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Characterization and Differentiation of Monovarietal Grape Pomace Distillate from Native Varieties of Galicia

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Monovarietal grape pomace distillates (orujo) of six native varieties of *Vitis vinifera* L. from Galicia (Albariño, Treixadura, Godello, Loureira, Dona Branca, and Torrontés) have been thoroughly analyzed considering esters, alcohols, major aldehydes, monoterpenes, sesquiterpenes, norisoprenoids, and diterpenes. Albariño and Loureira distillates showed similar profiles of terpenic compounds, with the Loureira products having higher contents of monoterpenols. Native Torrontés distillate from Galicia is principally characterized by marked levels of some sesquiterpenes such as cadinene isomers and epizonarene. On the other hand, Treixadura, Godello, and Dona Branca grape pomace distillates seem not to have any marked terpenic content, and their single separation is difficult. PCA data treatments showed a good separation among the terpenic-rich varieties. Also, the *p*-menthen-9-al isomers, typical flavors in honey citrus and dill herb (derived from 8-hydroxylinalool), are reported for the first time in grape pomace distillate.

KEYWORDS: GC-MS; grape pomace distillate; variety; sesquiterpenes

INTRODUCTION

The name "Orujo" identifies the spirit, produced in Galicia (Spain) by the distillation of fermented grape pomace, yielding a distillate with ethanol contents of < 86% (v/v) (Regulation EEC N.110/2008). Attachment II describes the denomination of origin "Orujo de Galicia", the only one in Spain. Similar spirits have equivalent appellations, such as Italian "grappa", French "eau-de-vie de marc", Portuguese "bagaçeira", and Greek "tsipouro".

Volatile compounds of grape pomace distillate vary according to yeast and bacteria metabolites, the conditions and duration of storage, and grape variety. Several variety markers such as monoterpenes, norisoprenoids, and benzenoids can be naturally present in the berry as both free and bound forms, the latter being more or less hydrolyzed into free forms during yeast fermentation and storage period by enzymatic and chemical processes or chemically by the distillation process itself. Macrocomponents such as higher alcohols, acetaldehyde, ethyl acetate, 1,1-diethoxyethane, methanol, fatty acid ethyl esters, and ethyl esters originate during fermentation (*1*−*3*).

Particular attention has been devoted in recent years to the analytical characterization of the varietal aroma of grape pomace distillate (orujo) from white grapes such as Albariño, Godello, and Treixadura (*4*−*6*), but in most of these cases the number of samples was insufficient to classify the varieties.

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In this work the aroma fraction of the spirits obtained from six grape varieties native to Galicia (Spain) was characterized by gas chromatography (GC) coupled either with flame ionization detection (FID) or mass spectrometry (MS). The grape pomace distillates of *Vitis vinifera* L., Albariño, Treixadura, Godello, Loureira, Dona Branca, and Torrontés varieties, were cultivated in Estación de Viticultura y Enología de Galicia (EVEGA) over 7 years, keeping constant both process of preparation and fermentation of the mash. The autochthonous grape varieties Loureira, Dona Branca, and Torrontés are not frequently used in industrial wineries for the elaboration of monovarietal grape pomace distillate. We focused our attention principally on compounds potentially linked to varietal peculiarities, extending our investigations to the other compounds that are being reported for the first time.

Therefore, the aims of the present work are twofold: (1) to develop and validate a simple method for direct determination of aromatic compounds (monoterpenols, minoritary alcohols, ethyl esters, and other compounds present in Galician orujo) and (2) to characterize more deeply the orujo distillate profiles of six varieties of autochthonous (*V. vinifera* L.) grapes from Galicia.

MATERIALS AND METHODS

Orujo Samples. White grapes of the Albariño, Treixadura, Godello, Loureira, Dona Branca, and Torrontés varieties were harvested at ripeness over the years 2003−2008. The vintages are not referred to all the quoted varieties because not all grape pomaces were available in each vintage.

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Table 1. Concentration Intervals, Absolute Reponse Factors of Standards, Correlation Coefficients of Calibration Curves, Detection Limits (LOD), and Relative Standard Deviations of 44 Volatile Compounds for Standard Solutions

compound[a]	range (mg/L, $n = 7$)	slope	r	LOD (mg/L)	%RSD[b]
ethyl butyrate	0.11−11.3	0.179	0.9951	0.201	4.55
isobutyl acetate	0.056−5.65	0.634	0.9975	0.026	7.80
butyl acetate	0.093−4.65	0.597	0.9955	0.036	10.27
isoamyl acetate	0.1525−15.25	0.404	0.9976	0.058	4.18
ethyl hexanoate	0.5015−50.15	0.437	0.9982	0.074	2.98
1-pentanol	0.072−7.15	0.828	0.9953	0.035	2.83
hexyl acetate	0.058−5.80	0.575	0.9982	0.042	9.28
3-hydroxy-2-butanone	0.1935−19.30	0.272	0.9968	0.085	10.44
ethyl heptanoate	0.076−7.65	0.733	0.9983	0.040	3.39
trans-3-hexen-1-ol	0.083−8.25	0.879	0.9998	0.019	5.15
3-ethoxy-1-propanol	0.103−10.40	0.313	0.9974	0.107	7.27
cis-3-hexen-1-ol	0.077−7.70	0.859	0.9993	0.046	6.11
trans-2-hexen-1-ol	0.1093−10.95	0.776	0.9992	0.107	1.13
ethyl octanoate	1.0623−106.23	0.633	0.9989	0.116	3.65
trans-furan linalool oxide	0.1078−10.78	0.562	0.9999	0.123	3.49
isoamyl hexanoate	0.0917−9.16	0.686	0.9990	0.078	7.71
1-octen-3-ol	0.055−5.50	0.975	0.9999	0.068	12.23
1-heptanol	0.108−10.88	0.932	0.9996	0.043	2.71
cis-furan linalool oxide	0.088−8.884	0.696	0.9930	0.043	7.40
furfural	0.147−14.73	0.736	0.9980	0.072	3.40
ethyl nonanoate	0.11−11.08	0.795	0.9999	0.046	3.15
linalol	0.086−8.63	1.012	0.9990	0.054	5.62
benzaldehyde	0.102−10.24	0.871	0.9998	0.047	4.56
1-octanol	0.108−10.79	0.919	0.9983	0.031	1.15
ethyl decanoate	1,051−105.1	0.741	0.9996	0.079	3.05
isoamyl octanoate	0.051−5.1	0.956	0.9988	0.114	4.71
1-nonanol	0.088−8.8	1.079	0.9991	0.019	5.29
diethyl succinate	0.1845−18.45	0.329	0.9953	0.152	4.17
α-terpineol	0.1945−19.45	0.709	0.9969	0.065	4.31
1-decanol	0.095−9.5	1.107	0.9993	0.127	9.19
citronellol	0.1855−18.55	0.859	0.9966	0.051	1.24
nerol	0.0695−6.95	1.430	0.9979	0.029	24.85
2-phenylethyl acetate	0.1215−12.15	0.552	0.9953	0.033	1.70
ethyl dodecanoate	0.4415−44.15	0.831	0.9999	0.063	2.21
geraniol	0.095−9.49	0.856	0.9946	0.055	6.72
benzyl alcohol	0.1451−14.51	0.542	0.9960	0.075	5.94
2-phenylethylethanol	0.670−67	0.468	0.9983	0.091	8.63
ethyl tetradecanoate	0.076−7.63	0.993	0.9998	0.026	3.99
isoamyl dodecanoate	0.074−7.35	1.004	0.9998	0.232	8.19
ethyl hexadecanoate	0.08−8.100	0.712	0.9997	0.025	5.73
ethyl octadecanoate	0.114−11.40	0.669	0.9991	0.052	4.93
ethyl 9-octadecenoate	0.0585−5.85	0.599	0.9986	0.113	8.54
ethyl 9,12-octadecadienoate	0.085−8.54	0.768	0.9987	0.041	7.17
ethyl 9,12,15-octadecatrienoate	0.076−7.64	0.733	0.9984	0.029	6.45

