefruit syrup, Pulco	20 drops in 30 mL of water[a]
red fruits		
cherry	cherry juice, Granini	30 mL[a]
strawberry	strawberry syrup, Teisseire	20 drops in 30 mL of water[a]
raspberry	raspberry topping, Vahiné	30 mL[a]
red currant	red currant jelly, Bonne Maman	5 teaspoons in 10 mL of boiling water[a]
black fruits		
black currant	aromatized black currant water, Volvic gourmande	30 mL[a]
blackberry	blackberry jam, Fruitée Intense Bonne Maman	5 teaspoons in 10 mL of water[a]
blueberry	blueberry syrup, Védrenne	5 mL in 10 mL of water[a]
dry fruits		
date	dry date	3 chopped units in 30 mL of boiling water[a]
fig	dry fig	3 chopped units[a]
prune	prune juice, Bio Carrefour	30 mL[a]
nuts		
almond	almond pastry	10 g[a]
walnut	walnut extract, Vahiné	10 drops in 30 mL of water[a]
hazelnut	hazelnut extract, Metarom	5 drops in 30 mL of water[a]
exotic fruits		
banana/English candy	banana nectar, Carrefour	30 mL[a]
pineapple	pineapple juice, Carrefour kids	30 mL[a]
passion fruit	passion fruit nectar, Caraïbos	30 mL[a]
lychee	syrup of canned lychees	30 mL[a]
mango	mango juice, Granini	30 mL[a]
coconut	coconut moisturizing cream, Suzi Wan	30 mL[a]
other fruits		
candied/cooked fruits	crystallized fruits (except orange pieces), Vahiné	50 g[a]
muscat	Rivesaltes muscat and grape juice/Muscat, Pampryl	10 mL of each[a]
bitter almond	bitter almond extract, Vahiné	10 drops in 30 mL of mineral oil[b]
cherries in alcohol	juice of canned cherries, crushed cherry, and Kirsch	10 mL of juice + 1 cherry + 2 mL of Kirsch[a]
cider	sweet cider, Carrefour	30 mL[a]
floral		
acacia	No. 25, Le Nez du Vin	50 μL impregnated in cotton[a]
chamomile	chamomile, Lipton	1 tea sachet in 50 mL of boiling water[a]
orange blossom	orange blossom extract, Elodie	40 drops in 30 mL of water[a]
jasmine	solution Firmenich	100 μg/L[b]
lilac	solution Firmenich	200 μg/L[b]
violet	violet syrup, Guillot	5 mL in 30 mL of water[a]
lime blossom	lime, Lipton	1 tea sachet in 50 mL of boiling water[a]
rose	rose syrup, Védrenne	40 drops in 30 mL of water[a]
honeysuckle	IFF, Dijon, France	100 μg/L[b]
geranium	geranium	4 chopped leaves and 4 petals[a]
honey	honey "touts les fleurs", Carrefour	2 teaspoons in 10 mL of boiling water[a]
spicy		
anise/fennel	anise syrup, Carrefour	10 drops in 30 mL of water[a]
licorice	licorice	stick (2 cm $\times$1 cm)[a]
clove	clove grains, Amora	2 units[a]
vanilla	vanilla extract, Vahiné	1 mL[a]
nutmeg	nutmeg, Amora	1 teaspoon[a]
black pepper	black pepper grains, Amora	2 units[a]
cinnamon	cinnamon in powder, Amora	bottom of the flask draped with product[a]
curry	curry, Indian Spices	bottom of the flask draped with product[a]
ginger	ginger berries, Cigalou	6 units[a]
thyme	thyme leaves	4 chopped leaves[a]
laurel	laurel leaves	4 chopped leaves[a]

Table 2. Continued

descriptor	odor reference	quantity or concentration
menthol/fresh	menthol syrup, Berger	20 drops in 30 mL of water[a]
roasted/woody		
roasted		
caramel	liquid caramel, Carrefour	30 mL in 30 mL of water[a]
toasted bread	fresh bread	half of a crushed toasted slice[a]
coffee	roasted coffee, Maison du Café	1 teaspoon[a]
woody		
fresh wood	oak wood, HM Arobois	1 g in 60 mL of hot water[a]
smoky	No. 12, Le Nez du Vin "*Le fût de chêne neuf*"	100 μL[b]
vegetal		
vegetables		
artichoke	juice of artichoke in conserve, Carrefour	30 mL[a]
asparagus	juice of asparagus in conserve, Carrefour	1 mL (diluted 1/10)[a]
cabbage	juice of cabbage in conserve, Daucy	5 mL in 5 mL of water[a]
green beans	juice of green beans in conserve, Carrefour	5 mL[a]
olives	olive juice, Carrefour	5 mL[a]
celery	celery leaf	1 chopped leaf[a]
bell pepper	green pepper	1 chopped unit[a]
other vegetables		
hay/dry leaf	dried herbs	a full 120 mL flask
pine/resin	No. 35, Le Nez du Vin	100 μL[b]
herbaceous	*cis*-3-hexen-1-ol, Sigma	100 μL[b]
fresh tobacco	fresh tobacco	half a cigarette[a]
animal		
musk/civet	standard Sentosphère	c
cat urine	standard Sentosphère	c
wet dog	wet dog hair	half flask[a]
leather	standard Sentosphère	c
transpiration/sweat	No. 8, Le Nez du Vin "*Les défauts*"	1 drop in 30 mL of water[b]
meat fumet	Viandox, Knorr	2 drops[b]
undergrowth		
mushroom	juice of mushrooms in conserve	diluted 1/10[a]
humus/earthy	humus	10 g[a]
mold	molds and tissues	in water[a]
others		
lactic	liquid cream, Délisse	30 mL[a]
butter	butter, Président	10 g
alcohol	ethanol, Sigma	diluted 1/2[a]
yeast	bakery yeast, Vahiné	5 g in 50 mL of hot water[a]
chocolate	pieces of chocolate, Vahiné	1 teaspoon[a]
rubber	No. 36, Le Nez du Café "*Passion révélation*"	
tar/bitumen	No. 26, Le Nez du Vin "1st edition"	
carboard/dust	cardboard	in pieces[a]
gun flint/silex	bis(2-methyl-1,3,4-thiadiazolyl)-5,5′-disulfane	100 μL[b]
sulfur	No. 6, Le Nez du Vin "*Les défauts*"	100 μL[b]

