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Assessment of Volatile and Sensory Profiles between Base and Sparkling Wines

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This paper focuses on the study of the volatile, olfactometric, and sensory composition of base wines and their corresponding sparkling wines (14−24 months aging) obtained at semi-industrial scale during three consecutive harvests. The sensory profile of sparkling wine is more complex than that of base wine, with toasty, lactic, sweet, and yeasty notes being described by the panelists and an even sharper increase of these tastes in the cava reserve. On the other hand, during the second fermentation and subsequent aging in contact with lees, some compounds such as acetate and ethyl esters decrease in amount while others such as norisoprenoids, acetal, diacetyl, and furans appear or increase over time. These volatile compounds could be responsible for the sensory profile depending on their notes, as determined by sniffing. The differences in volatile composition are responsible for the changes observed in the sensory profile of cava with respect to base wine.

KEYWORDS: Aroma; cava; aging; GC-O; HS-SPME; sensory descriptive analysis

INTRODUCTION

Spanish sparkling wine (cava) (Certified Brand of Origin) is produced in limited geographical areas by a traditional method consisting of two stages. The base wine is elaborated in a first phase and then left to undergo alcoholic fermentation in a sealed bottle in a second phase, followed by aging in contact with lees for at least 9 months (*1*). The characteristics of the base wine, the yeast, and the aging time in contact with lees are the factors that contribute the most to the quality of cava. The process implies chemical and biochemical changes that involve the modification of the final quality of wine (*2*).

The quality of the aroma constitutes the first quality factor of a wine (*3*), and its analysis is today a multidisciplinary science (*4*). The aroma could be studied by three approaches: chemical composition of volatile compounds, sensory analysis, and olfactometric analysis. The volatile profile of base (*5*) and sparkling wines has been widely investigated (*6*−*8*), usually by means of GC-MS and SPME. Sensory analysis could also be used as an effective quantitative method to assess sparkling wine quality, provided trained judges are used (*9*, *10*). Hence, chemical and sensory analyses could be two complementary techniques that could provide a lot of information about the aroma of the wine. On the other hand, few papers deal with the characterization of the aroma profile of sparkling wines by olfactometry (GC-O) (*2*, *11*) due to the difficulty of detecting some volatile compounds with high olfactometric impact by instrumental detectors. This technique cannot accurately predict flavor mixtures from the wine's raw aromatic component because odors are not additive variables (*10*).

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However, no paper has yet sought to compare the sensory and volatile profiles between base wines and their corresponding sparkling wines. The aim of the current work was to find the volatile, olfactometric, and sensory profiles of base and sparkling wines with different aging times with the objective of finding which volatiles are responsible for the characteristic and complex bouquet of cava (sparkling wine). Volatile composition was obtained by an easy, rapid, and solvent-free method (HS/SPME), whereas sensory attributes were determined by quantitative descriptive analysis. In addition, the odorants involved in the aromatic profile of base wine and cava were determined by GC-O, which made it possible to determine some of compounds that are specific to cava and not to base wine.

MATERIALS AND METHODS

Samples. The wines were manufactured in the Freixenet S.A. winery in three consecutive harvests (2003, 2004, and 2005) from the autochthonous *Vitis vinifera* from the Macabeu, Xarel·lo, and Parellada grapevine varieties (10000 kg of each grape variety) (Spain). The varietal musts were fermented at semi-industrial scale (1000 L of fermentation tanks) with six different yeast strains selected according to the commercial suppliers' recommendations to obtain white wines with floral and fruity odor and with high resistance to alcohol and sulfur dioxide (*5*). Each harvest, varietal wines were blended to obtain six base wines (6 wines × 3 harvests = 18 base wines) to elaborate the corresponding sparkling wines according to the traditional method, which involves a second fermentation in a closed bottle and subsequent aging in contact with lees and which provides the cava with its special and characteristic bouquet. The second fermentations were always made with the yeast strain belonging to the Freixenet private collection. The sparkling wines were sampled and analyzed at 14 (young cava, $n = 18$) and 24 months (reserve, $n = 18$) of aging (*1*).

Chemical Standards and Reagents. 2-Octanol and 2-methylhexanoic acid were purchased from Sigma-Aldrich (St. Louis, MO) with a

Table 1. Means of the General Parameters of Base Wines and Sparkling Wines and Significance (*p*) Obtained by One-Way ANOVA[a]

	base wines (n = 18)	cava (n = 18)	cava reserve (n = 18)	p
total SO_2	69 a	52 b	49 b	<0.0001
total acidity (g/L)	4.0 a	3.5 b	3.5 b	<0.0001
pH	3.02	3.01	2.99	ns
OD 420 nm	0.05 a	0.07 b	0.08 c	<0.0001
alcohol (vol %)	10.6 a	11.8 b	11.9 b	<0.0001
total polyphenols (mg/L)	123 a	128 a	117 b	<0.05
malic acid (g/L)	1.33 a	0.73 b	0.76 b	<0.0001
lactic acid (g/L)	0.04 a	0.32 b	0.40 b	<0.001
protein (mg/L)	12.33 a	5.89 b	6.17 b	<0.0001

