Analytical Methods

Effect of skin contact on bound aroma and free volatiles of Listán blanco wine

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Abstract

Listán blanco is the major grape variety of the Canary Islands. Aroma precursors in musts and free volatiles in wines and their variations due to the skin contact process (10 °C and 0–12 h of maceration) were determined in samples of the Listán blanco grape variety. Aroma precursors of must were isolated by absorption on XAD-2 resin and the aglycone liberated by means of acid hydrolysis. Free volatiles from wines and from aroma precursors were extracted with dichloromethane and then analysed by GC-MS. The results of two consecutive vintages show that only aroma precursors of some terpenes and phenols may affect the final wine aroma. However, the majority of the free compounds of the wines did not present differences in content that could be related to the skin contact process. © 2008 Elsevier Ltd. All rights reserved.

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1. Introduction

Compounds from the grape variety can contribute to the aromatic characteristics of wines. Such compounds are present in grapes as free volatiles, which may contribute directly to the aroma, and as non-volatile bound forms, called aroma precursors. These bound forms are mainly volatile compounds linked to the sugars as O-glycosides (Günata, Bayonove, Baumes, & Cordonnier, 1985a, 1985b) and cysteine derivatives (Tominaga, Peyrot des Gachons, & Dubourdieu, 1998) and they can contribute to wine aroma after hydrolysis during the wine-making process and storage.

The enzymatic or acid hydrolysis of glycosidic precursors can yield free volatiles, mainly monoterpenenes, C13 nor-isoprenoids and phenolic derivatives (Günata et al. 1985a, 1985b; Sefton et al., 1993; Selli et al., 2003; Versini et al., 1994). Other compounds such as higher alcohols,

organic acids, lactones and carbonyl compounds have also been determined after acid hydrolysis (Cabaroglu, Canbas, Lepoutre, & Günata, 2002; Cabaroglu et al., 1997; Sánchez-Palomo, Pérez-Coello, Dıaz-Maroto, González-Viñas, & Cabezudo, 2006; Selli et al., 2003).

Taking into account that the compounds responsible for varietal aroma predominate in grape skins (Cordonnier, Günata, Baumes, & Bayonove, 1989; Günata et al., 1985b; Sánchez-Palomo, Dıaz-Maroto, & Pérez-Coello, 2005), the prefermentative "skin contact" technique can be used to extract these compounds and probably improve wine quality.

Studies performed by Baumes, Bayonove, Barillere, Escudier, and Cordonnier (1988), in white varieties (Chenin, Chardonnay and Bourboulenc) showed that the macerated musts presented total contents of free volatiles greater than control musts, mainly in aldehydes and alcohols with 6 carbon atoms. In wines the effect observed was an increase in the greater part of volatile compounds with the exception of volatile acids (Baumes, Bayonove, Barillere, Escudier, & Cordonnier, 1989).

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Other studies in musts of Muscat of Bornova and Narince showed that the concentration of bound aroma compounds increased due to the skin contact process, while bound C6 aldehydes and alcohols contents presented lower values than free compounds (Selli et al., 2003). Arnold and Noble (1979), in Chardonnay wines from different maceration times (6, 12 and 16 h) observed that total aroma of wine from 16 h macerated must was higher than that of other wines with shorter contact times. Moreover, fruity aroma exhibited a non-linear increase and was higher in non-macerated and 16 h macerated wines. Bitterness and astringency of wines did not present differences with the maceration time. Other studies in Muscat wines macerated for 6 and 12 h did not present a uniform increase in the levels of aromatic compounds related to maceration time. Nevertheless, the wine macerated for 6 h presented a higher fruity aroma than the 12 h macerated wine and, contrarily, the wine macerated for 12 h presented a lower quality than the wine macerated for 6 h (Selli, Canbas, Cabaroglu, Erten, & Günata, 2006a).

Listán blanco is the main white variety of the Canary Islands and represents 90% of white cultivars. This variety has good yields but it is limited in aromas. One possibility to improve the quality of the aroma of its wines may be to exploit the different aromas present in must and skins as aroma precursors.

The aim of this work is to determine the aroma liberated by the aroma precursors present in the must of Listán blanco variety after 0, 4, 8 and 12 h of skin contact, and to study their effect on the volatile composition of the wines elaborated with these musts.

2. Materials and methods

2.1. Reagents and solvents

Dichloromethane, diethyl ether, methanol, *n*-pentane and ethyl acetate of HPLC quality was obtained from Lab-Scan (Dublin, Ireland), absolute ethanol p.a. from Merck (Darmstadt, Germany) and pure water was obtained from a Milli-Q purification system (Millipore). Amberlite XAD-2 resins from Supelco (Bellefonte, PA). Ammonium sulphate (anhydrous), sodium hydroxide, $NaH_2PO_4–H_2O$ and L-(+)-tartaric acid from Panreac (Barcelona, Spain). Pure reference compounds were supplied by Aldrich (Gillinghan, UK), Fluka (Buchs, Switzerland), Riedel de Häen (Seelze, Germany) and Firmenich (Geneva, Switzerland).

2.2. Samples and winemaking

Listán blanco grapes of two consecutive vintages (10-09-2002 and 12-09-2003) harvested in La Guancha (Tenerife) were destemmed, lightly crushed and 20 mg/L of sulphites and 4 g/Hl of pectolytic enzymes Novo speed – B100 (Novo Nordisk Ferment, Switzerland) added. Then the paste was kept at 10 °C and after 0, 4, 8 and 12 h of skin

contact parts of the paste were taken and pressed and the musts were fermented in duplicate in 1000 L-stainless steel tanks. Simultaneously, samples of must were taken at 0, 4, 8 and 12 h for analysis. To the must samples were added 30 ml of a $CaCl_2$ solution to inhibit the enzymatic processes and the mixtures were then stored frozen until analysis.

2.3. Standard chemical analysis

The different parameters were established as follows: Brix was measured by using a refractometer (Comecta, Barcelona, Spain); pH using a pH-meter pH 197-S (WTW, Weilheim, Germany), % vol by using an ebullometer (Gab, Barcelona, Spain), total acidity by potentiometric titration with sodium hydroxide 0.1 M until pH 7.0 (MAPA, 1993); tartaric acid by reaction with ammonium metavanadate and measuring the absorbance at 500 nm in a Cary 50 spectrophotometer (Varian, Walnut Creek, CA) (Vidal & Blouin, 1978); malic acid by use of an enzymatic kit (Boehringer-Manhein, Germany) (MAPA, 1993); and residual sugars by addition of an excess of a cupric solution, iodide and titration of the iodine formed with sodium thiosulphate (Rebelein, 1973).

2.4. Isolation of bound aroma of must

The aroma precursors were isolated from the must by adsorption on Amberlite XAD-2 resins (Günata et al., 1985a). The samples were passed through the Amberlite XAD-2 resins and the water-soluble compounds were eluted with 50 ml of water, the free volatiles with 75 ml of pentane and the aroma precursors with 75 ml of ethyl acetate. The flow rate was about 2 ml/min. The ethyl acetate eluate was concentrated to dryness in vacuo and dissolved in 5 ml of a model solution at pH 3.2 (6 gr/L tartaric acid; 13% v/v ethanol; pH was adjusted with a NaOH solution) to hydrolyze at 50 °C over 28 days to liberate the free aroma.

