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Article

Correlation between Chemical Composition and Sensory Properties of Brazilian Sugarcane Spirits (*Cachaças*)

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A correlação entre a composição química e os dados sensoriais de 28 amostras de cachaças foi investigada através de análise de componentes principais (PCA). Um modelo químico usando análise discriminante linear (LDA) para classificar as amostras de cachaças de acordo com suas qualidades sensoriais foi então elaborado. Este modelo apresentou habilidades preditivas de calibração e validação de 87,4 e 100%, respectivamente, e foi capaz de reconhecer corretamente 7 dentre 9 amostras adicionais, apresentando-se como uma ferramenta alternativa potencial para o reconhecimento das qualidades sensoriais de cachaças.

The correlation between the chemical composition and the sensory data for 28 *cachaça* samples was investigated using principal component analysis (PCA). A chemical model was then developed using linear discriminant analysis (LDA) to classify the distillate samples according to their sensory qualities. This model presented predictive abilities of calibration and validation of 87.4 and 100%, respectively, and was able to recognize correctly 7 out of 9 additional samples according to their sensory evaluations, showing itself as a potential alternative tool of recognizing *cachaça* sensory qualities.

Keywords: sugarcane spirits, *cachaça* sensory and chemical properties, multivariate analysis

Introduction

Similar to other distillates, the chemical composition of the Brazilian sugarcane spirit (*cachaça*) will depend on the raw material, yeasts, fermentation, distillation and aging processes.[1] The molecular structures of the minor compounds and their concentrations can provide positive or negative notes in the sensory and chemical characteristics of beverages.[2] Therefore, the concentrations of volatile components, such as alcohols, ethyl acetate, acetic acid, aldehydes and ketones, and that of nonvolatile compounds, like metal ions in beverages, can provide important information for the improvement of their production process and their typification.[3-6]

The qualitative and quantitative descriptions of the chemical compounds in sugarcane spirits have received considerable attention aiming to improve *cachaça* quality. However, the characterization based only on the chemical composition, although extremely important, is not enough and needs to be complemented with the beverage sensory attributes. Indeed, the sensory impact of substances that compose a distilled beverage is a key step to monitoring and guiding the production modifications in order to gain control of their characteristics and qualities.[2]

In comparison to other spirits, scarce information has been published on the sensory analysis of *cachaça* and its correlation with minor compounds that influence the spirit quality.[7-17] In addition to the chemical analysis, sensory tests in *cachaças* have been gaining importance. Although sensory evaluation of the *cachaça* attributes is not yet required by the Brazilian laws, its inclusion would be expected to occur in the future as a consequence of improvements on the beverage quality requirements and to attend consumer demands.[18]

Sensory evaluation is an important aspect in the quality authenticity. This requires appraisals by a highly trained *cachaça* panel in order to determine whether or not there are

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consistent sensory attributes expected for a good product. However, this approach is subject to bias since personal preferences are involved, hence, an objective method should be necessary for this evaluation. In the present study, *cachaça* samples were evaluated by sensory and chemical analysis in order to gain in depth knowledge for a relationship between the chemical and sensory profiles of Brazilian sugarcane spirits.

Experimental

Samples

The samples were provided and certified by Brazilian producers from various regions throughout Brazil. A total of twenty eight samples of unsweetened commercial *cachaças*, all distilled in pot stills (alembics), was analyzed. From these samples, nineteen were aged and nine were not aged.[18] The *cachaças* were codified using different letters and numbers as following: for the not aged *cachaças* (D1, D2, D3…) and for the aged *cachaças* (E1, E2, E3…). The time and the recipient used for *cachaças* storage, as informed by the producers, are shown in Table S1 in the Supplementary Information (SI) section.

The chemical compounds were selected based on their occurrences and quantitative profiles previously reported for other alcoholic beverages, including *cachaça*. Alcohol content (% vol.) was evaluated using density meter (pycnometer).

