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ORIGINAL RESEARCH ARTICLE

Effect of the alcoholic strength of unaged wine distillates on the final composition of Brandy de Jerez aged in Sherry Casks®

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ABSTRACT

Brandy is a spirit obtained from distilled wine that has an alcohol content equal to or greater than 36 % ABV (Alcohol by Volume). It undergoes an ageing process in oak wood casks with a capacity of up to 1000 L for a minimum of six months. During this process, a series of physicochemical and sensory changes take place that confer the initial wine distillate with a series of improvements to its sensory profile. Such changes are mainly determined by the intrinsic characteristics of the wood and by those associated with the manufacturing process of the casks. The previous use of the casks, ageing time and the alcoholic strength of the wine distillate are also important factors, among others. The casks, which will have previously contained some type of Sherry wine (such as Fino, Amontillado, Oloroso and Pedro Ximénez), are known as Sherry Casks® and they must be used in the production of Brandy de Jerez. During the ageing of Brandy de Jerez, Sherry Casks® contribute to the final brandy via the compounds that are both inherent to the wood they are made of and from the wine that they initially contained and that were retained in the wood pores. The alcohol content of the wine distillate to be aged significantly affects not only the quality of the brandy, but also the financial cost of the process. This study aimed to determine the influence on brandy of the alcoholic strength of wine distillates aged in static ageing systems using Sherry Casks®. Specifically, we assessed the physicochemical composition and sensory profile of Brandy de Jerez made from wine distillates with three different alcoholic strengths (40 %, 55 % and 68 % ABV) and aged for 24 months. The Brandy de Jerez with lower alcoholic strengths (40 % - 55 % ABV) were found to contain a higher concentration of polyphenolic compounds deriving from the wood as well as from the constituents of the cask-seasoning Sherry wine. The brandies with higher alcoholic strengths exhibited a marked colour change, while the 40 % and 55 % ABV brandies were perceived to have the best sensory characteristics.

KEYWORDS: Brandy, Sherry Cask, alcoholic strengths, ageing, spirit drinks, wine distillate

INTRODUCTION

Brandy is a spirit obtained from distilled wine aged for a minimum of six months in oak casks of up to 1000 L in capacity. It has a minimum alcoholic strength of 36 % ABV (Alcohol by Volume) and is usually commercialised at between 36 % ABV and 45 % ABV (Regulation (EU) 2019/787 European Parliament and Council of 17 April 2019, 2019).

The final quality of brandy is greatly influenced by its ageing stage. This is a process during which a number of physicochemical and sensory changes take place, modifying the colour, flavour and aroma of the initial wine distillate (Canas, 2017; Mosedale, 1995). These changes are influenced by the specific ageing process used (static and/or dynamic), the characteristics of the wooden casks used for ageing (botanical origin of the oak, level of toasting and size), the previous use of the casks (new, previously used to age other brandies or for seasoning), the length of the ageing process and the alcohol content of the wine distillate (Canas, 2017; García-Moreno *et al.*, 2020; Guerrero-Chanivet *et al.*, 2020; Valcárcel-Muñoz *et al.*, 2022a; Valcárcel-Muñoz *et al.*, 2020; Valcárcel-Muñoz *et al.*, 2021b).

Produced in southern Spain, Brandy de Jerez is a unique spirit produced in compliance with the requirements defined in the product specification of the most prominent Protected Geographical Indication (PGI) in Spain, "Brandy de Jerez PGI". According to these specifications, Brandy de Jerez must be produced in the area known as Marco de Jerez, which is located between the municipalities of Jerez de la Frontera, El Puerto de Santa María and Sanlúcar de Barrameda in the province of Cádiz, applying the traditional dynamic *Criaderas* y *Solera* ageing system characteristic of the Jerez region in which Sherry Casks® are exclusively used (Orden de 28 de Junio de 2018, 2018, por la que se aprueba el expediente técnico de Indicación Geográfica "Brandy de Jerez"); these casks have previously contained some type of Sherry wine (such as Fino, Amontillado, Oloroso and Pedro Ximénez) in a seasoning process known as "envinado" (Especificación técnica de envinado de vasijas, 2021) that modifies the characteristics of the casks in different ways. The first benefit of using seasoned casks is the reduction of the amount of compounds that are transferred from the new wood to the ageing brandy (some of them even undesirable due to their organoleptic impact, like astringent sensations, very bitter oak notes and low smoothness) (Guerrero-Chanivet *et al.*, 2023a; Valcárcel-Muñoz *et al.*, 2021b). The second obvious benefit is that some of the compounds in the composition of the seasoning Sherry wine are transferred to the ageing brandy (Valcárcel-Muñoz *et al.*, 2021b). Thus, during the ageing of Brandy de Jerez in Sherry Casks®, both the compounds from the wood and those from the Sherry wine which are retained in the wood pores contribute to the composition of the final brandy (Sánchez-Guillén *et al.*, 2019; Schwarz *et al.*, 2009b; Schwarz-Rodríguez *et al.*, 2011).

Another very important factor to consider is the alcoholic strength of the wine distillate to be aged. This has an impact, both logistically and economically on the winery (Valcárcel-Muñoz *et al.*, 2022a), as well as on the physicochemical processes that take place during ageing. In fact, the capacity of the wine distillate to extract certain compounds from the Sherry Cask® depend on its alcoholic content, but it also has a strong influence on the chemical reactions that take place between the distillate's own compounds and those that are obtained during the ageing process (Baldwin and Andreasen, 1974; Delgado-González *et al.*, 2017; Mayr Marangon *et al.*, 2021; Puech, 1984). Wine distillates for the production of brandy are traditionally aged with an alcohol content of between 50 % ABV - 70 % ABV, but some wineries adjust it to the alcoholic strength of the final product for consumption; i.e., between 36 % and 40 % ABV (Puech, 1984; Valcárcel-Muñoz *et al.*, 2021a).

The major influence of alcohol content of wine distillates to be aged has already been documented by other authors (Baldwin and Andreasen, 1974; Guerrero-Chanivet *et al.*, 2022; Puech, 1984). Valcárcel-Muñoz *et al.* (2022a) specifically studied the impact of using a dynamic Criaderas and Solera system to age wine distillates of different alcohol contents of between 65 % ABV and 80 % ABV on the physicochemical and sensory characteristics of the final Brandy de Jerez. Their study confirmed that alcoholic strength has a relevant influence on both the extraction processes (lower ABV resulted in a higher content of water-soluble compounds and less ethanol-soluble compounds) and the nature of the chemical reactions that take place between the compounds already present in the brandy.

Because of the importance of alcoholic strength with respect to the ageing of the wine distillates, we investigated its effect on the physicochemical composition and sensory profile of Brandy of Jerez aged for 24 months in Sherry Casks®. The wine distillates used in the ageing process had three different alcoholic strengths: 68 % ABV, which is the traditionally used alcoholic strength for Marco de Jerez Brandy (Valcárcel-Muñoz *et al.*, 2022a); 55 % ABV, the typical alcoholic strength used for ageing in other regions (Cognac, Armagnac) (Puech, 1984); and 40 % ABV, which is the standard alcoholic strength of brandy for consumption.

MATERIALS AND METHODS

1. Samples

The distillate used for this study was obtained from the continuous column distillation of wines from the Airén grape variety (Castilla La Mancha) in accordance with the European regulation. Distillates at 77 % ABV were produced to be later diluted in demineralised water and adjusted to the different alcoholic strengths to be investigated: 40 %, 55 % and 68 % ABV (Regulation (EU) 2019/787 European Parliament and Council of 17 April 2019, 2019).

The research was carried out in 500 L American oak casks (*Quercus alba*) of medium toasting level. These casks had previously been seasoned for 3 years with Oloroso Sherry wine (Sherry Cask®) - a dry wine made from the *Palomino* variety and which had been fortified at 18 % ABV and aged for 2 years. After 3 years of seasoning, the casks were emptied of the Sherry wine and filled with 485L of wine distillate of the alcoholic strength corresponding to each experiment. Both, the wine distillates and the Sherry Casks® were supplied by Bodegas Fundador S.L.U., a winery that belongs to the Brandy de Jerez Protected Geographical Indication. The average humidity and temperature of the cellar remained constant at 71.5 ± 7.7 g/m^3 and 19.2 ± 5.8 ºC respectively during the whole time required to complete the assays.

Each experiment was conducted in duplicate, with two different casks for each alcoholic strength (n = 2). The wine distillate was aged statically and sampled periodically in order to monitor its evolution over two years in the following months: 0.5, 1, 2, 3, 4, 6, 8, 10, 12, 16, 20 and 24 for each of the three experiments. During the ageing process a total of 75 samples were analysed: 12 ageing samples (periodically sampling for two years) x 2 barrels for each experiment x 3 experiments (three alcoholic strengths studied) + 3 initial wine distillates.

2. Reagents

Ultrapure water (EMD Millipore, Bedford, MA, USA), 0.1M sulfuric acid (Sigma-Aldrich, Saint Louis, MO, USA) and UHPLC quality acetone (VWR International, Radnor, PA, USA) were used to prepare the eluents to determine the organic acids. The tartaric acid used for calibration was purchased from PanReac (Barcelona, Spain) and the rest of the standards were supplied by Sigma Aldrich (Saint Louis, MO, USA).

UHPLC-grade acetonitrile and acetic acid (PanReac, Barcelona, Spain), as well as ultrapure water (EMD Millipore, Bedford, MA, USA), were used to prepare the eluents for the phenolic compounds and furanic aldehydes analysis, and the standards for calibration were purchased from Sigma Aldrich (Saint Louis, MO, USA).

The standards for the calibration of acetaldehyde, methanol, diethylacetal, higher alcohols, ethyl acetate, fatty acid esters, organic acid esters, glycerol, 2,3-butanediol, as well as the internal standards used, 2-pentanol and ethyl undecanoate, were purchased from Sigma Aldrich (Saint Louis, MO, USA).

In all cases, ultrapure water (EMD Millipore, Bedford, MA, USA) and ethanol of HPLC quality ≥ 99 % (Scharlab, S.L. Barcelona, Spain) were used for the preparation of the calibration standards.

3. Methods

3.1. Oenological control parameters

All the oenological parameters were determined according to the official methods for the analysis of spirits described by the International Organization of Vine and Wine (OIV). Alcoholic strength (% ABV) was determined by measuring the strength of the distillate by means of a DMA-5000 density meter (Anton Paar, Ashland, OR, USA) (OIV, 2019); pH was analysed using a Basic 20 pH meter (Crison Instruments SA, Barcelona, Spain); total acidity was determined by potentiometric titration up to pH 7.5 and expressed in g acetic acid/L of 100 % vol. alcohol (OIV, 2015); and volatile acids contents were determined using a segmented flow analyzer AA3 HR Autoanalyzer (Seal Analytical, Norderstedt Stadt, Germany) (Saris *et al.*, 1970), the results are expressed as g acetic acid/L of 100 % vol. alcohol.

