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ARTICLE

Phenolic Compounds and Furanic Derivatives in the Characterization and Quality Control of *Brandy de Jerez*

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This article shows the results obtained in the study of the extraction profiles from oak wood to distillate of several compounds, low molecular weight phenolics, and furanic derivatives, and the relationship of their contents with those found in commercial sherry brandies and other aged distillates of different geographical origin, in order to research the utility of these analytical variables for explaining the highly specific character of *Brandy de Jerez*. Using multivariate statistic techniques, the aging system (static by *añadas*, or dynamic, well known as *Soleras y Criaderas*) has been confirmed as having a great influence on the analytical profile of aged distillates (discrimination is up to 100%). Differences between commercial brandies and those aged experimentally of equivalent average age have also been confirmed. The *Solera Gran Reserva Brandies de Jerez* show a clear differentiation from the rest of the distillates of different origin (discrimination is up to 80%), indicating their highly specific character.

KEYWORDS: Sherry; brandy; polyphenols; furanic derivatives; spirits

INTRODUCTION

After the initial fermentation and distillation processes, *Brandy de Jerez* does not reach its organoleptic equilibrium until it has been aged in casks of American oak (*Quercus alba*). *Brandy de Jerez* is aged according to the traditional dynamic system known as *Soleras y Criaderas* and sometimes, additionally, by the static system known as *Añadas* (*1*).

During the aging period, slow physicochemical changes involving both brandy and wood take place. These changes result in radical modifications of the product, producing well-known changes in color, taste, and flavor. In this evolution, there are changes in both the composition and concentration of many compounds related to the sensorial characteristics of the brandy (*2*). For distillates aged in oak wood, there are descriptions in the literature of processes of direct extraction of wood components or degradation products of macromolecules of the wood, as well as reactions between the components of the distillate itself and/or those originating from the oak wood (polymerizations, esterifications, acetalyzations, and hydrolysis), in addition to major oxidation processes (*3*−*6*).

In the *Soleras y Criaderas* aging system, the extraction processes are influenced by several variables: the contents of compounds in the casks, the dilution effect of mixing with younger distillates, the difference in the extractive power of the distillates (since the lower compound concentrations in the younger scales involve a greater extractive power from the casks), the different extraction kinetics of each compound, the extraction of compounds from the wine previously contained in the casks, and the degradation compounds derived from chemical reactions such as oxidations.

Another differentiating characteristic of *Brandy de Jerez* is that the casks in which it is aged have previously contained sherry wine. This prior procedure is known as the *wining* of the casks. Butts which have previously been soaked in sherry wine give a particular personality which can be clearly appreciated in its organoleptic characteristics. The characteristics of each *Brandy de Jerez* will vary according to the type of sherry which the oak-wood casks have previously contained. They may have contained *Finos* or *Manzanillas* (straw colored and totally dry), *Amontillados* (dry but darker in color), dry or sweet *Olorosos* (darker still in color), or sweet wines such as *Pedro Ximenez* (very dark and sweet). In this way, the brandy takes on characteristics of color, bouquet, and taste from the wines which the casks have previously held, partially due to the extraction of compounds such as sugars, organic acids, furanic derivatives, and polyphenols from the wine into the cask to the distillate.

As a result, the content of brandy in some compounds, particularly phenols of low molecular weight and furanic derivatives, increases considerably during aging. Thus, although some furans and phenols as phenyl ethanol can already be found in a fresh distillate of wine (*7*, *8*), it is considered that the maturation of the brandy in oak casks is the major factor responsible for its final polyphenolic and furaldehyde content (*9*).

With respect to the final product, several authors have studied the polyphenolic content of commercial spirits aged in wood (*10*−*16*), although there have been few analytical studies on *Brandy de Jerez* (*12*−*19*).

Because of the increase in counterfeit products and consumer demands for protection against fraud, producer companies and

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Table 1. Analytical Parameters for the Identification and Calibration of the Compounds under Study

compound	calibration range (mg/L)	detection system	quantitation wavelengths (nm)[a]	retention time (min)
gallic acid	0.1−30	ultraviolet absorption	271.7	6.2
hydroxymethylfuraldehyde	0.37−372	ultraviolet absorption	283.5	10.5
furaldehyde	0.02−31	ultraviolet absorption	276.5	15.0
p-hydroxybenzaldehyde	0.01−1	ultraviolet absorption	283.5	28.3
vanillic acid	0.04−3	ultraviolet absorption	261.0	30.3
methylfuraldehyde	0.02−5.4	ultraviolet absorption	291.5	30.7
caffeic acid	0.01−0.76	ultraviolet absorption	324.1	32.4
syringic acid	0.01−12	ultraviolet absorption	274.3	34.8
vanillin	0.04−12	ultraviolet absorption	281.2	35.4
syringaldehyde	0.03−9	ultraviolet absorption	308.5	38.4
p-coumaric acid	0.01−3	ultraviolet absorption	310.0	39.8
coniferaldehyde	0.01−1.6	ultraviolet absorption	343.2	43.1
sinapaldehyde	0.02−5	ultraviolet absorption	344.4	44.2
aesculetin	0.003−5.4	fluorescence emission	351/453	31.1
umbelliferon	$(0.078-8) \times 10^{-3}$	fluorescence emission	329/455	39.1
scopoletin	0.003−2.5	fluorescence emission	347/457	40.8

[a] Shown are the maximum absorption wavelengths for the compounds quantified by UV and the maximum excitation and emission wavelength (ex/em) for those detected by fluorescence.

other professionals of the food and drinks industry need effective means for guaranteeing the authenticity of their products. Consequently, the reliable and objective characterization of *Brandy de Jerez* seems to be interesting as this makes it possible to differentiate a particular product analytically from all other similar products on the market, thus confirming its authenticity.

