FIRST STUDY ON VOLATILE COMPOSITION OF THREE *VITIS VINIFERA* CULTIVARS FROM BETANZOS (NW SPAIN): BLANCO LEXÍTIMO, AGUDELO AND SERRADELO

M. Vilanova [1*], Z. Genisheva [2], A. Masa [1] and J.M. Oliveira.[2]

(1) Misión Biolóxica de Galicia (CSIC). PO Box 28, 38080, Pontevedra (España)
(2) Institute for Biotechnology and Bioengineering-Centre of Biological Engineering. Universidade do Minho, 4710-057 Braga (Portugal)
*mvilanova@mbg.cesga.es

ABSTRACT

Wine aroma is formed by volatile compounds of different chemical nature and origins. Compounds arising from grape metabolism vary as a function not only of the variety but also of climatic conditions and others. Betanzos is the most northern viticole geographic area from Galicia (NW Spain). Wines produced from *Vitis vinifera* cv. Blanco lexítimo, Agudelo and Serradelo from Betanzos (NW Spain), harvest in 2006 and 2007, were submitted to gas chromatography (GC/FID).
A total of 35 varietal and fermentative aroma compounds were identified and quantified which include terpenes and C_{13}-norisoprenoids, alcohols, acids, esters, phenol volatiles and C6 compounds. The results for quantification of the aroma compounds in the three varieties from Betanzos shows that the mean concentration between years was 25039.42ug/L for Blanco lexítimo 21913.2ug/L for Agudelo and 19804.6μg/L for Serradelo variety. Alcohols, acids and esters were the most important volatile compounds in the varieties from Betanzos.

RESUMEN

El aroma del vino está formado por compuestos volátiles de diferente naturaleza y origen. Estos compuestos varian no solo con la variedad de uva sino también con las condiciones climáticas y otros factores. Betanzos es la zona vitícola situada más al norte de Galicia (Noroeste de España). Los vinos producidos con tres variedades de Betanzos, Blanco lexítimo, Agudelo y Serradelo cultivadas en las cosechas 2006 y 2007, fueron analizados mediante GC/FID.
En los vinos fueron identificados y cuantificados un total de 35 compuestos varietales y fermentativos, en cuales se incluyen C_{13}-norisoprenoides, alcoholes, acidos, esters, fenoles volatiles y otros. Los resultados de la cuantificación de los compuestos del aroma en los vinos de las tres variedades de Betanzos muestra que la concentración mediaentre los años estudiados fue de 25039.42ug/L para Blanco lexítimo 21913.2ug/L para Agudelo y 19804.6μg/L para Serradelo. Alcoholes, acidos and esteres fueron los compuestos más importantes en los tres vinos elaborados con las variedades de Betanzos, siendo el más aromático el elaborado con la variedad Blanco lexítimo, caracterizado por aromas frutales.

INTRODUCTION

Wine aroma is formed by volatile compounds of different chemical nature and origin and they vary as a function of grape metabolism, variety and also certain cultural and climate-related factors (Sanchez Palomo, 2007).
Among the compounds responsible for the wine aroma can be found terpenols, norisoprenoids, alcohols, acids and phenols volatiles (Aznar et al. 2001; Ferreira et al., 1998; Rapp and Mandery 1986). Monotepens and norisoprenoids are characteristics of the grape, forming the varietal aroma of wines. Some of these volatiles compounds are modified during yeast fermentation. (Lambrets and Pretorius 2000). The secondary aromas, produced by yeast metabolims during fermentation are esters, acetates, alcohols and others.
During the last few years, there has been a growing interest in the recuperation of the denominated autochthonous varieties from Galicia. This is the case of the traditional grape varieties grown in Betanzos.
Betanzos is an ancient winemaking area sited in the most northern viticole geographic area from Galicia (NW Spain). White cultivar Blanco lexítimo and Agudelo and red cultivar Serradelo are three *Vitis vinifera* grape varieties traditionally grown in Betanzos. As far as we known aroma composition of these cultivars have not yet been studied.
This paper reports the results of the first study on volatile composition of the monovarietal wines elaborated with *cv*. Blanco lexítimo, Agudelo and Serradelo grown in the same geographic area and made under the same fermentation condition during two consecutive vintages (2006 and 2007). The main objective of this study was to identify and quantify the principal volatile compounds present in these cultivars and contribute to their characterization according to the aromatic profile.

MATERIALS AND METHODS

Grapes and Wines

Two white grape varieties from *Vitis vinifera*, Blanco lexítimo and Agudelo and one red grape variety, Serradedo, grown in Betanzos (Galicia) from 2006 and 2007 vintages were consider in this study. Monovarietal wine production was carried out in the Bescansa Winery from Betanzos. Ethanol, total acidity, volatile acidity, reducing sugar, pH and tartaric acid content of wines were determined according to OIV Official Methods (OIV, 1990).