3.2. Organic acids

Ion chromatography was applied for the analysis of the organic acids using a 930 Compact IC Flex chromatograph (Metrohm, Madrid, Spain) equipped with a Metrosep Organic Acids column of 250 mm × 7.8 mm (i.d.) and 9µm particle size. A mixture of ultrapure water:acetone:sulfuric acid (84:12:4), at a flow rate of 0.4 mL/min, was used as the eluent and 20 µL of sample was injected. The acids to be determined were acetic, lactic, malic, succinic and tartaric acids and they were identified by a comparison of the retention time and the standard used. Data processing and acquisition was carried out using the software application MagicNet 3.3 (Metrohm, Madrid, Spain) (Valcárcel-Muñoz *et al.*, 2022b). The results are expressed as mg/L of 100 % vol. alcohol.

3.3. Aldehydes, Acetal, Methanol, Higher Alcohols, Esters, Glycerol and 2,3-Butanediol

An Agilent 7890B Gas Chromatograph (Agilent Technologies, Santa Clara, CA, USA) coupled to a flame ionisation detector was used to determine the acetaldehyde, diethylacetal, methanol, higher alcohols, ethyl acetate, fatty acid esters, organic acid esters, glycerol and 2,3-butanediol contents (Valcárcel-Muñoz *et al.*, 2021b). The 55 % ABV and 68 % ABV samples were diluted in ultrapure water to 40 % ABV and injected immediately after their preparation. The samples that already contained 40 % ABV were injected directly. The results are expressed as mg/L of 100 % vol. alcohol.

Total aldehydes are obtained from the sum of the concentrations of acetaldehyde and diethylacetal, with diethylacetal being expressed as acetaldehyde (1 mg diethylacetal equals 0.373 mg acetaldehyde) (Valcárcel-Muñoz *et al.*, 2022a). The results are expressed as mg acetaldehyde/L of 100 % vol. alcohol.

3.4. Chromatic characteristics

The chromatic characteristics were evaluated using the CIELab coordinates, following the calculations established by the regulations and the methodology described in previous studies (Delgado-González *et al.*, 2018). Transmittance spectra between 380 and 830 nm with a resolution of 1 nm were performed on each sample using an Agilent Cary 60 UV-Vis spectrophotometer (Agilent, CA, USA) and glass cuvettes with 10 mm path length.

The chromatic differences between the aged samples and the unaged wine distillate were determined according to the CIEDE2000 parameter (ΔE_{00}).

The absorbance measurements at 420 and 520 nm were determined following the methodology described by the

OIV (OIV, 2009), and the absorbance at 470 nm (brown hue) relevant to these samples (Canas *et al.*, 2016; Martins and Van Boekel, 2003) was determined by means of an Agilent Cary 60 UV-Vis spectrophotometer (Agilent, CA, USA). The results of the absorbances at 420, 520 and 470 nm are expressed as absorbance units/L of 100 % vol. alcohol.

3.5. Total Polyphenol Index

The absorbance at 280 nm was used to determine the total polyphenol index (TPI) in the samples by means of a Lambda25 spectrophotometer (Perkin Elmer, Boston, MA, USA) and quartz cuvettes with a 10mm path length. A calibration curve of gallic acid solutions at concentrations of between 0 and 50 mg/L was generated to quantify the samples (Guerrero-Chanivet *et al.*, 2023b). The samples were diluted at 1:10 in ultrapure water. The results are expressed as mg gallic acid equivalent (GAE)/L of 100 % vol. alcohol.

3.6. Phenolic Compounds and Furanic aldehydes

The phenolic compounds and furanic aldehydes were quantified by UHPLC (Guerrero-Chanivet *et al.*, 2020; Schwarz *et al.*, 2009a). A Waters Acquity UPLC instrument equipped with a PDA detector and an Acquity UPLC C18 BEH column, 100 × 2.1 mm (i.d.) with 1.7 µm particle size (Waters Corporation, Milford, MA, USA) was used. Seven phenolic acids (caffeic acid, p-coumaric acid, ellagic acid, gallic acid, protocatechuic acid, syringic acid, vanillic acid), four phenolic aldehydes (coniferaldehyde, sinapaldehyde, syringaldehyde and vanillin) and three furanic aldehydes (5-hydroxymethylfurfural, 5-methylfurfural and furfural) were identified.

The samples and the standards were filtered through nylon membranes with a pore size of 0.22 µm prior to injection. The compounds were identified by comparison of their retention times and the UV-Vis spectra of the samples and the standards used. The calibration curves obtained covered the range from 0.1 mg/L to 20.0 mg/L. The results are expressed as mg/L of 100 % vol. alcohol.

3.7. Sensory analysis

The sensory evaluations were conducted in a room that had a constant temperature of 20 ºC and was set up according to ISO 8589 (2007) to facilitate the concentration of the judges.

The tasting panel consisted of 7 judges who had previous experience working with aged wine spirits. Details regarding the selection of the descriptors of the samples and the training of the judges on using these descriptors with the aid of the reference standards have been published in previous articles (Guerrero-Chanivet *et al.*, 2022; Valcárcel-Muñoz *et al.*, 2022a; Valcárcel-Muñoz *et al.*, 2021b). The olfactory descriptors were aromatic intensity, fruity, vinous, vanilla, toasted, spicy and dried fruits. For the olfactory-gustatory evaluation, sweetness, alcoholic, smoothness, oak, balance and persistence were included.

For the descriptive evaluation, the 4 samples were presented to the judges in random order. During the tasting sessions, the reference standards for the different descriptors were available to the judges on request. The initial wine distillate and the Brandy de Jerez aged for 24 months were evaluated. In a preliminary session, a triangular test (ISO 4120, 2021) was carried out to evaluate whether any differences could be perceived between the samples. After verifying that there were no defects or significant differences between the two samples of each experiment, they were combined at the same ratio in a single sample (n = 1) 72 hours prior to tasting. The samples were diluted with demineralised water to 30 % ABV and rounded to 4g/L of inverted sugars using rectified grape-must concentrate (Guerrero-Chanivet *et al.*, 2022; Regulation (EU) 2019/787 European Parliament and Council of 17 April 2019, 2019). Ten minutes prior to the evaluation, 35 mL of each sample was poured into black wine glasses (ISO 3591, 1977), which were covered with a glass lid to stabilise their headspace. After the descriptive analysis, the judges were asked to rank the samples from lowest to highest in terms of olfactory quality (in correlation with their highest aromatic complexity and intensity), and also according to their olfactory-gustatory balance; i.e., overall mouthfeel that defines a well-structured Brandy de Jerez: full-bodied, with presence, rounded, no outstanding notes, no sharp edges, complex diversity of notes, containing well-integrated alcohol, no remarkable astringency or bitterness and a long aftertaste. Each judge evaluated each sample in duplicate.

3.8. Statistical analysis

The software package Statgraphics 18 (Statgraphics Technologies, Inc., The Plains, VA, USA) was used for ANOVA and PCA. Microsoft® Excel® version 2210 (Microsoft Corp., Redmond, WA, USA) was used for the rest of the statistical data management and to generate graphs.

Two-way Analysis of Variance with interaction (Judge x Sample) was applied for the treatment of the descriptive test data (ISO 13299, 2016) using the software application Statistica 8.0 (StatSoft Inc., Tulsa, OK, USA). Least Significant Difference (LSD) tests were applied to identify the different samples. The data from the ranking tests were processed according to the Friedman test, as prescribed by the preference ranking standard ISO 8587 (2006), by means of Excel 2016 (Microsoft Corp., Redmond, WA, USA), which was also used to produce the spider charts.

RESULTS AND DISCUSSION

In order to clearly display the differences in the physicochemical evolution of the three brandies of different alcoholic strengths in the study, the resulting data were standardised to litres of absolute alcohol.

1. Oenological control parameters

The evolution of the alcoholic strength of the Brandy de Jerez that had been aged for 24 months can be seen in Figure 1. An initial drop in alcoholic strength was observed in all three experiments, consisting in a more drastic fall in the first 4-6 months followed by a gradual decline until months 8 to 10. This reduction in alcoholic strength was due to two main factors: the dilution of the brandy with the Oloroso Sherry wine (18 % ABV) that had remained trapped in the wood after the seasoning procedure, and the losses in volatile compounds resulting from transpiration and evaporation from the casks. This reduction was more marked in the first 1-2 months of the ageing process, because during the filling of the casks evaporation had occurred due to the liquid's larger surface area being in contact with the air (Russell, 2003; Wang *et al.*, 2022). In addition, the initial contact with the seasoned wood may have produced a greater dilution effect than in the later months (8 to 10 months), after which a minimum alcoholic strength was reached, when both the liquid inside the wood and the ageing brandy seemed to have the same alcoholic strength. From that moment on, and as a consequence of the losses in volatile compounds by evaporation and the resulting higher concentration attributable to the phenomenon known as *merma* (transpiration of water through the wood pores), slight increases in alcoholic concentration occurred between the 12th and 24th months in all three experiments: around 0.20 % ABV in the 40 % ABV brandy and roughly 0.40 % ABV in the 55 % and 68 % ABV brandies. From these results it can be concluded that *merma* was favoured by the higher presence of water molecules in the 40 % ABV brandy, with easier transpiration of water through the wood pores, together with some volatile losses attributable to the evaporation of certain compounds, including ethanol, that took place in the casks.

The values for pH, total acidity and the volatile acids of the initial wine distillate and those corresponding to the Brandy de Jerez after 0.5, 12 and 24 months of ageing are given in Table 1.

The pH of the initial wine distillates decreased as the alcoholic strength dropped. The wine distillate at 40 % ABV showed a pH of 3.11, while the distillate at 68 % ABV had a pH of 5.01. The decreasing trend exhibited by the pH of hydrated distillates - which had a lower alcohol content - coincides with that observed in previous experiments (Valcárcel-Muñoz *et al.*, 2022a). During the ageing period, different trends were displayed by the 40 % ABV brandy to those exhibited by the 55 % and 68 % ABV brandies: with ageing, pH increased in the 40 % ABV brandy, reaching values of 3.41 after 24 months, while the pH of the 55 % and 68 % ABV brandies decreased. The latter fall in pH was more pronounced in the 68 % ABV distillate. These results coincide with the trends that had previously been observed in young brandies, with initial pH values of 4-5 decreasing as they aged (Bertrand, 2003; Valcárcel-Muñoz *et al.*, 2022a; Valcárcel-Muñoz *et al.*, 2021b). These changes in pH are attributable to the extraction and transformation of certain slightly acidic components intrinsic to ageing wood, like phenolic acids, of which mainly gallic and ellagic acid (Canas, 2017). Furthermore, in the particular case of the present experiments, the decreases in pH were mainly due to the transfer of organic acids (such as tartaric acid) originally provided by the Sherry wine used to season the Sherry Casks® (Sánchez-Guillén *et al.*, 2019). On the other hand, the trend of increasing pH observed in the 40 % ABV brandy might be due to the presence of certain metallic compounds in the medium, such as potassium, calcium or magnesium from the Sherry Cask®, which exert a certain buffering effect on the organic acids that are produced during ageing (Álvarez Batista, 1997).

