JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Influence of Type of Distillation Apparatus on Chemical Profiles of Brazilian Cachaças

RONI VICENTE RECHE, ALEXANDRE FERREIRA LEITE NETO, ALEXANDRE ATAIDE DA SILVA, CARLOS ALEXANDRE GALINARO, RENATA ZACHI DE OSTI, AND DOUGLAS WAGNER FRANCO*

Departamento de Química e Física Molecular, Instituto de Química de São Carlos, Universidade de São Paulo (USP), Avenida Trabalhador São-carlense 400, CP 780, CEP 13560-970 São Carlos, SP, Brazil

Brazilian cachaças (115 samples; 73 samples derived from distillation in copper pot stills, 42 samples derived from distillation in stainless steel columns), collected directly at the producers, were analyzed for the contents of 34 constituents by chromatography, inductively coupled plasma optical emission spectrometry, and atomic absorption spectrometry. The analytical data were subjected to principal component analysis (PCA) and linear discriminant analysis (LDA). The PCA treatment led to discrimination of the two groups of cachaças, explaining 65.0% of the database variance. Using LDA and ethanal, ethyl carbamate, dimethyl sulfide, isobutyl alcohol, *n*-propanal, copper, ethyl acetate, and phenylmethanal as chemical descriptors, a model was developed that presented 95.1% accuracy in predicting the type of distillation apparatus.

KEYWORDS: Cachaças; distillation; chemical profiles

INTRODUCTION

During recent years, the export of Brazilian sugar cane spirit, known as cachaça, has shown a considerable increase. It is estimated that the cachaça industry produces more than 5000 brands, and exports are expected to reach U.S. $30 million in 2010 (*1*). Therefore, it is essential that the existing production process be improved and that chemical and sensory qualities be rigidly controlled (*1*−*6*). Distillation of the sugar cane-derived fermented must or "wine" in copper pot stills (group 1) or stainless steel columns (group 2) and the fermentation are the most important steps in the production of cachaça (*7*, *8*). The resulting cachaças can be distinguished as the so-called homemade or "artisanal" cachaças that are distilled in copper pot stills and "industrial" cachaças that are distilled in stainless steel columns. There is ongoing debate as to which production method results in better qualities.

During the distillation process, a heated rich mixture of volatile compounds obtained from the fermentation step is in contact with the hot surface of the equipment, which behaves as a reactor, and the metals present in the walls of the distiller, which behave as catalysts (*7*−*10*). As a consequence, a high number of reactions such as esterification, acetalization, dehydration, and oxidation take place during the distillation (*9*−*13*). The yields of these reaction products as well as their relative ratio are therefore dependent on the type of distillation apparatus, the material employed in their construction, and the intensity and homogeneity of the heat source (*7*, *8*, *10*−*14*). For example, low levels of volatile sulfur compounds such as dimethyl sulfide and high contents of aldehydes and copper ions in the spirits are related to the presence of copper in the ascendant part of the distiller (*8*, *12*, *14*). Nonuniform heating or overheating of the wine (fermented must), which is rich in sugars (pentose or hexose), increases the concentration of 2-furfuraldehyde and 5-hydroxymethyl-2-furfuraldehyde (*10*, *12*, *14*−*16*, *33*).

The copper pot still (or alembic) process is known as a batch distillation corresponding to one theoretical plate; a column is a continuous process involving many assembled theoretical plates (*7*, *8*, *17*). When the distillation is carried out in a pot still, the alcoholic degree of the spirits is monitored during the distillation process and three fractions, namely, head, heart, and tail, are separated on the basis of their alcoholic contents. The main objective of this separation is to ensure that the heart fraction has a low concentration of toxic and sensorial negative compounds, acceptable concentrations of ethanol, and compounds that are favorable to the aroma and flavor of the cachaça. The head (alcoholic degree of 50−70% v/v) distills in the temperature range of 70−75 °C, whereas the tail (alcoholic degree of 10−38% v/v) distills in the temperature range of 85−100 °C (*9*, *18*). These two fractions make up 20% of the total volume of the distilled cachaça. The tail and the head can be reused in subsequent distillations. The heart (alcoholic degree of 38−50% v/v) distills in the range of 75−85 °C and makes up 80% of the total volume of distilled cachaça (*9*, *14*, *18*). After alcoholic degree correction through water addition, the heart becomes the cachaça sold in the market (*14*). When a

* Author to whom correspondence should be addressed (telephone/fax +55 16 3373 9976; e-mail douglas@iqsc.usp.br).

10.1021/jf0704110 CCC: $37.00
Published on Web 07/13/2007

column is used in the distillation process, the three fractions are not separated, because it is a continuous process (*9*). The distilled portion shows an alcoholic degree of 35−65% (v/v), which is adjusted with water to 38−48% (v/v) to yield the commercial product. The temperature in the base of the column is usually between 103 and 105 °C and that at the top around 94 °C (*9*, *14*).