[a] Compounds are listed in order of elution from the Supelcowax 10 capillary column. [b] %RSD = reproducibility per 10 analyses.

Therefore, 25 samples were selected for this research: Albariño samples, vintages 2003, 2004, and 2007 (two samples from different systems of distillation); Dona Branca samples, vintages 2004, 2007, and 2008; Loureira samples, vintages 2003, 2006, 2007, and 2008; Godello samples, vintages 2003, 2004, 2005 (two samples), 2006, 2007, and 2008; Treixadura samples, vintages 2003, 2004, 2005, and 2007; and Torrontés samples, vintages 2007 and 2008. The mash was fermented at a controlled temperature in two types of plastic recipients of approximately 50−120 kg. The mash conserved under the residual CO_2 was distilled 4−8 weeks after fermentation in a copper pot still or steam pressure system carrying out the same head and tail cutss (the same alcoholic grade). All samples were distilled in an experimental distillery, and these were stored without dilution to the moment of performance of analysis. Whereas Albariño and Godello, major white grape varieties cultivated in Galicia, are usually elaborated separately for industial distilleries and their distillates are available commercialy, distillates from Treixadura, Loureira, Dona Branca, and Torrontés grape pomace are not available.

Reagents. *trans*-2-Hexen-2-ol, isobutyl acetate butyl acetate, isoamyl acetate, 3-hydroxy-2-butanone, ethyl heptanoate, 3-ethoxy-1-propanol, ethyl octadecanoate, isoamyl hexanoate, isoamyl octanoate, ethyl hexadecanoate, ethyl tetradecanoate, 1-octen-3-ol, 1-heptanol, furfuraldehyde, benzaldehyde, 1-octanol, isoamyl dodecanoate, β-damascone, α-ionone, and β-ionone were purchased from Sigma-Aldrich (Madrid, Spain) at the highest purity available. Isoamyl lactate and isoamyl decanoate were supplied from TCI Europe N.V. (Belgium). Hexanol, ethyl lactate, benzyl alcohol, ethyl butyrate, hexyl acetate, ethyl dodecanoate, diethyl succinate, 2-phenylethyl acetate, and 2-phenylethylethanol were supplied by Merck (Darmstadt, Germany). *trans*-3-Hexen-1-ol, *cis*-3-hexen-1-ol, ethyl hexanoate, 1-pentanol, ethyl octanoate, ethyl 9-octadeceneoate, ethyl 9,12-octadecadienoate, ethyl 9,12,15-octadecatrienoate, linalol, geraniol, citronellol, nerol, α-terpineol, ethyl octadecanoate, ethyl decanoate, 1-nonanol, 1-decanol, 5-methylfurfural, and eugenol were purchased from Fluka (Madrid, Spain). *trans*-Furan linalool oxide/*cis*-furan linalool oxide (preparation of mixture of isomers) was provided from Instituto Agrario San Michelle all'Adige (IASMA, Trento, Italy).

Chemical Analysis. *Classical Parameters*. The most common parameters were determined according to the Office International de la Vigne et du Vin (OIV). Ethanol (%, v/v) and total acidity were determined according to the methods given in ref *7*.

GC-FID and GC-MS Conditions. The distillates were submitted to analysis of the volatile compounds by GC-FID, with direct injection of the rough distillate, and by GC-MS with solid phase extraction.

Table 2. Content of Macroconstituents Present in Distillates Obtained from Grape Pomace from Various Galician Varieties

	Albariño		Dona Branca		Loureira		Godello		Treixadura		Torrontes	
	mean[a] (*n* = 5)	SD	mean[a] (*n* = 3)	SD	mean[a] (*n* = 4)	SD	mean[a] (*n* = 7)	SD	mean[a] (*n* = 4)	SD	mean[a] (*n* = 2)	SD
ethanol/ % v/v	62.88	13.33	64.87	7.49	52.00	13.40	55.90	10.36	51.53	11.15	57.90	4.60
total acidity/$g_{acetic\ ac}$/hL p.a.	19.85	4.10	33.32	30.44	47.39	46.11	75.30	60.72	25.14	5.37	18.74	7.05
pH	4.96	0.40	4.81	0.28	4.42	0.33	4.56	0.39	4.50	0.27	4.76	0.14
methanol	635.01	206.91	590.60	298.63	484.81	122.53	423.6	81.36	458.46	142.01	403.38	104.17
ethyl acetate	100.02	51.09	121.65	124.56	55.40	37.91	135.50	107.74	115.04	74.36	83.25	34.61
acetaldehyde	52.48	27.53	46.89	32.64	43.54	44.98	53.45	34.73	48.05	13.55	26.60	11.93
1,1-diethoxyethane	47.43	27.33	38.65	30.72	23.41	16.42	52.14	38.87	42.48	16.96	12.34	10.14
$\sum$ acetaldehyde + 1,1-diethoxyethane	99.91	45.71	85.55	37.19	66.95	59.39	105.50	70.12	90.53	19.12	38.94	1.79
higher alcohols												
1-propanol	58.97	5.25	42.58	10.666	46.27	13.735	43.39	9.253	57.17	13.937	35.39	9.223
2-methyl-1-propanol	70.93	6.51	53.67	13.758	67.30	28.124	40.87	9.241	53.82	20.609	43.99	5.942
1-butanol	3.11	0.50	2.02	0.277	1.51	0.718	2.40	0.368	3.19	0.566	2.36	0.284
2-butanol	0.82	0.58	0.10	0.023	0.22	0.102	0.33	0.272	0.26	0.058	0.15	0.061
allylic alcohol	0.61	0.44	0.14	0.164	0.15	0.165	0.22	0.122	0.36	0.425	0.22	0.136
2-methyl-1-butanol	52.34	10.15	36.42	3.183	49.82	11.164	31.27	9.546	33.77	7.303	35.78	6.964
3-methyl-1-butanol	139.13	21.68	119.63	14.732	164.71	16.742	118.22	18.800	131.18	13.062	133.24	26.781
$\sum$ total higher alcohols[b]	324.48		254.32		329.61		236.16		279.13		250.76	
ethyl lactate	21.30	10.37	41.12	17.90	26.86	12.22	44.89	19.51	51.70	26.35	49.81	8.23
1-hexanol	7.42	3.66	3.49	0.56	3.08	2.22	4.63	1.73	6.94	3.95	5.17	1.53
isobutyraldehyde	1.84	2.02	2.11	1.19	0.52	0.32	1.35	1.82	0.49	0.21	0.85	0.41
ethyl formate	4.25	4.12	3.49	1.53	1.69	0.65	2.34	2.35	1.95	0.91	2.20	0.10
methyl acetate	7.53	6.33	3.63	2.59	1.21	0.56	7.14	7.63	7.45	9.14	1.31	0.20
2-propenal	6.99	8.40	2.87	2.04	0.79	0.48	3.37	3.66	2.76	1.34	0.32	0.29

