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Influence of the use of sulfur dioxide, the distillation method, the oak wood type and the aging time on the production of brandies

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ABSTRACT

Brandies are spirits produced from wine spirit and wine distillates. The original wines selected to be distilled to produce the wine spirits as well as the distillation method used determine, to a large extent, the organoleptic characteristics of the final products. The young wine spirits evolve during their aging in oak casks, this being another key stage that affects the chemical and sensorial characteristics of the final brandy. In this work, seven different brandies have been studied. They were obtained from wine produced with and without the addition of sulfur dioxide, during their fermentation, using different distillation methods (single, double or serial distillation using pot stills and continuous column distillation) and aged for 14 or 28 months in three different types of oak wood (*Quercus alba, Quercus robur* and *Quercus petraea*) previously toasted to two different grades (medium or light).

The use of unsupervised pattern recognition methods (HCA and FA) determined that the addition of sulfur dioxide during the fermentation of the base wine has a major influence on the aromatic and phenolic profile of the aged distillates. On the other hand, by means of supervised pattern recognition methods such as LDA and ANNs, the most significant variables that would allow to discriminate between the classes of brandies identified in the study were evaluated. Thus, the results obtained should cast some light on the most significant variables to be taken into account regarding Brandy production processes if a better control over these production processes is to be achieved, so that more exclusive and better quality products are obtained.

1. Introduction

Brandy is a wine spirit drink produced from wine spirit and wine distillates. According to EU Regulation 2019/787 (European Parliament & Council of the Europeo, 2019) brandy is produced from wine spirit to which wine distillate may be added, provided that that wine distillate has been distilled at less than 94.8% ABV and does not exceed a maximum of 50% of the alcoholic content of the finished product. The wine spirit is aged either for at least one year when oak casks whose capacity is equal to or greater than 1000 L are used or for just six months when oak casks less than 1000 L. are used. Its total volatile content must be equal to or greater than 125 g/hL alcohol at 100% ABV (Alcohol by Volume) and such volatile content must come exclusively from the distillation of the raw materials used. Its maximum methanol content is 200 g/hL alcohol at 100% ABV. The minimum alcohol content of this beverage is 36% ABV. The addition of alcohol is not permitted, but the use of caramel is allowed in order to adjust the color and to round off its final flavor (sweetening must not exceed 35 g invert sugar/L).

Four different sources of aromas are distinguished in brandy: primary aromas, which are inherent to the grape variety and mainly develop during the maturation of the fruit; secondary aromas, which are generated during the fermentation of the grape juice (must); tertiary

Abbreviations: ABV, Alcohol by Volume; ANN, Artificial Neural Networks; CF, Classification Function; DF, Discriminant Function; FA, Factor Analysis; HCA, Hierarchical Cluster Analysis; LDA, Linear Discriminant Analysis; LDR, Linear Dynamic Ranger; LOD, Limit Of Detection; OIV, International Organisation of Vine and Wine; TPI, Total Polyphenol Index; WS, Wine Spirit; VF, Varifactor.

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aromas, which are an effect of the distillation process of the varietal wine; and quaternary aromas, which are produced during the aging of the distillate (Spaho et al., 2013).

Some factors, such as the grape variety (Cacho et al., 2013; Xiang et al., 2020), the fermenting conditions or the oenological practices that are implemented to produce the wine to be later on distilled (Tsakiris et al., 2014; Xiang et al., 2020; Zierer et al., 2016) have an influence on the character and quality of the wine spirit to be produced. Similarly, certain traditional oenological practices, such as the use of sulfur dioxide (OIV, 2021a), also determine the organoleptic profile of the wines (Korenika et al., 2020) and, as a result, that of the wine spirits produced from them (Nedjma and Maujean, 1995; Tsakiris et al., 2014).

Aldehydes, higher alcohols and major esters are among the compounds that compose the aromatic fraction of brandies. These major volatile compounds in brandies are influenced by the grape variety (Lukić et al., 2011) and they are the result of the must fermentation (Berry and Slaughter, 2003; Swiegers et al., 2005; Valero et al., 2002). Their greater or lesser content levels in the distillate is governed by the distillation method used (Silva and Malcata, 1999). This is why the selection of the base grape variety and the oenological practices that are implemented during the wine making process, together with the distillation method employed, are decisive with regard to the brandy to be obtained, (García-Llobodanin et al., 2007; Hernandez-Gomez et al., 2003), since the presence and concentration levels of these compounds in the aged product will depend on them (Spaho et al., 2013).

The distillation method used to obtain the wine spirit is also a determining factor with respect to its organoleptic characteristics (Balcerek et al., 2017; Spaho et al., 2013; Tsakiris et al., 2014).

Two of the most commonly used distillation techniques for the production of wine spirits are continuous column distillation (Spaho, 2017; Tsakiris et al., 2014; Xiang et al., 2020) and pot still distillation, which can be carried out in one or two steps (Balcerek et al., 2017). This is one of the most critical stages in the production of brandies, since pot still distillation not only delivers fruity aromas (primary aromas) but also the "memories" of the raw material in the distilled product is more accentuated. On the other hand, the distillates that are obtained by column distillation are usually richer in higher alcohols, since these are separated, to a greater extent, from the rest of the compounds due to the own nature of this distillation process (Spaho, 2017).

The character of brandies will also be shaped by another fundamental stage in its production process: aging, during which the wine spirit is stored inside of a wood cask for a period of time for the purpose of allowing that spirit drink to undergo natural reactions that impart specific characteristics to that spirit drink. The content of phenolic compounds and furanic aldehydes in aged wine spirits is mainly derived from wood yields during this stage. Wood is composed by 90% of polysaccharides (cellulose and hemicellulose) and lignin, the remaining 10% consisting of phenolic compounds, fatty acids, alcohols and inorganic substances. (Mosedale and Puech, 1998). The thermal degradation of lignin during the manufacturing and heat treatment of the casks results in the transferring into the wine spirit certain compounds such as vanillin, coniferaldehyde, syringaldehyde, sinapaldehyde, benzoic or cinnamic acids. (Canas, 2017; Conner et al., 1992; Mosedale and Puech, 1998). Furfurals and derivatives result from the degradation of hemicellulose. (Le Floch et al., 2015; Sarni et al., 1990). However, furfural can also be found in young unaged brandies as a consequence of the distillation process (Briones et al., 2012; Spaho, 2017). This will determine its presence in aged brandies in variable quantities.

The casks used for the aging of the wine spirit are a crucial element, as both the wood type (De Rosso et al., 2009; Jordao et al., 2005; Martínez-Gil et al., 2018; Prida and Puech, 2006) and the thermal treatment that it is subjected to during its manufacturing (Canas, 2017; Martínez-Gil et al., 2018; Soares et al., 2012) have a heavy influence on the compounds that will be found in them and that are susceptible to be transferred into the wine spirit during its aging process.

Quercus alba (American oak) is the most commonly used oak species in the Sherry area for the manufacturing of casks. However, we may also find other oak species, such as French oak (*Quercus petraea*) or Spanish oak (*Quercus robur*), being used for the aging of these wine spirits. Casks are usually medium toasted, although some casks may also be lightly or heavily toasted, which results in a different combination of compounds being released into the aged product.

The complexity of aged brandies increases during the aging period with respect to that of young brandies. The freshness and fruitiness of the raw material is replaced by aromas of vanilla, smoked, toasted and dried fruits, which are positively correlated with the quality of the brandies (Rodríguez Dodero et al., 2010; Tsakiris et al., 2014).

In order to evaluate the influence of the aforementioned factors on the brandies from the Sherry area, this study proposes the use of certain chemometric tools as follows: unsupervised Hierarchical Cluster Analysis (HCA) and Factor Analysis (FA), as well as supervised Linear Discriminant Analysis (LDA), and Artificial Neural Networks (ANNs). These tools should provide insights regarding the effect that the following variables have on the physicochemical characteristics of the aged distillates: base wines produced with and without the addition of sulfur dioxide; distillation method and alcohol content of the distillates; botanical origin the wood and heat treatment applied to the aging casks and finally, the length of time that the wine spirits remain in their respective aging casks.

2. Material and methods

2.1. Samples

Seven wine spirits (Table 1), all of them supplied by Bodegas Fundador, S.L.U. and compliant with the technical specifications set forth in the regulations governing brandy (European Parliament & Council of the Europeo, 2019) were used for this study.

The 7 types of brandy that have been studied were aged in three different types of oak wood: *Quercus alba* L., *Quercus robur* L. and *Quercus petraea* (Matt.) Liebl., which, in turn, had undergone two different toasting treatments: light toasting and medium toasting, so that 6 different types of vessels were used for the study. All the vessels used in the study were brand new oak casks (Tonelería Huberto Domecq, Jerez de la Frontera, Spain), with a total capacity of 350 L and filled up to 335 L with wine spirit. The wood was toasted by the supplier's staff following to the traditional manual process: for medium toasting, once the barrel

Table 1
Description of the wine distillates used for the experiments.

Wine Spirit	Wine distillation time[b,c]	Distillation method	Strength (in % ABV) of	
			Wine Spirit	Aging
WS1	1 month	Double distillation in pot stills	70%	55%
WS2	1 month	Single distillation in pot still	65%	55%
WS3	1 month	Serial distillation using two pot stills	65%	55%
WS4[a]	6 months	Continuous column distillation	77%	55%
WS5[a]	6 months	Serial distillation using two pot stills	65%	55%
WS6[a]	6 months	Continuous column distillation	77%	65%
WS7[a]	6 months	Serial distillation using two pot stills	65%	65%

[a] Spirits produced from wines with the addition of SO_2 during their fermentation.
[b] Time after fermentation.
[c] In the case of sulfur-added wines, the distillation may be performed between 1 and 6 months after their fermentation without any noticeable consequence.

reaches an internal temperature of 180 °C and an external temperature of 60 °C, it is vertically kept in contact with a flame of 70 cm height located in its central axis for 15 min on each side. For light toasting, once the aforementioned temperatures are reached, the barrel is kept in contact with a flame of 25 cm height for no more than 10 min on each side. All the experiments were carried out, at least, in duplicate. The samples for analysis were taken after 14 and 28 months of aging and analyzed in triplicate. The young unaged wine spirits were also analyzed. All the experiments were conducted in the same cellar belonging to the facilities provided by the company Bodegas Fundador, S.L.U. The average humidity of the cellar during the experiments was 71.5 ± 7.7 g/m^3, and the average temperature was 19.2 ± 5.8 °C, being constant through the years.

The wines selected for the production of the wine spirits for the study had been produced using the same variety: Airén (Castilla La Mancha). All wines come from the same harvest year and were produced by several wineries following the same standard conditions of the suppliers in the area, all being suitable for distillation. The wine distillates were obtained through five different distillation methods and subsequently diluted with demineralized water until the appropriate strength for aging was reached (Table 1):

- WS1 was a wine spirit with 70% ABV obtained through a double distillation of a wine that had just finished fermentation and where no sulfur dioxide was used for the process (a 30% ABV distillate was obtained from the first distillation, which was then re-distilled to produce a wine spirit at 70% ABV). Demineralized water was added to reduce alcohol content down to 55% ABV.
- WS2 was a wine spirit with 65% ABV, obtained through a simple distillation of a wine that had just finished fermentation and to which no sulfur dioxide had been added during this process. The alcohol content was reduced to 55% ABV by dilution.
- WS3 was a wine spirit with 65% ABV, obtained through two pot stills in series by distilling a wine just after its fermentation and without any sulfur dioxide added. This method allows the vapors from the first pot still to come into contact with the wine from the second pot still. It was subsequently diluted to reduce its alcohol content down to 55% ABV.
- WS4 and WS6 were wine spirits with 77% ABV. They were obtained by the continuous column distillation of a specific wine which had been added sulfur dioxide during its production process. The alcohol content of WS4 and WS6 were adjust to 55% ABV and 65% ABV respectively, by dilution.
- WS5 and WS7 were wine spirits with 65% ABV. They had been obtained by distilling a selected wine which had been added sulfur dioxide during its production process through two stills in series. Demineralized water was added to bring the alcohol content of WS5 down to 55% ABV.

