

## Volatile Composition and Sensory Characters of Commercial Galician Orujo Spirits

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

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

Nineteen samples of commercial Galician orujo spirits were analyzed by gas chromatography and distinguished from one another on the basis of the concentrations of major volatile compounds (methanol, higher alcohols, esters, acetates, and aldehydes). The spirits were also sensorily analyzed to emphasize this differentiation and to establish a sensory profile as a function of the attributes defined by the tasters. The results show that the Galician orujo spirits present notably significant differences in the concentrations of 2-butanol, methanol, acetaldehyde, and ethyl lactate, whereas their ethylic esters contents are similar. Sensorily, the orujo spirits can be differentiated by taste but have similar characteristics of bouquet, the best of which are from the Godello variety. The descriptions employed to define the orujo spirits were herbaceous, floral, fruity, vegetal, alcohol, toasted, and "others". Floral and fruity were predominant in the Albariño orujo spirits; herbaceous was predominant in the plurivarietal orujo spirits, vegetal in the Godello spirits, and dried fruit or toasted in the Mencia spirits. The orujo spirits from Treixadura have the most diverse profile, with the participation of most of the attributes.

**KEYWORDS:** Orujo spirits; commercial; volatile compounds; gas chromatography; taste

### INTRODUCTION

In Galicia, a region situated in northwestern Spain, the spirit produced by the distillation of grape pomace (called "orujo") after alcoholic fermentation was traditionally considered to be an alcoholic beverage produced and consumed by the common people; however, during the past few years its characteristics are tending to adapt to the demands of the new market (specifically by reducing the alcohol degree), but without losing authenticity.

What was previously valued as a homemade product of a marked traditional character, now must have been subjected to a process of quality control. More and more aspects of the spirit are controlled and, although it is still defined as a "subproduct", the wineries now have their own brand of orujo as a distinctive feature. At the present time, apart from quality, special attention is being given to the presentation of the product: design of the label, bottle style, packaging, etc. Thus, although the design and quality of alcoholic drinks similar to orujo have always been attributed to the Italian grappas, today, orujo and grappa are competitors in the same market.

There are some references which indicate that the two most influential factors in the volatile composition of the orujo spirits are delay in the distillation of the raw material after alcoholic fermentation of the residual sugars contained therein and the conditions of storage previous to this operation (1, 2). After a

prolonged period of ensilage of the grape pomace, the orujo spirit obtained shows (in most cases) a high content of certain volatile compounds that are negative from both sanitary and toxicological points of view. Among these, methyl alcohol and 2-butanol (3–7) stand out from an organoleptic point of view, as a result of the increase in the concentrations of ethyl lactate, allyl alcohol, and, principally, acids and their high molecular weight ethyl esters (8, 9). Moreover, if the grape pomace has been stored in the presence of oxygen, the orujo spirit will also present an especially high content of acetaldehyde, acetal, and methyl and ethyl acetates (9, 10–13), as well as a considerable loss of ethanol.

The basic process for obtaining orujo spirits is the same, but the characteristics of the raw material, storage system, storage time, and the equipment used for distillation are different and dependent on the possibilities of the winery. For this reason, the orujo spirits offered commercially will also be very different. The commercialization of orujo spirits under the label of the Regulating Commission of the Geographic Denomination *Orujo de Galicia* demands that each sample must, on the one hand, pass a chemical test to determine that a series of parameters are within a determined range (Table 1) and, on the other hand, must be submitted to the sensory evaluation of the Official Tasting Panel of the Regulating Commission.

One of the main problems of the Galician orujos is their high concentration of methyl alcohol (6, 14). In some cases, this concentration can be reduced to the maximum value fixed by the Regulating Commission of 1000 g hL<sup>-1</sup> absolute ethanol

\* Author to whom correspondence should be addressed (telephone +34 988 38 70 83; fax +34 988 38 70 01; e-mail smcortes@uvigo.es).

**Table 1.** Chemical Parameters Controlled by the Regulating Council

	maximum	minimum
alcohol degree (% v/v)	50	37.5
methanol (g hL <sup>-1</sup> aa) <sup>a</sup>	1000	200
total acidity (in acetic acid, g hL <sup>-1</sup> aa)	150	
acetaldehyde (g hL <sup>-1</sup> aa)	150	
ethyl acetate (g hL <sup>-1</sup> aa)	250	
higher alcohols (g hL <sup>-1</sup> aa)	600	225
Cu (mg L <sup>-1</sup> sample)	10	

<sup>a</sup> Grams per 100 L of absolute ethanol.

(aa) by the addition of distillates that are poorer in methanol, such as lees or wine (15), although this process also modifies the rest of the components of the spirit and can spoil the initial organoleptic characteristics. Moreover, the mixing of spirits is not allowed, only the combined distillation of grape pomace with up to 25% of lees.

In this study, gas chromatography and sensory analysis have been performed on samples of commercial Galician orujo spirits to establish the average composition, with regard to both the volatile compounds that have concentration limits fixed by the Regulating Commission and the other components that are important for quality evaluation. Their sensory profile, as a function of the attributes employed by the tasting panel to describe them, was defined, too.