2.5. Extraction of the volatile compounds liberated by the precursors

After liberation of the volatile compounds, 100 μl of an internal standard solution (50 mg/L of 4-methyl-2-pentanol and 2-ethyl-1-hexanol in 13% v/v ethanol), 5 ml of Milli-Q water and 1.5 g of ammonium sulphate were added and the volatiles were then extracted with 1 mL of dichloromethane with continuous shaking for 1 h at room temperature (25 °C). The organic phase was recovered and transferred to a 2 ml glass vial and stored at −20 °C. The calibration graphs were made by extraction of standard solutions with dichloromethane.

2.6. Extraction of volatile compounds of the wines

Free volatiles of wines were extracted with dichloromethane based on a method proposed by Ferreira, López,

Escudero, and Cacho (1998). To 10 ml of wine, 100 μl of an internal standard solution and 1.5 g of ammonium sulphate were added and the volatiles extracted with 100 μl of dichloromethane with continuous shaking for 1 h at room temperature (25 °C). The organic phase was recovered and transferred to a 200 μl glass vial and stored at −20 °C. The calibration graphs were made by extraction of standard solutions with dichloromethane.

2.7. Chromatographic analysis

The separations were performed using a gas chromatograph (Varian CP-3800) equipped with a mass spectrometer detector (Varian Saturn 2000). The chromatographic column was a capillary column DB-WAXETR (60 m × 0.25 mm i.d. × 0.5 μm film thickness, J&W Scientific) and the oven temperature programme was 40 °C (15 min), 2 °C/min up to 240 °C and 240 °C (45 min). The flow of car-

rier gas (He) was 2 mL/min. The volume of injection was 1 μL in splitless mode. Data acquisition was made in different segments with electronic impact mode and chemical ionization mode (CI reagent: Methanol). The identification of each compound was carried out using the spectra obtained with standard compounds and from the NIST library. Retention times and quantification ions of each compound are presented in Table 1.

2.8. Major volatile compound analysis

The analysis of major volatile compounds of wine (methanol, isobutanol, 1-propanol, 2-methyl-1-butanol, 3-methyl-1-butanol and ethyl acetate) was performed by direct injection of wine into a gas chromatograph (Varian Star 3400) equipped with a FID detector. The chromatographic column was a capillary column Chrompack CP Wax 57 (50 m × 0.25 mm i.d. × 0.20 μm film thickness,

Table 1
Retention times and quantification ions of each compound analysed

Compound	Time	Q ions	Compound	Time	Q ions
Ethyl isobutyrate	14.58	43 + 71 + 29	Acetophenone	66.82	105
Propyl acetate	15.33	43 + 73 + 61	Furfuryl alcohol	67.24	97 + 98 + 41 + 42
2,3-Butanedione	15.93	43 + 42	Ethyl benzoate	67.69	105 + 77
Isobutyl acetate	18.68	43 + 56	2-Methylbutyric acid	67.87	87
Ethyl butyrate	20.83	71 + 43 + 88	Isovaleric acid	67.95	60
1-Propanol	21.16	31	Diethyl succinate	67.97	101 + 129
2-Methyl-3-buten-2-ol	21.36	71 + 43	α-Terpineol	69.13	59 + 93 + 121 + 136
Ethyl 2-methylbutyrate	22.23	57 + 102 + 41	3-(Methylthio)-1-propanol	70.42	106 + 61 + 57 + 31
Butyl acetate	24.23	56 + 43	Benzyl acetate	71.27	108 + 91 + 90
Hexanal	25.06	41 + 44 + 56	β-Phenylethyl acetate	76.08	104
Isobutanol	25.89	41 + 42 + 31	β-Damascenone	76.25	69 + 121 + 190
Isoamyl acetate	28.71	43 + 55 + 70	Ethyl dodecanoate	76.97	88 + 101
1-Butanol	30.57	41 + 56 + 31	Hexanoic acid	77.61	60
4-Methyl-2-pentanol (IS)	32.41	45 + 43 + 69	Guaiacol	78.55	109 + 81 + 124
(2 + 3)-Methyl-1-butanol	35.83	41 + 55 + 70	Benzyl alcohol	79.34	79 + 108 + 107
Ethyl hexanoate	38.03	88 + 99 + 43	Ethyl hydrocinnamate	79.73	104
Hexyl acetate	41.08	43 + 56	Phenylethyl alcohol	81.15	91 + 92 + 65
Propyl acetate	42.28	45 + 43	γ-Nonalactone[a]	87.18	139
2-Heptanol	44.47	45	4-Ethylguaiacol[a]	87.22	153 + 152
Ethyl lactate	46.50	45	Furaneol[a]	87.22	129 + 128
1-Hexanol	46.96	56 + 43 + 41 + 55	Octanoic acid	88.46	60 + 73
cis-3-Hexen-1-ol	49.29	41 + 67 + 55 + 82	2-Methoxy-4-propylphenol	90.99	137
Ethyl octanoate	52.64	88 + 57 + 101	γ-Decalactone	92.70	85
trans-Linalool oxide[a]	53.20	153 + 152 + 135	Eugenol	93.77	164 + 139 + 103
1-Heptanol[a]	53.98	57 + 55 + 56	4-Ethylphenol	94.16	107 + 122
cis-Linalool oxide[a]	55.07	153 + 152	2-Methoxy-4-vinylphenol	95.16	135 + 150 + 107 + 77
2-Furaldehyde[a]	55.23	97 + 96 + 98	2.6-Dimethoxyphenol	98.19	154 + 139 + 93
2-Ethyl-1-hexanol (IS)[a]	56.27	57	Decanoic acid	98.33	60 + 73
Ethyl 3-hydroxybutyrate	58.39	43 + 45	4-Vinylphenol	103.89	120 + 91
Benzaldehyde	59.02	77 + 105 + 106	Benzophenone[a]	107.68	183 + 184
Linalool	59.97	71 + 93	4-Allyl-2.6-dimethoxyphenol[a]	109.78	195
1-Octanol	60.53	41 + 56	Vanillin[a]	111.05	153
Isobutyric acid[a]	61.81	89	Methyl vanillate[a]	112.50	183 + 182 + 151
Ethyl 2-furoate	65.06	112	Ethyl vanillate[a]	113.52	197 + 196 + 151
Methyl benzoate	65.10	105	4-Hydroxy-3-methoxyacetophenone[a]	113.92	167
Butyric acid	65.45	60	Vanillylacetone[a]	120.59	137
Ethyl decanoate	65.45	88 + 101	Methyl 4-hydroxybenzoate[a]	129.43	153
Isoamyl octanoate	66.59	70	4-Hydroxybenzaldehyde[a]	130.15	123

IS = Internal Standard.
[a] Analysed by chemical ionization.

