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Characterization and Differentiation of Sherry Brandies Using Their Aromatic Profile

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ABSTRACT: Aroma compounds of 48 Sherry brandies have been identified and quantified by the stir bar sorptive extraction method coupled to gas chromatography−mass spectrometry (SBSE−GC/MS). Analysis of variance and multivariate analysis techniques have been used to classify these brandy samples according to the commercial category (Solera brandy, Solera Reserva brandy, and Solera Gran Reserva brandy). From an univariate point of view (analysis of variance), several of the volatile compounds considered showed significant differences. Principal component analysis, using the global data matrix, showed that only the Solera brandy samples, with the shortest aging in wood, were well-differentiated from the others. Partial least-squares discriminant analysis (PLS-DA) results provided evidence of the ability of the content of volatile compounds to discriminate among the different commercial categories. Linear discriminate analysis allowed for a 93% differentiation according to the commercial category and, thus, the length of its aging process in wood. The results obtained show that it would be possible to ensure the commercial category of a Sherry brandy using its content of volatile compounds.

KEYWORDS: SBSE, Sherry brandy, differentiation, flavor, aging

INTRODUCTION

Sherry brandy is an oenological distilled product from wine. For its manufacturing, alcohol derived from wine is stored in American oak casks for a certain period of time. During this period, the typical traditional dynamic aging system known as solera y criaderas is carried out[1,2] as follows: part of the content of the oldest barrel in the ground (solera) is tapped, which is bottled. Then, that barrel is refilled from the next oldest cask (first criadera), and that one in succession from the second oldest (second criadera), up to the youngest cask, which is refilled with new product. The transferred product mixes with the older product in the next barrel. Martínez Montero et al.[3] showed an explanatory design of this process.

Dependent upon the length of time that the Sherry brandy is submitted to aging in wood, three different categories of commercial product can be found in the market: Solera brandy (S, from 6 months to 1 year), Solera Reserva brandy (SR, from 1 to 3 years), and Solera Gran Reserva brandy (SGR, more than 3 years). This type of aging implies an important financial cost that should be recovered in the final price of the product. Therefore, as important as obtaining a high-quality Sherry brandy is the need to determine objectively the appropriate parameters that allow us to characterize and differentiate Sherry brandies from different categories and/or from others produced in different regions.

During the period of aging in oak wood, important and diverse physicochemical changes occur.[4,5] All of the modifications that oenological products experience during their aging in wood depend upon several factors, such as the duration of the aging period, the origin and state of the wood, the environmental conditions, etc.[4,6,7] These modifications include both extraction phenomena and reactions that take place during this period, such as oxido−reductions, esterifications, Maillard reactions, polymerizations, and polycondensations, and involve both compounds present in the raw distillate and compounds extracted from the wood.

Among all of these processes, the direct or indirect extraction of the wood components by the distillate plays a decisive role in the sensorial properties of the final product.[4] *trans*- and *cis*-β-Methyl-γ-octalactone, furfural, eugenol, and vanillin are some of the volatile compounds derived from the wood, which provide sensorial notes, such as sweet, oak woody, coconut, spice, and vanilla, among others.[8]

Hundreds of volatile compounds, some of them already present in the raw material and others from the distillation process and from the wood, constitute the aroma of brandies.[9] Several ethyl esters and terpenes provide fruity and floral notes,[10] whereas herbaceous attributes are produced by C_6-alcohols.[11] The smoky and toasted odor notes are associated with some volatile phenols.[12] A high number of the compounds extracted from the wood have a poor volatility, and thus, their direct contribution to the aroma is low. However, it is known that some of these nonvolatile compounds have influence indirectly on the aroma by reducing the volatility of other more volatile compounds.[13] Otherwise, some of the volatile compounds already present in the fresh distillate undergo significant and specific modifications during the aging in wood. For instance, Rodríguez et al.[14] found different evolutions of some volatile compounds throughout aging in wood of cider brandies. The concentration of acetates and fatty acids decreased, whereas the content of their ethyl esters increased.

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For all of this, the time that brandy spends in the cask is now considered as a fundamental factor that contributes to the final taste and aroma of this product. On the basis of this fact, several attempts have been made to correlate the concentration of particular compounds and the length of this aging.