The aim of this study is to define both the extraction curves from the cask to the distillate during the aging process and the final contents of phenolic compounds and furanic derivatives, on the one hand to make a comparison between static and dynamic systems and on the other hand to describe and explain the differences from those contents in the commercial brandies.

MATERIALS AND METHODS

Chemicals. The ethanol (Merck, Darmstadt, Germany), methanol (Panreac, Barcelona, Spain), and acetic acid (Scharlau, Barcelona, Spain) used were of HPLC grade. Water was supplied by a Milli-Q water purifier system from Millipore (Bedford, MA, USA).

Furaldehyde, hydroxymethylfuraldehyde, coniferaldehyde, sinapaldehyde, and aesculetin were from Sigma−Aldrich Chemie GmbH (Steinheim, Germany). Syringic acid was from Eastman Kodak (Rochester, NY) and gallic and *p*-coumaric acids from Merck (Darmstadt, Germany). Methylfuraldehyde, *p*-hydroxybenzaldehyde, vanillin, syringaldehyde, umbelliferon, scopoletin, and vanillic and caffeic acids were purchased from Fluka (Buchs, Switzerland). Compound standards were dissolved in a model solution consisting of 40% (v/v) ethanol in water.

Analytical Instrumentation. The analysis was performed by HPLC using a Waters (Milford, MA, USA) chromatographic system (two 510 pumps, PCM module, 717 automatic injector, 996 photodiode array detector, 474 fluorimetric detector, and Millennium 2010 software) using an RP-18 LiChrospher column, 250 × 4 mm, 5 μm (Merck, Darmstadt, Germany).

Methodology. An elution gradient was used according to the method proposed by the authors (*20*). Briefly, two solvents were used: solvent A (5% methanol and 2% acetic acid in water) and solvent B (90% methanol and 2% acetic acid in water). The solvents were filtered through a 0.45 μm filter and degassed with He bubbling. The initial conditions were flow-rate at 1 mL/min and 100% A, reaching 90:10 (A/B) in 20 min, and 25:75 (A/B) in 60 min, the column being re-equilibrated between injections. The compounds were identified by matching the retention times and spectra (absorption UV−visible, 240−390 nm) of the standards. Comparison between data from 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 using the two methods; therefore, quantification was done by external calibration using peak areas. Compounds were quantified at their own maximum absorbance wavelength to maximize sensitivity. With respect to compounds with fluorescent properties, excitation and emission spectra were recorded and maximum wavelengths used in order to obtain the best signals. **Table 1** shows the compounds identified and quantified.

A volume of 50 μL of the samples, previously filtered through nylon filters of 0.45 μm (Scharlab, Barcelona, Spain), was injected in all of the cases. *Statistica* software v. 4.5 (StatSoft, Inc. 1993) was used for the treatment of results.

Samples. Three types of samples were studied. First of all, an experimental aging system was set up in Jerez Viticulture and Enology Centre for the analytical monitoring of brandy aging. It consisted of 15 American oak casks of 500 L capacity each, medium toasting. Twelve of the casks 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. These are differentiated according to their mean time of aging: The *Solera* scale, designated S, was the oldest; the first *criadera* (F), the next oldest; the second *criadera* (C), 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* (A). All of the casks had previously contained sherry wine type *Oloroso* 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, supplied by the Regulatory Commission for the Specific Denomination of *Brandy de Jerez*.

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 average of the whole scale.

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 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. Experimental aging was carried out for 5 years (or 20 decantings).

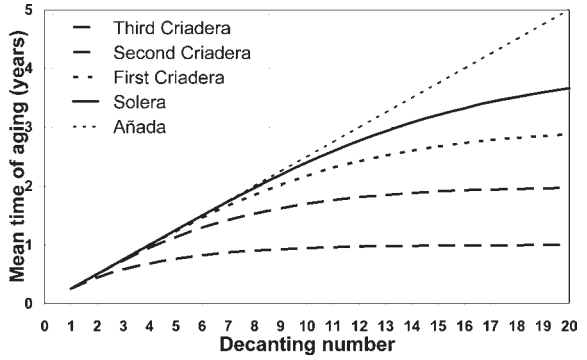

Figure 1. Evolution of the mean time of aging in the experimental system of dynamic aging by *Soleras y Criaderas*. (— — —) Third Criadera; (— - —) second Criadera; (- - -) first Criadera; (————) Solera; (- - -) Añada.

An *average time of aging* arises as a consequence of the drawing-off and refilling operations in the dynamic system and indicates the average time that all of the brandy contained in a certain cask has been aged. It can be assessed for each sample using sampling dates and the calculation formula (*21*). 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 1**) reveals their aging aims: 4 years for the *Solera* scale, 3 years for the first *Criadera*, 2 years for the second, and 1 year for the third *Criadera*.

