Sugar Contents of Brandy de Jerez during Its Aging

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Brandy de Jerez is aged in American oak casks according to the traditional dynamic system (Soleras y Criaderas) and sometimes additionally by the static system (Añadas). The experimental arrangement used here for the analytical monitoring of brandy aging consisted of 15 casks, 12 of which were set up for aging by the dynamic system, which is well established in the denomination of origin area, whereas the other 3 contained the same brandy but aged according to the static system. This paper studies the kinetics of sugar extraction from oak wood to distillate, as well as the possible correlations between the sugar contents in brandy and its age or the commercial type it belongs to (Solera, Solera Reserva, or Solera Gran Reserva). High-performance anion-exchange chromatography with pulsed amperometric detection was used as the analytical tool to measure the concentrations of glucose, fructose, arabinose, galactose, and xylose, the presence of which in brandy has previously been described.

KEYWORDS: Brandy; sugars; aging; cask; chromatography; amperometry

INTRODUCTION

After the initial fermentation and distillation processes, Brandy de Jerez does not reach its organoleptic equilibrium until it has been aged in American oak (*Quercus alba*) casks (*1*). Brandy de Jerez is aged by following the traditional dynamic system (Soleras y Criaderas, **Figure 1**) and sometimes additionally the static system (Añadas). During the aging period, slow physicochemical changes involving both brandy and wood take place (*2*, *3*). The results of these changes are radical modifications of the product, with well-known changes in color, taste, and flavor. This evolution comprises changes in the composition and concentration of compounds related to its sensorial characteristics. In distillates stored in oak wood, there are descriptions in the literature of processes of direct extraction of wood components or degradation products of wood macromolecules, as well as reactions between the components of the distillate itself and/or those that come from oak wood (polymerizations, esterifications, acetalyzations, hydrolysis), in addition to major oxidation processes.

As a result of some of these reactions, the sugar content of brandy increases considerably during aging. Increases of sugar content to a maximum of 2 g L^{-1} have been described in brandies aged for 40 years, whereas a cognac aged in oak for 30 years can reach 0.5 mg L^{-1} of sugars (*4*). The presence of arabinose, glucose, xylose, rhamnose, and fructose has been reported in a brandy aged in Limousin oak for 6 months (*5*). The process of transference of sugars from the cask to the brandy
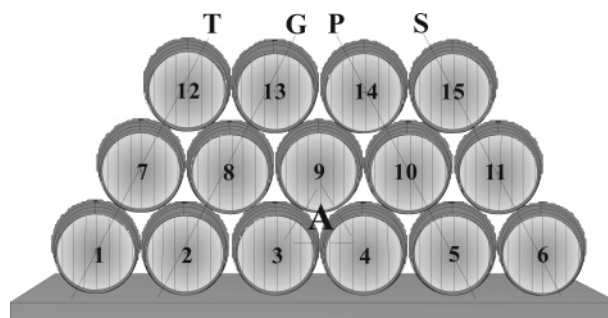

Figure 1. Dynamic system of Soleras y Criaderas.

during the aging process has been the subject of study in the present work.

The sugar determination was carried out by high-performance anion-exchange chromatography (HPAEC) with pulsed amperometric detection (PAD), which is now the most commonly used method for the detection of nonderivatized sugars because it is fast, sensitive, and selective and requires minimal pretreatment (*6*−*15*). This type of chromatography is based on the weak acidic nature of carbohydrates (the hydroxyl groups of which have pK_a values in the 12−14 range). This property allows their ionization and chromatographic separation in alkaline solutions by high-performance (or pH) anion-exchange chromatography. At a high pH, carbohydrates are oxidized at the surface of a gold electrode by applying a positive potential. The electrical current generated is proportional to the concentration of sugars, which can be consequently detected and quantified.