## MATERIALS AND METHODS

**Samples.** Nineteen samples of commercial orujo spirits were used for this study, 7 plurivarietal and 12 monovarietal, obtained from the distillation of grape pomace of the main varieties of grape grown in Galicia: white grapes [Albariño (6), Godello (2), and Treixadura (2)] and red grapes [Mencia (2)]. A larger number of monovarietal samples of Albariño were used as the amount of this wine, and thus the amount of monovarietal grape pomace available, is also more abundant. The samples were collected directly from the distilleries themselves.

**Reagents.** Ethanol, of analytical grade, was purchased from Merck (Darmstadt, Germany). 2-Butanol, 1-butanol, 1-propanol, 2-methyl-1-propanol, 4-methyl-2-pentanol, *trans*-2-hexenol, *cis*-2-hexenol acetaldehyde, 1,1-diethoxyethane, diethyl succinate, and ethyl mirystate were supplied by Aldrich (Aldrich Chemical, Buchs, Switzerland); methanol, benzyl alcohol, 2-phenylethanol, allyl alcohol, 2-methyl-1-butanol, hexanol, ethyl butyrate, ethyl laurate, hexyl acetate, isoamyl acetate, ethyl acetate, and methyl acetate were purchased from Merck; ethyl hexanoate, ethyl octanoate, ethyl decanoate, *trans*-3-hexenol, *cis*-3-hexenol, 3-methyl-1-butanol, and furfural were supplied by Fluka (Buchs, Switzerland), and ethyl lactate was from Sigma (Buchs, Switzerland).

A stock solution of reference standards was prepared in distilled water containing 40% (v/v) of ethanol. The internal standard, 4-methyl-2-pentanol, was prepared in absolute ethanol.

**Statistical Analysis.** A computer program, Statgraphics Plus for Windows, version 3.1 (1997), was used for the statistical study of the results. A multifactor analysis of variance (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 orujo spirits.

A significance value ( $p$  value), calculated using the nonparametric test of Kruskal–Wallis, lower than the estimated theoretical value (in this case 0.05), indicates the existence of significant differences between the analyzed data. Likewise, the multiple-range test (LSD) was applied to confirm the results obtained.

**Aromatic Compound Determination.** The analyses were carried out using a Hewlett-Packard 5890 series II gas chromatograph equipped with an HP 6890 automatic injector and a flame ionization detector. The compounds were separated on a Chrompack CP-Wax 57CB (polyethylene glycol stationary phase; 50 m × 0.25 mm i.d. with 0.25 μm film thickness) fused-silica capillary column. Instrumental condi-

tions were as follows: injector temperature, 250 °C; detector temperature, 260 °C; carrier gas, helium at 1.07 mL min<sup>-1</sup>; makeup gas, nitrogen at 15 mL min<sup>-1</sup>. The detector gas flow rates were 40 mL min<sup>-1</sup> for hydrogen and 400 mL min<sup>-1</sup> for air.

For determination of the volatile compounds, 1 mL of an internal standard solution (5 g of 4-methyl-2-pentanol per liter of ethanol) was added to a 10 mL sample of spirit. A 1 μL aliquot was injected directly into the chromatograph and split 1:1. The temperature program of the oven was as follows: initial  $T^a$ , 40 °C (isotherm for 6 min); ramp, 1.5 °C min<sup>-1</sup> to 80 °C and afterward to 200 °C at a rate of 3 °C min<sup>-1</sup>.

All of the volatile compounds were identified by comparing GC retention times and MS data, in agreement with those of pure compounds available in the laboratory, using an HP 5890 series II coupled to an 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.

For the quantification, the internal standard method was utilized. Quantitative data were obtained from GC-FID analyses. Integration was performed on compounds eluted from the CP-Wax column. Response factors of 31 reference compounds from different classes (alcohols, aldehydes, acetates, and esters) were determined. The GC-FID chromatogram of a reference solution is shown in **Figure 1**.

All analyses were done in triplicate.

**Sensory Tasting.** The sensory evaluation of the commercial Galician orujos was carried out using the wine glasses and official taste evaluation forms of the Regulating Commission of the Geographic Denomination *Orujo de Galicia*. On this form, the aspects evaluated and the number of points that could be achieved in each case are visual aspect (6–10), bouquet (18–30), taste and retrobouquet (24–40), response to type (6–10), general impression (6–10) [total points (60–100)]. The tasting panel was formed by five tasters trained in the characteristic aromas of orujo spirits and in the correct tasting terminology. Apart from their score, the tasters were asked to use descriptors to define the spirits. Tasting was carried out in the morning, and the session was divided into two parts, with an interval of 30 min, to avoid fatigue in the tasters. This was especially important because of the high degree of alcohol in the orujo spirits [40–45% (v/v)].

