JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Volatile Components of Loureira, Dona Branca, and Treixadura Wines

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White wines experimentally produced from the white grape varieties Loureira, Dona Branca, and Treixadura have been analyzed over four consecutive harvests. The contents of monoterpenes, volatile phenols, alcohols, sulfur components, acetates, fatty acids, and ethyl esters were determined by gas chromatography (FID) and gas chromatography−mass spectrometry. The mean values from four vintages confirmed that these wines have characteristic profiles. Loureira wines are characterized by a high content of free terpenes, 1-hexanol, ethyl acetate, and fatty acids. Dona Branca wines present the highest concentrations of methanol and sulfur constituents, and the lowest concentrations of higher alcohols, acetates, diethyl succinate, and ethyl esters. The levels of monoterpenes in Treixadura wines are very low, but they have the highest concentrations of volatile phenols, principally due to the vanillin, diethyl succinate, ethyl lactate, and ethyl esters. These results were confirmed by principal component and linear discriminant analysis, which show a clear differentiation among these wines as a function of the varietal origin.

KEYWORDS: Loureira wine; Treixadura wine; Dona Branca wine; aromatic composition; GC−MS analysis; principal component analysis; linear discriminant analysis

INTRODUCTION

Loureira, Treixadura, and Dona Branca are white grape varieties of *Vitis vinifera* typical of Galicia (a region of Northwest Spain) and the north of Portugal. The production of monovarietal wines with these grapes is frequent in Portugal, but in Galicia, because of their limited production, they are normally mixed together or with other varieties, as in the case of Albariño. The different Denominaciones de Origen (appellations of controlled origin) that exist in Galicia have begun, in the past few years, to promote a reconversion of their vineyards, promoting the planting of these varieties (considered to be autochthonous) instead of other external varieties that were planted originally because of phylloxera (*1*).

Commercial wines produced from each of these individual varieties exist in Portugal. An example is the highly valued Loureira wines, appreciated even more than the Albariño wines that are recognized worldwide. In contrast, in Galicia, because commercial monovarietal wines are practically nonexistent, there are very few data on the composition of this type of wine, with the exception of the classical parameters obtained by the Estación de Viticultura y Enología de Galicia (EVEGA) in its study of Galician Autochthonous Varieties (*2*) and some studies of differentiation of Albariño wines from other Galician wines as a function of the volatile compounds (*3*, *4*) or the trace elements content (*5*, *6*).

The present study analyzes the volatile composition of monovarietal wines produced from Loureira, Treixadura, and Dona Branca grapes obtained over four consecutive vintages (1992 to 1995), with the objective of possibly finding typical profiles. Because the grapes of the three varieties were from the same vineyard, they should have common characteristics of soil, climate, etc. Therefore, any differences that might be found in the volatile compositions of their wines should only be due to the variety used for winemaking. These profiles were compared to establish differentiation criteria as a function of the varieties from which the wines were made. Multivariate techniques of data analysis (principal component and linear discrimination analysis) were employed for these comparisons.

MATERIALS AND METHODS

Sample Wines. Grapes of *Vitis vinifera* cultivars Loureira, Dona Branca, and Treixadura, supplied for the Estación de Viticultura y Enología de Galicia (EVEGA), collected at the final stage of ripening were used. The vinification of all varieties was carried out in the same way. Grapes of each variety were crushed, destemmed, racked, and pressed. The musts were fermented in flasks in the laboratory with spontaneous yeasts. Alcoholic fermentation was carried out at 17 °C, then malolactic fermentation occurred at 20 °C. When fermentation was finished, the wines were stored at −5 °C for 10−15 days, filtered, and then bottled.

Volatile Compound Determination. Methanol and the higher alcohols were determined by direct injection, using a Carbowax 1540

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10.1021/jf010631s CCC: $22.00
Published on Web 12/29/2001

column (7.5 m × 2.3 mm i.d.) in a Hewlett-Packard 5890 gas chromatograph at 80 °C isothermic temperature (carrier gas, hydrogen at 8 psi), following the method described by Bertrand (*7*).