For the cases where no sulfur dioxide had been added to the wine, the distillation processes of the wines were carried out after the alcoholic fermentation. All the analyses were performed in triplicate.

2.2. Parameters of oenological control

A pH-Meter Basic 20 (Crison Instruments SA, Barcelona, Spain) was used to determine the pH of the samples. The alcoholic strength (%AVB) (OIV, 2021b), was determined by measuring the density of the wine spirits with a DMA-5000 density meter (Anton Par, Ashland, OR, USA). Th total acidity of the wines was determined by potentiometric titration at pH 7 (OIV, 2021c) and the results were expressed as g tartaric acid/L; the total acidity of wine spirits was determined by potentiometric titration at pH 7.5 (OIV, 2009) and the results were expressed as mg acetic acid/L, both following the official method stablished by the OIV. Total sulfur dioxide content of the wines purchased for the production of the different wine spirits were determined by following the official methods established by the OIV (OIV, 2021d). All the reagents used for routine oenological analyses were supplied by Sigma-Aldrich (Saint Louis, MO, USA).

2.3. Total polyphenol index

The Total Polyphenol Index (TPI) corresponding to the wine spirits' absorbance at 280 nm was measured using a PerkinElmer spectrophotometer, Lambda 25 model (PerkinElmer, Waltham, MS, USA), in quartz cuvettes of 10 mm light path. Depending on the sample, the wine spirits were directly measured or previously diluted in ultrapure water (EMD-Millipore, Beldord, MA, USA) when necessary. The results from the analyzed samples were expressed as mg/L gallic acid equivalent (GAE). Gallic acid was supplied by Sigma-Aldrich (Saint Louis, MO, USA). The linear dynamic ranger (LDR) of the calibration curves was 10–50 mg/L gallic acid.

2.4. Phenolic and furfural compounds

Eight phenolic compounds (gallic acid, syringic acid, vanillic acid, p-hydroxybenzaldehyde, coniferylaldehyde, sinapaldehyde, syringaldehyde and vanillin) and three furanic aldehydes (furfural, 5-metylfurfural and 5-hyhdroxymethylfurfural) were determined and quantified by UPLC using a Waters Acquity UPLC equipped with a PDA detector and a 100 × 2.1 mm (i.d.) with a 1.7 μm particle size Acquity UPLC C18 BEH column (Waters Corporation, Milford, MA, USA) according to the methodology developed by Schwarz et al. (2009). The standards for the calibration of the compounds and samples were filtered through 0.22 μm pore size nylon membranes. The compounds were identified by comparing samples against standards using their retention times and UV–Vis spectra. The LDR of the calibration curves was 0.1–100 mg/L (Valcárcel-Muñoz et al., 2022). All the results were expressed as mg analyte/L distillate. For the preparation of the UPLC phases, HPLC-grade acetonitrile (Panreac, Barcelona, Spain), acetic acid (Merck, Darmstadt, Germany) and ultrapure water (EMD Millipore, Bedford, MA, USA) were used. The standards used for the calibration were supplied by Sigma-Aldrich (Saint Louis, MO, USA).

2.5. GC-FID analysis

An Agilent 7890 B Gas Chromatograph (Agilent Technologies, Santa Clara, CA, USA) coupled to a flame ionization detector was used for the analysis of the volatile compounds. To determine the acetaldehyde, acetaldehyde-diethylacetal, methanol, ethyl acetate, n-propanol, iso-butanol, n-butanol, 2-methyl-1-butanol and 3-methyl-1-butanol, a 30 m × 250 μm x 1.4 μm DB-624 column (Agilent Technologies, Santa Clara, CA, USA) was used. 2-pentanol was used as the internal standard. For the determination of n-hexanol, 2-phenylethanol, ethyl lactate, diethyl succinate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl dodecanoate, ethyl tetradecanoate and ethyl hexadecanoate a 25 m × 250 μm x 0.2 μm CP-WAX 57 CB column (Agilent Technologies, Santa Clara, CA, USA) was employed. In this case, ethyl undecanoate was used as the internal standard. The methodology followed for the analysis of the wine spirits by GC-FID has been described in previous works. (Valcárcel-Muñoz et al., 2021a, 2022). The calibration standards and aged wine spirits were injected directly (0.5 μL sample volume was used for the analysis of the major esters and 1.0 μL for the analysis of the higher alcohols). The standards used for the calibration of volatile compounds were supplied by Sigma-Aldrich (Saint Louis, MO, USA).

2.6. Statistical analysis

The data from the chemometric study, the Hierarchical Cluster Analysis (HCA), the Factorial Analysis (FA), Artificial Neural Networks (ANNs) and Linear Discriminant Analysis (LDA) were treated by means of the software application Statgraphics 19™ (Statgraphics

Technologies, Inc., The Plains, VA, USA). For other statistical studies Microsoft Excel 2016™ (Microsoft Corp., Redmond, WA, USA) utilities were employed.

3. Results and discussion

3.1. Analytical characterization of the wines to be distilled

The general oenological parameters of the wines selected to be distilled and to produce the spits in this study are shown in Table 2. All the wines used for this study were obtained from clean musts produced from healthy grapes, which were fermented to produce wines suitable for direct consumption. The measured parameters were within the normal range for this type of wine.

The alcoholic strength values (10.50–11.50% ABV) were within the ranges previously described for wines of the Airén variety (Bueno et al., 2006; Jurado-Córdoba, 2016; Pérez-Navarro et al., 2020), with low total acidity, so that acidification was required in order to reach content levels that guarantee their stability until the distillation time. It should be noted that no sulfur dioxide was added during the production of wines for WS1, WS2 and WS3. While those intended for the production of WS4, WS5, WS6 and WS7 had a sulfur dioxide content of 36–73 mg/L. These latter wines turned out to be richer in total aldehydes and higher alcohols than the former. The total aldehyde content was in line with the previously described results (Flanzy, 2003), which some authors believe to be related to the resistance of the yeasts against SO_2 (Liu and Pilone, 2000). The concentration of higher alcohols is almost double in wines made with SO_2 compared to those without the addition of this antioxidant and bacteriostatic agent, used in winemaking to prevent oxidation, obtain microbiological stability and select fermentative yeasts. Higher alcohols appear during the alcoholic fermentation process, basically by deamination of amino acids by yeast to obtain ammoniacal nitrogen for consumption. Regarding the results obtained, it should be noted that in the selection of fermentative yeasts the sulfur dioxide favored the presence of species more prone to the formation of these congeners (Sun et al., 2016), as well as the higher initial concentration of sugars in the musts with SO_2 would cause a greater need for ammoniacal nitrogen in the yeasts to be able to finish the fermentations (Younis and Stewart, 1998). As for the major esters that were determined, their high content in the wine used for the production of WS5 and WS7 stands out when compared against the rest of the wine spirits — all of them with a similar lower content.

Table 2
Characteristics of the wines selected for the production of the spirits.

	Wine to produce			
	WS1	WS2 and WS3	WS4 and WS6	WS5 and WS7
Alcoholic strength (% ABV)	10.50 ± 0.06	10.60 ± 0.08	11.56 ± 0.07	11.50 ± 0.05
Total acidity (g/L Tart. Ac.)	6.41 ± 0.07	5.33 ± 0.11	5.76 ± 0.12	5.19 ± 0.09
Volatile acidity (g/L Acet. Ac.)	0.31 ± 0.03	0.51 ± 0.05	0.33 ± 0.04	0.28 ± 0.03
Total sulfur dioxide (mg/L)	<10	<10	73	36
Total aldehydes[a] (mg/L)	19.3 ± 2.4	23.3 ± 3.5	56.8 ± 2.1	33.9 ± 2.7
Higher Alcohols[b] (mg/L)	160.4 ± 7.2	175.3 ± 8.3	374.6 ± 8.7	349.5 ± 9.5
Major esters[c] (mg/L)	63.9 ± 6.5	84.8 ± 8.2	74 ± 5.5	117.5 ± 3.9

[a] Total aldehydes are defined as the sum of acetaldehyde, acetaldehyde-diethylacetal and acetoin.

[b] Higher alcohols are defined as the sum of n-propanol, isobutanol, n-butanol, isoamyl alcohols, 1-hexanol and 2-phenylethanol.

[c] The major esters are defined as the sum of ethyl acetate, ethyl lactate, diethyl succinate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl dodecanoate, ethyl tetradecanoate and ethyl hexadecanoate.

3.2. Analytical characterization of the wine spirits

3.2.1. General parameters

3.2.1.1. pH and total acidity. The pH range of the brandies that have been studied was between 4.91 (WS2) and 3.98 (WS4), which are typical pH values for young brandies (Tsakiris et al., 2014) (Table SM1, SM: Supplementary Material). When considering just the starting 55% ABV alcohol degree for aging, we can observe the influence attributable to the distillation method on the pH of the wine spirits used to make the brandies, where continuous column distillation was the method that generated brandies with a higher acidity, while single pot still distillation resulted in slightly less acidic brandies. The initial pH of the wine spirits intended for aging determines, to some extent, the aggressiveness of the distillate with regard to the extraction of compounds from the casks' wood (Tsakiris et al., 2014). pH shows a general declining trend with respect to aging time, although in certain cases it remains practically unchanged.

The total acidity of the different young wine spirits used for this study varies greatly (Table SM1), ranging between 60 and 168 mg/L acetic acid. This depends on the volatile acidity of the wines being distilled (Table 2) and on the greater or lesser separation of these compounds as a result of the different distillation methods applied when using either modern industrial equipment (columns) or more traditional ones (pot stills). The aged wine spirits in the WS2 and WS5 experiences were those that presented a higher total acidity level regardless of the type of oak and toasting degree of their aging casks. Total acidity was already determined by the young wine spirit of origin.

It is noteworthy that the total acidity of those wine spirits that had been aged at 55% ABV (WS4 and WS5) is higher than that of their respective wine spirits when aged at 65% ABV (WS6 and WS7). This may be due to the higher solubility of the acids, which is greater in water than it is in alcohol (Carrascal García, 2004; Sánchez-Guillén et al., 2019) and that given the lower alcohol concentration in the medium, the esterification reactions between acids and ethanol are less favored (Valcárcel-Muñoz et al., 2022), which in turn affects pH values. According to several authors (Canas, 2017; Guerrero-Chanivet et al., 2020), total acidity is one of the parameters that evolves the most during aging, clearly increasing as time passes. This is explained by the fact that the casks' wood yields a variety of acids (carboxylic, fatty and phenolic), and also because, during aging, a variety of chemical reactions that generate acids take place, mainly acetic acid (Valcárcel-Muñoz et al., 2021a), that are also transferred into the brandy thereby increasing its acidity (Guerrero-Chanivet et al., 2020).

In the case of wine spirits produced from wines that had been treated with sulfur dioxide during their fermentation process, the increasing acidity may also be due to hydrolytic reactions that allow the release of part of the sulfur dioxide combined with acetaldehyde. As this oxidizes sulfuric acid is produced.