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Table 1. Operating Parameters and Columns

analytical column	CarboPac PA1 (250 × 4 mm) Dionex
guard column	CarboPac PA1 (10-32) Dionex
eluent A	30 mM NaOH, degassed with He
eluent B	100% water, degassed with He
eluent C	300 mM NaOH, degassed with He
gradient, %A + %B + %C (time)	30% A + 70% B (0–25 min), 100% C (30–35 min), 30% A + 70% B (40–50 min)
eluent flow rate	1 mL min^{-1}
sample loop volume	25 μL
detection	PAD
detection mode	integrated amperometry
detection settings, *E* (time)	0.05 V (0.00 s), 0.05 V (0.20 s), 0.05 V (0.40 s), 0.75 V (0.41 s), 0.75 V (0.60 s), −0.15 V (0.61 s), −0.15 V (1.00 s)
Aaquisition time	25 min

MATERIALS AND METHODS

Chemicals. D-(+)-xylose, D-galactose, and D-(−)-arabinose were purchased from Extrasynthese, d-(−)-fructose was from Sigma, and D-(+)-glucose was from Panreac. All solutions, including the eluents, were prepared with distilled deionized water.

Chromatographic Instrumentation. All analyses were performed on a Dionex DX-500 ion chromatograph (Sunnyvale, CA). The system consisted of a quaternary gradient pump (GP40), an eluent degassing module, and an electrochemical detector (ED40) including a detection cell with a gold working electrode and a pH−Ag/AgCl reference electrode. The pump had a standard bore configuration and polyether ether ketone (PEEK) pump heads and flow paths. Data were acquired by Millennium version 2.10 software, connected to the instrumental equipment by a System Interface Module (Waters).

Methodology. Eluents were degassed and pressurized daily under helium using the Eluent Degas Module (Dionex). Eluents were kept in plastic bottles, and a helium headspace was maintained on the solutions. The anionic mobile phase was prepared from carbonate-free 50% (w/w) NaOH solutions, previously factorized by titration with potassium acid phthalate (dried for 12 h in the oven and then kept in a desiccator), using a 2% solution of phenolphthalein in ethanol as the indicator. **Table 1** summarizes the details of the operating parameters and columns (*13*).

Samples. The experimental system set up in the Jerez Centre of Viticulture and Enology for the analytical monitoring of brandy aging consisted of 15 casks of 500 L capacity each. Twelve of them were used to age brandy according to the dynamic system of Soleras y Criaderas (traditionally used in the denomination of origin area), in groups of three casks for each aging scale or step (according to length of aging period). The Solera scale, designated S, was the oldest; the first Criadera (P), the next oldest; the second Criadera (G), the next; and the third Criadera (T), the youngest. The other three casks held the same new distillate but for static aging according to the system of Añadas, designated A. All of the casks had previously contained sherry wine for at least 3 years, as established in the regulations for the manufacture of Brandy de Jerez.

The four scales contained distillate with a 40% v/v graduation. Programmed decantings every 3 months involved first drawing off one-fourth (125 L) of the total volume of brandy held in each of the casks of the oldest Solera scale. Then, a similar proportion of the volume

held in the first Criadera casks was drawn off; these amounts (from the first Criadera casks) were then mixed together, divided into three parts, and used to refill the three Solera casks to their original volume. This procedure of partially refilling older casks with younger brandy drawn off the preceding scale is repeated through all of the aging scales of the system. In the final decanting, the youngest scale (the third Criadera in this system) is refilled with new distillate from the distillery.

Sampling was carried out every 3 months in the dynamic system, taking advantage of the operations of drawing off and refilling. Small sample volumes (20 mL) were obtained from the product after the mixing of the partial volumes drawn off the three casks belonging to the same scale, which thus constitutes a representative mean of the whole scale. Consequently, the sample classification consisted of an initial letter corresponding to the aging scale (Solera, S; first Criadera, P; second Criadera, G; third Criadera, T), followed by two digits indicating the decanting number (from 00 to 19).

The three casks used for the Añadas were filled with the same new distillate and at the same time as the casks of the dynamic system. The only product drawn off from these static system casks was that needed for sampling (20 mL).

In the static system, the sample was drawn up directly from the casks with a pipe. Finally, the sample was obtained by mixing the aliquots from the three casks of the static system. A similar arrangement but on a larger scale was used for the drawing off and refilling operations in the dynamic system.

The sugar composition was determined for those samples from the dynamic system with decanting numbers 1−19 in their four scales and for those samples from the static system corresponding to the decanting numbers 4, 6, 8, 9, 11, 13, 15, and 19. Samples were filtered (nylon syringe filters, 0.45 μm) before injection.