[a] Average of each sample of this variety made in triplicate (mg%mL p.a.). [b] $\sum$1-butanol, 2-butanol, 1-propanol, 2-methyl-1-propanol, allylic alcohol, 2-methyl-1-butanol, 3-methyl-1-butanol, 3-methyl-1-butanol.

Analyses were carried out using two different columns. A capillary column CP-WAX-57 CB (Varian) (50 m × 0.32 mm i.d. × 0.2 μm film thickness) on an Agilent 6890 (Agilent Technologies, Waldbronn, Germany), equipped with split/splitless injector and FID, was used for evaluation of the macroconstituents according the method given in ref *8*.

Separations of the rest of the compounds were done using a Supelcowax 10 capillary column (30 m, 0.32 mm, 0.25 μm film thickness; Supelco Inc., Bellefonte, PA) in a Varian CP3900. The carrier gas used was hydrogen at a constant flow rate of 2.3 mL/min. The injector and detector temperatures were 270 and 250 °C, respectively. The temperature program was from 55 to 190 °C (held for 6 min) at 2.5 °C/min using spilt injection mode (spilt ratio 1:12). All measurements were made in triplicate.

With the aim of verifying the FID dosage of some compounds and determining that of other compounds present in low quantities after a solid phase extraction, an Agilent 6890 gas chromatograph equipped with a mass spectrometric detector (MSD) model 5973N *inert* was employed (Agilent Technologies). The column used was a Supelcowax 10, the same column previously described. The mass spectrometer was operated in the electron ionization mode at a voltage of 70 eV. The source and transfer line temperatures were 230 °C; the quadrupole temperature selected was 150 °C.

Peak identification was carried out by comparing two spectral libraries: Registry of Mass Spectral Data with Structures, Wiley 6.l (New York) and NIST Mass (rev 05) Spectral Database (Hewlett-Packard Co., Palo Alto, CA). MS identifications were confirmed by comparing GC retention times with pure standards when available; in the other cases, the compounds were tentatively identified. We also used the injection of retention index standards (Sigma, St. Louis, MO) of C8−C32 aliphatic hydrocarbons dissolved in methanol to calculate the Kovats type gas chromatographic retention indices in Carbowax phase (PEG).

Isolation of Microconstituents. The extraction of some monoterpenes, sesquiterpenes, diterpenes, norisoprenoids, and other compounds was carried out with a solid extraction procedure. The extraction was performed according to the method given in ref *9*, with some modifications to the distillate. An Isolute (IST Ldt., Mid Glamorgan, U.K.) ENV+ cartridge packed with 1 g of highly cross-linked styrene−divinylbenzene (SDVB) polymer was sequentially conditioned with methanol (15 mL) and distilled water (20 mL). Then, a sample of 10 mL diluted with 50 mL of distilled water and containing 0.25 mL of internal standard (2-octanol at 112 mg/L in 50% hydroalcoholic solution) was passed through the SPE cartridge at around 2 mL/min. The sample was washed first with 20 mL of a methanol/water mixture (15% v/v) and 20 mL of water. The analytes were recovered by elution with 30 mL of dichloromethane. At the solution was added 60 mL of pentane, was dried Na_2SO_4 and concentrated to 1.0 mL on a small Vigreux column and further reduced to 200 μL prior to GC analysis. All samples were carried out in duplicate.

Quantification was carried out by the internal standard method (4-methyl-2-pentanol for macroconstituents and 2-octanol for the rest of the compounds) with appropriate calibration curves based on pure compounds. In the case of absence of pure products, the compounds were quantified as 2-octanol equivalents (response factor = 1), with target ions selected for each compound identified. The concentrations of volatile compounds were calculated as milligrams in 100% ethanol (mg%mL p.a.) following CE Regulation 2870/2000.

Statistical Analyses. Univariate statistical analysis (one-way ANOVA) was applied to the data to determine significant differences between the orujo samples depending on variety; the model was statistically significant with a value of $P \leq 0.01$ and post hoc multiple-comparison tests using Duncan's test. The variables that showed high significance were used in the principal component analysis (PCA). PCAs were applied to obtain visualization in a reduced dimension of the structure of the data. All statistical analyses were performed with the software package SPSS 14.0 (SPSS Inc., Chicago, IL).