According to the type of wood used for the casks, it has been observed that, in general, those wine spirits aged in *Quercus alba* (pH range: 4.49–3.96; total acidity range: 396–696 mg acetic acid/L), under the same conditions, show slightly higher pH values and slightly lower total acidity when compared to those aged in *Quercus robur* (pH range: 4.29–3.70; total acidity range: 399–756 mg acetic acid/L) or *Quercus petraea* casks (pH range: 4.21–3.74; total acidity range: 408–912 mg acetic acid/L), with very similar pH values in the latter two cases.

This more pronounced fall of pH values and rising of the total acidity in those brandies that were aged in *Quercus robur* or *Quercus petraea* may be explained by a greater extraction of the acids from the wood (Canas, 2017; Guerrero-Chanivet et al., 2020; Martínez-Gil et al., 2018). *Quercus robur* and *Quercus petraea* woods have a larger pore size than *Quercus* *alba*, which allows an easier penetration of the wine spirit into the wood. This means that there is a greater wood contact surface, which results in a greater extraction of compounds from it (Guerrero-Chanivet et al., 2020).

Based on the type of toasting used for the manufacturing of the barrel, it can be observed that as the wood toasting process is intensified, there is an increment of the total acidity and therefore a decrease in the pH values. This fact may be explained by the fact that the longer the wood is toasted, the greater its degradation, which in turn favors the release of a series of compounds that contribute to the acidity of the wine spirit. Furthermore, as the aging time of the wine spirit is increased, the total acidity rises and therefore a drop of the pH values, regardless of the type of wood or toasting used, takes place.

3.2.1.2. Density and alcoholic strength. The density of the wine spirits was measured in order to establish the alcoholic strength of the same. In all the cases studied (Table SM1), an increment in the alcoholic content was observed as a consequence of the concentration due to the phenomenon known as *merma*. Thus, given that the barrel is not airtight, some alcohol evaporation takes place during the aging stage, which is in turn offset by certain loss of water through the wood pores (Guymon and Crowell, 1970; Singleton, 1995). The water molecules permeate through the pores of the wood and, therefore, the alcohol concentration in the aged wine spirit increases. Table 3 shows the loss of volume experienced during the aging of the wine spirits studied.

The *merma* during the first 14 months is more noticeable than that corresponding to the remaining 14 months (Valcárcel-Muñoz et al., 2021a), specifically 4.48% higher. This represents about 15 L less that the initial volume of brandy poured into the casks. Given that the casks used for this study had been made with new wood, the significant reduction in the liquid volume during the first period would be explained by a considerable soaking of the liquid into the wood. The average incremental percentage of alcoholic strength after the wine spirits had been aged for 28 months in *Quercus alba* casks was 1.3%; in *Quercus petraea* 1.2% and in *Quercus robur* 1.6%. The brandies from the WS6 experiment were those that experienced the greatest increment of their alcohol concentration, going from 2.2% up to 2.4%. No relevant differences in the brandies' alcoholic strength were observed attending to the wood toast grades. The fact that *Quercus robur* is a highly porous wood explains why the increment in alcoholic strength is more pronounced in the brandies that were aged in these casks.

Given that the longer the aging time, the higher the concentration due to *merma* (Valcárcel-Muñoz et al., 2021a), the alcohol content in the brandies aged for 28 months was greater than the alcohol content in the 14-month old ones.

3.2.1.3. Total polyphenol index. Phenolic and furfural compounds are the main substances transferred from the wood into the wine spirit, being these a clear marker of the aging time, and are usually quantified as TPI. However, in young wine spirits, the content of these compounds is mainly explained by the presence of furfural and some of its derivatives, that are originated during the distillation of the wines. The values registered for this parameter are shown in Table SM1. It can be seen that those distillates obtained through column distillation have a considerably lower TPI than those obtained through traditional distillation in pot stills.

On the other hand, and in general terms, the evolution of this parameter increased with aging time in all the cases studied and is greater when using woods that favor the extraction of these compounds because of their greater porosity, according to the following ranking: $TPI_{Quercus\ alba} \ll TPI_{Quercus\ robur} < < TPI_{Quercus\ petraea}$.

With respect to the wood toasting grade, greater TPIs contents are found in the brandies aged in medium toasted oak than in those aged in lightly toasted oak. The brandies aged at 65% ABV have a slightly lower TPI than those aged at 55% ABV (Valcárcel-Muñoz et al., 2022), which has traditionally been the optimum aging strength for the wine spirits produced under the P.D.O. Cognac or Armagnac (Puech, 1984).

Table 3
Loss of volume experience by the brandy in the casks during the experience.

Wine spirit	14 months (%)	28 months (%)	Average volume loss per year (%)
WS1	6.71	2.54	3.96
WS2	6.83	2.97	4.20
WS3	7.36	2.27	4.12
WS4	7.43	2.73	4.35
WS5	7.53	2.64	4.35
WS6	6.61	2.41	3.87
WS7	7.10	2.62	4.17
Average volume loss per year	7.08	2.60	4.15

The values given are the average loss in all the wood types studied and for each one of the wine spirits.

3.2.2. Aldehydes, methanol and higher alcohols

From the results presented in Table SM2, it can be observed that the content of volatile compounds such as aldehydes, methanol or higher alcohols in the aged brandies is marked not only by the content of these compounds in the young wine spirits but also by the distillation method used. Thus, the wine spirits produced by column distillation (WS4 and WS6) are richer in aldehydes and higher alcohols than the rest of the them. The continuous distillation process in columns facilitates the permanence of certain desired volatile compounds and that typify its oenological quality (aldehydes and higher alcohols) in the final brandy, due to the large number of distillation plates. On the contrary, in discontinuous "pot still" systems, with less separation capacity, there is the possibility of a significant loss of aromatic compounds (fruity, floral, notes of varnish, etc.) during the elaboration of the wine spirit, when an important separation of heads and tails are required.

If we consider traditional pot still distillation with different modalities and the use or non-use of sulfur dioxide during the wine fermentation process as an oenological practice, for the same level of final ABV, we can observe that the wine spirits made from wine treated with sulfur dioxide during its fermentation have a slightly greater content of both aldehydes and higher alcohols than the rest, since some compounds as acetaldehyde and its diethyl-acetal are influenced by the sulfur dioxide presence (Cantagrel et al., 1998). This was the case of WS5, which had been produced from wine treated with sulfur dioxide during its fermentation process.

Acetaldehyde and its diethyl-acetal are two compounds whose balance is largely affected by the alcoholic strength of the wine spirits being aged. According to Valcárcel Muñoz et al. (Valcárcel-Muñoz et al., 2022) the lower the alcoholic strength of the wine spirits to be aged, the higher the percentage of acetaldehyde in relation to its diethylacetal content relative to the total aldehydes, when studying the aging of wine spirits with alcoholic strengths between 65% ABV and 80% ABV. This same trend can also be observed in the case of lower alcoholic strengths (Valcárcel-Muñoz et al., 2021b). The proportions of these two compounds observed in this study are the same as previously mentioned, and they both present an increasing trend during their aging as a consequence of the *merma* (loss of volume) resulting from the evaporation of liquid through the wood (see Table 4), which in turn represents an increment of the concentration of the compounds present in the wine spirits (higher alcohols, acetaldehyde and acetals formed).

3.2.3. Major esters

The behavior of the major esters is very similar to that of the higher alcohols (Table SM3). In this respect, and with regard to the young wine spirits and the use of sulfur dioxide, it is worth noting the increment that was registered by the esters derived from fatty acids (ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl dodecanoate, ethyl tetradecanoate and ethyl hexadecanoate) in those wine spirits that had not been

Table 4
Loads received from each of the analytes in the five vector factors (VF) extracted in the Factor Analysis.

	VF1	VF2	VF3	VF4	VF5
Acetaldehyde	0.884412	0.002045	−0.406101	−0.094539	0.032867
Methanol	0.946659	−0.078171	−0.095560	0.140369	−0.115009
n-propanol	0.990647	−0.076478	−0.014836	0.018290	−0.048419
Ethyl acetate	0.187919	0.449788	0.589150	0.244467	0.392341
Isobutanol	0.981435	−0.054193	0.144530	−0.040447	−0.021370
n-butanol	0.921357	−0.034487	0.222394	−0.224393	0.022729
Diethyl-acetal	0.942043	−0.063879	−0.214458	0.084937	−0.064487
3-Methyl-1-butanol	0.957425	−0.062124	0.251271	−0.067030	−0.021013
2-Methyl-1-butanol	0.950388	−0.072635	0.271528	−0.052870	−0.022770
Ethyl hexanoate	−0.664172	0.131473	−0.103215	0.678210	0.069316
Ethyl lactate	0.420937	−0.085875	0.876959	−0.100045	−0.125902
Hexanol	0.981836	−0.053770	0.118881	−0.071477	−0.022565
Ethyl octanoate	−0.581551	0.161285	−0.394270	0.641421	0.163238
Ethyl decanoate	−0.793978	0.118412	−0.365435	0.388762	0.074215
Diethyl succinate	0.932788	−0.028800	0.253085	−0.186332	−0.007912
Ethyl dodecanoate	−0.873211	0.077021	−0.238434	0.368747	0.010533
2-phenylethanol	0.041608	−0.012684	0.980309	−0.103519	−0.003146
Ethyl tetradecanoate	−0.834006	0.054492	−0.059263	0.504681	−0.008873
Ethyl hexadecanoate	−0.723756	0.092419	0.282685	0.575940	0.016137
Gallic acid	−0.051683	0.271051	−0.111564	0.122490	0.908783
HMF	−0.145154	0.893514	−0.079175	0.026218	0.265873
Furfural	−0.417377	0.811213	0.257720	−0.093356	0.099406
Vanillic acid	−0.179294	0.456020	0.197356	−0.152801	0.450421
p-hydroxybenzaldehyde	−0.057957	0.894185	−0.067487	0.026478	0.045435
5-methyfurfural	−0.112159	0.928808	0.027414	−0.040870	0.158525
Siringic acid	0.026472	0.963092	0.007320	0.117183	0.112943
Vanillin	0.000477	0.943203	−0.104250	0.115991	0.154911
Syringaldehyde	0.023670	0.966156	−0.049166	0.049128	0.045993
Coniferylaldehyde	−0.104055	0.947411	0.000586	0.004625	−0.141858
Sinapaldehyde	0.061969	0.951883	0.072136	0.095641	−0.018198

Note. Those loads with a value higher than 0.45 or lower than −0.45 have been highlighted in grey.

treated with sulfur dioxide during the wine fermentation process (WS1-WS3).

The evolution of the major esters during the aging time depends both on the profile of the young wine spirit, where changes in the concentration of some esters may occur as a consequence of esterifications of the corresponding acids in the alcoholic medium, and of the aging process itself. In general terms, an major esters content increments are during aging, mainly due to: i) the increasing concentration of the distillates due to alcohol evaporation, ii) the air permeability of the vessel, iii) the water transpiring through the wood pores (see Table 3), and iv) the transferring of some fatty acids from the wood (Guerrero-Chanivet et al., 2020) that can be esterified in the presence of alcohol.