Schwarz et al.[15] concluded that antioxidant activity and polyphenolic content of Sherry brandies increased with rising age. By means of different chemometric techniques, a clear correlation between the age of a wine and certain parameters related to the process of aging has been developed. Guillén et al.[16] established a partial least-squares (PLS) regression model that allowed for the prediction of the age of a wine, with a mean deviation of 1.6 years in relation to its true age. In this model, short-chain organic acids, polyphenols, and higher alcohols were employed as predictive variables. Moreover, Ortiz et al.[17] observed a high correlation between the age of a series of Vintage Port wines and parameters, such as some major volatile compounds, several polyphenols, and color parameters.

Therefore, the cession of compounds from the wood and the modifications in the composition of oenological products because of the different chemical reactions that take place during the aging in wood depend upon the length of this period. Taking this into account, it could be expected that Sherry brandies from different categories (S, SR, and SGR) could be differentiated according to their content of volatile compounds. This fact, the correlation between the length of aging in wood for Sherry brandies, and their content of volatile compounds could provide the wineries with an easy method to differentiate them.

To date, this is the first paper in the literature regarding the differentiation of Sherry brandies with different aging periods. It is very important progress, taking into account the complexity of the employed aging system, which could facilitate the classification of this high-quality product. Moreover, it is the first approximation to estimate the actual age of a Sherry brandy using its aromatic profile.

MATERIALS AND METHODS

Chemical and Standards. All of the aroma standards employed in this work were supplied by Merck (Darmstadt, Germany) and Sigma (Steinheim, Germany). NaCl were purchased from Scharlau (Barcelona, Spain). 4-Methyl-2-pentanol was employed as an internal standard.

Samples. A total of 48 commercial Sherry brandies were studied, from the Protected Designation of Origin (PDO) "Brandy de Jerez", belonged to three different categories: 15 Solera brandy (S), 15 Solera Reserva brandy (SR), and 18 Solera Gran Reserva brandy (SGR). The studied samples had an ethanol content ranging between 37 and 42%.

Analysis of Brandy Volatile Compounds. A total of 33 volatile compounds were determined, in duplicate, by stir bar sorptive extraction (SBSE) and gas chromatography (GC). The SBSE method had been previously optimized and validated for the determination of volatile compounds in brandies, by means of a factorial design 2^{5-1}. Detection and quantification limits, recovery, and intra- and interassay precision were satisfactorily determined in this previous work for all of the studied compounds.[18]

Briefly, the extractions were carried out with 10 × 0.5 mm (length × film thickness) polydimethylsiloxane (PDMS) commercial stir bars, supplied by Gerstel (Mülheim a/d Ruhr, Germany). A volume of 35 mL of sample was pipetted and placed in a 100 mL Erlenmeyer flask with 140 μL of a solution of 4-methyl-2-pentanol (internal standard, 2.294 g/L in an alcohol−water solution at 40% of alcohol). To reduce the alcoholic content, which negatively affected the analytical signals,[18] 35 mL of Milli-Q water was also added to the Erlenmeyer flask. Then, it was placed on a 15 position magnetic stirrer (Mülheim a/d Ruhr, Germany). The stir bar was rotated at 1100 rpm for 100 min at 25 °C. After removal from the brandy sample, the stir bar was placed for a few seconds in distilled water and gently dried with a lint-free tissue. Then, it was transferred to a glass thermal desorption tube. The coated stir bars were thermally desorbed using a commercial thermal desorption unit (TDU) (Gerstel) connected to a programmed-temperature vaporization (PTV) injector CIS-4 (Cooled Injection System, Gerstel) by a heated transfer line. The PTV was installed in an Agilent 6890 GC-5973 mass spectrometry (MS) system (Agilent Technologies, Palo Alto, CA). An empty baffled linear was used in the PTV. The thermodesorption unit was equipped with a MPS 2 L autosampler (Gerstel) capable of handling the program for 98 coated stir bars. The desorption temperature was programmed from 40 to 300 °C (held for 10 min) at 60 °C/min under a helium flow (75 mL/min), and the desorbed analytes were cryofocused in the PTV system with liquid nitrogen at −140 °C. Finally, the PTV system was programmed from −140 to 300 °C (held for 5 min) at 10 °C/s for analysis by GC−MS. Capillary GC−MS analyses in the electron impact mode were performed on an Agilent 6890 GC-5973N MS system (Agilent, Little Falls, DE), equipped with a DB-Wax capillary column (J&W Scientific, Folsom, CA), 60 m × 0.25 mm inner diameter, with a 0.25 μm coating. The carrier gas was helium at a flow rate of 1.0 mL/min. The GC oven was programmed as follows: held at 35 °C for 10 min and then ramped at 5 °C/min to 100 °C. Then, it was raised to 210 °C at 3 °C/min and held for 40 min. The mass detector operated in EI+ mode at 70 eV in a range from 30 to 400 amu.

