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Characterisation of volatile fraction of monovarietal wines: Influence of winemaking practices

Z. Piñeiro [a], R. Natera [a], R. Castro [a], M. Palma [a,*], B. Puertas [b], C.G. Barroso [a]

[a] *Departamento de Química Analítica, Facultad de Ciencias, Universidad de Cádiz, Campus Universitario de Puerto Real, P.O. Box 40, 11510 Puerto Real, Cádiz, Spain*

[b] *CIFA Rancho de la Merced, I.F.A.P.A. C.I.C.E. (Junta de Andalucía), Apdo. 589, 11471 Jerez de la Frontera (Cádiz), Spain*

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Abstract

Twenty-three monovarietal wines from 13 white and red grapes have been analysed by solid phase extraction–gas chromatography and solid phase micro-extraction–gas chromatography. The content of some varietal terpenic and fermentative volatile compounds was determined. The 13 studied varieties were characterised as well as the influence of winemaking practices like cold soaking and addition of glycosidase enzymes.

Terpenic compounds showed a high variability between the 13 varieties which allows for its characterisation. The winemaking practices devoted to increase the aromatic properties of wines produced different results depending on the variety of grape. For example, cold soaking produced very different results if applied on Palomino fino variety or on Traminer variety, whereas for Viura variety few changes were found.

Regarding the volatile compounds generated during the alcoholic fermentation, its relative amount is clearly related to the kind of fermentation process carried out, and particularly according to whether maceration of the solid parts has or has not been done during the process. In the case of vinification without maceration, there is a relative increase of fatty acids and their ethyl esters, whereas in vinification with maceration, the ethyl esters of lactic, acetic and succinic acids are the compounds that are relatively more abundant. Additionally, none of these compounds was affected by the techniques applied to increase varietal aroma, i.e. cold soaking, and addition of glycosidase enzymes showed very low influence in the levels of this kind of compounds.

Keywords: Wine; Grape; Aroma; Terpenic compounds; Varietal aroma; Fermentation

1. Introduction

The variety of grape employed in making a particular wine, in many cases, determines completely the aroma of that wine. This is due to the persistence of certain compounds present in the grape throughout the entire process of vinification. Many of these compounds are of the terpenic type, although there are also others that are particular to certain varieties. In all the cases, these compounds present much higher concentrations in the marc or skins of the grape than in its pulp [1].

Diverse types of terpenic derivatives have been identified in grapes, most of them of the monoterpenic type, and among these, basically, are alcohols and aldehydes, fundamentally. Many wines present levels of these compounds above the thresholds of perception, and thus in many cases they form active components of the aroma [2].

The persistence of these compounds from the grape through to the wine is going to be influenced by the conditions of the vinification, as they tend both to be increased by techniques of maceration of the solid parts or through the release of glycosylated precursors, and to be decreased by high temperatures or by oxidations.

The techniques leading to their increased concentration fall into two types. The first is the greater extraction of the solid parts by means of their maceration in the must before the fermentation (cold soaking) [3]. The second technique open to the winemaker is the release of the aromatic compounds that are found in the grape combined with sugars in non-aromatic form, and for this, enzymes with glycosidase activity are employed [4].

* Corresponding author. Tel.: +34 956016360; fax: +34 956016460.
E-mail address: miguel.palma@uca.es (M. Palma).

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On the other hand, the process of vinification itself and particularly the alcoholic fermentation carried out by the yeasts generates the greater part of the aromatic compounds present in the wine: in this case, compounds of the acid type, alcohol and esters. The relative quantities of these compounds are largely conditioned by the composition of the fermentation medium, in respect of pH, quantity of sugars, amino acids and aromatic precursors, as well as by the specific yeast that is responsible for the fermentation [5,6]. On the other hand, another influential factor is the conditions in which the fermentation takes place, in respect of temperature and supply of oxygen, since these condition the metabolism of the yeast [7].

Among these compounds there are many that present levels above the limits of detection, which are therefore important in wines, from the point of view of the wine aroma [8].

The concentrations in which these compounds occur, both the terpenic type of compounds and those of the non-terpenic type that participate in the aroma of a wine, are customarily low. For this reason, prior to their analysis by gas chromatography, processes of not only extraction but also concentration are usually applied. Among these extraction and concentration processes, methods based on solid phase extraction (SPE) [9,10] and on solid phase micro-extraction (SPME) [11,12] have been developed; these methods have enabled both terpenes and non-terpenic compounds to be determined efficiently.

In this study the object is to evaluate the influence of two main variables, the variety of grape and the conditions of vinification, on the resulting aroma of the wines produced, by determining the presence in the monovarietal wines of both terpenic type and volatile non-terpenic type compounds. For this, diverse varieties of grape have been utilised, all cultivated in the Jerez wine-producing district, and made using different enological variations that may condition the aromatic composition of the wines. For the analysis of the results, cluster and principal components analyses have been applied.