Ethyl acetate stands out among the esters that have been analyzed, since this compound experiences a considerable concentration increment over the aging process. In fact, the initial ethyl acetate content in wine spirits is affected not only by the fact has already been commented above, but also by the type of wine used and the distillation method employed, given that wines with volatile acidity values higher than 0.8 g/L usually present high concentrations of ethyl acetate when transformed into wine spirits and, according to several researchers (Balcerek et al., 2017; Louw and Lambrechts, 2012; Xiang et al., 2020), the distillation method also determines a greater or lesser separation of the compounds. Additionally, it should be taken into account that ethyl acetate is involved in numerous esterification reactions between acetic acid (generated during aging) and ethanol, as established in the works of Reazin et al. (Reazin, 1981, 1983; Reazin et al., 1976). There are also recent studies (Guerrero-Chanivet et al., 2020) that have demonstrated that wood is susceptible of yielding acetic acid into the wine spirits that are aged in contact with it, thus explaining why aged wine spirits have a higher acetic acid content than younger wine spirits. This implies that, because of this esterification, a greater amount of ethyl acetate is generated over time, thereby making of this compound a clear marker of the age of the brandies.

3.2.4. Phenolic and furfural derivative compounds

The content of TPI of unaged wine spirits may be due to the presence of furanic aldehydes, such as furfural, 5-hydroxymethylfurfural and 5-methylfurfural, which are originated during the distillation of the wines by the dehydration of pentoses and hexoses involving Maillard reactions (Balcerek et al., 2017), favored in pot still distillation. It can also be due to the phenolic compounds present in the wine that are thermally stable (Volf et al., 2014) at the temperatures reached with the pot still distillation. These reasons explain that the TPI content is greater in those wine spirits that were had been obtained through traditional distillation in pot stills than in those obtained by column distillation (Table SM4).

The aging process in the casks plays an important role with regard to the profile of these compounds, since aging in wood tends to increase their concentration. Therefore, the longer the contact time with the wood, the greater the presence of these compounds in the brandy. The greatest differences have been observed between brandies aged for 14 months in relation to young wine spirits, this difference being less pronounced when the aging period spanned for 28 months.

It should be noted again how the porosity of the wood has an influence on the extraction of all these compounds, since the values observed for the phenolic compounds in this study are higher in the wine spirits aged in *Quercus robur* and *Quercus petraea* than in those aged in *Quercus alba* (Guerrero-Chanivet et al., 2020).

In terms of the wood toast grade, those brandies aged in medium toasted oak have a higher content of compounds that are extracted from the wood as a consequence of the greater degradation of the wood lignin during the toasting process (i.e. vanillin, syringaldehyde, sinapaldehyde and coniferaldehyde) than those aged in lightly toasted oak barrels reported by several authors (Canas, 2017; Mosedale and Puech, 1998; Sarni et al., 1990). This factor also affects the concentration of furfural and derivatives, with higher values again being observed in the brandies that had been aged in medium toast casks.

Attending to the % ABV, the wine spirits aged at 55% ABV (WS4 and WS6) presented slightly higher concentrations of the phenolic and furfural compounds when compared to the respective ones aged at 65% ABV (WS5 and WS7), which is in agreement with the findings reported by other authors (Puech, 1984; Valcárcel-Muñoz et al., 2022).

Finally, as with other families of compounds, slight variations in their concentrations as a consequence of the *merma* have been registered.

3.3. Chemometric study

In order to evaluate the influence that winemaking practices have on the quality of the final product, a chemometric study has been carried out on the families of compounds that can have an influence on secondary, tertiary and quaternary aromas. Thus, aldehydes, acetal, methanol, higher alcohols, major esters and phenolic and furanic compounds contents have been considered as analytes of interest to be evaluated: the effect of using wines produced with and without the addition of sulfur dioxide; the distillation method used and the alcohol content of the distillates; the botanical origin of the wood and the thermal treatment applied to the wood to produce the casks for aging as well as the aging time of the brandies produced for this study. For this purpose, different distillation procedures have been considered (continuous column distillation and single, double or serial distillation using pot stills). We have, therefore, started by distinguishing wines produced with and without the addition of sulfur dioxide, as well as a number of qualitative parameters related to the aging process, such as the type of oak wood used, its toasting grade and the aging time of the brandy in the casks.

In this study we worked with a single data matrix (232 samples × 30 variables) that contained the concentrations of the different analytes from each of the families that had been quantified (aldehydes, acetal, methanol, higher alcohols, major esters, phenolic and furanic compounds). In those cases, where the analytes were below the limit of detection (<LOD), mean gap-filling and self-scaling were applied as a preprocessing step prior to the application of pattern-recognition methods.

3.3.1. Non-supervised chemometric studio

3.3.1.1. Hierarchical Cluster Analysis. A HCA was applied to the previously defined matrix using the quadratic Euclidean distance and Ward's method as the metric distance and the nesting criterion respectively. In the same way, two linkage distances were considered as internal criteria to define the natural grouping of the clusters, $D_{linkage} = 2/3\ D_{max}$ and $1/2\ D_{max}$.

In Fig. 1, according to $D_{linkage} = 2/3\ D_{max}$, two distinctive clusters (Group I and II) could be observed depending mainly on the addition, or not, of sulfur dioxide during the fermentation of the wine used to obtain the wine spirit. If a less strict criterion was established, such as $D_{linkage} = 1/2\ D_{max}$, these clusters divided into four new groups. The first of them (highlighted as pale yellow), was composed by the wines spirits before their aging in casks; the second one (highlighted as pale pink) was formed by those wine spirits obtained from SO_2 treated wines and distilled using a column (WS4 and WS6); the third one (highlighted as pale orange) was constituted by wine spirits treated with SO_2 and distilled by column (WS4 and WS6) or pot still (WS5 and WS7), and finally the fourth group (highlighted as pale green) was composed by the remaining wine spirits from wine without a SO_2 treatment (WS1, WS2 and WS3).

It should therefore be noted that, regardless of the origin of the wood as well as its toasting degree or aging time, the use of sulfur dioxide during the fermentation of the wine used to obtain the wine spirits has a highly significant influence on the volatile and phenolic fractions of the final product.

3.3.1.2. Factor Analysis. In order to corroborate the results obtained from the HCA, a FA was conducted by applying a "varimax" rotation by means of PCA to the data matrix on the space generated. The minimum number of factors (called varifactors, VFs) was selected according to an Eigenvalue >1. As a result of this analysis, 5 VFs were extracted, which explained 92.67% of the total variance of the data.

Table 4 shows the loadings received from each of the analytes in their corresponding VFs. It can be observed that VF1 is mainly composed by alcohols, which are mainly associated to young wine spirits, while VF2 is mainly made up of phenolic and furfural compounds, mainly related to the aging of the wine spirits. The remaining three VFs were populated by ethyl acetate, ethyl lactate and 2-phenyl ethanol (VF 3), ethyl hexanoate, ethyl octanoate, ethyl tetradecanoate (VF 4) and gallic and vanillic acids (VF 5). Based on these last contributions, it can be concluded that the influence of the young wine spirit can be observed in VFs 1, 3 and 4, while the influence of the wood is reflected in VFs 2 and 5.

Fig. 2a shows the scores received by the brandies in the space VF1 *vs* VF2 *vs* VF3. Two different behaviors can be observed: i) according to the use of SO_2 during the fermentation of the base wine, such that those wine spirit coming from wines that have not been treated with SO_2 (WS1, WS2 and WS3) received negative scores for VF1 and VF3 and positive and negative scores for VF2. This clustering can be explained by the contribution of fatty acid-derived esters in VF1 and VF3. These wines

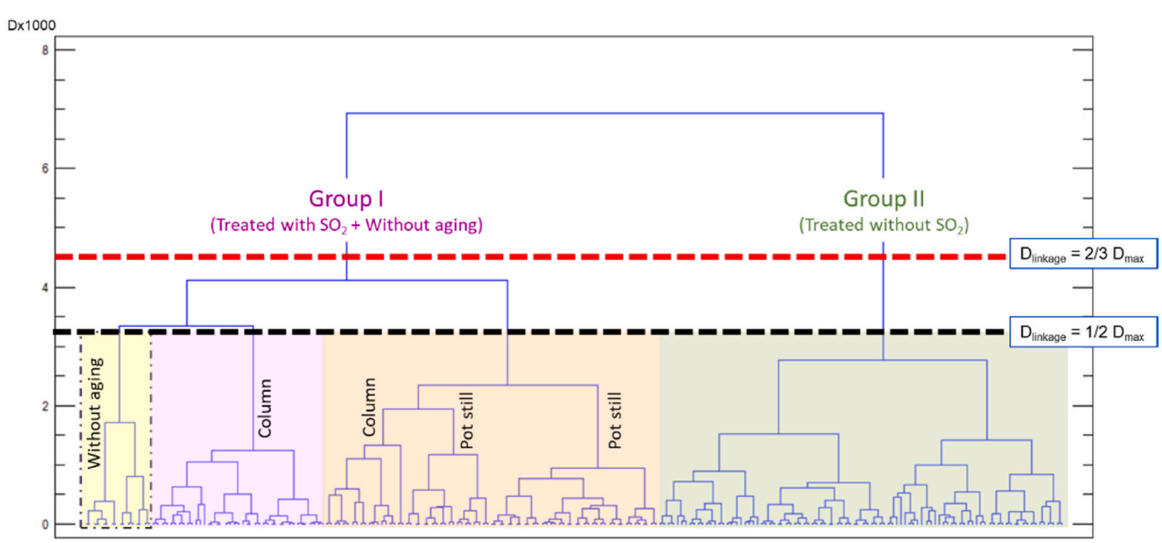

Fig. 1. Dendrogram obtained from the HCA.

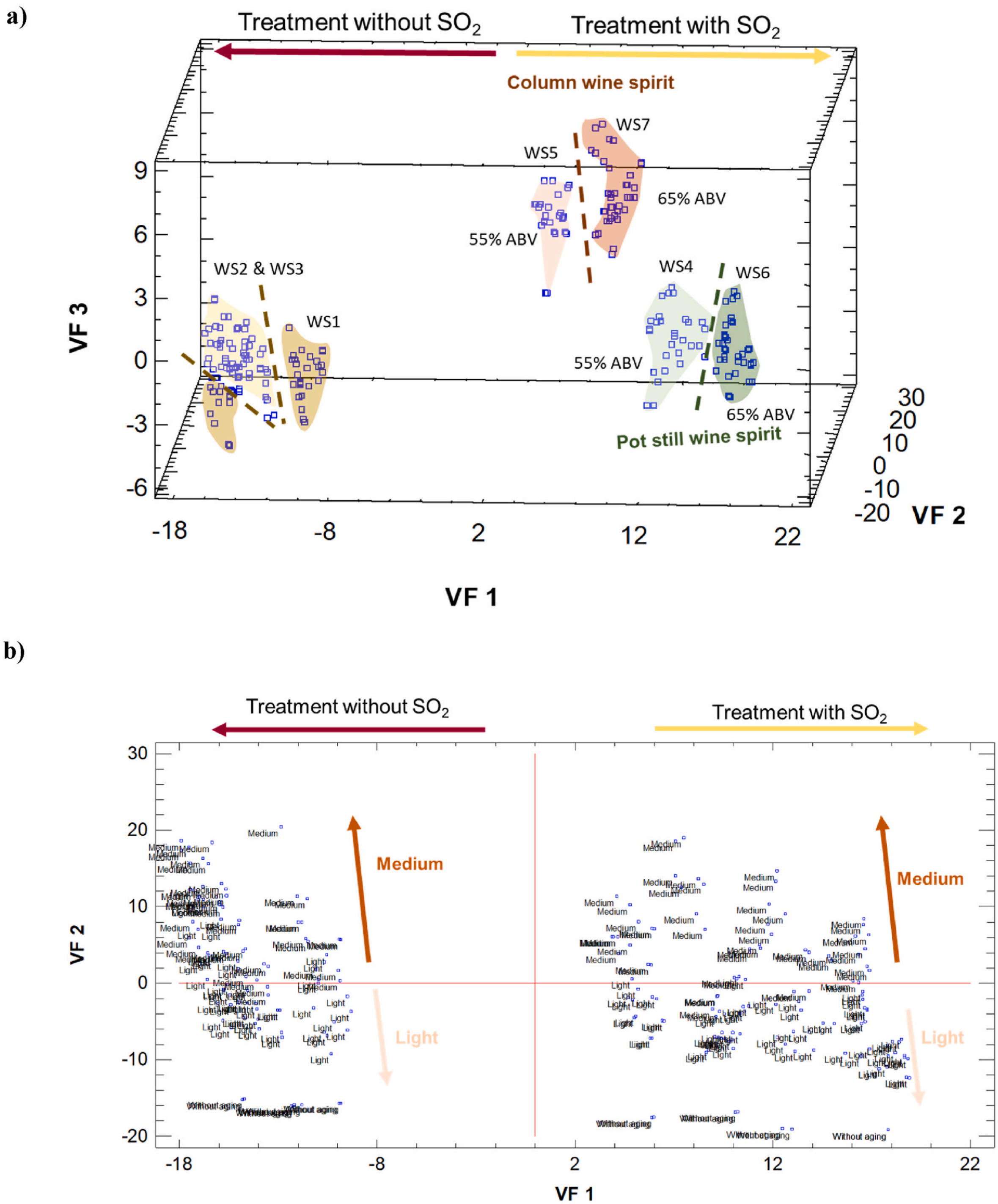

Fig. 2. Scores in (a) the three-dimensional space defined by the first three VFs; (b) the two-dimensional space defined by VF2 *vs.* VF1.