Peak identification was carried out using the Wiley library by analogy of mass spectra and confirmed by retention indices of standards. Quantitative data from the identified compounds were obtained by measuring the molecular ion relative peak area in relation to that of 4-methyl-2-pentanol, the internal standard.

Statistical Techniques. Univariate analysis of variation (ANOVA) and multivariate analysis of data including principal component analysis (PCA, using the statistical computer package Statgraphics Centurion, version 15.0, Statpoint, Inc., Warrenton, VA), partial least-squares discriminant analysis (PLS-DA) regression (using the statistical package The Unscrambler 9.6, CAMO, ASA, Oslo, Norway), and linear discriminant analysis (LDA, employing SPSS statistical software, version 14.0, SPSS, Inc., Chicago, IL) were performed. PLS-DA regression is a variant of partial least-squares (PLS) regression. Each sample in the calibration set is assigned to a dummy variable[15] as a reference value (Solera brandy, S = 1; Solera Reserva brandy, SR = 2; Solera Gran Reserva brandy, SGR = 3). The classification of each sample is made as a function of the predicted value by the PLS model. This value should be ideally close to the values used to codify the classes. A cutoff value between the numbers assigned to each class is normally established. For example, if "1" is used to indicate that the sample belongs to the correct category, "0" is used to indicate that the sample belongs to the other category, and in the prediction, the value assigned to the sample is larger than the cutoff value, then the sample is assigned to its real category. Normally, an arbitrary cutoff value between the numbers assigned to each category is used. In this study, the classification of the brandy samples was on the basis of the 0.5 cutoff value.

RESULTS AND DISCUSSION

Mean Values and ANOVA. With the aim to guarantee the age of the different categories of Brandy de Jerez and make the method to check the age of the brandy easier and faster, the main and representative volatile compounds for each chemical family have been identified: acids, ethyl esters, acetates, alcohols, terpenes, benzenic compounds, and C_{13}-norisoprenoids.

Table 1 shows the mean values and standard deviations calculated for each volatile compound and Sherry brandy

Table 1. Mean ± Standard Deviation (μg/L) of Volatile Compounds Found for the Different Sherry Brandy Categories and ANOVA

