Characterization of Cider Brandy on the Basis of Aging Time

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ABSTRACT: To characterize cider brandies on the basis of age, chemometric techniques (principal component analysis, linear discriminant analysis, and Bayesean analysis) together with contents of volatile, furanic, and phenolic compounds were used. Significant principal components computed by a double cross-validation procedure allowed us to visualize the structure of the database as a function of the aging time to which the cider brandies had been subjected. Feasible and robust discriminant rules were computed and validated by a cross-validation procedure that allowed suitable classification of fresh and aged brandies, obtaining classification hits > 90%. The most discriminant variables for characterizing cider brandies according to their aging level were as follows: ethyl caprylate > ethyl isovalerate > 1-propanol > hexyl acetate.

Keywords: characterization, cider brandy, aging, volatile, phenolic

Introduction

CIDER BRANDY IS A TRADITIONAL BEVERAGE ELABORATED BY DISTILLING fermented apple juice in alembics and subsequent maturing in oak wood casks to improve its sensory characteristics.

During aging, many reactions take place that involve substances present in the fresh distillate and in the wood staves. The changes detected in the aromatic profile of aged spirits are brought about by evaporation of volatiles through the barrel, substances extracted or derived from the wood, reactions by the compounds present in the fresh distillates, and reactions by compounds derived from the wood with raw distillate components.

The ethanol in these beverages is subjected to esterification with fatty acids, thus enhancing the characteristic fruity aroma of intermediate-chain and long-chain ethyl esters. However, nonethyl esters decrease by transesterification (Onishi and others 1977; Mangas and others 1996a). Fatty acids decrease in parallel, but acetic acid arises as a consequence of its extraction from wood where it is formed during barrel making or by the oxidation of ethanol (Reazin and others 1976; Reazin 1981). Likewise, carbonyl compounds react with ethanol to yield cetals and acetals (Williams and Strauss 1975), which are more pleasant than the respective cetones and aldehydes.

On the other hand, ethanol also degrades lignin of wood in a 2-step process. First, ethanol extracts lignin to yield ethanol-lignin compounds and, subsequently, ethanol-lignin is degraded into phenolic compounds. Although these phenolic compounds, mainly aromatic acids and aldehydes, also originate directly from the staves (Puech 1981), where they are generated during the seasoning, charring, and toasting of wood to make the casks (Chatonnet 1995). Tannins, responsible for astringency (Viriot and others 1993; Singleton 1995), sugars (Belchior and Carneiro 1972; Reazin 1981), and furan and pyran derivatives formed from heating carbohydrates and associated with a "toasty-caramel" aroma (Onishi and others 1977; Cutzach and others 1997, 1999), are also incorporated into the distilled product.

An important compound related to maturation in oak wood is oak or whiskey lactone (β-methyl-γ-octalactone), a volatile compound whose odor is defined as "wood" or "coconut." Only 2 of the 4 stereoisomers are present in oak (Masson and others 1995) and the quantity of extractable oak lactones in American oak is sometimes so high that it could have a negative influence on the aroma of wine (Chatonnet and Dubourdieu 1998).

Some authors have proposed the relationships between phenolic compounds of low molecular weight (Delgado and others 1990), or the presence of coumarines (Otsuka and Zenibayashi 1974; Tricard and others 1987), as indicators of wine and spirits really aged in oak, but the use of caramel and oak extracts, which contain these substances, prevents their sole employment as markers (Fernández Izquierdo and others 2001). Other compounds proposed as aging markers, such as furfural, 5-methylfurfural, and 5-hydroxymethylfurfural, were also discarded due to their being present in caramel (Quesada Granados and others 1996) and the fact that their concentration can be affected by the distillation system (Onishi and others 1977) and the type of raw cider (Mangas and others 1996b).