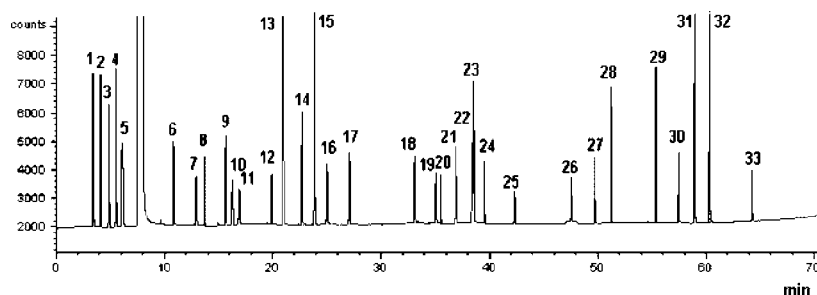
## RESULTS AND DISCUSSION

**Results of Chromatographic Analysis.** The concentrations of volatile compounds, in the different groups of orujo spirits analyzed, are shown in **Table 2**.

**Alcohols.** No significant differences were found in the average concentration of ethanol [43–45% (v/v)], which was slightly higher in the orujo spirits from Mencia and Godello, although lower than the maximum permitted by the standards of the Regulating Commission of 50% (v/v). This is, on the one hand, due to economic criteria and, on the other, perhaps the more important, because the present-day consumer rejects drinks that have a very high alcoholic content.

The highest values of methanol were detected in the orujo spirits obtained from Treixadura (752 g hL<sup>-1</sup> aa) and Albariño (680 g hL<sup>-1</sup> aa), with concentrations that were significantly different from the others (<565 g hL<sup>-1</sup> aa). This could be due to the storage of grape pomace from grapes that had been excessively pressed to produce more must and therefore contained less moisture (6). In these conditions, the pectinases are more active and produce larger quantities of methanol (16). The values of methanol in the orujo spirits obtained from Mencia and in the plurivarietal orujo spirits are significantly lower. The reason of this lower value of methanol is due to the vinification process, which in red wine includes the must alcoholic fermentation with the skins of the grape. In the case of plurivarietal orujo spirits, being a mixture of varieties, this could possibly include pomace from red grapes.

The quality of an orujo spirit can be evaluated as a function of the concentration of the higher alcohols (2-butanol to



**Figure 1.** Chromatogram of a standard solution of methanol, aldehydes, higher alcohols, acetates, and esters. Peak identification (retention time is given in parentheses): 1, acetaldehyde (4.06 min); 2, methyl acetate (4.72 min); 3, ethyl acetate (4.99 min); 4, 1,1-diethoxyethane (5.88 min); 5, methanol (6.41 min); 6, ethyl butyrate (10.82 min); 7, 2-butanol (11.09 min); 8, 1-propanol (11.72 min); 9, 2-methylpropanol (15.30 min); 10, isoamyl acetate (15.54 min); 11, allyl alcohol (16.84 min); 12, 1-butanol (19.48 min); 13, 4-methyl-2-pentanol (IS) (20.9 min); 14, 3-hexanol (22.95 min); 15, 2-methyl-1-butanol + 3-methyl-1-butanol (23.65 min); 16, ethyl hexanoate (23.82 min); 17, hexyl acetate (27.03 min); 18, ethyl lactate (33.77 min); 19, 1-hexanol (35.34 min); 20, *trans*-3-hexen-1-ol (35.81 min); 21, *cis*-3-hexen-1-ol (37.16 min); 22, *trans*-2-hexen-1-ol (38.64 min); 23, cyclohexanol (38.75 min); 24, ethyl octanoate (39.47 min); 25, furfural (40.80 min); 26, benzaldehyde (43.86 min); 27, ethyl decanoate (49.62 min); 28, diethyl succinate (51.24 min); 29, 2-phenylethyl acetate (55.32 min); 30, ethyl laurate (57.47 min); 31 = benzyl alcohol (59.05 min), 32, 2-phenylethanol (60.28 min); 33, ethyl myristate (64.22 min).

**Table 2.** Mean Concentration (Milligrams per Liter)<sup>a</sup> and Standard Deviation for the Five Groups of Orujo Spirits Analyzed

