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Influence of alcoholic strength on the characteristics of Brandy de Jerez aged in *Sherry Casks*®

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ABSTRACT

Brandy de Jerez is produced by ageing wine distillates in casks that have previously contained Sherry wine. A *Criaderas and Solera* system is used according to the corresponding Technical File. However, the alcohol content of the distillate that is subjected to ageing is not specified, even if this is a factor that affects both brandy quality and production costs. This paper studies the influence that alcohol content has on the physicochemical and sensory characteristics of aged Brandy de Jerez. Six Criaderas and Solera systems have been characterised with alcoholic strengths between 65% and 80% ABV. The brandies with 65% ABV showed a higher concentration of the polyphenolic compounds extracted from the wood and from the wine used to season the casks, and also a higher colour intensity. In addition, these brandies were preferred by the tasters and were granted better scores for the descriptors that characterize Brandy de Jerez.

1. Introduction

The Technical File for the Geographical Indication Brandy de Jerez defines this product as a spirit beverage obtained from wine distillates and spirits aged in wooden casks of less than 1000 L volume (Consejería de Agricultura Pesca y Desarrollo Rural, 2018) with a minimum alcohol content of 36% ABV (Alcohol by Volume), where commercial brandies exhibit between 36% and 45% ABV. During the ageing process of distilled beverages, a series of physicochemical and sensory changes take place, which are manifested by colour, flavour or aroma variations that improve the quality of the initial distillate (Canas, 2017; Mosedale, 1995). Such changes are influenced by several factors related with the nature of the ageing process and the characteristics of the wooden casks; such as botanical origin, volume, manufacturing process, toasting degree, previous usage (Canas, 2017; García-Moreno et al., 2020) and pre-treatments, such as the wine-seasoning process. In fact, the Brandy de Jerez must age in casks that have previously contained some type of Sherry wine (Fino, Oloroso, Pedro Ximenez, etc.). This Sherry-seasoning process gives rise to the so-called Sherry Casks® (Consejería de Agricultura Pesca y Desarrollo Rural, 2018; Especificación técnica de envinado de vasijas, 2017). The characteristics of Sherry Casks® depends on the Sherry wine that they have previously contained and, during brandy ageing, they contribute to the brandy, not only with the compounds inherent to the cask wood, but also with those from the wine they initially contained and that were retained in the wood's pores (Sánchez-Guillén et al., 2019). The ageing method is another important factor, since Brandy de Jerez undergoes a dynamic ageing process by which brandies with different ageing times are blended in the casks as they pass from one into another according to their ageing scale, thus achieving a final commercial product with a uniform ageing time. The organoleptic characteristics and the quality of Brandy de Jerez, that differentiate it from other related beverages, are due to its special method of elaboration.

The traditional dynamic ageing system, characteristic from the Sherry area, is known as Criaderas and Solera. This system involves periodic removal of part of the brandy contained in each of the oak casks

Abbreviations: ABV, Alcohol by Volume; 1-CRA, 1st Criadera; 2-CRA, 2nd Criadera; n.d., not detected; OIV, International Organization of Vine and Wine; REP, Replenishment with unaged distillate; SM, Supplementary Material; SRA, Solera.

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that make up the same ageing scale followed by the corresponding replenishment with the brandy removed from the next ageing level (Regulation (EU) 2019/787 European Parliament and Council of 17 April 2019, 2019, Sherry Wines web site, 2022).

Each ageing scale is made up of a number of oak casks containing brandy with the same ageing time. Each scale is known as Criadera, except for the final one, which is the oldest and is known as Solera.

This dynamic system operates as follows: a portion of the brandy contained in each of the casks that make up the Solera is removed for consumption, allowing some empty space in them. This empty space is filled with brandy from the casks on the next oldest scale, 1st Criadera. Then, the partial empty volume in the 1st Criadera is replenished with

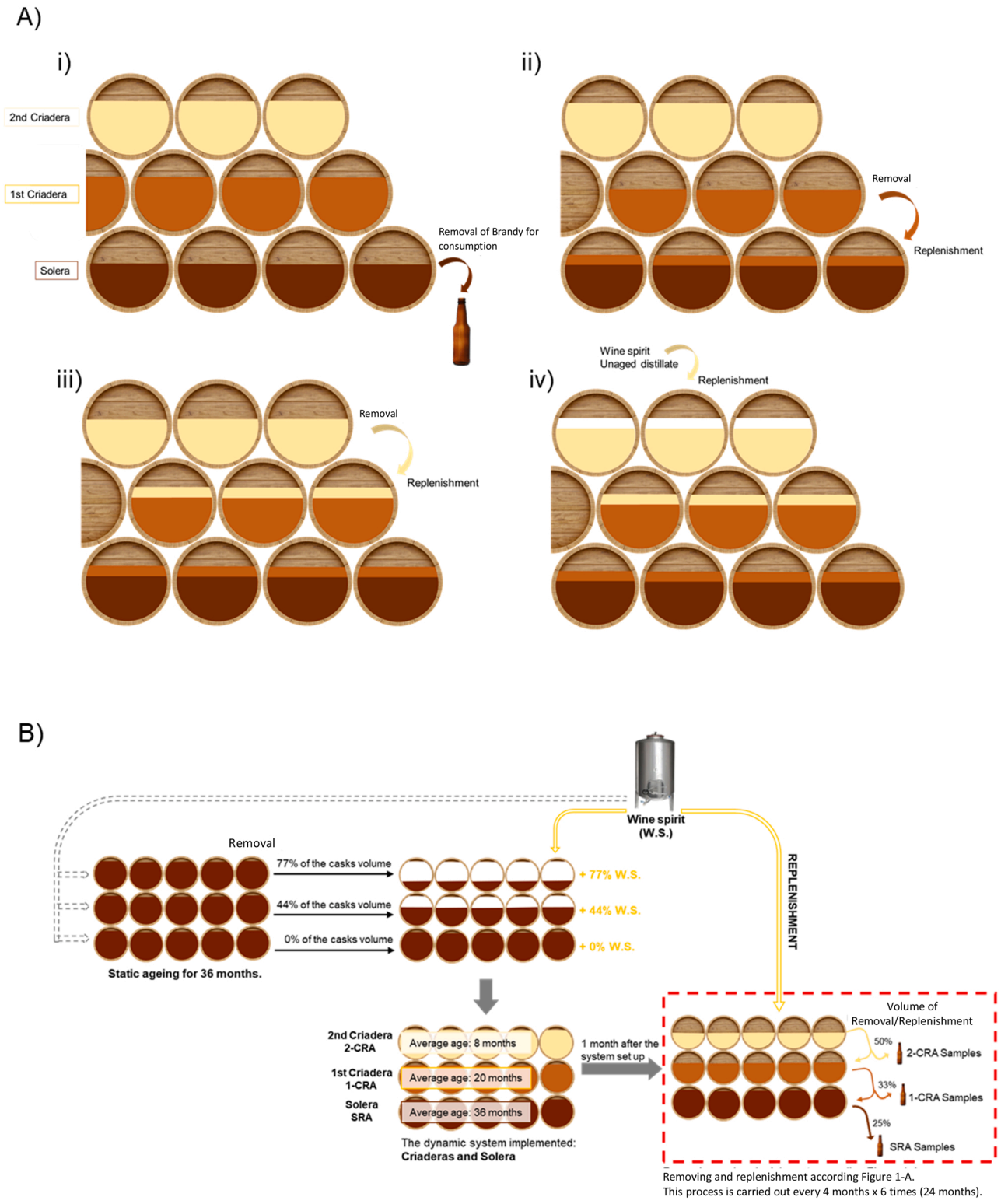

Fig. 1. A) Removal and replenishment operations in a *Criaderas and Solera* system: a) Removal from *Solera* for bottling; b) Removal from *1st Criadera* and replenishment from *Solera*; c) Removal from the *2nd Criadera* and replenishment from the *1st Criadera*; d) Replenishment from the *2nd Criadera* with distillate to complete the *Criaderas and Solera* system; B) System of the *Criaderas and Solera* system being studied.

brandy from the 2nd Criadera, and this process is repeated until the youngest tier casks are reached. These are replenished with unaged wine distillate (Fig. 1-A).

The average age of an ageing scale is defined as the ratio between the total volume of brandy contained in that scale and the volume of the removals in one year (Regulation (EU) 2019/787 European Parliament and Council of 17 April 2019, 2019).

The Criaderas and Solera system allows the maintenance of the characteristics of the brandy in the Solera over the years avoiding the possible heterogeneities due to the origin of the distillate that is being aged.

Alcoholic strength of the distillate to be aged is an important factor to be considered in the process, as has been observed in previous studies of different beverages such as whisky or brandy among others spirits (Baldwin and Andreasen, 1974; Delgado-González et al., 2017; Mayr Marangon et al., 2021; Puech, 1984; Singleton and Draper, 1961). Traditionally, distillates are aged at between 50% and 70% ABV, although in some wineries it is aged at the alcoholic strength for consumption. Moreover, it is also known that such alcoholic strength not only influences the physicochemical evolution of the product, but also has a direct impact on the logistics of the winery. Thus, wine spirits intended for brandy production must be produced at less than 86% ABV, while wine distillates are produced at over 86% ABV and less than 94.8% ABV, provided that the latter do not exceed the maximum limit of 50% alcoholic strength in the finished product. In addition, the total coefficient of volatile substances constitute by ethyl acetate, aldehydes, higher alcohols and volatile acids, whose minimum levels in brandy are described by the European regulation (Regulation (EU) 2019/787 European Parliament and Council of 17 April 2019, 2019), and in the Brandy de Jerez regulation for its different categories (Consejería de Agricultura Pesca y Desarrollo Rural, 2018). Demineralised water is used to dilute the distillate and adjust the desired alcoholic strength from the ageing process. However, an ageing process where distillates of a higher alcoholic strength allows to obtain a greater volume of the final product (36% ABV) while a smaller number of barrels are required for the procedure. Barrels represent an immobilised asset for the wineries that directly affect facilities operability and work management. In other words, it has an impact on the production costs. However, despite its physicochemical, sensory and economic significance, only a few studies related with the influence of the alcohol strength on the extraction process during the ageing distillate can be found in the literature, and no studies in particular have been found to deal with the effect from the alcoholic content in the distillates that are aged through the traditional Criaderas and Solera system in Sherry Casks®.

This work tries to determine the influence that the different alcoholic strengths of distillates have on the physicochemical and sensory characteristics of Brandy de Jerez as it is aged through a Criaderas and Solera system. For that purpose, the behaviour of the Soleras and Criaderas in six different systems with alcoholic strengths between 65% ABV and 80% ABV have been evaluated.