Analytical method description

Higher alcohols and acetic acid

The presence of methanol, propanol, isobutanol, 1-butanol, 2-butanol, isoamyl alcohol and acetic acid were determined through direct injection of 1.0 μL aliquots of the sample (spiked with 4-methyl-1-propanol, internal standard, 126 mg L^{-1}) into a gas chromatography system (Hewlett-Packard, HP 5890-A GC) using a flame ionization detector (FID) and a HP-FFAP column (cross-linked polyethylene glycol esterified 50 m × 0.20 mm × 0.33 μm film thickness). The inlet and detector temperatures were 250 °C. The split ratio was 1:20 and the carrier gas (hydrogen) flow 1.2 mL min^{-1}. The oven temperature program was 55 °C (5 min); 2 °C min^{-1} to 100 °C (3 min), 5 °C min^{-1} to 190 °C (30 min); 5 °C min^{-1} to 220 °C (15 min).[19]

Aldehydes and ketones

Acetylacetone, formaldehyde, 5-hydroxymethylfurfural (5-HMF), acetaldehyde, acrolein, furfuraldehyde, propionaldehyde, butyraldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde and 2,3-butanedione (diacetyl) were determinated as their 2,4-dinitrophenyihydrazones (aldehyde-DNPHs) using a high-performance liquid chromatograph (HPLC) Shimadzu model LC-10AD equipped with a UV-Vis diode array detector (Shimadzu SPD M6A, wavelength = 365 nm). The HPLC separation was performed with a Shimadzu Shim-Pak C_{18} column (25 cm × 4.6 mm i.d. × 5.0 μm particle size) and a gradient system of water and methanol/acetonitrile (80:20 v/v) solution. The injection volume was 20.0 μL and the following gradient (methanol/acetonitrile)-water was used: (methanol:acetonitrile) (8:2), water 60:40 (v/v) isocratic for 9 min (1.0 mL min^{-1}), from 60:40 to 95:5 in 16 min (1.1 mL min^{-1}), from 95:5 to 60:40 in 9 min (1.0 mL min^{-1}), 60:40 isocratic for 15 min (1.0 mL min^{-1}).[20]

Ethyl carbamate

The determination of the ethyl carbamate concentration was performed through direct sample injection without previous treatment into a gas chromatograph model GC17A (Shimadzu, Tokyo, Japan) interfaced to a mass selective detector model QP 5050A (Shimadzu, Tokyo, Japan) using electron ionization (70 eV) as the ion source. The mass spectrometer detector operated in SIM (single ion monitoring) mode (*m/z* 62), and propyl carbamate was used as an internal standard (150 μg L^{-1}). A HP-FFAP capillary column was used in the ethyl carbamate separation. The inlet and detector interface temperatures were 250 and 230 °C, respectively. The oven program temperature used was: 90 °C (2 min); 10 °C min^{-1} for 150 °C (0 min); 40 °C min^{-1} for 230 °C (10 min), using helium (1.5 mL min^{-1}). The injected volume was 1.0 μL in the splitless mode.[21]

Esters

Ethyl acetate, ethyl butyrate, ethyl hexanoate, ethyl lactate, ethyl octanoate, ethyl nonanoate, ethyl decanoate, ethyl laurate and isoamyl octanoate were determined by direct sample injection. The volume of 1 μL was injected into a gas chromatography model GC17A (Shimadzu, Tokyo, Japan) linked to a mass selective detector model QP 5050A (Shimadzu, Tokyo, Japan) using electron impact (70 eV) as the ionization source and 4-methyl-2-pentanol as an internal standard. The target analytes were separated on the HP-FFAP capillary column. The temperature of the injector and of the detector interface was 220 °C. The oven temperature was programmed from 35 to 180 °C at a rate of 5 °C min^{-1} and then raised at 20 °C min^{-1} from 180 to 220 °C (5 min), using split mode 1:15.[22]

Organic acids

Nine organic acids (lactic, glycolic, pyruvic, succinic, capric, citramalic, lauric, myristic and palmitic) were

determined in distilled samples. The methodology was based on the evaporation of 20 mL of *cachaça* to dryness at room temperature and the subsequent addition of 200 μL of a derivatizing solution, which contains 100 μL of *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA) and 100 μL of nonanoic acid (internal standard, 100 mg L^{-1}) in an acetonitrile solution. A Hewlett-Packard 5890 model gas chromatograph (GC) equipped with flame ionization detector was used with a capillary column DB-5 (5%-phenyl-methylpolysiloxane) with dimensions of 50 m × 0.20 mm × 0.33 μm. The oven temperature program used was: 60 °C (2 min) to 100 °C at a programming rate of 25 °C min^{-1} and raised at 10 °C min^{-1} increments from 100 to 300 °C (5 min), using split mode (1:15).[23,24]