RESULTS AND DISCUSSION

Validation of the Analytical Method. Triplicate calibration graphs at seven concentration levels were constructed by least-squares linear regression using the results for a standard solution of minor compounds. Concentration ranges, slopes, correlation

Table 3. Content of Microconstituents (Esters) Present in the Aromatic Fraction of Distillates Obtained from Grape Pomace from Various Galician Varieties

	Albariño		Dona Branca		Loureira		Godello		Treixadura		Torrontés	
	$n = 5^a$	SD	$n = 3^a$	SD	$n = 4^a$	SD	$n = 7^a$	SD	$n = 4^a$	SD	$n = 2^a$	SD
Acetates of Higher Alcohols												
isobutyl acetate	0.10	0.09	0.05	0.02	0.06	0.05	0.05	0.02	0.05	0.03	0.16	0.11
butyl acetate	0.40	0.36	0.20	0.15	0.11	0.11	0.43	0.55	0.13	0.08	0.08	0.07
isoamyl acetate	0.67	0.42	0.50	0.29	0.26	0.11	0.45	0.31	0.37	0.20	0.31	0.12
hexyl acetate	0.05	0.03	0.05	0.01	0.01	0.01	0.02	0.01	0.02	0.02	0.01	0.01
2-phenylethyl acetate	0.16	0.17	0.06	0.03	0.20	0.16	0.03	0.02	0.06	0.05	0.07	0.03
acetates of higher alcohols	1.36		0.82		0.52		0.99		0.64		0.63	
Esters												
ethyl butyrate	0.17	0.13	0.19	0.13	0.10	0.05	0.16	0.10	0.14	0.10	0.09	0.03
ethyl hexanoate	1.23	0.48	0.88	0.38	0.81	0.53	0.68	0.22	0.68	0.17	1.96	1.30
ethyl heptanoate	0.04	0.02	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ethyl octanoate	2.96	1.51	1.61	0.21	2.81	1.83	0.92	0.34	1.08	0.59	3.02	1.66
ethyl nonanoate	0.05	0.01	0.03	0.01	0.06	0.01	0.04	0.01	0.04	0.02	0.06	0.01
ethyl decanoate	3.75	1.67	3.62	1.06	4.66	3.14	2.01	0.72	1.98	1.21	3.76	1.73
ethyl dodecanoate	1.50	0.47	1.87	0.63	1.90	1.23	1.21	0.53	0.88	0.52	1.39	0.60
$\sum$ ethyl esters C6−C12[b]	7.94		6.12		8.28		3.61		3.73		8.75	
ethyl tetradecanoate	0.42	0.14	0.43	0.07	0.32	0.17	0.35	0.17	0.21	0.14	0.25	0.08
ethyl hexadecanoate	4.50	2.39	5.95	1.71	2.52	1.45	4.59	2.85	2.56	2.53	5.09	1.41
ethyl octadecanoate	0.07	0.05	0.11	0.07	0.06	0.04	0.11	0.07	0.06	0.06	0.15	0.01
ethyl 9-octadecenoate	0.46	0.28	0.55	0.16	0.34	0.18	0.40	0.24	0.32	0.30	0.76	0.22
ethyl 9,12-octadecadienonate	2.20	1.15	3.48	1.10	1.35	0.74	2.89	1.66	1.74	1.35	4.07	0.99
ethyl 9,12,15-octadecatrienoate	1.07	0.57	1.74	0.56	0.81	0.43	1.38	0.74	0.76	0.48	1.70	0.32
$\sum$ ethyl esters C14−C18	10.24		14.13		7.29		10.92		6.54		13.40	
isoamyl hexanoate	0.03	0.01	<LOD		0.02	0.01	<LOD		0.03	0.01	0.01	0.01
isoamyl octanoate	0.06	0.04	0.04	0.02	0.11	0.04	0.02	0.01	0.02	0.01	0.06	0.05
isoamyl dodecanoate	0.01	0.01	0.03	0.03	0.02	0.01	0.01	0.01	<LOD		0.01	0.01
$\sum$ isoamyl esters	0.07		0.07		0.10		0.02		0.02		0.08	
diethyl succinate	1.94	0.40	3.27	2.01	1.73	1.36	4.76	3.34	4.82	4.00	2.24	0.15

[a] Average of each sample of this variety made in triplicate mg%mL p.a. [b] $\sum$ ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl dodecanoate.

coefficients of calibration curves, detection limits (LOD), and reproducibility (%RSD) are shown in **Table 1**. The values correlations coefficients (r) obtained were from 0.9930 for *cis*-furan linalool oxide to 0.9999 for *trans*-furan linalool oxide, 1-octen-3-ol, ethyl nonanoate, and ethyl dodecanoate. LOD showed values below 0.25 mg/L in all cases. Method reproducibility (intralaboratory) was essayed by the repeated analysis of one distillate on five different days during 1 month: 10 analyses (1 distillate × 2 injections × 5 days). Results showed that the method is satisfactory in terms of reproducibility. The highest RSDs are for nerol (24.8%) and 1-octen-3-ol (12.2%). The rest of the compounds are below 10.5% (%RSD).

Major Volatile Compounds in Orujo Distillate. With regard to the macroconstituents in **Table 2**, we observed the methanol mean content of each variety varied from 403.4 mg%mL p.a. for Torrontés to 635.0 mg%mL p.a. for Albariño distillate and never exceeded the legal limit of 1000 mg%mL p.a. (Council Regulation EEC N. 110/2008).

Acetaldehyde is a direct alcoholic fermentation byproduct, and neither the grape cultivar nor the presence of wine in the orujo to be distilled affects its content. The sum of acetaldehyde and 1,1-diethoxyethane (acetal) shows rather low values. This means that, generally, the spirits have been fermented, distilled, and aged under favorable conditions and without intervention of unwanted bacteria. The mean concentration of ethyl acetate in the studied samples ranged between 135.5 and 83.3 mg%mL p.a. These values are similar to others (*4*, *8*, *10*−*11*). The sum of higher alcohols ranged from 236.2 mg%mL p.a. for Godello distillate to 329.6 mg%mL p.a. for Loureira distillate. The amount of 2-butanol increase by means of bacterial spoilage in the ensiled pomace when the pomace pH value is quite high and below 2.0 mg%mL p.a. is considered to be marc without bacterial events. In this case, 2-butanol ranged from 0.10 mg%mL p.a. for Dona Branca distillate to 0.82 mg%mL p.a. for Albariño distillate. The compound 1-hexanol is partially an alcoholic fermentation product (it mostly derives from 1-hexanal and *trans*-2-hexen-1-al/*trans*-2-hexen-1-ol by yeast reduction activity), and its origin may be linked to grape variety for the lipoxygenase activity, which can be connected also to the grape maturity, according to ref *12*, as well as to the type of skin contact−pressing technology. In our case, Dona Branca and Loureira distillates have shown the lowest concentrations of 1-hexanol, but differences were not significant ($P \leq 0.01$).

Ethyl lactate concentrations ranged between 21.3 and 51.7 mg/mL aa. Lactic acid bacteria spoilage increases its concentration and contributes negatively to the distillate organoleptic quality (*13*), but not in studied cases.

