

## Approaches to Spirit Aroma: Contribution of Some Aromatic Compounds to the Primary Aroma in Samples of *Orujo* Spirits

SANDRA C. DIÉGUEZ,\* MA. LUISA G. DE LA PEÑA, AND ESPERANZA F. GÓMEZ

Departamento de Química Analítica y Alimentaria, Área de Química Analítica, Universidad de Vigo, Facultad de Ciencias, As Lagoas s/n, 32004 Ourense, Spain

Terpenes and C<sub>13</sub> norisoprenoids are among the most important aromatic compounds found in a volatile and nonvolatile form in grapes. Aromatic typicity of a spirit could be attributed to these compounds despite the very important presence of volatile compounds produced during alcoholic fermentation. In this study, following a solid phase extraction stage, the determination of the varietal aromatic compounds by gas chromatography was performed on 15 samples of Galician orujo spirits. The results show that significant differences ( $p < 0.05$ ) exist in the concentrations of varietal aromatic compounds in Galician spirits obtained from different varieties of grapes.  $\alpha$ -Ionone is the varietal aromatic compound that is most likely to contribute to the aroma of all of the spirits studied. The spirits from Catalan Roxo are the most aromatic, with floral and fruity nuances, while the spirits from Godello were the less aromatic group as far as the varietal compounds studied are concerned. Spirits from Mencia and Treixadura show a similar profile, but the former has a more intensive aroma due to  $\beta$ -pinene, citronellol, and  $\alpha$ -ionone. Albariño spirits stand out because of their profile that is marked by the contributions of eugenol and linalool.

**KEYWORDS:** Orujo; spirit; varietal aroma; terpenes; C<sub>13</sub>-norisoprenoids; solid phase extraction; gas chromatography

### INTRODUCTION

One of the most influential factors in the characteristics and chemical composition of an orujo spirit is the quality of the raw material (1–4). The raw material or grape pomace, apart from contributing (after alcoholic fermentation of the residual sugars) principally ethanol, higher alcohols, volatile organic acids, and their ethyl esters, aldehydes, acetates, etc. also contributes a series of aromatic compounds responsible for the primary or varietal aroma. These compounds are principally in the nature of terpenes and C<sub>13</sub> norisoprenoids and are characterized by their contribution of fruity or floral nuances (5). Although these compounds are found in low concentrations as most of them have very low perception threshold levels, their presence in wines and spirits is going to be very important from the sensory and organoleptic point of view.

Several studies exist, which indicate that although the varietal compounds are distributed throughout the berry, their concentration is especially high in the cells on the internal part of the grape skin (6–9). Besides being present in free and volatile forms and therefore with a direct participation in the aroma, terpenes and C<sub>13</sub> norisoprenoids are found in important amounts bound to sugar molecules (10–13) by  $\beta$ -bonds and need to be liberated so that in a volatile form, the varietal compounds can participate in the aroma. It must also be taken into account that

the concentration of bound varietal aromatic compounds for most of the varieties is higher than the volatile forms (14). In the process of liberation or hydrolysis of the aglycone–sugar bonds, the most important elements that intervene are temperature, pH of the medium, and enzymes with  $\beta$ -glucosidase activity (15–19).

In very aromatic varieties, the concentration of a compound in its free form is normally higher than its perception threshold. Occasionally, in less aromatic varieties, the liberation of the bound compounds might cause the total concentration of this compound to raise to a level close to the perception threshold or even beyond; therefore, the aromaticity is notably increased.

Because of the presence of these varietal compounds in the different varieties of *Vitis vinifera*, the performance of a varietal differentiation has been attempted for many of them (20). It has been demonstrated, after carrying out various studies, that although the compounds detected in all the varieties are usually the same, their concentration changes from one variety to another (21). Of all of the compounds, linalool and citronellol among the terpenols and  $\alpha$ - and  $\beta$ -ionone among the norisoprenoids are especially important. The former have very low perception thresholds (50 and 18  $\mu\text{g L}^{-1}$ , respectively) (22) and contribute, respectively, rose and citrus aromas to the wine and the latter contribute an aroma of violets and have low perception thresholds of 2.6 and 4.5  $\mu\text{g L}^{-1}$ , respectively (23, 24).