had been distilled just after their fermentation, which implies that their ester content was greater due to the presence of yeast remains in the wines. ii) Among the wine spirits produced from wines treated with SO_2 (WS4-WS7), some differences could also be observed regarding the scores received depending on the distillation method used (pot still or distillation column). The wine spirits coded WS5 and WS7, which had been produced through a more "artisanal" method, were richer in compounds such as 2-phenylethanol or ethyl acetate (as they have a stronger "memory" of the base wine), as well as being richer in furfural and its derivatives (because of the distillation method used). These wine spirits appear apart from WS4 and WS6 wine spirits, which had undergone column distillation, the latter being a well-defined industrial process intended to achieve the desired quality of wine spirits and, therefore, they may "lose or reduce" the presence of the aforementioned compounds, as well as be enriched with higher alcohols.

In turn, a new subgrouping of the distillation method can be observed that correlates with the final % ABV of the brandy obtained (55 or 65% ABV), with those aged at 65% ABV (WS6 and WS7) getting higher positive values in the VF1 area while those aged at 55% ABV (WS4 and WS5) presented lower values in the same positive area. Acetaldehyde and its diethyl-acetal are two of the compounds most influenced by the alcoholic strength of the aged wine spirits. As previously mentioned, the lower the alcoholic strength, the higher the percentage of acetaldehyde versus its diethyl-acetal with respect to total aldehydes (Valcárcel-Muñoz et al., 2021b, 2022).

When the scores in the two-dimensional space VF2 *vs.* VF1 are analyzed, we can observe a trend to group together according to the degree of toasting, even if these groups are not clearly defined, since the toasting of the casks is a manual process that allows some space for variations of the final toasting (Fig. 2b). The toasting process, in addition to the compounds resulting from lignin degradation, also involves furfural and its derivatives, which are among the major compounds found in the aged brandies that have been analyzed.

In order to evaluate the influence of the type of wood used for the manufacturing of each cask, we assessed the correlation between VF5 and VF1 and between VF5 and VF2. Fig. 3a shows the scores received in the two-dimensional space VF5 *vs.* VF1, in which we can again observe that the groupings that occurred were mainly attributable to the use of SO_2 during the fermentation of the young wines (with a clear differentiation between the young wine spirits and the aged brandies). Regardless of this, it could also be observed that, for each grouping of aged brandies, the samples that had been aged in *Quercus alba* were apart from the rest, which had been aged in other wood types. Only the wines that had not been treated with SO_2 and were later on aged in *Quercus robur* or *Quercus petraea* were slightly, even if not clearly, located apart, since these two types of wood present a high similarity. VF5 is associated to the oak variety. The botanical origin of the wood has a strong impact on its composition (De Rosso et al., 2009; Prida and Puech, 2006) and, although *Quercus robur* and *Quercus petraea* are from close geographical areas and present some similarities (Martínez-Gil et al., 2018), their composition, and in turn, the compounds and corresponding proportions that are susceptible to be transferred into the distillates differ. Vanillic and, particularly, gallic acid have a highly positive influence on this variable factor. It can be seen from Table SM1 that in most of the cases studied, these compounds are found in slightly greater proportions in *Quercus petraea*, which results in the brandies aged in this wood type being positioned in higher positive areas of VF5. On the other hand, when the scores of the samples in the two-dimensional space VF5 *vs.* VF2 (Fig. 3b) are examined, the wine spirits aged in either *Quercus petraea* or *Quercus robur* can be distinguished, as the former registers higher scores in VF2 and VF5. Nevertheless, just a trend and not a clear clustering can actually be observed in this figure.

The scores received by the labeled samples as a function of aging time were evaluated to determine whether there is any influence of the aging time on the evolution of the concentrations of the compounds studied. According to all the projections of the two-dimensional spaces defined by the VFs (Fig. 4) the distribution of the different samples within the two-dimensional space VF 5 *vs.* VF 1 presents differences that of the wood type that correlate with the aging time in the casks. As already mentioned, those brandies that had not been aged (time 0) have a notably different behavior from the rest of the samples. This is explained by the fact that, since they have not been in contact with the wood, they have not been transferred any of the substances responsible for certain aromas.

In order to fix the wine spirit variable and study the behavior of the brandies according to the variables related to the aging process, a new FA was performed by selecting a subgroup of samples consisting of the

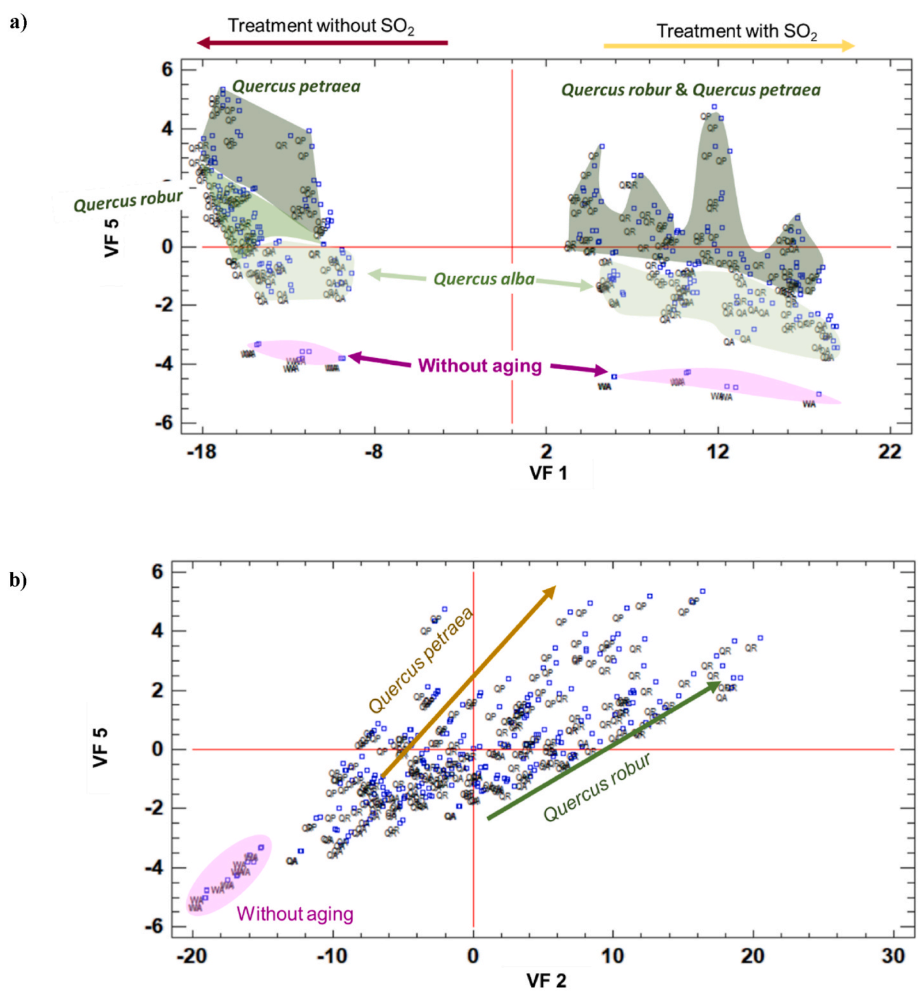

Fig. 3. Scores in the two-dimensional spaceVF5 *vs.* (a) VF1; (b) VF2.

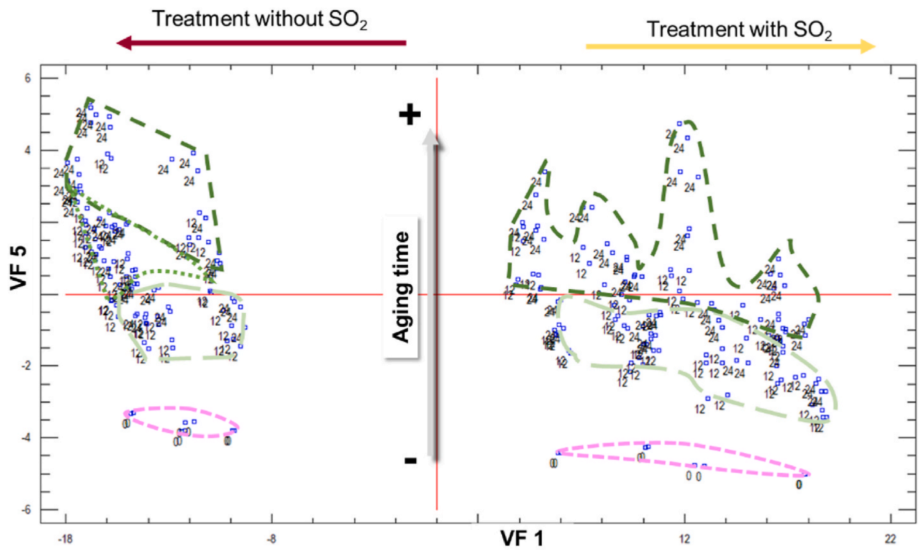

Fig. 4. Scores in the two-dimensional space VF5 *vs.* VF1 according to the aging time of the brandies.

wine spirits coded as WS6 (36 × 30 matrix). In this analysis we again extracted 5 VFs that explained 84.39% of the total variance of the system (eigenvalue >1). Fig. 5a shows the scores received by these brandies in the two-dimensional space VF2 *vs.* VF1. This figure clearly shows the separation of the samples' data according to the different oak wood types used for aging. The clustering obtained was conditioned by the values of the first two VFs. Thus, VF2 is capable of differentiating, and therefore grouping, the wine spirits aged in casks made from oak of the *Quercus alba* variety from the other oak varieties (*Quercus petraea* and *Quercus robur*), i.e. American oak versus European oaks. The *Quercus petraea* and *Quercus robur* varieties are quite similar and, for this reason, no clear differences were found between them. VF1 is capable of differentiating the samples by the wood toast grade used for the manufacturing of the casks, which explains the wide dispersion of the samples that make up the two groups that had been identified. Fig. 5b shows the same scores, but in this case, the toasting grade is used as a code for each of the samples, with VF1 being the main responsible for this behavior.