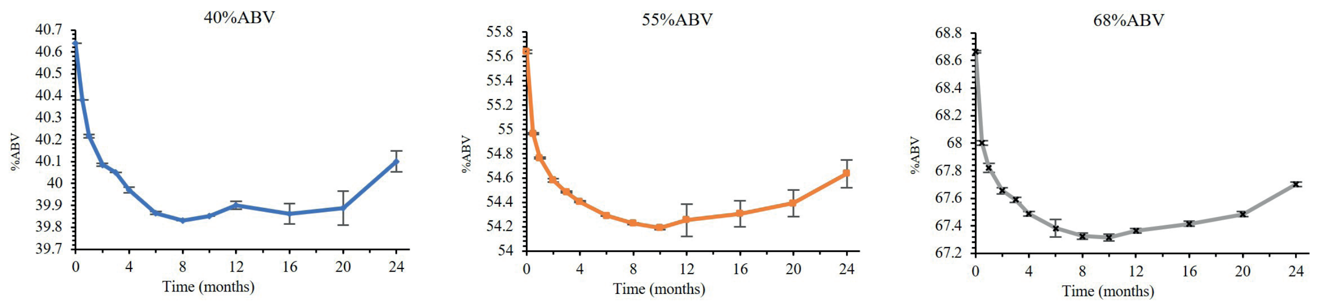

FIGURE 1. Evolution of the alcoholic strength of the brandies over 24 months of ageing in Sherry Casks®.

TABLE 1. pH, total acidity and volatile acids (g acetic acid/L of 100 % vol. alcohol) of brandies aged for 0.5, 12 and 24 months.

Ageing time (months)	UWD*	40 % ABV			55 % ABV			68 % ABV		
		0.5	12	24	0.5	12	24	0.5	12	24
pH	3.11 ± 0.10 (40 % ABV)	3.25 ± 0.05	3.32 ± 0.02	3.41 ± 0.05	-	-	-	-	-	-
	4.35 ± 0.01 (55 % ABV)	-	-	-	3.95 ± 0.00	4.11 ± 0.04	4.07 ± 0.04	-	-	-
	5.01 ± 0.01 (68 % ABV)	-	-	-	-	-	-	4.81 ± 0.49	4.42 ± 0.02	4.33 ± 0.02
Total acidity	0.06 ± 0.00 a	0.15 ± 0.00 a	0.92 ± 0.13 b, c	1.26 ± 0.21 d	0.10 ± 0.00 a	0.75 ± 0.02 b, e	0.96 ± 0.01 c	0.07 ± 0.00 a	0.51 ± 0.01 f	0.67 ± 0.00 e, f
Volatile acids	0.05 ± 0.00 a	0.10 ± 0.00 a	0.39 ± 0.03 b	0.62 ± 0.04 c	0.10 ± 0.00 a	0.24 ± 0.03 d	0.44 ± 0.05 c	0.07 ± 0.00 a	0.16 ± 0.02 e	0.29 ± 0.01 d

*UWD = Unaged wine distillate. Data are mean ± standard deviation (n=4); for a particular parameter, significant differences are indicated with different letters in the same row, according to Tukey HSD test ($p < 0.05$)

Total acidity increased with ageing for the three studied alcoholic strengths, with higher values at 24 months than at 12 months. Of the different alcoholic strengths, the acidity level of the 40 % ABV brandy was higher than that of the 55 % or 68 % ABV brandies, a trend that is consistent with the literature (Álvarez Batista, 1997; Valcárcel-Muñoz *et al.*, 2022a). After 24 months of ageing, the 40 % ABV brandy showed a total acidity of 1264 mg/L of 100 % vol. alcohol, while the 55 % ABV and 68 % ABV brandies showed acidity levels of 955.4 and 673.5 mg/L of 100 % vol. alcohol respectively.

The same trend that had been observed for total acidity was also observed for volatile acids; i.e., they increased with ageing in all three experiments, with higher values being registered for the lower alcoholic strength brandies after 24 months of ageing: 721.9 mg/L of 100 % vol. alcohol in the 40 % ABV brandy compared to 480.4 and 399.2 mg/L of 100 % vol. alcohol in the 55 % and 68 % ABV brandies respectively (Table 1). This increase in volatile acids with ageing can be explained by several processes occurring during the extraction of compounds from the Sherry Casks®, such as acetic acid or lactic acid, and the reactions in which these compounds are involved (Álvarez Batista, 1997; Guerrero-Chanivet *et al.*, 2020; Valcárcel-Muñoz *et al.*, 2022a; Valcárcel-Muñoz *et al.*, 2021b).

2. Organic acids

The concentrations of all the organic acids increased with ageing (Figure 2): the highest initial content – along with some increases - were recorded in the 40 % ABV brandy, followed by the 55 % ABV and 68 % ABV brandies, which had the lowest content after the same ageing time. Given that tartaric, malic and succinic acids were not found in the initial unaged wine distillate, it can be concluded that the cause of their increase in concentration is exclusively due to the ageing process, and specifically to the compounds transferred to the brandy from the Sherry Casks® (Álvarez Batista, 1997; Valcárcel-Muñoz *et al.*, 2021b). Tartaric acid was the majority acid in the three experiments, as after 24 months of ageing it reached 700 mg/L and 200 mg/L of 100 % vol. alcohol in the 40 % and 68 % ABV brandies respectively.

Lactic and acetic acids, on the other hand, were present in the initial wine distillate and exhibited a similar increase during ageing. Lactic acid increased as a result of the contributions from the Sherry wine seasoning in the Sherry Casks® (Sánchez-Guillén *et al.*, 2019). Acetic acid proved to be the second most abundant organic acid, with up to 500 mg/L and 200 mg/L of 100 % vol. alcohol after 24 months in the 40 % and 68 % ABV brandies respectively. This increase can be explained by three factors: the contributions from the wine seasoning of the Sherry Cask® (Sánchez-Guillén *et al.*, 2019), the contributions by the wood itself of certain compounds extracted from degraded hemicellulose (Guerrero-Chanivet *et al.*, 2020; Tarko *et al.*, 2023), and oxidative reactions taking place between ethanol and/or acetaldehyde to form the acids (Valcárcel-Muñoz *et al.*, 2021b).

In general, the greater amounts of these organic acids in the brandies with lower alcoholic strength would be due to their higher solubility in water rather than in ethanol (Valcárcel-Muñoz *et al.*, 2022a). This would be consistent with the observations regarding total acidity and volatile acids as explained in the previous paragraphs.

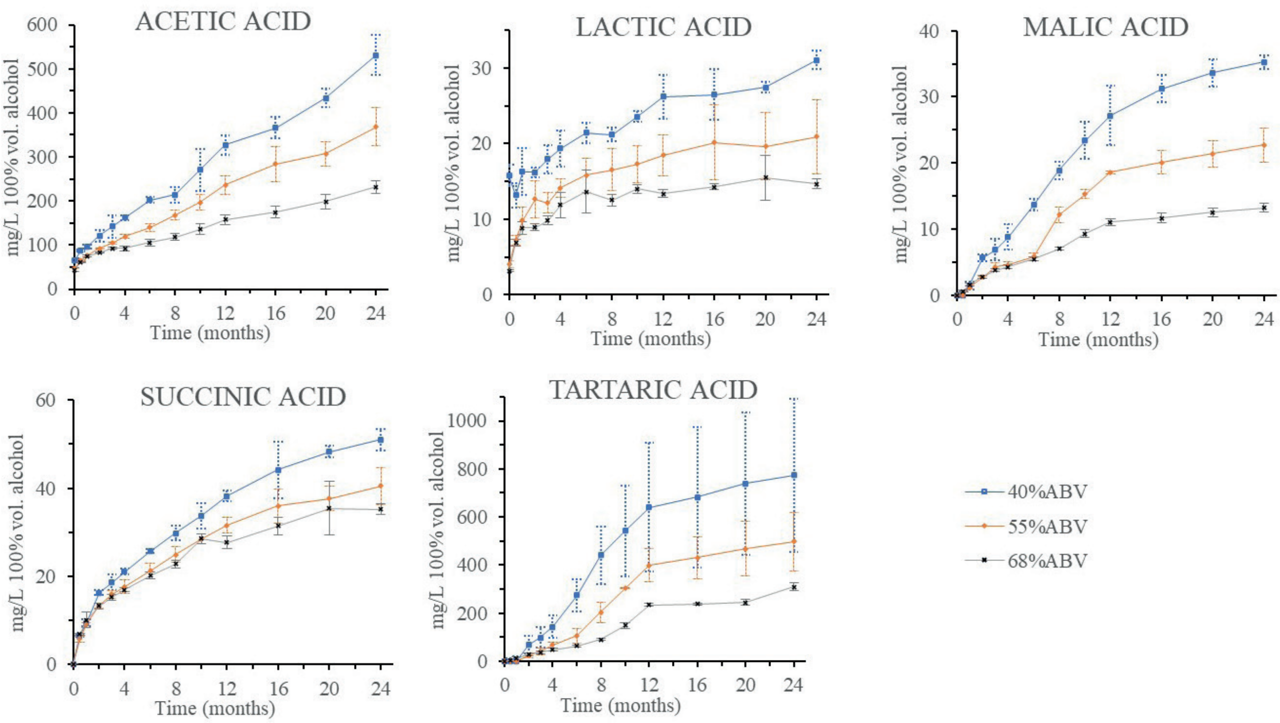

FIGURE 2. Evolution of organic acid content in the brandies attributable to the use of Sherry Casks® (□ = 40 % ABV; ♦ = 55 % ABV; X = 68 % ABV).