Very aromatic varieties of grapes are cultivated in Galicia, among which can be found Albariño, Loureira, and Treixadura,

\* To whom correspondence should be addressed. Tel: +34 988 38 70 83. Fax: +34 988 38 70 01. E-mail: smcortes@uvigo.es.

within the white *V. viniferas* and Mencia as a red variety of *Vitis*. From these grapes, wines obtained have an important acid content and a large number of varietal aromas (25–27). The grape pomace resulting from pressing these grapes during winemaking is employed, after fermentation and distillation, in the production of Orujo, the name of Galician spirits.

In this Spanish region, a large number of hectares of vineyards are dedicated to the production of hybrid direct product or Catalan Roxo. Its use for the production of wine is prohibited because it is not *V. vinifera*, but there is nothing in the legislation against its use for the production of spirits, and there are various orujos in the market that have used, totally or partially, hybrid grape pomace. This variety is characterized by its high acidity, principally in malic acid, and also an important sugar content, when the climate permits, but it stands out for being a very aromatic variety with very intense fruity and floral nuances that evoke some types of muscat (28).

For all of these reasons, it can be considered that the spirits produced from Galician grape pomace are characterized by their significant aromaticity and excellence because of the presence of these varietal compounds in the initial raw material. Moreover, during the fermentation of the grape pomace, the most favorable conditions are found for two processes that take place. The first is the extraction of the aromatic compounds that are present mainly in the grape skins, as the alcoholic fermentation of the grape pomace implies a lengthy maceration of the solid parts of the grape, and the second is that during the fermentation stage and later storage period, conditions are adequate for endogenous enzyme activity in the grape, liberating the aromatic compounds that might be bound to the sugar molecules.

Despite an ever widening knowledge about the compounds responsible for the aromaticity of quality Galician varieties, their study in spirits (for characterization or even just for identification and quantification) has not yet been carried out, and the limited number of publications about Galician grape pomace do not mention this important group of compounds. Very little information exists in the bibliography that mentions the study of varietal compounds in other kinds of spirits (29–32).

Knowledge of the varietal compounds will permit characterization of the spirits produced from Galician grape pomace and their differentiation from other European spirits that are produced like Galician spirits (i.e., Italian grappas, Greek tsipouro, French marc, and Portuguese bagaçoiras) (33).

In this study, through the determination of the varietal aromatic compounds (terpenes and C<sub>13</sub> norisoprenoids) present in spirits produced from monovarietal Galician grape pomace, the objective sought is to identify and quantify the compounds responsible for the varietal aroma of the Galician monovarietal orujo spirits, obtained from the distillation of grape pomace from the principal varieties of aromatic grapes cultivated.

## MATERIALS AND METHODS

**Samples.** Fifteen samples were available for the study of the varietal aromatic compounds, mainly terpenes and C<sub>13</sub> norisoprenoids present in spirits produced from Galician grape pomace. The samples had been collected, in most cases, directly from the distilleries; whenever this was not possible, they were provided by the Regulating Council of the Specific Denomination "Galician Orujo", so that the authenticity of the product was patent. Samples of monovarietal spirits from the principal varieties of *Vitis* cultivated in Galicia were employed in this study. These varieties were Albariño, Treixadura, Godello, and Mencia. In addition, an analysis of spirits of the hybrid Catalan Roxo was performed, to determine if there were marked differences in its composition and similarities to spirits of the other varieties studied.