Therefore, taking into account all of these differences in the distillation step, some differences in the qualitative and quantitative chemical profiles of artisanal and industrial cachaças are expected to occur.

As a part of our efforts to better understand the cachaça's chemistry, this study aims at establishing sound scientific criteria to distinguish cachaças according to the production technique.

MATERIALS AND METHODS

Samples. All of the samples of cachaça had been collected from the producer at the moment of the distillation and stored in the refrigerator (6−8 °C), hence eliminating variables such as aging time, addition of water, or storage effects. One hundred and fifteen samples of cachaças were analyzed. From these, 82 samples (55 samples distilled in copper pot stills, heart fraction, group 1; 27 samples distilled in stainless steel columns, group 2) constituted the evaluation group, and 33 samples were used as a test group (18 distilled in copper pot stills, 15 distilled in stainless steel columns; LDA analysis). The complete list of the place of production is available as Supporting Information.

Standards. Methanol, ethanal (formaldehyde), ethyl acetate, propyl alcohol, isobutyl alcohol, isoamyl alcohols (3-methyl-1-butanol and 2-methyl-1-butanol), acetic acid, *sec*-butyl alcohol, and *n*-butyl alcohol were purchased from Mallinckrodt (Xalostoc, Mexico); ethyl carbamate, dimethyl sulfide, 3-methylbutanal, *n*-pentanal, 2,3-butanedione monoxime, methyl phenyl ketone, cyclopentanone, methanal (formaldehyde), *n*-propanal, 5-hydroxymethyl-2-furfuraldehyde (5-HMF), 2-furfuraldehyde (furfuraldehyde), 2-butenal, 2-methyl-1-propanal, 1-butanal, and phenylmethanal (benzaldehyde) from Sigma-Aldrich (Milwaukee, WI) were used as purchased. The standard solutions for analyzing the elements (manganese, aluminum, sodium, calcium, magnesium, copper, strontium, iron, cadmium, and potassium) were obtained by diluting a multielement standard solution obtained from Carlo Erba (Milano, Italy) using distilled water, which was deionized using a Milli-Q system (Millipore, Bedford, MA).

Analytical Procedures. All analyses were performed as described previously (*1*, *2*, *4*, *6*, *15*, *19*, *20*). The organic compounds were analyzed using chromatographic techniques. Except when using a gas chromatography−mass spectrometry (GC-MS) technique, the identification of the desired compounds was carried out by comparing relative retention time with that of a standard obtained from a chromatogram containing the standards dissolved in an ethanol/water (40:60% v/v) mixture and also by spiking the sample with an aliquot of the known compound and observing the changes in the chromatogram. When using GC-MS, the identification was also carried out by comparing the fragmentogram of the desired compound with that of the standard in the same experimental condition. Quantitative analyses were realized using a standard addition method and performed in triplicate.

Organic Compounds. *Alcohols, Ethyl Acetate, and Acetic Acid (2, 3, 20).* Samples were spiked with internal standard (*n*-hexanol). Aliquots of 1.0 μL were injected into the gas chromatograph system (Hewlett-Packard, HP 5890 series II) using a flame ionization detector (FID) and an HP-FFAP column (cross-linked polyethylene glycol esterified, 50 m × 0.20 mm × 0.33 μm film thickness). The analyses were performed at a 1:50 split ratio. Hydrogen was used as carrier gas (flow rate of 1.2 mL min^{-1}). The temperatures of both injector and detector (FID) were set at 250 °C. The oven temperature program was 40 °C for 2 min, followed by an increase to 150 °C at 10 °C min^{-1}, then kept for 4 min, and then up to 200 °C at 5 °C min^{-1}, and maintained for 15 min.

Aldehydes and Ketones (4, 5). The samples were analyzed in a HPLC Shimadzu model LC-10AD equipped with a UV−vis diode array detector (high-performance liquid chromatography, Shimadzu SPD M6A, wavelength = 365 nm). The HPLC separation was accomplished using a Shimadzu Shim-Pak C18 column (25 cm × 4.6 mm i.d. × 5 μm particle size) with water−methanol/acetonitrile (80:20) as elution gradient. The following methanol/acetonitrile−water gradient was used: methanol/acetonitrile (80:20)−water 60:40 (v/v) isocratic for 9 min (1.00 mL min^{-1}), from 60:40 to 70:30 in 6 min, from 70:30 to 80:20 in 15 min, from 80:20 to 90:10 in 10 min, from 90:10 to 60:40 in 2 min, and 60:40 isocratic for 3 min.