Sugar Quantification and Validation. Peak areas were used for the quantification. The calibration curve for each sugar was made from the analysis in triplicate of six sugar mixtures at different concentrations. The linear range for each sugar included the concentrations found in all of the samples analyzed. Standard solutions of the sugars for calibration were prepared in 40% v/v ethanol/water in order to match the aqueous alcoholic matrix of brandy samples. The calibration curves and the analytical parameters related to them are summarized in **Table 2**. Comparison between these data (external calibration) and those obtained from the standard addition method revealed that there were no significant differences (at a significance level of 0.05) between the slopes of the calibration curves obtained by using both methods. Detection limits were calculated by external calibration (*16*). Repeatability was acceptable for all compounds (CV < 7.5%). The chromatographic separation was characterized by the capacity factor (>4.3), separation factor (>1.12), and resolution (≥1.39).

Statistics. External calibration and standard addition calibration were obtained using ALAMIN (*17*), which is a DOS program that establishes the performance characteristics of the analytical method from the calibration data set. The program QUIMIOMETRÍA PRÁCTICA (*18*) enabled us to compare the regression curves obtained by external calibration and standard addition method. The previous study of data (to find outliers), linear discriminant analysis (LDA), and the validation of the multiple correlation function were carried out with the program STATISTICA version 4.5. Program SPSS version 11.5 for Windows was used for the multivariate linear correlation.

Table 2. Calibration Curves and Related Analytical Parameters (*Y*, Area; *X*, Concentration, mg L^{-1}; R^2, Correlation Coefficient)

	standard addition calibration		external calibration						
sugar	calibration curve (*Y* = *a* + *bX*)	R^2	calibration curve (*Y* = *a* + *bX*)	SD (*a*)	SD (*b*)	R^2	linearity (%)	detection limit (mg L^{-1})	range (mg L^{-1})
arabinose	*Y* = 7559.7*X*	1	*Y* = 4.825 + 7559.359*X*	1298.121	149.169	0.990	98.027	1.991	0.48–21
galactose	*Y* = 6255.8*X*	0.9999	*Y* = −503.732 + 6316.065*X*	804.718	166.238	0.983	97.368	1.495	0.24–12
glucose	*Y* = 8527.5*X* + 4137.6	1	*Y* = 4137.603 + 8527.463*X*	3237.458	279.309	0.983	96.725	3.829	1.104–27.6
xylose	*Y* = 10885*X* − 918.66	1	*Y* = −918.665 + 10885.297*X*	991.584	215.039	0.994	98.025	0.919	0.4392–10.98
fructose	*Y* = 5290.6*X* − 151.25	1	*Y* = −151.253 + 5290.605*X*	737.183	121.143	0.992	97.710	1.405	0.5796–14.49

RESULTS AND DISCUSSION

The curves of sugar extraction from the cask (**Figure 2**) reveal that the concentration of the five sugars studied increases in brandy until reaching a certain decanting number (this may be between 6 and 9 depending on the sugar and the aging scale). Beyond this decanting number, the sugar concentration stabilizes or even decreases gradually in some cases, such as xylose and galactose. The decanting number at which the sugar stabilization/decrease starts (∼1.5−2.25 years from the start of aging) varies as a function of the scale and different extraction kinetics of each sugar.

The sugars found in Brandy de Jerez could come from the breakdown of the wood hemicellulose and also from the sherry wine that was previously aged in the same casks (at the end of the aging of sherry wine, the casks will be impregnated with some of the components of the wine).

The profile of the extraction curve is influenced by several variables: the content of sugars in the casks, the dilution effect of mixing with younger distillates, the difference in the extractive power of the distillates (the lower the sugar concentration, the greater the extractive power), and the different extraction kinetics of each compound. The initial rise in the sugar concentrations (common to all of the sugars studied) is produced by the predominance of the extraction phenomenon over the dilution effect produced by the addition of younger distillate. This situation changes after a certain decanting number, with a stabilization and slight decrease in the sugar concentrations.

From the comparison among scales (**Figure 2**), it is concluded that the highest concentration (for each decanting number) corresponded to the Solera, followed by the first Criadera and the second Criadera, with the third Criadera having the lowest sugar concentration. The explanation for this is that, in the dynamic aging system, the Solera is the scale containing the brandy that has spent the most time in the aging system and, therefore, has been able to extract the largest amounts of sugars from the casks. These data clearly indicate the exhaustion shown by the third Criadera, when the decanting number increases: sugar concentrations decrease progressively, and this will affect the sugar contents of the oldest scale (Solera). To maintain the sugar levels in the Solera scale, and in the final product, we suggest the replacement of the casks of the third Criadera with new casks (which have previously contained sherry wine for at least 3 years).