no.	compound	GE	A	ME	GD	TR
	samples (n)	7	6	2	2	2
<b>alcohols</b>						
1	ethanol (% v/v)	43.2a ± 0.49	44.2a ± 2.76	44.8a ± 0.14	45.6a ± 1.27	42.4a ± 3.25
2	methanol	2374a ± 17.4	3007b ± 12.4	1928a ± 20.2	2578ab ± 23.2	3190b ± 9.32
3	2-butanol	138a ± 3.74	29.8b ± 0.96	6.65ab ± 0.09	0.56ab ± 0.01	0.77ab ± 0.09
4	1-propanol	191a ± 4.70	167a ± 0.60	162a ± 0.48	135a ± 2.54	147a ± 0.53
5	2-methylpropanol	238ab ± 2.71	210b ± 0.83	265ab ± 1.11	195ab ± 3.02	302a ± 0.78
6	1-butanol	8.42a ± 0.22	6.17a ± 0.73	5.10a ± 0.02	7.40a ± 0.68	4.19a ± 0.26
7	2-methyl-1-butanol	171ab ± 2.27	129b ± 1.13	220a ± 0.80	135ab ± 2.33	164ab ± 0.08
8	3-methyl-1-butanol	584ab ± 8.19	401b ± 2.52	755a ± 2.20	459ab ± 8.55	506ab ± 1.08
	<b>total alcohols (3–8)</b>	<b>1331a ± 382</b>	<b>943b ± 216</b>	<b>1413a ± 3.53</b>	<b>932ab ± 183</b>	<b>1125ab ± 62.9</b>
9	1-hexanol	33.9a ± 1.40	34.6a ± 0.48	37.2a ± 0.82	30.4a ± 0.01	79.9b ± 0.16
10	<i>cis</i> -3-hexen-1-ol	3.64ab ± 0.53	2.41bc ± 0.16	5.58a ± 0.07	1.61c ± 0.06	2.57bc ± 0.07
11	<i>trans</i> -3-hexen-1-ol	0.31a ± 0.01	0.76bc ± 0.10	0.32ab ± 0.02	1.45c ± 0.10	1.35d ± 0.02
12	<i>trans</i> -2-hexen-1-ol	1.89a ± 0.24	2.18a ± 0.09	2.49a ± 0.02	1.56ab ± 0.21	0.73b ± 0.05
	<b>total hexenols (10–12)</b>	<b>5.84ab ± 2.00</b>	<b>5.36a ± 1.99</b>	<b>8.39b ± 1.09</b>	<b>4.62a ± 0.53</b>	<b>4.64a ± 0.86</b>
	<b>R<sub>1</sub><sup>b</sup></b>	<b>11.74</b>	<b>3.17</b>	<b>17.44</b>	<b>1.11</b>	<b>1.90</b>
13	allyl alcohol	5.84a ± 1.29	0.35b ± 0.05	0.44ab ± 0.09	nd	nd
14	benzyl alcohol	3.57a ± 0.31	0.99a ± 0.08	0.64a ± 0.01	0.72a ± 0.08	1.29a ± 0.02
15	2-phenylethanol	7.65a ± 0.65	4.45a ± 0.16	9.78ab ± 0.09	3.45a ± 0.11	15.2b ± 0.86
<b>esters and acetates</b>						
16	methyl acetate	3.41a ± 0.36	3.70a ± 0.16	nd	4.64a ± 0.13	7.64a ± 0.23
17	ethyl acetate	432a ± 5.20	453a ± 4.59	565a ± 1.28	338a ± 1.17	567a ± 2.09
18	isoamyl acetate	10.4a ± 0.48	3.73a ± 0.34	6.75a ± 0.32	7.76a ± 1.35	7.50a ± 0.18
19	hexyl acetate	1.48a ± 0.33	20.0a ± 0.20	2.24a ± 0.07	1.42a ± 0.13	3.06a ± 0.03
	<b>total acetates (18–19)</b>	<b>11.8a ± 11.9</b>	<b>4.93a ± 2.71</b>	<b>8.99a ± 0.45</b>	<b>9.17a ± 3.28</b>	<b>10.6a ± 1.06</b>
20	ethyl butyrate	2.60a ± 0.25	1.28a ± 0.09	1.22a ± 0.09	1.25a ± 0.33	nd
21	ethyl hexanoate	10.3a ± 0.84	4.14a ± 0.34	9.83a ± 0.38	7.92a ± 0.38	10.1a ± 0.12
22	ethyl octanoate	39.9a ± 2.01	16.9a ± 0.70	32.5a ± 0.08	9.40a ± 0.37	13.2a ± 0.06
23	ethyl decanoate	127a ± 4.84	41.9b ± 0.18	51.8ab ± 0.54	11.5b ± 0.30	35.6b ± 0.34
	<b>total esters (20–23)</b>	<b>179a ± 97.2</b>	<b>64.2b ± 51.5</b>	<b>95.4ab ± 0.22</b>	<b>30.1b ± 7.64</b>	<b>58.9b ± 48.0</b>
24	diethyl succinate	28.9a ± 0.66	3.10b ± 0.25	6.69ab ± 0.83	2.39ab ± 0.63	4.96ab ± 0.08
25	ethyl laurate	35.7a ± 1.60	14.1b ± 0.22	16.5ab ± 0.61	3.21b ± 0.03	14.1b ± 0.33
26	ethyl myristate	1.98a ± 0.20	2.19a ± 3.95	2.17a ± 0.01	nd	1.98a ± 0.58
27	ethyl lactate	383a ± 4.97	154a ± 0.08	93.2a ± 0.58	99.3a ± 0.37	128a ± 2.36
	<b>R<sub>2</sub><sup>c</sup></b>	<b>1.50</b>	<b>0.61</b>	<b>0.40</b>	<b>0.45</b>	<b>0.40</b>
<b>aldehydes and acetal</b>						
28	acetaldehyde	103a ± 1.96	232b ± 0.98	382b ± 0.42	380b ± 6.42	403b ± 9.38
29	furfural	6.65a ± 0.39	5.87a ± 0.02	2.68a ± 0.01	2.30a ± 0.01	3.67a ± 0.24
30	benzaldehyde	0.60a ± 0.07	1.49a ± 0.08	1.76a ± 0.01	1.43a ± 0.01	2.16a ± 0.01
31	1,1-diethoxyethane	6.30a ± 0.29	15.2a ± 0.69	2.83a ± 0.15	6.62a ± 1.47	9.86a ± 0.04

<sup>a</sup> Values, within the same row, with the same letter are not significantly different at 95% confidence. GE, generics or plurivarietales; A, Albariño; ME, Mencia; GD, Godello; TR, Treixadura. nd, not detected. <sup>b</sup> R<sub>1</sub>, relationship of concentrations *cis*-3-hexenol/*trans*-3-hexenol. <sup>c</sup> R<sub>2</sub>, relationship of concentrations of total esters/ethyl acetate.