Table 1. Compounds Studied and Their Aromatic Characteristics

compd	odor threshold (mg L <sup>-1</sup> )	matrix	odor descriptor
α-pinene	1 <sup>44</sup>	water	mint, eucalyptus <sup>44</sup>
β-pinene	0.14 <sup>44</sup>	water	mint, eucalyptus <sup>44</sup>
limonene	0.21 <sup>44</sup>	water	citrus, fruity <sup>44</sup>
1,8-cineol			mint, eucalyptus <sup>23</sup>
linalool	0.05 <sup>23</sup>	wine	rose, <sup>22</sup> aniseed, floral <sup>47</sup>
α-terpineol	0.40 <sup>22</sup>	wine	floral, iris, <sup>22</sup> pine, lime tree <sup>47</sup>
citronellol	0.018 <sup>22</sup>	wine	grapefruit, <sup>22</sup> green lemon <sup>47</sup>
nerol	0.40 <sup>22</sup>	wine	lime tree, floral, <sup>47</sup> rose <sup>22</sup>
geraniol	0.13 <sup>22</sup>	wine	floral, <sup>47</sup> rose <sup>22</sup>
theaspirane			tea, rose <sup>6</sup>
α-ionone	0.0026 <sup>23</sup>	wine	floral (violet) <sup>23</sup>
β-ionone	0.0045 <sup>24</sup>	wine	floral (violet) <sup>24</sup>
citronellal			
eugenol	0.006 <sup>23</sup>		clove <sup>24</sup>
4-allyl-1,2-dimethoxybenzene	0.82 <sup>45</sup>	water	floral <sup>45</sup>

Within the varietal spirits, the highest number of samples corresponds to the variety Albariño. This is because a large number of wineries produce wine and spirits exclusively from this variety. However, it was difficult to obtain spirits that were 100% Godello, Treixadura, or Mencia, as they are scarce and their production as monovarietal spirits is rare.

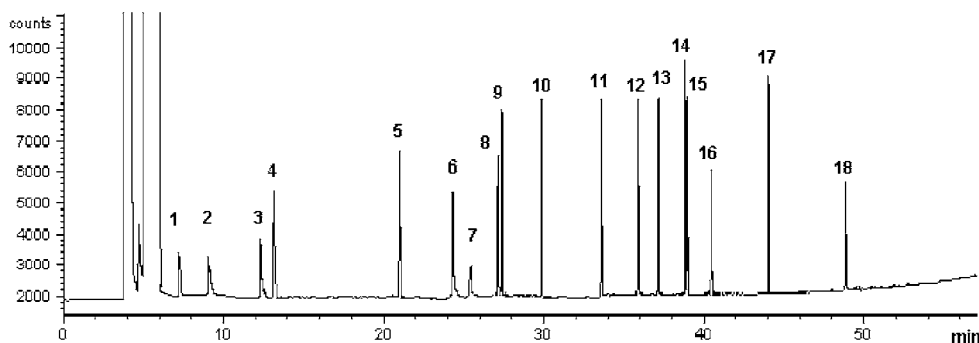
**Reagents.** Methanol, dichloromethane, pentane, and ethanol were of analytical grade from Merck (Germany). All standards were purchased from Sigma (Sigma Chemical, U.S.A.). **Table 1** shows perception threshold, matrix, and odor descriptor of each volatile compound studied.

**Statistical Analysis.** A computer program, Statgraphics Plus for Windows, Version 3.1 (1997), was used for the statistical study of the results. A multifactor variance analysis (ANOVA) was also applied, to establish whether significant differences ( $p < 0.05$ ) existed between the values obtained for the concentration of aromatic compounds in the different groups of spirits.

**Aromatic Compound Determination.** Given the very low concentration of these compounds and the complex volatile composition of the spirit samples, an extraction of the sample must be performed for its determination, which will allow the separation of terpenes and C<sub>13</sub> norisoprenoids from other compounds that may interfere in the analysis. It must then be concentrated so that these can be detected by gas chromatography (GC). Various methods of extraction for these types of compounds are cited in the bibliography, such as liquid–liquid extraction, headspace, solid phase extraction, ultrasound, and micro-extraction (34–40). In our case, a solid phase extraction was performed using C-18 cartridges and a mixture of dichloromethane and pentane (1:2), previously distilled, as the elution solvent.