Table 4. Content of Microconstituents (Minor Alcohols, Monoterpenols, and Other Compounds) Present in the Aromatic Fraction of Distillates Obtained from Grape Pomace from Various Varieties

	Albariño		Dona Branca		Loureira		Godello		Treixadura		Torrontés		
	$n = 5$[a]	SD	$n = 3$[a]	SD	$n = 4$[a]	SD	$n = 7$[a]	SD	$n = 4$[a]	SD	$n = 2$[a]	SD	ANOVA[c]
Alcohols													
trans-3-hexen-1-ol	0.17	0.05	0.15	0.03	0.14	0.11	0.21	0.04	0.17	0.06	0.22	0.05	
cis-3-hexen-1-ol	0.35a	0.03	0.25b	0.03	0.11c	0.08	0.16c	0.05	0.32ab	0.11	0.28b	0.08	*
trans-2-hexen-1-ol	0.95	0.78	0.15	0.08	0.20	0.21	0.09	0.05	0.11	0.06	0.04	0.01	
R^1[b]	0.48		0.59		1.28		1.33		0.53		0.79		
1-pentanol	0.82a	0.12	0.37b	0.07	0.38b	0.23	0.43b	0.06	0.53ab	0.15	0.41b	0.03	*
1-heptanol	0.15	0.05	0.10	0.02	0.12	0.08	0.13	0.05	0.13	0.06	0.12	0.01	*
1-octanol	0.24a	0.09	0.13b	0.02	0.14b	0.02	0.13b	0.03	0.13b	0.02	0.15b	0.02	
1-nonanol	0.15a	0.03	0.09b	0.01	0.08b	0.03	0.09ab	0.02	0.11a	0.03	0.09ab	0.01	*
1-decanol	0.09	0.06	0.05	0.03	0.05	0.01	0.05	0.02	0.06	0.04	0.04	0.01	
benzylic alcohol	0.53a	0.24	0.26a	0.18	0.38a	0.18	0.35a	0.12	0.38a	0.13	2.32b	0.20	*
2-phenylethanol	5.14ab	1.82	4.27a	1.28	7.77bc	4.33	3.24a	0.90	3.66a	1.24	9.74c	0.67	
Other Compounds													
benzaldehyde	0.52	0.24	0.26	0.06	0.11	0.06	0.45	0.25	0.28	0.14	0.15	0.01	
furfural	0.42	0.29	0.89	0.19	0.59	0.24	0.75	0.61	0.31	0.13	0.80	0.35	
3-ethoxy-1-propanol	0.48	0.19	0.39	0.28	0.33	0.15	0.29	0.11	0.46	0.23	0.31	0.03	
1-octen-3-ol	0.09a	0.04	0.04b	0.02	0.01bc	0.01	0.06c	0.02	0.05b	0.03	0.03b	0.01	*
3-hydroxy-2-butanone	0.96	0.93	0.81	0.97	0.68	0.87	2.62	4.99	0.79	0.64	0.16	0.03	
Monoterpenols													
trans-furan linalool oxide	0.41a	0.21	0.09b	0.05	0.79a	1.10	0.08b	0.07	0.07b	0.04	0.04b	0.02	*
cis-furan linalool oxide	0.36a	0.34	0.02b	0.01	0.28a	0.33	0.03b	0.03	0.03b	0.01	<LOD		*
linalol	0.81a	0.30	0.24b	0.01	2.22c	1.13	0.11a	0.06	0.09a	0.02	0.05a	0.02	*
α-terpineol	0.18a	0.07	0.11b	0.03	0.82c	0.32	0.05b	0.02	0.06b	0.01	0.09b	0.04	*
citronellol	0.21a	0.06	0.07b	0.03	0.13b	0.04	0.05b	0.02	0.11b	0.04	0.12b	0.05	*
nerol	0.06a	0.01	0.02b	0.01	0.05a	0.01	<LOD		0.02b	0.01	0.02b	0.01	
geraniol	0.33a	0.08	0.16b	0.07	0.35a	0.07	0.08b	0.04	0.14b	0.04	0.14b	0.03	*
hotrienol[d]	0.47a	0.07	0.01b	0.01	0.63c	0.16	0.05b	0.03	0.02b	0.01	<LOD		*
∑ monoterpenols	2.79		0.70		5.22		0.42		0.49		0.45		

[a] Average of each sample of this variety made in triplicate mg%mL p.a. [b] R^1, *trans* 3-hexen-1-ol / *cis*-3-hexen-1-ol. [c] *, significance depending on variety ($P \leq 0.01$). Different letters in a row represent significantly different means (Duncan's test). [d] Quantification as linalol (RF = 1.02).

Esters. The results are summarized in **Table 3**. The content of ethyl esters of fatty acids from hexanoate to ethyl dodecanoate, with a ripe fruit aroma, is lower for Godello and Treixadura. Esters of higher molecular weight from ethyl tetradecanoate to 9,12,15-octadecatrienoate, with a waxy-rancid hint, are dependent on yeast level in the fermented pomaces by working on raw distillates (*14*). They derived from the yeast from which they are extracted by distillation. Higher levels are in products with more yeasts. The C18 acid ethyl esters profile depends also on the yeast type and relevant nutrition. Treixadura and Loureira are the distillates with the lowest values. Isoamyl esters are compounds previously identified in other beverages with fruit aroma such as sparkling wine cava (*15*) and also in grappa from Moscato (*16*). The results are not significantly different. Diethyl succinate ranged from 1.73 to 4.82 mg/mL aa. The amount of this compound can increase by means of bacterial spoilage in the ensiled pomace when the pomace pH value is quite high (*13*), although it may be linked to the intensity of the tail cut at the distillation.

Minor Alcohols, Monoterpenols, and Other Compounds. The ratio of *trans*-3-hexen-1-ol and *cis*-3-hexen-1-ol (the last one with results significantly different) is a marker of the variety. This fact is shown in **Table 4**, where R (ratio of the isomers *trans*-/*cis*-3-hexen-1-ol) is higher in Loureira and Godello varieties. This fact was also found in wines (*17*). Loureira and Albariño distillates have in common higher contents of *trans*-2-hexen-1-ol. The minor alcohols, 1-pentanol, 1-octanol, and 1-nonanol, showed significantly higher values in Albariño distillates. We can also observe very high values of benzylic alcohol in Torrontés distillates, which may be linked to the variety [typical of a hybrid variety (*18*)]. Varietal flavor contributions (sum of monoterpenols) were highest for Albariño and, even more markedly, for the Loureira grape pomaces, as can be deducted from the high values shown in **Table 4**. The sum of monoterpenols in Loureira distillate is double that of Albariño distillate. We recall the small content of geraniol, nerol, and citronellol, the so-called "skin monoterpenols", with respect to linalool, and the dominance of *trans*-furan linalool oxide on the *cis* isomer, according to the work on Albariño and Loureira wines by Versini et al. (*17*) and that on Loureira, Dona Branca, and Treixadura wines by Falqué et al. (*19*). Benzaldehyde values showed differences in Albariño and Godello distillates. It could come from microbiological problems, but, on the other hand, the reported bound benzaldehyde of Godello wines (*17*) can be a marker of this variety.