2. Materials and methods

2.1. Distillates samples

In this work has been used an initial wine distillate, at 80.54% ABV, obtained by blending of two wine distillates, whose formulation was: 58% of pot-still wine spirit (70% ABV) and 42% of wine distillate obtained by a Coffey column still (94.7% ABV). This mixture was then diluted with demineralised water to reach the different alcoholic strengths to be tested: 80% ABV, 75% ABV, 72% ABV, 70% ABV, 68% ABV and 65% ABV. All the distillates used were obtained from Airén wines.

2.2. Establishment of Criaderas and Solera system

The brandies were aged in 600 litre capacity, medium toast, American oak (*Quercus alba*) casks, which had been seasoned by containing 18% ABV Oloroso Sherry wine for 12 years. The pot-still spirit, the wine distillate and the Oloroso wine used for the different experiments complied with the technical specifications established by the regulations governing Brandy de Jerez (Consejería de Agricultura Pesca y Desarrollo Rural, 2018; Regulation (EU) 2019/787 European Parliament and Council of 17 April 2019, 2019) and Sherry Casks® (Especificación técnica de envinado de vasijas, 2017). The distillates and the Sherry Casks® were supplied by Bodegas Fundador SLU., a Company affiliated to the Protected Geographical Indication Brandy de Jerez.

For each one of the six experiments a Criaderas and Solera dynamic system was set up. Each set of casks was made up of 15 units, arranged in three 5-cask layers according to the age of the brandy: two Criaderas and the Solera scale. A total of 90 casks were employed.

The 15 barrels that were initially used to start the Criaderas and Solera system were filled with the same unaged distillate, at a specific alcoholic strength level. The distillate from these barrels underwent static ageing for 36 months. After completing the first 36 months, the following operations were carried out (Fig. 1-B):

- The 5-cask group that made up the 2nd Criadera (2-CRA) were extracted 77% of the volume of the aged distillate they contained and were subsequently refilled with the same initial unaged distillate. In this way, the casks now would contain a distillate with an average ageing period of 8 months.
- The group of 5-cask that made up the 1st Criadera (1-CRA) had 44% of the volume of the aged distillate they contained extracted and were subsequently refilled with the same initial unaged distillate. In this way these casks came to contain a distillate with an average ageing period of 20 months.
- The last 5-cask group remained intact, representing the Solera (SRA), with an average age of 36 months.

These barrels were left to settle for a month before the first removal according to this dynamic ageing system was performed.

2.3. Criaderas and solera systems

The dynamic system implemented on each one of the 6 Criaderas and Solera systems that had been set up involves extracting part of the casks' content to be replenished with a distillate (either aged or unaged) according to the scale of the system. This process is carried out every 4 months, starting one month after the system has been set up, and as above mentioned, it has been continued for 24 months. Specific removal and replenishment procedures were performed as follows:

- First, 25% of the volume of the aged distillate was extracted from each of the 5 casks that made up the Solera in a particular system. The empty volume was filled with aged distillate from the 5 casks of the 1st Criadera.
- 33% of the distillate volume in each of the 5 casks that made up the 1st Criadera was extracted and mixed. This mixture was used to replenish the Solera casks that had been partially emptied. The empty volume in the 1st Criadera was refilled with aged distillate from the 2nd Criadera.
- From each of the 5 casks that made up the 2nd Criadera, 50% of its volume was extracted, and as in the previous case, a blend was formed with the content extracted from the five casks. It is with this distillate that the empty volume in the barrels of the 1st Criadera was replenished. The empty partial volume that was then available in the 2nd Criadera casks was filled up with the corresponding unaged distillate.

2.4. Sampling

During the 24 months of the study, every 4 months and just before proceeding with the removal and replenishment operations, 375 mL samples were taken from all 5 casks that set up each scale. In order to avoid any diversions, the five samples extracted from each scale in the same system were mixed into a single combined sample per scale and system.

A combined sample was obtained as a representative sample of the scale and thus avoid or reduce the variability that each barrel contributes individually.

In total, six combined samples were obtained from each ageing scale and system (n = 6), one combined sample every 4 months for 24-month study: six combined samples for Solera, six for 1st criadera and six for 2nd criadera which made a total of 18 samples for each system to be characterised. The unaged distillate was also sampled for analysis.

2.5. Solvents and reagents

To determine the Folin-Ciocalteau Index: ultrapure deionised water (EMD-Millipore, Bedford, MA, USA), Folin-Ciocalteau reagent, anhydrous sodium carbonate (ACS reagent) and gallic acid (certified reference material) as the calibration standard (Sigma-Aldrich, Saint Louis, MO, USA) were used. UHPLC-grade acetonitrile (PanReac, Barcelona, Spain), acetic acid (PanReac, Barcelona, Spain) and ultrapure deionised water (EMD-Millipore, Bedford, MA, USA) were used for the preparation of the UHPLC phases. The eluent preparation used to determine tartaric acid was made up of ultrapure deionised water (EMD-Millipore, Bedford, MA, USA); 0.2 N concentrated sulphuric acid (Sigma-Aldrich, Saint Louis, MO, USA, grade ACS reagent, 95.0–98.0%) and UHPLC-grade acetone (VWR-International, Radnor, PA, USA). Tartaric acid was supplied by PanReac (Barcelona, Spain, grade for analysis, 99%). All the other standards were supplied by Sigma Aldrich (Saint Louis, MO, USA) with different grades of purity depending on the compound: acetaldehyde – ACS reagent, ≥ 99.5%, acetaldehyde-diethylacetal ≥ 98.00% FG, ethyl acetate, puriss. p.a., ACS reagent ≥ 99.5% (GC), 1-butanol - ACS reagent, ≥ 99.4%, 2-butanol - anhydrous, 99.5%, isobutanol – 99.5%, 2-methyl-1-butanol - ≥ 99%, 3- methyl-1-butanol - reagent grade, 98%, 1-propanol - ACS reagent, ≥ 99.5%, 2-propanol - suitable for HPLC, 99.9%, 2-pentanol – 98%, ethyl hexanoate - ≥ 99% (GC), ethyl octanoate - ≥ 98%, ethyl decanoate - ≥ 99% (GC), ethyl dodecanoate - ≥ 98.0% (GC), ethyl tetradecanoate - 99% (GC), ethyl hexadecanoate - analytical standard ≥ 98.5% (GC), ethyl lactate - ≥ 98.5% (GC), ethyl undecanoate – 97%, diethyl succinate - ≥ 99% (GC), diethyl tartrate - ≥ 99%, glycerol - ≥ 99.5%, 2,3-butanediol – 98%, ellagic acid - ≥ 95.0% (HPLC), vanillic acid - ≥ 97.0% (HPLC), syringic acid - ≥ 95.0% (HPLC), vanillin - 97%, syringaldehyde - 98%, coniferaldehyde - 98%, sinapaldehyde - 98%, furfural - ≥ 98.5% (GC), 5-methylfurfural - ≥ 98% and 5-hydroxymethylfurfural - ≥ 99%.

2.6. Alcoholic strength, pH, dry extract, total acidity and volatile acids

Each parameter was determined according to the official method established by International Organization of Vine and Wine (OIV). The alcoholic strength (% ABV) was achieved by measuring the density of the distillate by means of a DMA-5000 densimeter (Anton-Paar, Ashland, OR, USA). The pH was determined using a pH-meter Basic-20 (Crison-Instruments, Barcelona, Spain). The dry extract was determined by gravimetry (International Organization of Vine and Wine, 2009a) and the results were expressed in g/L 100% vol. alcohol. Total acidity was determined by potentiometric titration at pH 7.5 (International Organization of Vine and Wine, 2009b) and expressed as mg acetic acid/L 100% vol. alcohol. The volatile acids were determined by means of a segmented flow analyser (AA3-HR Autoanalyzer, Seal-Analytical, Norderstedt Stadt, Germany) (Saris et al., 1970) and the results were expressed as mg acetic acid/L 100% vol. alcohol. All the analyses were conducted in duplicate. Nevertheless, the number of independent samples analysed is 6 (n = 6), since the results are expressed as the average data of the 6 combined samples obtained at the end of the 24-month study.

2.7. Tartaric acid

The tartaric acid was determined by ion chromatography, using a 930 Compact IC Flex (Metrohm, Madrid, Spain), equipped with a Metrosep Organic Acids column, whose dimensions were 250 × 7.8 mm with 9 μm particle size. The eluent used was a mixture of deionised water:acetone:sulphuric acid (84:12:4), pumped at a flow rate of 0.4 mL/min. The software used to acquire and process the data was MagicNet 3.3 (Metrohm, Madrid, Spain). The identifications were performed by comparing the retention time of the samples with that of the corresponding standard. The results have been expressed in mg/L 100% vol. alcohol. Standards and samples were injected in duplicate and the number of independent samples analysed is 6 (n = 6).

2.8. Aldehydes, acetal, higher alcohols, esters, glycerol and 2,3-butanediol

The aldehydes, acetal, higher alcohols, esters, glycerol and 2,3-butanediol were determined by GC-FID. An Agilent 7890B Gas Chromatograph (Agilent-Technologies, Santa Clara, CA, USA) coupled to a flame-ionisation detector was used for these analyses. The methodology used has been described in previous works by our research group (Valcárcel-Muñoz et al., 2021a). The samples were diluted in ultrapure deionised water at 40% ABV and all of them were injected in duplicate immediately after their preparation. The results have been expressed as mg/L 100% vol. alcohol.

The total aldehydes, quantified in mg acetaldehyde/L 100% vol. alcohol, were obtained from the sum of the concentrations of acetaldehyde and its acetal, acetaldehyde-diethylacetal, the latter being expressed as acetaldehyde (1 mg acetal equals 0.373 mg acetaldehyde).

The higher alcohols were defined as the sum of the concentrations of [1-butanol] + [2-butanol] + [isobutanol] + [2-methyl-1-butanol] + [3-methyl-1-butanol] + [1-propanol], expressed in mg/L 100% vol. alcohol.

The fatty acids ethyl esters were defined as the sum of the concentrations of [ethyl hexanoate] + [ethyl octanoate] + [ethyl decanoate] + [ethyl dodecanoate] + [ethyl tetradecanoate] + [ethyl hexadecanoate], expressed in mg/L 100% vol. alcohol.