Monoterpene alcohols were extracted as described by Dubourdieu et al. (*8*). A sample of 100 mL of wine was adjusted to pH 7 by the addition of NaOH, and 1 mL of 3-octanol (10 mg/L) was added as an internal standard. The sample was extracted three times (10, 5, and 5 mL) with diethyl ether-pentane (1:1, v/v). This organic extract was concentrated to 0.5 mL under nitrogen. A Hewlett-Packard HP5890 chromatograph, with flame ionization detector (FID) and equipped with a Carbowax 20M (50 m × 0.25 mm i.d., 0.25 μm film tickness) capillary column, was used. A 1-μL sample of the extract was injected in splitless mode (30 s). Temperature program was as follows: held 1 min at 45 °C, raised at 3 °C/min to 230 °C, and held for 25 min. Hydrogen was used as the carrier gas (18 psi). Temperature of the injector and detector was 230 °C.

Fatty acids and their ethyl esters, acetates, 1-hexanol, diethyl succinate, and 2-phenyl ethanol were extracted and quantified with the method described by Bertrand (*9*): 2 mL of 3-octanol (50 mg/L) as internal standard and 1 mL of sulfuric acid (1/3) were added to 50 mL of wine. These were extracted three times (4, 2, and 2 mL) with diethyl ether−hexane (1:1, v/v). The organic extract (1 μL) was injected into a Varian 3400 chromatograph under the same capillary column and chromatographic conditions indicated above for the terpenes.

Volatile phenols were extracted according to the method proposed by Chatonnet and Boidron (*10*). After adjustment of the ionic strength of the medium with ammonium sulfate and addition of an internal standard (3,4-dimethylphenol), liquid−liquid extraction with dichloromethane was performed. The organic extract obtained was washed two times at pH 8.5 to eliminate the carboxylic acids, and then the phenolates were extracted with NaOH (pH 13). Hydrochloric acid (7.5 mL) was added to the aqueous phase to isolate the phenolic fraction, and then it was extracted three times with diethyl ether. The final organic extract was concentrated under nitrogen and injected in the same capillary column and chromatographic conditions as the esters and terpenes.

Sulfur constituents (boiling point > 90 °C) of the wines were analyzed by gas chromatography on a Hewlett-Packard HP5890 chromatograph with photometric flame detection (absorbance at 393 nm) (*11*), under the same capillary column and chromatographic conditions indicated for the other mentioned compounds.

Determinations of the different compounds were made in triplicate.

All compounds were identified by comparing retention times with pure substances and confirmed by GC−MS using a HP 5890 Series I coupled to HP 5970 mass spectrometer. Each family of compounds was identified in splitless mode (temperature, 230 °C; injection volume, 3 μL; purge time, 30 s; purge rate, 70) on a capillary column Carbowax 20M (50 m × 0.25 mm i.d., 0.25 μm film, He; 18 psi). The temperature was held at 45 °C for 1 min, raised to 230 °C at 3 °C/min, then held for 30 min. The detection was performed by an HP-5970 mass spectrometer in the EI mode (ionization energy, 70 eV; source temperature, 250 °C). The acquisition was made in scanning mode (mass range, 30−300 amu, 1.9 spectra/s).

Statistical Analysis. Significant differences among wines for each of the compounds were assessed with a one-way analysis of variance (ANOVA) using the Excel 5.0 program. Fischer's least significant differences (LSD) was used to evaluate the significance of the analysis.

To establish the relationship between the composition and the grape variety, principal component analysis (PCA) and linear discriminant analysis (LDA) were carried out using Statistica 5.0 program (StatSoft, Inc.).

RESULTS AND DISCUSSION

The mean values for the volatile compounds determined in the Loureira, Dona Branca, and Treixadura wines over the four vintages studied are presented in Table 1.