Other Microconstituents of Grape Pomace Distillate. (*a*) *Analytical Profile Peculiarities*. GC-MS analysis allowed the identification of 65 compounds. We could find compounds as monoterpenes, sesquiterpenes, diterpenes, norisoprenoids, volatile phenols, minority esters, and alcohols. In **Table 5** are shown compounds identified by SPE-GC-MS and semiquantified that showed differences significant among the six varieties studied. In **Table 6** are summarized other compounds identified without differences ($P \leq 0.01$). Also, as far as we know, most of the compounds we report here had not yet been found in these

Table 5. Identification of Minor Volatile Compounds in Distillates Obtained from Grape Pomace

		Albariño		Dona Branca		Loureira		Godello		Treixadura		Torrontés		
compound	KI[a]	(*n* = 5)[b]	SD	(*n* = 3)[b]	SD	(*n* = 4)[b]	SD	(*n* = 7)[b]	SD	(*n* = 4)[b]	SD	(*n* = 2)[b]	SD	ANOVA[c]
styrene	1257	141.4a	141.5	50.5b	50.4	17.2b	34.4			15.0b	11.7	59.5b	31.6	*
α-terpinene	1278	4.8a	4.4			49.7b	42.5	0.2a	0.6			1.7a	0.1	*
trans-2-penten-1-ol	1307	32.8a	18.3	10.8b	18.7	tr		16.2ab	15.1	16.6ab	19.2			*
cis-2-penten-1-ol	1314	369.8a	250.4	153.3b	22.5	tr		1032b	252.2	76.5b	105.6	67.4b	95.4	*
linalyl ethyl ether	1319	22.9a	14.4			209.6b	160.0	5.2a	8.2	3.0a	6.0			*
α-terpenyl ethyl ether	1433	7.2a	4.3	3.3a	3.0	65.3b	52.0	3.3a	6.4	0.5a	1.0			*
α-copaene	1476	1.5a	3.6			10.9a	21.7	1.7a	3.5	6.3a	11.2	39.2b	17.7	*
vitispirane A	1504	68.4bc	39.4	77.4bc	46.4	126.5c	61.4	29.5ab	16.3	13.2ab	8.7	73.7bc	50.7	*
vitispirane B	1506	93.8bc	50.5	67.2bc	39.5	154.3c	67.1	26.4a	16.9	13.6a	6.7	44.7ab	26.4	*
isobutyl octanoate	1551	36.4b	30.3	20.4ab	16.2	44.0b	14.7	9.2a	4.9	7.1a	9.7	25.6ab	17.6	*
p-menthen-9-al (primary isomer)[d]	1593	134bc	104.1	78.6ab	28.2	174.1c	172.5	24.1ab	25.5	7.5a	15.0	86.3ab	74.9	*
p-menthen-9-al (secondary isomer)[d]	1596	126ab	108.5	75.1ab	22.0	182.8b	185.8	22.2a	23.8	6.9a	13.9	87.4ab	78.7	*
ethyl benzoate[e]	1651	59.8a	62.3	112.9b	100.5	72.3a	88.6	75.4a	64.1	52.3a	38.5	100.3b	21.9	*
epizonarene	1703	17.5a	33.0	29.2a	26.4	88.7a	31.9	16.9a	25.3	8.1a	12.4	252.5b	189.1	*
β-cadinene	1706	0.5a	1.4	5.6a	5.1	19.3b	5.3	2.5a	4.1	1.3a	2.5	39.8c	21.4	*
2,6-dimethyl-3,7-octadiene-2,6-diol	1714	63.9b	41.8			49.7ab	51.1	4.5a	12.8					*
TDN	1724	21.4ab	19.8	84.8c	39.5	66.2bc	23.2	30.4ab	19.7	10.0a	8.2	84.9c	77.7	*
trans-pyran linalool oxide	1740	263.9a	141.5	37.9b	26.7	116.0c	100.4	25.0b	22.7			7.2b	4.5	*
γ-cadinene	1746	38.4a	47.6	65.8a	57.1	97.4a	52.7	42.1a	34.9	18.0a	33.0	378.8b	317.0	*
δ-cadinene	1752	22.7ab	30.4	32.9ab	28.8	74.6b	24.9	29.6ab	21.6	8.2a	12.6	146.9c	86.1	*
cis-pyran linalool oxide	1764	43.9a	22.6	7.8b	11.6	75.7a	107.3	9.8b	10.5	1.6b	3.2	1.9b	2.7	*
methyl dodecanoate[e]	1815	123bc	79.6	86.1ab	87.3	197.5c	81.9	52.8ab	31.9	16.8a	33.6	75.0ab	39.7	*
unknown (*m*/*z*85, 128)	2001	78.0ab	67.4	168.5ab	52.5	61.7a	67.9	139a	71.6	73.8a	91.9	202.0b	74.6	*
eugenol	2138	75.0b	40.7	18.0a	11.3	40.4a	34.8	20.4a	20.7	14.3a	17.1	84.2b	36.7	*
nerolidol	2043	tr		33.8ab	25.0	14.9ab	22.5	33.5ab	48.6			64.7b	70.3	*
mannoyl oxide	2278	50.9a	39.0	56.7a	45.8	29.9a	11.7	52.4a	42.1	92.8a	60.4	390.2b	185.4	*

[a] Retention indices relative to C8−C32 *n*-alkanes on Carbowax phase (PEG). [b] Values represent averages of samples of each variety made in duplicate. [c] *, significance depending on variety ($P \leq 0.01$). Different letters in a row represent significantly different means. (Duncan's test). [d] Correct isomer not identified. [e] Co-elution with pure component.