Varian) and the oven temperature programme was 60 °C (5 min), 8 °C/min up to 130 °C and 20 °C/min up to 180 °C. Head column pressure was 20 psi and the injection volume was 1 μL in split mode (1/60).

3. Results and discussion

3.1. Classical parameters of musts and wines

The values of classical parameters of control musts and wines of each vintage are given in Table 2. As can be seen, both musts presented similar pH and total acidity, but the control must of the first vintage had higher values in Brix and tartaric acid, and a lower value in malic acid than the control must of the second vintage. On the other hand, the control wine of the second vintage presented a lower pH and higher values in total acidity and tartaric acid, which is due to a correction of the acidity with tartaric acid. Likewise, the wines of the second vintage presented a higher value in reducing sugar and malic acid and a lower value in % of ethanol.

3.2. Bound aroma compounds of the musts

The results obtained in the analysis of the volatile compounds released by aroma precursors after acid hydrolysis of control musts (non-macerated) and at three maceration times (4, 8 and 12 h) of the two vintages are presented in Table 3. Fifteen and sixteen compounds from the more important chemical families of aroma precursors were quantified, respectively, in the first and second vintages, at least in one of the samples. These compounds included terpenes (4 in both vintages), phenols (3 and 5 in first and second vintages, respectively) and phenol derivatives (8 and 7 in first and second vintages, respectively). Fourteen of these compounds were common to both vintages. Moreover, further compounds from other chemical families (esters, alcohols, carbonyl compounds, lactones and acids) were quantified in much lower yields than those generated during the alcoholic fermentation.

With the exception of total terpenes, phenols and benzenic derivatives presented significant differences in total content between the control musts of both vintages. Thus, the total content of phenols was significantly higher in the control musts of the first vintage, while to the contrary the total content in benzenic derivatives showed significantly higher levels in the control musts of the second vintage. These differences between years are related to the climatic conditions of each year. In general, in the majority of published works important differences are observed in aroma precursor content among several vintages, which are attributed to differences in climatic conditions (Sefton et al., 1993; Schneider, Razungles, Augier, & Baumes, 2001).

In general, the macerated musts of both years showed higher contents than the control musts in the greater part of the compounds released by the aroma precursors. Furthermore, the majority of these compounds presented their highest content in the musts macerated for 8 h in the first vintage and either four or eight hours in the second vintage.

The content of terpenes, linalool, α-terpineol, benzene derivatives, benzyl alcohol and β-phenylethanol found in Listán blanco musts, as expected, were lower than those of aromatic varieties such as Muscat or Riesling (Günata et al. 1985a, 1985b). Other varieties such as Chardonnay (Sefton et al., 1993), Melon B. (Schneider et al., 2001), Narince (Selli et al., 2003), Amaral and Avesso (Oliveira et al., 2003) showed contents in bound terpenes similar to or lower than those of Listán blanco. In the case of benzyl alcohol, Listán blanco musts showed similar levels to those found in other non-aromatic varieties such as Chardonnay (Sefton et al., 1993) and Narince (Selli et al., 2003) or lower levels than in Albillo, Airén, Jaén and Malvar blanco musts (Muñoz-Organero & Ortiz, 1997) or Albariño musts (Diéguez, Lois, Gómez, & de la Peña, 2003). Finally, β-phenylethanol presented higher levels in Listán blanco musts than those found in Chardonnay musts and lower values than those of the other five above-mentioned varieties.

3.3. Free aroma compounds of the wines

The results of the analysis of wine volatiles at 4 maceration times (0 or control wines, 4, 8 and 12 h) of two vintages are presented in Tables 4 and 5. Fifty-eight and fifty-one compounds (including terpenes, norisoprenoids, phenols, alcohols, esters, acids, carbonyl compounds, lactones and others) were identified and quantified in the first and second vintages, respectively.

Control wines of the first vintage presented significantly higher mean contents than control wines of the second vintage in phenols, benzenic derivatives, esters (both ethyl esters and acetate esters), acids and thiols. In contrast, control wines from the second vintage showed a significantly higher mean content in alcohols (even in C6 alcohols). The differences between the two vintages may be related to the initial composition of musts and to the fermentation

Table 2
Classical parameters of control musts and wines of each vintage

	First vintage	Second vintage
Control musts		
pH	3.30	3.34
Total acidity (g/L tartaric acid)	5.52	5.66
Brix	21.2	20.6
Malic acid (g/L malic acid)	0.52	0.96
Tartaric acid (g/L tartaric acid)	4.81	4.52
Control wines		
pH	3.22	2.92
Total acidity (g/L tartaric acid)	5.81	7.34
Ethanol (% v/v)	12.3	12.1
Residual sugars (g/L)	0.5	1.0
Malic acid (g/L malic acid)	0.40	0.64
Tartaric acid (g/L tartaric acid)	4.40	5.10

Table 3
Bound aroma compounds of control and macerated musts (µg/Kg of must)