Free Monoterpenes. The Loureira wines, contrary to Treixadura and Dona Branca wines, showed a high free monoterpene content. Linalool was markedly the most abundant monoterpene, being present at levels higher than its perception threshold (50 μg/L) (*12*). The next most abundant free monoterpenes in Loureira wines were the α-terpineol and geraniol, which corroborates the results obtained by Ortega et al. (*13*) and by Orriols et al. (*14*). In addition, studies of this variety cultivated in Portugal show similar values for these terpenes (*15*, *16*). The 1992 vintage showed an abnormally high content of monoterpenes compared to that in the other vintages, which, in most cases, caused significant differences between the concentrations of the different vintages.

Recent studies on the glycosylated monoterpenes of this variety cultivated in Portugal (*15*) revealed that, with the exception of geraniol, combined forms were almost non-existent and that the addition of enzymes to unfermented grape juice did not significantly increase the terpene. Ortega et al. (*13*) tested different prefermentation maceration times and reached the conclusion that a 6-h contact increased the geraniol content by four times. This could mean that this compound may surpass its perception threshold (130 μg/L) (*12*) and give the wine a "rose" nuance.

The Dona Branca wines, similarly to the Treixadura wines, showed a generally low free monoterpene content, although in the 1992 vintage, the linalool content was found to be above its perception threshold. Geraniol was the second most abundant free monoterpene in the wines of this variety. Because of the low levels obtained for the four grape harvests, it is possible that the use of glycosylated enzymes or a prefermentation maceration might lead to an increase in the terpene content of the wines obtained from Dona Branca. There is no information available, either on the aromatic potential of this grape or on the resulting wines, despite the fact that they are now very much appreciated commercially.

Treixadura is the variety that shows by far the lowest content of free monoterpenes (*17*). The concentration of linalool remained constant throughout the four vintages that were studied, but was present at only one-tenth of the perception threshold. The nerol content was constant in the last three vintages analyzed (12 μg/L). However, in the first year it showed a low value, with the result that it was significantly different. Geraniol was the terpene present at the highest concentration in the four vintages, showing values between the 12 μg/L and 21 μg/L, extremely low amounts compared to the perception threshold. The fact that the terpenes nerol and geraniol were the most abundant in this variety, within the minimum amounts that are present, confirmed the results obtained by Orriols et al. (*14*). Therefore, the free monoterpene alcohols do not play an important part in the varietal profile of the Treixadura wines. Moreover, studies made by Pereira (*15*) of this variety cultivated in Portugal (Região Demarcada de Vinhos Verdes) showed that the content of terpene glycosylates is also not high. In fact, combined linalool was not detected and, although it appeared that the content of α-terpineol and geraniol, in the form of precursor, was higher than in the free state, they were still at very low concentrations. Therefore, neither the use of prefermentation maceration nor the addition of pectolytic enzymes, before or after the alcoholic fermentation (*18, 19*), will sufficiently increase the terpene content to give Treixadura wines the typical floral character attributed to this family of volatile compounds.

Volatile Phenols. The Loureira and Treixadura wines contained low levels of guaiacol. In fact, only the Loureira wine of 1993 had a concentration above its perception threshold (95 μg/L) (*20*), which was significantly different from the wines of 1993 and 1995. The content of vinylphenols of Loureira and

Table 1. Mean Values for Volatile Compounds of Loureira, Dona Branca, and Treixadura Wines from Different Vintages[a]