It can be seen from Fig. 5c that the positive contribution of phenolic and furfural compounds to FV1 is the main factor that differentiates the two toasting grades, even if this fact is also influenced by the presence of fatty acid esters (positive and negative contribution to this FV). Finally, it can be seen that gallic acid, ethyl lactate, acetaldehyde, diethyl acetal, hexanol and methanol are responsible for the distinction between the *Quercus alba* variety and the others (positive and negative contributions to FV2).

The phenolic and furfural compounds show an increasing trend with longer aging time, since their presence in aged wine spirits is attributable to the wood yields. Their presence in the distillate is related not only to the nature of the cask wood, but also to the toasting treatment applied to the wood for the manufacturing of the cask. Changing from a light toast to a medium toast involves a greater degradation of the wood lignin, which allows a greater release of phenolic compounds into the medium that results in distillates with a greater phenolic compound content than those aged in casks made with lightly toasted wood (Canas, 2017).

The behavior observed in VF2 is explained, on the one hand, by the heavier transfer of gallic acid from *Quercus robur* and *Quercus petraea* wood into the distillates during the aging process, in comparison with the transfers registered from *Quercus alba* wood. This latter wood is poorer in tannins, which results in aged distillates with a lower concentration of gallic acid than those aged in the *Quercus robur* or *Quercus petraea* oak varieties (Cadahía et al., 2001; Guerrero-Chanivet et al., 2020). Furthermore, *Quercus petraea* in particular is the one with the greatest gallic acid content. (Cadahía et al., 2001). Also noteworthy is the higher concentration of HMF as well as the lower concentration of vanillic acid in both *Quercus petraea* and *Quercus robur* in comparison to that found in *Quercus alba*.

3.3.2. *Supervised chemometric studio*

With the aim of establishing chemometric models capable of discriminating/classifying brandy samples according to the oak wood variety and to the wood toasting grade as well as to the time that these samples have been aged in the casks, a supervised pattern recognition study was carried out. The variables described are considered to have a great influence on the secondary, tertiary and quaternary aromas of this category of wine spirits. The supervised pattern recognition study consisted in the development of hard classification models based on Artificial Neural Networks and Linear Discriminant Analysis.

3.3.2.1. Artificial Neural Networks. Based on the data matrix described above, three neural networks were developed according to the following: i) the variety of wood used to make the casks (*Quercus alba*, *Quercus petraea* and *Quercus robur*), ii) the toasting grade (light or medium toasting) and iii) the aging time that each brandy remained in the cask (0, 12 or 24 months). All the cases were estimated as a 3-layer neural network with a single hidden unit. Each neural network was developed by evaluating the prior probability of belonging to the class (Parzen, 1962) as well as the equal error cost for all the classes. In addition, the models were trained using jackknifing as a sphere of influence to estimate the nonparametric probability of density function. For each neural network, the 30 variables that had been determined and 232 cases were selected as the input layer and the hidden layer, respectively. The output layer consisted of as many outputs as classes were estimated according to the unsupervised pattern recognition methods. Table 5 shows the results obtained for the three trained ANNs.

The three ANNs showed successful classification rates above 95%. In fact, the first ANN (wood variety) reached a 100% success rate when classifying the samples, while the second one (toasting grade) only failed to correctly classify a single medium toasted sample which was wrongly classified as a light toasted one. All in all, a successful performance of the developed network could be considered. As previously mentioned, the toasting of the wood is an artisan process where two identical toasting results are rather difficult to obtain and that may inevitably vary depending on the craftsman's criteria with respect to the proper degree of toasting. The last of the neural networks (ANN based on the aging

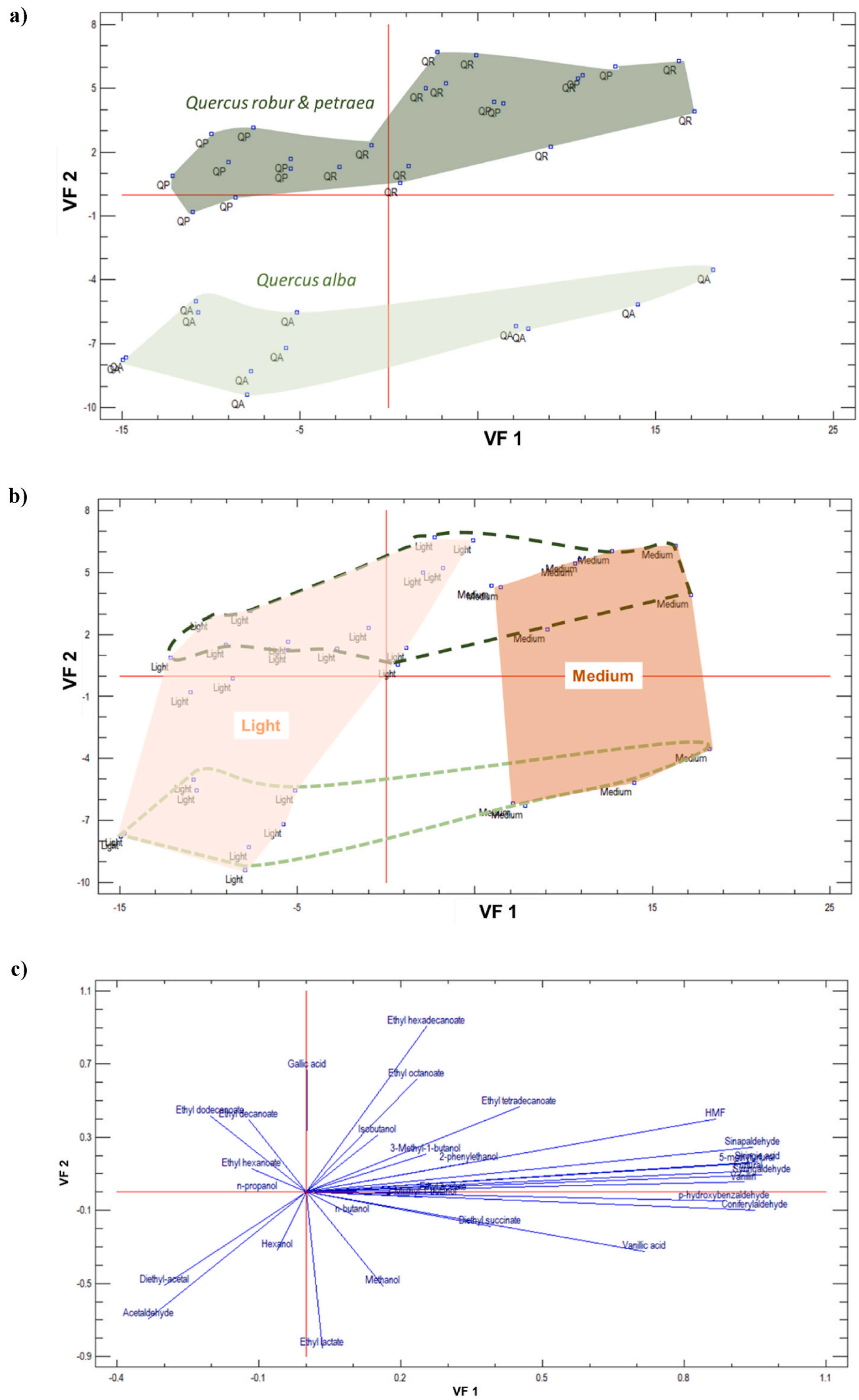

Fig. 5. (a) Scores of the two-dimensional space VF2 vs. VF1 attending to the wood type employed for the manufacturing of the cask; (b) Scores of the two-dimensional space VF2 vs. VF1 attending to the wood toasting grade and (c) Loadings received in the two-dimensional space VF2 *vs.* VF1.

time) was the one, out of the three models, to be granted the poorest classification performance, as it wrongly classified 8 of the samples in the data set (2 of the samples labeled as 12-month old were classified as 24-month old samples and 6 of the samples labeled as 24-month old were classified as 12-month old samples). This erroneous response of the trained network could be explained by the following facts:

i) The major esters determined have a greater influence when it comes to discriminating/classifying different types of aged brandies. The presence of these compounds is originated by the raw material, with the exception of ethyl acetate which, despite also being influenced by its concentration in the unaged wine spirit, evolves increasingly during the aging time due to the wood yields and to the chemical reactions that take place during this period between the wine spirit and the wood.

Table 5
Classification obtained through the trained neural networks attending to the following: oak wood type, toasting grade & aging time.

Oak wood type						
	Prior probability	Nº. of samples	*Quercus alba*	*Quercus petraea*	*Quercus robur*	*Unaged*
Quercus alba	31.03%	72	70 (97.22%)	0 (0.00%)	2 (2.78%)	0 (0.00%)
Quercus petraea	31.03%	72	0 (0.00%)	71 (98.61%)	1 (1.39%)	0 (0.00%)
Quercus robur	31.03%	72	1 (1.39%)	3 (4.17%)	68 (94.44%)	0 (0.00%)
Unaged	6.9%	16	0 (0.00%)	0 (0.00%)	0 (0.00%)	16 (100.00%)
Total correct classification	100%					
Toasting grade						
	Prior probability	No. of samples	Light	Medium	Unaged	
Light	5.00%	116	116 (100.00%)	0 (0.00%)	0 (0.00%)	
Medium	43.10%	100	1 (1.00%)	99 (99.00%)	0 (0.00%)	
Unaged	6.90%	16	0 (0.00%)	0 (0.00%)	16 (100.00%)	
Total successful classification	99.57%					
Aging time						
	Prior probability	No. of samples	0 months	12 months	24 months	
0 months	6.90%	16	16 (100.00%)	0 (0.00%)	0 (0.00%)	
12 months	46.55%	108	0 (0.00%)	106 (98.15%)	2 (1.85%)	
24 months	46.55%	108	0 (0.00%)	6 (5.56%)	102 (94.44%)	
Total successful classification	96.55%					

ii) Some higher alcohols such as hexanol or 2-phenylethanol are also affected by the aging process since, and particularly the latter, they are closely related to the base wine used for the production of the wine spirit, and these compounds "recall memories" of the raw material.

Although the number of samples used for this study could be deemed adequate for the training of the developed networks, it is nevertheless not high enough to enable each ANN to provide a fully reliable prediction on new brandy samples based on the attributes considered. Therefore, in order to create a classification/discrimination model that would allow more successful predictions without any further training, the potential of LDA was evaluated.

3.3.2.2. Lineal discriminant analysis. In order to verify the feasibility of this method and given that the regular working procedures in wineries focus on the production of brandy, in this study, we have used a 216 × 30 matrix that comprises exclusively those samples that had been in contact with the wooden casks.

Similarly, to what was described in the previous subsection, three independent models were developed based on: i) the type of wood of the casks (classes: *Quercus alba*, *Quercus petraea* and *Quercus robur*), ii) the toasting grade of the wood (classes: light and medium toasting) and iii) the aging time that each brandy remained in the cask (classes: 12 and 24 months). All the models were developed by dividing the matrix into two subsets, where the first one was used for model training (144 × 30) and the second one (72 × 30) for prediction (external validation).

a) Wood type

The first LDA was intended to discriminate the brandy samples according to the type of wood used to make the casks in which they had been aged. This discrimination model required two Discriminant Functions (DFs) to explain 100% of the total variance of the samples. The percentage of relative variance explained by the first DF was 90.26% while the percentage corresponding to the second DF was 9.74%. Three Classification Functions (CFs) were established for each of the established classes (*Quercus alba*, *Quercus robur* and *Quercus petraea*) for the development of the model. The results are shown in Table 6 below.