It is important that the degree of alcohol in the spirit used for determining the compounds is reduced to avoid interferences due to the high graduation of alcohol in the sample (41, 42). For this, 20 mL was taken from each spirit and diluted to 100 mL so that the degree of alcohol of the sample was reduced to between 10 and 15% (v/v). One milliliter of 3-octanol (10 mg L<sup>-1</sup>) was added to the sample as internal standard. This prepared sample was then subjected to solid phase extraction following the methodology adapted in our laboratory for the determination of the same compounds in samples of grapes and wine (43). The extract obtained was concentrated under nitrogen gas flow to 1 mL. Determinations were made in triplicate. All extracts were analyzed by GC with a flame ionization detector using a Hewlett-Packard 5890 Series II gas chromatograph equipped with an HP 6890 automatic injector.

Aromatic compounds were identified by comparing retention times with those of pure compounds and confirmed by GC-MS using a HP5890 Series II coupled to HP 5989 A mass spectrometer in the EI mode (ionization energy, 70 eV, source temperature 250 °C). The acquisition was made in scanning mode from  $m/z$  10 to 1000 at 5 scan/s.



**Figure 1.** Chromatogram of a standard solution of varietal aromatic compounds. Peak identification (in parentheses; retention time (min)): 1,  $\alpha$ -pinene (7.11 min); 2,  $\beta$ -pinene (9.25 min); 3, limonene (12.25 min); 4, 1,8-cineol (13.07 min); 5, 3-octanol (I.S.) (20.97 min); 6, citronellal (24.23 min); 7, theaspirano a (25.42 min); 8, theaspirano b (27.10 min); 9, linalool (27.33 min); 10, 4-terpineol (29.85 min); 11,  $\alpha$ -terpineol (33.55 min); 12, citronellol (35.90 min); 13, nerol (37.14 min); 14, geraniol (38.77 min); 15,  $\alpha$ -ionone (38.92 min); 16,  $\beta$ -ionone (41.95 min); 17, 4-allyl-1,2-dimethoxybenzene (43.97 min); and 18, eugenol (48.80 min).