Pattern recognition techniques, such as principal components analysis (PCA), linear discriminant analysis (LDA), Bayesean analysis, soft independent modeling of class analogy, and partial least squares, have been successfully used for the classification of alcoholic beverages according to their geographical origin and raw material (Miyashita and others 1989; Mazerolles and others 1992; Bindler and others 1992; Moret and others 1994; Mangas and others 1997; Picinelli and others 2000; Cameán and others 2001). Hence, the classification of matured spirits according to their time of aging could be carried out by these techniques using their chemical composition.

The aim of this study was to characterize cider brandy on the basis of its time of aging by means of the compounds involved in this process, namely volatile, furanic, and phenolic compounds, and multivariate techniques.

Materials and Methods

Reagents and standards

Major volatiles. Standard solutions were prepared in ethanol/water (35/65, vol/vol). Samples and standards were filtered through a 0.45-μm polyvinylidene difluoride (PVDF) membrane. 3-Pentanol was used as internal standard at 0.5 g/L.

Minor volatiles. Standard solutions were prepared in ethanol/water (30/70, vol/vol) and filtered through a 0.45-μm PVDF mem-

brane. Samples were subjected to microextraction with Freon 113, according to the method optimized by Ferreira and others (1993). Ten milliliters of cider brandy, previously diluted to 30% (vol/vol) in ethanol, were introduced into the extraction centrifuge tubes with 150 μL of Freon 113, 2 g of ammonium sulfate, and 5 μL of a solution of 2-ethyl-1-hexanol (13 g/L in ethanol at 30%, vol/vol) used as internal standard. The tubes were shaken by means of a water shaking bath at 20 °C for 60 min and centrifuged (12000 × *g* for 10 min). One microliter of the organic phase was recovered and injected into the chromatographic system.

Phenolic and furanic compounds. Standards were prepared in a solution of 2% acetic acid and 0.02 M sodium acetate, and samples were previously subjected to an ethanol removal process under vacuum at 30 to 35 °C, and then filtered through a 0.45-μm PVDF membrane.

Chromatographic equipment and conditions

Major volatiles. The following equipment and column were used for gas chromatography analysis of the major volatiles: a Hewlett-Packard 5890 gas chromatograph fitted with a flame ionization detector and 5 m × 1/8 in. stainless steel column packed with carbowax 1500 on carbopack C 8/100 to 0.5%. Chromatographic conditions were as follows: initial temperature 45 °C for 10 min; program rate, 3.5 °C/min; final temperature 125 °C; isothermal to 125 °C for 25 min; injector and detector temperature 170 °C; carrier gas, He at 60 psi; injection volume 1 μL.

Minor volatiles. The following equipment and column were used for the gas chromatography analysis of the minor volatiles: a Hewlett-Packard 5890 gas chromatograph interfaced with a Hewlett-Packard 5972 mass-selective detector (MSD), fitted with a column (FFAP 50 m × 0.22 mm i.d.; phase thickness, 0.33 μm), and inserted into a split/splitless injector (splitless mode, 1 min). Chromatographic conditions were as follows: initial temperature 40 °C for 5 min; program rate, 3.0 °C/min; final temperature 220 °C; isothermal to 220 °C for 60 min; injector and detector temperature 250 °C; carrier gas, He at 1 mL/min; injection volume 1 μL. The analysis was performed in the electron impact (EI) mode, the ionization voltage was fixed at 70 eV and the quantification was carried out in selected-ion-monitored (SIM) mode.