				ANOVA	
compound	Solera brandy (S)	Solera Reserva brandy (SR)	Solera Gran Reserva brandy (SGR)	*F*	*p*
ethyl butyrate	463 ± 185	973 ± 503	$1.49 \times 10^4 \pm 1.21 \times 10^4$	2.94	0.0583
ethyl 2-methyl-butyrate	103 ± 83.7 b,c[a]	216 ± 142 b	241 ± 128 c	6.39	0.00262[b]
ethyl isopentanoate	142 ± 121 b	354 ± 200	443 ± 238 b	6.73	0.000101[b]
isopentyl acetate	130 ± 159	310 ± 215	533 ± 280	0.421	0.661
ethyl pentanoate	51.1 ± 17.1 b	61.2 ± 29.9 c	106 ± 90.9 b,c	6.81	0.00181[b]
α-terpinene	1.53 ± 0.08	1.55 ± 0.12	1.58 ± 0.27	0.523	0.598
isoamyl alcohol[c]	222 ± 60.6	253 ± 74.8	298 ± 83.0	0.698	0.504
2-methyl-1-butanol[c]	101 ± 18.0	115 ± 30.7	135 ± 30.9	0.691	0.502
ethyl hexanoate	463 ± 299	821 ± 436	963 ± 547	0.232	0.797
hexyl acetate	0.880 ± 0.880	2.66 ± 2.15	3.32 ± 1.91	1.38	0.256
ethyl heptanoate	<DL[d] b	57.4 ± 104	83.4 ± 144 b	4.85	0.0101[b]
1-hexanol[c]	5.49 ± 1.63	5.22 ± 1.99	5.74 ± 1.78	1.03	0.361
cis-3-hexen-1-ol[c]	0.860 ± 0.340	1.05 ± 0.66	1.29 ± 0.63	0.494	0.615
ethyl octanoate[c]	1.58 ± 1.10 b	2.65 ± 1.31	3.04 ± 1.60 b	3.29	0.0421[b]
benzaldehyde[c]	11.9 ± 10.7	11.8 ± 9.83	13.3 ± 9.63	0.153	0.863
linalool	53.4 ± 26.1 b	164 ± 122 c	303 ± 295 b,c	9.12	0.000312[b]
(*E*)-methyl 2-octenoate	0.720 ± 0.360	0.780 ± 0.730	1.17 ± 0.840	0.803	0.451
ethyl nonanoate	<DL[d]	<DL	<DL		
methyl decanoate	1.81 ± 2.04 b,c	4.43 ± 2.96 c	4.72 ± 3.35 b	5.41	0.00613[b]
ethyl decanoate[c]	1.75 ± 1.42	3.28 ± 1.71	3.61 ± 2.01	0.172	0.840
diethyl succinate[c]	1.89 ± 2.13	3.82 ± 5.28	5.40 ± 6.01	0.204	0.818
isoamyl octanoate	1.80 ± 3.75	13.3 ± 12.5	7.53 ± 8.53	0.402	0.671
α-terpineol	16.5 ± 13.1	53.7 ± 63.5	58.7 ± 35.2	1.45	0.241
phenylethyl acetate	14.3 ± 8.33 b	36.3 ± 23.0 c	58.4 ± 23.7 b,c	8.14	0.000621[b]
β-damascenone	2.60 ± 1.67	3.14 ± 2.02	2.99 ± 2.20	0.834	0.439
ethyl laureate	231 ± 204	407 ± 297	541 ± 387	1.15	0.321
2-phenylethanol[c]	5.18 ± 3.45	9.73 ± 4.55	12.9 ± 6.22	0.181	0.836
4-ethylguaiacol	82.2 ± 50.0	113 ± 59.2	121 ± 65.5	0.453	0.639
nerolidol	3.47 ± 6.68	4.14 ± 10.6	1.99 ± 7.36	1.14	0.324
octanoic acid[c]	9.12 ± 4.07	12.0 ± 5.5	13.4 ± 7.01	0.494	0.617
eugenol	6.79 ± 5.20 b,c	31.7 ± 29.2 c	26.1 ± 14.8 b	7.50	0.00103[b]
decanoic acid[c]	6.83 ± 2.93	9.20 ± 3.54	9.89 ± 4.73	0.401	0.675
lauric acid [c]	2.04 ± 1.05	2.89 ± 1.60	3.82 ± 2.79	0.222	0.802

[a] Mean values in the same row with the same letter indicate that they are significantly different at $p < 0.05$. [b] Values are significant at $p < 0.05$. [c] Values are in units of mg/L. [d] <DL = below the detection limit.

category. The results obtained from ANOVA according to the commercial category and, consequently, the duration of the aging in wood are also shown (Table 1). A study of the comparison of means was carried out using Tukey's test.

High standard deviations were found for some of the volatile compounds studied (Table 1). The employed method presented limits of detection and quantitation low enough to determine the volatile compounds in brandy samples, good recoveries with values ranging from 85 to 115% for all of the compounds studied, inter- and intra-assay precision lower than 10% in most cases, and very low standard deviations between duplicate samples.[18,19] Therefore, these high standard deviation values should not be produced by the analytical methodology employed. The data for each volatile compound were calculated as the mean values for every brandy with the same category. These brandies belonged to different wineries with different guidelines in relation to the cask wining operations. Therefore, the high standard deviations found could be explained on the basis of a close relationship between the content of this type of compound and the raw material together with the specific conditions of the production process: distillation process, aging conditions, including the exact duration of its aging in wood, etc. The major volatile compounds quantified were isoamyl alcohol, 2-methyl-1-butanol, benzaldehyde, diethyl succinate, 2-phenylethanol, octanoic acid, decanoic acid, lauric acid, ethyl decanoate, and ethyl octanoate. Panosyan et al.[20] found, in general, a higher content of these compounds in brandies from different origins (Armenia, Moldavia, France, etc.). However, Caldeira et al.[21] obtained similar contents to us for most of these volatile compounds in Portuguese brandies.