Dimethylsulfide (DMS)

The analysis was carried out in a purge-and-trap concentrator (OI Analytical model 4560) using high purity helium, coupled to a gas chromatograph (Shimadzu, model GC17A) equipped with a mass selective detector (Shimadzu, model GCMS-QP5050A) using 70 eV as the ionization mode. Aliquots of 6 mL of sample were injected in the purge-and-trap concentrator and purged for 5 min at a helium flow rate of 45 mL min^{-1}. The trap was then flash-heated (20 to 180 °C in 2 min) to desorb the volatile compounds. The gas chromatograph was operated in the on-column injection mode. The oven temperature program used was: 60 °C for 5 min to 200 °C (10 °C min^{-1}). Helium at a flow rate 1 mL min^{-1} was used as the carrier gas. The mass spectrometer detector was operated in the SIM mode (*m/z* 62). The temperatures of the injector and interface were set at 100 and 200 °C, respectively.[25]

Metals

The determination of metal ions (copper, iron and lead) was carried out by atomic absorption spectrophotometry using a Polarized Zeeman atomic absorption spectrophotometer (Hitachi Z-8100), equipped with an air acetylene burner and hollow cathode lamps.[26]

The compound identification was carried out, as described previously, through relative retention time, standard addition and confirmed by mass spectrometry analysis. The analytical data reported herein are the average values obtained from the analysis performed in triplicate.

Sensory evaluation

General conditions

Two different levels of evaluation were performed, a descriptive sensory analysis and a consumer hedonic test. The descriptive sensory analysis was performed at Instituto de Química de São Carlos (USP, São Carlos-SP, Brazil) and the consumer hedonic test at Escola de Engenharia Lorena (USP, Lorena-SP, Brazil). On both cases, air conditioned conference-style rooms were used, their dimensions, disposition, illumination (white fluorescent lighting), temperature (25 ± 3 °C) and humidity conditions (62 ± 7%) were comparable.[27] The beverages were served as supplied by the producers. Their alcoholic content (exception for samples D6, E15 and E29) ranged from 38.0 to 45.3% (% vol.) as reported in the following section. The *cachaça* bottles were opened just before the sensory test. The *cachaças* (30 mL) were served at a temperature of 21 ± 2 °C and in encoded ISO-standard sherry glasses (120 mL), not covered. The samples were offered on a random presentation order for all the assessors. Aged samples and non-aged samples were presented on separated sets.

Descriptive sensory analysis

To examine the *cachaça* samples, a similar approach to the one described in the literature was used.[28] The descriptive sensory analysis method was applied by a panel of thirteen assessors, six males and seven females, between 22 and 60 years old. All assessors were trained in descriptive analysis with *cachaça* samples before participating in the experiment. This was based on a vocabulary previously used in our laboratory (Table S2 in the SI section) for a sensory analysis of *cachaça*.[15] The assessors scored the samples for every vocabulary descriptor, using a structured numerical scale anchored from one (not present) to nine (very much present).

Each day, the assessors received fourteen samples in two sets (in the morning and afternoon sessions) of eight samples (seven new samples and one replicated).

Consumer hedonic test

A category hedonic scale ranging from 1 (dislike extremely) to 9 (like extremely) was used to assess the appearance, aroma and taste by 240 different consumers of both genders (21 to 70 years old). They are all *cachaça* consumers, mostly students and professionals from various Brazilian regions and from other countries, without any given information about the origin and kind of the *cachaça* samples.[27,28] Four series of seven samples were presented in a random mode, without replicates. Aged samples and non-aged samples were presented on separated sets. Each sample was evaluated forty times. The consumer hedonic score averages for *cachaça* sensory qualities (taste and aroma) were used to generate the hedonic index (HI) which describes the acceptability of the consumers by the tasted product. Since 4.5 is the middle point in the hedonic scale

used and represent neither like nor disliked, the number 6.0 was arbitrarily chosen as reference parameter for ensure the sample classification according to their qualities (samples with HI < 6 and HI ≥ 6). Simulations using HI = 5.9 ± 0.1 led to similar results.[29]

Statistical analysis

Analysis of variance (ANOVA) was used to verify significant differences among sensory descriptors and the chemical descriptors, for all the *cachaças*. The variance was estimated considering the variation of these descriptors within the samples of the full group and between the samples of each one of the two groups (HI > 6 and HI < 6).[30]

Principal component analysis (PCA) was used to observe if there were groups of samples according to their respective chemical and sensorial similarities.[31] For the chemical descriptors, a matrix was built up with 28 rows representing the *cachaça* samples and 36 columns corresponding to the chemical variables (autoscaled). Similarly, a matrix of 28 rows (*cachaças*) and 10 columns (sensory descriptors) was built up. The HI data were not used in the matrix build up but only to identify samples after the end of the PCA treatment.