[a] Different letters indicate significant differences between samples; ns, nonsignificant result.

purity of >98%. They were prepared in a hydroalcoholic solution (11%) and used as internal standards at concentrations of 0.253 and 0.748 mg/L, respectively. Isobutyl acetate, ethyl isobutyrate, ethyl butyrate, ethyl isovalerate, isoamyl acetate, ethyl hexanoate, hexyl acetate, *cis*-3-hexenyl acetate, ethyl lactate, hexanol, *cis*-3-hexenol, 1-octen-3-one, ethyl octanoate, octyl acetate, furfural, γ-decalactone, linalool, isobutyric acid, butyric acid, ethyl decanoate, diethyl succinate, isovaleric acid, methionol, benzylic alcohol, 2-phenylethyl acetate, β-damascenone, hexanoic acid, 2-phenylethanol, octanoic acid, 4-vinylguaiacol, acetaldehyde, ethyl acetate, isobutanol, isoamyl alcohol, acetal, diacetyl, sotolon, methional, and acetoin were purchased from Sigma-Aldrich and Fluka (St. Louis, MO) with a purity of >98%.

Analytical Determinations. L-Malic acid, lactic acid (enzymatic kits were obtained from Roche Diagnostic, Mannheim, Germany), polyphenols (Folin−Ciocalteu method), acidity (potentiometric method), and SO_2 (iodometric method) were determined by analytical methods according to Commission Regulation (EC) 1990/2004 (*12*). Moreover, alcohol and protein contents were determined by NIR and Bradford method (Bio-Rad Laboratories, Munchen/Germany), respectively. **Table 1** shows the means (n = 18) of the general parameters of the samples and the significance obtained by one-way ANOVA. The general parameters were mainly influenced by the type of wine. Total SO_2, acidity, malic acid, polyphenols, and protein contents decreased in the transition from base wine to cava, whereas alcohol, OD 420 nm, and lactic acid increased.

Analysis of Volatile Composition. Acetaldehyde, ethyl acetate, isobutanol, isoamyl alcohol, and acetoin were determined by direct injection GC-FID.

The volatile composition was quantified in duplicate by headspace-solid phase microextraction (HS-SPME) coupled to gas chromatography (GC) with flame ionization detection (FID) (Agilent Technologies 6890A series II gas chromatograph equipped with a FID, Palo Alto, CA), according to the method described by Torrens et al. (*5*). Compounds were identified by comparison of their retention times with those of pure standards when available. In addition, GC−mass spectrometry (MS) was applied to confirm the identification of volatile compounds under the same conditions (Agilent Technologies 6890A series II gas chromatograph equipped with a split−splitless injection port coupled to a 5973A mass spectrometer).

Quantification was done using the internal standard (IS) method. Calibration was performed according to the method of Torrens et al. (*5*) as milligrams per liter for most compounds. Only octyl acetate, vitispiranes 1 and 2, and TDN were quantified as milligrams per liter equivalents of IS 2-octanol, whereas isovaleric acid and β-damascenone were quantified according to 2-methylhexanoic acid.

Sensory Analysis. The wines were evaluated by a panel of seven winery experts with previous experience in sparkling wine sensory analysis. The panelists were trained with fortified wines with standard hydroalcoholic solutions of different concentrations. The training was realized during several sessions. Samples were stored at the appropriate light, humidity, and temperature conditions. Previously, the close-ended list was discussed by the panelists to obtain consensus-based descriptors (**Table 2**). Odor attributes were evaluated by the panelists, assigning a value ranging from 1 to 9 (**Table 2**). Samples were tasted in a randomized order. Wine was presented to the panelists in tasting glasses (NF V09-110 AFNOR, 1995) marked with three-digit random numbers. Tasting was performed at 20−22 °C, and water was provided to rinse the palate between tastings.

Table 2. Selected Sensory Attributes of the Close-Ended List for the Sensory Evaluation by Base Wine and Sparkling Wines

wine descriptor	sparkling wine descriptor	reference aroma
floral	floral	rose, geranium, daisy, jasmine...
citrus fruit		lemon, grapefruit...
tree fruit		apple, pear...
tropical fruit	fruity	banana, pineapple...
ripe fruit		jam, stewed fruit...
	toasty	almond, nuts...
sweet	sweet	honey, caramel...
chemical	chemical	petroleum, plastic, sulfur...
lactic	lactic	milk, cheese, yogurt, butter...
yeasty	yeasty	bread, baker's yeast...

Olfactometric Analysis. *Preparation of Wine Extracts.* Volatiles were obtained by liquid−liquid extraction: 150 mL of wine was extracted with 20 mL of a mixture of pentane/dichloromethane (60:40). Next, the extracts were concentrated under a stream of pure nitrogen to a final volume of 0.1 mL.