3. Volatiles

3.1. Total aldehydes, methanol

The content of total aldehydes (comprising acetaldehyde and its acetal, diethylacetal) in the Brandy de Jerez after 0.5, 12 and 24 months of ageing are shown in Table 2. In all three experiments, the same trend can be observed over the 24 months of ageing: total aldehydes increase with respect to the initial wine distillate. However, after 0.5 months of ageing of all three brandies, total aldehyde concentrations were not found to be significantly different from those in the initial wine distillate. When comparing the concentrations of total aldehydes in the brandies of different alcoholic strengths after 12 months of ageing, the 55 % and 40 % ABV brandies did not show any significant differences between them; meanwhile the 68 % ABV brandy exhibited lower values than 55 % ABV but was not significantly different to 40 % ABV. Furthermore, after 24 months of ageing, the 55 % ABV brandy had the highest concentration of total aldehydes, followed by the 68 % and 40 % ABV brandies in that order. These data indicate that equilibrium and synthesis reactions occurred as a result of the ethanol concentration and pH; for example, the formation of acetaldehyde from ethanol oxidation, were favoured in the 55 % ABV brandy. However, the 40 % ABV and 55 % ABV brandies did not show an increase in total aldehydes between the 12th and 24th month of ageing, as was the case for the 68 % ABV brandy. This could be explained by the fact that reactions involving aldehydes - mainly oxidation reactions of acetaldehyde into acetic acid - were favoured, resulting in a reduction in their concentration (Valcárcel-Muñoz *et al.*, 2021a).

It is worth noting that, since methanol is a volatile compound that comes from the wine distillate, its slight decrease in content during ageing is due to both the evaporation and formation of methyl acetate (Álvarez Batista, 1997). No significant differences in its concentration were observed between the different brandies aged at different alcoholic strengths (Table 2).

3.2. Higher Alcohols

Higher alcohols are volatile compounds that also originate from the wine distillation process (Awad *et al.*, 2017). As can be observed in Table 2, no major differences in content were observed between the three experiments.

The total concentrations of the higher alcohols in both the 40 % and 55 % ABV brandies decreased at the beginning of the ageing period (0.5 months) with respect to that of the initial wine distillates, after which they increased over the rest of the ageing period. Meanwhile, the total content of higher alcohols in the 68 % ABV brandy did not differ to that in the initial wine distillate until month 12, after which a decrease was observed until month 24. In the case of the 40 % and 55 % ABV brandies, lower total concentrations higher alcohols were observed throughout the whole ageing period than in the initial wine distillate, with the lowest values corresponding to the 40 % ABV brandy.

A detailed analysis of the data on the higher alcohols revealed that the 40 % ABV brandy contained lower concentrations of some of the compounds (N-propanol, 2-methyl-1-butanol and 3-methyl-1-butanol) after 0.5 months of ageing than the initial wine distillate. As already mentioned, this initial decrease may have been caused by the dilution of the compounds transferred by the seasoning Sherry wine to the ageing wood and that had remained attached to the wood until the casks were filled with the wine distillate. However, no significant differences were found in the concentrations of other higher alcohols (isobutanol, N-butanol, hexanol and 2-phenylethanol) between 0.5 months of ageing and the initial wine distillate. Some of them (N-propanol, N-butanol, 3-methyl-1-butanol and 2-phenylethanol) increased over the whole 24-month ageing period in the 40 % and 55 % ABV brandies. No clear trend in higher alcohol concentrations in the brandies was observed: their variation during the first 12 months of ageing was significantly influenced by the compounds that the seasoning Sherry wine had contributed. As already discussed regarding the different alcoholic strengths, all the wine distillates in the casks showed a certain homogeneity at 8-10 months of ageing. The slight variation that then takes place between the 12th and 24th month of ageing can be attributed to the evaporation of volatile compounds and/or a reduction in alcohol content as a result of the *merma* effect. As in the 40 % ABV brandy, a lower total higher alcohol content was found in the 55 % ABV brandy after just 0.5 months of ageing; however, it exhibited a greater higher alcohol content (N-propanol, 2-methyl-1-butanol and 3-methyl-1-butanol) during the first months of ageing, followed by minor variations between months 12 and 24 without any significant differences. Meanwhile, the higher alcohol content measured in the 68 % ABV brandy after 0.5 months of ageing remained constant throughout the 12- and 24-month ageing periods.

In general, for the same ageing time, significant differences in higher alcohol content were detected between the 40 % ABV brandy and the 55 % and 68 % ABV brandies, but not between the 55 % and 68 % ABV brandies.

3.3. Esters

The concentrations recorded for ethyl acetate, fatty acid ethyl esters and organic acid ethyl esters in the Brandy de Jerez aged for 0.5, 12 and 24 months are shown in Table 2.

Ethyl acetate is a volatile compound present in the initial wine distillate and its concentration increases with ageing (Valcárcel-Muñoz *et al.*, 2021b). This is due to the esterification of acetic acid; thus the higher the concentration of acetic acid in the medium, the higher the concentration of ethyl acetate will be. It was therefore observed in the three experiments that ethyl acetate concentrations increased with ageing, the values obtained at 24 months of ageing being higher than those at 12-months. Overall, for the same ageing time, no significant differences were found between the three alcoholic strengths studied.

Given that fatty acid ethyl esters come from the wine distillate and that they are found in very low concentrations,

TABLE 2. Concentrations of total aldehydes (acetaldehyde and diethylacetal), methanol, ethyl acetate, glycerol, 2,3-butanediol, higher alcohols, ethyl esters of fatty acids and ethyl esters of organic acids (mg/L of 100 % vol. alcohol) of brandies aged for 0.5, 12 and 24 months.