Linear discriminant analysis (LDA) is one of the parametric classification methods of pattern recognition that uses linear boundaries to define the groups.[32] A predictive classification model was built with the LDA model which has as purpose to evaluate the possibility of classifying *cachaça* samples according to their HI values (HI < 6 and HI > 6) using chemical descriptors. The predictive ability of the LDA model was evaluated by calibration using 22 samples and validation using 6 samples. The multivariate analyses were applied using Minitab 15.1.1 release software (Minitab® and the Minitab logo™ are trademarks of Minitab Inc.)

Results and Discussion

Sensory and chemical analysis data

All the analytical data collected from the analyses of 13 sensory attributes, 33 organic compounds and 3 metal ions for the 28 *cachaça* samples (15 aged and 13 non-aged) are presented in Tables 1 and 2, respectively.

In general, methanol and higher alcohols followed by acetic acid, lactic acid, ethyl acetate and ethyl lactate were present in larger concentrations than other analytes in the *cachaças*. Higher alcohols are important contributors to the aroma of the distillates and are formed during the metabolism of amino acids in the fermentation process.[1] The higher contents of isoamyl alcohol (709 mg L^{-1}), isobutanol (198 mg L^{-1}), methanol (33.6 mg L^{-1}), 1-butanol (3.44 mg L^{-1}) and 2-butanol (13.9 mg L^{-1}) were found in the aged samples, whereas 1-hexanol (5.46 mg L^{-1}) and propanol (182 mg L^{-1}) predominated in the non-aged *cachaças*. Propanol has a pleasant, sweetish odor, but at higher concentration it will introduce solvent notes that mask all the positive notes in distillates.[33]

The highest average values for acetic acid (367 mg L^{-1}) were observed for the aged *cachaças*, probably a consequence of the aldehyde oxidation into their respective acids during the aging of *cachaça* in woody barrels.[34,35]

Partial degradation of amino acids present in the sugarcane broth could account for the formation of higher alcohols which, in the presence of oxygen, can be converted into aldehydes.[35] In *cachaças*, acetaldehyde (176 mg L^{-1}) predominates among aldehydes, followed by formaldehyde (6.50 mg L^{-1}) and benzaldehyde (4.35 mg L^{-1}). The higher acetaldehyde levels in aged *cachaças* can be explained as a consequence of the chemical oxidation of ethanol during the aging process.[36]

Dehydration of hexoses generates 5-hydroximethyl-furfural (5-HMF), more abundant in aged *cachaças* (2.65 mg L^{-1}) than in non-aged ones. It is not a fermentation product, appearing in sugarcane juice as consequence of the non-uniform heating and even overheating of the alembics.[36] The extraction process due to the contact of the spirit with the wood would account for the higher concentration of 5-HMF in aged *cachaças* regarding to the non-aged ones.[37] Acrolein which can be produced via fermentation, distillation and aging, predominated in aged *cachaças* (1.44×10^{-1} mg L^{-1}) and it is associated to a spicy taste.[36,38]

As expected, ethyl acetate is the major ester present in *cachaças* (366 mg L^{-1}), followed by ethyl lactate (42.8 mg L^{-1}).[22,34] Excess of ethyl lactate has been proposed as an indication of *Lactobacillus spp*. contamination during the fermentation process and of an incorrect distillation.[5,22]

DMS, a sulfur-containing amino acid degradation product, is the major volatile sulfur component in *cachaças* and exhibits a strong negative influence on the beverage sensory qualities.[25] It is more present in the non-aged *cachaças* (2.73 mg L^{-1}) than in the aged ones (7.0×10^{-2} mg L^{-1}), which could be partially explained by the high DMS volatility (b.p. = 38 °C) leading to its concentration decrease during the aging process.