Sniffing. Concentrated extracts were used in the GC-O analyses. Extracts were subjected to GC-FID in an olfactory detector outlet (ODO-1 SGE) connected by an outlet splitter system (OSS-1, SGE) at the column exit. The column used was TRWAX (60 m × 0.53 mm × 1 μm) (Tecknokroma, Sant Cugat del Vallès, Barcelona, Spain). The temperature program was from 40 to 225 °C (held for 10 min) at 3 °C/min. The helium carrier gas flow was set at a velocity of 5 mL min^{-1}, and the temperature of the injector and detector was 250 °C. A panel of six judges carried out the sniffing of the extracts. All of the judges that participated in the olfactometry have extensive experience in GC-O analysis. The judges were the same that realized the sensory descriptive analysis, and they were trained with hydroalcoholic solutions of standards at different concentrations. Every judge evaluates the wine extract once a day to avoid fatigue. The panelists were asked to provide a descriptor to characterize the eluted odor and to rate its intensity using a 5-point category scale (0 = not detected; 1 = weak; hardly recognizable odor; 2 = clear but not intense odor; 3 = medium intensity odor; 4 = intense odor; 5 = very intense odor). In this way the data processed was a mixture of the intensity and the frequency of an odorant. This parameter is labeled as modified frequency (MF) and is calculated according to the formula proposed by Dravsnieks (*13*): $MF(\%) = F(\%)I(\%)^{1/2}$, where $F(\%)$ is the detection frequency of an aromatic attribute expressed as percentage of total number of judges and $I(\%)$ is the average intensity expressed as percentage of the maximum intensity. In this study, those odorants that did not reach a maximum score of 15% in any wine were considered to be noise.

The identification of the odorants was carried out by comparison of their odors, reference standards, and mass spectra.

Statistical Analysis. Statgraphics Plus 5.1 (1999) was used to carry out the statistical data analysis. One-way ANOVA was used to analyze general parameters and volatile composition, whereas two-sample comparison analyses were used to study if there were any statistically significant differences between the two samples in relation to the frequency obtained by the values of the tasters. This analysis was performed to study the descriptive profile of cava wines and their corresponding aged cavas. In all of the statistical analyses, differences were considered to be significant at $p < 0.05$.

RESULTS AND DISCUSSION

Sensory Characterization of Base Wines and Sparkling Wines. Sensory analysis was an efficient tool to characterize the sensorial properties of wine. Descriptive analysis was previously used to characterize and discriminate champagne despite the difficulties of applying sensory analysis to sparkling wines (*10*). In the current study, experienced panelists established a close-ended list for wine and cava obtained by consensus on the basis of their experience in wine sensory analysis (**Table 2**). The current work focused mainly on the sensory profile to relate it with the volatile profile.

The means and standard deviations of the sensory profile obtained by base wine and young and reserve sparkling wine

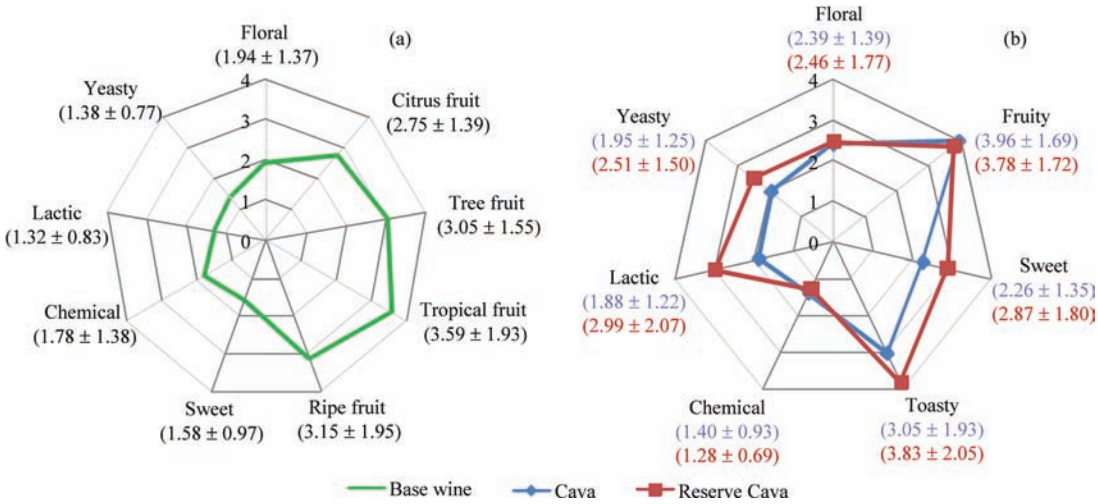

Figure 1. Aroma profiles of wine (**a**) and cava (**b**) obtained by the mean and standard deviation of the scores given by the panelists.