In the static aging system (Añadas), the content in sugars increases throughout the entire process, because the distillate remains in the same cask all of the time and there is no dilution effect by adding younger distillate (**Figure 2**). Arabinose and galactose concentrations in the static system are lower than those from the Solera, the last stage in the dynamic system. In the case of xylose, glucose, and fructose, beyond decanting no. 11, sugar concentrations in the static system are higher than those of the Solera.

As shown in **Figure 2**, the curves corresponding to the Solera and first Criadera tend to overlap in the initial stage of increasing concentration (the overlapping is clearest in the case of arabinose, galactose, and xylose). This overlapping can be understood by introducing a new parameter used in the dynamic aging system: the "average time of aging", which arises as a consequence of the decanting and refilling operations and indicates the average time that all of the brandy contained in a certain cask has been aged. To calculate this parameter, the number of decantings in a year, the total system volume, the volume of each decanting, and the number of scales were the variables considered. The graph relating the average time of aging and the decanting number for each of the four aging scales (**Figure 3**) reveals that the Solera and first Criadera curves present the greatest overlap. This explains the overlapping observed in the curves of concentration against decanting number: these brandies have similar average times of aging. The higher the decanting number, the greater the separation between average times of aging of the four scales, and as a result, the curves of concentration against decanting number (**Figure 2**) diverge for high decanting numbers.

The divergence observed when the decanting number is increased has been quantitatively measured by LDA. LDA is suitable when a dependent variable (aging scale, in this case) and several continuous independent variables (the concentrations of sugars) are used. The aim of LDA is to obtain classification rules based on the punctuation of the independent variables. For this purpose, LDA gives one or more discriminant functions, which are linear combinations of the independent variables, in such a way as to obtain a maximum discrimination between groups. In this work, LDA was applied to differentiate among the aging scales (Solera, first Criadera, second Criadera, and third Criadera) by means of the concentrations of sugars. The percentages of samples classified in the correct scale (which is previously assigned) by LDA using sugar concentrations, as well as the decanting numbers of the samples included in every scale, are summarized in **Table 3**. As the differentiation is greater for high decanting numbers, the percentage of classification when using all decanting numbers was lower than when only those samples with decanting numbers beyond 6 were considered. As shown in **Table 3**, the percentage of classification increases when using samples with decanting numbers beyond 6, 7, 8, and 9, in that order. One hundred percent classification was achieved with decanting numbers in the 9−19 range. The classification function corresponding to 100% of classification is presented in **Table 4**. The variable with the most discriminating power was arabinose, followed by xylose and fructose. The graph of the samples on the plane of canonical variables shows the differentiation among the four aging scales (**Figure 4**).

As a function of their average time of aging, brandies can be classified commercially as Solera (aged for >6 months), Solera Reserva (aged for >1 year), and Solera Gran Reserva (aged for >3 years). Chromatograms of Solera, Solera Reserva, and Solera Gran Reserva brandies are presented in **Figure 5**. Given the generally predictable behavior in the concentrations of certain sugars, we were able to study by LDA the possibility of using arabinose, galactose, xylose, glucose, and fructose concentrations to classify brandies according to their commercial category as Solera, Solera Reserva, or Solera Gran Reserva. For this purpose, the average time of aging of the samples from the experimental system was calculated, which allowed us to classify those samples as Solera, Solera Reserva, and Solera Gran Reserva. It is noteworthy that there was no overlap among the three categories because they were classified using ranges of average time of aging (for example, between 6 months and 1 year for a Solera brandy), instead of the official definitions of Solera, Solera Reserva, and Solera Gran Reserva (for instance, a Solera Reserva brandy could be classified as a Solera because it has been aged for >6 months).