compound	Loureira wines				Dona Branca wines				Treixadura wines			
	1992	1993	1994	1995	1992	1993	1994	1995	1992	1993	1994	1995
monoterpenes												
linalool	213^{a}	80^{b}	101^{c}	186^{d}	56^{a}	31^{b}	46^{c}	36^{d}	5	5	5	5
α-terpineol	107^{a}	36^{b}	38^{b}	38^{b}	20^{a}	6^{b}	20^{a}	16^{c}	3^{a}	1^{b}	n.d.^{b}	n.d.^{b}
citronellol	1^{a}	11^{b}	7^{c}	9^{d}	n.d.^{a}	8^{b}	n.d.^{a}	n.d.^{a}	n.d.	n.d.	n.d.	n.d.
nerol	5^{a}	4^{a}	1^{b}	2^{b}	n.d.	5^{b}	n.d.^{a}	n.d.^{a}	1^{a}	12^{b}	12^{b}	11^{b}
geraniol	69^{a}	9^{b}	11^{bc}	13^{c}	47^{a}	17^{b}	47^{a}	26^{c}	12^{a}	17^{b}	16^{b}	21^{c}
volatile phenols												
guaiacol	87^{a}	101^{b}	88^{a}	79^{c}	65^{a}	237^{b}	186^{c}	202^{d}	n.d.	n.d.	n.d.	n.d.
4-vinylguaiacol	96^{a}	21^{b}	35^{c}	45^{d}	31^{a}	173^{b}	201^{c}	195^{c}	40^{a}	42^{b}	35^{c}	35^{c}
4-vinylphenol	250^{a}	235^{b}	234^{b}	251^{a}	643^{a}	209^{b}	218^{b}	238^{c}	510^{a}	562^{b}	589^{c}	613^{d}
4-methylguaiacol	13^{a}	n.d.^{b}	n.d.^{b}	n.d.^{b}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
vanillin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	68^{a}	57^{b}	33^{c}	22^{d}
alcohols												
methanol	50^{a}	37^{b}	45^{c}	47^{d}	53^{a}	70^{b}	63^{c}	68^{d}	40^{a}	42^{b}	40^{a}	42^{b}
1-propanol	41	33	39	37	50^{a}	21^{b}	48^{c}	37^{d}	40	40	40	38
2-methyl-propanol	71	61	66	66	23^{a}	70^{b}	26^{c}	29^{d}	29	29	28	29
2-methyl-butanol	31	24	30	32	18^{a}	38^{b}	21^{c}	22^{c}	31	31	32	33
3-methyl-butanol	93^{a}	117^{b}	94^{a}	96^{c}	83^{a}	171^{b}	93^{a}	98^{d}	126^{a}	128^{b}	125^{c}	120^{d}
1-hexanol	3.35	3.52	3.24	3.19	0.55^{a}	2.37^{b}	0.61^{a}	0.51^{a}	1.51^{a}	1.53^{a}	1.37^{b}	1.49^{a}
2-phenylethanol	20.29	19.35	20.45	21.34	10.21^{a}	35.18^{b}	12.12^{c}	10.24^{a}	16.36^{a}	13.33^{b}	14.42^{c}	15.04^{d}
acetates												
ethyl acetate	79^{a}	81^{b}	98^{c}	96^{d}	14^{a}	16^{ab}	12^{a}	18^{b}	36	36	36	36
isoamyl acetate	0.317	0.304	0.355	0.364	0.600^{a}	0.148^{b}	0.624^{a}	0.600^{a}	0.777	0.756	0.754	0.698
hexyl acetate	0.015	0.006	0.018	0.023	0.031	0.045	0.049	0.048	0.056	0.061	0.049	0.046
phenethyl acetate	0.286	0.264	0.286	0.296	0.067	0.044	0.053	0.061	0.092	0.089	0.078	0.076
ethyl esters												
ethyl butyrate	0.707	0.741	0.728	0.695	0.352^{a}	0.239^{b}	0.253^{b}	0.206^{c}	0.334	0.352	0.323	0.302
ethyl hexanoate	0.176	0.185	0.160	0.164	0.866^{a}	0.167^{b}	0.267^{c}	0.192^{d}	1.005	0.992	0.994	1.005
ethyl octanoate	0.401	0.383	0.395	0.404	1.350^{a}	0.207^{b}	0.137^{c}	0.124^{c}	1.103	1.023	0.994	1.006
ethyl decanoate	0.045	0.055	0.061	0.073	0.453^{a}	0.035^{b}	0.042^{c}	0.034^{b}	0.107	0.099	0.095	0.091
ethyl dodecanoate	0.005	n.d.	0.005	0.007	0.033^{a}	n.d.^{b}	n.d.^{b}	n.d.^{b}	0.006	n.d.	n.d.	n.d.
ethyl tetradecanoate	n.d.	n.d.	n.d.	0.001	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ethyl lactate	7.93^{a}	6.53^{b}	6.97^{b}	6.65^{b}	9.50^{a}	28.67^{b}	28.67^{b}	26.67^{b}	34.15	34.61	30.01	29.96
diethyl succinate	0.377	0.369	0.341	0.366	0.35^{a}	0.35^{b}	0.35^{a}	0.30^{c}	1.95	2.00	1.82	1.66
fatty acids												
butyric acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.013	1.983	1.963	1.880
isobutyric acid	n.d.	n.d.	n.d.	n.d.	n.d.^{a}	1.81^{b}	n.d.^{a}	n.d.^{a}	0.988^{a}	0.974^{b}	1.004^{c}	0.899^{d}
hexanoic acid	3.487	3.180	3.230	3.307	4.987^{a}	2.623^{b}	2.973^{c}	2.740^{d}	0.420^{a}	0.401^{b}	0.395^{b}	0.254^{c}
octanoic acid	3.983	3.873	3.907	3.987	6.523^{a}	2.543^{b}	1.523^{c}	1.317^{c}	0.507^{a}	0.477^{b}	0.456^{c}	0.302^{d}
decanoic acid	1.177	1.277	1.267	1.137	1.660^{a}	0.861^{b}	0.632^{c}	0.553^{c}	0.105	0.100	0.096	0.099
dodecanoic acid	0.092	0.084	0.093	0.101	n.d.	n.d.	n.d.	n.d.	0.052^{a}	0.034^{b}	n.d.^{c}	n.d.^{c}
sulfur constituents												
thiophenone	11	13	12	13	72^{a}	41^{b}	50^{c}	45^{b}	n.d.	n.d.	n.d.	n.d.
methionol	731^{a}	751^{b}	721^{c}	732^{a}	1147^{a}	2857^{b}	3027^{c}	2986^{d}	780^{a}	945^{b}	826^{c}	856^{d}
methionyl acetate	n.d.	n.d.	n.d.	n.d.	16^{a}	n.d.^{b}	n.d.^{b}	n.d.^{b}	n.d.	n.d.	n.d.	n.d.