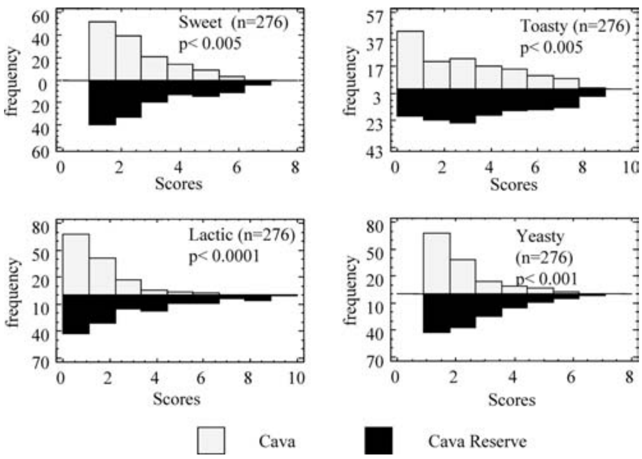

Figure 2. Frequency histograms of the data obtained by sweet, yeasty, lactic, and toasty flavors between cava and cava reserve by means of the two-sample comparison analysis.

are shown in the spiderweb diagrams in **Figure 1**. As shown in **Figure 1**, citrus, tree, tropical, and ripe fruit notes could be identified in the sensory profile of base wine, and in sparkling wines this fruity profile became more chemically complex with toasty, lactic, sweet, and yeasty nuances. With regard to the sensory profile between cava and reserve, it could be rated as yeasty ($p < 0.001$), sweet ($p < 0.005$), lactic ($p < 0.0001$), and toasty ($p < 0.005$), with these nuances being noticeably higher in more aged cava (**Figure 1b**). The evolution during aging from ripe fruit to butter and toasted notes was previously described in champagne samples (*10*).

To study the descriptive profile of cava wines and their corresponding aged cavas, the two-sample comparison analysis was performed (**Figure 2**). **Figure 2** shows the frequency histograms of the data obtained by sweet, yeasty, lactic, and toasty nuances between cava and reserve with the scores of the panelists on the horitzontal axis and the frequencies on the vertical axis. The height of each bar is the number of observations that fall within that interval. In the graph, two histograms are displayed; one for each sample, young cava and reserve. This analysis is often used to understand patterns. First, this analysis calculates the confidence intervals and then compares the hypothesis test of the mean, variances, and median. The results showed a significant difference in the frequency obtained by the values of the tasters regarding sweet, lactic, toasty, and yeasty flavors (**Figure 2**). The cava reserve with a high aging time has a high frequency of high values on all of the notes tested (**Figure 2**). As shown in **Figure 2**, 1 was the most frequently given score by the panelists to sweet (19%), lactic (25%), toasty (16%), and yeasty (25%) flavor nuances in young cava. One was also the most frequently given score to sweet (15%), lactic (16%), and yeasty (16%) nuances in cava reserve. However, for toasty nuances, 3 was the most frequently given score. The samples were significantly different on the basis of these notes in all cases ($p < 0.01$). At the same time, higher scores were obtained with higher frequencies in all of the notes studied by long-aged cava. These results confirm the data shown in **Figure 1**.

Changes in Volatile Compounds from Base Wine to Cava. Table 3 shows the volatile composition of base wine and its corresponding young and aged cavas. Most of the odorants shown in the table have been positively identified with pure standards and mass spectra similar to those of standards. About 35 compounds could be identified and quantified (mg/L), and qualitative and quantitative changes could be observed on the volatile composition through the elaboration process of the sparkling wine. When one-way ANOVA was performed according to the type of wine considered (base wine, cava, and reserve), most of the volatile compounds were significantly different ($p < 0.001$). Only ethyl hexanoate, ethyl acetate, isobutanol, isoamyl alcohol, isovaleric acid, acetoin, and hexanoic acid were not significantly different, showing a similar amount in the three types of wines measured (**Table 3**). **Table 4** shows the results of the GC-O analysis. This table describes the odorants identified only in cava or those compounds that increase by > 100% with regard to base wine as well as volatile compounds with similar perception in cava and base wine. As can be seen, 69 compounds were detected by GC-O, with some of them being detected only in cava. The aroma compounds are listed according to their retention time.

As expected, the acetate esters (hexyl acetate, phenylethyl acetate, octyl acetate...) determined in the current study decreased their amounts in cava to a point to where they were no longer detectable (**Table 3**). According to the literature, these compounds decrease during cava production and could also be used as age markers (*7*). These compounds are mainly described by the judges as having a fruity or sweet nuance (**Table 4**). This fact confirms the loss of fresh and fruity descriptors between base wine and sparkling wine (**Figure 1**). However, the most abundant esters in aged cava were ethyl lactate and diethyl succinate (**Table 3**). These two compounds were previously described as volatile compounds that increase their amount in long-aged cava (*7*).