2. Experimental

2.1. Samples

The samples consisted of a total of 23 wines corresponding to 13 varieties of grape cultivated in Jerez and made under different conditions of vinification. Table 1 indicates the particular wines analysed, and the different processes of vinification that differentiate these wines.

2.2. Reagents and standards

Dichloromethane (HPLC grade) and methanol (Lichrosolv grade) were purchased from Merck (Darmstadt, Germany); ethanol (ACS grade) and *n*-pentane (ACS grade) were purchased from Panreac (Barcelona, Spain). Water (HPLC grade) was provided by a Milli-Q system (Millipore Bedford, MA, USA). Linalol, γ-terpinene and terpineol were from Sigma–Aldrich Chemie GmbH (St. Louis, MO, USA), geraniol, nerol, (+)-limonene and D-citronelol were from Extrasynthèse (Genay, France).

All standards used in the non-terpenic compound analyses were supplied by Sigma–Aldrich. 4-Methyl-2-pentanol was employed as internal standard.

2.3. SPE method

This was performed in a Visiprep SPE vacuum manifold 12-port model from Supelco, in which there are 12 positions available for performing the SPE simultaneously. During the extraction, prior to use, 3 mL cartridges (Strata SDB-L, Phenomenex, Torrance, CA, USA) were conditioned by rinsing with 4 mL of dichloromethane, 4 mL of methanol and finally 4 mL of an ethanol–water mixture (12%, v/v). Then, 50 mL of wine was rinsed through the cartridge by vacuum suction (−0.67 atm). Clean-up was obtained by flushing the cartridge

Table 1
Samples analysed, classified in function of the variety of grape and type of vinification

Variety of grape	Code assigned, type of sample			
Chardonnay	Ch, non-irrigated (c.v.w.w.)			
Cabernet sauvignon	Cs, non-irrigated (c.v.r.w.)			
Garrido	Gd, non-irrigated (c.v.w.w.)			
Graciano	Gr, non-irrigated (c.v.w.w.)			
Moscatel Alejandría	Ms, non-irrigated (c.v.w.w.)		Msi, irrigated (c.v.w.w.)	
Palomino fino	Pf, non-irrigated (c.v.w.w.)	Pfir, irrigated (c.v.w.w.)	Pfen, non-irrigated glycosidase enzymes	Pfcs, non-irrigated cold soaking
Palomino negro	Pn, non-irrigated (c.v.r.w.)	Pnlt, low temperature fermentation		Pncm, carbonic maceration
Syrah	Sy, non-irrigated (c.v.r.w.)			
Tempranillo	Tm, non-irrigated (c.v.r.w.)			
Gewürtztraminer (Traminer)	Tr, non-irrigated (c.v.w.w.)		Trcs, non-irrigated cold soaking	
Tintilla de Rota	Tn, non-irrigated (c.v.r.w.)		Tnir, irrigated (c.v.r.w.)	
Vijiriega	Vj, non-irrigated (c.v.w.w.)			
Viura	Vr, non-irrigated (c.v.w.w.)	Vrcs, non-irrigated cold soaking		Vren, non-irrigated glycosidase enzymes

c.v.w.w.: classic vinification for white wines; c.v.r.w.: classic vinification for red wines.

with water (10 mL). The cartridge was then dried under vacuum (−0.67 atm). Finally, terpenoids were eluted from the solid phase using dichloromethane (2 mL) [10].

2.4. SPME method

Twenty-five millilitres of wine was pipetted and placed in a 50 mL glass vial with 3.0 g of NaCl. Each sample was spiked with 75 μL of a solution of 4-methyl-2-pentanol (2.516 g L^{-1} in Milli-Q water containing 15%, v/v, of ethanol). A small magnetic stirring bar was also added. The vial was tightly capped with a PTFE-faced silicone septum and placed in a thermostated block on a stirrer. The sample was equilibrated for 15 min at sampling temperature (40 °C) and, after this, the SPME fibre (CAR/PDMS 85 μm) was inserted into the headspace. During the sampling time (45 min), the sample was stirred at constant speed. After completion of sampling, the fibre was removed from the sample vial and inserted into the GC injection port [12].

2.5. GC analysis

Separation and quantification of terpenic compounds were performed on a Hewlett-Packard (Palo Alto, CA) 5890 Series II gas chromatograph equipped with a 60 m × 0.32 mm i.d. fused silica capillary column coated with DB-WAX (J&W Scientific, Folsom, CA), and flame ionization detector (FID). Separation conditions were as follows: injector temperature 200 °C; GC column temperature 40 °C (5 min) at 2 °C min^{-1} to a final temperature of 230 °C (20 min); carrier gas He at 40 kPa.

For non-terpenic compounds, the injection was made in the splitless mode for 2 min. For the desorption of the analytes inside the GC injection port, the temperature was 280 °C. The GC was equipped with a DB-WAX capillary column 60 m × 0.25 mm i.d., with a 0.25 μm coating (J&W Scientific), and FID. The carrier gas was helium at a flow rate of 1.1 mL min^{-1}. The detector temperature was 250 °C. The GC oven was programmed as follows: held at 35 °C for 10 min, then ramped at 5 °C min^{-1} to 100 °C. Then it was raised to 210 °C at 3 °C min^{-1} and held for 40 min.