Compound	Control	4 h	8 h	12 h	F	p
First vintage						
Terpenic compounds						
trans-Linalool oxide	$3.5 \pm 0.10_a$	6.8 ± 0.19^b	7.8 ± 0.21^d	5.3 ± 0.15^c	374.11	0.0000
cis-Linalool oxide	2.2 ± 0.06^a	3.9 ± 0.11^b	4.6 ± 0.13^d	2.9 ± 0.08^c	352.76	0.0000
Linalool	d.m.s.	0.5 ± 0.02^c	0.4 ± 0.01^b	0.2 ± 0.01^a	374.46	0.0000
α-Terpineol	7.7 ± 0.22^a	15.1 ± 0.43^c	16.6 ± 0.47^d	11.3 ± 0.32^b	347.5	0.0000
Total	13.4^a	26.3^c	29.4^d	19.7^b	363.0	0.0000
Volatile phenols						
4-Ethylphenol	0.7 ± 0.02^b	0.5 ± 0.01^a	1.7 ± 0.05^c	2 ± 0.06^d	1051.74	0.0000
2-Methoxy-4-vinylphenol	11.1 ± 0.42^b	7.1 ± 0.27^a	14.8 ± 0.56^d	12.5 ± 0.48^c	159.29	0.0000
4-Ethylguaiacol	0.3 ± 0.01^a	0.3 ± 0.02^a	0.5 ± 0.03^b	d-n.q.	137.53	0.0000
Total	12.1^b	7.9^a	17.0^d	14.5^c	182.9	0.0000
Benzenic compounds						
Benzyl alcohol	23.9 ± 0.50^a	30.4 ± 0.63^b	61.2 ± 1.27^d	35.2 ± 0.73^c	1155.94	0.0000
Phenylethyl alcohol	18.2 ± 0.53^a	23.4 ± 0.68^b	59.9 ± 1.74^c	32 ± 0.93^d	892.05	0.0000
Methyl vanillate	0.8 ± 0.05^a	n.d.	2.4 ± 0.15^c	1.5 ± 0.09^b	176.68	0.0000
Ethyl vanillate	0.3 ± 0.03^a	n.d.	1.3 ± 0.10^b	0.3 ± 0.02^a	228.45	0.0000
Methyl 4-hydroxybenzoate	d-n.q.	n.d.	4.5 ± 0.60^b	2.7 ± 0.36^a	26.12	0.0105
Vanillin	10.4 ± 0.6^b	3.2 ± 0.19^a	16.2 ± 0.93^d	12.4 ± 0.72^c	201.78	0.0000
4-Hydroxybenzaldehyde	28.6 ± 4.06^b	9.1 ± 1.30^a	75.3 ± 10.7^d	43.2 ± 6.13^c	54.99	0.0000
Vanillylacetone	1.0 ± 0.17^a	d-n.q.	4.1 ± 0.72^c	2.3 ± 0.41^b	30	0.0008
Total	83.2^a	66.1^a	225^c	130^b	155	0.0000
Second vintage						
Terpenic compounds						
trans-Linalool oxide	5.2 ± 0.14^a	5.5 ± 0.15^b	6 ± 0.16^c	5.7 ± 0.15^b	17.02	0.0008
cis-Linalool oxide	2.6 ± 0.07^a	2.8 ± 0.08^b	2.9 ± 0.08^c	$2.8 \pm 0.08^{b,c}$	11.77	0.0003
Linalool	0.4 ± 0.01^b	0.4 ± 0.01^b	0.5 ± 0.01^c	0.4 ± 0.01^a	43.21	0.0000
α-Terpineol	5.3 ± 0.15^a	7.3 ± 0.21^c	5.8 ± 0.16^b	5.3 ± 0.15^a	91.96	0.0000
Total	13.5^a	16.0^b	15.2^b	14.1^a	21.53	0.0003
Volatile phenols						
Guaiacol	d-n.q.	d-n.q.	0.2 ± 0.01^a	0.2 ± 0.01^b	22.79	0.0088
Eugenol	0.6 ± 0.02^a	0.8 ± 0.02^d	0.7 ± 0.02^b	0.7 ± 0.02^c	59.65	0.0000
4-Ethylphenol	1.5 ± 0.04^b	1.5 ± 0.04^b	1.5 ± 0.04^b	1.4 ± 0.04^a	8.59	0.0070
2-Methoxy-4-vinylphenol	2.7 ± 0.10^a	4.1 ± 0.16^c	3.2 ± 0.12^b	4.0 ± 0.15^c	71.86	0.0000
4-Ethylguaiacol	0.9 ± 0.04	n.d.	n.d.	n.d.		
Total	5.7^a	6.4^b	5.6^a	6.3^b	13.6	0.0017
Benzenic compounds						
Benzyl alcohol	20 ± 0.41^a	38.5 ± 0.80^b	43.5 ± 0.90^c	52.8 ± 1.09^d	813.64	0.0000
Phenylethyl alcohol	29.7 ± 0.86^a	67.3 ± 1.96^c	57.7 ± 1.68^b	78.3 ± 2.28^d	413.27	0.0000
Methyl vanillate	0.5 ± 0.03^a	1 ± 0.07^b	0.5 ± 0.03^a	1 ± 0.06^b	91.96	0.0000
Ethyl vanillate	d-n.q.	0.3 ± 0.03	n.d.	n.d.		
Methyl 4-hydroxybenzoate	d-n.q.	2.6 ± 0.34	d-n.q.	d-n.q.		
Vanillin	12.5 ± 0.72^b	16.0 ± 0.92^c	9.1 ± 0.52^a	9.7 ± 0.56^a	61.11	0.0000
4-Hydroxybenzaldehyde	40.9 ± 5.81^a	85.9 ± 12.2^b	40.7 ± 5.77^a	40.9 ± 5.81^a	24.76	0.0002
Total	104^a	212^d	151^b	183^c	51.05	0.0000

Different superscripts (a–d) mean significant differences ($p < 0.05$) between the average values.
±SD; d.m.s. = detected by mass spectrometry; d-n.q. = detected not quantified; n.d. = not detected.

conditions in each year. The levels of esters, acids and alcohols generated during alcoholic fermentation are affected by fermentation conditions. Lower levels of esters in the second vintage may be related to the lower pH of the wine in this vintage. On the other hand, the contents in some phenols and benzenic derivatives may be related to free or bound compounds of the grapes and to chemical transformations or may be generated during alcoholic fermentation (Etievant, 1991). Moreover, higher contents in

ethylphenols may be related to the presence of the brettanomyces bacterium (Chatonnet, Dubordieu, Boidron, & Lavigne, 1993).

Regarding the maceration process, in both vintages the total content of volatiles was higher in the macerated wines (381–398 mg/L and 356–360 mg/L) than in the control wines (358 and 351 mg/L) but these differences were not significant. The most dominant compounds of wines were higher alcohols, followed by esters, acids and phenols.

Table 4
Free aroma compounds (first vintage) of control and macerated wines (mg/l)