Table 3. 95% Confidence Intervals for the Means of Volatile Compounds Determined in Base Wines (n = 18) and Sparkling Wines (n = 18 Young Cava and n = 18 Cava Reserve)

		identification[a]	base wines[b] (mg/L)	young cava[b] (mg/L)	cava reserve[b] (mg/L)
	ethyl esters				
2	ethyl butyrate	S, MS, KI	0.385−0.435 a	0.443−0.504 b	0.486−0.557 c
3	ethyl isovalerate	S, MS, KI	nd	0.021−0.030 a	0.035−0.046 b
5	ethyl hexanoate	S, MS, KI	0.824−0.913	0.808−0.898	0.865−0.932
8	ethyl lactate	S, MS, KI	6.44−8.62 a	49.98−87.45 b	64.61−123.13b
11	ethyl octanoate	S, MS, KI	1.083−1.258 a	0.983−1.076 b	1.012−1.124 b
15	ethyl decanoate	S, MS, KI	0.226−0.297 a	0.063−0.065 b	0.057−0.072 b
16	diethyl succinate	S, MS, KI	nd	5.545−6.974 a	9.18−10.75 b
	acetate esters				
1	isobutyl acetate	S, MS, KI	0.049−0.058	nd	nd
4	isoamyl acetate	S, MS, KI	2.787−3.385 a	0.179−0.255 b	0.064−0.121 b
6	hexyl acetate	S, MS, KI	0.291−0.344	nd	nd
7	*cis*-3-hexenyl acetate	S, MS, KI	0.027−0.032	nd	nd
13	octyl acetate[c]	S, MS, KI	0.008−0.010	nd	nd
19	2-phenylethyl acetate	S, MS, KI	0.224−0.285	nd	nd
30	ethyl acetate	S, MS, KI	39.559−45.105	35.925−42.493	37.398−45.105
	alcohols				
9	hexanol	S, MS, KI	0.877−0.999 a	1.186−1.279 b	1.216−1.389 b
10	*cis*-3-hexenol	S, MS, KI	0.189−0.244 a	0.273−0.328 b	0.304−0.356 b
18	methionol	S, MS, KI	3.041−4.091 a	3.758−4.842 b	2.449−2.829 c
22	benzylic alcohol	S, MS, KI	nd	0.024−0.071 a	0.143−0.178 b
31	isobutanol	S, MS, KI	18.914−23.922	20.413−25.004	19.448−23.585
32	isoamyl alcohol	S, MS, KI	150.08−167.08	156.07−171.09	149.73−161.03
23	2-phenylethanol	S, MS, KI	12.221−13.651 a	16.871−19.392 b	18.718−20.578 c
	furans, volatile phenols				
12	furfural	S, MS, KI	nd	0.279−0.443 a	0.713−0.871 b
25	4-vinylguaiacol	S, MS, KI	0.112−0.185	nd	nd
	terpenes, lactones, C[13] norisoprenoids				
14	linalool	S, MS, KI	0.004−0.005 a	0.005−0.006 b	0.005−0.006 b
20	β-damascenone[d]	S, MS, KI	0.120−0.138 a	0.061−0.067 b	0.062−0.071 b
33	vitispirane 1[c]	MS, KI	nd	0.108−0.169	0.132−0.185
34	vitispirane 2[c]	MS, KI	nd	0.090−0.149	0.109−0.155
35	TDN[c,e]	MS, KI	nd	0.051−0.091	0.070−0.094
	acids				
17	isovaleric acid[d]	S, MS, KI	0.064−0.083	0.070−0.087	0.070−0.084
21	hexanoic acid	S, MS, KI	5.977−6.548	5.833−6.449	5.875−6.492
24	octanoic acid	S, MS, KI	8.298−9.085 a	5.957−6.467 b	6.207−6.693 b
	carbonyl compounds				
26	acetal (1,1-diethoxyethane)	S, MS, KI	nd	1.120−1.220 a	2.490−2.667 b
27	diacetyl	S, MS, KI	nd	nd	0.034−0.087
28	acetoin (3-hydroxybutanone)	S, MS, KI	0.690−5.960	3.251−6.641	3.251−7.473
29	acetaldehyde	S, MS, KI	42.952−51.883 a	32.190−38.974 b	38.200−46.134 ac

[a] S, identified by comparison with standard compound; MS, tentatively identified by mass spectra; KI, tentatively identified by KI. [b] Different letters indicate significant differences ($p < 0.05$). [c] mg/L equivalents of 2-octanol (IS). [d] mg/L equivalents of 2-methylhexanoic acid (IS). [e] 1,2-Dihydro-1,1,6-trimethylnaphthalene.

The same results were obtained in the present study. The formation of these two esters could be favored by the presence of lees and the time of contact (*14*).

Some main varietal compounds increase their amount in cava (benzylic alcohol, 2-phenylethanol, linalool, vitispiranes, and TDN) (**Table 3**). The amount of varietal compounds changes, during bottle storage, as a result of acid-catalyzed reactions (*15*). TDN and vitispiranes originate from carotenoid degradation in the presence of oxygen, high temperatures, or exposure to the sun (*16*). These compounds increase their amount during aging even though this cannot be established by olfactometric analysis (**Table 4**). 2-Phenylethanol and benzylic alcohol increase their amount during aging and are related with yeast metabolism. Benzylic alcohol was found in grapes as glucopyranoside (*17*). The enzymatic activity of yeast lees could release the volatile compound during aging of wine. An increased amount of volatile compounds during commercial or fermentation lees contact has been previously described (*14*) (**Table 3**). β-Damascenone decreases its amount in cava. The literature reports that some mannoproteins secreted by yeast could interact with volatile compounds at concentrations at which these mannoproteins could cause sensory consequences in the wine (*18*).