The model obtained by LDA could classify correctly 86.7% of Solera brandies, 84.6% of Solera Reserva brandies, and 60.0% of Solera Gran Reserva brandies. Overall, 82.6% of brandies studied were classified correctly. The classification function is shown in **Table 5**. The variables with the most discriminating power were fructose, arabinose, and glucose, followed by xylose
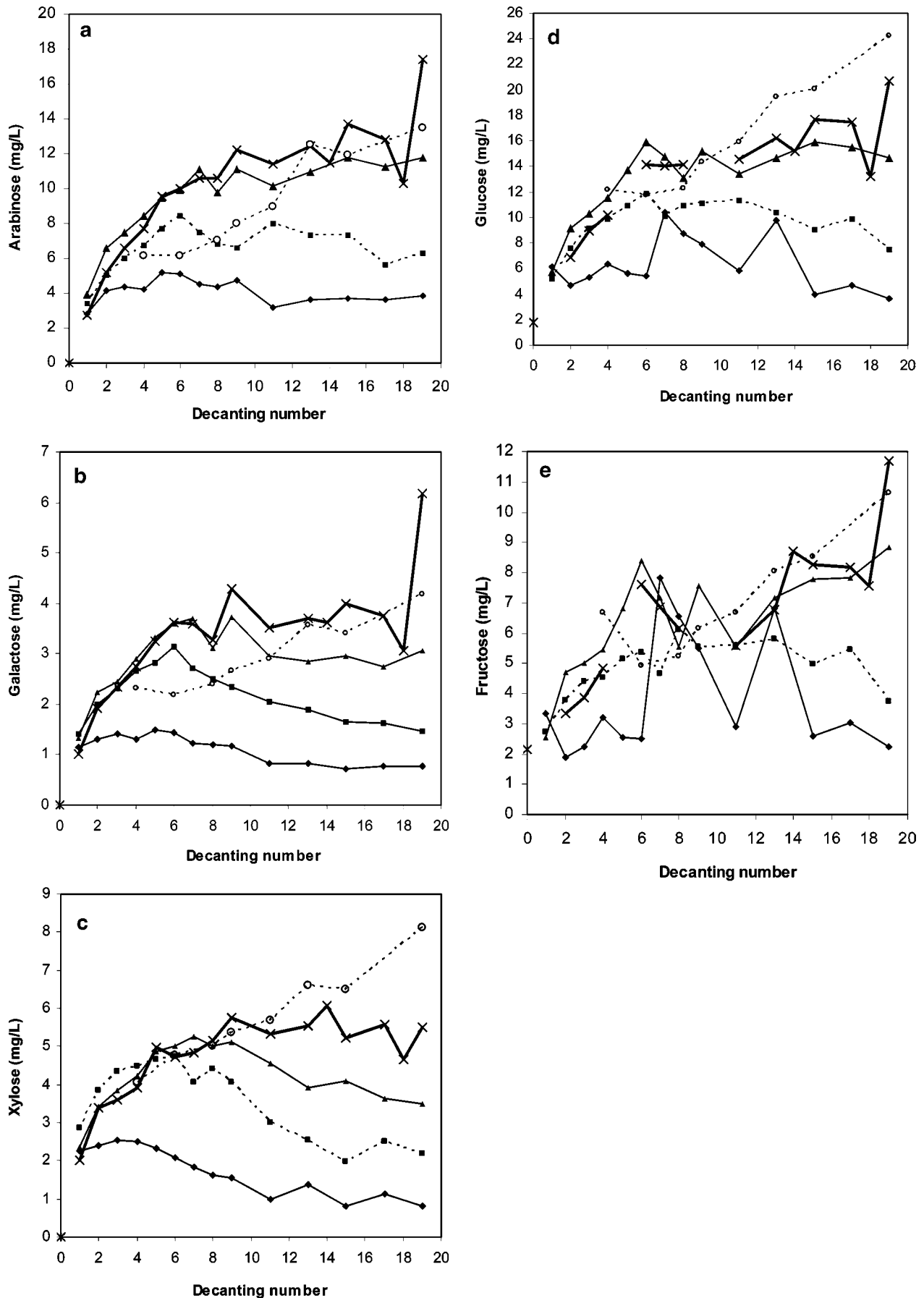
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Figure 2. (**a**) Arabinose, (**b**) galactose, (**c**) xylose, (**d**) glucose, and (**e**) fructose in the aging system: (◆) third Criadera; (■) second Criadera; (▲) first Criadera; (×) Solera; (✳) new distillate; (○) Añada.
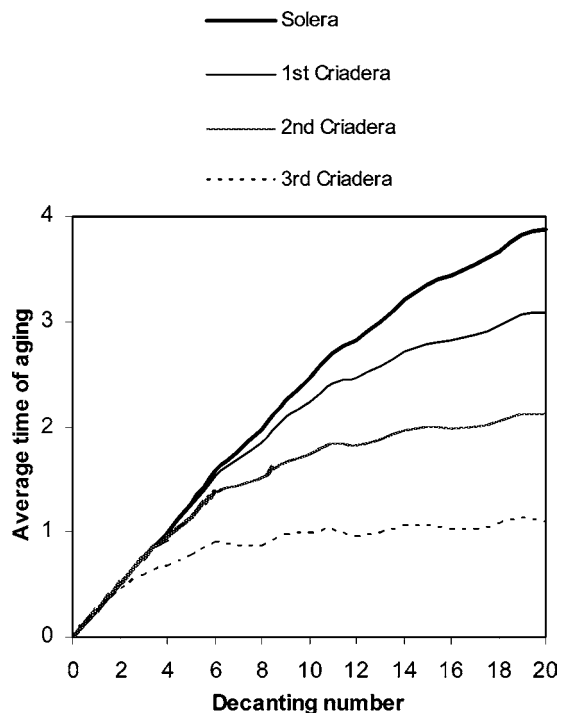
Figure 3. Relationship between the average time of aging and the decanting number.