In a second part, the study covered a total of 64 commercial samples of *Brandy de Jerez*, of which 21 were of the *Brandy de Jerez Solera* (S) type, 18 were of the *Brandy de Jerez Solera Reserva* (SR) type, and 25 were of the *Brandy de Jerez Solera Gran Reserva* (SGR) type. The sampling represented brandies of 100% of the producers registered with the Regulatory Council and a coverage of all products sold approaching 90%. The authenticity of the commercial brandies used in this study was guaranteed by the Regulatory Council for the Specific Denomination of *Brandy de Jerez*.

Finally, another 35 commercial bottled brandies were included in the study, all acquired in the market; of these, 12 are from different regions of Spain without quality denomination, 19 are French products (11 Cognacs, 4 Armagnacs, and 4 without quality denomination), and 4 are from South Africa.

Statistical Studies. External calibrations were obtained using ALAMIN (*22*), which is a DOS program that establishes the performance characteristics of the analytical method from the calibration data set. ANOVA and multivariate analysis of data included principal component analysis (PCA) and linear discriminant analysis (LDA) performed using the statistical computer package Statistica 7.0 (Tulsa, OK, USA).

RESULTS AND DISCUSSION

Pilot Scale Systems of Dynamic and Static Aging. From the extraction curves given as **Figure 2** several points can be made. The initial rise in the concentrations (common to all of the compounds studied) is produced by the predominance of the extraction phenomenon over the dilution effect resulting from the addition of the younger distillate. This situation changes after a certain number of decantings, and the concentrations tend to stabilize and/or decrease slightly.

At the date of termination of the experiment (5 years), the third and second scales have entered the phase of apparent exhaustion of the wood for most of the compounds. This phase is defined as the state in which the supply from the wood is not capable of compensating for the dilutions of the drawing-off/refilling operations. The explanation for this exhaustion is that the third *Criadera* is refilled with new distillate with a greater extractive power than those aged because it is not saturated in compounds from the casks. However, the first scale and the *Solera* scale have stabilized their content in most of the polyphenols. As can be observed, the decanting at which stabilization is reached is more advanced for the scales of greater age.

In compounds such as caffeic and *p*-coumaric acids, very intense initial extractions take place, followed by a sharp decline; therefore, we hypothesized about these compounds originating mainly from the wine previously held by the cask: the operation of wining the casks facilitates the occlusion of these species in the pores of the wood or their coprecipitation with tartaric acid in forms that are not chemically bound, which promote a rapid extraction kinetic.

Some other compounds derived from the thermal degradation of wood (hydroxymethylfuraldehyde, furaldehyde, coniferaldehyde, and sinapaldehyde) show a great difference among the scales at decanting number one. This fact could be due to these compounds being very affected by the toasting intensity of casks (*23*, *24*), which is carried out in a traditional way that involves some variation.

It can also be observed that, over the passage of time, the scales tend to be ranked from higher to lower levels of concentration, in the direction S, F, C, and T, and that this relative classification coincides with that of the average periods of aging, the evolution of which is shown in **Figure 1**. Finally, the syringic compounds (acid and aldehyde), together with furaldehyde and gallic acid, are of most importance quantitatively.

As a summary of the extraction curves, the maximum contents reached in each scale, together with the decanting number, are given in **Table 2**. As can be seen, the contents of the analyzed compounds in the distillate increase with mean time of aging.

With respect to the brandy aged according to the static system of *Añadas*, increasing contents for most of the compounds are observed over the entire course of the experiment, although the kinetic is slower in the samples from the later decantings. When this evolution is compared with that of the *Solera* scale (S), an overlap becomes evident, which is more or less pronounced according to the compound; this can be seen until approximately the end of the third year (decanting number 12), when the concentrations in the *Añada* exceed those of the *Solera* scale. This continuous growth in the concentration of compounds from the *Añada* could allow producers to obtain brandies with a character of greater age than those from the dynamic system, in which the concentrations in the brandy stabilize at a particular point in time.

Since the samples of the same average age extracted from the *Solera* scale and the *Añada* system presented similar concentrations, a study was conducted to determine if they could be differentiated statistically. Samples extracted from *Solera* and *Añada* were classified according to the commercial category that would correspond to them in the function of its average time of aging: a minimum of 1 year for the *Solera Reserva* (SR) and 3 years for the *Solera Gran Reserva* (SGR). The LDA shows a 100% differentiation for the samples of age corresponding to both the SR and the SGR, with syringic and gallic acids selected as the variables with the best power of discrimination; these results confirm the findings reported by some authors (*25*).

Therefore, significant differences have been observed in the composition of brandies of equivalent age, between those aged by the *Añadas* system and others aged by the *Soleras y Criaderas* system; therefore, the influence of the type of aging system on the profiles of the distillates is confirmed. The existence of such differences could be relevant for setting quality standards.