Ageing time (months)	UWD*	40 % ABV			55 % ABV			68 % ABV		
		0.5	12	24	0.5	12	24	0.5	12	24
Total aldehydes	265.0 ± 0.5 ^{a,b,c}	253.8 ± 8.8 ^{a}	293.7 ± 6.0 ^{d,e}	289.7 ± 12.5 ^{d,e}	260.6 ± 1.5 ^{a,b}	305.3 ± 12.6 ^{e,f}	315.2 ± 3.2 ^{f}	273.0 ± 3.0 ^{b,c}	277.5 ± 1.4 ^{c,d}	300.2 ± 1.1 ^{e}
Methanol	658.3 ± 1.4 ^{a}	626.2 ± 10.6 ^{b}	641.8 ± 3.5 ^{b}	637.2 ± 9.0 ^{c}	631.0 ± 3.6 ^{a}	648.1 ± 19.4 ^{b}	636.9 ± 2.4 ^{b,c,d}	654.2 ± 3.7 ^{c,d}	642.0 ± 1.3 ^{b}	628.4 ± 2.3 ^{c}
Ethyl acetate	208.0 ± 1.8 ^{a}	197.7 ± 5.6 ^{a}	286.8 ± 10.8 ^{b}	340.6 ± 29.7 ^{c}	205.4 ± 2.8 ^{a}	300.3 ± 19.6 ^{b}	367.6 ± 12.0 ^{c}	224.9 ± 1.4 ^{a}	288.6 ± 10.4 ^{b}	370.6 ± 15.1 ^{c}
Glycerol	n.d.	32.2 ± 10.4 ^{a}	475.6 ± 24.3 ^{b}	642.4 ± 36.5 ^{c}	25.5 ± 3.7 ^{a}	329.9 ± 7.0 ^{d}	395.3 ± 41.6 ^{e}	52.0 ± 11.0 ^{a}	271.5 ± 22.9 ^{f}	310.4 ± 15.9 ^{d,f}
2,3-Butanediol	n.d.	7.5 ± 0.3 ^{a}	41.5 ± 1.7 ^{b}	50.4 ± 3.8 ^{c}	5.8 ± 0.6 ^{a}	28.4 ± 0.8 ^{d}	34.9 ± 2.2 ^{e}	8.3 ± 0.4 ^{a}	27.7 ± 1.2 ^{d}	32.6 ± 1.2 ^{e}
					Higher alcohols					
N-Propanol	327.8 ± 1.2 ^{a}	316.0 ± 1.9 ^{b,c,d}	314.6 ± 1.8 ^{c,d,e}	308.0 ± 2.7 ^{e}	312.3 ± 2.0 ^{d,e}	323.1 ± 8.2 ^{b}	322.3 ± 2.6 ^{b}	326.3 ± 0.8 ^{a}	326.0 ± 0.5 ^{a}	322.6 ± 3.2 ^{a,b}
Isobutanol	343.4 ± 0.6 ^{a,b,c}	334.6 ± 1.9 ^{a}	334.8 ± 1.6 ^{a}	334.7 ± 4.0 ^{a}	335.9 ± 1.9 ^{a,b}	344.0 ± 9.3 ^{b,c}	344.2 ± 2.3 ^{b,c}	347.4 ± 4.0 ^{c}	348.2 ± 1.7 ^{c}	345.1 ± 2.2 ^{c}
N-Butanol	16.1 ± 0.3 ^{a,b}	14.4 ± 0.7 ^{a}	22.2 ± 1.8 ^{d,e}	22.9 ± 1.4 ^{e}	15.9 ± 1.5 ^{a,b}	19.4 ± 1.7 ^{c,d,e}	19.0 ± 2.3 ^{c,d}	16.0 ± 1.3 ^{a,b,c}	18.4 ± 1.0 ^{b,c}	18.0 ± 1.5 ^{b,c}
2-Methyl-1-butanol	415.5 ± 0.7 ^{a}	402.5 ± 2.2 ^{b}	403.3 ± 10.2 ^{b}	387.3 ± 3.2 ^{b}	397.7 ± 2.4 ^{b,c}	406.0 ± 10.2 ^{a,b}	405.5 ± 1.5 ^{a,b}	408.1 ± 2.2 ^{a,b}	404.5 ± 2.6 ^{a,b}	401.4 ± 3.7 ^{b}
3-Methyl-1-butanol	1928.4 ± 6.2 ^{a,b}	1874.6 ± 5.2 ^{c,d}	1889.3 ± 8.8 ^{b,c,d}	1863.2 ± 10.5 ^{d}	1868.7 ± 8.8 ^{c,d}	1927.8 ± 45.0 ^{a,b}	1923.2 ± 13.1 ^{a,b}	1938.7 ± 12.5 ^{a}	1935.8 ± 8.0 ^{a}	1906.4 ± 4.4 ^{a,b,c}
Hexanol	16.4 ± 0.2 ^{a,b}	16.1 ± 0.5 ^{b,c}	16.3 ± 0.1 ^{a,b,c}	17.3 ± 0.9 ^{a}	15.2 ± 0.9 ^{c}	15.8 ± 0.6 ^{b,c}	16.2 ± 0.1 ^{a,b,c}	15.7 ± 0.3 ^{b,c}	15.6 ± 0.2 ^{b,c}	15.7 ± 0.3 ^{b,c}
2-Phenyl ethanol	8.6 ± 0.2 ^{a}	10.2 ± 0.3 ^{a}	17.7 ± 0.6 ^{b}	20.3 ± 1.9 ^{d}	9.3 ± 0.7 ^{a}	16.1 ± 0.9 ^{b,c,d}	17.5 ± 2.5 ^{c,d}	9.9 ± 0.2 ^{b,a}	13.9 ± 0.3 ^{b}	14.9 ± 0.6 ^{b,c}
Total	3054.7 ± 6.8 ^{a,b}	2968.6 ± 9.7 ^{c,d}	2998.2 ± 18.3 ^{b,c,d}	2953.8 ± 14.1 ^{d}	2955.0 ± 11.4 ^{d}	3052.1 ± 72.1 ^{a,b}	3047.8 ± 17.6 ^{a,b}	3062.0 ± 19.2 ^{a}	3062.6 ± 11.4 ^{a}	3024.2 ± 9.9 ^{b,c}
					Ethyl esters of fatty acids					
Ethyl hexanoate	2.2 ± 0.1 ^{a,b,c}	2.0 ± 0.1 ^{b,d}	2.1 ± 0.1 ^{b,c,d}	2.3 ± 0.2 ^{a,b,e}	1.9 ± 0.1 ^{d}	2.3 ± 0.1 ^{a,b,e}	2.5 ± 0.2 ^{e,f}	2.3 ± 0.1 ^{a,b,e}	2.4 ± 0.1 ^{a,e,f}	2.7 ± 0.1 ^{f}
Ethyl octanoate	8.2 ± 0.1 ^{a,b,c,d}	7.9 ± 0.3 ^{c,d}	7.9 ± 0.1 ^{b,c,d}	8.5 ± 0.4 ^{a,b,c,e}	7.6 ± 0.3 ^{d}	8.8 ± 0.4 ^{a,e}	9.0 ± 0.3 ^{e,f}	8.5 ± 0.2 ^{a,b,e}	9.6 ± 0.1 ^{f,g}	10.0 ± 0.3 ^{g}
Ethyl decanoate	6.6 ± 0.0 ^{a}	6.0 ± 0.1 ^{b}	6.1 ± 0.2 ^{b}	6.6 ± 0.2 ^{a}	7.0 ± 0.1 ^{b,c}	7.3 ± 0.3 ^{c,d}	7.7 ± 0.2 ^{d,e}	7.7 ± 0.4 ^{d,e}	8.2 ± 0.3 ^{e,f}	8.3 ± 0.3 ^{f}
Ethyl dodecanoate	1.5 ± 0.2 ^{a,b}	1.1 ± 0.0 ^{a}	1.8 ± 0.1 ^{c,d}	2.3 ± 0.2 ^{e}	1.3 ± 0.1 ^{a,b}	1.8 ± 0.1 ^{c,d}	2.0 ± 0.1 ^{d}	1.4 ± 0.0 ^{a,b}	1.7 ± 0.1 ^{c}	1.8 ± 0.1 ^{c,d}
Ethyl tetradecanoate	0.4 ± 0.1 ^{a,b,c}	0.3 ± 0.0 ^{b,c}	0.2 ± 0.0 ^{d}	0.3 ± 0.0 ^{b,c,d}	0.3 ± 0.0 ^{b,c}	0.3 ± 0.0 ^{c,d}	0.3 ± 0.0 ^{a,b,c}	0.3 ± 0.0 ^{a,b,c}	0.4 ± 0.0 ^{b,c}	0.4 ± 0.0 ^{a}
Ethyl hexadecanoate	1.3 ± 0.2 ^{a}	0.7 ± 0.1 ^{b,c}	0.5 ± 0.0 ^{c}	0.6 ± 0.1 ^{c}	0.9 ± 0.1 ^{a,b}	1.2 ± 0.1 ^{a,c}	1.3 ± 0.1 ^{a}	1.4 ± 0.1 ^{a}	1.8 ± 0.2 ^{d}	1.9 ± 0.1 ^{d}
Ethyl octadecanoate	0.6 ± 0.0 ^{a}	0.4 ± 0.1 ^{a,b,c}	0.3 ± 0.0 ^{b,c,d}	0.3 ± 0.1 ^{b,c,d}	0.2 ± 0.0 ^{d}	0.3 ± 0.1 ^{c,d}	0.4 ± 0.1 ^{a,b,c}	0.5 ± 0.1 ^{a,b}	0.8 ± 0.1 ^{e}	0.8 ± 0.2 ^{e}
Total	20.3 ± 0.1 ^{a,b}	18.4 ± 0.8 ^{c}	18.9 ± 0.2 ^{c}	21.0 ± 0.6 ^{a,d}	19.2 ± 0.3 ^{a,c}	21.9 ± 0.7 ^{d,e}	23.2 ± 0.5 ^{e}	22.2 ± 0.5 ^{d,e}	24.9 ± 0.5 ^{f}	25.9 ± 0.6 ^{f}
					Ethyl esters of organic acids					
Ethyl lactate	68.9 ± 2.2 ^{a,b}	68 ± 1.4 ^{a,a,b}	71.6 ± 0.7 ^{b,c}	79.5 ± 4.5 ^{d}	64.5 ± 3.8 ^{a}	73.7 ± 0.9 ^{b,c,d}	77.0 ± 5.4 ^{c,d}	70.8 ± 1.9 ^{a,b,c}	73.0 ± 1.1 ^{b,c,d}	75.0 ± 2.0 ^{c,d}
Diethyl succinate	11.9 ± 0.4 ^{a}	13.6 ± 0.5 ^{a}	20.1 ± 0.3 ^{b}	24.4 ± 1.4 ^{c}	12.6 ± 0.8 ^{a}	19.2 ± 0.9 ^{b}	27.3 ± 2.8 ^{d}	13.9 ± 0.4 ^{a}	18.5 ± 0.5 ^{b}	21.1 ± 0.7 ^{b}
Diethyl tartrate	n.d.	2.6 ± 0.0 ^{a}	2.7 ± 0.0 ^{a}	5.4 ± 0.7 ^{a}	1.94 ± 0.0 ^{a}	16.4 ± 4.0 ^{b}	19.0 ± 3.7 ^{b}	1.57 ± 0.0 ^{a}	3.4 ± 0.1 ^{a}	3.8 ± 0.6 ^{a}
Diethyl malate	n.d.	0.7 ± 0.1 ^{a}	4.4 ± 0.1 ^{c}	6.0 ± 0.5 ^{d}	0.9 ± 0.1 ^{a}	4.3 ± 0.4 ^{c}	5.7 ± 1.0 ^{d}	1.1 ± 0.2 ^{a}	3.2 ± 0.2 ^{b}	4.2 ± 0.2 ^{c}

*UWD = Unaged wine distillate. Data are mean ± standard deviation (n=4); for a particular parameter, significant differences are indicated with different letters in the same row, according to Tukey HSD test ($p < 0.05$)

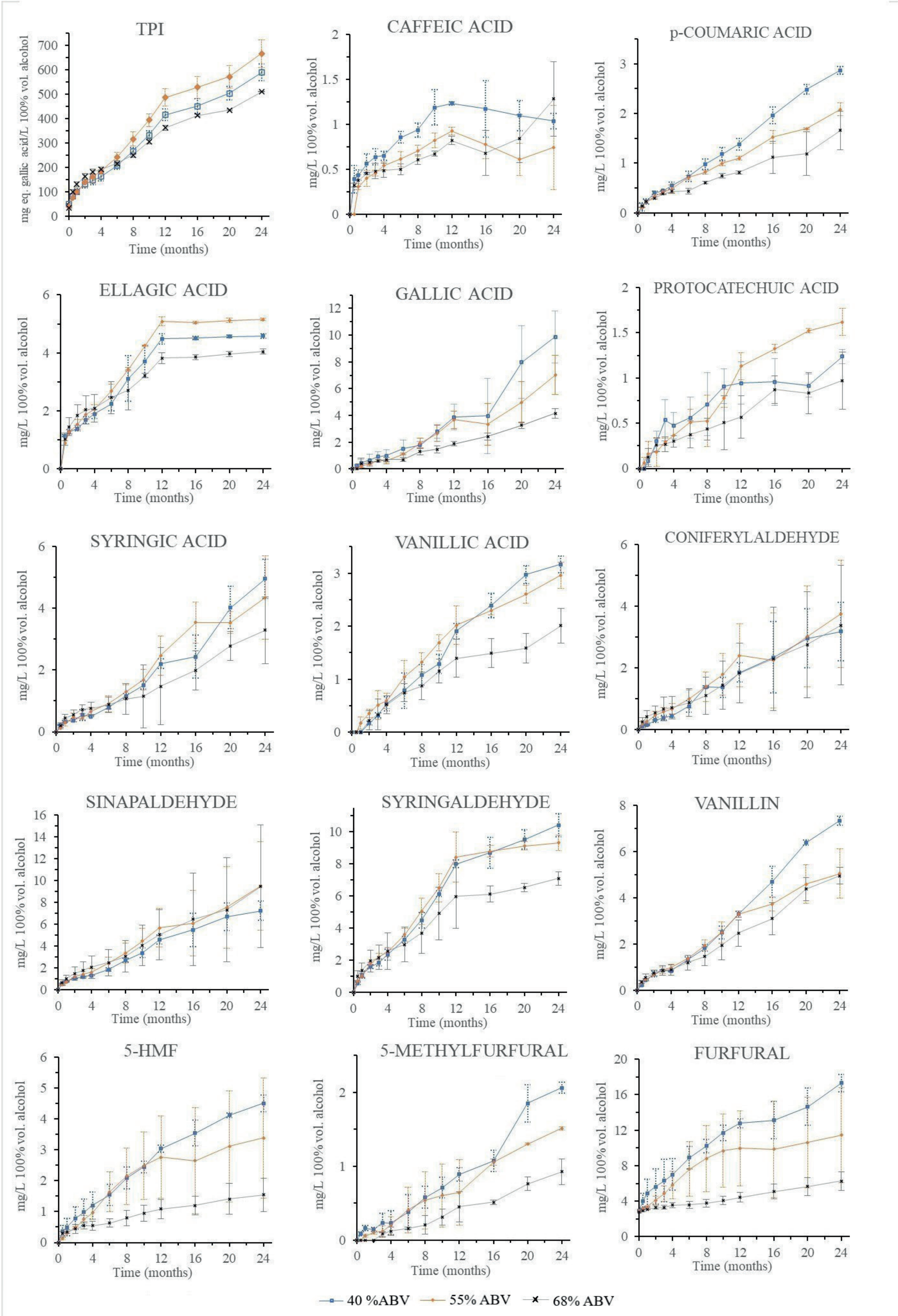

FIGURE 3. Evolution of Total Phenolic Index (TPI), phenolic compounds and furanic aldehydes in the brandies attributable to the usage of Sherry Casks®. (□ – 40 % ABV; ♦ - 55 % ABV; X - 68 % ABV).

they did not show any relevant evolution during the ageing of the brandies. In the 40 % and 55 % ABV brandies, the total content of fatty acid ethyl esters after 0.5 months initially decreased with respect to the initial wine distillate and then increased during the ageing period, the increase being more pronounced in the case of the 55 % ABV brandy. In general, when comparing the initial wine distillate with the brandies aged for 24 months, a slight increase was observed, especially in the 68 % ABV brandy, with a value of 25.9 g/L of 100 % vol. alcohol; meanwhile, values of 23.2 and 21.0 mg/L of 100 % vol. alcohol were recorded for 55 % ABV and 40 % ABV brandies respectively - just slightly higher than the initial 20.3 mg/L of 100 % vol. alcohol of the unaged wine distillate. This trend can be explained by the fact that higher alcohol solutions favour both the dissolution of fatty acid esters and a more pronounced *merma* phenomenon (Balcerek *et al.*, 2019; Puškaš *et al.*, 2013).