3-methyl-1-butanol). Thus, Rodríguez and Mangas (4) indicate that total concentrations of higher alcohols of 350 g hL<sup>-1</sup> aa are a sign of poor quality. According to this criterion, the orujo spirits from Godello (204 g hL<sup>-1</sup> aa) and Albariño (213 g hL<sup>-1</sup> aa) will have the highest quality. The orujo spirits from Mencia

are the richest in higher alcohols among the Galician orujos (315 g hL<sup>-1</sup> aa), which is related to their production from red grape pomace (2).

2-Butanol is found at a significantly higher concentration in the plurivarietal orujo spirits (31.9 g hL<sup>-1</sup> aa) than in the other

spirits listed ( $<6.7 \text{ g hL}^{-1}$  aa). The spirits from the varieties Godello, Treixadura, and Mencia are so low in this alcohol that it suggests that the grape pomace employed to produce the orujo spirit was correctly stored. Although the Regulating Commission does not, at the present time, fix a maximum value, it is considered that at a value  $>30 \text{ g hL}^{-1}$  aa the quality of the orujo spirit deteriorates (8). This concentration was exceeded only in the plurivarietal orujo spirits, although the fact that significant differences of concentration did not exist for this compound between the plurivarietal orujo spirits and those of Treixadura, Mencia, and Godello indicates a very high range of variation and, therefore, that these orujo spirits with a low level of 2-butanol are of good quality.

Significant differences in the concentrations of 1-propanol and 1-butanol were not found in any of the groups of orujo spirits analyzed. Both compounds increased their concentrations as a function of the microbiological processes that took place during ensilage of the grape pomace (5). They are strongly odorous compounds, but in no case surpassed their perception thresholds, fixed at 800 and 450  $\text{mg L}^{-1}$  for 1-propanol and 1-butanol, respectively (8). On the contrary, 2-methyl-1-propanol, with a perception threshold of 200  $\text{mg L}^{-1}$  (8), is higher than this value in all of the groups of orujo spirits analyzed, except the Godello.

2-Methyl-1-butanol and 3-methyl-1-butanol are found at their highest levels in the Mencia and Treixadura orujo spirits and at their lowest in the Godello and Albariño orujo spirits. In all cases, they are higher than their perception threshold, 65  $\text{mg L}^{-1}$  (8). According to Silva et al. (3), low levels of isoamyl alcohols indicate orujo spirits with very little body. In this case, the Mencia and plurivarietal orujo spirits have the highest concentrations of isoamyl alcohols and so a better body, which could be associated with the use of red grapes, whereas the white grape Albariño orujo spirits are lighter.

1-Hexanol was detected in all of the groups with similar average concentrations (30.4–37.2  $\text{mg/L}$ ), with the exception of Treixadura (79.7  $\text{mg/L}$ ). The hexanol will contribute an herbaceous aroma as it exceeds, in all cases, the 4  $\text{mg L}^{-1}$  of its perception threshold (8). According to Versini et al. (5), its concentration depends on the raw material employed in the distillation.

*cis*-3-Hexenol is the most abundant hexenol in all of the groups of orujo spirits analyzed, although its concentration is significantly higher in the Mencia (5.58  $\text{mg/L}$ ) and lower in the Godello orujo spirits (1.61  $\text{mg/L}$ ). *trans*-3-Hexenol is at a higher concentration in the Godello (1.45  $\text{mg/L}$ ) and Treixadura orujo spirits (1.35  $\text{mg/L}$ ) and at lower concentrations in the plurivarietals (0.31  $\text{mg/L}$ ). However, *trans*-2-hexenol is found at higher concentrations in the Mencia, Albariño, and plurivarietal orujo spirits, whereas the lowest concentrations were found in the Treixadura orujo spirits. These compounds, together with hexanol, appeared at high concentrations when the pH of the grape pomace had not been controlled during fermentation–storage (3). According to Versini et al. (7), the relationship that exists between the concentrations of *cis*-3-hexenol and *trans*-3-hexenol could be associated with a varietal characteristic. In this study low values are obtained for Treixadura, Godello, and Albariño orujo spirits, compared to those registered for the variety Mencia.

Allyl alcohol was detected in only the plurivarietal orujo spirits (5.84  $\text{mg/L}$ ) and in those from Albariño (0.35  $\text{mg/L}$ ) and Mencia (0.44  $\text{mg/L}$ ), although its concentration was significantly higher in the former. 2-Butanol and allyl alcohol are associated with a deficient storage of the raw material during ensilage (17).

The concentration of benzyl alcohol in the orujo spirits, although not significantly different, was higher in the plurivarietal orujo spirits. On the contrary to what should be expected, 2-phenylethanol is not richer in the Albariño orujo spirits, despite their marked floral character. Therefore, the intense floral nuance of this group of orujo spirits cannot be attributed to this compound alone (18). The concentration of this compound is significantly higher in the Treixadura and Mencia orujo spirits, and the Godello and Albariño varieties have the lowest values for this compound.