[a] Concentrations are reported in mg/L, except for monoterpenes, volatile phenols (except vanillin), and sulfurs, which are reported in μg/L. n.d., Not detected. Means within each row with the same letter superscript are not singnificantly different at 95%.

Treixadura wines was also lower, with less 4-vinylguaiacol in wines from Loureira grapes and less 4-vinylphenol in those from Treixadura grapes. This could be explained (due to their similarity to the respective Portuguese varieties) by decarboxylation of the higher level of ferulic acid in Loureira unfermented grape juice (*21*), and of *p*-coumaric acid in Treixadura (*22*). The concentration of 4-vinylphenol in the Treixadura wines was significantly different for the four grape harvests. Although this is lower than their perception threshold (770 μg/L), according to Boidron et al. (*20*) the presence of both of the vinylphenols in the same sample of wine would reduce the perception threshold to 375 μg/L for the 4-vinylphenol, and for this reason the “paint” or “watercolor” aroma that this provides could be appreciated. A skin contact time of only 5 h, according to Falqué and Fernández (*23*), will cause tripling of the content of 4-vinylphenol.

The Dona Branca wines, with the exception of the 1992 vintage, were those that showed the highest content of guaiacol. This compound supplies wines with a “smoked” aroma at levels above 95 μg/L (*20*). The 4-vinylguaiacol content was also significantly different for the four grape harvests, and the Dona Branca wines showed concentrations of these compounds two or three times higher than those in Loureira and Treixadura wines, although these contents were lower than its perception threshold of 440 μg/L (*20*). 4-Vinylphenol, which had a significantly different concentration between the 1992 and 1995 vintages, had a tripled concentration in the 1992 wine. This was more than the perception threshold of 375 μg/L (*20*) attributed to this compound, when 4-vinylguaiacol is present in the sample. For this reason, in the 1992 vintage, the undesirable nuance of “paint” or “watercolor” supplied by this compound could be detected. It should also be noted that it was in the 1992 Dona Branca wine that the minimum levels of guaiacol and 4-vinylguaiacol were produced, coinciding with the maximum concentration detected for 4-vinylphenol. In the 1992 Loureira wine, 4-methylguaiacol was also detected, but in concentrations below its perception threshold (65 μg/L) (*20*). This was significantly different with respect to other grape harvests.