Lactones are desirable compounds in wines because of their floral and fruity odor (*19*). In the present study, these notes were confirmed by olfactometric analysis (**Table 4**), but they are difficult to quantify because they are at very low level.

Volatile phenols usually considered to be off-flavors decrease in cava (4-vinylguaiacol) (**Table 3**). However, these compounds could be detected by GC-O in cava reserve (**Table 4**). 4-Ethylphenol and 4-ethylguaiacol were described by the analysts as unpleasant odors such as pharmacy, horse, or leather (**Table 4**). Some studies performed with red wine aged in contact with lees showed that some volatile phenols are retained in yeast lees, decreasing their concentration in wine in correlation with the amount and the time

Table 4. Comparison of Odorants Detected by GC-O in Cava and Base Wines

KI Wax	compound	odor descriptor	MF (%)	
			base wine (n = 18)	cava reserve (n = 18)
	ethyl esters			
924	ethyl propanoate + ni[a,c]	alcohol	59.6	73.9
987	ethyl isobutyrate	fruity, sweet	25.6	62.8
1053	ethyl butyrate	fruity, sweet	46.3	60.1
1067	ethyl 2-methylbutyrate[a]	fruity, sweet	20.9	64.5
1084	ethyl isovalerate	fruity, sweet	44.8	63.4
1230	ethyl butenoate[a]	fruity, floral	14.1	42.6
1258	ethyl hexanoate	fruity, strawberry, sweet	85.1	78.3
1370	ethyl lactate	cheese	9.0	26.3
1452	ethyl octanoate	fruity, strawberry, sweet	64.8	62.2
1708	diethyl succinate + ethyl 3-hydroxyhexanoate[a]	fruity, sugary, floral	0.0	37.5
2172	ethyl cinnamate[a]	sweet, smoked	24.8	2.9
	acetate esters			
1142	isoamyl acetate	banana, fruity, sweet	74.0	36.6
1296	hexyl acetate	ripe fruit	27.1	0.0
1851	2-phenylethyl acetate + β-damascenone	fruity, rose, jam	71.7	50.8
	alcohols			
1108	isobutanol	alcohol	24.1	20.5
1226	isoamyl alcohol	alcohol, cheese	70.2	65.7
1375	1-hexanol	grassy, floral	51.2	69.6
1408	*cis*-3-hexenol	grassy, vegetable, floral	57.1	58.9
1551	2-methylthioethanol[a]	grassy, vegetable	14.3	52.1
1750	methionol	boiled vegetable	42.4	47.5
1948	2-phenylethanol	floral, rose	66.5	67.8
2036	*o*-cresol + phenol[a]	species, celery, smoked	17.3	47.5
	aldehydes, ketones			
965	3-methylbutanal[a]	alcohol, solvent	31.6	28.6
1327	1-octen-3-one	mushroom	15.1	49.0
1415	2-nonanal[a]	grassy, acid, damp	25.8	36.9
1493	methional	vegetable, boiled potato	29.5	26.9
1512	decanal[a]	grassy, arugula	4.3	32.0
1685	phenylacetaldehyde[a]	floral	0.0	16.4
2621	vanilla[a]	vanilla	40.0	60.8
	furans, volatile phenols			
1342	2-methyl-3-furanthiol[a]	toasty, fried	6.0	41.1
1458	furfurylthiol[a]	dried fruits, toasty	3.0	15.5
1500	furfural	fruity, caramel	0.0	20.1
1533	acetylfuran[a]	balsamic	10.4	30.5
1613	5-methylfurfural[a]	fruity, caramel	0.0	18.0
2209	4-ethylphenol[a]	horse, leather	28.3	47.5
2066	Furaneol + 4-ethylguaiacol[a]	caramel	81.5	74.4
2114	ethylfuraneol + *m*-cresol[a]	plasteline, leather, rubber	36.7	63.0
	terpenes, lactones, C^{13} norisoprenoids			
1738	γ-hexalactone[a]	vegetable, legume	0.0	25.7
1897	guaiacol[a]	pharmacy, wood, toasty	24.6	49.5
2021	δ-octalactone[a]	cinnamon, caramel, fruity	24.9	51.0
2192	γ-decalactone	peach, syrup	28.6	53.4
2239	sotolon	species, caramel, maple	73.5	82.2
2248	δ-decalactone[a]	fruity, species, sweet	30.3	29.5
	acids			
1474	acetic acid	vinegar	66.0	77.0
1589	isobutyric acid	cheese, unpleasant	53.5	63.3
1651	butyric acid	cured cheese	84.1	87.0
1690	isovaleric acid	sweat, cheese	87.3	78.8
1866	hexanoic acid	cheese, acid	86.8	88.1
2076	octanoic acid	sweat, cheese	77.0	64.4
2303	decanoic acid + syringol[a]	rancid, phenol	53.2	50.0
	carbonyl compounds			
1004	diacetyl	butter, yeasty	0.0	59.6
1305	acetoin	rancid	0.0	25.2
	other compounds			
910	ni	alcohol	36.5	33.7
924	ni	fruity, sweet	70.7	77.7
1431	ni	mushroom	0.0	25.1
1566	*m*/*z* 42, 55, 102[b]	gas	51.6	77.8
1629	ni	caramel	22.4	48.1