2.9. Total polyphenol index (TPI)

The total content of phenolic compounds was determined through the Folin-Ciocalteau index, according to the method established by the OIV, measuring the absorbance at 750 nm (Singleton and Rossi, 1965) by means of a Lambda-25 spectrophotometer (Perkin-Elmer, Boston, MA, USA). The results from such analyses were expressed as mg gallic acid/L 100% vol. alcohol. For this purpose, a calibration curve of the gallic acid at a concentration range between 0 and 750 mg/L was realized and the R^2 obtained was 0.9998. The standards and the samples were analysed in duplicate the number of independent samples analysed is 6 (n = 6).

2.10. Phenolic and furfural compounds

The phenolic and furfural compounds were quantified by UHPLC following the methodology that had been previously developed by our research group (Schwarz et al., 2009; Valcárcel-Muñoz et al., 2021a). The equipment used to determine these compounds was a Waters Acquity UPLC equipped with a PDA detector and a 100 × 2.1 mm (i.d.) with 1.7 μm particle size Acquity UPLC C18 BEH column (Waters Corporation, Milford, MA, USA). Eight phenolic compounds (gallic acid, ellagic

acid, p-hydroxybenzaldehyde, vanillic acid, vanillin, syringic acid, syringaldehyde, sinapaldehyde and coniferaldehyde) and three furanic aldehydes (furfural, 5-methylfurfural and 5-hydroxymethylfurfural) were identified.

The samples and standards were filtered through 0.22 μm pore size nylon membranes and injected in duplicate. The compounds were identified by comparison of their retention times and the UV-Vis spectra of the sample and standards used. The calibration curves comprised the range 0.1–10.0 mg/L.

The results expressed in mg/L 100% vol. alcohol, for each family of polyphenolic compounds and furanic aldehydes identified, were obtained from the sum of the concentrations of the following compounds:

- ∑ Hydroxybenzoic acids: [gallic acid] + [ellagic acid] + [vanillic acid] + [syringic acid].
- ∑ Hydroxybenzaldehydes: [vanillin] + [syringaldehyde].
- ∑ Hydroxycinnamaldehydes: [coniferaldehyde] + [sinapaldehyde].
- ∑ Furfurals: [furfural] + [5-methylfurfural] + [5-hydroxymethylfurfural]

2.11. Chromatic characteristics

The colour of the samples was determined by measuring absorbance at 420 nm according to the official method established by the OIV (International Organization of Vine and Wine, 2009c) by means of a Lambda-25 spectrophotometer (Perkin-Elmer, Boston, MA, USA). In addition, the absorbance at 470 nm regarding the brown hue, because of its relevance in this type of samples, was measured also using the same equipment (Canas et al., 2019). All the results have been expressed in units Absorbance/L 100% vol. alcohol. All the measurements were performed in duplicate, the number of independent samples analysed is 6 (n = 6).

2.12. Sensory analysis

The tastings were carried out in a room with characteristics that facilitated the concentration and isolation of the assessors (ISO, 8589, 2007), who tasted in at individual tasting booths at a constant temperature of 20ºC. The tasting panel consisted of 7 assessors, including winery personnel who regularly work with this type of samples, and were trained in the specific sensory attributes to be evaluated according to the selection applied in a previous work (Valcárcel-Muñoz et al., 2021a). The 6 samples from the most aged scale, i.e. the *Solera*, where the brandy intended for consumption is delivered from, were tasted in duplicate. 72 h before the tastings, the samples were diluted using demineralised water and adjusted to 36% ABV (standard graduation for the commercial product). Ten minutes before the tasting, 50 mL of each sample were poured into black glass wine glasses (ISO, 3591, 1977) and covered with a glass lid to stabilize their headspace. The olfactory descriptors to be evaluated were aromatic intensity, fruity, vinous, vanilla, toasted/caramel, and spicy/aniseed; for the flavour evaluations, alcoholic, smoothness, oxidative sweetness, equilibrium, and oak were considered. All of these were scored according to a structured 9-point scale. After the descriptive analysis, the judges were requested to rank the 6 samples according to their overall quality by considering their highest aromatic intensity and complexity, and their proper equilibrium on the palate.

2.13. Statistical analysis

All the analyses were carried out in duplicate and the results were presented as the average of the 6 combined samples from each scale evaluated (n = 6). Before performing an analysis of variance, it was verified whether the data followed a normal distribution (Shapiro-Wilk W statistic and Kolmogorov-Smirnov test). Then, an ANOVA was applied to each parameter to determine if any relevant differences between the means could be observed. Finally, a Principal Component Analysis (PCA) was performed on all the variables considered for the 6 combined samples from each scale evaluated. Statgraphics-18 software package (Statgraphics Technologies, Inc., The Plains, VA, USA) was used for the ANOVAs and PCAs.

An analysis of variance of one and two factors was applied to process the sensory data from the descriptive tests (ISO 9, 1329, 2016), using Statistica 8.0 software (StatSoft Inc., Tulsa, OK, USA). The ranking-test data were processed by applying Friedman test, according to the standard (ISO, 8587, 2006).

Microsoft Excel-2016 (Microsoft Corp., Redmond, WA, USA) was used for the rest of the statistical parameters and graphs.

3. Results and discussion

The physiochemical results registered for the *Criaderas and Solera* systems have been presented according to their ageing scales to facilitate their comparison between similar scales with different alcoholic strengths.

The alcoholic strength of *Brandy de Jerez* for consumption ranges between 36% and 45% ABV. To clearly show the similarities and differences between the different systems with similar alcohol content in this study, the standardized results have been expressed as number of measurement units per litre of absolute alcohol.

3.1. pH, dry extract, total acidity, volatile acids and tartaric acid

The values of pH, dry extract, total acidity, volatile acids and tartaric acid established for the systems studied are shown in Table 1.

As can be observed, the pH values decreased slightly as the alcohol content also decreased, and for the same ageing system (equal alcohol content), it decreased with ageing. Thus, it is observed that in the younger ageing scales the pH values were around 4, while in the older scale it decreased to 3.7. These results are consistent with those found in the literature, where young brandies exhibit pH values between 4 and 5 and, as they age, they decrease to 3.5 (Bertrand, 2003; Valcárcel-Muñoz et al., 2021a). This pH drop is explained by the extraction and transformation of certain wood components (Canas, 2017) and to the transfer of acidic compounds from the wine used for the seasoning of the *Sherry Casks*® (Sánchez-Guillén et al., 2019).

The dry extract values obtained are exclusively attributable to the ageing process, since the initial distillate does not contain any compounds that contribute to this parameter at any quantifiable level. Therefore, the values determined for dry extract in the brandies provide us with direct information on the evolution undergone by the product because of the ageing process itself. As can be seen in Table 1, the dry extract values are higher in the samples from the systems with lower alcoholic strength levels (0.98 g/L 100% vol. alcohol in the 2-CRA and 2.95 g/L 100% vol. alcohol in the SRA of the system at 65% ABV vs. 0.59 g/L 100% vol. alcohol in the 2-CRA and 1.99 g/L 100% vol. alcohol in the SRA of the system at 80% ABV). Thus, for the same age scale, the systems with 80% ABV present lower dry extract values than those with 65% ABV, with a difference of 1 g/L 100% vol. alcohol between the oldest ageing scales (SRAs). One of the processes that leads to physicochemical changes in brandy during its ageing is the direct extraction of certain compounds from the casks' wood (Canas, 2017). Among these compounds that contribute to the dry extract are the wood's own compounds such as polyphenols, sugars and those contributed by the seasoning wine, such as tartaric acid, lactic acid, glycerol, etc. (Álvarez, 1997). These are, in general, more water-soluble compounds, which favours those aged distillates with lower alcohol content, and therefore with a greater water concentration, present higher values.

The total acidity values displayed the same behavioural pattern, so that in each system, the total acidity values increased with ageing time, being higher in the samples from the *Soleras* than in the 2-CRA (Table 1). Therefore, the samples from the systems with lower alcoholic strength

Table 1
Alcoholic strength (%ABV), pH, Dry extract (g/L 100% vol. alcohol), Total Acidity and Volatile Acids (mg acetic acid/L 100% vol. alcohol) and Tartaric Acid (mg/L 100% vol. alcohol).

	Alcoholic strength					
	80	75	72	70	68	65
REP - Wine Spirit						
Alcoholic strength	80.43 ± 0.04	75.22 ± 0.08	72.21 ± 0.07	70.12 ± 0.05	68.03 ± 0.04	65.03 ± 0.06
pH	4.14 ± 0.04^{a}	4.12 ± 0.03^{a}	4.11 ± 0.04^{a}	4.07 ± 0.03^{a}	4.05 ± 0.02^{a}	4.03 ± 0.04^{a}
Dry Extract	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total Acidity	302.0 ± 4.3^{a}	312.0 ± 5.8^{a,b}	318.0 ± 7.0^{b,c}	320.0 ± 6.7^{b,c}	326.0 ± 9.4^{b,c}	331.0 ± 5.6^{c}
Volatile Acids	112.0 ± 5.7^{a}	117.0 ± 4.5^{a,b}	122.0 ± 6.0^{a,b}	122.0 ± 3.4^{a,b}	125.0 ± 8.5^{a,b}	128.0 ± 7.6^{b}
Tartaric Acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2nd *Criadera*						
Alcoholic strength	80.00 ± 0.02	74.94 ± 0.11	72.07 ± 0.04	69.99 ± 0.06	67.98 ± 0.04	65.10 ± 0.03
pH	4.07 ± 0.02^{a}	4.04 ± 0.02^{b}	4.02 ± 0.02^{c}	3.98 ± 0.01^{d}	3.94 ± 0.02^{e}	3.93 ± 0.02^{e}
Dry Extract	0.59 ± 0.04^{a}	0.65 ± 0.05^{a}	0.72 ± 0.03^{b}	0.81 ± 0.04^{c}	0.88 ± 0.06^{d}	0.98 ± 0.07^{e}
Total Acidity	375.8 ± 9.8^{a}	393.0 ± 9.5^{b}	408.5 ± 7.8^{c}	422.5 ± 7.6^{d}	432.0 ± 8.2^{d}	452.7 ± 9.9^{e}
Volatile Acids	152.7 ± 6.6^{a}	160.0 ± 8.7^{a,b}	166.7 ± 7.2^{b,c}	172.8 ± 6.5^{c,d}	179.3 ± 4.2^{d}	187.0 ± 5.4^{e}
Tartaric Acid	39.7 ± 4.2^{a}	48.2 ± 4.3^{b}	55.3 ± 3.6^{c}	60.3 ± 5.6^{c,d}	65.3 ± 5.0^{d}	72.3 ± 5.6^{e}
1st *Criadera*						
Alcoholic strength	79.41 ± 0.03	74.54 ± 0.09	71.88 ± 0.05	69.81 ± 0.04	67.91 ± 0.05	65.19 ± 0.05
pH	3.98 ± 0.02^{a}	3.94 ± 0.02^{b}	3.91 ± 0.02^{c}	3.87 ± 0.02^{d}	3.87 ± 0.02^{d}	3.82 ± 0.02^{e}
Dry Extract	1.22 ± 0.04^{a}	1.41 ± 0.05^{b}	1.53 ± 0.07^{c}	1.64 ± 0.06^{d}	1.74 ± 0.06^{e}	1.88 ± 0.06^{f}
Total Acidity	465.3 ± 8.4^{a}	497.8 ± 8.4^{b}	532.3 ± 5.8^{c}	563.2 ± 12.5^{d}	590.7 ± 8.0^{e}	624.8 ± 8.0^{f}
Volatile Acids	194.5 ± 7.4^{a}	210.5 ± 6.2^{b}	227.0 ± 3.9^{c}	236.8 ± 4.3^{d}	245.3 ± 5.0^{e}	255.2 ± 9.5^{f}
Tartaric Acid	83.2 ± 5.2^{a}	107.0 ± 5.0^{b}	121.3 ± 5.2^{c}	131.2 ± 8.1^{d}	146.0 ± 7.4^{e}	162.5 ± 9.3^{f}
Solera						
Alcoholic strength	78.56 ± 0.06	73.99 ± 0.08	71.62 ± 0.07	69.55 ± 0.05	67.82 ± 0.05	65.32 ± 0.04
pH	3.87 ± 0.02^{a}	3.84 ± 0.02^{b}	3.80 ± 0.02^{c}	3.74 ± 0.02^{d}	3.76 ± 0.02^{e}	3.71 ± 0.02^{f}
Dry Extract	1.99 ± 0.06^{a}	2.22 ± 0.05^{b}	2.39 ± 0.10^{c}	2.58 ± 0.08^{d}	2.72 ± 0.12^{e}	2.95 ± 0.06^{f}
Total Acidity	559.7 ± 10.8^{a}	610.2 ± 11.6^{b}	650.2 ± 10.3^{c}	697.7 ± 14.5^{d}	730.5 ± 7.6^{e}	787.3 ± 7.1^{f}
Volatile Acids	251.2 ± 8.2^{a}	277.0 ± 10.2^{b}	298.7 ± 8.2^{c}	312.2 ± 5.9^{d}	327.5 ± 4.6^{e}	339.0 ± 5.7^{f}
Tartaric Acid	144.0 ± 6.4^{a}	176.3 ± 5.9^{b}	198.2 ± 6.6^{c}	223.7 ± 9.8^{d}	245.2 ± 11.7^{e}	280.2 ± 11.3^{f}