The software used to develop the model allowed to establish during the cross-validation stage the prior probability of fitting into each one of the classes as 32.64% for the *Quercus alba* class, 35.42% for the *Quercus petraea* class and 31.95% for the *Quercus robur* class. Regarding the classification results, 100% of the samples both from the training set, 47 samples of the *Quercus alba* class, 51 samples of the *Quercus petraea* class and 46 samples of the *Quercus robur* class, and from the prediction set, 25 samples of the *Quercus alba* class, 21 samples of the *Quercus petraea* class and 26 samples of the *Quercus robur* class, were successfully classified. While the FA could only clearly discriminate between individual brandies, the LDA was able to clearly and unambiguously discriminate all the samples as a whole according to the type of wood in which the brandies had been aged.

Table 6
Classification of the LDA training sample set according to the type of wood.

		Nº of samples	*Quercus alba*	*Quercus petraea*	*Quercus robur*
Quercus alba	32.64%	47	47 (100.00%)	0 (0.00%)	0 (0.00%)
Quercus petraea	35.42%	51	0 (0.00%)	51 (100.00%)	0 (0.00%)
Quercus robur	31.94%	46	0 (0.00%)	0 (0.00%)	46 (100.00%)
	Total successful classification			100.00%	

b) Toasting grade

The LDA that had been developed to discriminate the samples according to the type of wood toasting (light and medium) only required a single DF to explain 100% of the samples' variance, for which 2 CFs were established. In this case, the software allowed to establish the percentage of probability of fitting into the light toast class as 52.08%, while the same parameter for the medium toast class was 47.92%. The resulting classification is presented in Table 7.

Out of the 144 samples that made up the training set (75 samples from the light toast and 69 samples from the medium toast class) only 4 of them were misclassified as follows: 3 samples from lightly toasted wood casks were classified as medium toast and one sample from

Table 7
Classification of the ADL training sample set according to the toasting grade.

		Nº of samples	Light toast	Medium toast
Light toast	52.08%	75	72 (96.00%)	3 (4.00%)
Medium toast	47.92%	69	1 (1.45%)	68 (98.55%)
	Total successful classification		97.22%	

medium toast wood casks were classified as lightly toasted wood. Furthermore, with regard to the prediction set, 41 light toast and 31 medium toast samples, all of the samples were correctly classified into their respective classes. The errors observed during the training of the model could be related to the toasting process itself, since, as previously mentioned, this is a fully handmade process.

c) Aging time

Finally, the LDA that had been conducted according to the aging time also required just one DF which explained 100% of the total variance of the data. 2 CFs corresponding to 12 and 24 months of aging were obtained. The prior probability of fitting into the 12-month aging class was established at 48.61%, while for the 24-month aging class this value was calculated as 51.39%. The classification results are listed in Table 8.

It can be seen from this table that 100% of the samples used as the training set: 70 samples of the 12-month class and 74 samples of the 24-month class, were correctly classified into their corresponding class. The samples used as the prediction set, 38 samples of the 12-month class and 34 samples of the 24-month class, were also correctly classified into their classes. When compared against the results obtained by the ANN for this particular case, we can see that the LDA provides a more accurate classification of the samples from both the training and the prediction set.

4. Conclusions

The volatile fraction of the brandies was strongly marked by the young wine spirit and presented a slight trend to increase over the aging process as a result of the growing concentration attributable to the *merma* phenomenon. The phenolic and furanic aldehyde compounds together with the ethyl acetate and the volatile acidity (as a consequence of acetic acid transfers) were the parameters that definitely presented a clearly rising curve during the aging time since, although some of the compounds studied are also present in the young wine spirit, their presence in the aged brandies was mainly related to the transferring of compounds from the wood into the distillate.

The unsupervised chemometric study of all the parameters studied revealed that the aged wine spirits formed different groupings depending mainly on whether or not sulfur dioxide had been used during the fermentation of the wines used to produce the wine spirit to be aged and on the distillation method used to obtain these wine spirit. Some differences were also observed between both studies according to the alcoholic strength of the wine spirits to be aged, although these differences were not so obvious. On the other hand, the botanical origin of the oak, the wood degree of toasting and the aging time did not prove to be so influential on the composition of the final brandy and, therefore, did not facilitate a clear discrimination of the brandies. With regard to the phenolic compounds and furanic aldehydes in the aged brandies, some differences were observed attending to the oak wood types once the groups of wine spirit under study were selected. It is particularly relevant to highlight that the oenological practices implemented during the fermentation of the base wine have a definite and significant impact on the characteristics of the final product, even after 28 months of aging. This, as well as the distillation method used to obtain the wine spirit to be aged, are crucial variables that must be seriously considered when selecting the wines to be used for the production of brandy.

The three ANNs demonstrated classification accuracy percentages above 95% according to the type of oak, the toasting grade and the aging time. This should be considered as a really successful performance of the developed networks. The majority esters identified were the most relevant compounds with regard to their capacity to discriminate/classify the different categories of aged brandies. Some higher alcohols, such as hexanol or 2-phenylethanol were also found to be quite decisive.

The 3 LDAs that were developed based on the classification of brandies according to the type of oak wood, toasting grade and aging time provided 100% successfully classified samples. While the FA provided reliable classifications only when single brandy samples were analyzed, LDA was capable of clear and successfully discriminate between all the samples in a set according to the type of wood in which the brandies had been aged. When comparing these results against those obtained from the ANNs with regard to this variable, it could be confirmed that LDA was a more reliable method. Only during the training of the ANN for toasting grade discrimination, some imprecise results were obtained, but this imprecision could be attributable to the manual nature of the toasting procedures. Despite the complexity of the data handled and the large number of variables that have been considered for this study, the models that have been developed have clearly revealed which are the key variables involved in brandy production that the industry can use as practicable and reliable reference for the classification of brandies, these being the use of wines made with or without the addition of sulfur dioxide during fermentation, the type of distillation methods used to obtain the distillate and the alcoholic strength of the distillates. However, the type of oak wood used, the aging time, or the degree of toasting of the wood are also variables to be considered for the classification of spirits.

Table 8
Classification of the training sample set for the LDA according to aging time.

		Nº of samples	12 months	24 months
12 months	48.61%	70	70 (100.00%)	0 (0.00%)
24 months	51.39%	74	0 (0.00%)	74 (100.00%)
	Total successful classification		100.00%	

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CRediT authorship contribution statement

María Guerrero-Chanivet: Conceptualization, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Fidel Ortega-Gavilán:** Conceptualization, Formal analysis, Methodology, Writing – original draft, Writing – review & editing. **M. Gracia Bagur-González:** Conceptualization, Formal analysis, Funding acquisition, Methodology, Supervision, Writing – original draft, Writing – review & editing. **Manuel J. Valcárcel-Muñoz:** Conceptualization, Formal analysis, Investigation, Methodology, Supervision, Writing – review & editing. **M. Valme García-Moreno:** Conceptualization, Formal analysis, Funding acquisition, Methodology, Project administration, Supervision, Writing – review & editing. **Dominico A. Guillén-Sánchez:** Conceptualization, Formal analysis, Funding acquisition, Methodology, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors are unable or have chosen not to specify which data has been used.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.crfs.2023.100486.

References

Balcerek, M., Pielech-Przybylska, K., Patelski, P., Dziekońska-Kubczak, U., Strąk, E., 2017. The effect of distillation conditions and alcohol content in 'heart' fractions on the concentration of aroma volatiles and undesirable compounds in plum brandies. J. Inst. Brew. 123, 452–463. https://doi.org/10.1002/jib.441.

Berry, D.R., Slaughter, J.C., 2003. Alcoholic beverage fermentations. In: Lea, A.G., Piggott, J.R. (Eds.), Fermented Beverage Production. Kluwer Academic/Plenum Publishers, New York, pp. 25–38.

Briones, A., Ubeda-Iranzo, J., Hernndez-Gmez, L., 2012. Spirits and liqueurs from melon fruits (cucumis melo L.). In: Distillation - Advances from Modeling to Applications. InTech. https://doi.org/10.5772/38702.

Bueno, J.E., Peinado, R.A., Medina, M., Moreno, J., 2006. Effect of a short contact time with lees on volatile composition of Airén and Macabeo wines. Biotechnol. Lett. 28, 1007–1011. https://doi.org/10.1007/s10529-006-9038-2.

Cacho, J., Moncayo, L., Palma, J.C., Ferreira, V., Culleré, L., 2013. The impact of grape variety on the aromatic chemical composition of non-aromatic Peruvian pisco. Food Res. Int. 54, 373–381. https://doi.org/10.1016/j.foodres.2013.07.019.

Cadahía, E., Muñoz, L., De Simón, B.F., García-Vallejo, M.C., 2001. Changes in low molecular weight phenolic compounds in Spanish, French, and American oak woods during natural seasoning and toasting. J. Agric. Food Chem. 49, 1790–1798. https://doi.org/10.1021/jf0006168.

Canas, S., 2017. Phenolic composition and related properties of aged wine spirits: influence of barrel characteristics. A review. Beverages 3, 55. https://doi.org/10.3390/beverages3040055.

Cantagrel, R., Galy, B., Jouret, C., 1998. Eaux-de-vie d'origine viticole. In: Flanzy, C. (Ed.), Oenologie Fondements Scientifiques et Technologies. Collection Sci. & Tech. Agr., New York, pp. 1085–1142.

Carrascal García, V., 2004. Estudio de los ácidos orgánicos en Brandy de Jerez y su relación con las prácticas tradicionales de elaboración. Universidad de Cádiz.

Conner, J.M., Paterson, A., Piggott, J.R., 1992. Analysis of lignin from oak casks used for the maturation of Scotch whisky. J. Sci. Food Agric. 60, 349–353. https://doi.org/10.1002/jsfa.2740600312.

De Rosso, M., Cancian, D., Panighel, A., Dalla Vedova, A., Flamini, R., 2009. Chemical compounds released from five different woods used to make barrels for aging wines and spirits: volatile compounds and polyphenols. Wood Sci. Technol. 43, 375–385. https://doi.org/10.1007/s00226-008-0211-8.

Europeo, Parlamento, Consejo de la Unión Europea, 2019. Reglamento (UE) 2019/787 del Parlamento Europeo y del Consejo de 17 de abril de 2019. D. Of. la Unión Eur. L130, 17–27.

Flanzy, C., 2003. Enología: Fundamentos Científicos Y Tecnológicos, second ed. Mundi-Prensa Libros S.A., Madrid, Spain.

García-Llobodanin, L., Achaerandio, I., Ferrando, M., Güell, C., López, F., 2007. Pear distillates from pear juice concentrate: effect of lees in the aromatic composition. J. Agric. Food Chem. 55, 3462–3468. https://doi.org/10.1021/jf0633589.

Guerrero-Chanivet, M., Valcárcel-Muñoz, M.J., García-Moreno, M.V., Guillén-Sánchez, D.A., 2020. Characterization of the aromatic and phenolic profile of five different wood chips used for ageing spirits and wines. Foods 9, 1613. https://doi.org/10.3390/foods9111613.

Guymon, J.F., Crowell, E.A., 1970. Brandy aging. Some comparisons of American and French oak cooperage. Wines Vines 23–25.

Hernandez-Gomez, L.F., Úbeda, J., Briones, A., 2003. Melon fruit distillates: comparison of different distillation methods. Food Chem. 82, 539–543. https://doi.org/10.1016/S0308-8146(03)00008-6.

Jordao, A.M., Ricardo-da-Silva, J.M., Laureano, O., 2005. Comparison of volatile composition of cooperage oak wood of different origins (Quercus pyrenaica vs. Quercus alba and Quercus petraea). Mitteilungen Klosterneubg 55, 22–31.