*Acetates and Esters.* High concentrations of methyl and ethyl acetate are indications of aerobiosis in the raw material during the fermentation process or the result of an incorrect separation of the first fraction (heads) during distillation. The lowest concentrations of methyl acetate are in the Mencia orujo spirits, although their average concentration is not significantly different from the rest of the orujo spirits analyzed. The ethyl acetate is, in general, the major ester in the alcoholic beverages distilled, although its concentration should not be too high as, if it exceeds its perception threshold (33  $\text{mg L}^{-1}$ ), it will contribute nuances of glue and solvents to the orujo spirit (8). This occurs in all of the groups of orujo spirits analyzed. Ethyl acetate is found at its highest concentrations in Treixadura (567  $\text{mg/L}$ ) and Mencia (565  $\text{mg/L}$ ). The relationship between the total concentration of esters and the concentration of ethyl acetate can be used to evaluate the quality of an aged alcoholic beverage. The higher this relationship, the higher will be the quality according to Guichard et al. (19). The plurivarietal orujo spirits are those with the highest value for this relationship (1.50), motivated by the high concentration of ethyl lactate and, therefore, cannot be considered as a sign of quality when the distillate is young.

Significant differences were not detected for the concentration of isoamyl acetate between the groups of orujo spirits; however, the Albariño orujo spirits are those with the least concentration of this compound, although above its perception threshold of 1.6  $\text{mg L}^{-1}$  in all of the samples analyzed, contributing fruity nuances of banana to the orujo spirit (8).

The hexyl acetate, highly favored for its fruity nuance of apple (10), has a higher concentration in the Albariño orujo spirits (20  $\text{mg/L}$ ). This agrees with the fact that an intense fruity aroma defines these orujo spirits. The group of orujo spirits as a whole does not show significant differences of concentration for this compound.

As Silva et al. (13) indicate, the short-chain fatty acid esters are very much appreciated for their contribution of fruity aromas. These compounds appear at their highest concentration in the group of plurivarietal orujo spirits. This could be due to the distillation of the grape pomace together with the fermentation bottoms or lees, which are very rich in esters. This hypothesis is also sustained by the fact that the Mencia red wine orujo spirit also contains a higher quantity of this type of compound, as it is soaked in the must because of the vinification system used and as a result shows the highest concentration of short-chain ethyl esters within the monovarietal orujo spirits (95.4  $\text{mg/L}$ ). Godello spirits are the poorest in short-chain ethyl esters (30.1  $\text{mg/L}$ ), although significant differences in their average concentrations were not found with respect to the rest of the orujo spirits analyzed. Ethyl butyrate presents the lowest concentration, but without significant differences between the orujo spirits analyzed, except those from Treixadura in which it was not detected. It contributes nuances of apple to the orujo spirit if it exceeds its perception threshold of 0.4  $\text{mg L}^{-1}$  (8), which it did in all of the groups of orujo spirits in which it was

**Table 3.** Punctuations Obtained for the Orujo Spirits in the Different Sensory Aspects Evaluated

	bouquet phase			tasting phase			global		
	mean	range, min–max	SD	mean	range, min–max	SD	mean	range, min–max	SD
Albariño	22.53	21.40–23.75	0.96	29.29	28.00–30.25	0.95	75.33	73.50–77.75	1.75
plurivarietal	21.50	19.50–22.80	1.45	27.44	25.25–30.00	1.51	69.56	61.60–74.40	4.73
Godello	22.78	22.75–22.80	0.04	30.65	30.00–31.20	0.85	77.10	76.00–78.20	1.56
Mencia	21.70	21.20–22.20	0.71	27.90	27.2–28.60	0.99	73.30	71.00–75.60	3.25
Treixadura	22.13	22.00–22.25	0.18	28.50	28.00–29.00	0.71	74.00	73.00–75.00	1.41

detected. Neither were statistical differences found between the orujo spirits as a function of the content of ethyl octanoate and hexanoate, although both were at higher concentrations in the Mencia and plurivarietal orujo spirits. Again, the highest concentration of decanoate was detected in the Mencia (51.8 mg/L) and plurivarietal orujo spirits (127 mg/L), and in the rest, especially in Godello, the concentration of this compound (11.5 mg/L) was significantly lower. The results confirm what was noted by Nykänen and Nykänen (11) in distilled alcoholic beverages: habitually, the concentration of ethyl octanoate is higher than that of ethyl hexanoate, whereas ethyl decanoate is the major ester in those of C<sub>6</sub>–C<sub>12</sub>.

Silva et al. (13) also indicate that, as the number of carbon atoms of the esters present in the orujo spirits increase, their organoleptic quality decreases, as these compounds contribute rancid, greasy, and soapy nuances. The spirits that contain a higher concentration of ethyl succinate and ethyl laurate are those from the plurivarietal orujos, whereas those with a lesser concentration are Godello orujo spirits, which do not exceed the perception threshold of ethyl laurate (3.5 mg L<sup>-1</sup>) (8). No significant differences were found for the average concentration of ethyl myristate.