Treixadura was the only variety studied in which the presence of appreciable quantities of vanillin were detected, varying between 68 and 22 mg/L and corroborating the amounts found in other studies (*24*). This compound has a perception threshold of 0.40 mg/L (*20*), for which reason the aroma of "vanilla" that it supplies will be present in the wines produced from this variety.

Higher Alcohols. For the wines produced from the variety Loureira, only the concentrations of methanol and of 3-methyl-1-butanol were significantly different for all the grape harvests. The average content of 2-methyl-1-propanol was the highest of all the wines analyzed, whereas in contrast the average levels of isoamyl alcohol were the lowest, together with those of the Dona Branca wines. The Loureira wines had a notably higher concentration of 1-hexanol of around 3−4 mg/L. The 2-phenylethanol content was not significantly different and showed values in accordance with those reported (*25*). Similar increases in the concentration of this substance on treating the musts of this Portuguese variety with glycosylated enzymes were found (*15*).

The concentrations of all the higher alcohols in the Dona Branca wines were significantly different for all the grape harvests, except for isobutanol in the 1994 and 1995 vintages. The average content of methanol in the Dona Branca wines was high compared to that found in the Loureira and Treixadura wines. With the exception of the 1993 vintage, which showed a much higher level of isoamyl alcohol than the rest of the vintages (a factor that was also found in Loureira wines), the Dona Branca and Loureira wines showed a low content of this higher alcohol. The concentration of 1-hexanol remained constant, with the exception of the 1993 vintage, which had a significantly higher value. Finally, the 2-phenylethanol content was also significantly different for the wines from 1993 and 1994, although in 1994 it showed a value close to those of 1992 and 1995. With the exception of the 1993 vintage, it can be noted that the contents of 1-hexanol and 2-phenylethanol of the Dona Branca wines are the lowest of all the varieties studied in this work.

In the Treixadura wines, only 3-methyl-1-butanol appeared in significant concentrations for the four vintages. The high contents of 2-methyl- and 3-methyl-1-butanol shown by these wines, at least with respect to those produced from Loureira grapes, could be justified by the higher content, of up to three times (*21*), of leucine and isoleucine, which are amino acid precursors of these alcohols (*26*). 1-Hexanol, which supplies the "green", "coconut", and "picant" aroma (*27*), were also significantly different for the 1994 grape harvest. Finally, 2-phenylethanol, which has an aromatic description of "rose" (*27*) and may contribute to the floral nuance of the wines, appeared in a significantly different concentration for the four vintages. It showed values similar to those reported by Falqué and Fernández (*28*) and slightly above those cited by Pereira (*15*) for this variety cultivated in Portugal, although the latter concentration could equal the level found in this investigation by including the combined form.

Acetates. The only acetate that showed significantly different values for the wines from all the Loureira vintages was ethyl acetate. In contrast, these wines showed the least content of isoamyl and hexyl acetates and the highest levels of phenylethyl acetate, around 0.26−0.30 mg/L, a content not significantly different for the four harvests analyzed.

In the Dona Branca wines, only ethyl and isoamyl acetates showed (in the 1993 vintage) significantly different values. The hexyl acetate was present at an average concentration of 0.040 mg/L and the phenylethyl acetate varied between the 0.044 mg/L for the 1993 vintage and 0.067 mg/L for the first year of the study. Again, the wines of this variety are those that showed a marked difference when compared with the other varieties studied, having a lower content of ethyl acetate and phenylethyl acetate.

In the Treixadura wines, ethyl acetate appeared in the highest concentrations and was constant throughout the four vintages analyzed (36 mg/L). Isoamyl acetate, which supplies a "fruity" and "banana" nuance (*29*), had very low values, although higher than those in the Loureira and Dona Branca varieties. Hexyl acetate, as in the case of ethyl acetate, showed higher values than those detected in wines of the other varieties. Finally, phenylethyl acetate also did not show significant differences between the four vintages analyzed, but had a higher concentration than that in Dona Branca wines, and a concentration three times lower than the other variety studied.