Phenolic and furanic compounds. Experimental data were obtained from a high-performance liquid chromatography system (Waters Associates) equipped with a 712 automatic injector, 2 M510 pumps, a Millenium v. 2.0 software data module, and a 996 photodiode array detector. Separation of analytes was carried out on Spherisorb ODS-2 (250 × 4.6 mm, 3 μm) at 40 °C using 2% acetic acid and 0.02 M sodium acetate (pH, 3.2; solvent A) and methanol (solvent B) as mobile phase. Elution conditions were as follows: starting, 97% A; isocratic for 4 min; linear increase of solvent B in solvent A to 30% solvent B for 21 min; isocratic for 25 min. Flow rate was 1 mL/min. Injection volume, 10 μL. Gallic, vanillic, syringic, furfural, 5-hydroxymethylfurfural, 5-methylfurfural, 2-furyl methyl ketone, vanillin, and syringaldehyde were detected at 280 nm, whereas scopoletin, ferulic acid, coniferaldehyde, and synapaldehyde were detected at 320 nm.

Database and statistics

The database was formed by 282 rows (cider brandies) and 43 columns (chemical variables). For its construction, samples were selected that could pick up the possible variance relative to the factors involved throughout the generation process of cider brandy. We employed 250 experimental distillates, divided as follows: 132 fresh spirits (months of aging < 12) were obtained from apple juice concentrate with different technologies: Charente alembic (n = 66), 33 aged in French oak and 33 aged in American oak, and rectification column (n = 66), 33 aged in French oak and 33 aged in American oak, and 6 fresh spirits were obtained from fresh apple juice, distilled by rectification column and aged in American oak. There were 138 total experimental fresh spirits. We onbtained 108 experimental aged spirits (months of aging ≥ 12) from apple juice concentrate with different technologies: Charente alembic (n = 54), 27 aged in French oak and 27 aged in American oak, and rectification column (n = 54), 27 aged in French oak and 27 aged in American oak; 4 aged spirits were obtained from fresh apple juice, distilled by column system and aged in American oak. There were 112 total experimental aged spirits. Furthermore, 32 commercial cider brandies also were included, of which 5 were AOC-Calvados (AOC, appelation d'origine contrôlée) and 27 originated in Spain; 17 were aged longer than 12 mo and the rest, 15 samples, were categorized as fresh cider brandies (aging time < 12 mo). The chemical variables analyzed were as follows: acetaldehyde, methanol, ethyl acetate, 1-propanol, isobutanol, 1-butanol, acetal, D-amyl alcohol, isoamyl alcohol, ethyl isovalerate, isoamyl acetate, ethyl caproate, hexyl acetate, 1,1,3-triethoxypropane, 1-hexanol, ethyl caprylate, 1-octanol, ethyl caprate, diethyl succinate, 2-phenylethyl acetate, ethyl laurate, *cis* and *trans* isomers of β-methyl-γ-octalactone, ethyl myristate, caprylic acid, ethyl palmitate, capric acid, lauric acid, ethyl linoleate, myristic acid, palmitic acid, gallic acid, 5-hydroxymethylfurfural, furfural, vanillic acid, 5-methylfurfural, syringic acid, vanillin, syringaldehyde, ferulic acid, scopoletin, coniferaldehyde, and sinapaldehyde. The data were autoscaled before multivariate analysis (PCA, LDA, and Bayesean analysis) and processed by means of the PARVUS statistical package (Forina and others 1988). Cider brandies were categorized according to their aging level as fresh brandies (F, < 12 mo of aging) and aged brandies (A, ≥ 12 mo of aging).

Results and Discussion

Univariate analysis

Before applying the multivariate techniques to classify the cider brandies, a univariate analysis was carried out to ascertain whether any variable by itself would allow us to distinguish fresh and aged brandies. With this aim in mind, we used the Fisher classification technique. Fisher weights (FW) were computed for classifying cider brandies, ethyl caprylate (FW: 0.67), ethyl caprate (FW: 0.54), and ethyl isovalerate (FW: 0.48) being found to be the variables with the highest FW. However, the use of these variables did not allow us to correctly differentiate between fresh and old cider brandies; therefore, a multivariate treatment was necessary.