Organic acid ethyl esters increased in concentration during ageing, the highest values being recorded after 24 months for all the wine distillates. Ethyl lactate and diethyl succinate were found in the initial wine distillate, but their levels increased during ageing due to esterification reactions between their respective free acids and ethanol (Table 2). Diethyl tartrate and diethyl malate were not present in the wine distillate. Their formation was exclusively attributable to the ageing process in the Sherry Casks®, as esterification reactions involving ethanol and both tartaric and malic acid took place. After 24 months of ageing, the 55 % ABV brandy showed the highest concentrations of diethyl tartrate (19.0 mg/L of 100 % vol. alcohol), while the 40 % ABV and the 55 % ABV brandies had the highest concentration of diethyl malate (6.0 mg/L of 100 % vol. alcohol and 5.7 mg/L of 100 % vol. alcohol respectively). In general, the 40 % and 55 % ABV brandies did not differ significantly from each other and had slightly higher values than the 68 % ABV brandy. It should be noted that the hydrolysis and/or esterification equilibrium reactions involved in the formation of these compounds is determined by alcoholic strength, pH and the amount of acid involved (Valcárcel-Muñoz *et al.*, 2022a). For this reason, this trend agrees with the results related to organic acids, of which the 40 % ABV brandy had the highest values.

3.4. Glycerol and 2,3-Butanediol

Glycerol and 2,3-butanediol are compounds that result exclusively from the Sherry Cask® seasoning process, since they are not found in the wine distillate. As can be seen in Table 2, alcoholic strength has a strong influence on the amount of these compounds in the brandies. In general, higher concentrations were obtained in the brandies with lower alcohol content than in those with higher alcohol content. Glycerol varied significantly depending on the experiment, a higher value being obtained in 40 % ABV brandy (642.4 mg/L of 100 % vol. alcohol) than in 68 % ABV brandy (310.4 mg/L of 100 % vol. alcohol) after 24 months of ageing. In the case of 2,3-butanediol, there were no significant differences between the 55 % and 68 % ABV brandies, but both showed lower concentrations than the 40 % ABV brandy after the same ageing length.

4. Total Polyphenol Index, Phenolic Compounds and Furanic aldehydes

4.1. Total Polyphenol Index

The evolution of the Total Polyphenol Index (TPI) in the Brandy de Jerez over 24 months of ageing can be observed in Figure 3. As expected, TPI increased with ageing in the three experiments and in practically the same manner (Figure 3). The 55 % ABV brandy showed a greater increase of over 650 mg GAE/L of 100 % vol. alcohol after 24 months. Very similar values with no significant differences were recorded for the 40 % ABV brandy (590 mg GAE/L of 100 % vol. alcohol), while slightly lower values were obtained for the 68 % ABV brandy (510 mg GAE/L of 100 % vol. alcohol).

4.2. Furanic aldehydes

The evolution of 5-hydroxymethylfurfural (5-HMF), furfural and 5-methylfurfural in all three experiments over 24 months of ageing can be seen in Figure 3. Furfural is the only compound in this family that is found in the initial wine distillate (Awad *et al.*, 2017), and is also the one that increased the most with ageing, as it was transferred from the wood of the casks (Tarko *et al.*, 2023). When comparing all three experiments, the influence of alcoholic strength can be seen, with the highest concentrations of 5-hydroxymethylfurfural (5-HMF), furfural and 5-methylfurfural found in the 40 % ABV brandy and the lowest in the 68 % ABV brandy.

4.3. Phenolic composition

The evolution of the phenolic aldehyde concentrations in the Brandy de Jerez (vanillin, syringaldehyde, coniferylaldehyde and sinapaldehyde) is shown in Figure 3. As expected, the concentrations of these compounds increased with ageing in all the experiments, with no significant differences being observed between the alcoholic strengths studied, except for vanillin, which reached higher values in the 40 % ABV brandy. Sinapaldehyde and coniferaldehyde had been extracted directly from the wood, after the thermal degradation of its lignin, allowing in turn syringaldehyde and vanillin to be obtained from each of them respectively. These aldehydes can subsequently be oxidised to their respective phenolic acid. (Cernîşev, 2017; Tarko *et al.*, 2023; Viriot *et al.*, 1993).

The concentration of phenolic acids (gallic acid, protocatechuic acid, vanillic acid, syringic acid, caffeic acid, p-coumaric acid and ellagic acid) evolved in the Brandy de Jerez as shown in Figure 3. As with the other phenolic compounds, they increased with ageing, and their presence was exclusively due to the usage of Sherry Cask®, since these compounds were not present in the initial wine distillate; they are derived from the wood itself and also from the wine used for seasoning (Schwarz *et al.*, 2009b; Tarko *et al.*, 2023). Gallic acid, which is derived from the hydrolysis of the gallotannins extracted from the wood (Canas *et al.*, 2019; Viriot *et al.*, 1993), showed the greatest increase in the 40 % ABV brandy (10 mg L of 100 % vol. alcohol at 24 months), followed by the 55 % ABV brandy and then the 68 % ABV brandy (4 mg/L of 100 % vol. alcohol at 24 months). Meanwhile, ellagic acid, which results from the hydrolysis of ellagitannins (Tarko *et al.*, 2023), showed higher values in the 55 % ABV brandy (5 mg/L of 100 % vol. alcohol after 24 months) than in the 40 % and 68 % ABV brandies. The slight increase observed after 12 months can be explained by the use of used wood barrels. During the 3-year cask seasoning, the wine had extracted an initial amount of ellagic acid from the new wood. Later, in the first year of ageing of the distilled wine, a significant increase in ellagic acid in the brandy was observed, which did not continue in the second year of ageing; this is probably due to a certain reduction in this compound or its precursors in the wood, as reported in the bibliography (Viriot *et al.*, 1993)

The hydroxycinnamic acids, p-coumaric and caffeic acid, can come from either the Sherry wine used for the seasoning of the Sherry Casks® or the oak wood of the casks itself (Cernîşev, 2017; Schwarz *et al.*, 2009a; Tarko *et al.*, 2023; Zhang *et al.*, 2015). p-Coumaric acid followed the expected usual trend, increasing during the ageing process and showing the highest values in month 24 in all three experiments. In addition, the influence of alcoholic strength was observed, with the highest concentrations of this compound being recorded in the 40 % ABV brandy, followed by the 55 % and the 68 % ABV brandies. An increase in caffeic acid was observed until 12-16 months of ageing, especially in the 40 % ABV and 55 % ABV brandies; from then on, no significant differences were observed when compared to the samples that had been aged for 20 or 24 months.

Finally, syringic acid and vanillic acid, which are derived from the oxidation of syringaldehyde and vanillin respectively and are also directly extracted from the wood, also showed the expected trend (Cernîşev, 2017); i.e. both of them increased over the ageing process, especially in the 40 % and 55 % ABV brandies, in which the highest contents of these compounds were recorded. For both compounds, the concentrations recorded after 24 months of ageing represented almost half the level of their respective aldehydes; for example, syringaldehyde concentrations were 10 mg/L of 100 % vol. alcohol in the 40 % ABV brandy, 9 mg/L of 100 % vol. alcohol in the 55 % ABV brandy and 7 mg/L of 100 % vol. alcohol in the 68 % ABV brandy, while syringic acid concentrations were 5 mg/L of 100 % vol. alcohol in the 40 % ABV brandy, 4 mg/L of 100 % vol. alcohol in the 55 % ABV brandy and 3 mg/L of 100 % vol. alcohol in the 68 % ABV brandy. This may be due to the progress of the oxidation reaction of phenolic aldehydes and to the reaction of the acids with other compounds, such as in esterification, to form ethyl vanillate and ethyl syringate (Cernîşev, 2017).

4.4. Chromatic characteristics

Figure 4 shows the effect of alcohol content on the colour of the Brandy de Jerez during the ageing process in terms of CIELab values and the absorbances at 420, 470 and 520 nm expressed as units abs/L of 100 % vol alcohol.