Dimethyl Sulfide (6, 20). Determinations of dimethyl sulfide was carried out in a purge and trap concentrator (OI Analytical, model 4560) using high-purity helium (99.999%) coupled to a gas chromatograph (Shimadzu, model GC17A) equipped with a mass selective detector (Shimadzu, model GC-MS-QP5050A) using 70 eV electron impact as the ionization mode. Separation was achieved in a column packed with esterified polyethylene glycol (HP-FFAP, 50 m × 0.2 mm × 0.3 μm; Hewlett-Packard). The gas chromatograph was operated in the "on" column injection mode. The column temperature was set at 60 °C for 5 min, after which it was raised to 200 °C at a rate of 10 °C min^{-1}. Helium at a flow rate of 1 mL min^{-1} was used as the carrier gas. The mass spectrometer detector was operated in the single ion monitoring (SIM) mode (*m*/*z* 62).

Ethyl Carbamate (15). The samples were analyzed with a gas chromatograph system (Shimadzu model GC17A) equipped with a mass selective detector (Shimadzu model GCMS-QP5050A) using 70 eV electron impact as the ionization mode. The mass spectrometer detector was operated in the SIM mode (*m*/*z* 62), and propyl carbamate was added as an internal standard. The oven temperature program was as follows: 90 °C (2 min), followed by an increase to 150 °C at 10 °C min^{-1} (0 min), then up to 230 °C at 40 °C min^{-1} (10 min). Helium was used as carrier gas (flow rate of 1.5 mL min^{-1}). Sample aliquots of 2.0 μL were injected into the gas chromatograph system.

Inorganic Compounds. *Metals (1).* The analyses were performed by inductively coupled plasma optical emission spectrometry (ICP OES) (Optima 3000 Dual View, Perkin-Elmer). A sample (50.0 mL) was placed in an open 150 mL beaker and then digested with 10.0 mL of HNO_3 under controlled heating (100−120 °C) until 5.0 mL of sample volume remained. After cooling at room temperature, the treated sample was transferred to a 25.0 mL volumetric flask, diluted to volume with 5.0% nitric acid solution, and then analyzed. The calibration curves were constructed by using the external standard method, and all of the analyses were performed in triplicate.

Multivariate Analyses. Using all sets of data (see Supporting Information) a data matrix was structured with 115 rows representing cachaças samples and 34 columns corresponding to the concentration values of the chemical variables analyzed. The chemical variables were autoscaled before statistical treatment. Principal component analysis (PCA) and linear discriminant analysis (LDA) were applied to distinguish between cachaças of group 1 (distilled in copper pot stills) and cachaças of group 2 (distilled in stainless steel columns) (*19*−*27*). First, an exploratory analysis was carried out by PCA using analytical data for 82 samples (55 samples of cachaças distilled in copper pot stills and 27 distilled in stainless steel columns) to verify group formation and data structure. Afterward, LDA was used for classification purposes. The training set used in the LDA was composed of the 82 samples used in the PCA. The self-consistency of the LDA model was examined through cross-validation using 33 unknown samples. During cross-validation, one sample at a time (of *n* samples) is left out, and the prediction ability is tested on the sample omitted. This procedure is repeated *n* times, resulting in *n* models, and will give an estimate of the average prediction ability for the *n* models. The multivariate analyses were carried out using the Minitab R14 software (MINITAB and the MINITAB logo are registered trademarks of Minitab Inc.).

RESULTS AND DISCUSSION

Studies realized with other spirits showed that it is possible to relate the type of distillation system to the composition of the spirits and characterize a spirit by considering its chemical composition (*11*, *12*, *19*−*23*, *26*−*33*).

Table 1. Average, Median, Low, and High Concentrations of Constituents in Brazilian Cachaças (Group 1, Cachaças Distilled in Copper Pot Stills; Group 2, Cachaças Distilled in Stainless Steel Columns; Concentrations of Organic Compounds in Milligrams per 100 mL of AA; Concentrations of Elements in Milligrams per 100 mL)