Table 4. Continued

			MF (%)	
KI Wax	compound	odor descriptor	base wine (*n* = 18)	cava reserve (*n* = 18)
1665	2-acetylpyrazine	toasty, smoked	15.4	22.8
1723	*m*/*z* 58, 83, 111[b]	fish, unpleasant, vegetable	18.7	38.4
1761	ni (*m*/*z* 43, 71, 115, 158)[b]	boiled rice	0.0	36.4
1802	ni	dried fruits, toasty	11.1	35.0
1819	ni	unpleasant	10.4	51.0
1857	ni	balsamic, toasty	0.0	35.0
2112	ni	fruity, caramel	19.6	6.4
2355	ni	vegetable	20.2	52.9
2426	ni	feet, damp, leather	36.1	15.7
2447	ni	sweet, fruity	11.1	28.6
2496	ni	wax, soap	43.0	23.1
2608	ni	cheese, acid, unpleasant	42.1	52.4

[a] Tentatively identified. [b] Main mass fragments identified. [c] Not identified.

of contact with the lees. The great complexity of the wine matrix could also modify the retention of the volatile compounds on lees surface (*20*). This fact could benefit the final profile of cava.

Furans are compounds derived by sugar degradation and are partially responsible for the yeasty and toasty notes of aged wines (**Table 3**). Specifically, the Maillard reaction is responsible for the formation of furans and their yeasty aroma (*16*, *21*). These compounds were described in the literature as bread, almond, or sweet, but in the work by Comuzzo et al. (*21*) they were described as having a cheese or pungent note, as determined by GC-O in white wine. In the present study, furans such as furfural, 5-methylfurfural, 2-methyl-3-furanthiol, furfurylthiol, and acetylfuran were identified by the analysts as caramel, toasty, or dried fruits by olfactometric analysis (**Table 4**). All of these compounds were detected by sniffing in cava more than in base wine. Some of them may be important for the cava bouquet (*22*, *23*).

Acetoin or 3-hydroxybutanone is a compound involved in the bouquet of the wine and a key compound in the biosynthesis of diacetyl and 2,3-butanediol (*24*). These three compounds are similar, representing three levels of oxidation of a four-carbon molecule. Their odorous signification is erratic because acetoin has little smell, as can be seen in **Table 4**, whereas diacetyl has a characteristic nuance with a high MF% value, detectable in wine at a very low level (8 mg/L). The analysts described diacetyl as butter or yeasty (**Table 4**).

Acetal or 1,1-diethoxyethane is produced by the reaction between acetaldehyde and ethanol. Acetaldehyde is a volatile compound that comes from yeast and varies depending on the strain. In the current study the acetal content increased (**Table 3**). It is a compound typically found in some singular wines such as sherries (*25*) but which also appears in cava samples. Acetal produces a biscuit-type note according to the literature and could also be responsible for this different profile, although it was not detected in the current samples.

In conclusion, vitispiranes, TDN, or furans are compounds that increase their amounts during the aging process of cava. Moreover, the odor descriptions of the furans by olfactometric analysis were mainly attributes that characterize the bouquet of cava described in the sensory analysis (toasty, lactic, or sweet) that corresponds to furfurylthiol, 2-methyl-3-furanthiol, diacetyl, and some lactones. These volatile compounds are probably responsible for the great complexity of the cava profile. On the other hand, the specific compounds from wine are mainly acetate and ethyl esters, usually described as fruity, which could explain the predominantly fruity note found in the sensorial descriptive analysis of the base wine. Finally, the results of volatile composition and the GC-O analyses confirm the loss of freshness and the appearance of new compounds and sensory notes.

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LITERATURE CITED

(1) Council Regulation (EC) No. 479/2008 of 29 April 2008 on the common organisation of the market in wine, amending Regulations (EC) No. 1493/1999, (EC) No. 1782/2003, (EC) No. 1290/2005, (EC) No. 3/2008 and repealing Regulations (EEC) No. 2392/86 and (EC) No. 1493/1999.

(2) Campo, E.; Cacho, J.; Ferreira, V. The chemical characterization of the aroma of dessert and sparkling white wines (Pedro Ximénez, Fino, Sauternes, and Cava) by gas chromatography−olfactometry and chemical quantitative analysis. *J. Agric. Food Chem.* **2008**, *56*, 2477–2484.

(3) Campo, E.; Ferreira, V.; Escudero, A.; Cacho, J. Prediction of the wine sensory properties related to grape variety from dynamic-headspace gas chromatography−olfactometry data. *J. Agric. Food Chem.* **2005**, *53*, 5682–5690.