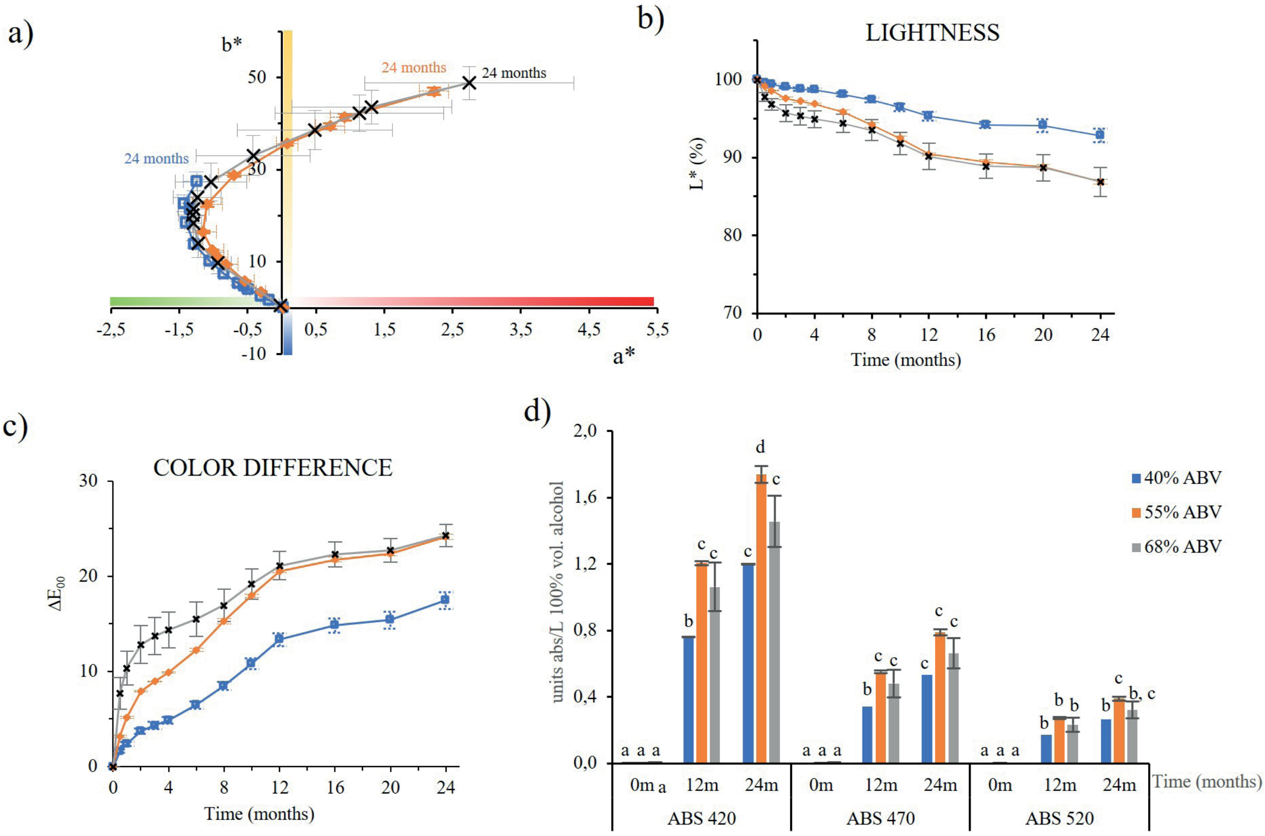

FIGURE 4. Evolution of CIELab values in the brandies according to their ageing alcohol strength: a) a* vs. b*; b) Lightness (%) and c) colour difference (ΔE00) (□ – 40 % ABV; ♦ - 55 % ABV; X - 68 % ABV) and d) absorbances at 420, 470 and 520 nm (units absorbance/L of 100 % vol. alcohol)

In all three experiments, the longer the ageing time, the higher the positive value of b* (blue-yellow hues); i.e., more yellow tones were obtained (García-Moreno *et al.*, 2020). The 55 % ABV and 68 % ABV brandies showed higher b* values than 40 % ABV brandy. Regarding the parameter a* (green-red hues) in the first months of ageing the brandies showed a trend of negative values, (green hues). However, after 10-12 months of ageing, a change in this trend was observed, especially in the 55 % and 68 % ABV brandies, with the a* value becoming positive (red hues). Slightly higher a* values were recorded for the 68 % ABV brandy.

Luminosity (L*) decreased over the ageing process, with lower percentages of luminosity being reached in the brandies after 24 months. No significant differences were detected between the 55 % and 68 % ABV brandies in terms of L*, while the 40 % ABV brandies showed higher values and less luminosity loss over the ageing process.

The colour variations of each brandy when compared to the initial wine distillate (ΔE_{00}) were higher during the first 10-12 months of ageing, after which, even though some chromatic changes continued to occur, they were not so marked. The highest values were recorded for the 55 % and 68 % ABV brandies, indicating that these wine distillates underwent the most significant chromatic changes.

The absorbance values of the brandies measured at 420, 470 and 520 nm increased with ageing. The 55 % and 68 % ABV brandies showed higher absorbance values than the 40 % ABV brandies after 12 months of ageing and at the three wavelengths. No relevant differences were detected between the 55 % and 68 % ABV brandies until after 24 months of ageing, when the 55 % ABV brandies showed the highest values, especially at 420 nm (which corresponds to yellow hues) and 470 nm (brown hues). For all three types of brandies, the values obtained at 520 nm (red hues) were the lowest, with the 55 % ABV brandy showing the highest values, while the 40 % and 68 % ABV brandies showed no relevant differences between them. The colour changes were due to the reactions between the compounds obtained both from the Sherry Casks® during ageing and from the wine distillate itself (Baldwin and Andreasen, 1974).

In general, these absorbance values agree with the observed TPI values (Figure 3). There was a significant increase in the first 10-12 months of ageing, followed by a slight increase from 12 to 24 months. The TPI values for all three experiments were similar at the beginning of ageing process, but at 24 months, the TPI of the 40 % and 55 % ABV brandies was higher than that of 68 % ABV. However, the absorbance values at 420 nm (yellow hues) were higher for 55 % ABV than for 40 % and 68 % ABV, and no significant differences were found at 470 nm and 520 nm.

5. Principal component analysis

To better understand the correlation between the alcohol content of the brandies and the evolution of their physicochemical parameters during 24 months of ageing in the Sherry Casks®, a Principal Component Analysis (PCA) was carried out. All the studied variables were analysed, except for the CIELab variables - because related variables were included (absorbances at 420, 470 and 520 nm and TPI) and they are not expressed in litres of 100 % vol. alcohol - as well as those not influenced by the ageing process, i.e. they are not correlated with ageing time ($p > 0.05$) (I-butanol, ethyl decanoate, ethyl tetradecanoate and hexanol). The analysis was carried out using 47 standardised variables, varimax rotation and eigenvalues greater than 1.0 as a factor selection criterion. Thus, 6 factors were found to meet this criterion, which in combination explained 90.48 % of the variability of the data.

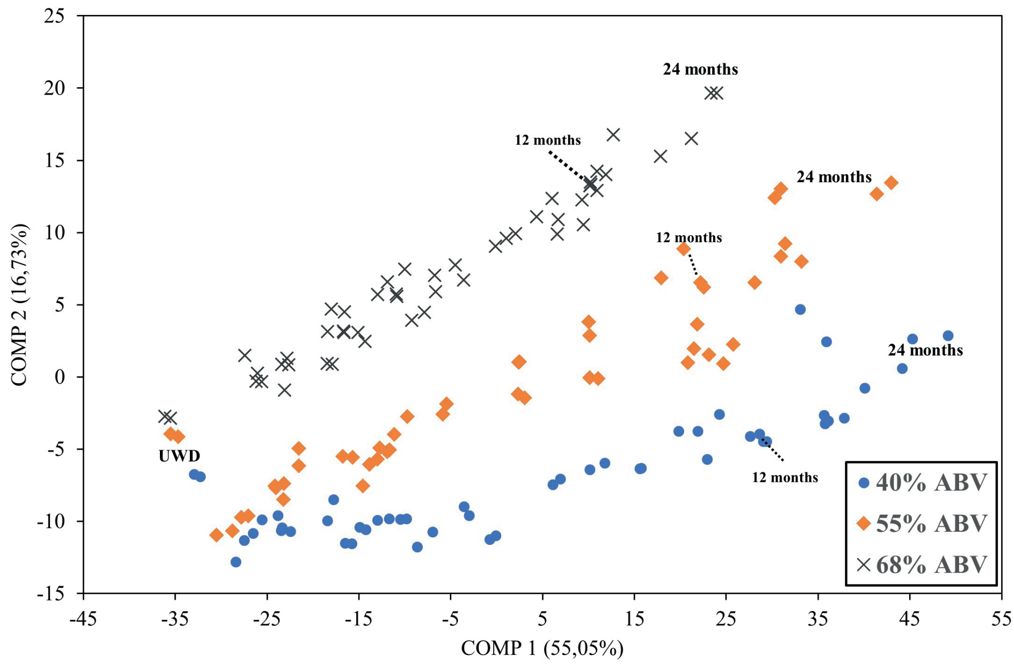

FIGURE 5. Graphical representation of the brandies on the plane formed by the two Principal Components, COMP-1 (55.05 %) and COMP-2 (16.73 %).

The distribution diagram of the Brandy de Jerez according to the two main components COMP-1 and COMP-2 is shown in Figure 5. Regarding COMP-1 (X-axis) the brandies are distributed from left to right with increasing ageing time. Meanwhile, COMP-2 (Y-axis) distributed the brandies according to their alcoholic strength, so that the 40 % ABV brandies are located mainly in the lower area, with negative values, while the 68 % ABV brandies are in the upper area.

Table 3 shows the weight of the components 1 and 2, but it only includes those with a coefficient r > |0.45| for both components; i.e., the most significant variables for each component. Component 1 is made up of all those variables that showed higher concentration levels or evolved positively during ageing, such as organic acids or their respective ethyl esters, as well as phenolic compounds or furanic aldehydes, among others. Component 2 has a close positive correlation with pH and fatty acid esters, both individually and in terms of the sum of their totals. This is due to the formation and stabilisation reactions which these compounds are involved in and which are largely dependent on the pH and alcohol content of the medium.

6. Sensory analysis

In order to confirm the homogeneity of the panel, a two-way analysis of variance (Judges x Samples) was performed on each of the descriptors (ISO 8587, 2006). As can be seen in Table 4, except for the p-value corresponding to the interaction between the factors associated with smoothness, the p-values were close to or greater than 0.05, allowing us to confirm that there were no significant differences attributable to the Judge factor or to its interaction with the Sample factor (pJudge and pJudge x pSample > 0.05). Table 4 also shows the mean scores awarded for each of the descriptors of the brandies by the tasting panel. The standard deviations were in all cases less than 2, which confirms the homogeneity of the panel.

The Analysis of Variance of the scores given to each sample indicates that ageing had a significant effect on almost all the descriptors, except for persistence in the mouth (pSample > 0.05).

In terms of olfactory, the unaged wine distillate had the lowest aromatic intensity, with an absence of vanilla, toast and dried fruit notes, as expected. It also had the lowest intensities for

TABLE 3. Principal Components 1 (COMP-1) and 2 (COMP-2) scores for the variables with high correlation (r > |0.45|).

Variables	COMP-1	COMP-2	Variables	COMP-1	COMP-2
2,3-Butanediol	0.912257		Ethyl octanoate		0.858956
2-Methyl-1-butanol			Furfural		-0.527033
2-Phenyl ethanol	0.868886		Gallic acid	0.775827	
3-Methyl-1-butanol			Glycerol	0.926554	
5-HMF	0.531812		Lactic acid	0.791316	
5-Methylfurfural	0.742035		Malic acid	0.930895	
ABS 420	0.672277	0.540258	Methanol		
ABS 470	0.667712	0.535073	N-Butanol	0.833506	
ABS 520	0.679494	0.511586	N-Propanol		
Acetic acid	0.941424		p-Coumaric acid	0.721694	
Total higher alcohols			pH		0.709072
Caffeic acid			Protocatechuic acid	0.45032	
Coniferylaldehyde			Succinic acid	0.879564	
Diethyl malate	0.876684		Sinapaldehyde		
Diethyl succinate	0.820977		Syringaldehyde	0.519925	
Diethyl tartrate			Syringic acid	0.600077	
Ellagic acid			Tartaric acid	0.890295	
Total ethyl esters of fatty acids		0.952065	Total aldehydes	0.577109	
Ethyl acetate	0.705596	0.540627	Total Acidity	0.93012	
Ethyl dodecanoate	0.769229		TPI	0.812288	
Ethyl hexadecanoate		0.91939	Vanillic acid	0.613875	
Ethyl hexanoate		0.777328	Vanillin	0.680022	
Ethyl lactate	0.632211		Volatile acids	0.934324	
Ethyl octadecanoate		0.792983			

TABLE 4. Scores awarded by the tasting panel.