One interesting aspect of the system of *Soleras y Criaderas* is that the final brandy tends to become homogenized in character due to the periodical mixing operations performed during the

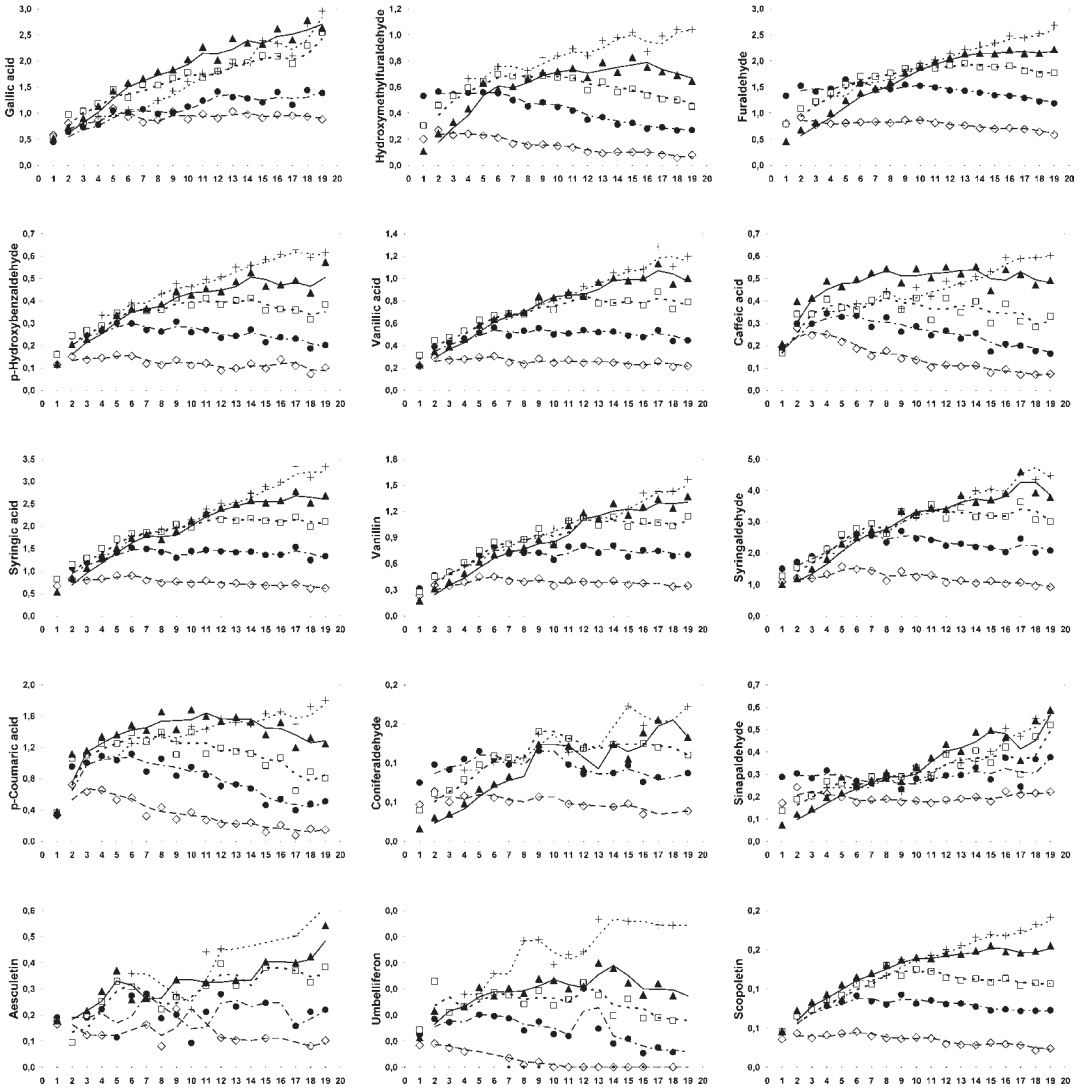

Figure 2. Time evolution curves of the compounds under study during the assay of experimental aging by *Añadas* and *Soleras y Criaderas*: (— ◊ —) Third Criadera; (- — ● — -) second Criadera; (- □ -)fFirst Criadera; (— ▲ —) Solera; (- + -) Añada. X-Axis is the decanting number. Y-Axis is the concentration of each compound expressed in mg/L.

Table 2. Maximum Contents (mg/L) of the Compounds Analyzed in the Experimental Aging Assay[a]

	third *Criadera*	second *Criadera*	first *Criadera*	*Solera*	*Añada*
gallic acid	1.09 (5)	1.44 (12)	2.55 (19)	2.78 (18)	2.95 (19)
hydroxymethylfuraldehyde	0.27 (2)	0.56 (5)	0.70 (6)	0.83 (15)	1.04 (19)
furaldehyde	0.92 (2)	1.64 (5)	1.95 (13)	2.22 (19)	2.68 (19)
p-hydroxybenzaldehyde	0.16 (5)	0.31 (9)	0.41 (14)	0.57 (19)	0.63 (17)
vanillic acid	0.31 (6)	0.56 (9)	0.88 (17)	1.13 (17)	1.28 (17)
caffeic acid	0.28 (2)	0.34 (4)	0.43 (8)	0.55 (14)	0.60 (16)
syringic acid	0.91 (6)	1.54 (11)	2.26 (11)	2.78 (17)	3.34 (19)
vanillin	0.46 (6)	0.81 (14)	1.15 (19)	1.37 (19)	1.57 (19)
syringaldehyde	1.59 (5)	2.71 (9)	3.65 (17)	4.61 (17)	5.12 (17)
p-coumaric acid	0.73 (2)	1.12 (6)	1.40 (8)	1.69 (10)	1.80 (19)
coniferaldehyde	0.06 (5)	0.12 (9)	0.14 (9)	0.16 (17)	0.17 (19)
sinapaldehyde	0.24 (2)	0.38 (19)	0.52 (19)	0.59 (19)	0.58 (19)
aesculetin	0.22 (9)	0.28 (7)	0.40 (12)	0.54 (19)	061 (18)
umbelliferon $\times 10^3$	0.45 (2)	0.10 (5)	0.16 (12)	0.20 (13)	0.28 (13)
scopoletin	0.05 (6)	0.09 (9)	0.13 (8)	0.16 (19)	0.19 (19)