Extraction and GC-FID analysis of wine volatiles

Extractions of volatiles and GC-FID from each wine were made in triplicate, were realized according to Oliveira et al (2006).

Statistical analyses

To establish the relationship between the aromas and the wines elaborated with different Betanzos cultivars, principal component analysis (PCA) was carried out. The calculations were performed using the Enterprise Guide 3 System Software (SAS Institute, Cary, NC, USA).

RESULTS AND DISCUSSION

Table 1 shows results for ethanol, total acidity, volatile acidity, reducing sugars, pH and tartaric acid of wines obtained from Blanco lexítimo, Agudelo and Serradelo varieties harvested in 2006 and 2007 vintages. All wines were fermented to dryness. The ethanol and acidity of the wines were very different for 2006 than 2007 vintages. The ethanol of the wines was higher in the 2006 than 2007 vintage. Moreover, 2007 vintage shows important levels of total acidity. Probably the climatic conditions are the principal factor that explains the existence of differences between years, in the general composition of wines from Betanzos in the two years studied. This indicates that the degree of maturation was possibly incomplete in 2007 vintage.

Table 1. Chemical composition of fermented must from cv Blanco lexítimo, cv Agudelo and cv Serradelo from Betanzos (2006 and 2007 vintage)

	Blanco lexítimo		***Agudelo***		***Serradelo***	
	2006	**2007**	**2006**	**2007**	**2006**	**2007**
Etanol (% vol)	12.8	12.0	11.7	10.6	11.0	11.1
Total acidity (g/L)	5.7	7.9	5.6	10.1	5.4	7.9
Volatile acidity (g/L)	0.5	0.3	0.50	0.5	0.6	0.3
Reducing sugars (g/L)	0.8	<1.0	<1.0	<1.0	0.5	<1.0
pH	3.1	3.4	3.3	3.0	3.2	3.0
Tartaric acid (g/L)	3.5	2.6	2.9	2.3	3.0	3.7
Malic acid (g/L)	<0.3	3.8	<0.3	5.4	<0.3	2.2

The volatile composition of monovarietal wines from Blanco lexítimo, Agudelo and Serradelo is shown in Table 2. The data are expressed as the means (µg/L) of the GC analyses of triplicate extractions.
A total of 35 compounds were identified and quantified in 2006 and 2007 vintage, 4 monoterpenic compounds, 1 C_{13}-norisoprenoid, 7 alcohols, 11 esters, 7 volatile fatty acids and 5 volatile phenols.

The total concentration of free volatile compounds was very different in the two vintages. White wine Blanco lexítimo had 28784.7 µg/L and 16808.2 µg/L in 2006 and 2007 vintage, respectively. White wine Agudelo shown 29945.3 µg/L and 133881.1 µg/L and red wine Serradelo 25899.1 µg/L and 13710.1 µg/L.
There were high differences in total volatile concentration between the two vintages. The results for volatile composition varied between vintages for the same variety and may be strongly influenced by weather factors as temperature and rainfall, during ripening, fermentation conditions and the yeast involved. (Nurgel et al.,2002; Dieguez et al. 2003).

Table 2. Volatile composition of fermented musts from Blanco lexítimo, Agudelo and Serradelo cultivars in consecutive vintages, 2006 and 2007.