	Control	4 h	8 h	12 h	F	p
Terpenic compounds						
Linalool	0.032 ± 0.007	0.041 ± 0.005	0.048 ± 0.002	0.049 ± 0.002	ns	
α-Terpineol	0.038 ± 0.000	0.046 ± 0.014	0.048 ± 0.000	0.051 ± 0.000	ns	
Total	0.070	0.087	0.096	0.100	ns	
C13 Nor-isoprenoids						
β-Damascenone	d-n.q.[a]	0.007 ± 0.001[b]	0.008 ± 0.000[b]	0.007 ± 0.000[b]	26.2	0.0043
Volatile phenols						
4-Ethylphenol	0.289 ± 0.203	0.226 ± 0.320	n.d.	n.d.	ns	
4-Ethylguaiacol	0.229 ± 0.323	0.161 ± 0.228	d.m.s.	d.m.s.	ns	
4-Vinylphenol	0.869 ± 0.653[a]	2.80 ± 0.40[b]	3.97 ± 0.21[b]	3.85 ± 0.56[b]	17.4	0.0093
2-Methoxy-4-vinylphenol	0.070 ± 0.046	0.105 ± 0.081	0.258 ± 0.026	0.214 ± 0.085	ns	
2,6-Dimethoxyphenol	n.d.	n.d.	0.014 ± 0.020	n.d.	ns	
4-Allyl-2,6-dimethoxyphenol	0.021 ± 0.004	0.021 ± 0.001	0.023 ± 0.001	0.012 ± 0.017	ns	
2-Methoxy-4-propylphenol	0.019 ± 0.027	n.d.	n.d.	n.d.	ns	
Total	1.50[a]	3.31[b]	4.26[b]	4.08[b]	9.97	0.0250
Benzenic compounds						
Benzyl alcohol	0.062 ± 0.039	0.098 ± 0.032	0.115 ± 0.015	0.179 ± 0.044	ns	
Phenylethyl alcohol	31.2 ± 20.8	32.2 ± 4.8	27.3 ± 13.9	26.7 ± 3.9	ns	
Methyl vanillate	0.033 ± 0.020	0.027 ± 0.003	0.031 ± 0.002	0.028 ± 0.004	ns	
Methyl 4-hydroxybenzoate	0.031 ± 0.008	n.d.	0.015 ± 0.021	n.d.	ns	
Total	31.3	32.4	27.5	26.9	ns	
Higher alcohols						
1-Hexanol	0.155 ± 0.158	0.119 ± 0.077	0.16 ± 0.013	0.158 ± 0.003	ns	
cis-3-Hexen-1-ol	0.199 ± 0.128	0.170 ± 0.063	0.170 ± 0.007	0.168 ± 0.005	ns	
Total C6 alcohols	0.354	0.289	0.330	0.326	ns	
Methanol	30.7 ± 3.3[a]	33.9 ± 1.5[a,b]	40.8 ± 3.2[b,c]	44.6 ± 4.3[c]	7.77	0.0382
1-Propanol	27.6 ± 3.3	31.7 ± 2.7	28.5 ± 3.5	30.1 ± 2.2	ns	
Isobutanol	16.5 ± 2.3	16.9 ± 2.6	17.1 ± 1.5	16.4 ± 0.5	ns	
1-Butanol	1.74 ± 0.89	1.55 ± 0.43	1.84 ± 0.19	2.11 ± 0.66	ns	
(2 + 3)-Methyl-1-butanol	160 ± 33	159 ± 11	165 ± 4	156 ± 1	ns	
2-Heptanol	0.021 ± 0.005	0.011 ± 0.015	0.021 ± 0.002	0.012 ± 0.016	ns	
1-Heptanol	0.262 ± 0.197	0.171 ± 0.061	0.240 ± 0.019	0.268 ± 0.034	ns	
1-Octanol	0.024 ± 0.005	0.024 ± 0.002	0.025 ± 0.001	0.028 ± 0.002	ns	
Furfuryl alcohol	0.132 ± 0.145	0.119 ± 0.127	d.m.s.	n.d.	ns	
Furaneol	0.134 ± 0.087	0.072 ± 0.102	0.116 ± 0.000	0.106 ± 0.003	ns	
Total	237	243	254	250	ns	
Esters						
Ethyl butyrate	0.164 ± 0.074	0.177 ± 0.044	0.262 ± 0.035	0.236 ± 0.034	ns	
Ethyl 2-methylbutyrate	0.010 ± 0.014	n.d.	0.023 ± 0.001	n.d.	ns	
Ethyl hexanoate	0.650 ± 0.151	0.758 ± 0.166	1.05 ± 0.04	0.919 ± 0.175	ns	
Ethyl octanoate	0.941 ± 0.295	1.00 ± 0.35	1.30 ± 0.02	1.01 ± 0.39	ns	
Ethyl 3-hydroxybutyrate	0.753 ± 0.668	0.979 ± 0.438	0.836 ± 0.032	1.11 ± 0.03	ns	
Ethyl 2-furoate	0.018 ± 0.010	0.022 ± 0.008	0.030 ± 0.003	0.034 ± 0.004	ns	
Ethyl decanoate	0.078 ± 0.065	0.068 ± 0.005	0.143 ± 0.029	0.093 ± 0.021	ns	
Ethyl benzoate	0.030 ± 0.001	n.d.	0.028 ± 0.000	n.d.	ns	
Ethyl dodecanoate	n.d.	n.d.	n.d.	0.091 ± 0.128	ns	
Ethyl hydrocinnamate	0.011 ± 0.016	n.d.	n.d.	n.d.	ns	
Total ethyl esters	2.65	3.01	3.67	3.49	ns	
Ethyl acetate	60.4 ± 9.7	67.4 ± 4.9	70.8 ± 4.1	77.2 ± 0.0	ns	
Isobutyl acetate	d-n.q.[a]	d-n.q.[a]	0.065 ± 0.001[b]	0.070 ± 0.003[c]	202.01	0.0001
Propyl acetate	0.068 ± 0.021	0.070 ± 0.024	0.104 ± 0.001	0.103 ± 0.004	ns	
Isoamyl acetate	1.56 ± 0.06[a]	1.69 ± 0.07[a]	2.39 ± 0.14[b]	2.36 ± 0.24[b]	17.29	0.0094
Hexyl acetate	0.115 ± 0.027	0.181 ± 0.046	0.162 ± 0.072	0.187 ± 0.053	ns	
Benzyl acetate	n.d.	n.d.	0.007 ± 0.009	n.d.	ns	
β-Phenylethyl acetate	0.222 ± 0.102	0.253 ± 0.015	0.285 ± 0.010	0.291 ± 0.032	ns	
Total acetates	62.4	69.6	73.8	80.2	ns	
Diethyl succinate	0.733 ± 0.592	0.913 ± 0.164	1.03 ± 0.02	1.21 ± 0.26	ns	

Table 4 (continued)

	Control	4 h	8 h	12 h	F	p
Total	65.8	73.5	78.5	84.9	ns	
Acids						
Butyric acid	4.34 ± 1.88	6.18 ± 1.99	4.90 ± 0.03	6.13 ± 0.65	ns	
2-Methylbutyric acid	1.12 ± 0.99	1.59 ± 0.62	1.50 ± 0.13	1.69 ± 0.12	ns	
Isovaleric acid	0.762 ± 0.729	1.19 ± 0.51	1.01 ± 0.14	1.17 ± 0.03	ns	
Hexanoic acid	6.12 ± 4.47	8.32 ± 2.39	8.54 ± 0.25	9.73 ± 0.15	ns	
Octanoic acid	5.77 ± 4.53	7.06 ± 0.74	8.46 ± 0.12	8.93 ± 0.41	ns	
Decanoic acid	0.954 ± 0.673	1.21 ± 0.50	1.19 ± 0.61	1.04 ± 0.17	ns	
Total	19.1	25.5	25.6	28.7	ns	
Carbonyl compounds						
Benzaldehyde	0.039 ± 0.004	0.040 ± 0.002	0.070 ± 0.006	0.059 ± 0.027	ns	
2,3-Butanedione	0.125 ± 0.011	0.288 ± 0.066	0.765 ± 0.761	1.59 ± 1.95	ns	
Acetophenone	0.007 ± 0.009	0.007 ± 0.010	0.013 ± 0.000	0.014 ± 0.000	ns	
Benzophenone	0.004 ± 0.004	d.m.s.	d.m.s.	n.d.	ns	
4-Hydroxy-3-methoxyacetophenone	0.064 ± 0.046	0.044 ± 0.017	0.060 ± 0.011	0.057 ± 0.000	ns	
Total	0.239	0.379	0.908	1.72	ns	
Lactones						
γ-Nonalactone	0.009 ± 0.002	0.003 ± 0.004	0.008 ± 0.000	0.008 ± 0.001	ns	
γ-Decalactone	0.006 ± 0.009	0.110 ± 0.156	n.d.	n.d.	ns	
Total	0.015	0.113	0.008	0.008	ns	
Thiols						
3-(Methylthio)-1-propanol	2.23 ± 2.41	1.94 ± 0.53	1.76 ± 0.08	1.71 ± 0.19	ns	
General Total	357	380	393	398	ns	

Different superscripts (a–d) mean significant differences ($p < 0.05$) between the average values.
±SD; d.m.s.=detected by mass spectrometry; d-n.q.= detected not quantified; n.d.=not detected.