	average		median		low		high	
	group 1	group 2	group 1	group 2	group 1	group 2	group 1	group 2
methanal	0.0673	0.0180	<QL[a,e]	<QL[a]	<QL[a]	<QL[a]	0.768	0.0690
5-hydroxymethyl-2-furfuraldehyde	0.491	0.520	0.159	0.156	<QL[a]	<QL[a]	4.55	2.52
ethanal	4.06	6.38	1.84	3.54	0.164	0.230	20.2	19.1
n-propanal	0.0410	0.0195	<QL[a]	<QL[a]	<QL[a]	<QL[a]	0.509	0.0760
2,3-butanedione monoxime	0.0342	0.0219	<QL[a]	<QL[a]	<QL[a]	<QL[a]	0.859	0.164
2-furfuraldehyde	0.0144	0.0214	<QL[a]	<QL[a]	<QL[a]	<QL[a]	0.335	0.170
2-butenal	0.162	0.0512	<QL[a]	0.0280	<QL[a]	<QL[a]	5.32	0.790
2-methyl-1-propanal + 1-butanal	0.0750	0.0729	0.0390	0.0645	<QL[a]	<QL[a]	0.662	0.152
cyclopentanone	<QL[a]	<QL[a]	<QL[a]	<QL[a]	<QL[a]	<QL[a]	0.117	0.107
phenylmethanal	0.0505	0.591	<QL[a]	0.559	<QL[a]	0.0500	0.600	1.50
3-methylbutanal	0.0349	0.0611	0.0310	0.0455	<QL[a]	<QL[a]	0.243	0.210
n-pentanal	0.0205	0.0258	<QL[a]	<QL[a]	<QL[a]	<QL[a]	0.546	0.140
methyl phenyl ketone	0.0537	<QL[a]	<QL[a]	<QL[a]	<QL[a]	<QL[a]	0.726	0.0330
ethyl carbamate	0.0246	0.180	0.0100	0.105	<QL[b]	<QL[b]	0.260	0.843
ethyl acetate	45.9	50.0	36.0	28.5	<QL[c]	3.33	180	623
acetic acid	50.3	17.4	27.6	0.524	<QL[c]	<QL[c]	304	444
3-methyl-1-butanol	132	151	123	136	13.6	2.92	379	314
methanol	20.2	17.5	20.9	20.4	<QL[c]	<QL[c]	68.9	45.2
sec-butyl alcohol	6.16	15.3	<QL[c]	4.14	<QL[c]	<QL[c]	96.8	66.9
propyl alcohol	44.3	65.7	34.5	40.2	<QL[c]	17.9	273	341
isobutyl alcohol	36.9	51.8	32.3	43.1	2.39	0.990	113	166
n-butyl alcohol	0.981	0.665	0.650	0.510	<QL[c]	<QL[c]	15.2	2.70
dimethyl sulfide	5.35	1.05	2.21	0.128	<QL[c]	<QL[c]	52.1	19.9
calcium	0.123	0.122	0.105	0.125	<QL[d]	0.0270	0.749	0.261
magnesium	0.0490	0.0500	0.0390	0.0480	<QL[d]	0.0180	0.729	0.131
copper	0.558	0.280	0.418	0.233	0.0245	0.0230	2.98	1.03
strontium	<QL[d]	<QL[d]	<QL[d]	<QL[d]	<QL[d]	<QL[d]	<QL[d]	<QL[d]
iron	0.0150	<QL[d]	0.0110	<QL[d]	<QL[d]	<QL[d]	0.114	0.0340
cadmium	<QL[d]	<QL[d]	<QL[d]	<QL[d]	<QL[d]	<QL[d]	<QL[d]	<QL[d]

[a] = 1.00E-2 mg 100 mL anhydrous alcohol (AA)$^{-1}$. [b] = 1.00E-3 mg 100 mL AA^{-1}. [c] = 0.100 mg 100 mL AA^{-1}. [d] = 1.00E-2 mg 100 mL^{-1}. [e] QL, quantification limit.

Table 1 summarizes in terms of average and median concentrations as well as the highest and lowest contents the analytical data for organic constituents and minerals in 115 cachaças. The copper pot still group of cachaças (group 1) was shown to exhibit higher median concentrations for acetic acid and copper, whereas in cachaças distilled in stainless steel columns (group 2), higher median concentrations were found for ethyl carbamate, phenylmethanal, *sec*-butyl alcohol, 2-methyl-1-propanal + 1-butanal, 2-butenal, and ethanal.

The levels of ethyl carbamate in the pot still apparatus are found to be smaller than those in the columns apparatus (**Table 1**). The fact that artisanal cachaças were made only from the heart fraction partly explains, although not always, this behavior. Because urethane is more soluble in ethanol than in water, ethyl carbamate would be more abundant in the head fraction than in the other two. In addition, the fact that the head is collected in alembics at a lower temperature (*9*, *18*) and at a lower throughput than columns would favor a smaller ethyl carbamate content (*9*).

It was observed that the median concentration values of higher alcohols (more than two carbons) were higher in group 2 than in group 1 (except for *n*-butyl alcohol, **Table 1**). In pot still products, higher alcohols are expected to be more abundant in the head fraction than in the heart fraction because they have a relatively low boiling point and are more soluble in ethanol than in water (*10*). When the head fraction is reused in the process, higher alcohol concentration in the heart fraction would increase.

Similarly to higher alcohols, ethyl acetate is expected to distill at the beginning of the distillation because it has a low boiling point and is more soluble in alcohol than in water. Highest concentration was found in cachaça distilled in pot stills (**Table 1**), suggesting that the producers maybe are mixing the head fraction in the next wine distillation (*10*).

Ethanal (acetaldehyde) is formed from the fermented raw materials (*34*). It was found in higher concentration in cachaças distilled in columns. Ethanal has a low boiling point (20 °C), so the head fraction, in the pot still distillation, is expected to have higher concentrations of this compound than the heart fraction.

The methanol produced during fermentation derived from the degradation of pectic substances (*35*) presents similar median concentrations in the two groups of cachaças.

As expected, because alembics are made of metallic copper, whereas columns have just some parts in metallic copper, the copper median was found to be higher in group 1 than in group 2.