	Blanco lexítimo			***Agudelo***			***Serradelo***		
	2006	**2007**	**Mean**±SD	**2006**	**2007**	**Mean**±SD	**2006**	**2007**	**Mean**±SD
Terpenols									
linalool	27.0	25.5	26.2±1.1	2.4	2.3	2.3±0.1	14.5	13.4	13.9±0.8
α-terpineol	4.4	2.9	3.6±1.1	3.1	1.8	2.5±1.0	20.3	3.5	11.9±11.9
citronellol	4.4	0.2	2.3±3.0	nd	2.4	-	5.6	1.5	3.6±2.9
nerol	1.0	1.2	1.1±0.1	nd	nd	-	9.2	0.8	5.0±5.9
C_{13}-norisoprenoids									
β-damascenone	1.9	0.8	1.3±0.7	1.9	1.1	1.5±0.5	5.1	1.6	3.35±2.5
Alcohols									
1-propanol	81.0	102.8	91.9±15.4	110.4	37.2	73.8±51.7	74.7	35.8	55.3±27.5
2-methyl-1-propanol	868.2	1142.6	1005.4±194.1	1018.4	1068.5	1043.5±35.4	1679.2	1296.4	1487.8±270.7
1-butanol	20.5	15.8	18.2±3.3	23.5	3.9	13.7±13.9	10.3	5.3	7.8±3.5
3-methyl-1-pentanol	22.4	17.6	20.0±3.4	42.4	17.6	30.0±17.5	11.9	23.6	17.8±8.3
1-hexanol	208.4	449.0	328.7±170.1	834.6	534.5	684.5±212.2	1080.4	1102.8	1091.6±15.8
3-(methylthio)propanol	95.0	30.6	62.8±45.6	55.8	45.9	50.9±7.0	75.6	52.0	63.8±16.7
2-phenylethanol	11903.4	4739.1	8321.2±5065.9	12740.3	6735.0	9737.7±4246.3	12466.9	7767.0	10116.9±3323.4
Esters									
ethyl butyrate	121.5	154.2	137.8±23.1	165.5	86.8	126.2±55.7	112.0	83.6	97.8±20.1
ethyl 2-methylbutyrate	7.7	0.2	4.0±5.3	13.4	1.4	7.4±8.5	6.7	0.9	3.8±4.1
ethyl 3-methylbutyrate	15.1	0.9	8.0±10.0	21.6	2.6	12.1±13.5	5.9	1.7	3.8±3.0
isoamyl acetate	268.3	1888.6	1078.5±1145.8	203.5	1371.1	787.3±825.6	141.3	460.7	301.0±225.8
ethyl hexanoate	462.1	349.8	406.0±79.4	429.2	209.3	319.3±155.5	123.2	204.9	164.1±57.7
hexyl acetate	9.2	138.2	73.7±91.2	13.6	80.1	46.8±47.0	2.5	29.3	15.9±18.9
ethyl lactate	4722.8	201.6	2462.2±3197.0	5754.2	103.7	2929.0±3995.5	3541.9	135.3	1838. 6±2408.8
ethyl octanoate	820.2	784.7	802.4±25.1	717.5	247.5	482.5±332.3	139.3	234.2	186.7±67.1
ethyl decanoate	173.8	93.7	133.8±56.7	158.7	18.8	88.8±98.9	34.0	31.5	32.8±1.7
diethyl succinate	1749.2	48.3	898.7±1202.7	1801.7	49.1	925.4±1239.3	3452.6	73.6	1763.1±2389.3
2-phenylethyl acetate	118.1	267.6	192.9±105.7	61.8	130.9	96.4±48.8	34.0	73.7	53.9±28.0
Volatile fatty acids									
2+3-methylbutyric acid	49.2	49.9	49.6±0.5	95.1	64.5	79.8±21.6	27.1	31.7	29.4±3.3
Butyric acid	506.7	353.8	430.2±108.1	803.9	179.0	491.5±441.9	962.7	201.1	581.9±538.5
hexanoic acid	957.7	1098.4	1028.1±99.5	945.9	469.2	707.5±337.1	281.9	379.0	330.5±68.7
octanoic acid	4191.1	4083.6	4137.4±76.0	3782.1	2042.6	2912.4±1230.0	809.8	1226.3	1018.0±294.5
decanoic acid	1229.2	605.4	917.3±441.1	33.0	218.4	125.7±131.1	280.0	227.4	253.7±37.2
dodecanoic acid	39.9	36.8	38.4±2.2	59.0	5.2	32.1±38.0	18.5	7.3	12.9±7.9
Volatile phenols									
guaiacol	4.2	nd	-	nd	nd	-	0.7	nd	-
4-ethylphenol	52.0	nd	-	7.5	2.0	4.7±3.9	409.0	nd	-
4-vinylguiacol	6.7	35.8	22.6±18.7	15.4	29.8	22.6±10.2	5.2	nd	-
4-vinylphenol	4.2	63.8	34.0±42.2	11.4	110.8	61.1±70.3	51.8	nd	-
vanillin	38.2	24.7	31.5±9.5	18.4	8.1	13.2±7.2	5.4	4.5	5.0±0.6