[a] Contained in a glass amber flask of 60 mL. [b] Glass amber flask (60 mL) containing an absorbent paper support (5 × 11 cm) impregnated with 10 mL of the odorant solution. [c] Standard Sentosphère directly placed in a glass amber flask of 125 mL.

A contingency table (wines in rows and descriptors in columns) containing the average citation frequency (2 repetitions and 30 panelists) of the most cited terms was then constructed and further analyzed by correspondence analysis (CA). To choose the number of factors that should be retained, dimensions with an eigenvalue greater than the mean eigenvalue (Kaiser law) were calculated for the CA space. The interpretation of the dimensions of the CA map was established by statistical indicators measuring the contributions of each term to the inertia on such dimensions. Only those attributes showing a contribution higher than the average were considered.

The effects linked to the presence of a given nonvolatile matrix (M_i) were measured by applying two-tailed paired t tests on the differences of the CFs for each attribute between the different pairs of samples $M_jA_k - M_iA_i$, where $j \neq i$ for all k aroma extracts.

RESULTS AND DISCUSSION

In the present work 18 different reconstituted wine samples were assessed by sensory analysis. The samples were made by mixing nonvolatile and volatile fractions of wines with different characteristics and further adjusting the ethanol degree (see Materials and Methods). With this strategy it was possible to have a series of reconstituted samples (M*i*A*j*) with the same nonvolatile matrix coming from a wine W*i* (denoted M*i*) and different volatile compositions taken from different real wines W*j* (denoted A*j*) or samples with the same volatile composition in different nonvolatile matrices. The six original wines were two Chardonnays and four Spanish reds with quite different sensory characteristics. A summary of the sensory and analytical characteristics of the original wines is given in **Tables 3** and **4**, respectively.

As can be seen, the two white wines were the fruitiest (30 to 25 CF versus 17 to 20.5 in the reds) and the sweetest. Among red wines, W3 is aromatically simple, its two major terms being fruity (CF = 19) and roasted/woody (CF = 12), and globally is the less intense. W4 has as major terms fruity (CF = 17) and vegetal (CF = 18), W5 fruity (CF = 18) and roasted/woody (CF = 21, defined mainly as roasted CF = 13), and W6 fruity (CF = 20.5) and roasted/woody (CF = 24, defined mainly as woody CF = 16).

Table 3. Summary of the Most Cited Odor Families (Numbers in Parentheses Indicate the Number of Panelists That Cited a Term (CF)) and the Sensory Attributes Evaluated in Mouth (Numbers in Parentheses Indicate the Mean Rating for Each Attribute) of the Original Wines Considered in the Study

wine code	wine type	odor attributes (CF)	in-mouth attributes (mean intensity[a])
W1	young Chardonnay	fruity (30), floral (12), alcohol (7), roasted/woody (7)	moderate sweetness (4.8), moderate acidity (5)
W2	Chardonnay *sur lies*	fruity (25), floral (11), roasted/woody (7), spicy (5)	low−moderate sweetness (4.1), moderate acidity (5.3)
W3	young Tempranillo	fruity (19), roasted/woody (12), spicy (8), floral (7), animal (5), undergrowth (5)	low−moderate global intensity (4.8), persistence (4.7), bitterness (4.3), astringency (4.2), and acidity (4)
W4	wooded Tempranillo	fruity (17), vegetal (18), spicy (11), roasted/woody (11), animal (6)	moderate−high astringency (5.4), moderate bitterness (4.7), moderate acidity (4.5)
W5	wooded Tempranillo	fruity (18), roasted/woody (21), undergrowth (10), vegetal (7), spicy (5), animal (5)	moderate−high astringency (6.1) and bitterness (5.1)
W6	wooded Tempranillo	fruity (20.5), roasted/woody (24), spicy (11), vegetal (6), animal (5)	low−moderate bitterness (4.3) and astringency (4.2)

[a] The intensity for tastes and astringency was measured on a 10-point scale (0 = absence, 1 = very low, 3 = low, 5 = moderate, 7 = high, and 9 very high), whereas global intensity was measured on a 9-point scale (1 = very low, 3 = low, 5 = moderate, 7 = high, and 9 = very high) as was persistence (1 = very short, 3 = short, 5 = moderate, 7 = long, and 9 = very long).