5-Hydroxymethyl-2-furfuraldehyde (5-HMF) has a boiling point of 114−116 °C and is very soluble in water. Therefore, it is described (*10*) to be more abundant in the heart fraction (middle of the fraction) and tail than in the head fraction. Thus, 5-HMF is in general more abundant in artisanal than in industrial cachaças. The nonuniform heating and even overheating of the alembics would in part account for that.

PCA (*24*, *26*, *30*) showed two distinct groups in the set of 82 samples (**Figure 1**) corresponding to the cachaças of group 1 (55 samples) and the cachaças of group 2 (27 samples). The analytical results (see Supporting Information) were autoscaled to construct the PCA correlation matrices. This procedure standardizes a variable according to the mean and the standard deviation of the variable (*31*).

The sum of the three first principal components [PC1 (30.0%), PC2 (20.0%), and PC3 (15.0%)], which account for 65.0% of

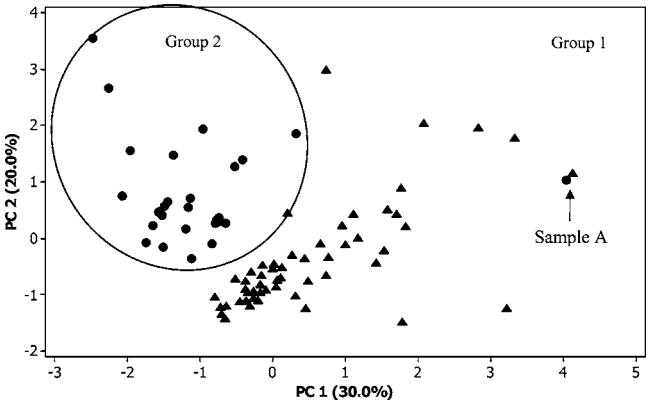

Figure 1. Score plot for Brazilian cachaças: group 1 (●), 27 samples, cachaças distilled in copper pot stills; group 2 (▲), 55 samples, cachaças distilled in stainless steel columns).

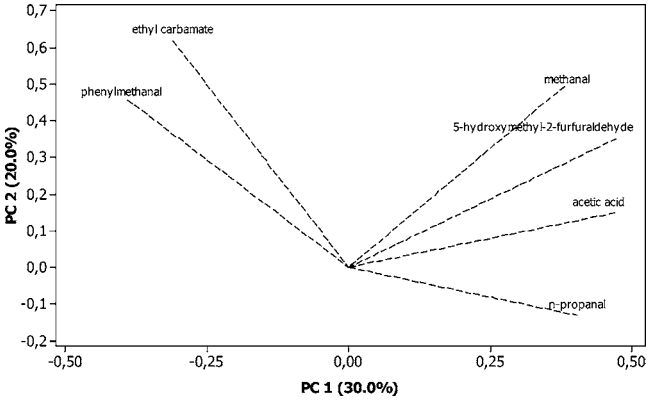

Figure 2. Loading plot of PC1 × PC2 to the set of 82 samples of Brazilian cachaças.

the total variability, was considered to be sufficient in the exploratory analysis to differentiate the two groups of cachaças. **Figure 1** presents the score plot obtained considering PC1 × PC2. A two-dimensional plot of the objects (cachaças) in the space defined by the two principal components shows a natural separation of the objects into two groups.

The cachaças distilled in stainless steel columns form a separate and homogeneous group, whereas those distilled in copper pot stills exhibit a distinct and less homogeneous group. This could in part be explained by the fact that columns are produced following standard industrial procedures and alembics are produced mainly in homemade factories (*9*, *18*, *14*). Therefore, the designs of alembics are not always the same. Among the 35 analytes, superior discriminant properties (**Figure 2**) were revealed for methanal, *n*-propanal, 5-hydroxymethyl-2-furfuraldehyde, ethyl carbamate, phenylmethanal, and acetic acid. Despite the above comments, copper ions did not exhibit a particular relevance as a descriptor in the PCA.

It is clear that phenylmethanal and ethyl carbamate contribute significantly to characterize the samples in group 2 (loading plot, **Figure 2**), whereas methanal, *n*-propanal, 5-hydroxymethyl-2-furfuraldehyde, and acetic acid are characteristic of the samples in group 1.

The coefficients (loadings) of the first and second principal components (**Figure 2**) suggest that phenylmethanal and 5-hydroxymethyl-2-furfuraldehyde are predominant features of the first principal component (30.0% of the total variability), whereas ethyl carbamate and *n*-propanal predominate the second principal component (20.0% of the total variability).

Only one sample from the 27 cachaças of group 1 (sample A) is found to be apparently misclassified in **Figure 1**. This is probably due to varying levels of acetic acid and 5-hydroxymethyl-2-furfuraldehyde as can be deduced from the loading plot shown in **Figure 2**. Indeed, only sample A was shown to present high levels of these two compounds that led to a discrimination of this cachaça from the other samples. Probably, in sample A, the heart fraction was separated in a different alcoholic degree from the other samples, which leads to a different composition in the cachaça (see Supporting Information).