(4) Noble, A. C.; Ebeler, S. E. Use of multivariate statistics in understanding wine flavor. *Food Rev. Int.* **2002**, *18*, 1–21.

(5) Torrens, J.; Urpí, P.; Riu-Aumatell, M.; Vichi, S.; López-Tamames, E.; Buxaderas, S. Different commercial yeast strains affecting the volatile and sensory profile of cava base wine. *Int. J. Food Microbiol.* **2008**, *124*, 48–57.

(6) Francioli, S.; Torrens, J.; Riu-Aumatell, M.; López-Tamames, E.; Buxaderas, S. Volatile compounds by SPME-GC as age markers of sparkling wines. *Am. J. Enol. Vitic.* **2003**, *54*, 158–162.

(7) Riu-Aumatell, M.; Bosch-Fusté, J.; López-Tamames, E.; Buxaderas, S. Development of volatile compounds of cava (spanish sparkling wine) during long aging time in contact with lees. *Food Chem.* **2006**, *95*, 237–242.

(8) Bosch-Fusté, J.; Riu-Aumatell, M.; Guadayol, J. M.; Caixach, J.; López-Tamames, E.; Buxaderas, S. Volatile profiles of sparkling wines obtained by gas chromatography−mass spectrometry (GC-MS) analysis. *Food Chem.* **2007**, *105*, 428–435.

(9) De la Presa-Owens, C.; Schlich, P.; Davies, H. D.; Noble, A. C. Effect of mèthode champenoise process on aroma of four *V. vinifera* varieties. *Am. J. Enol. Vitic.* **1998**, *49*, 289–294.

(10) Vannier, A.; Brun, O. X.; Feinberg, M. H. Application of sensory analysis to champagne wine characterisation and discrimination. *Food Qual. Pref.* **1999**, *10*, 101–107.

(11) Escudero, A.; Charpentier, M.; Etiévant, P. X. Characterization of aged champagne wine aroma by GC-O and descriptive profile analyses. *Sci. Aliment.* **2000**, *20*, 331–346.

(12) EC regulation No. 2676/90. 1990 Reglamento por el que se determinan los métodos de análisis aplicables en el sector del vino.
(13) Dravnieks, A. *Atlas of Odor Character Profiles*; ASTM: Philadelphia, PA, 1985; p 354.
(14) Bautista, R.; Fernández, E.; Falqué, E. Effect of the contact with fermentation-lees or commercial lees on the volatile composition of white wines. *Eur. Food Res. Technol.* **2007**, *224*, 405–413.
(15) Rapp, A. Volatile flavour of wine: correlation between instrumental analysis and sensory perception. *Nahrung* **1998**, *42*, 351–363.
(16) Genovese, A.; Gambuti, A.; Piombino, P.; Moio, L. Sensory properties and aroma compounds of sweet Fiano wine. *Food Chem.* **2007**, *103*, 1228–1236.
(17) García, E.; Chacón, J. L.; Martínez, J.; Izquierdo, P. M. Changes in volatile compounds during ripening in grapes of Airén, Macabeo and Chardonnay white varieties grown in La Mancha region (Spain). *Food Sci. Technol. Int.* **2003**, *9*, 33–41.
(18) Chalier, P.; Angot, B.; Delteil, D.; Doco, T.; Gunata, Z. Interactions between aroma compounds and whole mannoprotein isolated from *Saccharomyces cerevisiae* strains. *Food Chem.* **2007**, *100*, 22–30.
(19) Pérez-Serradilla, J. A.; Luque de Castro, M. D. Role of lees in wine production: a review. *Food Chem.* **2008**, *111*, 447–456.
(20) Jiménez Moreno, N.; Ancín Azpilicueta, C. Binding of oak volatile compounds by wine lees during simulation of wine aging. *LWT—Food Sci. Technol.* **2007**, *40*, 619–624.
(21) Comuzzo, P.; Tat, L.; Tonizzo, A.; Battistutta, F. Yeast derivatives (extracts and autolysates) in winemaking: release of volatile compounds and effects on wine aroma volatility. *Food Chem.* **2006**, *99*, 217–230.
(22) Blanchard, L.; Tominaga, T. Y.; Dubordieu, D. Formation of furfurylthiol exhibiting a strong coffee aroma during oak barrel fermentation from furfural released by toasted staves. *J. Agric. Food Chem.* **2001**, *49*, 4833–4835.
(23) Tominaga, T.; Dubourdieu, D. A novel method for quantification of 2-methyl-3-furanthiol and 2-furanmethanethiol in wines made from *Vitis vinifera* grape varieties. *J. Agric. Food Chem.* **2006**, *54*, 29–33.
(24) Romano, P.; Suzzi, G. Origin and production of acetoin during wine yeast fermentation. *Appl. Environ. Microbiol.* **1996**, *62*, 309–315.
(25) Peinado, R. A.; Moreno, J. A.; Muñoz, D.; Medina, M.; Moreno, J. Gas chromatographic quantification of major volatile compounds and polyols in wine by direct injection. *J. Agric. Food Chem.* **2004**, *52*, 6389–6393.

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