Table 3. LDA of Classification between Aging Scales

decanting no. of samples included	correct global classification (%)
6–19	84.375
7–19	92.857
8–19	96.000
9–19	100.000

Table 4. Classification Function (between Aging Scales)[a]

	T	G	P	S
arabinose	8.937	17.975	30.881	37.705
xylose	4.880	12.085	19.268	25.244
fructose	−1.966	−5.238	−10.143	−14.084
constant	−17.878	−65.741	−175.656	−256.805

[a] T, third Criadera; G, second Criadera; P, first Criadera; S, Solera.

and galactose. The canonical analysis shows the differentiation among the groups Solera, Solera Reserva, or Solera Gran Reserva (**Figure 6**).

The high percentage of classification obtained by using sugar concentrations and the validity of the average time of aging to estimate the age of a brandy in the dynamic system led us to the next step of this study: to predict the average time of aging of a certain brandy by using its sugar concentrations. The statistical tool used to predict the average time of aging was multivariate linear correlation. Previously, the Kolmogorov−Smirnov test was applied to every variable, which ensured that all of them (the concentrations of the five sugars) verified the necessary condition of normality. The multivariate linear correlation produced a model with 88.3% of reliability, in which all variables took part significantly:

$$t = -1.103 - 1.264\text{Ln[galactose]} - 0.134\text{[glucose]} +$$
$$0.393\text{[xylose]} + 0.192\text{[fructose]} - 0.890\text{[galactose]} +$$
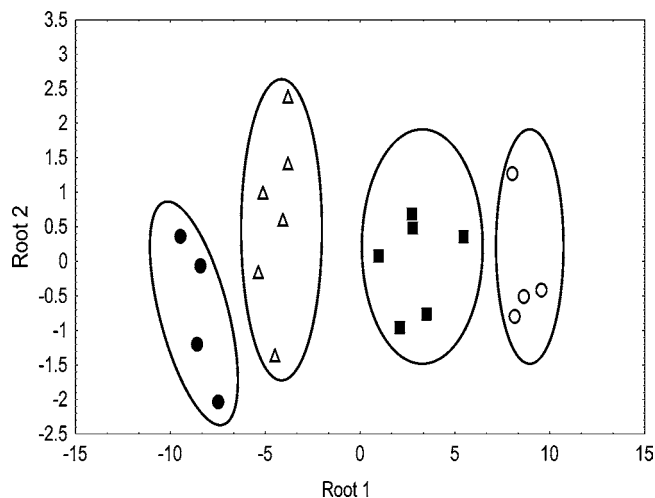$$0.622\text{[arabinose]}$$