[a] In parentheses are the decanting numbers in which each scale reached the maximum value.

successive decantings and refillings. To confirm this, in some decantings, samples were taken individually from the three casks of both *Solera* scale and *Añada*. By way of example, **Figure 3** shows the graphs of evolution of the coefficients of variation between the casks for gallic acid, hydroxymethylfuraldehyde, and vanillin. As can be observed, the variability is always greater between the casks that constitute the *Añada* than between those that constitute the *Solera*, which also presents a tendency to

diminish. In contrast, the variability in the *Añada* does not follow a clear trend for all of the compounds: some, like gallic acid, *p*-hydroxybenzaldehyde, or scopoletin, increase; some, like hydroxymethylfuraldehyde, syringaldehyde, or coniferaldehyde stay constant; and others, like vanillin, furaldehyde, or vanillic syringic, caffeic acid, or *p*-coumaric acids decrease.

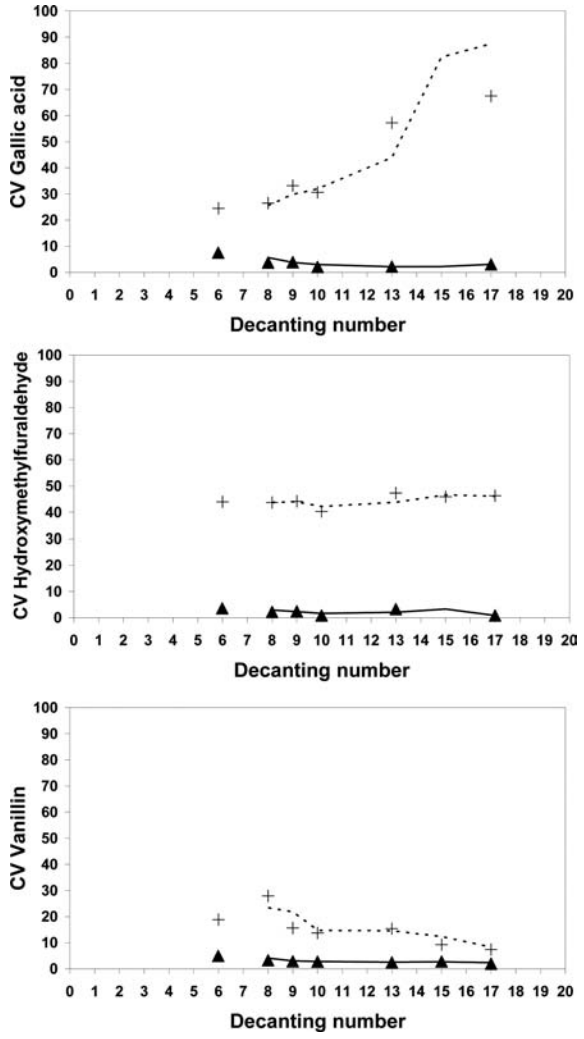

Figure 3. Time evolution of the coefficients of variation (CV) of the concentrations between casks of the same aging scale. (— ▲ —) Solera; (- + -) Añada.

Last, it was considered of interest to study the possibility of discriminating between the samples according to the commercial category that would correspond to the sample as a function of its average time of aging: a minimum of 6 months for the *Solera* (S), 1 year for the *Solera Reserva* (SR), and 3 years for the *Solera Gran Reserva* (SGR). Thus, using the variables previously selected by PCA, a global classification of 91% is obtained by application of LDA, with the following identified as the most discriminant variables, in this order: sinapaldehyde, *p*-coumaric acid, gallic acid, vanillin, and syringaldehyde.

Commercial *Brandies de Jerez*. Table 3 gives the mean values for each of the species by commercial categories and also for the samples as a whole. The mean values show increases passing from the S to the SR group and from the SR to the SGR group, although the high variability (SD) within each group does not allow the statistical differentiation of the types with any of the compounds ($p > 0.05$ in all of the cases). It should be recalled in this context that the typification of the brandies is based on the criterion of a minimum time of aging. Quantitatively, the most important species are hydroxymethylfuraldehyde, followed by gallic acid, furaldehyde, and the benzoic aldehydes syringaldehyde and vanillin.