Mean values ± standard deviation (n = 6) are shown; ANOVA: different letters (a, b, c, d, e, f) indicate significant individual parameter differences ($p < 0.05$) between scales from different alcoholic strength systems; REP: Replenishment with unaged distillate. n.d., not detected.

presented higher acidity values than with a higher alcoholic strength. Thus, the lower alcoholic strength systems such as SRA-65% ABV showed a total acidity of 787.3 mg/L 100% vol. alcohol, while SRA-80% ABV just had a total acidity of 559.7 mg/L 100% vol. alcohol.

Similarly to the total acidity, the tartaric acid concentration of the samples also increased with the ageing time, and decreased with the distillate higher alcoholic strength. Thus, the tartaric acid concentrations were as follows: 280.0 mg/L 100% vol. alcohol in the SRA-65% ABV samples versus just 144.0 mg/L 100% vol. alcohol in the SRA-80% ABV samples. However, it is important to note that the initial distillate did not present any detectable tartaric acid content. The presence of this acid in the aged samples could be due to the previous seasoning of the wooden casks, i.e. the casks conditioning. This acid precipitates in the form of potassium and calcium salts during the cask preconditioning process and subsequently passes into the brandy during the ageing stage (Álvarez, 1997; Valcárcel-Muñoz et al., 2021b). The solubility of tartaric acid is greater in water with respect to ethanol; therefore, the lower the alcoholic strength of the distillate, the greater the amount of solubilized acid.

The concentration of the volatile acids follows the same behavioural pattern, which reinforces the observations that explain the increases in the total acidity of the samples from the systems with lower alcoholic content. Thus, the volatile acids presented a concentration of 339.0 mg/L 100% vol. alcohol in the SRA-65% ABV, while in the SRA-80% ABV they were only found at 251.2 mg/L 100% vol. alcohol. The increment of volatile acids contents during ageing is due to the extraction of compounds such as acetic acid from the wood (Guerrero-Chanivet et al., 2020), the lactic acid that are yielded because of the casks' preconditioning and the oxidation of the ethanol itself (Valcárcel-Muñoz et al., 2021a). Furthermore, many of these acids are involved in multiple processes that include their own evaporation, their concentration because of the transpiration of water through the wood pores or esterification reactions with ethanol that turn them into ethyl acetate, ethyl lactate, etc. (Canas, 2017; Valcárcel-Muñoz et al., 2021a).

3.2. Aldehydes, acetal and higher alcohols

As for acetaldehyde and its acetal (acetaldehyde-diethylacetal), there is a significant influence from the alcoholic strength on the balance between the two (Table 2 and Fig. 2-A). Thus, the samples from the 65% ABV system presented the highest acetaldehyde concentration values and the lowest of acetaldehyde-diethylacetal, while the samples from the 80% ABV system exhibited the opposite behavioural pattern. This is because the equilibrium reaction between acetaldehyde and acetaldehyde-diethylacetal is influenced by alcoholic strength and pH, so that the higher the hydration the more the equilibrium tends to cause the hydrolysis of the acetal into acetaldehyde and ethanol (Valcárcel-Muñoz et al., 2020c). On the other hand, the content value of the total aldehydes did not show any significant difference regarding the different alcoholic strengths. The small fluctuations were attributable to the volatility of these substances, which was compensated by their generating ethanol through an oxidative process. Comparing the values registered for these parameters between the different scales with the same alcoholic strength, we can see that there were practically no differences between them; therefore, no evolution of these parameters was observed over the ageing process in preconditioned casks, which is in agreement with the observations by (Valcárcel-Muñoz et al., 2021b). This behavioural pattern is the opposite to that observed in other alternative ageing systems such as micro-oxygenation (Rodríguez Madrera et al., 2013), where an evolution in the concentration of these compounds as the brandy is aged can be observed.

The content of higher alcohols did not significantly differ between samples with different alcoholic strength (Table 2). Nevertheless, slightly higher values were observed in the samples from 65% ABV with respect to those from 70% and 80% ABV. However, there were no relevant differences between the SRA samples from the 80% and 75%

Table 2
Acetaldehyde, Acetaldehyde-diethylacetal, Total Aldehydes, Higher Alcohols, Ethyl Acetate, Ethyl Lactate, Diethyl Succinate, Diethyl Tartrate and ∑Fatty Acids Ethyl Esters, 2,3-Butanediol and Glycerol (mg/L 100% vol. alcohol).