Jurado-Córdoba, M.S., 2016. Potential agronómico y enológico de diez variedades blancas de vid como materia prima en la obtención de aguardientes para Brandy de Jerez. Cádiz.

Korenika, A.M.J., Biloš, J., Kozina, B., Tomaz, I., Preiner, D., Jeromel, A., 2020. Effect of different reducing agents on aromatic compounds, antioxidant and chromatic properties of sauvignon blanc wine. Foods 9, 996. https://doi.org/10.3390/foods9080996.

Le Floch, A., Jourdes, M., Teissedre, P.-L., 2015. Polysaccharides and lignin from oak wood used in cooperage: composition, interest, assays: a review. Carbohydr. Res. 417, 94–102. https://doi.org/10.1016/j.carres.2015.07.003.

Liu, S.Q., Pilone, G.J., 2000. An overview of formation and roles of acetaldehyde in winemaking with emphasis on microbiological implications. Int. J. Food Sci. Technol. 35, 49–61. https://doi.org/10.1046/j.1365-2621.2000.00341.x.

Louw, L., Lambrechts, M.G., 2012. Grape-based brandies: production, sensory properties and sensory evaluation. In: Alcoholic Beverages. Woodhead Publishing Limited. https://doi.org/10.1533/9780857095176.3.281.

Lukić, I., Tomas, S., Miličević, B., Radeka, S., Peršurić, D., 2011. Behaviour of volatile compounds during traditional alembic distillation of fermented Muscat blanc and Muškat ruža porežki grape marcs. J. Inst. Brew. 117, 440–450. https://doi.org/10.1002/j.2050-0416.2011.tb00491.x.

Martínez-Gil, A., del Alamo-Sanza, M., Sánchez-Gómez, R., Nevares, I., 2018. Different woods in cooperage for oenology: a review. Beverages 4, 94. https://doi.org/10.3390/beverages4040094.

Mosedale, J.R., Puech, J.L.L., 1998. Wood maturation of distilled beverages. Trends Food Sci. Technol. 9, 95–101. https://doi.org/10.1016/S0924-2244(98)00024-7.

Nedjma, M., Maujean, A., 1995. Improved chromatographic analysis of volatile sulfur compounds by the static headspace technique on water-alcohol solutions and brandies with chemiluminescence detection. J. Chromatogr. A 704, 495–502. https://doi.org/10.1016/0021-9673(95)00218-C.

OIV, 2009. Method OIV-MA-BS-12. Determination of the acidites of spirit drinks of vitivinicultural origin. In: Compendium of International Methods of Analysis of Spirituous Beverages of Vitivinicultural Origin. OIV, Paris, France. OIV-MA-BS-12: R2009: 1-8.

OIV, 2021a. Sulfiting (oeno 3/04). In: International Code of Oenological Practices, 1. OIV, Paris, France, pp. 18–19 p. II.1.

OIV, 2021b. Method OIV-MA-F1-03. Determination of the acquired alcoholic strength by volume (ASV) of concentrated musts (CM) and grape sugar (or rectified concentrated musts, RCM). In: Compendium of International Methods of Wine and Must Analysis, 2. OIV, Paris, France. OIV-MA-F1-03: R2011:1-6.

OIV, 2021c. Method OIV-MA-AS313-01. Total acidity. In: Compendium of International Methods of Wine and Must Analysis, 1. OIV, Paris, France. OIV-MA-AS313-01: R2015: 1-3.

OIV, 2021d. Method OIV-MA-AS323-04B. Sulfur dioxide. In: Compendium of International Methods of Wine and Must Analysis, 2. OIV, Paris, France. OIV-MA-AS323-04B: R2009 1-3.

Parzen, E., 1962. On estimation of a probability density function and mode. Ann. Math. Stat. 33, 1065–1076. https://doi.org/10.1214/aoms/1177704472.

Pérez-Navarro, J., Izquierdo-Cañas, P.M., Mena-Morales, A., Chacón-Vozmediano, J.L., Martínez-Gascueña, J., García-Romero, E., Hermosín-Gutiérrez, I., Gómez-Alonso, S., 2020. Comprehensive chemical and sensory assessment of wines made from white grapes of vitis vinifera cultivars albillo dorado and montonera del casar: a comparative study with airén. Foods 9, 1–17. https://doi.org/10.3390/foods9091282.

Prida, A., Puech, J.L., 2006. Influence of geographical origin and botanical species on the content of extractives in American, French, and East European oak woods. J. Agric. Food Chem. 54, 8115–8126. https://doi.org/10.1021/jf0616098.

Puech, J.L., 1984. Characteristics of oak wood and biochemical aspects of Armagnac aging. Am. J. Enol. Vitic. 35, 77–81.

Reazin, G.H., 1981. Chemical mechanisms of whiskey maturation. Am. J. Enol. Vitic. 32, 283–289.

Reazin, G.H., 1983. Chemical analysis of whiskey maturation. In: Piggott, J.R. (Ed.), Flavor of Distilled Beverages. Origin and Development. Ellis Horwood Limited, West Sussex, England, pp. 225–240.

Reazin, G.H., Bladwin, S., Scales, H.S., Washingotn, H.W., Andreasen, A.A., 1976. Determination of the congeners produced from ethanol during whiskey maturation. JAOAC (J. Assoc. Off. Anal. Chem.) 59, 770–776.

Rodríguez Dodero, M.C., Guillén Sánchez, D.A., Rodríguez, M.S., Barroso, C.G.G.G., Rodríguez Dodero, M.C., Guillén Sánchez, D.A., Rodríguez, M.S., Barroso, C.G.G.G., Dodero, M.C.R., Sánchez, D.A.G., Rodríguez, M.S., Barroso, C.G.G.G., 2010. Phenolic compounds and furanic derivatives in the characterization and quality control of Brandy de Jerez. J. Agric. Food Chem. 58, 990–997. https://doi.org/10.1021/jf902965p.

Sánchez-Guillén, M.M., Schwarz-Rodríguez, M., Rodríguez-Dodero, M.C., García-Moreno, M.V., Guillén-Sánchez, D.A., García-Barroso, C., 2019. Discriminant ability of phenolic compounds and short chain organic acids profiles in the determination of quality parameters of Brandy de Jerez. Food Chem. 286, 275–281. https://doi.org/10.1016/j.foodchem.2019.02.006.

Sarni, F., Moutounet, M., Puech, J.L., Rabier, P., 1990. Effect of heat treatment of oak wood extractable compounds. Holzforschung 44, 461–466. https://doi.org/10.1515/hfsg.1990.44.6.461.

Schwarz, M., Rodríguez, M.C., Guillén, D.A., Barroso, C.G., 2009. Development and validation of UPLC for the determination of phenolic compounds and furanic derivatives in Brandy de Jerez. J. Separ. Sci. 32, 1782–1790. https://doi.org/10.1016/j.lwt.2014.05.060.

Silva, M.L., Malcata, F.X., 1999. Effects of time of grape pomace fermentation and distillation cuts on the chemical composition of grape marcs. Eur. Food Res. Technol. 208, 134–143. https://doi.org/10.1007/s002170050390.

Singleton, V.L., 1995. Maturation of wines and spirits - comparisons, facts, and hypotheses. Am. J. Enol. Vitic. 46, 98–115.

Soares, B., Garcia, R., Freitas, A.M.C., Cabrita, M.J., 2012. Phenolic compounds released from oak, cherry, chestnut and robinia chips into a syntethic wine: influence of toasting level. Ciência Técnica Vitivinícola 27, 17–26.

Spaho, N., 2017. Distillation techniques in the fruit spirits production. Distill. - Innov. Appl. Model. https://doi.org/10.5772/66774.

Spaho, N., Dürr, P., Grba, S., Velagić-Habul, E., Blesić, M., 2013. Effects of distillation cut on the distribution of higher alcohols and esters in brandy produced from three plum varieties. J. Inst. Brew. 119, 48–56. https://doi.org/10.1002/jib.62.

Sun, Y., Zhang, T., Lü, H., Yu, Z., Li, X., 2016. Effect of added sulphur dioxide levels on the fermentation characteristics of strawberry wine. J. Inst. Brew. 122, 446–451. https://doi.org/10.1002/jib.342.

Swiegers, J.H., Bartowsky, E.J., Henschke, P.A., Pretorious, I.S., 2005. Yeast and bacterial modulation of wine aroma and flavour. Aust. J. Grape Wine Res. 11, 139–173. https://doi.org/10.1111/j.1755-0238.2005.tb00285.x.

Tsakiris, A., Kallithraka, S., Kourkoutas, Y., 2014. Grape brandy production, composition and sensory evaluation. J. Sci. Food Agric. 94, 404–414. https://doi.org/10.1002/jsfa.6377.

Valcárcel-Muñoz, M.J., Guerrero-Chanivet, M., García-Moreno, M.V., Rodríguez-Dodero, M.C., Guillén-Sánchez, D.A., 2021a. Comparative evaluation of brandy de Jerez aged in American oak barrels with different times of use. Foods 10, 288. https://doi.org/10.3390/foods10020288.

Valcárcel-Muñoz, M.J., Guerrero-Hidalgo, R.F., Cantos-Villar, E., Muñoz-Redondo, J.M., Beña-Parra, B., Moreno-Rojas, J.M., Puertas-García, B., 2021b. Evolución de parámetros fisicoquímicos, composición volátil y compuestos polifenólicos del Brandy de Jerez durante su envejecimiento en Sistemas de Criaderas y Solera. Rev. Enólogos 132, 76–91.

Valcárcel-Muñoz, M.J., Butrón-Benítez, D., Guerrero-Chanivet, M., García-Moreno, M.V., Rodríguez-Dodero, M.C., Guillén-Sánchez, D.A., 2022. Influence of alcoholic strength on the characteristics of Brandy de Jerez aged in Sherry Casks. J. Food Compos. Anal. 111, 104618 https://doi.org/10.1016/j.jfca.2022.104618.

Valero, E., Moyano, L., Millan, M., Medina, M., Ortega, J., 2002. Higher alcohols and esters production by Saccharomyces cerevisiae. Influence of the initial oxygenation of the grape must. Food Chem. 78, 57–61. https://doi.org/10.1016/S0308-8146(01)00361-2.

Volf, I., Ignat, I., Neamtu, M., Popa, V.I., 2014. Thermal stability, antioxidant activity, and photo-oxidation of natural polyphenols. Chem. Pap. 68, 121–129. https://doi.org/10.2478/s11696-013-0417-6.

Xiang, X.F., Lan, Y. Bin, Gao, X.T., Xie, H., An, Z.Y., Lv, Z.H., Yin-Shi, Duan, C.Q., Wu, G. F., 2020. Characterization of odor-active compounds in the head, heart, and tail fractions of freshly distilled spirit from Spine grape (Vitis davidii Foex) wine by gas chromatography-olfactometry and gas chromatography-mass spectrometry. Food Res. Int. 137, 109388 https://doi.org/10.1016/j.foodres.2020.109388.

Younis, O.S., Stewart, G.G., 1998. Sugar uptake and subsequent ester and higher alcohol production by Saccharomyces cerevisiae. J. Inst. Brew. 104, 255–264. https://doi.org/10.1002/j.2050-0416.1998.tb00998.x.

Zierer, B., Schieberle, P., Granvogl, M., 2016. Aroma-Active compounds in bartlett pears and their changes during the manufacturing process of bartlett pear brandy. J. Agric. Food Chem. 64, 9515–9522. https://doi.org/10.1021/acs.jafc.6b04612.