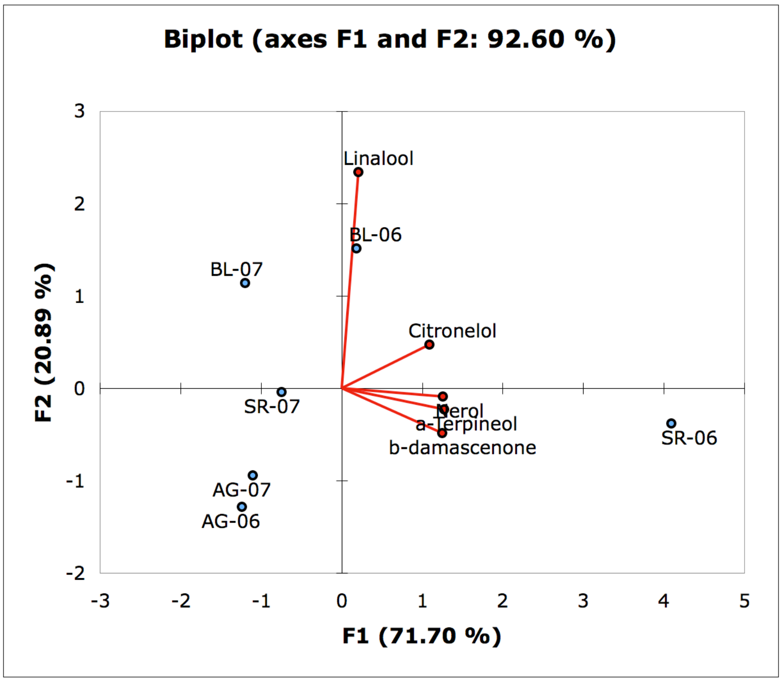
Alcohols were quantitatively the largest group of the volatile compounds in Blanco lexítimo, Agudelo and Serradelo wines from 2006 vintage (45.8 %, 49.5 % and 59.5 % respectively) and 2007 vintage (38.6%, 60.8% and 75% respectively)
Alcohols are produced by yeast metabolism during alcoholic fermentation and play an important role in the flavour of the wines depending of the type de compounds and their concentration (Swiegers and Pretorius, 2005). Among varietal compounds, four monoterpenols and one C_{13}-norisoprenoid were identified in wines from Betanzos.
Linalool, with floral aroma and low perception threshold, was quantitatively the main terpenol in Blanco lexítimo wine from the two vintages, 2006 and 2007, representing 73.6 % and 85.8 % respectively of total terpenols analyzed. Similar results were found by Oliveira et al. (2004) for the Loureiro variety from Vinhos Verdes in Portugal, where linalool represented the 75 % of the total monoterpenic concentration, followed by Alvarinho, Avesso, Amaral and Vinhão.
For Serradelo from 2006 vintage, α-terpineol is the most important terpenol at 20.3 µg/L and it accounts for 41% of total monoterpenic concentration. Nerol and β-damascenone were important varietal compounds in Serradelo wines from 2006 vintage.

With regard to fermentative compounds, alcohols and esters were lower in 2007 for the three wines studied; however, volatile phenols were higher in 2007 for Blanco lexítimo and Agudelo.
Given that fermentation conditions were the same, the differences of wines composition may be attributed to the different must composition between vintages.
Volatile phenols were high in Serradelo wines from 2006 vintage, where 4-ethylphenol represented the 86.6 % of phenols analyzed. Phenols present in young wines arise from the grapes and from the yeast metabolism (Belitz et al. 1999).

In terms of the number of compounds identified, esters represent the largest group (11 compounds). Table 2 shows ethyl hexanoate, ethyl lactate and diethyl succinate with the highest concentrations in 2006 vintage for the Blanco lexítimo and Agudelo wines. Similar results were found in volatile composition of Zalema white wines (Gomez–Miguez et al. 2007). Isoamyl acetate shown the highest concentrations from the three wines from 2007 vintage.
Among volatile fatty acids, the concentration of octanoic acid was the highest for the three wines, Blanco lexitimo, Agudelo and Serradelo, from the two vintages studies.

PCA were used with varietal compounds to identify the aromas that discriminated best among the wines of the different varieties (Fig. 1). The PCA shows the varietals compounds where the first two principal components accounted for 92.60 % of the total variance (71.70 % and 20.89% respectively). The effect of cultivar was very important when the varietals compounds were analyzed.

Figure 1. Principal component Analysis (PCA) for varietal volatile compounds of Blanco lexítimo (BL), Agudelo (AG) and Serradelo (SR) wines cultivated from 2006 and 2007 vintages



CONCLUSIONS

This work shows the first study of volatile composition of wines produced from white varieties Blanco lexítimo and Agudelo and red variety Serradelo grown in Betanzos and determined the most powerful odorants compounds in these wines. Varietal and fermentative aroma compounds were identified and quantified in free form. A total of 35 compounds were determined with more influence in the aroma of Betanzos wines from 2006 and 2007 vintages. For the three monovarietal wines studied, this approach provides proof that white varieties from Betanzos are much richer than red one. Blanco lexítimo is the most aromatic wine dominated by citric, banana apple and pineapple aroma. Agudelo wine which is poorer than Blanco lexítimo present high levels of fruity aromas and the red Serradelo wine is the most flowery wine with minor aroma.

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