Table 2. Model for Classification of Brazilian Cachaças Derived from Linear Discriminant Analysis (Group 1, Cachaças Distilled in Copper Pot Stills; Group 2, Cachaças Distilled in Stainless Steel Columns)

	correct classification	
	group 1	group 2
group 1	55	2
group 2	0	25
total number of samples	55	27
total number correctly classified	55	25
percentage	100	92.6
total number of samples	82	
total number correctly classified	80	
correctly classified (percentage)	97.6	

Table 3. Cross-Validation for Classification of Brazilian Cachaças Using the Model Derived from Linear Discriminant Analysis (Group 1, Cachaças Distilled in Copper Pot Stills; Group 2, Cachaças Distilled in Stainless Steel Columns)

	correct classification	
	group 1	group 2
group 1	54	3
group 2	1	24
total number of samples	55	27
total number correctly classified	54	24
percentage	98.2	88.9
total number of samples	82	
total number correctly classified	78	
correctly classified (percentage)	95.1	

For the second step, LDA was applied to the data set to generate a classification model rule (*27*, *29*). To study the prediction ability, the cross-validation method was applied and, subsequently, the model was tested with unknown samples. The LDA technique was applied in a data matrix structured with 115 rows representing cachaças samples and 34 columns corresponding to the analytical results of the chemical variables analyzed (see Supporting Information).

The results for 82 samples are presented in **Table 2**, the cross-validation is displayed in **Table 3**, and **Table 4** gives the results obtained from checking the model with unknown samples. The descriptors considered in the LDA were ethanal, ethyl carbamate, dimethyl sulfide, isobutyl alcohol, *n*-propanal, copper, ethyl acetate, and phenylmethanal, which discriminate cachaças depending on the distillation apparatus with an accuracy of about 95.1%.

It is interesting to point out that six compounds exhibited relevant discriminant properties in the PCA, whereas this number increases to eight using the LDA technique. Ethyl carbamate, *n*-propanal, and phenylmethanal are the compounds for which discriminant properties were pointed out by the two methodologies.

All samples in group 1 (copper pot stills) are classified correctly (**Table 2**), and only two samples in group 2 (stainless steel columns) are misclassified, leading to a discrimination with

Table 4. Application of the Model Derived from Linear Discriminant Analysis for Classification of Brazilian Cachaças from Unknown Origin (Group 1, Cachaças Distilled in Copper Pot Stills; Group 2, Cachaças Distilled in Stainless Steel Columns)

	correct classification	
	group 1	group 2
group 1	16	0
group 2	2	15
total number of samples	18	15
total number correctly classified	16	15
percentage	88.9	100
total number of samples	33	
total number correctly classified	31	
correctly classified (percentage)	93.9	

97.6% accuracy. The cross-validation of the LDA model (**Table 3**) shows an accuray of 95.1%, showing the robustness of the resulting model.

Application of the LDA model to the 33 unknown samples (18 samples from group 1 and 15 samples from group 2) led to a misclassification of only two samples in group 1 and a correct classification of all samples in group 2 (**Table 4**).

The obtained data strongly suggest that, as described for others spirits (*11*, *12*, *19*−*23*, *26*−*33*), the chemical profiles of Brazilian cachaças are substantially determined by the type of distillation apparatus, either copper pot stills (homemade cachaça) or stainless steel columns (industrial cachaça). Considering the sum of the three first principal components (PC1, PC2, and PC3) and phenylmethanal, ethyl carbamate, methanal, 5-hydroxymethyl-2-furfuraldehyde, acetic acid, and *n*-propanal as a chemical descriptors, the PCA accounts for 65.0% of the variance of the original database. According to this analysis, ethyl carbamate and phenylmethanal are the most important compounds in the clustering of the samples distilled in stainless steel columns, whereas methanal, *n*-propanal, 5-hydroxymethyl-2-furfuraldehyde, and acetic acid predominate in the samples distilled in copper pot stills. LDA classified 93.9% of the unknown samples correctly using ethanal, ethyl carbamate, dimethyl sulfide, isobutyl alcohol, *n*-propanal, copper, ethyl acetate, and phenylmethanal as chemical descriptors.

All of the compounds considered in the results of the PCA and LDA except dimethyl sulfide and phenylmethanal are currently controlled by Brazilian legislation. This study shows the feasibility, with only minor additional effort, of the above-described methodology application in routine analysis to distinguish the origin of the products.

ACKNOWLEDGMENT

We gratefully Dr. Denis De Keukeleire (Faculty of Pharmaceutical Sciences, Laboratory of Pharmacognosy and Phytochemistry, Ghent University, Belgium) for helpful comments and suggestions. This paper is dedicated to the memory of our master and friend Eduardo Fausto de Almeida Neves.