These compounds are mainly formed during alcoholic fermentation. In general, most compounds and chemical families, in both vintages, did not show significant differences between the macerated wines and the control wines. Nevertheless, phenols and C13 nor-isoprenoids (β-damascenone) in the first vintage and terpenes in the second vintage showed significantly higher mean contents in macerated wines than in control wines. This increasing content in terpenes, some phenols and C13 nor-isoprenoids had already been observed by other authors (Cabaroglu et al., 1997; Castro Vázquez, Pérez-Coello, & Cabezudo, 2002; Sánchez-Palomo et al., 2006; Selli et al., 2006a) and may be related to varietal compounds of the grapes (free or bound) that were present in macerated musts and to the different compositions of the macerated must.

According to Selli et al. (2006a), high levels of C6 alcohols in wines of Muscat de Bornova diminished the quality of wines. However, in another work (Cabaroglu et al., 2002) the contents of 1-hexanol and *cis*-3-hexen-1-ol have been correlated with fresh aroma. Several authors have observed an increase in C6 alcohols in wines due to the skin contact process in several varieties such as Chardonnay, Bourboulenc, Chenin (Baumes et al., 1989), Emir (Cabaroglu et al., 1997) and Muscat (Sánchez-Palomo et al., 2006). In our case, the Listán blanco wines did not present an increase in C6 alcohols with increased skin contact time, which may be due to the fact that the maceration temperature was 10 °C, lower than in the other works (between 15 °C and 18 °C), these compounds being related to the

oxidation of fatty acids and thus with the maceration conditions.

The greater part of the analysed compounds presented slight variations in content between the wines from different maceration times and only a few compounds showed statistically significant differences. In both vintages, only methanol, an odourless compound, presented significantly higher contents in macerated wines than in control wines. Their increased content with a longer maceration time may be due to the fact that the methanol is originated by action of the methylpectinestearase on the pectines present in the skins (since it is derived from the demethylation of the pectins). The same behaviour was observed by Darias Martín, Rodríguez, Díaz, and Lamuela Raventós (2000), in the same variety, and by Sánchez-Palomo et al. (2006) and Falqué and Fernández (1996), in other varieties.

Moreover, in the first vintage the macerated wines presented a significantly higher mean content in β-damascenone, 4-vinylphenol, isobutyl acetate (contents below odour threshold) and isoamyl acetate than control wines. In the second vintage some compounds presented significant differences between control and macerated wines, but did not follow a defined pattern. These compounds were two alcohols: 1-butanol (contents below odour threshold) and isoamyl alcohols; five esters: ethyl hydroxybutyrate (contents below odour threshold), ethyl furoate (contents below odour threshold), diethyl succinate (contents below odour threshold), ethyl acetate and ethyl octanoate; butyric acid and γ-nonalactone (contents below

Table 5
Free aroma compounds (second vintage) of control and macerated wines (mg/l)

	Control	4 h	8 h	12 h	F	p
Terpenic compounds						
Linalool	d-n.q.	0.026 ± 0.001	0.025 ± 0.003	0.034 ± 0.006	ns	
α-Terpineol	0.052 ± 0.000	0.054 ± 0.003	0.062 ± 0.000	0.061 ± 0.000	ns	
Total	0.052^a	$0.08^{a,b}$	$0.087^{b,c}$	0.095^c	12.66	0.0165
Volatile phenols						
4-Ethylphenol	0.232 ± 0.027	0.221 ± 0.131	0.288 ± 0.222	0.171 ± 0.242	ns	
4-Ethylguaiacol	0.084 ± 0.033	0.050 ± 0.069	0.030 ± 0.042	0.039 ± 0.053	ns	
4-Vinylphenol	0.372 ± 0.005	0.606 ± 0.290	0.440 ± 0.077	0.602 ± 0.271	ns	
2-Methoxy-4-vinylphenol	0.033 ± 0.000	0.047 ± 0.016	0.037 ± 0.008	0.048 ± 0.024	ns	
Guaiacol	d-n.q.	d.m.s.	0.005 ± 0.001	0.003 ± 0.003	ns	
Eugenol	n.d.	0.028 ± 0.040	0.028 ± 0.040	0.029 ± 0.040	ns	
4-Allyl-2,6-dimethoxyphenol	0.018 ± 0.000	0.018 ± 0.000	0.018 ± 0.000	0.018 ± 0.000	ns	
Total	0.739	0.971	0.846	0.910		
Benzenic compounds						
Benzyl alcohol	d-n.q.	0.053 ± 0.027	d-n.q.	0.047 ± 0.007	ns	
Phenylethyl alcohol	9.49 ± 0.65	12.5 ± 0.8	10.8 ± 1.0	11.2 ± 0.1	ns	
Methyl vanillate	d-n.q.	d-n.q.	d-n.q.	d-n.q.	ns	
Methyl 4-hydroxybenzoate	0.011 ± 0.016	n.d.	0.021 ± 0.001	0.011 ± 0.016	ns	
Total	9.50	12.5	10.8	11.3	ns	
Higher alcohols						
1-Hexanol	0.442 ± 0.003	0.369 ± 0.090	0.362 ± 0.020	0.306 ± 0.014	ns	
cis-3-Hexen-1-ol	0.298 ± 0.006	0.270 ± 0.001	0.285 ± 0.012	0.258 ± 0.015	ns	
Total C6 alcohols	0.740	0.639	0.647	0.564	ns	
Methanol	43.1 ± 5.2^a	$50.3 \pm 0.1^{a,b}$	52.0 ± 3.4^b	58.8 ± 0.1^b	8.72	0.0315
1-Propanol	69.1 ± 0.6	48.0 ± 14.3	71.0 ± 1.6	61.2 ± 1.2	ns	
Isobutanol	18.3 ± 0.8	20.0 ± 4.9	22.5 ± 0.1	19.6 ± 0.3	ns	
1-Butanol	1.46 ± 0.18^c	1.07 ± 0.06^b	$0.823 \pm 0.027^{a,b}$	0.793 ± 0.034^a	21.06	0.0065
(2 + 3)-Methyl-1-butanol	138 ± 0^b	170 ± 3^c	142 ± 1^b	128 ± 4^a	108.44	0.0003
2-Heptanol	0.021 ± 0.000	0.019 ± 0.004	0.021 ± 0.004	0.021 ± 0.002	ns	
1-Heptanol	0.126 ± 0.001	0.147 ± 0.069	0.130 ± 0.010	0.126 ± 0.004	ns	
1-Octanol	0.023 ± 0.000	0.024 ± 0.002	0.024 ± 0.000	0.021 ± 0.000	ns	
Total	270	290	289	269	ns	
Esters						
Ethyl isobutyrate	d-n.q.	d-n.q.	0.104 ± 0.030	0.104 ± 0.030	ns	
Ethyl butyrate	0.233 ± 0.008	0.233 ± 0.013	0.259 ± 0.014	0.240 ± 0.011	ns	
Ethyl 2-methylbutyrate	0.020 ± 0.005	0.022 ± 0.000	0.022 ± 0.000	0.022 ± 0.000	ns	
Ethyl hexanoate	0.234 ± 0.003	0.299 ± 0.023	0.302 ± 0.019	0.323 ± 0.033	ns	
Ethyl octanoate	0.038 ± 0.015^a	0.152 ± 0.018^b	0.150 ± 0.017^b	0.212 ± 0.043^b	16.00	0.0108
Ethyl 3-hydroxybutyrate	0.512 ± 0.01^b	0.534 ± 0.036^b	0.291 ± 0.027^a	0.243 ± 0.041^a	47.96	0.0014
Ethyl 2-furoate	0.043 ± 0.004^b	0.024 ± 0.004^a	0.044 ± 0.002^b	0.032 ± 0.003^a	15.04	0.0121
Ethyl decanoate	d-n.q.	d-n.q.	d-n.q.	0.022 ± 0.032	ns	
Ethyl benzoate	0.045 ± 0.003	0.042 ± 0.003	0.049 ± 0.002	0.045 ± 0.003	ns	
Total ethyl esters	1.13	1.31	1.22	1.24	ns	
Ethyl acetate	50.3 ± 0.0^c	40.0 ± 0.3^a	49.2 ± 1.8^b	56.5 ± 1.1^d	91.64	0.0004
Propyl acetate	0.085 ± 0.004	0.079 ± 0.004	0.098 ± 0.011	0.093 ± 0.023	ns	
Isoamyl acetate	0.292 ± 0.003	0.409 ± 0.087	0.351 ± 0.064	0.523 ± 0.120	ns	
Hexyl acetate	0.166 ± 0.024	0.220 ± 0.076	0.142 ± 0.011	0.072 ± 0.002	ns	
β-Phenylethyl acetate	0.096 ± 0.002	0.11 ± 0.006	0.110 ± 0.004	0.123 ± 0.013	ns	
Total Acetates	50.9	40.8	49.9	57.3	ns	
Diethyl succinate	1.83 ± 0.28^a	$2.41 \pm 0.38^{a,b}$	2.97 ± 0.04^b	4.11 ± 0.03^c	34.32	0.0026
Methyl benzoate	n.d.	n.d.	0.008 ± 0.011	n.d.	ns	
Total	53.9	44.5	54.1	62.6	ns	
Acids						
Butyric acid	3.28 ± 0.08 c	3.00 ± 0.37 bc	2.20 ± 0.11 a	2.28 ± 0.39 ab	7.38	0.0416