Table 4. Conventional Enological Parameters of the Studied Wines

wine code	pH	volatile acidity[a]	titratable acidity[a]	reducing sugar[b]	malic acid[b]	lactic acid[b]	etanol (v/v)	TPI
W1	3.47	0.36	3.71	3.7	2.87	0.05	13.7	10.1
W2	3.36	0.29	3.78	2.7	1.91	0.54	14.6	13.6
W3	3.66	0.32	3.62	5.8	0.29	1.88	13.1	59.5
W4	3.74	0.46	3.53	2.2	0.10	2.08	14.7	68.2
W5	3.59	0.51	4.13	3.0	0.00	1.87	14.8	60.1
W6	3.57	0.38	3.51	2.1	0.02	1.56	13.9	64.0

[a] Expressed as grams of acetic or tartaric acid per liter, respectively. [b] Expressed as grams per liter.

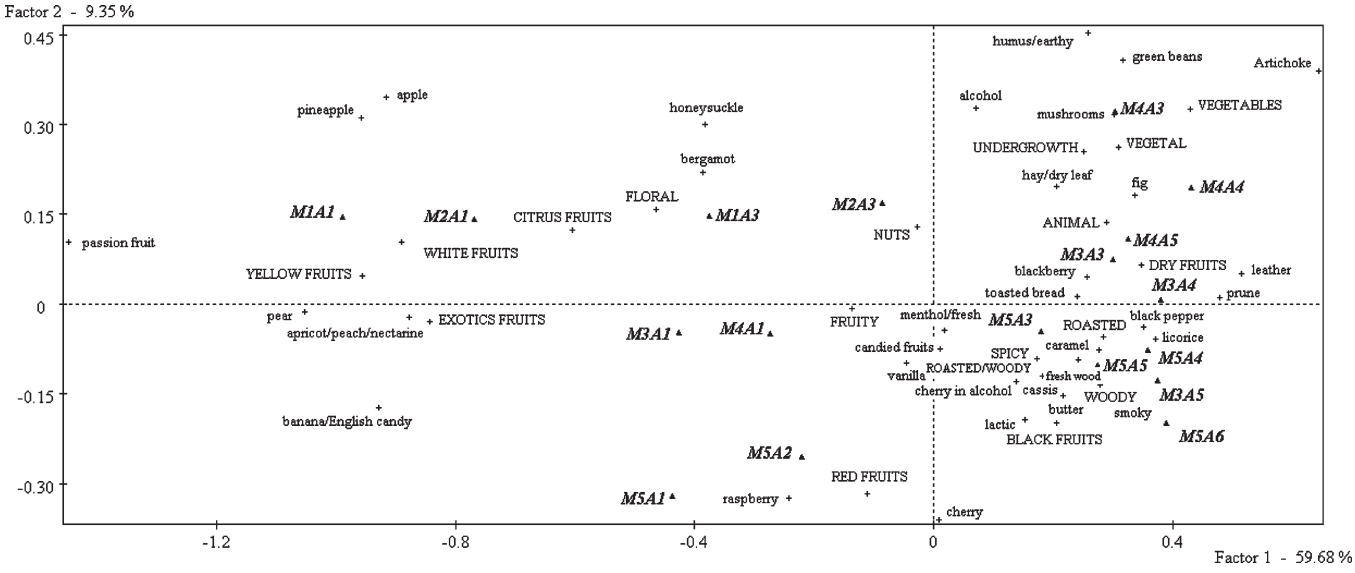

Figure 1. Projection of samples and aromatic descriptors in the CA map (dimensions 1 and 2).

With regard to the attributes evaluated in mouth, W4 is the most acid among red wines; it presents the maximum value for total polyphenol index, and it is together with W5 the most astringent (at a significance level of 95%), whereas it is the most bitter.

The reconstituted samples were made up by mixing nonvolatile and volatile fractions of those six wines as shown in **Table 1**. The results of, exclusively, the aroma sensory analysis carried out on those 18 reconstituted samples are summarized in **Figure 1**, where the projections of wines and terms (average of two replications) into a bidimensional CA plot (retaining nearly 70% of the original variance) are shown. The complete data set with the CFs is given in **Table 5**, and the results of the statistical tests carried out to evaluate the effects linked to the presence of a given nonvolatile matrix are presented in **Table 6**. The first factor in **Figure 1**, explaining >59% of the total variance, reveals an aromatic opposition between fruity terms characteristic of young white wines ("yellow, white, exotic, and citrus fruits") versus terms such as "vegetal", "dry fruits", "animal", "woody", "roasted", and "black fruits", most often related to red wines. The second factor, explaining 10% of the total variance, opposes "red fruits" (cherry and raspberry) to the "vegetal" and "undergrowth" (humus/earthy, green beans, artichoke) families.