Sample	40 % ABV	55 % ABV	68 % ABV	UWD*	P_{Judge}	P_{Sample}	$P_{Judge \times Sample}$
Aromatic intensity	6.5 ± 0.7^{b}	6.9 ± 1.0^{b}	6.3 ± 0.9^{a,b}	5.4 ± 1.5^{a}	0.055	0.034	0.268
Fruity	3.2 ± 1.2^{b}	3.0 ± 0.7^{b}	3.5 ± 0.5^{b}	5.5 ± 1.5^{a}	0.082	0	0.051
Vinous	6.5 ± 0.6^{c}	5.2 ± 0.9^{b}	4.7 ± 0.6^{b}	2.8 ± 0.9^{a}	0.705	0	0.050
Vanilla	6.3 ± 1.1d	5.4 ± 0.9^{c}	4.4 ± 1.2^{b}	1.1 ± 0.3^{a}	0.065	0	0.298
Toasted	5.0 ± 1.0^{c}	4.2 ± 0.9^{b,c}	3.5 ± 1.0^{b}	1.0 ± 0.0^{a}	0.043	0	0.412
Spicy	6.8 ± 1.3^{c}	4.4 ± 0.9^{a,b}	5.3 ± 1.7^{b}	3.5 ± 1.4^{a}	0.661	0.002	0.049
Dried fruits	3.8 ± 0.9^{b}	4.0 ± 0.0^{b}	3.2 ± 0.9^{b}	1.2 ± 0.5^{a}	0.392	0.006	0.963
Sweetness	2.5 ± 1.1^{a}	2.1 ± 0.6^{a}	2.3 ± 0.7^{a}	3.2 ± 0.9^{b}	0.091	0.021	0.062
Alcoholic	4.0 ± 0.9^{a,b}	4.0 ± 0.7^{a,b}	3.4 ± 0.5^{a}	4.6 ± 1.9^{b}	0.270	0.050	0.053
Smoothness	2.8 ± 0.9^{a}	3.5 ± 1.0^{a,b}	3.5 ± 1.3^{a,b}	4.5 ± 1.9^{b}	0.170	0.050	0.012
Oak	5.8 ± 1.5^{c}	5.8 ± 1.3^{c}	4.3 ± 0.8^{b}	1.0 ± 0.0^{a}	0.059	0	0.048
Balance	6.7 ± 1.1^{b}	5.7 ± 0.9^{b}	4.0 ± 1.4^{a}	3.0 ± 0.0^{a}	0.130	0.007	0.540
Persistence	5.7 ± 1.2	5.5 ± 1	5.3 ± 1	4.3 ± 1.7	0.047	0.112	0.053

*UWD = Unaged wine distillate. Mean ± standard deviation; P_{ANOVA}<0.05 indicates significant differences. Same letters indicate that the descriptors belong to similar groups (without differences in their intensities).

vinous and spicy notes and the highest for fruity aromas. Thus, cask ageing improved the aromatic intensity of the distillate and contributed vinous, vanilla, toasted, spicy and dried fruit notes to the brandy, although the effect of ageing alcoholic strength differed for each of these notes. After the ageing process, the fruitiness of the brandy decreased and the dried fruit notes increased to a similar degree and regardless of ageing time. The mean scores for vinous, vanilla and toast increased in the 68 % ABV brandy and to a greater degree in the 55 % ABV brandy, reaching the highest intensities in the 40 % ABV brandy. Nonetheless, only the vanilla notes were given significantly different scores depending on the brandy, while with respect to vinous and toast notes, only the 40 % ABV brandy was scored significantly higher than the 68 % ABV ones. Finally, the scores for the spicy notes were also significantly the highest for the 40 % ABV brandy, slightly lower for the 68 % ABV brandy and even lower for the 55 % ABV brandy, although the difference between the latter two was not significant. Generally, the brandy with the highest aromatic intensity (6.9) was the one that had been aged at 55 % ABV, even if the difference with the other two was not statistically significant.

On the palate, the aged brandies were perceived as being slightly less sweet and less alcoholic than the unaged wine distillate, as well as being slightly less smooth and better balanced, with more intense oak notes. As with the olfactory descriptors, the different olfactory and gustatory descriptors were directly affected by ageing time; thus, the alcohol content of the brandies did not influence how much the sweet notes had decreased after ageing. However, oak sensations and balance were significantly higher in the brandies aged either at 40 % ABV or 55 % ABV than in the one aged at 68 % ABV. The lowest alcoholic sensation was perceived in the brandy aged at 68 % ABV, although no significant differences were recorded.

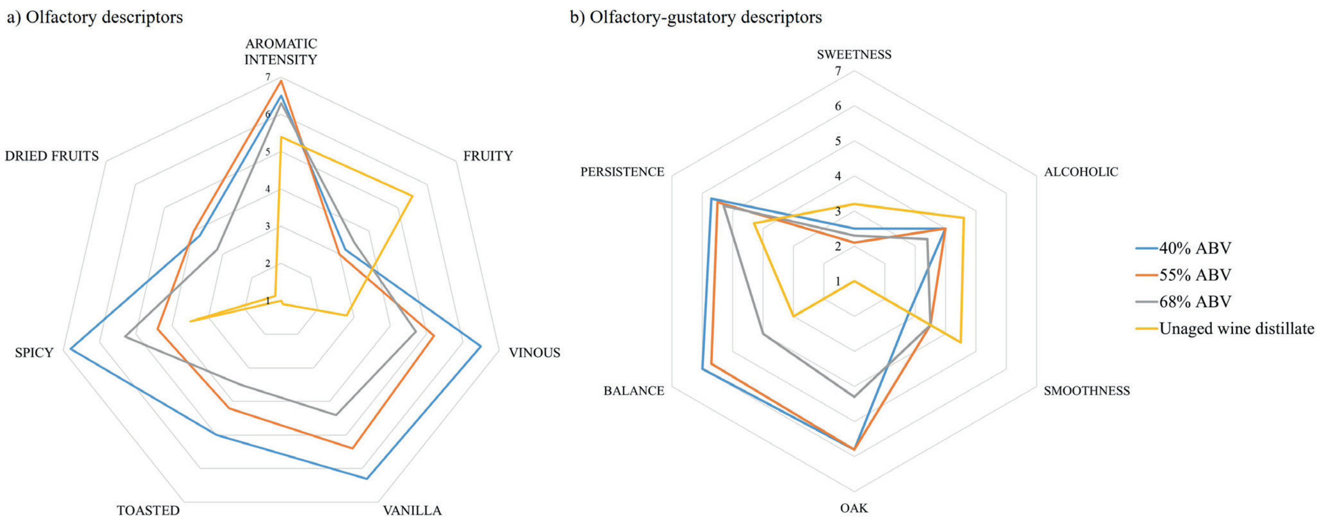

FIGURE 6. Spider graphs comparing the sensory profile of the unaged wine distillate with that of the brandies aged at different alcohol strengths.

As for smoothness, the 40 % ABV brandy was given a slightly lower score than the 55 % and 68 % ABV brandies, but again, the difference was not significant. Finally, the average persistence scores were also slightly higher for the aged brandies, although, as already mentioned, the differences with the unaged wine distillate were not significant. These profiles, which are represented in the spider graphs in Figure 6, are in agreement with the ranking that had been established previously.

In the ranking test based on olfactory quality criteria, the sums of the scores corresponding to each sample were: unaged wine distillate: 16; 40 % ABV: 33; 55 % ABV: 29; and 68 % ABV: 22. Calculated F (10.20) exceeded the critical value for 10 evaluations, 4 samples and 5 % error (7.67), thus confirming the significant differences found in one or more of the brandies. The least significant difference (LSD) test established a critical value of 11.32 for 10 evaluations, 4 samples and 5 % error that allowed differentiate between the brandies. Thus, the panel rated the 40 % ABV and 55 % ABV brandies as having a superior olfactory quality than the unaged wine distillate, but this difference was not confirmed regarding the 68 % ABV brandy.

According to the ranking established with regard to palate balance, calculated F was 13.44 and the total scores for each sample were: unaged wine distillate: 23; 40 % ABV: 43; 55 % ABV: 39; and 68 % ABV: 35. In this case, the panel confirmed that the ageing process had a clear positive effect on mouthfeel, but it was not able to discriminate the brandies according to their ageing times.

CONCLUSIONS

This study demonstrates the influence of alcohol content on the ageing of Brandy de Jerez in Sherry Casks®. In general, the brandies aged at lower alcoholic strength showed a greater evolution of their oenological parameters, such as total acidity or volatile acids, as well as of the compounds derived from both the wood, such as phenolic compounds or furanic aldehydes, and the Sherry wine used to seasoned the casks (organic acids and their corresponding ethyl esters, glycerol, and 2,3-butanediol). The highest TPI values were found in the 55 % ABV brandy. With regard to the brandies' volatile composition, after 24 months of ageing or longer, the concentration of higher alcohols decreased in the 40 % ABV brandy with respect to the initial content in the wine distillate. By contrast, the fatty acid ethyl esters increased slightly during ageing in the 55 % and 68 % ABV brandies, while the 40 % ABV brandy showed the lowest levels after 24 months of ageing due to their poorer solubility at lower concentrations of alcohol. A marked chromatic change to a^* (green-red hues) and b^* (blue-yellow hues) and ΔE_{00} was observed in the 55 % and 68 % ABV brandies, and even greater changes in the 55 % ABV brandies in terms of their absorbances at 420 nm (yellow hues) and 470 nm (brown hues).

These differences were revealed in the chemometric study of the Principal Components: three groups of samples were observed, which were differentiated by alcoholic strength and ageing time according to the first two principal components produced in the study.

In the sensory analysis conducted on the initial wine distillate and the brandies aged for 24 months after adjustment to 30 % ABV, the judges perceived the 40 % ABV and 55 % ABV brandies to have better sensory characteristics than the 68 % ABV brandy and that the differences between the 40 % ABV and the 55 % ABV brandies were better perceived via smell than taste.

This study confirms that the physicochemical and sensory profile changes that take place in Brandy de Jerez aged in Sherry Cask® are significantly influenced by the alcohol strength of the wine distillate being aged.

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