Each compound was quantified by comparison with a calibration curve, obtained using the relative peak area in relation to that of 4-methyl-2-pentanol, the internal standard.

Identification was performed by mass spectrometric analysis. In these analyses, a GC 8000 coupled to a MD 800 mass detector (Fisons Instruments, Milan, Italy) was used. The mass detector operated in EI+ mode at 70 eV in the range 30–450 amu. The signal was recorded and processed with Masslab software supplied with the Wiley 6.0 MS library. Peak identification was carried out by analogy of mass spectra and confirmed by retention indices of standards.

2.6. Statistical packages

Two statistical packages were used: the Unscrambler Version 7.5 (CAMO ASA, Norway) for principal components analyses and Statistica Version 5.0 (StatSoft, Tulsa, OK, USA) for cluster analyses.

3. Results and discussion

Terpenic type compounds, esters, acids and alcohols, have been determined with the object, first, of characterising the varieties studied, and second, of evaluating the effects that different vinification conditions have on some of these compounds.

3.1. Terpenic type compounds

The SPE–GC method previously developed by the authors [10] was applied. The mean results of the determinations of terpenic compounds are presented in Table 2.

The data obtained have been analysed to determine both variability in concentrations among the different varieties of grape and the possible influence on these concentrations of the vinification conditions that have been assayed.

When a cluster analysis (CA) of all the samples analysed is performed, employing the terpenic compounds as variables, the dendogram of Fig. 1 is obtained. This diagram shows that the terpenes allow for some well established groups among the varieties analysed.

Firstly, a fairly homogeneous group formed by most of the white varieties can be distinguished. Then another more heterogeneous group is found, in which a subgroup constituted by the autochthonous red varieties (Tintilla de Rota (Tr and Trir), Palomino negro (Pn)) can be distinguished; this is fairly well differentiated from the subgroup formed by the other red

Table 2
Concentrations of terpenic compounds (μg L^{-1}) in the wines assayed

	γ-Terpinene	Linalol	Terpineol	Citronelol	Nerol	Geraniol
Ch	113.76	n.d.	n.d.	n.d.	30.42	n.d.
Cs	101.61	16.35	n.d.	n.d.	n.d.	n.d.
Gd	108.59	7.09	n.d.	n.d.	19.55	n.d.
Gr	18.20	15.59	n.d.	n.d.	90.79	n.d.
Ms	137.43	76.35	123.78	18.22	22.50	13.01
Msir	132.85	86.89	89.17	18.70	37.91	12.65
Pf	133.99	9.72	5.26	n.d.	32.81	n.d.
Pfir	155.89	n.d.	3.86	n.d.	37.40	n.d.
Pfen	261.38	9.63	5.32	n.d.	35.76	n.d.
Pfcs	246.24	5.16	3.55	n.d.	21.84	n.d.
Pn	69.09	6.35	4.15	n.d.	67.83	n.d.
Pnlt	84.81	n.d.	3.82	n.d.	61.85	n.d.
Pncs	95.38	n.d.	4.37	n.d.	47.38	n.d.
Sy	70.25	15.81	3.90	n.d.	96.78	n.d.
Tm	21.07	14.49	n.d.	n.d.	100.33	n.d.
Tr	147.65	13.32	15.91	n.d.	18.91	n.d.
Trcs	127.68	49.63	47.31	31.44	47.95	n.d.
Tn	55.64	8.99	3.89	n.d.	52.47	n.d.
Tnir	63.18	13.18	5.25	n.d.	72.48	n.d.
Vj	110.95	n.d.	n.d.	n.d.	16.62	n.d.
Vr	122.13	8.90	n.d.	n.d.	29.47	n.d.
Vrcs	140.11	10.87	n.d.	n.d.	45.67	n.d.
Vren	84.08	9.95	4.25	n.d.	28.08	n.d.

n.d.: not detected.

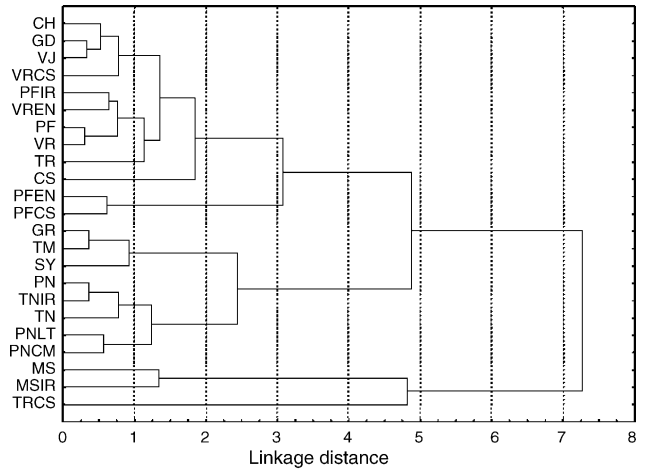

Fig. 1. Dendogram representing the groupings of the varieties analysed, in function of terpenes.

varieties that are not autochthonous to Jerez (Graciano, Tempranillo, Syrah). It is also possible to distinguish other subgroups formed by the red variety Cabernet sauvignon (Cs), another corresponding to the Palomino fino variety (Pf) and lastly a group comprising the most aromatic varieties: Moscatel non-irrigated and irrigated (Ms and Msir) and Traminer (with maceration (Trcs)); this group appears to be completely separate from the rest of the wines analysed.