The plot shows that samples are classified in the first dimension into three categories: reconstituted samples exclusively from white wines (M1A1 and M2A1) are on the far left; those exclusively from reds are grouped on the right; and those reconstituted samples containing fractions from both white and red wines are found in the center-left. The second dimension of the plot (accumulating 9.3% of the original variance) separates samples M1A3 and M2A3 from M3A1, M4A1, M5A1, and

Table 5. Aromatic Sensory Profiles (CF Average between Replicates) of Samples

	M1A1	M2A1	M3A1	M4A1	M5A1	M1A3	M2A3	M3A3	M4A3	M5A3	M3A4	M4A4	M5A4	M3A5	M4A5	M5A5	M5A2	M5A6
fruity	28	27	28	28.5	29.5	26.5	24.5	25	22	23.5	19.5	19.5	22	25.5	22.5	22	28	21.5
white fruits	10.5	12.5	7.5	9	7.5	8.5	5	1.5	2.5	2	0.5	0	1	1.5	2.5	0.5	5.5	1
yellow fruits	7	8	5.5	3.5	6	6	6	0	0.5	0.5	0.5	0	1.5	0.5	0.5	1.5	4.5	0
citrus fruits	6.5	6.5	5	4.5	4.5	5.5	4.5	2.5	1	3.5	2	2	0.5	2	1	2	2.5	0.5
red fruits	3.5	3	10	12	12	3	2	5	4.5	7	3	4.5	6	4.5	5.5	5	10	7
black fruits	2	3	3	7	7.5	2.5	3	6	5.5	10	8.5	6.5	8	9	5	6.5	9	6
dry fruits	2.5	1	3.5	6	3	4.5	5.5	10.5	8.5	7.5	7.5	7	7	9.5	10.5	7	4.5	8
nuts	4.5	2	1	1	2	4.5	5	2	2	1.5	4.5	3.5	3	4.5	2	3	3	2
exotic fruits	21.5	16.5	14	12	15	9.5	6	3	3.5	4.5	1.5	1.5	2.5	1.5	3	5	11.5	2
floral	12	13.5	10.5	8.5	7	12	7.5	6.5	6.5	6	5.5	4	3	2	3.5	5	8	3.5
vegetal	3	5.5	6	7	2	5.5	10	8.5	15.5	9	11	15	11	9.5	12.5	9	4.5	6.5
vegetables	0.5	3	5	5.5	0	3	7.5	10	13.5	7.5	8.5	14	8.5	7.5	9.5	7	3	4
spicy	8	7	12	11.5	12.5	11.5	11	12.5	9.5	15	20	14	18	16	15.5	18	12.5	18.5
animal	2.5	2.5	1.5	4.5	2	3	4	4	6	2.5	6.5	5.5	4	4	6	6.5	1	7
roasted/woody	4.5	8.5	11	12.5	14.5	10.5	17	14	15	17	22	16.5	22	21	18	20.5	17	23
roasted	1.5	2.5	6.5	3	4	3	5.5	9	7	6.5	7.5	5.5	8.5	7.5	5.5	8	6	8
woody	3	6	5	9.5	12	8	13.5	10	10.5	13	17	12.5	16	19	12.5	16.5	12.5	20.5
undergrowth	1	2.5	1	3	2	2	3	2	6	2	5	3	3.5	2	5.5	2	1	3

Table 6. Sensory Effects Linked to the Replacement of the Nonvolatile Matrix by That of a Specific Red Wine (Mean Differences and Significances Obtained in a Two-Tailed Paired *t* Test Comparison)

	M1		M2		M3		M4		M5	
descriptor	effect	*P*	effect	*P*	effect	*P*	effect	*P*	effect	*P*
fruity		ns		ns		ns	−1.25	0.040		ns
white fruits	3.56	0.012	2.63	0.028	−1.50	0.043		ns	−1.71	0.027
yellow fruits	2.75	0.025	3.38	0.004		ns	−2.17	0.005		ns
citrus fruits	2.00	0.004	1.38	0.026		ns	−1.42	0.012		ns
red fruits	−3.69	0.029	−4.63	0.006		ns		ns	3.13	0.005
black fruits	−3.38	0.007	−2.44	0.042		ns		ns	3.17	0.004
dry fruits	−2.19	0.035	−2.50	0.008	1.59	0.048	2.00	0.007		ns
exotic fruits	6.19	0.000		ns	−2.18	0.021	−2.46	0.017		ns
floral	3.75	0.004		ns		ns		ns	−2.00	0.035
vegetables	−4.75	0.004		ns		ns	4.58	<0.000	−2.21	0.031
spicy		ns	−2.56	0.024		ns		ns	2.79	0.001
animal		ns		ns		ns	1.83	0.001		ns
roasted	−3.25	0.001		ns	2.50	0.001		ns		ns
woody	−4.44	0.002		ns		ns		ns	3.21	0.007
undergrowth	−1.19	0.043		ns		ns	2.08	0.004		ns

M5A2 and also the samples made exclusively from red wines: those made with the matrix M4 have a positive score in this component, whereas those made with M5 have a negative score.