Ethyl Esters. The Loureira wines showed the lowest concentrations of ethyl esters of fatty acids (6 to 10 carbon atoms). Only the concentration of ethyl lactate was significantly different for the 1992 vintage. However, the values found for this compound and for diethyl succinate agree with those previously reported (*25*). The maximum values for all the ethyl esters were found in the 1992 Dona Branca vintage, being higher than the respective vintages of Loureira and Treixadura. With regard to ethyl lactate, with a significantly different concentration for the first year, it appeared that, as in Treixadura, this variety showed a somewhat higher malic acid content which spontaneously causes a partial malolactic fermentation. The concentration of diethyl succinate was about 0.30−0.35 mg/L, except for 1993, in which it was lower. These wines, together with those produced from Loureira, were the Galician wines with the least concentration of this compound.

The concentrations of all the ethyl esters in the Treixadura wines were reasonably constant over the four vintages, and in fact, the differences were not significant. The high content of these wines in ethyl hexanoate, octanoate, and decanoate were noteworthy when compared to the respective values obtained for the Loureira wines. The high content of diethyl succinate was similar to the levels previously reported (*23*). In contrast, the level of ethyl lactate was higher than that in the rest of the wines analyzed. As this is the second highest autochthonous Galician variety in average malic acid content (*2*), this could be due to spontaneous malolactic fermentation.

Fatty acids. The fatty acid concentrations in the Loureira wines were not significantly different for any of the vintages. Butyric and isobutyric acids were not detected in these wines, and the contents of 6-, 8-, and 10-carbon atom fatty acids, although high, were in agreement with those found by Versini et al. (*25*), showing levels of 3.3, 3.9, and 1.2 mg/L, respectively. With regard to dodecanoic acid, the detected contents were very similar for the four vintages analyzed, showing an average value of around 0.090 mg/L, higher than that found for Dona Branca and Treixadura.

The butyric, isobutyric, and dodecanoic acids appeared in scarcely appreciable quantities in the Dona Branca wines, and fatty acids of 6-, 8-, and 10-carbon atoms showed significantly different values. All of these had higher values in the 1992 vintage. Finally, the Treixadura wines stand out for their high content of butyric acid, with concentrations not significantly different for the four grape harvests, and of isobutyric acid. The

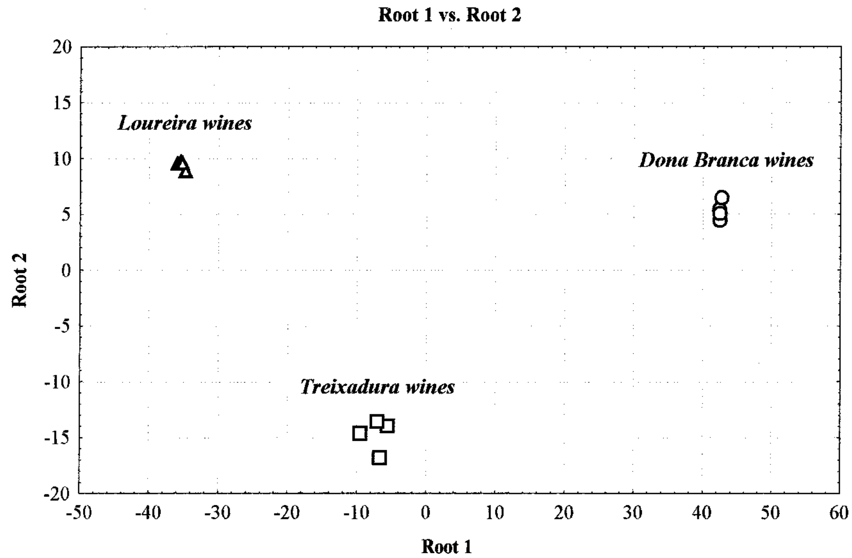

Figure 1. Differentiation between Treixadura, Loureira, and Dona Branca wines by applying LDA.

rest of the acids, excepting decanoic acid, showed values that are significantly different in the cases of hexanoic, octanoic, and dodecanoic acids. The fatty acids from 6−12 carbon atoms did not show a constant average level in the four vintages studied.