Factor analysis of the internal structure

Principal component analysis (PCA) and a double cross-validation procedure with 5 groups for cancellation was used to reduce dimensionality of data matrix, to compute the predictive factors, to choose the most relevant variables, and to ascertain the data structure. Five predictive factors were chosen, which accounted for 82.6% of the variance. The 1st (40.5% of explained variance) and 3rd (8.3% of explained variance) axes were related to the age of the spirits. In this sense, it may be pointed out that fresh brandies presented lower scores for the 1st principal component than aged brandies, and higher scores on the 3rd axis.

Loadings are the correlation coefficients between original variables and the principal components. Therefore, those chemical variables more correlated to the 1st and 3rd factors should be the most relevant ones for discriminating cider brandies by their aging level. Using this criterion, and with the aim of maximizing the clas-

Table 1—Classification matrix by the LDA method[a]

	Assigned category		
True category	F	A	Hits (%)
F	153	0	100
A	9	120	93.0
Overall			96.8

[a]F, fresh distillate; A, aged distillate.

Table 2 —Prediction matrix by the LDA method[a]

	Assigned category		
True category	F	A	Hits (%)
F	148	5	96.7
A	14	115	89.2
Overall			93.3

[a]F, fresh distillate; A, aged distillate; 3 groups for cancellation.

sification capacity of the discriminant methods, we selected those chemical variables that presented loadings in absolute values > 0.08 for the 1st and 3rd principal components. Therefore, the original variables selected were as follows: acetaldehyde, methanol, ethyl acetate, 1-propanol, isobutanol, 1-butanol, D-amyl alcohol, isoamyl alcohol, ethyl isovalerate, hexyl acetate, 1,1,3-triethoxypropane, 1-hexanol, ethyl caprylate, 1-octanol, ethyl caprate, diethyl succinate, 2-phenylethyl acetate, ethyl laurate, *trans*-oak lactone, ethyl myristate, ethyl linoleate, myristic acid, palmitic acid, gallic acid, 5-hydroxymethylfurfural, vanillic acid, syringic acid, vanillin, syringaldehyde, scopoletine, and coniferaldehyde. Thus, the new database was a matrix of 282 rows × 31 columns.

Linear discriminant analysis

Table 1 presents the classification matrix obtained from the LDA method. Table 2 shows the prediction matrix computed from a cross-validation procedure (internal validation), using 3 groups for cancellation. As can be seen, classification and prediction hits were very similar, > 93%. Taking into account these results, we can consider that the discriminant rule computed is both sufficiently feasible and robust for the purposes of classifying cider brandies on the basis of their degree of aging. At the same time, a stepwise LDA analysis, using Wilks' lambda criterion, was carried out to ascertain the most discriminant variables. Values of *F*-to-enter and *F*-to-remove of, respectively, 3.84 and 2.71 (confidence level of 90%) were used. Wilks' lambda was computed as 0.40, thus 60% of total variance is explained by within-group differences. The most important variables selected were as follows: ethyl caprylate > ethyl isovalerate > 1-propanol > hexyl acetate > gallic acid > diethyl succinate > 2-phenylethyl acetate. In this sense, we must highlight the low capacity for classifying phenolic substances, traditionally related to the maturation process. This could be due to the high variability included in the database with respect to the factors that influence the concentration of these substances in the spirit (oak type, barrel size, and so on). In contrast, the more discriminant compounds were basically esters, which exert an important influence on the sensory characteristics of the final product. The concentration of esters is affected by the aging process as a consequence of the high ethanol level. This molecule esterifies fatty acids and transesterifies acetate esters (Mangas and others 1996a); thus, high concentrations of ethyl esters and low concentrations or the absence of acetate esters, such as hexyl and 2-phenylethyl acetate, are good indicators of the degree of aging. On the other hand, gallic acid is a relevant variable to distinguish cider brandies for their aging level. As is well known, this phenolic increases during cider brandy maturing (Mangas and others 1996c) as a consequence of hydrolysis of gallotannins. At the same time, note that furanic compounds are not relevant variables for distinguishing cider brandies by their aging level, which is in agreement with the results obtained in other brandies (Quesada Granados and others 1996).