Figure 4. Differentiation among aging scales (canonical analysis): root 1, canonical variable 1; root 2, canonical variable 2; (○) T; (■) G; (△) P; (●) S.
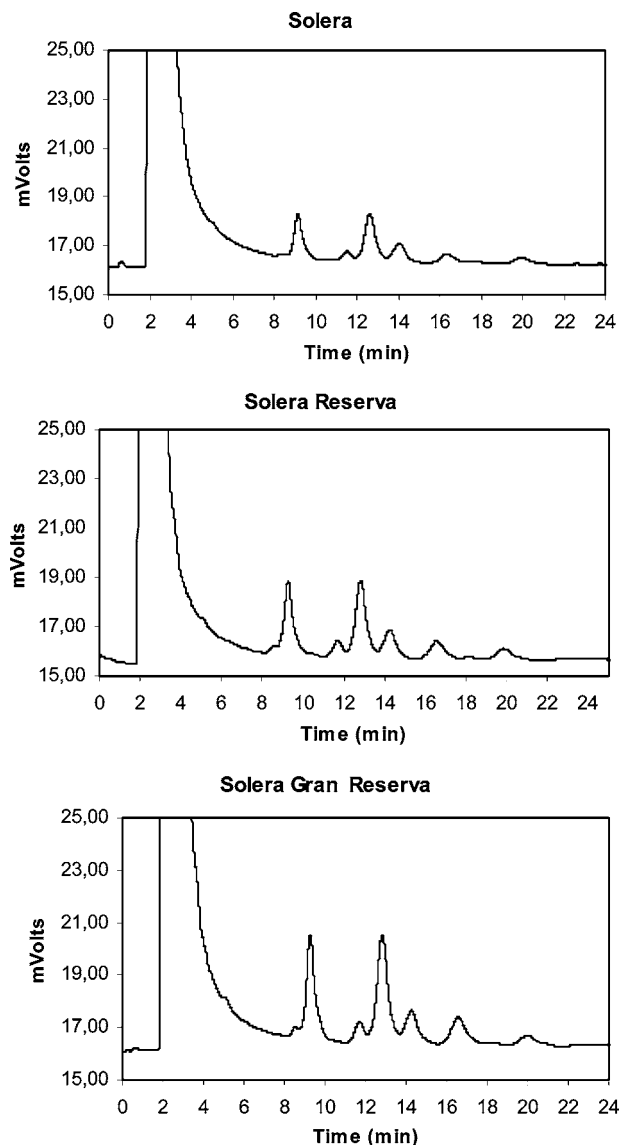

Figure 5. Chromatograms of Solera, Solera Reserva, and Solera Gran Reserva brandies.

where *t* is the average time of aging (years) and [arabinose], [glucose], etc. are the concentrations of sugars (mg L^{-1}). The

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Table 5. Classification Function (between Commercial Types)[a]

	S	SR	SGR
arabinose	3.425	4.090	9.106
fructose	4.856	4.566	10.606
glucose	−2.692	−2.084	−7.279
xylose	7.845	6.996	12.319
galactose	−13.390	−13.723	−22.740
constant	−9.506	−14.724	−35.152

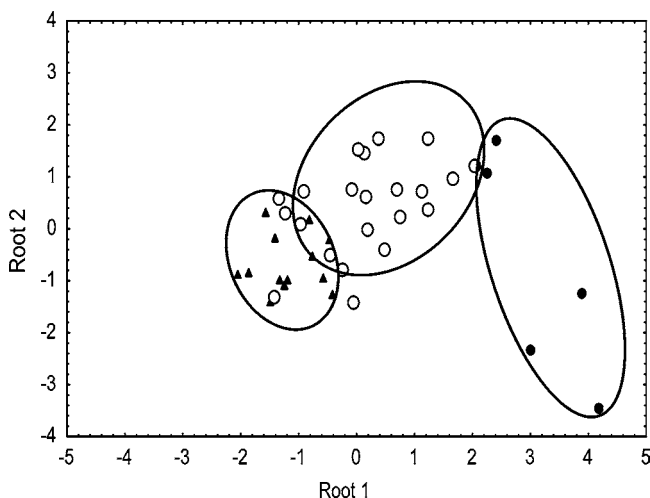[a] S, Solera; SR, Solera Reserva; SGR, Solera Gran Reserva.