	Alcoholic strength					
	80	75	72	70	68	65
REP - Wine Spirit						
Acetaldehyde	105.0 ± 3.9^{a}	130.0 ± 4.9^{b}	145.0 ± 3.7^{c}	156.0 ± 5.9^{d}	163.0 ± 3.9^{e}	181.0 ± 4.6^{f}
Acetal[1]	515.0 ± 6.0^{a}	446.0 ± 6.2^{b}	415.0 ± 5.4^{c}	394.0 ± 5.9^{d}	360.0 ± 7.7^{e}	321.0 ± 5.8^{f}
Total Aldehydes	297.0 ± 4.0^{a}	296.0 ± 3.5^{a}	300.0 ± 4.7^{a}	303.0 ± 4.1^{a}	297.0 ± 4.5^{a}	301.0 ± 3.7^{a}
Higher Alcohols	1691.1 ± 8.6^{a}	1690.1 ± 10.4^{a}	1695.9 ± 5.6^{a}	1688.2 ± 10.4^{a}	1699.1 ± 14.2^{a}	1683.9 ± 15.4^{a}
Ethyl Acetate	394.2 ± 1.9^{a}	393.6 ± 1.9^{a}	395.1 ± 1.9^{a}	395.6 ± 1.9^{a}	397.4 ± 1.9^{a}	398.7 ± 1.9^{a}
Ethyl Lactate	134.5 ± 0.6^{a}	134.5 ± 1.6^{a}	134.5 ± 1.5^{a}	134.5 ± 1.7^{a}	134.5 ± 2.5^{a}	134.5 ± 2.0^{a}
Diethyl Succinate	8.1 ± 0.1^{a}	8.0 ± 0.1^{a}	8.3 ± 0.1^{a}	8.2 ± 0.1^{a}	8.0 ± 0.1^{a}	8.1 ± 0.1^{a}
Diethyl Tartrate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
∑Fatty Ac. Ethyl Esters	64.0 ± 0.5^{a}	64.6 ± 0.5^{a}	63.4 ± 0.5^{a}	63.8 ± 0.5^{a}	64.6 ± 0.5^{a}	64.3 ± 0.5^{a}
2,3-Butanediol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Glycerol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2nd *Criadera*						
Acetaldehyde	103.0 ± 3.8^{a}	127.7 ± 4.2^{b}	143.2 ± 3.7c	158.2 ± 3.8^{d}	165.7 ± 3.9^{e}	182.5 ± 5.3^{f}
Acetal[1]	510.3 ± 6.3^{a}	436.3 ± 6.9^{b}	408.5 ± 3.3^{c}	394.3 ± 6.3^{d}	367.3 ± 8.8^{e}	325.8 ± 8.0^{f}
Total Aldehydes	293.4 ± 4.3^{a}	290.5 ± 6.2^{a}	295.6 ± 4.5^{a,b}	305.3 ± 6.0^{c}	302.7 ± 7.1^{b,c}	304.1 ± 8.3^{c}
Higher Alcohols	1753.6 ± 14.3^{a}	1753.0 ± 9.5^{b}	1755.1 ± 8.6^{c}	1759.4 ± 16.9^{d}	1764.5 ± 14.5^{e}	1763.3 ± 17.2^{f}
Ethyl Acetate	421.8 ± 6.4^{a}	428.2 ± 6.6^{a,b}	432.8 ± 4.0^{b}	433.0 ± 6.8^{b}	440.5 ± 5.8^{c}	443.5 ± 7.2^{c}
Ethyl Lactate	138.2 ± 3.7^{a}	138.3 ± 2.5^{a}	138.0 ± 3.3^{a}	138.8 ± 2.6^{a}	138.7 ± 2.9^{a}	139.7 ± 2.6^{a}
Diethyl Succinate	10.1 ± 0.4^{a}	11.9 ± 0.5^{a}	12.1 ± 0.3^{a}	12.9 ± 0.7^{a}	13.1 ± 0.4^{a}	13.6 ± 0.5^{a}
Diethyl Tartrate	51.4 ± 2.8^{a}	58.3 ± 5.8^{b}	60.2 ± 6.7^{b}	72.5 ± 5.1^{c}	73.0 ± 4.2^{c}	82.5 ± 5.2^{d}
∑Fatty Ac. Ethyl Esters	66.1 ± 0.6^{a,b,c}	66.3 ± 0.7^{b,c,d}	65.6 ± 0.6^{a}	65.9 ± 0.6^{a,b}	66.8 ± 0.5^{c,d}	67.0 ± 0.6^{d}
2,3-Butanediol	7.2 ± 2.1^{a}	8.5 ± 1.9^{a,b}	8.7 ± 1.6^{a,b}	8.3 ± 1.4^{a,b}	8.2 ± 1.2^{a,b}	9.7 ± 2.5^{b}
Glycerol	29.7 ± 3.7^{a}	32.0 ± 4.2^{a,b}	31.5 ± 3.2^{a,b}	34.2 ± 3.3^{b,c}	36.5 ± 2.5^{c}	40.8 ± 3.5^{d}
1st *Criadera*						
Acetaldehyde	100.7 ± 3.1^{a}	125.8 ± 6.7^{b}	141.3 ± 4.4^{c}	157.5 ± 3.6^{d}	165.0 ± 5.0^{e}	184.7 ± 4.5^{f}
Acetal[1]	501.2 ± 4.5^{a}	430.7 ± 10.4^{b}	405.5 ± 4.3^{c}	389.3 ± 4.4^{d}	369.5 ± 9.9^{e}	328.8 ± 7.3^{f}
Total Aldehydes	287.7 ± 4.8^{a}	286.5 ± 10.5^{a}	292.6 ± 5.4^{a}	302.8 ± 5.1^{b}	302.9 ± 8.6^{b}	307.4 ± 7.2^{b}
Higher Alcohols	1793.7 ± 14.4^{a}	1793.4 ± 7.7^{a}	1796.4 ± 11.0^{a}	1805.1 ± 8.2^{a,b}	1820.1 ± 18.8^{b}	1817.8 ± 23.1^{b}
Ethyl Acetate	459.3 ± 7.2^{a}	478.7 ± 5.0^{b}	485.2 ± 4.5^{b,c}	489.3 ± 6.2^{c}	503.8 ± 7.2^{d}	510.2 ± 8.2^{d}
Ethyl Lactate	140.8 ± 3.4^{a}	141.7 ± 2.8^{a}	140.8 ± 2.9^{a}	142.5 ± 3.3^{a}	143.3 ± 2.8^{a}	144.5 ± 3.7^{a}
Diethyl Succinate	14.0 ± 0.4^{a}	15.3 ± 0.2^{b}	15.4 ± 0.2^{b}	16.9 ± 0.4^{c}	17.1 ± 0.4^{c}	18.7 ± 0.5^{d}
Diethyl Tartrate	95.5 ± 3.4^{a}	109.2 ± 9.9^{b}	111.5 ± 4.2^{b}	131.7 ± 5.0^{c}	130.3 ± 6.3^{c}	160.2 ± 8.3^{d}
∑Fatty Ac. Ethyl Esters	67.6 ± 0.5^{a,b}	68.1 ± 0.7^{b,c}	67.2 ± 0.6^{a}	67.7 ± 0.9^{a,b}	68.6 ± 0.8^{c}	69.5 ± 0.5^{d}
2,3-Butanediol	16.8 ± 2.6^{a}	17.2 ± 2.6^{a}	17.0 ± 2.4^{a}	19.0 ± 2.3^{a}	17.8 ± 2.0^{a}	22.5 ± 2.1^{b}
Glycerol	69.5 ± 4.5^{a}	76.3 ± 5.6^{b,c}	74.0 ± 4.1^{a,b}	81.8 ± 6.5^{c}	88.0 ± 4.4^{d}	97.8 ± 4.8^{e}
Solera						
Acetaldehyde	97.7 ± 3.1^{a}	124.0 ± 5.7^{b}	139.2 ± 4.0^{c}	160.3 ± 3.1^{d}	168.0 ± 5.4^{e}	188.0 ± 5.0^{f}
Acetal[1]	492.3 ± 6.2^{a}	428.7 ± 9.8^{b}	402.2 ± 5.8^{c}	396.8 ± 5.8^{c}	372.3 ± 8.8^{d}	332.3 ± 8.3^{e}
Total Aldehydes	281.4 ± 5.3^{a}	284.0 ± 8.8^{a}	289.2 ± 6.0^{a}	308.4 ± 5.0^{b}	306.9 ± 8.4^{b}	312.0 ± 7.7^{b}
Higher Alcohols	1850.6 ± 10.8^{a}	1849.5 ± 11.8^{a}	1858.4 ± 12.8^{a,b}	1870.8 ± 15.4^{b}	1894.2 ± 14.4^{c}	1894.3 ± 22.2^{c}
Ethyl Acetate	511.8 ± 5.7^{a}	545.8 ± 5.1^{b}	558.7 ± 4.6^{c}	569.5 ± 7.7^{d}	592.5 ± 6.8^{e}	605.0 ± 8.6^{f}
Ethyl Lactate	143.8 ± 3.1^{a}	144.3 ± 3.7^{a,b}	144.3 ± 3.7^{a,b}	146.2 ± 2.9^{a,b,c}	148.0 ± 3.6^{b,c}	149.8 ± 2.9^{c}
Diethyl Succinate	16.9 ± 0.5^{a}	18.6 ± 0.5^{b}	19.5 ± 0.4^{c}	20.7 ± 0.5^{d}	22.1 ± 0.5^{e}	23.6 ± 0.5^{f}
Diethyl Tartrate	143.0 ± 5.5^{a}	157.8 ± 10.9^{b}	177.2 ± 5.2^{c}	190.3 ± 6.7^{d}	202.8 ± 6.4^{e}	235.7 ± 7.2^{f}
∑Fatty Ac. Ethyl Esters	69.3 ± 0.8^{a}	69.6 ± 0.7^{a}	69.0 ± 0.6^{a}	69.8 ± 0.6^{a}	71.3 ± 1.0^{b}	71.9 ± 0.6^{b}
2,3-Butanediol	30.5 ± 4.3^{a}	31.0 ± 4.6^{a}	30.8 ± 4.2^{a}	34.7 ± 2.7^{a,b}	36.0 ± 3.0^{b}	41.3 ± 4.0^{c}
Glycerol	126.3 ± 8.5^{a}	130.8 ± 6.3^{a,b}	134.7 ± 2.3^{b}	148.5 ± 4.7^{c}	158.2 ± 6.1^{d}	178.7 ± 6.9^{e}

Mean values ± standard deviation (n = 6) are shown; ANOVA: different letters (a, b, c, d, e, f) indicate significant individual parameter differences ($p < 0.05$) between scales from different alcoholic strength systems; REP: Replenishment with unaged distillate. n.d.: not detected. [1]Acetal: Acetaldehyde-diethylacetal.

ABV systems or between the SRA samples from the 68% and 65% ABV ones. Because of the origin of these compounds, the increments that were observed in the older scales (SRA > 1-CRA > 2-CRA) can be attributed to the concentration process caused by the transpiration and evaporation of the water molecules that pass through the wood pores to the outside of the casks (Canas, 2017). Higher alcohols are volatile compounds that come from the distillate, as they appear in the distillate just after being produced by yeast metabolism during the vinification stage (Bortoletto and Alcarde, 2013).

3.3. Esters, glycerol and 2,3-butanediol

The esterification of the acetic acid explains the increment of ethyl acetate as the age of the brandies in the ageing scales increases (Table 2). Ethyl acetate was already obtained from the wine distillation process itself with values around 400 mg/L 100% vol. alcohol, which is in agreement with the figures reported in the literature (Tsakiris et al., 2014). These values rose in the 2-CRA up to 440 mg/L 100% vol. alcohol, to 510 mg/L 100% vol. alcohol in the 1-CRA and reached as much as 605 mg/L 100% vol. alcohol in the SRA-65% ABV. Regarding the systems with higher alcoholic content, the increment was not so noticeable, reaching just 512 mg/L 100% vol. alcohol in SRA-80% ABV (Table 2). Therefore, a considerable influence from the starting alcoholic strength of the systems was observed, which resulted in significant concentration differences between the different SRAs confirming the close correlation between volatile acids and ethyl acetate, (r = 0.996) (Fig. 3-A).

The esters of organic acids (ethyl lactate, diethyl succinate and diethyl tartrate) were detected at higher concentrations in the experiments with lower alcoholic strengths (Table 2). Ethyl lactate and diethyl succinate were already found in the distillate. The wine presents these compounds in its constitution and, in addition, in the distillation columns themselves some esterification with ethanol of the free lactic and succinic acids in the wines had occurred (Awad et al., 2017). They can