Such distribution of samples reveals a surprisingly intense effect of the nonvolatile matrix on the aroma perception; the aroma properties of reconstituted wines containing the same aroma extract can be very different because of the kind of nonvolatile matrix they contain. This is clearly shown in the case of the reconstituted samples containing the aroma extract from wine 1. The plot shows that replacing the original nonvolatile matrix (M1A1) by a nonvolatile matrix from a second white wine (M2A1) has a small sensory effect, but that replacing it by a red wine nonvolatile matrix (M3A1, M4A1, or M5A1) has a deep effect on the sensory properties of the reconstituted wine, changing its aroma to terms related to the "red fruit" aroma family in detriment to the terms typical of white wines observed in the M1A1 and M2A1 samples. The specific sensory changes associated with such replacements can be seen in **Table 5**. As can be seen, the CFs of the terms white, yellow, and citrus fruits slightly decrease (1−3.5 CF units) as does floral (up to 5 CF units); exotic fruit strongly decreases (6.5−9.5 CF units), whereas the red and black fruit terms clearly increase (up to 8.5 CF units). Other terms that also increase are spicy (up to 4.5 CF units) and woody (up to 9 CF units). It should be noted that the effect is most intense when the nonvolatile matrix comes from the astringent red wine (W5). The opposite effect, that is, a red wine aroma becoming closer to that of a white when the matrix is replaced by a white wine matrix, seems to be also true. This can be seen by studying the distribution of samples containing the aroma extract from wine 3. Replacing the original matrix (M3A3) by that of a white wine (M1A3 and M2A3) brings about a clear increase in the white (3.5−7 CF units), yellow (6 CF units), citrus (2−3 CF units), and tropical fruit notes (3−6.5 CF units) and also of the floral note (1−5 CF units) (see **Table 5**), and those increments are at the expense of corresponding decrements on the red (minus 2−3 CF units), black (minus 3−3.5 CF units), and dry fruit notes (minus 5−6 CF units) and of roasted (minus 3.5−6 CF units), more typically associated with red wines.

The intensity and significance of the effects caused by the change in the nonvolatile matrix are presented in **Table 6**. As shown in the table, the presence of a white wine matrix increases significantly the CFs of the white, yellow, and citrus fruity notes and decreases those of black, red, and dry fruits. The effects are strongest for M1, for which important increases in exotic fruits and flowery nuances are noted, as well as sensible decrements in vegetal, roasted, woody, and undergrowth notes. The effects caused by the presence of matrices from red wines are more complex, slightly weaker and more matrix-dependent, as shown

Table 7. Gas Chromatographic−Olfactometry (GC-O) Data (Linear Retention Indices, Odor Descriptions, Identities, and GC-O Scores), Quantitative Data (Micrograms per Liter) of the Odorants Found in the Nonvolatile Matrices Used in the Study and in the Original Wines Used To Prepare the Matrices, and Percent of Compound Remaining after the Dearomatization Process

LRI DB-WAX	odor descriptor	identity		M1	M2	M3	M4	M5
957	lactic, strawberry	2,3-butanedione (diacetyl)	**GC-O**	**35**	**25**	**40**	**53**	**54**
			GC-FID	nd	nd	88	11	372
			original	450	2380	1490	680	7800
			% remaining	0	0	5.9	1.6	4.8
1011	sweet	isobutyl acetate	**GC-O**	**24**	**0**	**10**	**14**	**0**
			GC-MS	0.63	0.45	0.45	0.55	0.48
			original	56.1	37.9	58.8	22	20.3
			% remaining	1.1	1.2	0.8	2.5	2.3
1099	bitter, green	isobutanol	**GC-O**	**29**	**25**	**14**	**10**	**20**
			GC-FID	nd	469	755	502	725
			original	11800	13500	36600	30200	25000
			% remaining	0	3.5	2.1	1.7	2.9
1124	banana	isoamyl acetate	**GC-O**	**0**	**30**	**0**	**0**	**0**
			GC-FID	nd	0.03	nd	nd	nd
			original	1910	1200	860	150	130
			% remaining	0	0.0	0	0	0
1215	fusel	isoamyl alcohol	**GC-O**	**68**	**61**	**76**	**54**	**68**
			GC-FID	6393	7946	11079	2549	10118
			original	137280	184000	318400	209600	190400
			% remaining	4.7	4.3	3.5	1.2	5.3
1240	fruity, anise	ethyl hexanoate	**GC-O**	**10**	**27**	**10**	**0**	**0**
			GC-FID	nd	nd	nd	nd	nd
			original	340	360	130	180	140
			% remaining	0	0	0	0	0
1296	lemon, orange, solvent	octanal	**GC-O**	**25**	**10**	**25**	**0**	**0**
1307	mushroom	1-octen-3-one	**GC-O**	**54**	**10**	**40**	**29**	**20**
1455	vinegar	acetic acid	**GC-O**	**41**	**25**	**32**	**25**	**25**
1502	green, metallic	*Z*-2-nonenal[a]	**GC-O**	**29**	**0**	**25**	**29**	**32**
1632	cheese	butyric acid	**GC-O**	**0**	**10**	**0**	**0**	**0**
			GC-FID	nd	nd	nd	nd	nd
			original	1000	940	630	890	890
			% remaining	0	0	0	0	0
1678	cheese	2-/3-methylbutyric acid	**GC-O**	**14**	**29**	**14**	**10**	**47**
			GC-MS	4.3	3.5	11.0	2.0	7.9
			original	160	234	330	157	226
			% remaining	2.7	1.5	3.3	1.3	3.5
1805	sweet, apple	β-damascenone	**GC-O**	**14**	**20**	**53**	**25**	**32**
			GC-MS	0.23	0.13	0.15	0.12	0.09
			original	2.44	1.51	2.23	1.17	0.72
			% remaining	9.5	8.3	6.9	10.0	13.1
1879	sweet, pleasant	ethyl dihydrocinnamate	**GC-O**	**20**	**0**	**32**	**20**	**0**
			GC-MS	nd	nd	nd	nd	nd
			original	2.2	2.4	1.6	0.9	0.1
			% remaining	0	0	0	0	0
1908	roses	β-phenylethanol	**GC-O**	**20**	**25**	**32**	**47**	**47**
			GC-FID	1049	1039	2118	1245	1641
			original	15552	15422	40480	27520	21280
			% remaining	6.7	6.7	5.2	4.5	7.7
1947	sweet wood	*Z*-whiskey lactone	**GC-O**	**0**	**0**	**10**	**14**	**58**
			GC-MS	2.0	4.5	nd	6.9	15.2
			original	30.6	204	4.52	267	419
			% remaining	6.4	2.2	0.0	2.6	3.6