Figure 6. Differentiation among commercial types S (▲), SR (○), and SGR (●) (canonical analysis): root 1, canonical variable 1; root 2, canonical variable 2.
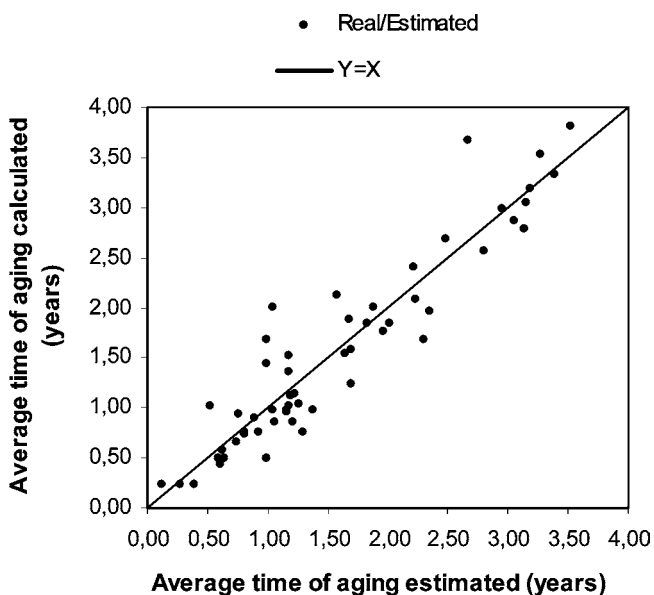

Figure 7. Degree of agreement between the model obtained to estimate the average time of aging (estimated value) and the values assigned to samples (calculated values).

most correlated variables were arabinose and galactose, followed by xylose, neperian logarithm of galactose, fructose, and glucose. The graph of the average times of aging calculated against the values estimated by the multiple correlation function is presented in **Figure 7**. To evaluate the ability of this function to estimate the average time of aging, we used it to obtain the average times of aging of four brandies (from the experimental system), which were not included in the multivariate linear correlation. These data were compared with the values calculated by means of a

t test for dependent samples, and no significant differences were found ($p = 0.058$). However, on the basis of this work, the equation obtained could not be used to estimate the average time of aging of a brandy from a different aging system, because it has been obtained for the particular conditions of the experimental system studied.

We conclude that, in the dynamic aging system, graphs of sugar concentration against decanting number are characterized by an initial increase in concentration, followed by a stabilization and slight decrease beyond a certain decanting number. From a comparison of the scales, the highest concentration usually corresponds to the Solera, followed by the first Criadera, the second Criadera, and the third Criadera, which presents the lowest sugar concentration (this would lead us to suggest the replacement of the casks of the third Criadera, to maintain the sugar levels in the Solera scale and in the final product). An ordering of scales according to age can be observed. This ordering is clearest beyond a certain decanting number and coincides approximately with the start of the separation in average time of aging for each scale. This divergence was confirmed by LDA, which obtained 100% correct classification after decanting no. 9. In the static aging system, sugar concentrations increase throughout the entire aging. LDA was also used to classify brandies from the experimental system into their three commercial categories (Solera, Solera Reserva, and Solera Gran Reserva). Overall, 82.6% of brandies studied were classified correctly. Moreover, a multivariate linear regression enabled us to obtain a function to estimate the average time of aging of a certain brandy with a reliability of 88.3%.

It is important to highlight the role that arabinose plays in aging: this sugar has a strong relationship with aging, as can be concluded from this work; it has a strong discriminating power in the classification functions both among scales and among commercial types, and it is one of the most correlated variables in the multiple correlation. The results of this work could be used to optimize the manufacturing processes of Brandy de Jerez: the replacement of the casks of the third Criadera, or the estimation of the time that Brandy de Jerez must be aged in casks as a function of the time needed to reach the highest sugar concentrations or the average time of aging necessary for belonging to a certain commercial type. In a more academic sense, this work tries to contribute to the characterization of the aging of Brandy de Jerez and studies the evolution of sugars during the aging of distillates and the influence of the wood casks in the sugar composition of Brandy de Jerez.

ABBREVIATIONS USED

A, Añada; CV, variation coefficient; DO, denomination of origin; G, second Criadera; HPAEC, high-performance anion-exchange chromatography; LDA, linear discriminant analysis; P, first Criadera; PAD, pulsed amperometric detection; S, Solera (aging scale or commercial type of brandy); SGR, Solera Gran Reserva; SR, Solera Reserva; T, third Criadera.

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