**Table 2.** Concentration (mg L<sup>-1</sup>) of the Varietal Aromatic Compounds in Orujo Spirits Analyzed<sup>a</sup>

samples	Treixadura				Mencia				Godello				Albariño				Catalán Roxo			
	mean	SD	range		mean	SD	range		mean	SD	range		mean	SD	range		mean	SD	range	
			min	max			min	max			min	max			min	max			min	max
	2				2				2			6					4			
	terpenes																			
$\alpha$ -pinene	ND				ND				0.07 <sup>a</sup>	0.10	0.00	0.14	ND						ND	
$\beta$ -pinene	1.26 <sup>a</sup>	0.26	1.07	1.44	2.80 <sup>b</sup>	0.12	2.72	2.88	0.86 <sup>a</sup>	0.28	0.67	1.06	1.07 <sup>a</sup>	0.58	0.33	1.93	0.54 <sup>a</sup>	0.34	0.22	0.95
limonene	ND				ND				ND				0.27 <sup>a</sup>	0.24	0.08	0.66	0.50 <sup>a</sup>	0.13	0.34	0.65
1,8-cineol	49.01 <sup>a</sup>	0.74	48.49	49.53	69.17 <sup>a</sup>	2.08	67.71	70.64	73.95 <sup>a</sup>	39.88	45.75	102.15	41.31 <sup>a</sup>	15.10	25.93	64.30	63.81 <sup>a</sup>	14.57	50.11	81.92
linalool	0.70 <sup>a</sup>	0.26	0.51	0.88	0.81 <sup>a</sup>	0.02	0.79	0.82	0.05 <sup>a</sup>	0.10	0.01	0.09	2.92 <sup>b</sup>	0.84	1.80	3.77	5.84 <sup>c</sup>	1.89	3.33	7.87
4-terpineol	0.17 <sup>a</sup>	0.01	0.16	0.17	0.35 <sup>a</sup>	0.01	0.35	0.36	ND				1.63 <sup>b</sup>	0.96	0.62	3.02	0.40 <sup>a</sup>	0.11	0.24	0.47
$\alpha$ -terpineol	0.34 <sup>a</sup>	0.09	0.27	0.40	0.38 <sup>a</sup>	0.10	0.31	0.45	0.025 <sup>a</sup>	0.03	0.03	0.02	0.65 <sup>a</sup>	0.06	0.56	0.71	4.98 <sup>b</sup>	1.67	2.95	6.44
citronellol	0.20 <sup>a</sup>	0.02	0.18	0.21	0.40 <sup>a</sup>	0.07	0.35	0.46	0.07 <sup>a</sup>	0.00	0.07	0.07	0.34 <sup>a</sup>	0.23	0.08	0.66	4.53 <sup>b</sup>	0.56	3.79	4.97
nerol	0.12 <sup>a</sup>	0.01	0.11	0.13	0.15 <sup>a</sup>	0.03	0.13	0.17	0.04 <sup>a</sup>	0.00	0.04	0.04	0.28 <sup>a</sup>	0.15	0.14	0.47	1.82 <sup>b</sup>	1.03	0.68	3.19
geraniol	0.37 <sup>a</sup>	0.06	0.33	0.42	0.40 <sup>a</sup>	0.02	0.38	0.42	0.165 <sup>a</sup>	0.01	0.16	0.17	0.67 <sup>a</sup>	0.31	0.40	1.03	2.55 <sup>b</sup>	0.78	1.87	3.63
	C <sub>13</sub> norisoprenoids																			
$\alpha$ -ionone	0.26 <sup>a,b</sup>	0.28	0.06	0.46	0.48 <sup>a,b</sup>	0.02	0.46	0.49	0.035 <sup>b</sup>	0.01	0.02	0.05	0.17 <sup>a</sup>	0.06	0.10	0.24	0.77 <sup>a</sup>	0.47	0.20	1.32
$\beta$ -ionone	0.02 <sup>a,b,c</sup>	0.01	0.01	0.03	0.03 <sup>b,c</sup>	0.00	0.02	0.03	0.01 <sup>a,b</sup>	0.00	0.01	0.02	ND				0.04 <sup>c</sup>	0.01	0.02	0.05
theaspirane a	ND				ND				ND				0.21 <sup>a</sup>	0.07	0.10	0.28	0.22 <sup>a</sup>	0.28	0.00	0.62
theaspirane b	0.29 <sup>a</sup>	0.03	0.27	0.31	0.35 <sup>a</sup>	0.03	0.34	0.37	0.20 <sup>b</sup>	0.03	0.18	0.22	ND				ND			
	other compounds																			
citronellal	0.44 <sup>a</sup>	0.21	0.30	0.59	0.28 <sup>a</sup>	0.01	0.28	0.29	0.23 <sup>a,b</sup>	0.02	0.22	0.24	ND				0.07 <sup>b</sup>	0.03	0.05	0.10
eugenol	ND				ND				ND				0.44 <sup>a</sup>	0.14	0.26	0.61	0.36 <sup>a</sup>	0.06	0.29	0.42
4-allyl-1,2-dimethoxybenzene	0.03 <sup>a</sup>	0.00	0.02	0.03	0.01 <sup>b</sup>	0.00	0.01	0.01	0.004 <sup>c,b</sup>	0.00	0.00	0.01	ND				ND			

<sup>a</sup> The value of a line with the same superindexed letter indicates that there are no significant differences between them ( $p < 0.05$ ); ND, not detected.

The compounds were separated in a CHROMPACK CP-WAX 57CB Wcot fused silica column (poly(ethylene glycol) stationary phase; 50 m  $\times$  0.25 mm i.d. with 0.25  $\mu$ m film thickness). Injections were made in splitless mode (30 s), and the sample size was 1  $\mu$ L. The injector temperature was 250  $^{\circ}$ C, and the oven was programmed from 60  $^{\circ}$ C for 5 min, increased at 3  $^{\circ}$ C min<sup>-1</sup> to 220  $^{\circ}$ C with 15 min isothermal. The carrier gas was helium, at a flow rate of 1.2 mL min<sup>-1</sup>. Detector (FID) Ta: 260  $^{\circ}$ C. H<sub>2</sub>: 42 mL min<sup>-1</sup>. Air: 360 mL min<sup>-1</sup>. Auxiliary gas (N<sub>2</sub>): 15 mL min<sup>-1</sup>.