Table 5 (continued)

	Control	4 h	8 h	12 h	F	p
2-Methylbutyric acid	0.175 ± 0.115	0.267 ± 0.048	0.163 ± 0.032	0.188 ± 0.005	ns	
Isovaleric acid	0.179 ± 0.000	0.281 ± 0.091	0.183 ± 0.048	0.216 ± 0.063	ns	
Hexanoic acid	4.93 ± 0.47	4.75 ± 0.28	4.69 ± 0.31	4.85 ± 0.23	ns	
Octanoic acid	3.98 ± 1.31	2.81 ± 0.33	3.66 ± 0.04	2.96 ± 0.99	ns	
Total	12.5	11.1	10.9	10.5	ns	
Carbonyl compounds						
Hexanal	0.338 ± 0.004	0.236 ± 0.012	0.331 ± 0.023	0.271 ± 0.067	ns	
Benzaldehyde	0.103 ± 0.003	0.102 ± 0.017	0.122 ± 0.008	0.116 ± 0.010	ns	
2,3-Butanedione	0.243 ± 0.159	0.142 ± 0.083	d-n.q.	0.249 ± 0.134	ns	
Acetophenone	0.013 ± 0.000	0.013 ± 0.000	0.013 ± 0.000	0.013 ± 0.000	ns	
Total	0.697	0.493	0.466	0.649	ns	
Lactones						
γ-Nonalactone	0.007 ± 0.001[b]	0.006 ± 0.000[a]	0.005 ± 0.000[a]	0.006 ± 0.001[a]	8.99	0.0299
γ-Decalactone	n.d.	0.177 ± 0.251	d-n.q.	d-n.q.	ns	
Total	0.007	0.183	0.005	0.006	ns	
Thiols						
3-(Methylthio)-1-propanol	0.387 ± 0.022	0.782 ± 0.311	0.735 ± 0.012	0.759 ± 0.110	ns	
General Total	348	361	367	356	ns	

Different superscripts (a–d) mean significant differences ($p < 0.05$) between the average values.
±SD; d.m.s.=detected by mass spectrometry; d-n.q.= detected not quantified; n.d.=not detected.

odour threshold). Only two of these compounds, diethyl succinate and ethyl octanoate, showed significantly higher contents in macerated wines than in control wines.

Several studies of contents in higher alcohols showed a higher content in macerated wines than in non-macerated wines (Baumes et al., 1989; Cabaroglu et al., 1997; Selli et al., 2006a, 2006b), although in other works the opposite effect has been observed (Sánchez-Palomo et al., 2006). In our case only in the second vintage the macerated wines showed significant differences compared with the control wines in 1-butanol and amylic alcohols. As for the esters and acids, other studies showed lower contents of esters and higher contents of acids in macerated wines than in control wines (Cabaroglu et al., 1997; Sánchez-Palomo et al., 2006; Selli et al., 2006a). In our case no significant differences were observed.

Thus, contrarily to what occurred with the precursors in musts, the macerated wines did not present significant differences in content for the majority of compounds with respect to the control wines. This may be due to the fact that the volatiles of the aroma precursors of musts were not released by the enzymes during the alcoholic fermentation. In this regard, several works have shown that the aroma precursors did not release all their volatiles during the alcoholic fermentation in wines elaborated with other neutral varieties (Cabaroglu et al., 1997, 2002; Selli et al., 2006b; Versini, Orriols, & Dalla Serra, 1994). Furthermore, the amounts of volatile compounds liberated by the aroma precursors may be smaller than the amounts generated by other mechanisms.

In order to relate the quantitative results of each compound with its sensorial importance in wine aroma, the odour activity values (OAVs) of each compound were calculated. The odour thresholds used have been previously reported by other authors (Etievant, 1991; Ferreira, Ortın, Escudero, López, & Cacho, 2002; Moyano, Zea, Moreno, & Medina, 2002; Ong & Acree, 1999). In non-quantified compounds, the limits of detection or quantification were used to calculate OAVs. Compounds with odour activity values higher than 1 OAV of each vintage are presented in Table 6.