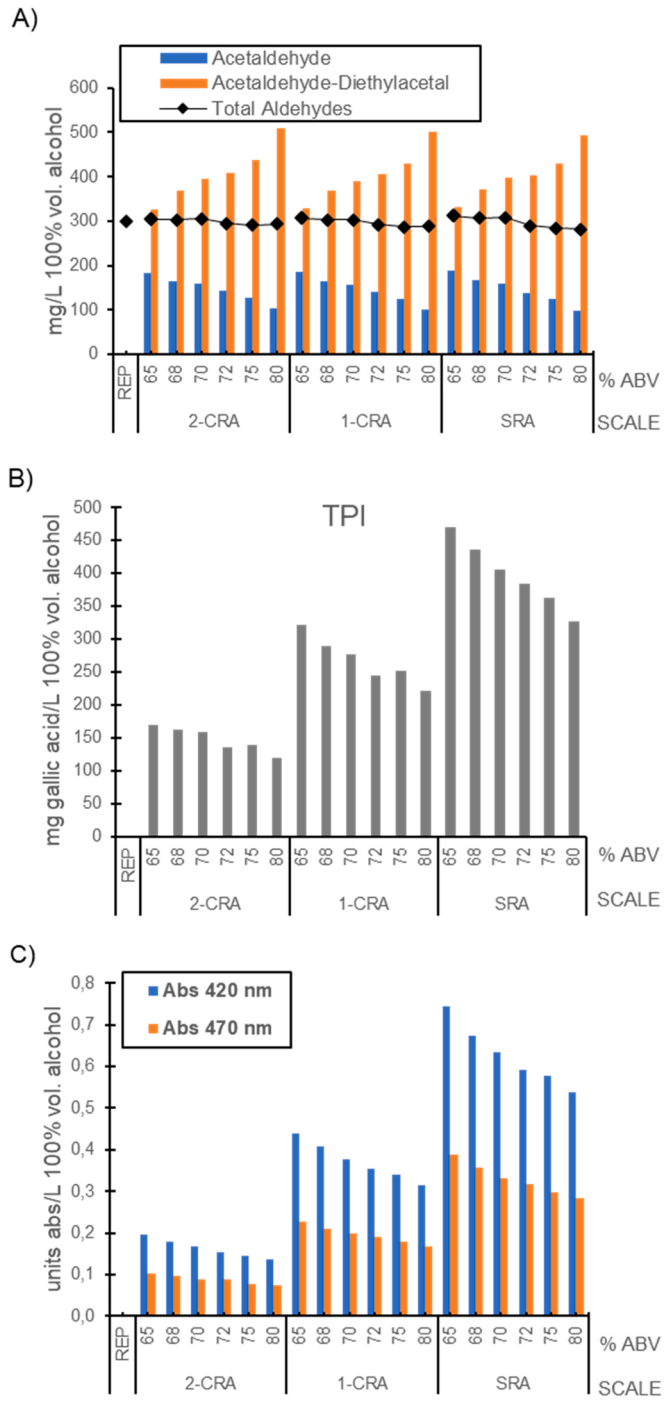

Fig. 2. A) Acetaldehyde, acetaldehyde-diethylacetal and total aldehydes; B) Total polyphenol index; C) Absorbance at 420 nm (A420) and at 470 nm (A470). Average value (n = 6).

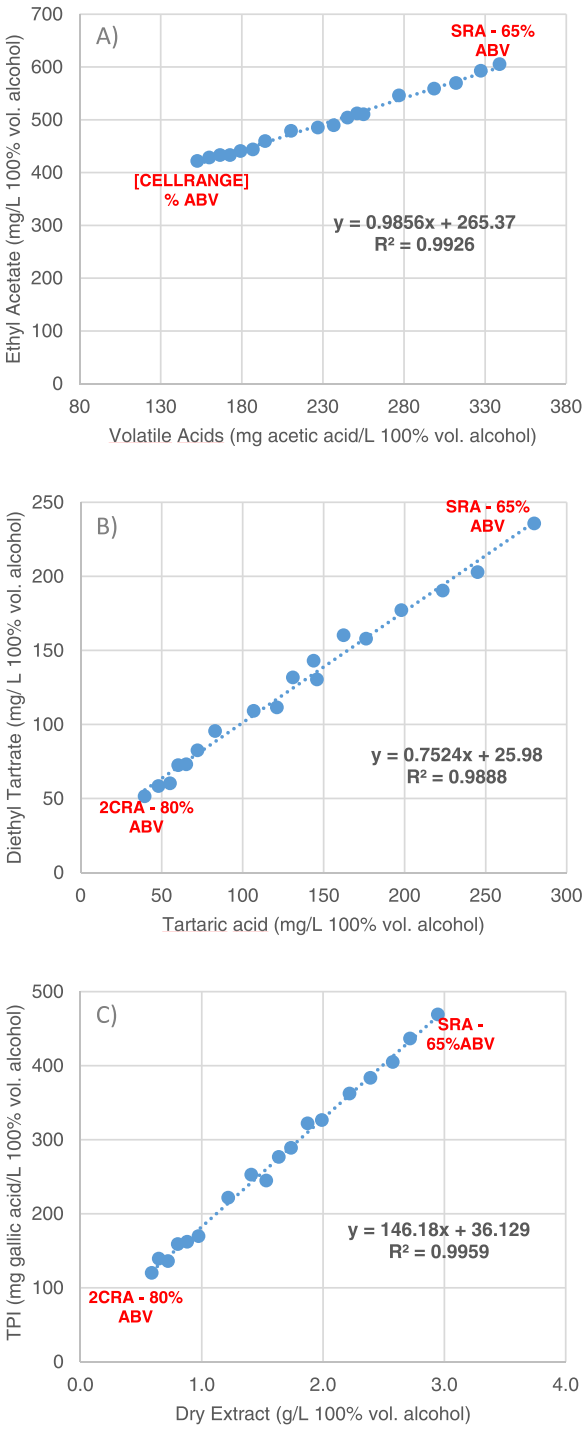

Fig. 3. Pearson correlation coefficient between the values for A) volatile acids and ethyl acetate, B) tartaric acid and diethyl tartrate, and C) dry extract and TPI.

also be formed during the ageing process through the esterification of the lactic and succinic acids derived from the wood seasoning (Sánchez-Guillén et al., 2019). However, these increments are lower degree when compared to diethyl tartrate increments. In fact, diethyl tartrate, with a high boiling point (272 °C), is not present in the distillate and is therefore very difficult to obtain through the distillation process. Therefore, this compound appears in the brandy because of the esterification of the ethanol in the distillate with the tartaric acid extracted from the seasoned wood, and since it is found in greater quantities with respect to those of lactic and succinic acids, a greater content increment is to be expected (Sánchez-Guillén et al., 2019). All in all, the amount of ethyl esters of organic acids is determined by the alcoholic strength, and, therefore, presents significant disparities between the different alcoholic strengths that have been tested. The achievement of equilibrium in these hydrolysis and/or esterification reactions will be then determined by the alcoholic strength, the pH of the medium and the amount of acid involved. For this reason, the experiments with a lower alcoholic strength, that present greater amounts of organic acids also contain greater amounts of esters in the three ageing scales of the *Criaderas and Solera* systems. It is also worth noting that a high correlation between the values for tartaric acid and diethyl tartrate contents as a function of

alcohol proportion could be observed (r = 0.995) (Fig. 3-B).

On the other hand, ethyl esters of fatty acids (ethyl caproate, ethyl caprylate, ethyl caprate, ethyl laureate, ethyl myristate and ethyl palmitate) did not present any differences as a function of alcoholic strength. These compounds are distillate-derived compounds and were found in small concentrations. When comparing 2-CRA with SRA, it could be observed that a slight increase had taken place over the ageing period, which could be mainly due to the concentration that results from the transpiration of water molecules through the pores of the wood towards the outside of the casks, as previously explained (Canas, 2017; Valcárcel-Muñoz et al., 2021b).

Glycerol and 2,3-butanediol are compounds that come exclusively from the Sherry wine that had been used to season the wood, as they are not present in the distillate because of their exceedingly high boiling point (Brown, n.d.). Their behaviour provides information regarding the extraction of compounds from the cask by the distillate. Thus, it can be observed from the data obtained, that the amount of these compounds detected is highly dependent on alcoholic strength (Table 2). In general, the experiments with lower alcohol content showed higher concentrations of these compounds. In the case of 2,3-butanediol, the amounts were relatively small compared to those of glycerol, with no relevant differences observed between the SRAs from the 80%, 75%, 72% and 70% ABV systems. However, in the 65% ABV unit, a higher concentration of 2,3-butanediol was registered. On the other hand, significant differences regarding glycerol content were detected between the SRAs from the different experiments. When the three scales were compared, it could be observed that both compounds increased over the ageing process, with the 65% ABV system exhibiting the most significant variations.

3.4. TPI and phenolic composition

The content of the phenolic compound families and the TPI is represented in Table 3 and Fig. 2-B. The polyphenol families quantified and the TPI values exhibited similar alcoholic strength depending on their particular trends: i.e. the samples from systems with lower alcoholic strengths are those with higher values for phenolic compounds concentration. As expected, the concentration levels increased with the age of the scales. Thus, the SRAs exhibit higher concentrations when compared against their respective *Criaderas* (2-CRA < 1-CRA < SRA) (Schwarz et al., 2011). The higher concentrations in the SRAs suggest that noticeable differences between experiments with different alcoholic strengths are to be found. On the contrary, there were no relevant differences between those experiments with closer alcoholic contents. Also, except for furfurals, none of the other families of the compounds studied are present in the initial distillate, which indicates that they come from the wood or from the wood seasoning process (Canas, 2017; Cernîşev, 2017; Schwarz et al., 2011; Valcárcel-Muñoz et al., 2021b). In the case of unaged distillates, the presence of the furfural family corresponds mainly to furfural, which is formed in the distillation columns themselves when residual wine sugars and certain organic matters are burnt (Awad et al., 2017).

Hydroxybenzoic acids are the ones that showed the greatest concentration increments during the ageing process, mainly because compounds such as gallic and ellagic acids are directly extracted from the casks' wood or through the hydrolysis of their hydrolysable tannins (gallotannins and ellagitannins) (Canas et al., 2019; Viriot et al., 1993). These processes were influenced by alcoholic strength, with higher amounts appearing in the systems with a lower alcoholic strength. Hydroxybenzaldehydes and hydroxycinnamaldehydes come from the

Table 3
∑Hydroxybenzoic Acids, ∑Hydroxybenzaldehydes, ∑Hydroxycinnamaldehy-des, ∑Furfurals (mg/ L 100% vol. alcohol), TPI (mg gallic acid/L 100% vol. alcohol), Abs 420 nm and Abs 470 nm (units Absorbance/L 100% vol. alcohol).