Fisher's weight and *p* values were calculated to establish the discriminate capacity of each volatile compound. From a univariate point of view, these volatile compounds were ethyl 2-methyl-butyrate, ethyl isopentanoate, ethyl pentanoate, ethyl heptanoate, ethyl octanoate, linalool, methyl decanoate,

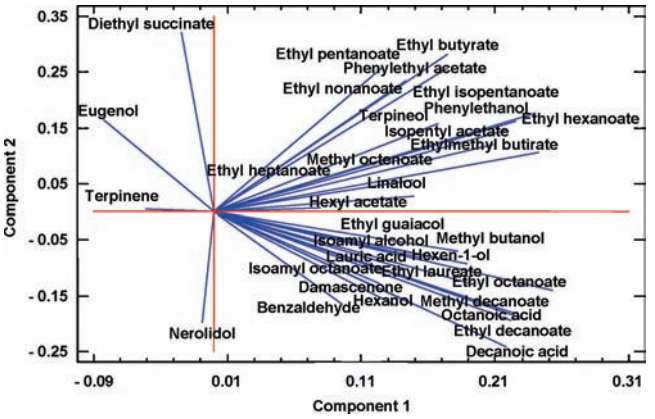

Figure 1. PCA performed on volatile compounds. Variable plot onto the plane defined by the two first PCs.

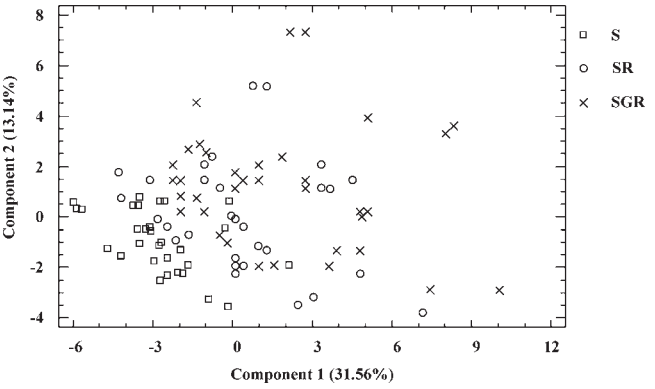

Figure 2. PCA performed on volatile compounds. Scatterplot of the samples onto the plane defined by the first two principal components. S, Solera Sherry brandy; SR, Solera Reserva Sherry brandy; and SGR, Solera Gran Reserva Sherry brandy.

2-phenylethyl acetate, and eugenol. The results obtained from the study of the comparison of means using Tukey's test (Table 1) showed that the content of these volatile compounds for the category "S" brandy differed significantly from that found for the category "SGR" brandy. In general, "S" brandies exhibited a lower content of these compounds than "SGR" brandies.

Rodríguez et al.[9] observed, in cider brandy, that the concentration of fatty acids decreased during the aging process, whereas their ethyl esters increased. These authors found that the concentration of alcohols, such as 1-hexanol and 1-octanol, decreased during the first steps of the aging process. Moreover, Panosyan et al.[20] found the same behavior for fatty acid esters and alcohols in brandies aged for 3, 10, and 20 years. This fact is also in concordance with Watts et al.,[22] who observed a clear relationship between the content of esters in brandy samples and their aging in wood. Panosyan et al.[20] explained these changes on the basis of non-enzymatic oxidation of alcohols and aldehydes to acids and the subsequent esterification of these last ones.

In our case, only the aforementioned ethyl esters showed significant increases of their concentration, according to the ANOVA test (Table 1). The contents of octanoic acid, decanoic acid, and 1-hexanol were similar for the three Sherry brandy categories. The stabilization of the content of these compounds could be explained according to possible kinetic differences between the oxidation and esterification reactions in which these compounds are involved.

Eugenol is a characteristic volatile compound of aged-in-wood oenological products;[4] therefore, it is logical that its content in aged products increases as the period of aging increases. In relation to linalool, the content found in Sherry brandies was also similar to those found in Portuguese brandies.[21] In our case, this monoterpenic alcohol appears in a higher amount in "SGR" brandies, despite the decreases that could be expected taking into account the different types of reactions (cyclation, hydratation, dehydration, isomerization, and oxidation) that are common for these compounds during the aging process.[23]

Although ANOVA shows statistical differences among data according to one factor, the use of multivariate analysis methods are necessary to deepen the differentiation among the Sherry brandy categories.

PCA. PCA is recommended as an exploratory tool to uncover unknown trends in the data. To examine the overall effect of the aging in wood on the content of volatile compounds, the global data matrix was subjected to PCA.

A total of 10 significant principal components (PCs) arose according to Kraiser's criterion (eigenvalues > 1). With these factors, 78.91% of the total variance is explained. The first PC, PC1, which explains 31.56% of the total variance, mainly contains ethyl esters, with a positive sign (Figure 1).