Finally, a study was made of the possibility of differentiating in a multivariate way the commercial types of *Brandy de Jerez*, which would be of interest to producers for quality control. The LDA selects the following as the most significant compounds, in decreasing order of discriminant capacity: vanillic acid, furaldehyde, scopoletin, syringaldehyde, vanillin, *p*-coumaric acid, hydroxymethylfuraldehyde, and *p*-hydroxybenzaldehyde. It was observed that the SR samples, with a correct classification of about 57%, overlap with the S and SGR categories. The reason for this overlapping is that the average times characterizing the different categories of *Brandy de Jerez* are minimum times, and this would also explain the greater dispersion seen for the SGR group, which is aged the longest.

Aged Distillates of Different Geographic Origins. The mean values for each species are given in **Table 4**, and several findings can be reported from their analysis in comparison with the contents in the commercial *Brandies de Jerez* (**Table 3**). For almost all of the compounds, the lowest contents are found in the French brandies, whereas the highest concentrations are seen in either Cognacs or SGR, according to the species. For most of the compounds, the S brandies present lower concentrations than

Table 3. Statistics of the Compounds in the Commercial *Brandies de Jerez*[a]

	Solera				*Solera Reserva*				*Solera Gran Reserva*				
	mean	min	max	SD	mean	min	max	SD	mean	min	max	SD	*p*-value
gallic acid	0.72	0.00	2.76	0.80	2.71	0.00	7.48	2.43	4.26	0.00	9.22	2.59	0.26
hydroxymethylfuraldehyde	18.04	1.97	53.67	10.79	42.82	5.36	149.18	41.50	58.12	15.65	191.09	41.01	0.40
furaldehyde	0.49	0.19	1.27	0.26	1.66	0.44	3.62	0.99	3.19	0.27	7.91	1.79	0.18
p-hydroxybenzaldehyde	0.07	0.00	0.19	0.07	0.23	0.00	0.66	0.18	0.43	0.14	0.98	0.27	0.52
vanillic acid	0.11	0.00	0.31	0.11	0.49	0.02	1.71	0.45	1.30	0.39	2.83	0.70	0.11
methylfuraldehyde	0.11	0.00	0.25	0.05	0.15	0.00	0.36	0.08	0.24	0.00	0.52	0.13	0.77
syringic acid	0.20	0.00	0.63	0.23	1.17	0.00	4.42	1.12	2.78	0.70	7.22	1.72	0.21
vanillin	0.86	0.00	4.07	1.01	2.45	0.46	5.94	1.80	2.66	0.67	5.80	1.48	0.30
syringaldehyde	0.38	0.00	1.26	0.46	2.20	0.20	10.59	2.51	4.59	0.84	10.77	2.61	0.26
p-coumaric acid	0.08	0.00	0.55	0.14	0.21	0.00	1.17	0.29	0.46	0.00	2.00	0.52	0.45
coniferaldehyde	0.06	0.00	0.20	0.06	0.12	0.00	0.48	0.14	0.18	0.05	0.35	0.08	0.66
sinapaldehyde	0.04	0.00	0.19	0.06	0.07	0.00	0.51	0.12	0.12	0.00	0.39	0.11	0.71
aesculetin	0.15	0.00	1.11	0.25	0.75	0.00	2.10	0.71	2.32	0.51	9.17	2.29	0.75
umbelliferon $\times 10^3$	0.20	0.00	3.18	1.10	0.36	0.00	2.08	0.71	1.08	0.06	2.62	0.82	0.39
scopoletin	0.01	0.00	0.06	0.02	0.06	0.01	0.19	0.06	0.20	0.02	2.36	0.47	0.18

[a] Values are in mg/L.

Table 4. Statistics of the Compounds in the Distillates of Different Geographic Origin[a]

	Spanish brandies				South African brandies				French brandies			
	mean	min	max	SD	mean	min	max	SD	mean	min	max	SD
gallic acid	5.04	0.00	29.11	8.94	1.04	0.00	2.07	1.47	0.00	0.00	0.00	
hydroxymethylfuraldehyde	26.83	11.17	64.78	17.35	18.86	1.00	30.99	13.00	24.87	11.13	55.42	20.74
furaldehyde	2.84	0.25	15.24	4.36	5.15	2.22	8.52	2.90	1.18	0.77	1.28	0.51
p-hydroxybenzaldehyde	0.19	0.00	0.75	0.21	0.13	0.00	0.29	0.12	0.01	0.00	0.03	0.01
vanillic acid	0.50	0.00	1.95	0.54	0.47	0.13	0.87	0.33	0.06	0.00	0.10	0.04
methylfuraldehyde	0.26	0.06	0.70	0.19	0.24	0.13	0.32	0.10	0.10	0.07	0.10	0.01
syringic acid	1.20	0.07	3.94	1.19	1.15	0.35	1.92	0.76	0.06	0.00	0.14	0.07
vanillin	2.87	0.03	10.30	3.56	1.07	0.51	1.65	0.53	0.05	0.00	0.07	0.03
syringaldehyde	2.48	0.10	8.20	2.51	1.97	0.59	3.30	1.33	0.23	0.19	0.26	0.03
p-coumaric acid	0.18	0.00	0.47	0.18	0.02	0.00	0.07	0.04	0.00	0.00	0.00	
coniferaldehyde	0.27	0.00	0.49	0.28	0.17	0.08	0.29	0.10	0.02	0.00	0.05	0.02
sinapaldehyde	0.28	0.00	1.03	0.30	0.11	0.00	0.29	0.13	0.08	0.03	0.21	0.08
aesculetin	1.02	0.00	4.51	1.36	0.91	0.20	2.20	0.89	0.05	0.00	0.09	0.04
umbelliferon $\times 10^3$	0.89	0.00	4.00	1.36	0.00	0.00	0.00		0.00	0.00	0.00	
scopoletin	0.07	0.00	0.17	0.07	0.04	0.01	0.08	0.03	0.01	0.00	0.01	0.00