	Alcoholic strength					
	80	75	72	70	68	65
REP - Wine Spirit						
∑Hydroxybenzoic Acids	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
∑Hydroxybenzaldehydes	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
∑Hydroxycinnamaldehydes	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
∑Furfurals	3.81 ± 0.12^{a}	3.86 ± 0.13^{a}	3.92 ± 0.10^{a}	$3.63 \pm 0.12^{a,b}$	3.65 ± 0.09^{b}	$3.70 \pm 0.07^{a,b}$
TPI	8.3 ± 0.8^{a}	8.3 ± 0.7^{a}	8.4 ± 0.9^{a}	8.1 ± 0.9^{a}	8.2 ± 0.8^{a}	8.2 ± 0.9^{a}
Abs 420 nm	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Abs 470 nm	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2nd *Criadera*						
∑Hydroxybenzoic Acids	9.15 ± 0.77^{a}	9.88 ± 0.82^{a}	9.18 ± 0.72^{a}	11.03 ± 0.63^{b}	10.92 ± 0.37^{b}	11.00 ± 0.60^{b}
∑Hydroxybenzaldehydes	2.48 ± 0.42^{a}	$2.83 \pm 0.55^{a,b}$	$2.53 \pm 0.48^{a,b}$	$2.95 \pm 0.32^{a,b}$	$2.88 \pm 0.37^{a,b}$	3.03 ± 0.32^{b}
∑Hydroxycinnamaldehydes	0.58 ± 0.10^{a}	0.65 ± 0.05^{a}	0.63 ± 0.12^{a}	0.83 ± 0.12^{b}	0.82 ± 0.13^{b}	0.88 ± 0.17^{b}
∑Furfurals	4.60 ± 0.30^{a}	$4.81 \pm 0.26^{a,b}$	$4.78 \pm 0.25^{a,b}$	$4.76 \pm 0.19^{a,b}$	$4.78 \pm 0.22^{a,b}$	4.94 ± 0.24^{b}
TPI	119.8 ± 9.6^{a}	139.2 ± 10.3^{b}	135.8 ± 5.5^{b}	158.8 ± 10.0^{c}	161.8 ± 10.3^{c}	169.5 ± 7.8^{c}
Abs 420 nm	0.137 ± 0.007^{a}	0.145 ± 0.006^{b}	0.155 ± 0.007^{c}	0.168 ± 0.006^{d}	0.181 ± 0.007^{e}	0.197 ± 0.009^{f}
Abs 470 nm	0.074 ± 0.005^{a}	0.078 ± 0.005^{a}	0.088 ± 0.006^{b}	$0.090 \pm 0.005^{b,c}$	0.096 ± 0.004^{c}	0.102 ± 0.008^{c}
1st *Criadera*						
∑Hydroxybenzoic Acids	$17.15 \pm 1.05^{a,b}$	$18.35 \pm 0.96^{b,c}$	17.02 ± 0.88^{a}	19.78 ± 0.97^{d}	$19.38 \pm 1.15^{d,c}$	21.43 ± 1.16^{e}
∑Hydroxybenzaldehydes	4.55 ± 0.74^{a}	$5.27 \pm 0.34^{a,b}$	4.72 ± 0.49^{a}	$5.17 \pm 1.12^{a,b}$	$5.12 \pm 0.53^{a,b}$	5.82 ± 0.66^{b}
∑ Hydroxycinnamaldehydes	1.03 ± 0.15^{a}	1.18 ± 0.15^{a}	1.13 ± 0.14^{a}	1.42 ± 0.20^{b}	1.47 ± 0.19^{b}	1.70 ± 0.26^{c}
∑Furfurals	5.42 ± 0.26^{a}	5.66 ± 0.36^{a}	5.48 ± 0.15^{a}	5.62 ± 0.34^{a}	5.54 ± 0.22^{a}	6.13 ± 0.19^{b}
TPI	221.5 ± 5.4^{a}	252.5 ± 8.1^{b}	244.5 ± 6.1^{b}	276.5 ± 8.2^{c}	288.8 ± 8.7^{d}	321.8 ± 13.1^{e}
Abs 420 nm	0.315 ± 0.008^{a}	0.341 ± 0.009^{b}	0.353 ± 0.007^{c}	0.376 ± 0.009^{d}	0.408 ± 0.006^{e}	0.440 ± 0.009^{f}
Abs 470 nm	0.169 ± 0.006^{a}	0.178 ± 0.005^{b}	0.190 ± 0.005^{c}	0.198 ± 0.008^{d}	0.211 ± 0.006^{e}	0.227 ± 0.005^{f}
Solera						
∑Hydroxybenzoic Acids	25.57 ± 1.87^{a}	$26.70 \pm 1.04^{a,b}$	$27.47 \pm 0.70^{b,c}$	$28.78 \pm 1.02^{c,d}$	$30.13 \pm 1.18^{d,e}$	31.50 ± 1.02^{e}
∑Hydroxybenzaldehydes	6.78 ± 1.07^{a}	7.60 ± 0.38^{b}	$7.70 \pm 0.58^{b,c}$	$7.90 \pm 0.50^{b,c}$	$8.02 \pm 0.42^{b,c}$	8.55 ± 0.47^{c}
∑ Hydroxycinnamaldehydes	1.58 ± 0.21^{a}	$1.70 \pm 0.21^{a,b}$	$1.88 \pm 0.08^{a,b}$	$2.00 \pm 0.32^{a,b}$	2.28 ± 0.35^{b}	2.48 ± 0.24^{c}
∑Furfurals	6.15 ± 0.33^{a}	$6.50 \pm 0.41^{a,b}$	$6.57 \pm 0.30^{a,b}$	$6.48 \pm 0.16^{b,c}$	$6.73 \pm 0.44^{c,d}$	7.33 ± 0.30^{d}
TPI	326.3 ± 6.5^{a}	362.0 ± 8.7^{b}	383.3 ± 10.5^{c}	404.7 ± 12.1^{d}	436.5 ± 9.91^{e}	469.0 ± 10.9^{f}
Abs 420 nm	0.537 ± 0.008^{a}	0.578 ± 0.009^{b}	0.593 ± 0.008^{c}	0.632 ± 0.010^{d}	0.674 ± 0.010^{e}	0.744 ± 0.009^{f}
Abs 470 nm	0.283 ± 0.007^{a}	0.297 ± 0.005^{b}	0.317 ± 0.005^{c}	0.331 ± 0.005^{d}	0.358 ± 0.007^{e}	0.387 ± 0.005^{f}

Mean values ± standard deviation (n = 6) are shown; ANOVA: different letters (a, b, c, d, e, f) indicate significant individual parameter differences ($p < 0.05$) between scales from different alcoholic strength systems; REP: Replenishment with unaged distillate. n.d., not detected.

thermal degradation of wood lignin (Cernîşev, 2017). The evolution of these compounds is similar to the hydroxybenzoic acids, although with a less marked difference between alcoholic strengths, since ageing time seemed to be more influential than the alcohol content. On the other hand, no major differences in the furfural family were observed between systems. Therefore, no relevant influence on furfurals content could be attributed to the different alcoholic strengths. Thus, while the 65% ABV system was detected greater furfural contents, the rest of the systems, with higher alcoholic strengths, did not exhibit significant differences between them.

The TPI data obtained, expressed in mg gallic acid/L 100% vol. alcohol were influenced by the alcoholic strength (Fig. 2-B). The TPI of the systems at 65% ABV presented higher values than those reported for any of the other ageing scales with higher alcoholic strengths, with significant differences between the SRAs of all the systems, as expected. According to this trend, a close correlation between dry extract and TPI values could be observed (r = 0.997) (Fig. 3-C). Such results are also in agreement with those found in the literature (Cruz et al., 2012).

3.5. Chromatic characteristics

As expected, the absorbance increased with ageing (Table 3 and Fig. 2-C). It was observed that alcoholic strength had a great influence on the evolution of the colour of the final brandy, with significant differences between every one of the experiments depending on their different alcoholic strengths. Thus, lower alcoholic strength experiments displayed higher values of A420 and A470 in the samples from their three ageing scales. The changes in colour were attributable to the extraction procedures and to the oxidation reactions that took place between the compounds obtained from the wood and its seasoning with the compounds present in the distillate (Baldwin and Andreasen, 1974).

A420, related to yellow shades, shows a greater variation than A470. Such difference in their intensity levels increases as the scales are aged for a longer time. The absorbance at 470 nm corresponds to brown shades and some studies have considered it an indicator of the melanoidin content. These compounds come from the Maillard reaction resulting from the wood roasting process (Cruz et al., 2012; Martins and Van Boekel, 2003). The greater increase displayed by A420, on the other hand, could be a consequence of the characteristics of the process itself, as during the removal and replenishment tasks the liquid extracted from the *Criaderas* comes into contact with air, which favours the oxidation reactions of the compounds that had been previously extracted from the wood. This has been associated by some studies with a more intense yellow colour A420 (Canas et al., 2019; Valcárcel-Muñoz et al., 2021a).

3.6. Principal component analysis

The effect of the alcohol content on the evolution of the different quantified parameters has been studied by means of a PCA on the data corresponding to all the variables from the three ageing scales. The results are shown in Fig. 4. Two components with eigenvalues greater than 1.0, COMP1 (80.2%) and COMP2 (9.5%), have been extracted and together they describe almost 90% of the variability of the original data (Table 4). Furthermore, an evident clustering of the samples according to their alcoholic strength and to their ageing time can be clearly observed in Fig. 4. Thus, COMP2 explains the differences observed between the various alcoholic strengths by clearly separating the samples according to alcohol content. Similarly, COMP1 explains the differences associated to the ageing time of the samples by clearly separating the groups of samples as a function of their scale, i.e. according to their coming from a 2-CRA, 1-CRA or from a SRA. It could be observed that the influence from the alcoholic strength is greater on the samples from the most aged scale (SRA) as can be seen by the clearer distinction between the SRA samples from the different systems with different alcoholic strengths.

Furthermore, the consistency of the brandy structure in the samples

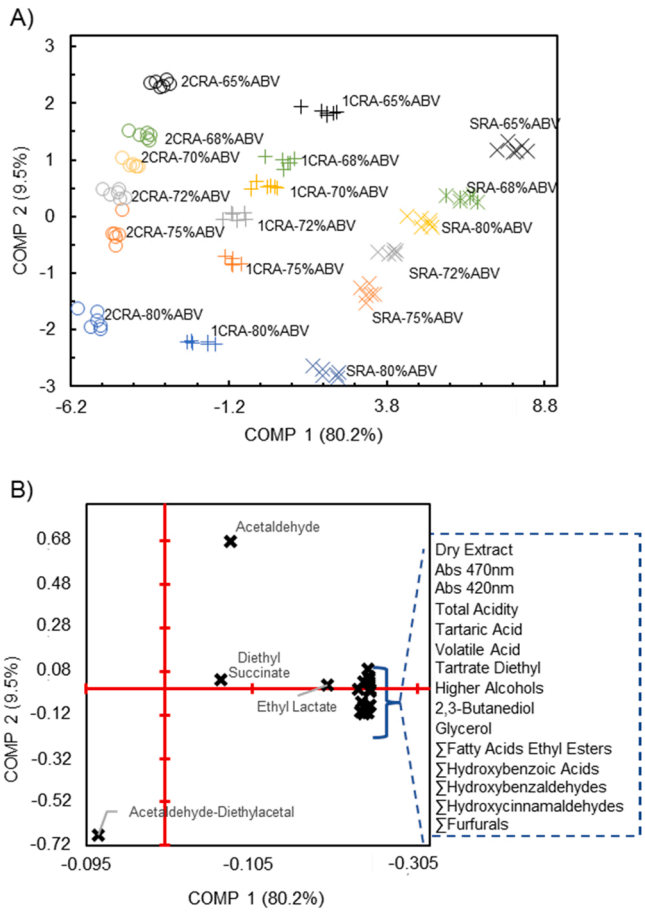

Fig. 4. Results from the Principal Component Analysis of all the samples analysed. A) Dispersion plot of the 2 principal components obtained from the PCA, with Scale-Grade labels; B) Graph of the weights of the components for each factor.