Sulfur Compounds. The presence of sulfur components in the Loureira and Treixadura wines was practically non-existent, with the exception of methionol. This compound was present in the wines in significantly different concentrations for almost all the vintages and was higher in Treixadura than in Loureira wines. This could be justified by the higher methionine content present in Treixadura (*21*). Methionine is an amino acid from which the yeasts presumably form methionol during alcoholic fermentation (*30*, *31*).

The Dona Branca wines showed the highest content of 2-methyl-3-tetrahydrothiophenone. Moreover, the amounts were significantly different for the 1992 and 1994 vintages. Although the methionol content did not reach the perception threshold of this compound (4.5 mg/L) (*11*), it appeared at a very high concentration, especially in the 1993 and 1995 vintages. These showed values of two or even three times that of the 1992 vintage. The methionyl acetate content was also significantly different for the 1992 vintage, being almost non-existent in the rest of the vintages.

Volatile Profile. With the exception of the higher alcohols and phenylethanol contents, there are clear differences in the average aromatic profiles of these Galician white wines. Loureira wines are characterized by the presence of higher levels of monoterpenes, acetates, fatty acids, and 2-phenyl-ethanol, which corroborates the typical floral and fruity nuance of these wines (*14*, *25*), despite their having higher concentrations of 1-hexanol. Dona Branca wines show the highest values of methanol and sulfur components, and high levels of free terpenes and fatty acids. In contrast, they have the lowest contents of 1-hexanol, diethyl succinate, acetates, and ethyl esters. Treixadura wines stand out clearly for their almost non-existent terpene content and for their high content of volatile phenols, due to the presence of significant quantities of vanillin, ethyl esters, ethyl lactate, and diethyl succinate.

Statistical Analysis. When PCA was applied to the concentrations of the 38 determined analytical variables, three factors were extracted and 99.7% of the total variance was explained. The most influential volatile compounds were methionol, 4-vinylphenol, guaiacol, vanillin, linalool, α-terpineol, ethyl lactate, ethyl acetate, 2-methyl-1-propanol, and 3-methyl-1-butanol. After a stepwise PCA using the more discriminant variables, a linear discriminant analysis (LDA) was run in order to optimize the separation of these Galician white wines. Figure 1 shows a projection of the wines in two-dimensional space, explaining 100% of the total variance. Three groups representing each variety were clearly observed. The two LDA factors were effective in discriminating between wine varieties.

Three wines (Loureira, Dona Branca, and Treixadura) from 1992 to 1995 vintages were analyzed by GC and GC−MS in order to characterize them according to their varietal origin. The effect of factors such as climatic conditions or winemaking techniques did not account for the differences between them, as these were the same for each year and for each variety. The content of volatile compounds shown by these wines remained relatively constant throughout the vintages studied, permitting the definition of volatile profiles that are typical for each wine and, in turn, perceptively different among the three varieties. Loureira, Dona Branca, and Treixadura wines were independently grouped according to variety when aromatic compounds were subjected to PCA. Two terpenes (linalool and α-terpineol), two acetates (ethyl acetate and ethyl lactate), two alcohols (2-methyl-1-propanol and 3-methyl-1-butanol), one sulfur compound (methionol), and three volatile phenols (guaiacol, 4-vinylphenol, and vanillin) were responsible for the separation of wines according to grape variety. Although a good varietal differentiation was obtained by LDA, this may be the result of unique variations in this small number of wines, and so a larger sample of wines should be examined in order to confirm our findings.

ACKNOWLEDGMENT

The authors thank the Estación de Viticultura y Enología de Galicia (EVEGA) for the grapes and wines provided.

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Received for review May 14, 2001. Revised manuscript received October 2, 2001. Accepted October 22, 2001. E.F. thanks the Caixa Galicia and Xunta de Galicia for a grant.

JF010631S