The effects of the processes of cold soaking and the employment of glycosidase enzymes in the vinification are also very interesting. In respect of cold soaking, it should be remembered that the fundamental objective of this is to enhance the phenomena of extraction from the solid parts, particularly extraction of terpenes and other aromatic compounds present in the grapes.

The results show that the effects of this process, in respect of terpenes, are dependent entirely on the variety employed. For

Table 3
Loadings of terpenes in PC1 and PC2

	PC1	PC2
Terpineol	0.520	0.058
Linalol	0.509	0.150
Geraniol	0.485	0.061
Citronelol	0.449	0.099
Nerol	0.137	0.732
γ-Terpinene	−0.123	−0.651

Viura variety there are no changes in the position in the dendograms between the reference wine and the wine obtained using cold soaking. Nevertheless, for Palomino fino and Traminer the resulting wines using cold soaking are grouped far away from the reference wines.

Something similar occurs when enzymes with glycosidase activity are employed. Thus, whereas in the Palomino fino (Pf and Pfen) variety there is a clear effect, for the Viura variety again the effect is smaller (Vr and Vren).

To corroborate the results obtained with the dendograms and check which are the terpenes that allow the differentiation of the varieties tested, a principal components analysis (PCA) was performed on the 23 wines analysed. From this analysis, a classification of the samples analysed can be established, as shown in Fig. 2.

It can be seen that, as with the principal components obtained in the PCA, there is a clear separation between the wines considered most aromatic (Traminer with cold soaking and Moscatel) and the rest of the varieties analysed.

The differentiation between aromatic and non-aromatic varieties is reflected in the principal component 1 (PC1); as can be seen in Table 3, it is in this PC that terpineol, linalool, geraniol and citronelol make the major contribution, with the contribution of the other terpenes being negligible. Therefore,

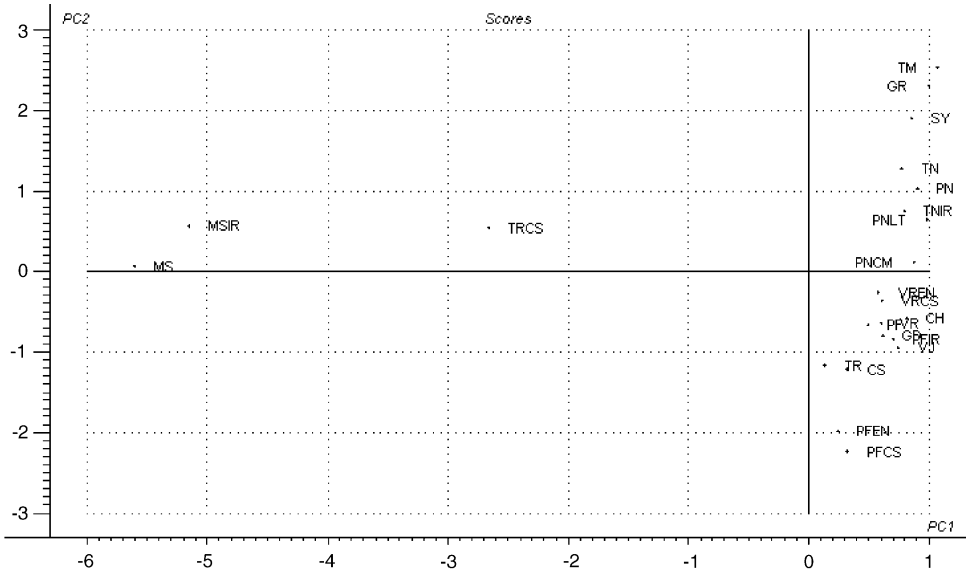

Fig. 2. Classification of the wines analysed in function of PC1 and PC2, for the terpenes variable.

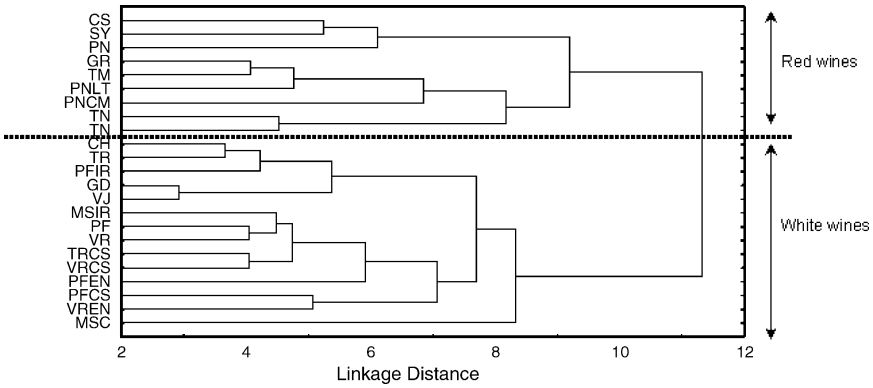

Fig. 3. Dendogram obtained from the cluster analysis of the samples, employing the volatile non-terpenic compounds as variables.

these terpenes must be the compounds that are most directly responsible for the differentiating characteristics of the aromatic varieties.