Twenty-six and twenty-two compounds presented higher concentrations than their corresponding odour thresholds, at least in one of the samples, in the first and second vintages, respectively. Nineteen of them were common to both vintages, including six esters (ethyl butyrate, ethyl octanoate, ethyl hexanoate and ethyl 2-methylbutyrate, and isoamyl acetate and ethyl acetate), five acids (butyric, 2-methylbutyric, isovaleric, hexanoic and octanoic acids), four phenols (4-ethylphenol, 4-ethylguaiacol, 4-vinylphenol and 2-methoxy-4-vinylphenol), an alcohol (2+3-methyl-1-butanol), a carbonyl compound (2,3-butanodione), a terpene (linalool) and a lactone (γ-decalactone).

Considering only those compounds common to both vintages, the families of compounds that presented the highest odour activity values were esters and acids. Esters are responsible for fruity aromas in wines and acids contribute to freshness and to equilibrate the fruity aroma (Etievant, 1991). The origin of these compounds is principally fermentative and the aroma of Listan blanco wines is therefore predominantly fermentative in nature. As for the differences found between maceration times, these could be related to the different composition of must that may affect fermentation.

Table 6
Odour activity values (>1) of volatiles of wine

Compounds	First vintage				Second vintage			
	Control	4 h	8 h	12 h	Control	4 h	8 h	12 h
Terpenic compounds								
Linalool	1.88	2.71	3.17	3.29	1.05	1.48	1.35	2.29
C13 Nor-isoprenoids								
β-Damascenone	85.0	148	152	149				
Volatile phenols								
Eugenol					n.d.	4.71	4.67	4.76
4-Vinylphenol	4.83	15.5	22.0	21.4	2.07	3.37	2.44	3.34
4-Ethylguaiacol	6.94	4.88	0.01	0.01	2.53	1.50	0.91	1.16
4-Ethylphenol					1.66	1.58	2.05	1.22
2-Methoxy-4-vinylphenol	1.75	2.63	6.45	5.36	0.82	1.17	0.91	1.19
4-Ethylphenol	2.06	1.61	n.d	n.d				
Total Vinylphenols	6.58	18.2	28.5	26.8	2.89	4.54	3.36	4.53
Total Ethylphenols	9.01	6.49	0.01	0.01	4.19	3.09	2.96	2.38
Total Phenols	15.6	24.7	28.5	26.8	7.08	12.3	11.0	11.7
Benzenic compounds								
Phenylethyl alcohol	2.23	2.30	1.95	1.91				
Alcohols								
Furaneol	23.7	14.4	23.1	21.2				
(2 + 3)-Methyl-1-butanol	2.47	2.45	2.53	2.4	2.12	2.61	2.18	1.98
Total alcohols	26.1	16.9	25.6	23.6				
Ethyl esters								
Ethyl octanoate	188	200	260	202	7.67	30.3	30.0	42.5
Ethyl hexanoate	46.4	54.2	75.1	65.6	16.7	21.3	21.6	23.1
Ethyl butyrate	8.22	8.85	13.1	11.8	11.6	11.7	13.0	12.0
Ethyl isobutyrate					4.36	4.36	5.78	5.77
Ethyl hydrocinnamate	6.98	n.d.	n.d.	n.d.				
Ethyl 2-methylbutyrate	0.54	n.d.	1.28	n.d.	0.92	1.22	1.24	1.22
Acetates								
Isoamyl acetate	52.1	56.4	79.8	78.6	9.73	13.6	11.7	17.4
Ethyl acetate	4.93	5.49	5.77	6.29	4.32	3.26	4.01	4.60
β-Phenylethyl acetate	0.888	1.01	1.14	1.16				
Total ethyl esters	250	263	350	279	41.3	68.9	71.5	84.5
Total acetates	58.0	62.9	86.7	86.0	14.1	16.9	15.7	22.1
Total esters	308	326	436	365	55.3	85.8	87.2	107
Acids								
2-Methylbutyric acid	33.4	47.5	44.9	50.7	4.64	8.00	4.88	5.62
Butyric acid	25.1	35.7	28.3	35.4	19.0	17.3	12.7	13.2
Isovaleric acid	22.8	35.5	30.4	35.1	11.7	11.3	11.2	11.5
Hexanoic acid	14.6	19.8	20.3	23.2	5.37	8.41	5.47	6.46
Octanoic acid	11.5	14.1	16.9	17.9	7.96	5.61	7.31	5.91
Decanoic acid	0.85	1.21	1.19	1.04				
Total acids	108	154	142	163	48.7	50.7	41.6	42.7
Carbonyl compounds								
Hexanal					67.6	47.2	66.2	54.2
2,3-Butanedione	1.25	2.88	7.65	15.9	2.43	1.42	0.54	2.49
Total carbonyl compounds					70.0	48.6	66.8	56.7
Lactones	1.38	3.02	7.88	16.1				
γ-Decalactone	0.07	1.25	n.d.	n.d.	n.d.	2.01	0.04	0.04
Thiols								
3-(Methylthio)-1-propanol	2.22	1.94	1.76	1.71				

n.d.: not detected.

Another important family is the phenolic compounds group. Phenols are considered to contribute to the wine aroma due to their low threshold levels and to the similarity of some of their aromatic descriptors (Etievant, 1991).

Some of these compounds were presented as aroma precursors in must (Table 3), even though only the 2-methoxy-4-vinylphenol they liberated presented contents that could influence final wine contents.

Terpenes (linalool) are responsible for floral aroma and presented odour activity values between 1 and 4 in Listán blanco wines. These levels, as expected, were lower than those in aromatic varieties such as Muscat (Baumes, Bayonove, Cordonnier, Torres, & Seguin, 1989b; Günata, Bayonove, Baumes, & Cordonnier, 1986; Sánchez-Palomo et al., 2006; Selli et al., 2006a), but similar to or higher than in wines of Albariño, Loureira and Godello (Versini et al., 1994), Bourboulenc, Chardonnay and Chenin (Baumes et al., 1989), Airén, Chardonnay and Macabeo (Castro Vázquez et al., 2002). The linalool content released by aroma precursors of Listán blanco were similar to the linalool content of the wines. Therefore, linalool released by aroma precursors had an influence on final wine aroma, although that compound could be presented in musts as a free volatile or be generated during the alcoholic fermentation (Carrau et al., 2005).

Some compounds presented higher odour activity values in one of the vintages, such as hexanal in the second vintage that could be related to enzymatic oxidation of linoleic and linolenic acids (Etievant, 1991), and β-damascenone and furaneol in the first vintage that could be related to free and bound varietal compounds and with the aroma of some hybrid varieties, respectively (Guedes de Pinho & Bertrand, 1995).

In summary, although the majority of aroma precursors presented higher contents in macerated musts than in control musts, the volatile compounds of wines, in general, did not present content differences that could be related with the skin contact process. This may be due to the fact that the volatiles of the aroma precursors of musts were not released by the enzymes during the alcoholic fermentation.

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