varieties, although they had been previously reported in Baga grapes (*20*), in grape pomace (*21*), and in Shiraz grapes (*22*). The major sesquiterpenoids isolated were α-ylangene, γ-cadinene (both of them a wood aroma), epizonarene, δ-cadinene, and α-calacorene. Beyond the observed differences between the six varieties, Torrontés is the variety with major presence of these sesquiterpenoids and one diterpene (β-cadinene, δ-selinene, α-humulene, aromandrene, nerolidol, manoyl oxide), which showed that their presence and their relative proportion may be a varietal marker for this variety, although only two samples have been studied. Due to the lack of availability of all commercial standards of these sesquiterpenoids, a tentative identification has been done. With regard to norisoprenoid compounds, two vitispirane isomers are present (**Table 5**), with the first one (vitispirane A) dominating the second one (vitispirane B) in most varieties, with the exception of Albariño and Loureira distillates. The compound 1,2-dihydro-1,1,6-trimethylnaphthalene (TDN) showed significant differences across the six varieties. Torrontés and Dona Branca have shown the highest amount of TDN. Within the norisoprenoid compounds, theaspirane isomers, α-ionone, and β-ionone are identified in only trace amount (around 20 μg/L for β-ionone and 10 μg/L for α-ionone), in disagreement with ref *5*, in which 10 times this value is reported. Focusing on the monoterpenoids, Loureira and Albariño show differences with respect to the rest of the varieties (α-terpinene, linalyl ethyl ether, α-terpenyl ethyl ether, *trans*-pyran linalool oxide, 2,6-dimethyl-3,7-octadiene-2,6-diol). The *p*-menthen-9-al isomers (**Table 5**) are compounds described from citrus honey (*23*−*25*) and from dill (*26*), but this is the first time that have been reported in grape pomace distillate and berries (**Figure 1**). These compounds, derived of linalool, may be derived from 8-hydroxylinalool (2,6-dimethyl-2,7-octadiene-1,6-diol) via the allylic rearranged 8-hydroxygeraniol under reaction conditions of acid pH (3−4) and high temperature (>100 °C). These compounds, 8-hydroxylinalool and 8-hydroxygeraniol, were not detected in this research. Albariño distillate and, even more markedly, Loureira distillate show high values of *p*-menthen-9-al according to ref *20*, in which a high concentration of bound 8-hydroxylinalool (both *trans* and *cis* isomers) was found in Loureira and Albariño wines.

Multivariate Statistical Analysis. As was shown in previous paragraphs, investigated distillates produced from different grape varieties generally differ in varietal aroma composition. Cross-validated (leave-one-out) PCA was performed excluding Torrontés samles (only two samples were available of this class). Raw data were autoscaled to avoid the effect of different size variables, and only 20 variables (compounds analyzed in each sample) were chosen as markers of grape pomace distillate varieties. Finally, Torrontés samples were projected with the remaining samples in PCA space for a better visualization of the results. The loadings plot (**Figure 2a**) shows that *trans*-furan linalool oxide (ox A), *cis*-furan linalool oxide (ox B), linalool, α-terpineol, *p*-menthen-9-al isomers, vitispirane isomers, hotrienol, and *trans*- and *cis*-pyran linalool oxide (ox C and D) were the dominant features in the first principal component, which represented 41.5% of the variance. The second principal component, which accounted for 24.7% of total data variance, is represented by sequiterpenes, epizonarene, β-cadinene, γ-cadinene, δ-cadinene, and mannoyl oxide. The third principal component (17.9%) is dominated by *cis*-3-hexen-1-ol, 1-pentanol, 1-heptanol. and 1-nonanol. The score analysis of

Table 6. Identification of Other Minor Volatile Compounds in Distillates Obtained from Grape Pomace

		Albariño		Dona Branca		Loureira		Godello		Treixadura		Torrontés	
compound	KI[a]	(*n* = 5)[b]	SD	(*n* = 3)[b]	SD	(*n* = 4)[b]	SD	(*n* = 7)[b]	SD	(*n* = 4)[b]	SD	(*n* = 2)[b]	SD
m-xylene	1207	14.8	6.3	3.1	5.3			6.9	5.3	10	10.7	17.8	12.1
2-pentylfuran[c]	1247	45.3	52.6	125.6	154.2			27.1	17.6	9.3	6.7	85.6	1.4
p-cymene	1269	14.8	10.3	8.1	14.1	13.8	17.3	2.2	2.5	7.6	8.9	8	1.2
methyl octanoate	1378	169.7	163.0	74.4	28.2	175.8	90.1	37.9	14.8	45.2	31.1	98.9	79.2
α-ylangene	1467	28.2	34.9	43.3	24.0	164	254.6	19.7	23.2	9	18.1	242.6	274.1
theaspirane A[c]	1478	5.1	4.5					tr		tr		tr	
theaspirane B[c]	1519	2.5	2.1									tr	
ethyl DL-2-hydroxyhexanoate	1538	453.2	361.0	355.9	99.3	656.9	742.2	414.4	224.7	378.9	326.5	486.8	202.3
5-methylfurfural[c]	1557	108.8	109.4	153.6	95.5	107.4	132.2	125.3	138.7	35.2	29.3	69.7	92.1
isoamyl lactate[c]	1564	626.5	419.5	786.7	429.1	1153	736.5	671.2	403.8	744.2	485.1	902	53.8
diethyl malonate	1578	29	10.4	26.4	4.7	19	6.3	27.3	19.3	9.5	11.0	36.7	10.6
4-terpineol	1590	78.4	47.5	73.3	73.3	104.6	72.3	16.1	27.5	84.1	114.2		
methyl decanoate	1593	235.3	205.7	154.7	74.8	231	245.8	73.1	33.4	78.7	49.4	134.7	98.7
β-cyclocitral	1593	9.6	10.7	8.4	14.6	2.1	4.2	tr					
aromandrene	1607			14.3	8.9	48.5	68.6	8.6	7.9	3.7	5.6	77	52.2
acetophenone	1629	13.3	10.5	tr				39.3	82.2	1.6	3.1	13.2	9.8
butanedioic acid ethyl methyl ester	1634	111.8	79.4	221.6	254.7	247.1	305.3	210	118.3	162.9	191.8	86.4	40.7
2-hydroxybenzaldehyde	1658	26	20.4	23.9	20.9	87.7	159.1	8.9	7.9	6.7	1.9	5.7	0.1
α-humulene	1661	9.8	15.2									10.4	5.9
ethyl 4-decenoate[d]	1668	3.8	3.4			3.5	2.6	4	4.0	3.6	1.2	3.6	5.0
δ-selinene	1683	3.2	6.7			28	36.7	4.3	5.9			36.9	22.7
ethyl 9-decenoate[d]	1696	95.5	76.2	22.1	21.8	90.1	60.3	27.5	14.3	17	12.9	9.5	4.9
β-damascone	1711	6.8	4.0	3.2	5.6	8.1	10.7	11	5.5	6.7	7.1		
α-muurolene	1717	13.6	15.7	11.5	19.9	55.5	59.5	12.9	13.4	2.9	4.1	54.9	41.2
benzyl acetate	1720	43.5	41.1	16.6	0.7	23.4	46.0	20	17.0	15	4.8	26.5	16.2
propyl decanoate	1732	6.2	8.2	9.3	10.4			9.5	12.4	2.2	3.1	6.6	5.0
ethyl undecanoate	1750	37.5	32.8	49.9	16.0	51.7	17.7	52.4	37.1	26.1	28.5	18	25.4
methyl salicylate[c]	1754	433.3	276.9	279.7	233.8	380.3	358.9	63.9	30.5	99.3	139.5	422	467.0
E,*E*-α-farnesene	1757	8.5	20.8			57.6	78.8	12.9	24.0			17.2	9.8
isobutyl decanoate	1767	29.5	31.1	36.9	23.5	54.6	13.7	9.4	10.7	8.1	16.2	32	27.8
ethyl phenylacetate	1781	188.2	53.3	188.3	75.7	128.9	152.4	228.2	227.7	838.7	1403	129.7	24.1
ethyl salicylate[c]	1791	1349	1449	218.2	111.7	442.4	446.0	59	36.3	132.3	112.5	325.3	363.3
β-damascenone	1806	tr						24.4	61.1			22.3	31.6
α-ionone [c]	1839							0.7	1.3			3.3	4.7
guaiacol	1850	16.4	12.1					14.4	20.4			3.7	5.2
α-calacorene	1896	38.8	29.1	47.5	26.0	135.5	108.1	35.2	23.7	69	123.0	144.8	84.3
β-ionone[c]	1921			28.4	25.8			21.5	17.1	11.6	14.6	17.9	6.3
3,7-dimethyl-1,7-octadiene-3,6-diol	1959	71.6	116.5			44.4	65.9						
4-ethylguaiacol	2016	410.9	500.9	344.3	526.3	163.2	185.8	363.9	487.4	29.8	41.0	10.8	1.8
ethyl cinnamate	2098	491.2	715.3	44.7	17.1	50.3	64.5	17.7	18.0	41.2	19.3	28.4	40.1
4-ethylphenol	2152			247.6	407.6	72.4	63.5	215.3	527.0			44.4	62.7
ethyl 9-hexadecenoate	2255	164.7	189.9	126.2	77.9	146.9	89.2	230.9	213.9	15.5	31.0	54.7	77.4