3.2. Volatile non-terpenic compounds

These compounds were determined by SPME–GC according to the methodology previously developed by the authors [12]. The compounds quantified were the following: ethyl acetate, ethyl butanoate, isoamyl acetate, 2-methyl-1-butanol, 3-methyl-1-butanol, hexyl acetate, hex-3-enyl acetate, ethyl lactate, 1-hexanol, methyl octanoate, ethyl octanoate, acetic acid, 2-furaldehyde, benzaldeyde, 2,3-butanediol, methyl decanoate, butanoic acid, ethyl decanoate, diethyl succinate, ethyl 2-phenylacetate, 2-phenylethyl acetate, hexanoic acid, benzyl alcohol 2-phenylethanol, 4-ethylguaiacol, octanoic acid and decanoic acid. The mean results of the determinations of these compounds are presented in Table 4.

Both the cluster analysis (Fig. 3) and the PCA (Fig. 4) show a clear differentiation between the varieties made with maceration during the fermentation (red varieties) and those made without this maceration (white varieties). In this case, no groupings of varieties that are autochthonous and non-autochthonous to Jerez are observed, as occurred in the case of the terpenic compounds.

Since the compounds analysed are not found in the grape, being produced during the alcoholic fermentation, it is clear from these results that the type of vinification affects the generation of these compounds, and therefore the resulting aroma of the wine. It can safely be assumed that both the higher temperature usually employed in the vinification used for red varieties and the greater quantity of oxygen available for the yeast in this kind of winemaking are the causes of the differentiation observed.

In the PCA shown in Fig. 4, PC1 is the component that effectively reflects the separation between the two types of

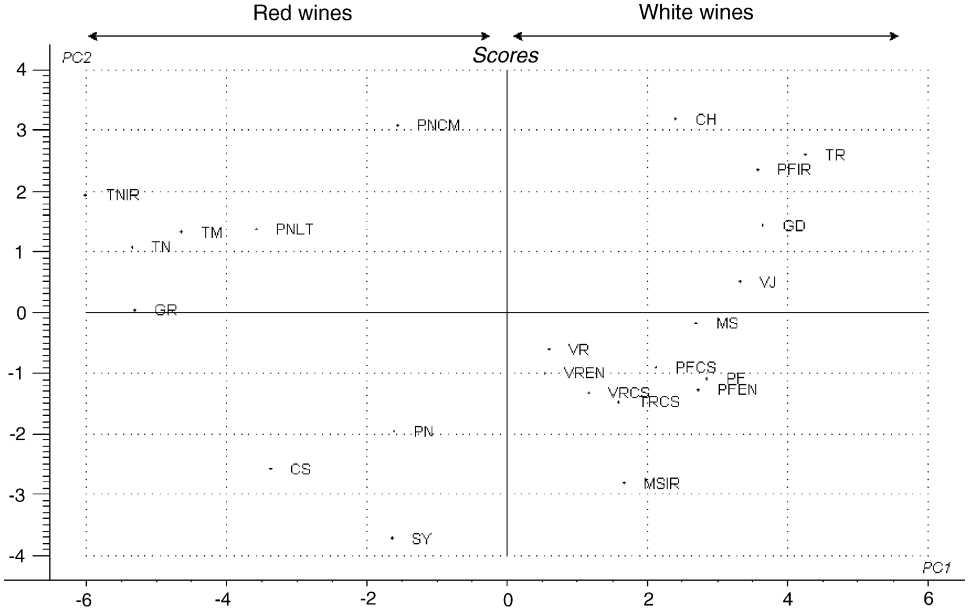

Fig. 4. PCA scores of the samples analysed, employing as variables the volatile non-terpenic compounds.