In the case of PC2, which explains 13.14% of the total variance, diethyl succinate and eugenol, both of them with a positive sign, and nerolidol, with a negative sign, are the main contributors (Figure 1).

Figure 2 shows the samples to the plane defined by these two PCs. As can be seen, "SGR" and "SR" brandy samples are intermingled. However, the "S" brandy samples, with shorter aging in wood, are clearly separated from the others, showing negative values for both PCs (lower concentration of ethyl esters and eugenol), although some overlapping can be noticed. The reason for this overlapping could be that the average times characterizing the different categories of Brandy de Jerez are minimum times (to acquire its own characteristics). This fact would also explain the high dispersion found for the samples.[24]

PLS-DA Regression. In the study of discrimination according to the commercial category (S, SR, and SGR) using PLS-DA regression, 10 factors were used. The global resulting coefficient of correlation (r) and the root-mean-square error of prediction (RMSEP) were 0.85 and 0.23, respectively. The global recognition values for the calibration and validation sets were 83 and 74%, respectively.

The calibration statistics indicated that the PLS-DA regression model developed could be acceptable to classify new brandy samples according to the commercial category using its volatile profile.

LDA. A forward stepwise LDA was carried out. This statistical analysis was performed according to the Wilks' λ statistic[25] to choose the descriptors that best distinguished the different classes. A F statistic is computed from the partial λ values, leading to a p level. The maximum discriminatory power corresponds to minimum p level values. The so-called "leave one out" method has been employed.[26] The three Sherry brandy commercial categories (S, SR, and SGR) have been considered.

With the samples grouped according to the commercial category, the variables included in the discriminant functions obtained were ethyl 2-methyl-butyrate, ethyl isopentanoate, ethyl pentanoate, hexyl acetate, ethyl octanoate, methyl decanoate, 2-phenylethyl acetate, and eugenol.

The "S" brandy samples are clearly differentiated (96.6% were correctly classified) from those belong to "SR" and "SGR" brandy

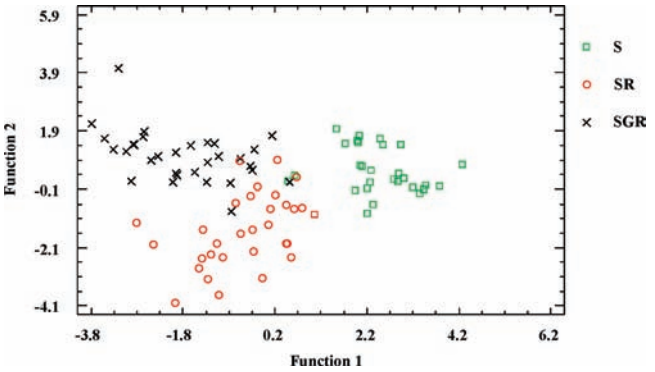

Figure 3. Forward stepwise LDA employing the commercial category as grouping criterion. Projection of samples on the discriminant space, selecting the two discriminant functions as axes. S, Solera Sherry brandy; SR, Solera Reserva Sherry brandy; and SGR, Solera Gran Reserva Sherry brandy.

samples (Figure 3). These two last samples, with some exceptions, are also separated by these two functions, with 90.0 and 93.6%, respectively, as a percentage of the correct classification in the check process. In summary, 93% of the total samples were correctly classified in the check process by the "leave one out" method.[26]

As the length of aging became higher, the concentration of the aforementioned ethyl esters increased, according to the results obtained by Rodríguez et al.[14] and Guillén et al.[16] in cider and Sherry wines, respectively. Also, the concentration of some acetates (2-phenylethyl acetate and hexyl acetate) and eugenol were higher, in agreement with Pérez-Coello et al.,[27] Díaz-Maroto et al.,[8] and Garde-Cerdán et al.[28]

In summary, the application of the SBSE to Sherry brandy samples together with multivariate statistical techniques showed that the Sherry brandy commercial categories (S, SR, and SGR) can be differentiated using their volatile profile.

Ethyl esters were the main family of volatile compounds responsible for the differentiation among the three different categories of Sherry brandies. For this type of oenological sample, the concentration of ethyl esters increased during the aging process, appearing in higher amounts in those Sherry brandies submitted to a longer aging in wood.

The results obtained show that it would be possible to guarantee the commercial category of a Sherry brandy using its content of volatile compounds. This fact means an important step forward in the field of oenology, because of the absence of scientific research about the differentiation among different categories of brandies using their aromatic profile.

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