	Cognacs				Armagnacs			
	mean	min	max	SD	mean	min	max	SD
gallic acid	5.74	3.27	7.91	1.45	5.86	3.08	7.61	1.97
hydroxymethylfuraldehyde	15.91	9.78	24.03	4.54	26.51	7.89	43.05	17.56
furaldehyde	8.68	5.34	14.62	3.11	10.58	2.32	34.05	15.66
p-hydroxybenzaldehyde	0.05	0.00	0.13	0.05	0.03	0.00	0.07	0.03
vanillic acid	0.29	0.00	0.81	0.22	0.28	0.20	0.39	0.08
methylfuraldehyde	0.39	0.14	1.01	0.31	0.15	0.12	0.18	0.03
syringic acid	0.86	0.00	2.24	0.65	0.80	0.43	1.34	0.40
vanillin	0.60	0.23	1.59	0.38	0.54	0.44	0.77	0.15
syringaldehyde	1.62	0.48	5.48	1.47	1.13	0.85	1.82	0.46
p-coumaric acid	0.00	0.00	0.00		0.02	0.00	0.07	0.04
coniferaldehyde	0.36	0.03	1.29	0.44	0.13	0.06	0.21	0.07
sinapaldehyde	0.72	0.04	3.91	1.15	0.31	0.20	0.49	0.13
aesculetin	0.67	0.10	1.75	0.43	0.77	0.55	1.06	0.21
umbelliferon $\times 10^3$	0.62	0.00	1.00	0.52	0.75	0.00	1.00	0.50
scopoletin	0.03	0.01	0.06	0.01	0.03	0.03	0.04	0.00

[a] Values are in mg/L.

Table 5. Comparison of the Mean Contents (mg/L) of the Compounds in the Commercial *Brandies de Jerez* against the Distillates Aged in the Experimental System of *Soleras y Criaderas*, of Equivalent Age to the Respective Commercial Categories

	Solera		*Solera Reserva*		*Solera Gran Reserva*	
	experimental	comercial	experimental	comercial	experimental	comercial
gallic acid	0.91	0.72	1.44	2.71	2.51	4.26
hydroxymethylfuraldehyde	0.34	18.04	0.45	42.82	0.70	58.12
furaldehyde	1.01	0.49	1.44	1.66	2.11	3.19
p-hydroxybenzaldehyde	0.20	0.07	0.29	0.23	0.48	0.43
vanillic acid	0.37	0.11	0.58	0.49	0.98	1.30
caffeic acid	0.29	0.00	0.30	0.00	0.48	0.00
syringic acid	1.01	0.20	1.55	1.17	2.54	2.78
vanillin	0.45	0.86	0.77	2.45	1.24	2.66
syringaldehyde	1.57	0.38	2.45	0.38	2.45	2.20
p-coumaric acid	0.82	0.08	0.89	0.21	1.32	0.46
coniferaldehyde	0.06	0.06	0.09	0.12	0.13	0.18
sinapaldehyde	0.21	0.04	0.29	0.07	0.48	0.12
aesculetin	0.10	0.15	0.24	0.75	0.39	2.32
umbelliferon $\times 10^3$	0.07	0.21	0.09	0.36	0.16	1.1
scopoletin	0.06	0.01	0.09	0.06	0.14	0.20

the other distillates (except for the French brandies), while the concentrations found in the SR are similar to those of the other Spanish brandies. These values are more widely dispersed, probably due to the differences of their geographic origin within the Spanish territory.

Joint Analysis of the Samples. The comparison by categories of the mean contents in commercial brandies with those of the samples from the pilot aging system of equivalent average age reported in the first part of this article is summarized in **Table 5**. There are few qualitative differences. Caffeic acid was not detected in the commercial *Brandies de Jerez*, whereas 2-methylfuraldehyde gave a signal. Some of the compounds (hydroxymethylfuraldehyde, vanillin, umbelliferon, and aesculetin) are found at much higher concentrations in the commercial brandies

Table 6. LDA of Commercial *Brandies de Jerez* and Aged Distillates of Different Geographic Origin[a]

	% correct classification	South African brandies	French brandies	Armagnacs	Spanish brandies	Cognacs	S	SR	SGR
South African brandies	100.0	4	0	0	0	0	0	0	0
French brandies	0.00	0	0	0	0	0	4	0	0
Armagnacs	75.0	0	0	3	0	1	0	0	0
Spanish brandies	58.3	0	0	0	7	1	4	0	0
Cognacs	90.9	1	0	0	0	10	0	0	0
Solera	85.7	0	0	0	1	0	18	2	0
Solera Reserva	58.8	0	0	0	0	0	6	10	1
Solera Gran Reserva	80.0	0	0	0	0	0	3	2	20
total	73.5	5	0	3	8	12	35	14	21

[a] Classification matrix.

than in the distillates from the aging assay, such that the quantities present in the commercial type S already exceed those present in the distillate aged for an average time of more than 3 years. Hydroxymethylfuraldehyde is found in caramel coloring, and vanilla is the principal component of the aromatic extract of vanilla pods; the addition of both of these products is authorized (*quantum Satis* dose) in the final phase of production of *Brandy de Jerez*, as part of the strategy for the definition of this type of brandy.