Table 7. Continued

LRI DB-WAX	odor descriptor	identity		M1	M2	M3	M4	M5
2078	phenolic, leather	*p*-cresol	GC-O	**53**	**68**	**14**	**43**	**14**
2204	burnt, curry	4,5-dimethyl-3-hydroxy-2-(5*H*)-furanone (sotolon)	GC-O	**43**	**29**	**40**	**31**	**25**

[a] Present in (*E*)-2-nonenal standard.

in **Table 6**. As can be seen, the presence of M3 brings about a significant increase in dry fruits and roasted notes and a significant decrease in white and exotic fruits. The introduction of M4 brings about significant increases in dry fruits, vegetal, animal, and undergrowth notes and significant decreases in fruitiness and in yellow, citrus, and exotic fruits. The introduction of M5 has as a consequence significant increases in red and black fruits and in spicy and woody character and significant decreases in vegetal, white fruit, and flowery notes. These results confirm that the nonvolatile matrix has a deep influence and that, in general, it can be said that white matrices enhance the perception of fruity notes typically linked to white wines, in detriment to those of reds, whereas red matrices have a more complex effect, highly dependent on the type of matrix, but whose effects, generally speaking, are opposed to those observed for white wine matrices.

It must be remarked that these results are unexpected, because although numerous previous studies had shown that nonvolatile compounds in the matrix can bind to some extent to some volatile components (*6*−*11*) and had suggested that such interactions could have some influence on wine aroma (*12*), we never thought that the effects on aroma perception could be of such a magnitude, nearly comparable to that of the aroma composition. Leaving aside the possibility that the results were biased by a cross-modal interaction effect caused by the perception of the color or taste of the wines, because the experiment was carried out in dark glasses and aromatic description was noted before panelists were allowed to introduce the sample into their mouths, there are three possibilities that could explain the strong effects exerted by the nonvolatile matrix on the aroma perception: (1) Limitations in the dearomatization process of the nonvolatile matrices. The presence in the nonvolatile matrices of some key volatiles, because they were not effectively removed or because they are continuously formed from nonvolatile precursors, could bias the results. (2) A strong and differential physical interaction effect of the nonvolatile matrix on the different aroma compounds of the wine. Such a differential interaction nonvolatile matrix × aroma extract should be able to create different aroma profiles (in the headspace) from the same aroma extract. (3) The existence of interactions more sophisticated than those purely physical between the nonvolatile matrix and the aroma extract, such as redox transformations induced by the matrix, or different forms of chemical binding of aroma molecules with components from the nonvolatile matrix.

The most important point is certainly to check whether the presence of some aroma compounds in the nonvolatile matrices could be biasing the results. Therefore, even if the nonvolatile matrices were odorless, they were reconstituted with water and ethanol and the corresponding reconstituted samples were analyzed by quantitative GC and GC-MS and were also submitted to a dynamic headspace sampling technique to obtain concentrated extracts of the remaining volatiles to be studied by GC-O.

Results of such studies are shown in **Table 7**. The GC-O study revealed that 18 odorants were present in the extracts from the nonvolatile matrices, in most cases at relatively low olfactometric scores (MF(%)). It should be noted that the MF(%) are most likely strongly overestimated in comparison with those found in real wine, because in samples extremely poor in odors, the sniffers tend to overmark the few appearing. This can explain why some of the GC-O scores of the nonvolatile matrices are even higher than those measured in the reconstituted wines M1A1, M5A1, M4A3, and M5A3 shown in **Table 8** (cases of 1-octen-3-one, acetic acid, ethyl dihydrocinnamate, *Z*-whiskey lactone, and *p*-cresol). On the other hand, the quantitative study confirmed that the amounts of odorants remaining in the nonvolatile matrices are very small and that in most cases the dearomatization process was nearly complete. As shown in **Table 7**, nonpolar odorants, such as esters, were almost completely removed, and just residual levels of the most polar odorants could be found. In the cases of diacetyl, isobutanol, isoamyl acohol, and butyric and isovaleric acids the levels found in the nonvolatile matrices are below the 6% of the wine original content in the odorant. In the worst case of β-phenylethanol the amount remaining peaks to 8% of the original wine content, yet the levels are well below the olfactory threshold of that compound. In addition, data in the table indicate that differences between the white and red nonvolatile matrices are in most cases not consistent. In fact, the 95% level of statistical significance for such difference is not reached in any case. We can therefore reasonably expect that the odorants remaining in the nonvolatile matrices are not a major cause explaining the strong sensory differences previously observed.