Supporting Information Available: Sample list, groups (pot still and column), and complete analytical data used in all of the statistical methods. This material is available free of charge via the Internet at http://pubs.acs.org.

LITERATURE CITED

(1) Nascimento, R. F.; Bezerra, C. W. B.; Furuya, S. M. B.; Schultz, M. S.; Polastro, L. R.; Lima-Neto, B. S.; Franco, D. W. Mineral profile of Brazilian cachaças and other international spirits. *J. Food Compos. Anal.* **1999**, *12*, 17−25.

(2) Boscolo, M.; Bezerra, C. W. B.; Cardoso, D. R.; Lima-Neto, B. S.; Franco, D. W. Identification and dosage by HRGC of minor alcohols and esters in Brazilian sugar cane spirit. *J. Braz. Chem. Soc.* **2000**, *11*, 86−90.

(3) Nascimento, R. F.; Cardoso, D. R.; Lima-Neto, B. S.; Franco, D. W. Determination of acids in Brazilian sugar cane spirits and other alcoholic beverages by HRGC-SPE. *Chromatographia* **1998**, *48*, 751−757.

(4) Nascimento, R. F.; Marques, J. C.; Lima-Neto, B. S.; De Keukeleire, D.; Franco, D. W. Qualitative and quantitative high-performance liquid chromatographic analysis of aldehydes in Brazilian sugar cane spirits and other distilled alcoholic beverages. *J. Chromatogr., A* **1997**, *782*, 13−23.

(5) Cardoso, D. R.; Bettin, S. M.; Reche, R. V.; Lima-Neto, B. S.; Franco, D. W. HPLC-DAD analysis of ketones as their 2,4-dinitrophenylhydrazones in Brazilian sugar-cane spirits and rum. *J. Food Compos. Anal.* **2003**, *16*, 563−573.

(6) Cardoso, D. R.; Andrade-Sobrinho, L. G.; Lima-Neto, B. S.; Franco, D. W. A rapid and sensitive method for dimethylsulphide analysis in Brazilian sugar cane spirits and other distilled beverages. *J. Braz. Chem. Soc.* **2004**, *15*, 277−281.

(7) Nascimento, R. F.; Cardoso, D. R.; Faria, J. B.; Lima-Neto, B. S.; Franco, D. W. Influência do material do alambique na composição química das aguardentes de cana-de-açúcar. *Quim. Nova* **1998**, *21*, 735−739.

(8) Cardoso, D. R.; Nascimento, R. F.; Lima-Neto, B. S.; Franco, D. W. Influência do material do destilador na composição química das aguardentes de cana − Parte II. *Quim. Nova* **2003**, *26*, 165−169.

(9) Bruno, S. N. F.; Vaitsman, D. S.; Kunigami, C. N.; Brasil, M. G. Influence of the distillation processes from Rio de Janeiro in the ethyl carbamate formation in Brazilian sugar cane spirits. *Food Chem.* **2007**, in press (doi:10.1016/j.foodchem.2007.01.048).

(10) García-LLobodanin, L.; Achaerandio, I.; Ferrando, M.; Guëll, C.; López, F. Pear distillates from pear juice concentrate: effect of lees in the aromatic composition. *J. Agric. Food Chem.* **2007**, *55*, 3462−3468.

(11) Madrera, R. R.; Alonso, J. J. M. Typification of cider brandy on the basis of cider used in its manufacture. *J. Agric. Food Chem.* **2005**, *53*, 3071−3075.

(12) Madrera, R. R.; Gomis, D. B.; Alonso, J. J. M. Influence of distillation system, oak wood type, and aging time on composition of cider brandy in phenolic and furanic compounds. *J. Agric. Food Chem.* **2003**, *51*, 7969−7973.

(13) Schehl, B.; Lachenmeier, D.; Senn, T.; Heinisch, J. J. Effects of stone content on the quality of plum and cherry spirits produced from mash fermentation with commercial and laboratory yeast strains. *J. Agric. Food Chem.* **2005**, *53*, 8230−8238.

(14) Mutton, M. J. R.; Mutton, M. A. Aguardente. In *Tecnologia de Bebidas*, 1st ed.; Venturini-Filho, W. G., Ed.; Edgard Blücher: São Paulo, Brazil, 2005; pp 485−524.

(15) Mangas, J.; Rodríguez, R.; Moreno, J.; Suárez, B.; Domingo, B. Evolution of aromatic and furanic congeners in the maturation of cider brandy: a contribution to its characterization. *J. Agric. Food Chem.* **1996**, *44*, 3303−3307.

(16) Apostolopoulou, A. A.; Flouros, A. I.; Demertzis, P. G.; Akrida-Demertzi, K. Differences in concentration of principal volatile constituents in traditional Greek distillates. *Food Control* **2005**, *16*, 157−164.

(17) Andrade-Sobrinho, L. G.; Boscolo, M.; Lima-Neto, B. S.; Franco, D. W. Carbamato de etila em bebidas alcoólicas (cachaça, tiquira, uísque e grapa). *Quim. Nova* **2002**, *25*, 1074−1077.