Qualitative and quantitative analyses of the compounds in the spirit samples analyzed were made by comparison of their retention times with those of the standards (Figure 1). In the calibration, the response factor of each compound, RFi, was calculated by  $R_{Fi} = (A_{is}/A_{si}) \cdot (C_{si}/C_{is})$ , where  $A_{is}$  and  $A_{si}$  are the peak areas of the chromatographic internal standard and of the chromatographic standard of the compound of interest, respectively, and where  $C_{is}$  and  $C_{si}$  are the molar concentrations of the chromatographic internal standard and of the chromatographic standard of the compound of interest, respectively. In the actual quantification, the molar concentration of each compound of interest,  $C_i$ , was determined via  $C_i = (A_i/A_{is}) \cdot C_{is} \cdot R_{Fi}$ , where  $A_i$  is the area of peak of interest.

## RESULTS AND DISCUSSION

The results obtained for the varietal compounds studied in each of the groups of orujo spirits analyzed are reflected in Table 2.

**Terpenic Hydrocarbons.**  $\alpha$ -Pinene is only detected in samples of the spirit obtained from Godello, although at a low concentration and only in one of the two samples of spirit of this variety was it analyzed. However, this compound does not participate directly in the aroma of any of the orujo spirits analyzed because of its high perception threshold (1 mg L<sup>-1</sup>) (44).

$\beta$ -Pinene was detected in all of the spirits analyzed, but significant differences of concentration were only found in spirits of the variety Mencia. These showed much higher contents of this compound than the rest of the spirits of the other varieties analyzed; those from the variety Catalán Roxo had the lowest content. However, in all of the spirits analyzed, the mean concentrations of  $\beta$ -pinene were much higher than its perception

threshold of  $0.14 \text{ mg L}^{-1}$  (44); therefore, the mint nuances of this aromatic compound could be clearly assessed.

Limonene was found at a higher concentration in spirits of Catalan Roxo, without significant differences with respect to the concentrations found in Albariño's orujos. For these two groups of spirits, the mean concentration of limonene is higher than its perception threshold of  $0.21 \text{ mg L}^{-1}$  (44); therefore, its presence will intensify the fruity and citrus nuances of the spirits. This compound was not detected in any of the samples of spirits analyzed from the varieties Treixadura, Mencia, or Godello.

**Terpenic Alcohols.** Of the terpenic alcohols identified, 1,8-cineol presented a higher concentration in all of the spirits analyzed. Although this alcohol did not show significant differences in its mean concentration between the different groups of orujo spirits analyzed, it reached its highest contents in those of Godello and slightly lower in those of Albariño. It is possible that this compound contributes balsamic nuances (eucalyptus) to the spirit, but as the value of its perception threshold is unknown, the extent of its contribution to the global aroma cannot be estimated.

Of the rest of the terpenic alcohols studied, linalool is one of the most important due to a low perception threshold ( $0.05 \text{ mg L}^{-1}$ ) (23) and aroma of roses. Of all of the spirits analyzed, those of Catalan Roxo have the highest concentration of this compound, with a mean concentration of double those of the Albariño spirits, in both cases; the mean concentration of linalool is above its perception threshold. The variety with the lowest linalool content is Godello, which is the only one whose spirits can show concentrations below the perception threshold.

4-Terpineol was not detected in the spirits from Godello and for the rest of the spirits analyzed their mean concentration did not show significant differences, with the exception of samples from Albariño, which contained an important amount of this compound. The value of the perception threshold of 4-terpineol is unknown, and so, its contribution to the aroma cannot be estimated.

$\alpha$ -Terpineol is also an important terpenic alcohol that is likely to contribute a floral aroma to the medium, although it has a high perception threshold ( $0.4 \text{ mg L}^{-1}$ ) (23) that is not always possible to surpass in the samples. In this case, once more, the spirits from Godello are the ones that present the lowest concentration, for which reason it is not going to be detected organoleptically. The mean concentration of  $\alpha$ -terpineol in the spirits from Treixadura and Mencia is also found at levels below its perception threshold. With respect to those of Albariño, no significant differences were detected. In these spirits, the mean concentration of this compound was, in all of the cases analyzed, above the perception threshold and therefore important in the aroma of the spirits produced from this variety. The concentration of  $\alpha$ -terpineol is significantly higher in the case of the spirits from Catalan Roxo, where the content of this compound widely exceeds the perception threshold.