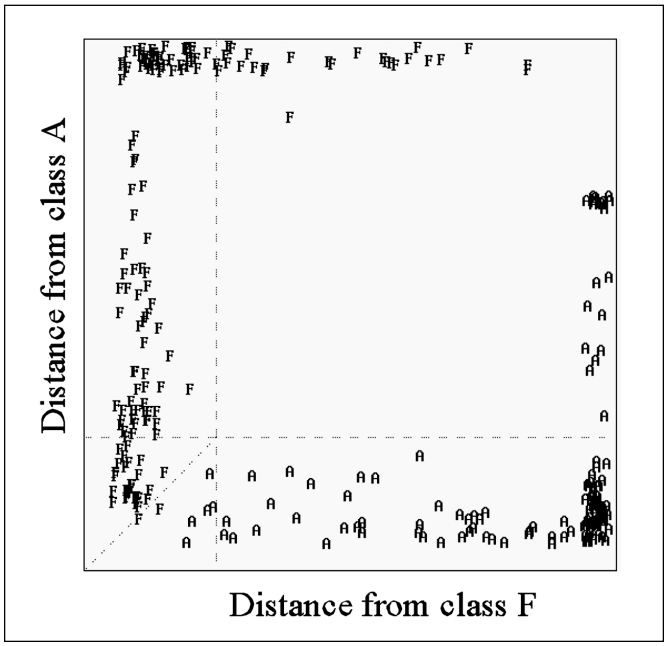

Figure 1—Coomans' diagram. A, aged brandies; F, fresh brandies.

Table 3—Sensitivities (S) and specificities (Sp) of fresh (F) and aged (A) models

	S (%)	Sp (%)
F	83.7	96.1
A	84.5	80.4

Bayesean analysis

This chemometric treatment is a modeling technique. In Bayesean analysis, the function of the probability density is estimated for each class, a normal multivariate distribution of the data being assumed. Boundaries are constructed for each class where 95% of probability is accumulated. From a geometrical viewpoint, a hyperellipsoid with a critical Mahalanobis distance is constructed for each category. First-class and second-class errors (α and β) related to model sensitivity ($1-\alpha$) and specificity ($1-\beta$) were estimated. As can be seen in Table 3 and Figure 1, where Coomans' diagram is displayed, the sensitivity of the fresh and aged models was > 83%. Thus, < 17% of samples belonging to each model are rejected of their own model, and the specificity of both models was > 80%. Therefore, < 20% of samples are accepted by a model to which they do not belong. The specificity of the Fresh model was very high (96%), which means that very few aged samples are included in this class. Correct classifications were > 97% (Table 4), and correct predictions, evaluated by cross-validation using 3 groups for cancella-

Table 4—Classification matrix by Bayesean analysis[a]

	Assigned category		
True category	F	A	Hits (%)
F	153	0	100
A	6	123	95.4
Overall			97.9

[a]F, fresh distillate; A, aged distillate

Table 5—Prediction matrix by Bayesean analysis[a]

	Assigned category		
True category	F	A	Hits (%)
F	151	2	98.7
A	23	106	82.2
Overall			91.1

[a]F, fresh distillate; A, aged distillate; 3 groups for cancellation.

tion, was 91% (Table 5). Therefore, we can assume the constructed model is both sufficiently feasible and robust for classifying cider brandies according to their degree of aging.

Conclusions

IN CONCLUSION, THE USE OF THE CHEMICAL COMPOSITION OF CIDER brandies, together with chemometric techniques (PCA, LDA, and Bayesean analysis), allowed the authors to characterize cider brandies on the basis of their aging level. The most discriminant variables were ethyl caprylate, ethyl isovalerate, 1-propanol, hexyl acetate, gallic acid, diethyl succinate, and 2-phenylethyl acetate.

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