(18) Marcos José Macedo. Personal communication.

(19) Arvanitoyannis, I. S.; Katsota, M. N.; Psarra, E. P.; Soufleros, E. H.; Kallithraka, S. Application of quality control methods for assessing wine authenticity: use of multivariate analysis (chemometrics). *Trends Food Sci. Technol.* **1999**, *10*, 321−336.

(20) Héberber, K.; Csomós, E.; Simon-Sarkadi, L.; Principal component and linear discriminant analyses of free amino acids and biogenic amines in Hungarian wines. *J. Agric. Food Chem.* **2003**, *51*, 8055−8060.

(21) Kokkinofta, R. I.; Theocharis, C. R. Chemometric characterization of the Cypriot spirit "Zivania". *J. Agric. Food Chem.* **2005**, *53*, 5067−5073.

(22) Lachenmeier, D. W.; Richling, E.; López, M. G.; Frank, W.; Schreirer, P. Multivariate analysis of FTIR and ion chromatographic data for the quality control of tequila. *J. Agric. Food Chem.* **2005**, *53*, 2151−2157.

(23) Fernandes, A. P.; Santos, M. C.; Lemos, S. G.; Ferreira, M. M. C.; Nogueira, A. R. A.; Nóbrega, J. A. Pattern recognition applied to mineral characterization of Brazilian coffees and sugar-cane spirits. *Spectrochim. Acta, Part B* **2005**, *60*, 717−724.

(24) Romero, R.; Sánchez-Viñas, M.; Gázquez, D.; Bagur, M. G. Characterization of selected Spanish table wine samples according to their biogenic amine content from liquid chromatographic determination. *J. Agric. Food Chem.* **2002**, *53*, 4713−4717.

(25) Latorre, M. J.; García-Jares, C.; Mèdina, B.; Herrero, C. Pattern recognition analysis applied to classification of wines from Galicia (northwestern Spain) with certified brand of origin. *J. Agric. Food Chem.* **1994**, *42*, 1451−1455.

(26) Dupuy, N.; Dréay, Y. L.; Ollivier, D.; Artaud, J.; Pinatel, C.; Kister, J. Origin of French virgin olive oil registered designation of origins predicted by chemometric analysis of synchronous excitation-emission fluorescence spectra. *J. Agric. Food Chem.* **2005**, *53*, 9361−9368.

(27) Nozal, M. J.; Bernal, J. L.; Toribio, L.; Alamo, M.; Diego, J. C. The use of carbohydrate profiles and chemometrics in the characterization of natural honeys of identical geographical origin. *J. Agric. Food Chem.* **2005**, *53*, 3095−3100.

(28) Mangas, J.; Rodríguez, R.; Moreno, J.; Blanco, D. Volatiles in distillates of cider aged in American oak wood. *J. Agric. Food Chem.* **1996**, *44*, 268−273.

(29) González-Arjona, D.; López-Pérez, G.; González-Gallero, V.; González, A. G. Supervised pattern recognition procedures for discrimination of whiskeys from gas chromatography/mass spectrometry congener analysis. *J. Agric. Food Chem.* **2006**, *54*, 1982−1989.

(30) Cardoso, D. R.; Andrade-Sobrinho, L. G.; Leite-Neto, A. F.; Reche, R. V.; Isique, W. D.; Ferreira, M. M. C.; Lima-Neto, B. S.; Franco, D. W. Comparison between cachaça and rum using pattern recognition methods. *J. Agric. Food Chem.* **2004**, *52*, 3429−3433.

(31) Lavine, B.; Workman, J. Chemometrics. *Anal. Chem.* **2006**, *78*, 4137−4145.

(32) Fernández, P. L.; Pablos, F.; Martín, M. J.; González, A. G. Multi-elemental analysis of tea beverages by inductively coupled plasma atomic emission spectrometry. *Food Chem.* **2002**, *76*, 483−489.

(33) Theobald, A.; Müller, A.; Anklam, E. Determination of 5-Hydroxymethylfurfural in vinegar by HPLC. *J. Agric. Food Chem.* **1998**, *46*, 1850−1854.

(34) Soufleros, E. H.; Mygdalia, A. S.; Natskoulis, P. Characterization and safely evaluation of the traditional Greek fruit distillate "Mouro" by flavor compounds and mineral analysis. *Food Chem.* **2004**, *86*, 625−636.

(35) Wang, M. L.; Wang, J. T.; Choong, Y. M. Simultaneous quantification of methanol and ethanol in alcoholic beverage using a rapid gas chromatographic method coupling with dual internal standards. *Food Chem.* **2004**, *86*, 609−615.

Received for review February 12, 2007. Revised manuscript received June 5, 2007. Accepted June 9, 2007. We acknowledge FAPESP, CAPES, and CNPq for financial support.

JF0704110