Table 4
Weights of the components for each factor extracted by means of a PCA on the data corresponding to all the variables from the three ageing scales.

	COMP 1 (80.2%)	COMP 2 (9.5%)
Dry Extract	0.247	-0.013
Abs 470 nm	0.246	-0.082
Abs 420 nm	0.247	-0.077
Total Acidity	0.245	0.090
Tartaric Acid	0.246	0.055
Volatile Acids	0.246	0.030
Acetaldehyde	0.079	0.680
Acetaldehyde-diethylacetal	-0.080	-0.674
Higher Alcohols	0.240	-0.081
Ethyl Lactate	0.236	-0.102
Diethyl Succinate	0.245	-0.083
Diethyl Tartrate	0.248	-0.003
2,3-Butanediol	0.233	-0.004
Glycerol	0.195	0.019
Ethyl Acetate	0.068	0.041
∑Fatty Acids Ethyl Esters	0.246	0.046
∑Hydroxybenzoic Acids	0.245	-0.109
∑Hydroxybenzaldehydes	0.239	-0.115
∑Hydroxycinnamaldehydes	0.240	0.034
∑Furfurals	0.237	-0.059

from each one of the systems can be noticed throughout the whole process. Thus, despite the samples being separated by 4 months, and despite a difference of 24 months between the first and the last sample, they can still be accurately classified by alcohol strength and scale. This

fact perfectly explains one of the main characteristics of the *Criaderas and Solera* dynamic ageing system, i.e. the consistency of the product over time, where no significant differences between the 1st and 6th removal can be detected.

In the graph representing the weights of the components (Fig. 4-B) we can see the variables that are responsible for the separation between the clusters that have been described. COMP1 is made up of most of the variables studied and, as we have seen, most of the variables displayed a similar behaviour, i.e. the *Solera* and the experiments with lower alcoholic content exhibited higher values for all the different variables. On the other hand, COMP2 is mainly dependent on acetaldehyde and acetaldehyde-diethylacetal contents. As we previously explained, both compounds are found in an equilibrium that depends on alcohol content and pH level, which means that they are not affected by the ageing process.

3.7. Sensory analysis

In the preference ranking test, the sums of the scores granted to each one of the aged brandies extracted from the Solera, whose alcohol content were adjusted to the product's standard marketing alcohol content of 36% ABV prior to the tasting, were: 80% ABV= 9; 75% ABV= 13; 72% ABV= 28; 70% ABV= 24; 68% ABV= 32; 65% ABV= 41. The calculated F (29.12) exceeded the critical value for 7 judges, 6 samples and 5% error (10.62), which confirmed a significant preference for one or more brandies over the others. The Least Significant Difference (LSD) test allowed to identify such preferred brandies. Thus, the members of the panel rated the brandy aged at 65% ABV higher than the others, except for the 68% ABV brandy, over which no relevant preference was noticeable, as it was also significantly preferred over the 70%, 75% and 80% ABV brandies.

The homogeneity of the panel was verified by two-factor analysis of variance with interaction (assessors x samples) for each of the descriptors (ISO 2, 1113, 2012), and no significant differences attributable to the judge factor or to the interaction assessors-sample (p-values >0.05) were confirmed.

Table 5 shows the mean scores that the panel awarded to each of the descriptors of the aged brandies. The standard deviations were, in all the cases, less than 1, which confirmed the uniformity of the tasting panel. An analysis of variance was applied, where the ageing alcoholic strength was the factor to be applied. Only the vinous descriptor was found to be significantly affected by alcoholic strength, although fruity, vanilla, spicy/aniseed, alcohol and equilibrium exhibited low p-values. It must be noted, that the brandy aged at 65% ABV received higher mean scores for vinous (8.3 ± 0.5), spicy/aniseed (7.3 ± 0.5), smoothness (7.8 ± 0.5), oxidative sweetness (7.8 ± 0.5) and equilibrium (7.8 ± 0.5), and lower for fruity (3.3 ± 0.5) and alcohol (3.3 ± 0.5); as well as a higher aromatic intensity (8.0 ± 0.8). The brandy aged at 68% ABV shared some of these notes. These profiles (Fig. 5) are consistent with the results that had been registered in the preference ranking test. According to these results, 65% ABV, followed by 68% ABV, are the alcoholic strengths that produce brandies with the best sensory characteristics through the ageing procedure used.

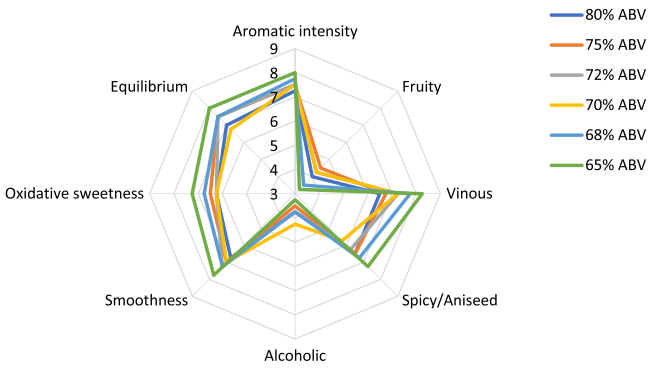

Fig. 5. Spider graph comparing the sensory profiles of *Solera* scale brandies aged with different alcoholic strength.

4. Conclusions

This study provides specific information on a physicochemical characterisation of brandies aged using the *Criaderas and Solera* system traditionally used for *Brandy de Jerez*. Distillates of different alcoholic strengths were aged following this unique system and the results were evaluated.

The brandies aged at 65% ABV contained a greater amount of compounds that are more soluble in water than in ethanol, both from the wood (phenolic compounds) and from the wine used to season the casks (organic acids, glycerol, 2,3-butanediol). In general, the brandies aged with lower alcoholic strength presented higher levels or dry extract, total acidity and volatile acids, higher concentrations of ethyl esters from organic acids, higher values of total polyphenol index and a greater colour evolution. About other parameters such as higher alcohols, ethyl esters from fatty acids or furfurals, their values were slightly higher in the brandies aged at 65% ABV, and generally just could be observed significant differences only compared to 80% ABV.

Alcoholic strength has a substantial influence on the balance of acetaldehyde and acetaldehyde-diethylacetal, so that the higher the alcoholic strength, the lower the acetaldehyde and the higher the

Table 5
Ratings of the tasting panel (as average value ± standard deviation) for spirits of the Solera scale aged to different alcoholic strengths. $p_{value} < 0.05$ means a significant difference.

Alcoholic strengths (% ABV)	Aromatic intensity	Fruity	Vinous	Vanilla	Toasted/ Caramel	Spicy/ Aniseed	Alcoholic	Smoothness	Oxidative sweetness	Equilibrium	Oak
80	7.3 ± 0.5	4.0 ± 0.8	6.5 ± 0.6	6.3 ± 0.5	7.0 ± 0.8	6.5 ± 0.6	3.8 ± 0.5	6.8 ± 0.5	6.3 ± 1.0	7.0 ± 0.8	6.3 ± 0.5
75	7.5 ± 0.6	4.5 ± 0.6	6.8 ± 1.0	7.3 ± 0.5	7.5 ± 0.6	6.5 ± 0.6	3.5 ± 0.6	7.0 ± 0.8	6.5 ± 0.6	7.5 ± 1.0	6.8 ± 1.0
72	7.5 ± 0.6	4.3 ± 0.5	7.3 ± 1.0	7.5 ± 0.6	7.8 ± 0.5	6.3 ± 0.5	3.8 ± 0.5	7.3 ± 0.5	6.3 ± 0.5	7.5 ± 0.6	7.3 ± 0.5
70	7.5 ± 0.6	4.3 ± 1.0	7.3 ± 1.0	6.8 ± 1.0	7.3 ± 0.5	5.8 ± 1.0	4.3 ± 0.5	7.0 ± 0.8	6.3 ± 0.5	6.8 ± 0.5	7.0 ± 0.8
68	7.8 ± 0.5	3.5 ± 0.6	7.8 ± 0.5	7.3 ± 0.5	7.5 ± 0.6	6.8 ± 1.0	3.8 ± 0.5	7.3 ± 0.5	6.8 ± 0.5	7.5 ± 0.6	7.0 ± 0.0
65	8.0 ± 0.8	3.3 ± 0.5	8.3 ± 0.5	7.3 ± 0.5	7.5 ± 0.6	7.3 ± 0.5	3.3 ± 0.5	7.8 ± 0.5	7.3 ± 1.0	8.0 ± 0.8	7.0 ± 0.8
p_{JUDGE}	*0.255*	*0.073*	*0.150*	*0.962*	*0.547*	*0.366*	*0.665*	*0.496*	*0.315*	*0.151*	*0.058*
$P_{JUDGE\ x\ SAMPLE}$	*0.332*	*0.184*	*0.449*	*0.772*	*0.281*	*0.551*	*0.710*	*0.227*	*0.575*	*0.411*	*0.121*
$P_{ALCOHOLIC\ STRENGTH}$	*0.604*	*0.119*	*0.051*	*0.094*	*0.604*	*0.127*	*0.192*	*0.348*	*0.299*	*0.161*	*0.426*

acetaldehyde-diethylacetal. However, total aldehyde values were similar in all the brandies regardless of their ageing alcoholic strength or scale, so that it could be concluded that this parameter is not affected by ageing time.

A sensory evaluation was carried out where the brandy samples to be tasted were previously adjusted to 36% ABV. The members of the tasting panel awarded the best scores to the brandies that had been aged at 65% and 68% ABV. Of all the descriptors evaluated, only the vinous character seemed to be significantly affected by alcoholic strength, followed by vanilla and fruity character. It should be noted that vinous character is one of the characteristics that *Sherry Casks*® provide to *Brandy de Jerez*. This is consistent with our conclusions regarding the improved singularity of the *Brandy de Jerez* produced through the *Criaderas and Solera* from the systems with lower alcoholic strengths in this study.

It can be therefore affirmed that the alcoholic strength of the distillate has a definite influence on the physicochemical and sensory changes that take place over the dynamic ageing system *Criaderas and Solera*. Such influence is originated by both, the removal operations that this methodology involves, and the chemical reactions that take place between the different compounds that can be found in the brandies, coming from the distillate, the casks' seasoning wine or from the wood itself.

Conflict of interest

Authors declare that they have no conflict of interest.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jfca.2022.104618.

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