It should be also observed that the presence in the nonvolatile matrices of small amounts of wine polar and major compounds, such as diacetyl, isobutanol, or isoamyl alcohol, is easily explained in terms of their solubility in the polar nonvolatile matrix: a kind of syrup composed mainly of glycerol. However, the presence of some other less polar and, theoretically easy to remove, compounds, such as octanal, 1-octen-3-one, (*Z*)-2-nonenal, or β-damascenone, should be attributed rather to their formation from nonvolatile precursors present in the nonvolatile matrix.

To check whether the nonvolatile matrix is really able to change the profile of aromas released out of the wine, the GC-O approach was also applied to the study of two sets of three reconstituted wine samples: M1A1, M5A1, and a third containing just A1 in hydroalcoholic solution (12% ethanol, pH 3.5); and M4A3, M5A3, and a third containing A3 in hydroalcoholic solution. Because the GC-O procedure is based on a dynamic headspace sampling system, differences in the olfactometric scores should be attributed to differences in volatility caused by the nonvolatile matrix. Results of this experiment are shown in **Table 8**. As can be seen, the highest GC-O scores were observed in most cases in the samples containing just the aroma extract and hydroalcoholic solution (samples A1 and A3), which indicates that nonvolatile matrices are exerting an effective opposition to the headspace release of odorants. On the other hand, comparison between the olfactometric signals obtained in M1A1 and M5A1 reveals that effectively, in most cases, the signals are higher when the nonvolatile matrix belongs to a white wine. In fact, and leaving aside (*Z*)-whiskey lactone, which comes from the M5 matrix, a paired *t* test reveals that the GC-O scores obtained in the M1A1 sample are significantly higher than those obtained in the

Table 8. GC−Olfactometries Carried out on Dynamic Headspace Extracts Obtained from Samples Containing the Same Aroma Formulation and Different Nonvolatile Matrices

IR	compound	A1	M1A1	M5A1	A3	M4A3	M5A3
989	2,3-butanedione (diacetyl)	82	76	73	87	73	82
1011	isobutyl acetate + unknown	38	38	22	61	33	0
1033−1036	ethyl butyrate	76	71	59	76	61	67
1053	ethyl 2-methylbutyrate	62	35	39	58	43	45
1068−1073	ethyl 3-methylbutyrate	75	76	76	83	65	78
1124−1129	isoamyl acetate	87	71	56	61	70	71
1192−1194	ethyl 4-methylpentanoate	0	0	0	36	17	46
1215−1218	isoamyl alcohol	85	83	83	88	73	87
1235−1238	ethyl hexanoate	78	78	66	75	73	67
1296−1297	octanal	7	29	7	0	0	0
1307−1309	1-octen-3-one	0	29	0	25	0	10
1434−1437	2-methoxy-3,5-dimethylpyrazine	0	0	0	26	0	0
1450	methional	0	0	0	29	0	10
1455−1457	acetic acid	14	29	29	0	0	10
1502	(*Z*)-2-nonenal[a]	0	19	45	17	14	0
1553	linalool	38	0	0	17	0	17
1625	2-acetylpyrazine	19	12	10	0	10	0
1632−1637	butyric acid	24	19	0	0	0	0
1678−1682	3-methylbutyric acid	35	71	41	57	47	39
1720	3-mercaptohexyl acetate	14	33	0	0	0	0
1725	methionol	14	25	19	41	19	24
1805	β-damascenone	51	47	39	53	51	43
1858	2-methoxyphenol (guaiacol)	41	22	22	41	43	38
1879	ethyl dihydrocinnamate	10	14	19	24	22	10
1908	β-phenethyl alcohol	70	70	70	58	47	54
1947	(*Z*)-whiskey lactone	0	0	24	0	0	19
2035	2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (Furaneol)	66	10	17	17	24	26
2063	2-ethyl-4-hydroxy-5-methyl-3(2*H*)-furanone (homofuraneol)	0	46	58	0	0	0
2078	*p*-cresol	33	43	14	17	36	43
2164	4.5-dimethyl-3-hydroxy-2-(5*H*)-furanone (sotolon)	58	29	48	0	38	45

[a] Present in (*E*)-2-nonenal standard.

Table 9. Amounts (in Arbitrary Units) of Odorants Released from Four Different Reconstituted Samples in a Dynamic Headspace Sampling System[a]