Citronellol is, together with linalool, one of the most important terpenic compounds, because it also presents a low perception threshold ( $0.018 \text{ mg L}^{-1}$ ) (23) with citrus aromas. Once again, significant differences for the mean concentration of this compound are only found in spirits from Catalan Roxo, which widely exceeds its perception threshold in all of the samples, and its concentration is much higher than in the other samples analyzed. The spirits from Godello again present a lower concentration of this compound, followed by those of Treixadura. The spirits from Mencia and Albariño show very similar mean concentrations of citronellol. In all of the groups of spirits analyzed, the mean concentration of citronellol exceeds the value

of its perception threshold, for which reason it can be expected that this compound will have a direct participation in the aroma.

There are no significant differences in the mean concentration of nerol for the spirits analyzed, except for the Catalan Roxo, where the concentration is again much higher than the rest of the spirits and even than its perception threshold ( $0.4 \text{ mg L}^{-1}$ ) (23). For this reason, its presence will be detected organoleptically in the spirits of this variety. For the rest of the spirits analyzed, its concentration is found at values below the perception threshold. In addition, in the case of the spirits of the variety Godello, it presents the lowest mean concentration of nerol, so that rose nuances of this compound cannot be appreciated in spirits produced from this variety.

Geraniol also is likely to contribute an aroma of flowers to the spirit if its concentration is found to be above its perception threshold ( $0.13 \text{ mg L}^{-1}$ ) (22). In this case, the concentrations of this compound in the samples of the spirits analyzed are very similar in all of them, except in the case of Catalan Roxo, which presents an important content of this compound. Following those of Catalan Roxo, the Albariño spirits are the ones that reach the highest concentrations of this compound. In all of the spirits analyzed, the concentration of geraniol exceeded its perception threshold, except in the spirits produced from Godello, in which the values are very close to this threshold.

**C<sub>13</sub> Norisoprenoids.**  $\alpha$ -Ionone was detected in all of the spirits analyzed, and its concentration is significantly lower in the case of the variety Godello. Again, the variety that presents the highest concentration of this compound is Catalan Roxo, although significant differences with respect to the mean concentration of other varieties no longer exist. This compound presents a very low perception threshold ( $2.6 \times 10^{-3} \text{ mg L}^{-1}$ ) (23), which is surpassed in all of the samples analyzed. As a result, it is likely to contribute an aroma of violets to the spirit.

$\beta$ -Ionone was detected at much lower concentrations than for its isomer  $\alpha$  in all of the spirits analyzed, and in the case of those from the variety Albariño, this compound was not present. The spirits from Catalan Roxo continue to be the most aromatic as the concentration of  $\beta$ -ionone is significantly higher, while the rest present concentrations of  $\beta$ -ionone are similar, although significantly lower for the spirits from Godello. This norisoprenoid also presents a low perception threshold ( $4.5 \times 10^{-3} \text{ mg L}^{-1}$ ) (24), which is surpassed in all of the cases.

The  $\alpha$ -isomer of the theaspriane was not detected in the spirits from the varieties of Treixadura, Mencia, and Godello, and in the rest (Albariño and Catalan Roxo), its concentrations are similar. However, its  $\beta$ -isomer was detected in the spirits from Treixadura, Mencia, and Godello without significant differences in concentration and was not detected in the spirits of Albariño and Catalan Roxo. As the perception threshold of this compound is unknown, its contribution to and importance in the aroma of the spirits in which it was detected cannot be evaluated.

In addition to terpenes and C<sub>13</sub> norisoprenoids, in several samples of spirits studied, citronellal, eugenol, and 4-allyl-1,2-dimethoxybenzene have been detected. Citronellal, for which there is no data available on the perception threshold of its fairly aggressive and sharp nuances, is found at its highest concentration in spirits from Treixadura, Mencia, and Godello, although their concentrations do not present statistically significant differences. This compound was not detected in spirits from Albariño, and its concentration is significantly lower in the case of the spirits from Catalan Roxo, contrary to what occurs with most of the compounds favorable to the aroma.