The concentration of ethyl lactate increases considerably in orujo spirits produced from grape pomace that has been poorly stored or fermented in inadequate conditions or ensilaged for a long time. The origin of the ethyl lactate and 2-butanol is associated with the activity of lactic acid bacteria (20), which also causes an increase in the concentration of hexanoate and octanoate (21) that can be seen in **Table 2**.

**Aldehydes and Acetal.** The content of acetaldehyde and 1,1-diethoxyethane will give an idea of the conservation of the raw material in anaerobiosis and the correct distillation of the orujo spirit (10). The plurivarietal spirits is the group that presents a significantly lower concentration of acetaldehyde (23.8 g hL<sup>-1</sup> aa). The rest of the orujo spirits contain higher quantities of this compound, principally Treixadura (95.0 g hL<sup>-1</sup> aa), Mencia (85.3 g hL<sup>-1</sup> aa), and Godello (83.3 g hL<sup>-1</sup> aa). The maximum concentration fixed by the Regulating Commission for this compound is 150 g hL<sup>-1</sup> aa, which is not reached by any of the samples, whereas its perception threshold of 25 mg L<sup>-1</sup> is widely exceeded in all of the groups analyzed. The average concentration of 1,1-diethoxyethane did not present significant differences, although the highest values appeared in the spirits from Albariño (15.2 mg/L).

No significant differences in the average concentration of furfural, a compound that is formed during distillation by thermal degradation of the sugars (22), were found.

The formation of benzaldehyde is associated with microbial development during the ensilage of the grape pomace and is favored by a high pH in the medium (5). No significant differences in the average concentration of this compound were found in the Galician orujo spirits. However, the highest concentration of benzaldehyde was found in the orujo spirits from Treixadura (2.16 mg/L) and the lowest in those from the plurivarietal spirits (0.60 mg/L).

**Table 4.** Variance Analysis for the Attributes Bouquet Phase and Tasting Phase of All of the Commercial Orujo Spirits Studied

	samples (n)	bouquet phase	tasting phase
Albariño	6	56.53	59.44
plurivarietal	7	43.18	39.77
Godello	2	57.77	64.86
Mencia	2	47.00	46.12
Treixadura	2	52.65	50.70
test statistic		4.665	11.104
p value		0.323	0.025

**Table 5.** Multiple-Range Test Applied to the Bouquet and Tasting Phases of All of the Commercial Orujo Spirits Analyzed

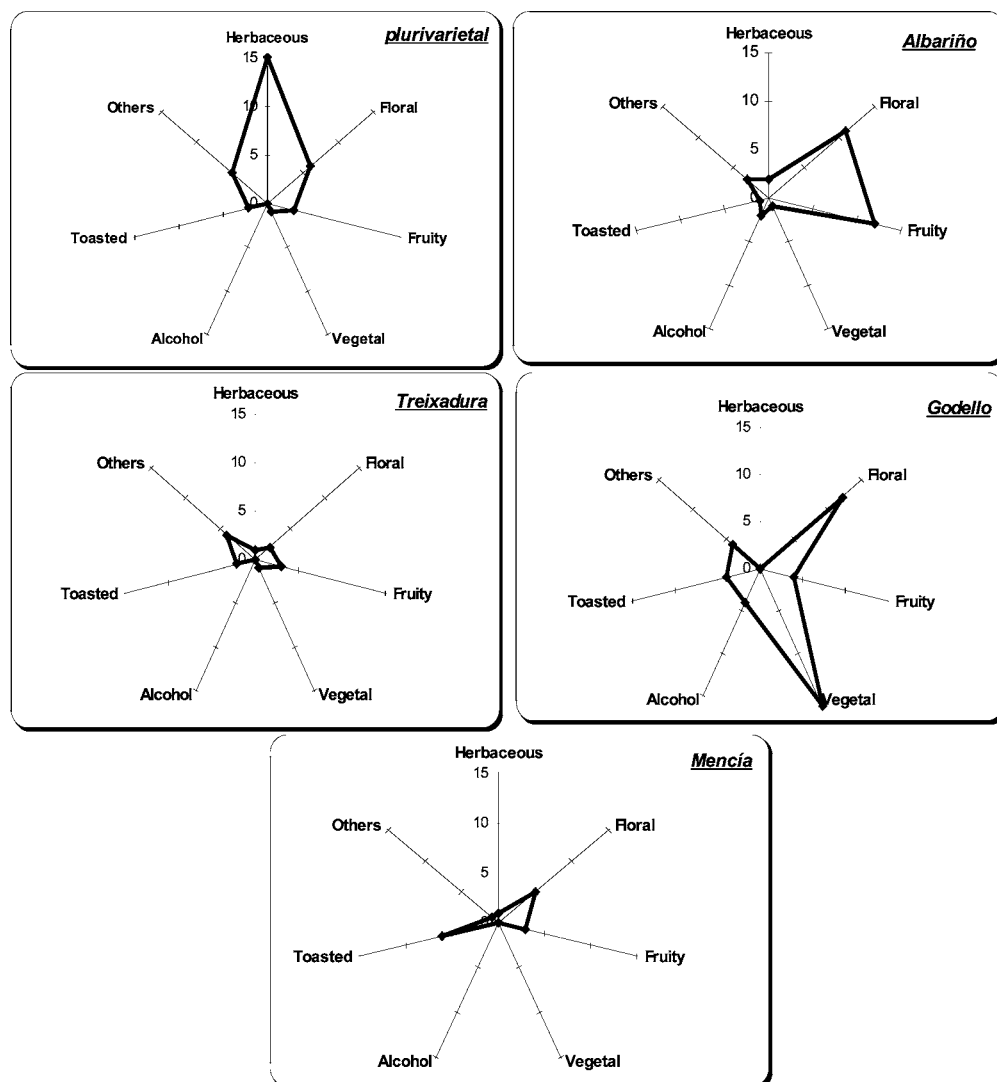
	count	bouquet phase		tasting phase	
		mean	homogeneous groups	mean	homogeneous groups
plurivarietal	7	21.50	X	27.44	X
Mencia	2	21.70	X	27.90	X X
Treixadura	2	22.23	X	28.50	X X X
Albariño	6	22.53	X	29.30	X X
Godello	2	22.77	X	30.65	X