	M1A1		M5A1				M4A3		M5A3			
	av	SD	av	SD	t^b	$P(t)$	av	SD	av	SD	t^b	$P(t)$
ethyl isobutyrate	nf						5.61	0.54	6.80	0.38	**3.14**	**0.035**
ethyl butyrate	1.85	0.11	1.42	0.11	**4.94**	**0.008**	1.39	0.09	1.41	0.11	0.21	0.846
ethyl 2-methylbutyrate	0.076	0.007	0.062	0.005	**2.87**	**0.046**	0.169	0.014	0.196	0.012	2.50	0.066
ethyl isovalerate	nf						0.053	0.007	0.068	0.004	**3.45**	**0.026**
ethyl hexanoate	16.42	0.18	14.08	0.72	**5.46**	**0.005**	4.03	0.24	3.48	0.39	−2.05	0.109
ethyl octanoate	18.45	1.23	15.88	1.03	**2.79**	**0.049**	4.21	0.33	3.90	0.35	−1.14	0.318
ethyl decanoate	1.06	0.09	0.84	0.11	2.74	0.052	0.159	0.022	0.226	0.007	5.02	0.007
isoamyl acetate	65.66	4.51	47.18	6.54	4.03	**0.016**	24.36	0.93	24.14	3.32	−0.11	0.919
isobutanol	0.656	0.043	0.668	0.030	−0.40	0.712	1.47	0.06	1.59	0.13	1.46	0.218
isoamyl alcohol	57.28	20.19	59.88	0.98	−0.22	0.834	89.13	0.45	91.42	3.60	1.09	0.337
hexanol	16.00	0.49	15.96	0.32	0.13	0.903	18.58	1.03	18.57	0.36	−0.02	0.983
β-phenylethanol	1.16	0.07	1.09	0.27	0.46	0.666	2.80	0.12	2.80	0.12	0.00	0.999
linalool	0.024	0.004	0.016	0.005	2.15	0.098	0.0040	0.0007	0.0062	0.0008	**3.65**	**0.022**
acetic acid	0.608	0.025	0.585	0.077	0.48	0.655	0.424	0.015	0.673	0.032	**12.05**	**0.000**
butyric acid	0.079	0.007	0.049	0.006	**5.83**	**0.004**	0.026	0.002	0.033	0.002	**3.93**	**0.017**
isovaleric acid	0.030	0.004	0.025	0.004	1.49	0.210	0.034	0.002	0.043	0.002	**6.25**	**0.003**
hexanoic acid	1.226	0.090	0.981	0.032	**4.44**	**0.011**	0.317	0.023	0.403	0.008	**6.08**	**0.004**
octanoic acid	0.84	0.05	0.71	0.05	**3.12**	**0.035**	0.191	0.015	0.227	0.012	**3.25**	**0.032**

[a] In all cases experiments were done in triplicate. Numbers in bold indicate significant differences ($\alpha \leq 0.05$). A 4-degree of freedom *t* reference distribution has been used. nf, not found. [b] *t* test for comparison of the two corresponding means.

M5A1 ($P = 0.019$), which confirms that, on average, the red wine nonvolatile matrix has a higher retention power, which reduces the volatility of the compounds. Moreover, differences are linked to the chemical nature of the odorants. Differences are particularly notable for esters and acids ($P < 0.001$), are null or negligible for alcohols, and even may be of opposite sign in the case of some very polar compounds, such as Furaneol, homofuraneol, and sotolon. Although not all of the compounds could be determined, a simple quantitative analysis of the headspace extracts obtained in triplicate in independent experiments confirmed the existence of such differences and the dependence on the polarity and functionality of the odorant. These results are given in **Table 9**. Esters are between 16 and 40% more concentrated in the headspace of M1A1 (the difference is not significant

in the case of ethyl decanoate), major alcohols are present at the same level in both headspaces, whereas butyric, hexanoic, and octanoic acid were found at levels also significantly higher in M1A1. In the cases of M4A3 and M5A3, GC-O data in **Table 8** show that olfactometric scores tend to be smaller in M4A3, the sample with highest total polyphenol content (total polyphenol index 68 vs 60). The smaller release rate of aroma compounds in this matrix is further confirmed by data in **Table 9**. Interestingly, the pattern of compounds affected is slightly different from that previously observed: in this case, the release of ethyl butyrate, hexanoate, and octanoate and isoamyl acetate was not affected, whereas ethyl isobutyrate, ethyl 2-methylbutyrate, and ethyl isovalerate were in all cases released at higher rates in M5A3. Differences between acids were also more notable in this other case.

It should be noted that all of these changes may have a relevant sensory influence and may even explain some of the sensory changes recorded in **Figure 1**. The importance of the ratio ethyl esters to fusel alcohol acetates in the qualitative profile of fruity notes of wines was highlighted years ago (*24*), the role of esters in the fruity notes and quality of reds has also been reported (*5*, *25*), and the relevance of the ratio linear esters to branched esters in the quality of the fruity perception has also been suggested (*26*). Another fact that may have a deep influence on the sensory properties of the reconstituted wines is the differential behavior of 3-mercaptohexyl acetate shown in **Table 8**. This outstanding aroma compound, which has been repeatedly found to play a significant role in the perception of fruitiness in white wines (*1*, *27*, *28*), was not even detected in the headspace of M5A1, whereas it reached a relatively high GC-O score (33) in M1A1. Such a major difference, which certainly will have a major sensory impact, may be due to the existence of specific interactions of the mercapto group with elements present in the red wine nonvolatile matrix.

Finally, data in **Table 8** also show some odorants with a relatively erratic behavior. These are octanal, 1-octen-3-one, (*Z*)-2-nonenal, and the polar compounds Furaneol, homofuraneol, *p*-cresol, and sotolon. Some of them were detected in the nonvolatile matrices (**Table 7**), but with the data at hand it is not feasible to do an accurate assessment of the roles that they may play in the aroma differences shown in **Figure 1**.

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