Eugenol, with an aroma of cloves, was not detected in the spirits from the varieties Treixadura, Mencia, and Godello.



**Table 3.** Contribution<sup>a</sup> of the Different Varietal Compounds to the Aroma of Orujo Spirits

compds	Albariño	Treixadura	Mencia	Godello	Catalán Roxo
terpenes					
$\alpha$ -pinene				0.35	
$\beta$ -pinene	38.21	45.00	100.00	30.71	19.29
limonene	6.43				11.90
linalool	292.00	70.00	81.00	5.00	584.00
$\alpha$ -terpineol	8.13	4.25	4.75	0.31	62.25
citronellol	94.44	55.56	111.11	19.44	1258.33
nerol	3.50	1.50	1.88	0.50	22.75
geraniol	25.77	14.23	15.38	6.54	98.08
C <sub>13</sub> norisoprenoids					
$\alpha$ -ionone	326.92	500.00	923.08	76.92	1480.77
$\beta$ -ionone		2.22	3.33	1.11	4.44
other compounds					
eugenol	366.67				300.00

<sup>a</sup> Mean concentration/20% perception threshold.

However, its concentration in the Albariño and Catalan Roxo spirits is higher than its perception threshold ( $6 \times 10^{-3}$  mg L<sup>-1</sup>) (23) and therefore very important for the aroma of these spirits. Significant differences were not found for the mean concentration of eugenol in the spirits from these two varieties.

4-Allyl-1,2-dimethoxybenzene also has a floral aroma, but with a very high perception threshold (0.820 mg/L) (45) that is not surpassed in the spirits in which it was detected (Treixadura, Mencia, and Godello), principally in Godello where its concentration is very low, for which reason this compound will only influence the aroma if there are synergic effects with other compounds. 4-Allyl-1,2-dimethoxybenzene was not detected in the spirits from Albariño or in those from Catalan Roxo.

According to Versini (46), an aromatic compound will take part directly in the aroma, not only when its concentration surpasses its perception index but also if this surpasses the corresponding limit of contribution, which is defined as 20% of the value of its perception threshold.

The coefficients obtained of the mean concentration of each compound of the five groups of spirits analyzed and their limits of contribution are shown in Table 3. Data are not included for citronellal, theaspirane, and 1,8-cineol or 4-terpineol, as their perception threshold is not available.

Those compounds, whose contribution to the aroma is higher than or equal to the unit, will be considered members of the aromatic profile of each group of spirit. The results obtained indicate that  $\alpha$ -ionone is the compound that most is likely contribute to the aroma of the Galician monovarietal orujo spirits, and this is principally due to its low perception threshold. This contribution is especially important in the case of spirits from Catalan Roxo, which is the variety of grape that gives rise to the richest grape pomace in aromatic compounds, with an important contribution of citronellol, linalool, and eugenol that have citrus, floral, and clove nuances, respectively.

$\beta$ -Pinene is, together with  $\alpha$ -ionone and citronellol, the most important compound in the aroma of the variety Mencia, with citrus nuances. The aromatic profile of Mencia spirits is similar to those of Treixadura, as the same compounds participate, although with a lower contribution.

The aroma of the spirits from the variety Godello cannot be attributed to the compounds studied, as it is the least rich and contributes less of these compounds to the spirit than any of the groups.

## CONCLUSIONS

There are significant differences in the concentrations of varietal aromatic compounds in the Galician spirits obtained from different varieties of grapes.  $\alpha$ -Ionone is the varietal aromatic compound that is most likely to contribute to the aroma of all of the spirits studied. The spirits obtained from Catalan Red are the most aromatic, with floral and fruit nuances due to  $\alpha$ -ionone and citronellol, while those from Godello were the least aromatic group, within the varietal compounds studied. The spirits from the varieties Mencia and Treixadura show a similar profile, but the former have a more intensive aroma. Albariño spirits stand out because of their profile that is marked by the contributions of eugenol and linalool.

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