Table 4
Concentrations of non-terpenic compounds ($\mu g\,L^{-1}$) in the wines assayed

	Ch	Cs	Gd	Gr	Ms	Msir	Pf	Pfir	Pfen	Pfcs	Pn	Pnlt	Pncs
Ethyl acetate	62.28	44.32	35.65	88.46	27.95	24.10	18.47	39.63	23.74	28.09	66.63	78.04	84.59
Ethyl butanoate	0.27	n.d.	0.76	0.02	0.33	0.11	0.12	0.59	0.06	0.05	0.01	0.40	0.39
Isoamyl acetate	2.77	0.82	1.22	0.96	0.52	0.68	0.46	2.48	0.53	0.68	1.22	0.99	1.74
2-Methyl-1-butanol	125.18	372.95	102.11	476.33	177.30	149.87	153.49	137.93	65.42	91.48	187.98	281.21	250.48
Isoamyl alcohol	149.89	52.47	160.65	75.26	137.38	58.21	102.27	99.52	155.03	155.59	76.52	116.57	152.26
Hexyl acetate	0.054	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.012	0.079	n.d.	n.d.	0.10	n.d.
cis-Hex-3-enyl acetate	n.d.	n.d.	n.d.	n.d.	1.893	1.000	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ethyl lactate	43.29	53.31	11.87	89.49	12.44	4.84	0.167	7.06	35.74	24.01	89.42	121.21	114.16
1-Hexanol	0.85	1.92	0.40	1.81	1.04	0.57	0.68	0.43	0.90	0.58	1.62	2.65	0.68
Methyl octanoate	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	0.01	0.02	n.d.	n.d.	n.d.	0.01	n.d.
cis-3-Hexen-1-ol	n.d.	n.d.	n.d.	0.04	0.05	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	0.01	0.10
Ethyl octanoate	1.20	0.17	1.34	0.32	1.19	0.59	1.15	1.12	1.04	1.09	0.35	0.61	0.89
Acetic acid	43.48	4.39	13.66	56.81	22.63	10.26	10.54	18.25	23.02	23.44	8.76	63.29	48.43
2-Furaldehyde	0.08	n.d.	0.02	0.19	0.05	0.03	0.03	0.07	0.05	0.17	n.d.	0.35	0.29
Benzaldehyde	n.d.	n.d.	n.d.	n.d.	0.016	n.d.	n.d.	n.d.	n.d.	0.009	n.d.	n.d.	n.d.
2,3-Butanediol	110.22	119.00	22.10	83.91	n.d.	n.d.	126.22	12.01	n.d.	95.17	83.39	135.12	290.93
Methyl decanoate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.09	0.09	n.d.	n.d.
Butanoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	0.128	0.177	0.088	0.039	n.d.	n.d.	n.d.	n.d.
Ethyl decanoate	0.29	0.01	0.27	0.02	0.30	0.15	0.33	0.25	0.72	0.19	0.02	0.11	0.13
Diethyl succinate	n.d.	3.24	1.27	4.11	0.42	1.21	n.d.	n.d.	n.d.	n.d.	1.50	1.42	3.43
Ethyl-2-phenyl acetate	n.d.	0.02	n.d.	0.02	0.02	0.03	n.d.	n.d.	0.05	0.09	n.d.	n.d.	n.d.
2-Phenylethyl acetate	0.24	0.07	0.15	0.08	0.26	0.13	0.28	0.42	0.18	0.14	0.10	0.09	0.38
Hexanoic acid	3.62	0.58	3.16	0.30	4.54	2.36	3.63	3.85	3.12	2.64	1.65	1.03	1.34
Benzyl alcohol	0.68	1.68	0.64	1.76	0.77	0.43	n.d.	0.55	0.82	0.35	0.20	0.84	n.d.
2-Phenylethanol	12.26	72.28	14.89	71.73	47.38	26.95	35.25	13.71	19.68	20.80	31.25	39.57	31.09
4-Ethylguaiacol	0.04	0.04	0.02	n.d.	0.03	n.d.	n.d.	0.02	n.d.	0.03	n.d.	n.d.	n.d.
Octanoic acid	10.27	1.09	13.75	1.31	12.04	5.92	9.87	12.95	6.89	10.63	2.65	4.12	6.21
Decanoic acid	0.91	0.04	3.28	0.07	2.99	1.60	2.38	2.75	0.75	1.92	0.29	0.61	0.06