For their part, the quantities of *p*-coumaric and caffeic acids are clearly lower in the commercial samples, in all three categories; this could reflect the evolution patterns of rapid extraction until exhaustion, characteristic of the origin of these compounds in cask wining, which was put forward as a hypothesis. Similarly, these cask wining operations typical of Jerez, which have been taken as a guideline by brandy producers in the rest of the peninsula, could explain the differences in the concentrations of caffeic and *p*-coumaric acid already described between the Spanish brandies and the rest of the distillates. With respect to the rest of the species, their relative contents vary according to the category. Among the *Soleras*, in general the concentrations are higher in the commercial brandies; while in the *Solera Gran Reserva* group, brandies aged experimentally present the highest values. The *Solera Reserva* brandies, however, are different in not presenting a clear tendency in this respect. However, the variability in the length of the useful life of casks in each winery could affect the profiles of phenolic and furfural compounds of the *Brandies of Jerez* on the market.

In addition, the classification obtained by LDA that is given in **Table 6** and presented graphically in **Figure 4** shows a Spanish brandy partially overlapped by the *Soleras of Jerez*. The identity of three of these samples that overlap, represented by a code during the course of the study, reveals a production process in which aging is performed by *Soleras y Criaderas*, which could be an explanation for the statistical similarity described. Among the Spanish brandies, the one that is classified as Cognac is the only one that shows an aging pattern in accordance with the tendencies of this French denomination of origin. The French brandies without denomination of origin are also found to show coincidences with the *Solera Brandies de Jerez*. The reason for this coincidence is that, when a brandy is introduced into the aging system, whether static or dynamic, a minimum time is required for it to acquire its own characteristics. The South African products are classified in a group of their own, but located in the area close to the *Solera* brandies. Armagnacs and Cognacs present a very good differentiation, both from the rest and from each other, even given the dispersion within each group. With respect to those of Jerez, the overlapping of the SR with the S and SGR groups, discussed above, is repeated; this makes it difficult to differentiate completely between the commercial categories. It should, however, be noted that the SR and SGR types, together, can be differentiated completely from the rest of

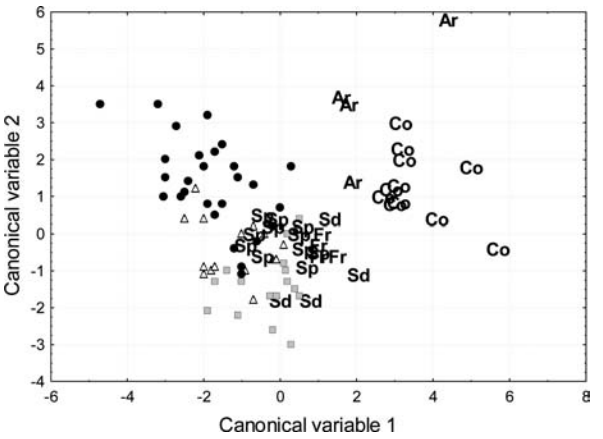

Figure 4. LDA of commercial *Brandies de Jerez* and aged distillates of different geographic origin. Projection of the samples in terms of the canonical variables. Sd, South African brandy; Fr, French brandy; Ar, Armagnac; Co, Cognac; Sp, Spanish brandy; shaded square, *Brandy de Jerez Solera*; △, *Brandy de Jerez Solera Reserva*; ●, *Brandy de Jerez Solera Gran Reserva*.

the aged distillates, thus pointing to the distinctive and exclusive character of these brandies.

If an imaginary horizontal line is traced that intercepts the second canonical variable by the origin, the set of samples are divided into two subgroups, the upper one of which includes the French denominations of origin, the *Solera Gran Reserva* and some of the *Solera Reserva* brandies; a correlation with quality can, therefore, be attributed to this function. Among the most discriminant variables, the statistical technique selects vanillic acid, coniferaldehyde, sinapaldehyde, and furaldehyde; this last compound is identified in the base distillate, which suggests that it could be considered a characteristic that marks the quality of the distillates used in the production of *Brandy de Jerez*.

In conclusion, a similarity is observed between the *Solera Brandies de Jerez* and some of the other Spanish brandies aged according to the system of *Soleras y Criaderas*, and with the French brandies without denomination of origin. The SR and SGR *Brandies de Jerez* similarly show a clear differentiation from the rest of the distillates of different origin, indicating their highly specific character.

ABBREVIATIONS USED

S scale, *Solera* scale; F, first *Criadera*; C, second *Criadera*; T, third *Criadera*; A, *Añada*; S brandy, brandy *Solera*; SR brandy, brandy *Solera Reserva*; SGR, brandy *Solera Gran Reserva*; Sp, Spanish brandy; Sd, South African brandy; Fr, French brandy; Ar, Armagnac; Co, Cognac; PCA, principal component analysis; LDA, linear discriminant analysis.

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