[a] Retention indices relative to C8−C32 *n*-alkanes on Carbowax phase (PEG). [b] The values represent averages of samples of each variety made in duplicate. [c] Co-elution with pure component. [d] Correct isomer not identified.

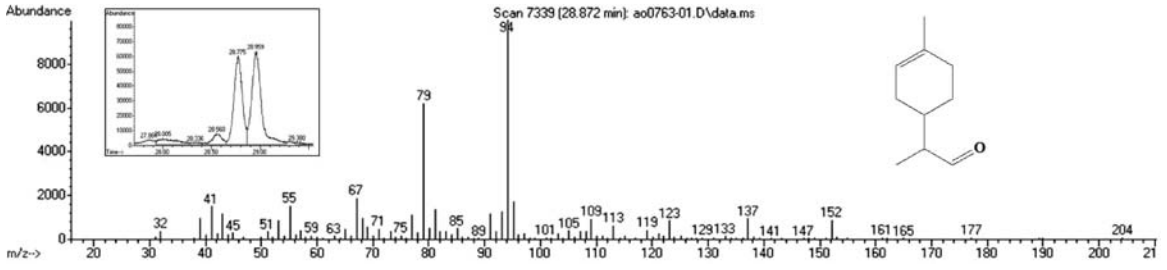

Figure 1. MS spectra of 1-*p*-menthen-9-al.

grape pomace distillate on the space formed by the three principal components (84.1%) was carried out (**Figure 2b**). The first axis was highly responsible for the separation between more aromatic varieties. The results showed that marc distillates from Loureira and Albariño are characterized by high contents of monoterpenols (linalool, α-terpineol, and hotrienol), furanic and pyranic oxides, C_{13}-norisoprenoids (vitispirane isomers), and *p*-menthen-9-al isomers, this content being higher in Loureira distillate, in contrast to the rest of the varieties, which exhibited poorer monoterpenol profiles. Treixadura, Godello, and Dona Branca appear as three groups partially overlapped. Among them, Treixadura is separated slightly by a high concentration of minority alcohols (PC3), and Dona Branca seems to show a contribution higher in PC1 than Treixadura and Godello. Torrontés distillates were

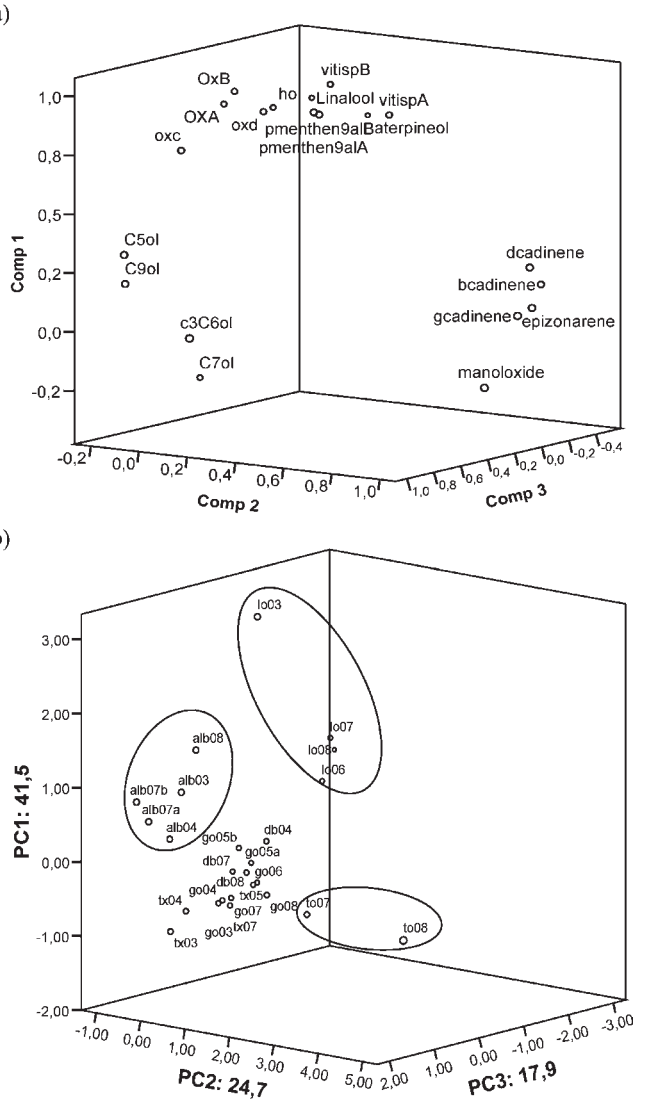

Figure 2. Principal component analysis of the volatile composition of monovarietal grape pomace distillates: (**a**) PCA loadings of some analyzed compounds; (**b**) PCA scores of Torrontés, Albariño, Loureira, Dona Branca, Treixadura, and Godello distillates.

positioned in PC2 and contained elevated sesquiterpene concentrations. Finally, on the basis of all volatiles investigated, it was possible to discriminate different distillates from different Galician varieties produced in several years by extracting several sesquiterpenes, C13-norisoprenoids, monoterpenols, and some minor alcohols.

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