	Sy	Tm	Tr	Trcs	Tn	Tnir	Vj	Vr	Vrcs	Vren
Ethyl acetate	51.15	69.39	48.64	29.18	85.77	100.34	32.14	35.45	38.85	25.85
Ethyl butanoate	n.d.	0.57	0.33	0.45	0.60	0.64	0.21	0.30	0.39	0.50
Isoamyl acetate	0.66	1.30	2.72	0.76	0.74	0.73	0.89	0.93	0.58	0.39
2-Methyl-1-butanol	209.47	383.66	111.15	75.36	407.71	347.60	136.35	207.83	200.18	119.31
Isoamyl alcohol	54.47	83.93	177.30	113.04	89.11	84.91	158.44	53.28	104.75	86.55
Hexyl acetate	n.d.	0.01	0.01	0.08	n.d.	n.d.	0.06	0.06	n.d.	n.d.
cis-Hex-3-enyl acetate	n.d.	n.d.	0.003	0.036	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ethyl lactate	71.24	81.26	6.37	85.29	112.23	125.76	9.93	52.25	0.167	44.63
1-Hexanol	1.30	1.98	0.65	1.18	1.99	1.78	0.653	0.75	0.87	0.62
Methyl octanoate	0.01	n.d.	0.01	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	n.d.
cis-3-Hexen-1-ol	0.14	0.06	n.d.	n.d.	n.d.	0.07	n.d.	0.10	n.d.	n.d.
Ethyl octanoate	0.28	0.41	1.48	0.79	0.39	0.33	1.43	0.97	0.95	0.78
Acetic acid	3.88	47.18	15.88	24.16	60.83	74.62	11.29	28.02	13.43	27.91
2-Furaldehyde	n.d.	0.35	0.08	n.d.	0.46	0.29	0.04	0.07	0.06	0.06
Benzaldehyde	n.d.	n.d.	0.02	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	0.01
2,3-Butanediol	238.09	99.38	163.22	18.45	130.22	189.33	13.18	131.08	37.24	n.d.
Methyl decanoate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.010	n.d.	n.d.
Butanoic acid	0.38	n.d.	n.d.	0.12	n.d.	n.d.	n.d.	0.104	n.d.	n.d.
Ethyl decanoate	0.02	0.02	0.36	0.13	0.05	0.04	0.41	0.25	0.260	0.14
Diethyl succinate	0.57	6.70	n.d.	n.d.	3.76	3.98	0.39	n.d.	0.07	n.d.
Ethyl-2-phenyl acetate	n.d.	n.d.	n.d.	0.01	0.01	0.03	n.d.	n.d.	n.d.	0.03
2-Phenylethyl acetate	0.06	0.15	0.18	0.10	0.07	0.06	0.21	0.15	0.08	0.09
Hexanoic acid	0.801	0.261	4.14	4.35	0.661	0.576	3.10	0.670	1.53	1.37
Benzyl alcohol	0.63	n.d.	n.d.	0.79	3.17	2.95	0.72	0.71	0.75	1.19
2-Phenylethanol	40.73	91.40	8.63	11.72	51.68	51.54	28.89	20.69	28.50	18.89
4-Ethylguaiacol	0.05	n.d.	0.04	n.d.	0.09	0.09	n.d.	n.d.	0.03	0.06
Octanoic acid	2.29	2.61	13.88	8.61	1.39	1.82	11.98	8.29	7.63	7.63
Decanoic acid	0.24	0.06	3.48	1.43	0.03	0.05	3.31	1.84	2.00	1.60

n.d.: not detected.

Table 5
Loadings of non-terpenic compounds in PC1 and PC2

	PC1	PC2
Octanoic acid	0.276	0.161
Ethyl octanoate	0.264	0.200
Hexanoic acid	0.258	0.078
Decanoic acid	0.257	0.066
Ethyl decanoate	0.225	0.064
Hexyl acetate	0.208	0.235
3-Metyl-1-butanol	0.171	0.280
2-Phenylethyl acetate	0.155	0.253
Methyl octanoate	0.120	−0.285
Hex-3-enyl acetate	0.078	−0.104
Isopropyl acetate	0.073	0.358
Methyl decanoate	0.046	−0.095
Butanoic acid	0.045	−0.270
Ethyl butanoate	−0.013	0.320
Benzaldehyde	−0.024	0.053
Ethyl 2-phenylacetate	−0.049	−0.128
4-Ethylguayacol	−0.100	0.078
Butane-2,3-diol	−0.125	0.134
cis-Hex-3-enol	−0.140	0.091
2-Furaldehyde	−0.173	0.313
Benzaldehyde	−0.180	0.020
Acetic acid	−0.199	0.299
2-Phenylethanol	−0.235	−0.050
Ethyl acetate	−0.243	0.246
Ethyl lactate	−0.255	0.090
Benzyl alcohol	−0.257	−0.016
Ethyl succinate	−0.272	0.063
2-Methyl-1-butanol	−0.273	0.052

vinification (positive values for vinification for white wines and negative values for vinification for red wines). If the contribution of each of the compounds to the principal components obtained (Table 5) is analysed, it can be concluded that the compounds whose concentration is increased more in the vinification in white than in red are principally fatty acids and their ethyl esters, specifically the decanoic, the octanoic and the hexanoic, together with other ethyl and methyl esters. In contrast, the compounds showing a greater presence in red than in white wines are ethyl esters of other organic acids, such as succinic, lactic and acetic acids. In addition, some alcohols like 2-methyl-1-butanol, benzyl alcohol and 2-phenylethanol also show a clear negative contribution to PC1.

It should also be emphasised that these differentiations are independent of the variations in vinification method evaluated in this study; that is, these differences remain irrespective of the use of prefermentation maceration or the employment of glycosidase enzymes. All the white varieties present positive values of PC1.

Finally, when a principal components analysis is performed employing all the variables determined in this study (Figs. 5 and 6), it can be observed that three types of wines are identified according to their aromatic composition: first there are the wines resulting from the most aromatic varieties, namely Traminer (with maceration (Trcs)), and Moscatel non-irrigated and irrigated (Ms and Msir) (negative values of PC1 and PC2); second, there are the rest of the white varieties, made with or without variations in vinification method (negative values of PC1 and positive values of PC2); third, there are the red varieties (positive values of PC1).