contrast	difference	± limits	difference	± limits
Albariño–plurivarietal	1.0313	1.146	1.866 <sup>a</sup>	1.502
Albariño–Godello	-0.243	1.637	-1.353	2.146
Albariño–Mencia	0.834	1.587	1.402	2.081
Albariño–Treixadura	0.409	1.695	0.802	2.221
plurivarietal–Godello	-1.27	1.575	-3.219 <sup>a</sup>	2.065
plurivarietal–Mencia	-0.197	1.523	-0.464	1.997
plurivarietal–Treixadura	-0.622	1.635	-1.064	2.143
Godello–Mencia	1.077	1.920	2.754 <sup>a</sup>	2.517
Godello–Treixadura	0.652	2.010	2.154	2.635
Mencia–Treixadura	-0.425	1.970	-0.600	2.582

<sup>a</sup> Denotes a statistically significant difference. Method 95% LSD.

**Results of the Sensory Analysis.** The results assigned by the tasters, to each group of spirits on the standard tasting form, for bouquet, taste, and global phases are shown in **Table 3**. The visual aspect was not analyzed separately, as all of the spirits obtained the same punctuation (good = 8 points). The most valued orujo spirits sensorily were those from the variety Godello, followed by those from Albariño. On the contrary, the plurivarietal orujo spirits obtained the lowest punctuation in the different aspects evaluated. To determine if the points assigned to each group of orujo spirits can be considered to be statistically different for a probability of 95%, an ANOVA was performed, using the nonparametric test of Kruskal–Wallis for each of the attributes, as a function of the variety of grape of the raw material. The results are shown in **Table 4**. There are no statistically significant differences in the case of bouquet with regard to aroma among the different orujo spirits analyzed. However, for the tasting phase, the samples present statistically significant differences. These results have been confirmed by application of the multiple-range test for the sensory attributes, and the results are shown in **Table 5**.



**Figure 2.** Sensory profile for the mono- and plurivarietal groups of orujo spirits analyzed.

In the bouquet phase no significant differences have been found between the different orujo spirits. However, for the tasting phase, the spirits from Godello are significantly different from those from Mencia and also from plurivarietal spirits, and these, in turn, are also significantly different from the Albariño spirits. It was not possible to establish significant differences for the rest of the orujo spirits. From these results it can be concluded that marked differences in the sensory evaluation of the Galician orujo spirits do not exist, if we limit the evaluation to the standard tasting form. However, it is possible that, depending on the grape variety of the pomace, the sensory characteristics of the spirits are different. It is for this reason that it was decided to study the attributes used by the tasters, to define them and so establish a descriptive profile of the different groups of orujo spirits, in a similar way to the method employed by López et al. (23) to study the influence of the production process of commercial liquors and by Cantagrel et al. (24) in a study of cognac.

The terms employed were listed, grouped by common categories (i.e., rose, violet, etc., formed the category floral; apple, citric, orange, mandarin, etc., formed the category fruity; asparagus, mushroom, etc., formed the category vegetal), until all six final descriptions were obtained: herbaceous, floral, fruity, vegetal, alcohol, toasted, and others. In this way a table was constructed for each type of orujo spirit, assigning one point to each term, within each category. The final attribute repre-

sented for each spirit would be the total sum of the points of all of the terms in this group. The aromatic profile of each variety of orujo spirit was constructed using the total values. The results are shown in **Figure 2**.

The aromatic profile of each group of orujo spirits is different. Thus, the plurivarietal orujo spirits are principally defined by herbaceous connotations (ensilage), although they are also slightly fruity and, very important, have toasted and floral nuances. Nuances of smoke and sulfur (grouped in "others") have been detected in these spirits, and these have an important influence on their aroma. The Mencia orujo spirits are described by fruity, floral, and principally toasted nuances; the latter term includes the aroma of dried fruit, which is logical when referring to orujo spirits from red grapes. The descriptive aromatic profile of Albariño is principally centered on floral and fruity nuances, contrary to Godello spirits, which are characterized by a strong vegetal component: mushroom, asparagus, and floral. The orujo spirits from Treixadura have the most diverse profile, with the participation of most of the attributes and a strong influence of those grouped under "others".

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