The loadings of each compound on the principal components show clearly that some terpenic compounds (terpineol, linalool, geraniol and citronelol) are mainly responsible for the grouping of the aromatic varieties (negative values of PC1 and PC2), the fatty acids and their esters are responsible for the differentiation of the other white varieties (negative values of PC1 and positive values of PC2) and lastly the ethyl esters of other acids are the compounds that condition the grouping of the red varieties made with classic vinification with maceration of solid parts of the bunches during fermentation (positive values of PC1).

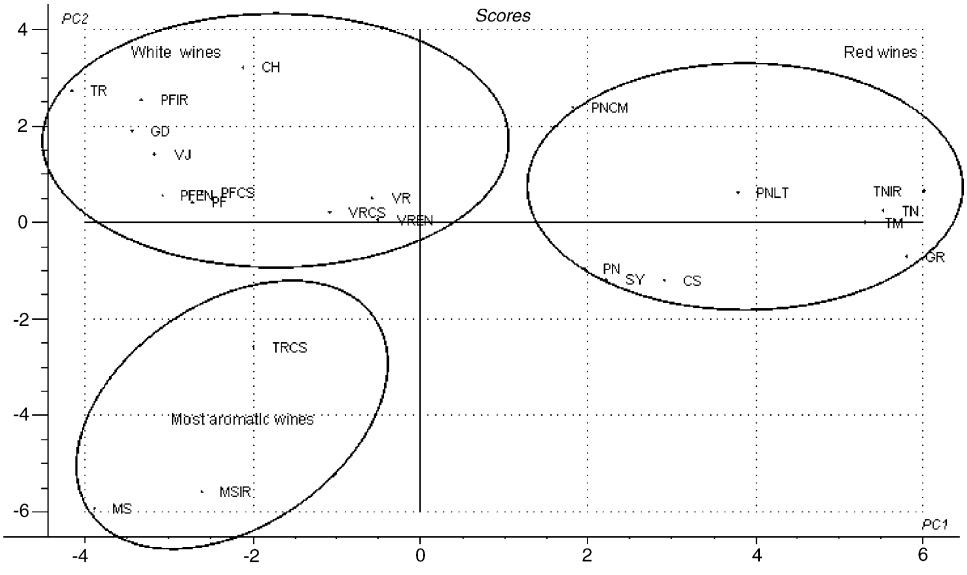

Fig. 5. Classification of the wines analysed in function of PCI and PC2, for all the analysed variables.

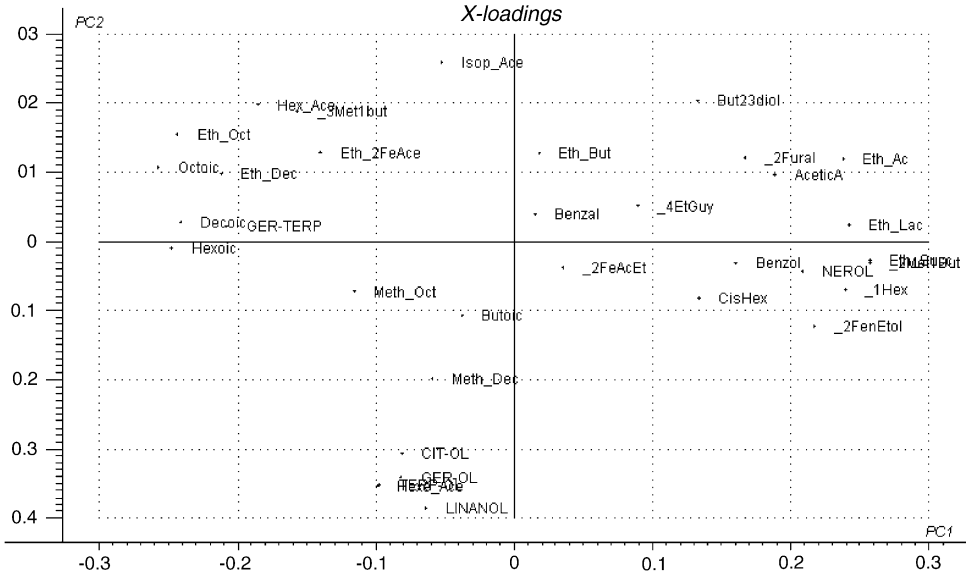

Fig. 6. PCA loadings of all analysed compounds.

4. Conclusions

The use of SPE–GC and SPME–GC has enabled the characterisation of the volatile composition of a series of monovarietal wines made from grapes cultivated in the same area. The chemometric analysis of these volatile compounds reveals that it is the terpenic compounds that are related most directly to the varietal aroma, and among these, specifically terpineol, linalol and geraniol.

The volatile compounds generated during the alcoholic fermentation present a relatively distinct composition depending on the type of fermentation carried out, and particularly according to whether maceration of the solid parts has or has not been done during the process. In the case of vinification without maceration, there is a relative increase of fatty acids and their ethyl esters, whereas in vinification with maceration, the ethyl esters of lactic, acetic and succinic acids are the compounds that are relatively more abundant.

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