Ethyl carbamate is generally found in fermented beverages and may be correlated to a carcinogenic effect.[39,40] The presence of ethyl carbamate in *cachaça* could suggest, at least partially, an incorrect distillation process, thus, being an important process quality descriptor.[5,21] A

Table 1. ANOVA (*F*-test) and hedonic and descriptive sensory data

Sample	*F*-test value	Average (HI < 6)	Average (HI > 6)	Median (HI < 6)	Median (HI > 6)	D3	D4	D5	D6	D7	D8	D9	D11	D12	E1	E7	E8	E24	E18	E22	E10	E11	E13	E14	E15	E6	E21	E23	E28	E29	E31	E3	E4
Hedonic index		5.4	6.3	5.3	6.3	5.3	5.3	5.7	5.0	5.8	4.8	5.1	5.2	5.4	5.9	5.4	5.8	5.3	5.1	5.6	6.4	6.1	6.4	6.5	6.2	6.1	6.3	6.6	6.6	6.2	6.3	6.2	6.0
Burnt	24	4.5	5.0	4.5	4.9	3.25	3.75	4.5	4.17	4.83	4.17	4.67	6.25	4.83	4.92	3.92	3.5	5.58	4.75	4.17	6.33	4.83	5.25	6.25	6.33	3.83	5.5	3.92	4.83	4.25	3.42	4.92	5.58
Sweetness	19	3.8	4.2	3.8	4.1	3.77	3.42	3.92	4.17	4.0	3.17	3.75	4.25	3.92	3.92	3.83	3.75	3.42	3.58	4.25	3.83	3.5	4.58	4.83	4.08	4.0	4.0	4.58	4.0	4.92	4.33	4.17	4.0
Bitterness	26	3.0	2.9	3.0	2.9	2.33	2.67	3.25	3.08	2.75	3.17	4.08	3.17	3.5	3.0	2.75	2.17	3.42	2.67	2.83	3.33	3.33	2.58	2.08	3.67	2.67	2.58	2.92	3.0	2.67	3.58	2.25	3.17
Floral	22	2.9	4.0	2.4	4.5	2.42	1.83	1.83	2.67	1.33	2.0	3.0	5.67	4.67	5.42	2.33	2.83	3.25	2.08	2.25	5.42	5.0	5.0	5.33	5.08	2.83	2.08	3.42	2.08	2.08	3.67	5.42	4.5
Fruity	23	4.8	5.4	4.8	5.6	4.08	4.25	3.92	5.0	4.0	8.83	3.25	5.25	4.91	5.42	4.75	5.33	3.5	4.17	5.33	5.58	4.83	6.33	5.67	5.25	5.67	5.08	5.58	5.5	4.5	5.75	5.92	5.17
Vegetable	24	2.6	2.9	2.3	2.8	2.0	3.0	2.0	2.17	3.67	1.83	3.25	3.42	3.08	1.83	3.08	2.33	2.33	2.5	2.33	3.0	3.33	2.75	2.67	3.0	2.17	3.17	3.83	2.67	2.75	2.67	2.33	2.92
Spicy	14	2.6	4.0	2.5	4.2	1.75	2.17	1.5	1.83	2.25	2.0	3.33	2.83	3.58	3.58	3.08	2.33	2.5	2.83	3.5	4.92	4.17	4.92	3.67	4.42	3.0	2.67	3.5	4.58	3.17	5.25	2.92	4.17
Woody	13	2.7	5.2	3.1	5.4	0.42	0.67	0.83	0.92	3.08	1.08	3.08	2.5	3.75	5.0	3.67	3.75	3.67	4.67	3.67	5.42	5.08	5.17	5.5	6.58	3.83	4.83	4.92	5.58	3.25	5.92	5.92	5.83
Bicochemistry/ Chemistry	26	1.4	1.3	1.8	1.5	1.0	1.75	0.25	0.75	0.75	1.83	2.42	2.5	1.92	1.83	1.0	0.33	1.75	1.25	1.75	1.83	1.5	1.5	1.25	2.25	0.41	1.0	1.75	0.33	0.58	1.58	1.33	2.08
Overall positive Odor	12	5.4	6.6	5.3	6.6	5.08	5.08	5.75	5.17	5.33	4.5	4.5	5.67	5.33	5.92	6.08	6.5	5.0	6.08	5.75	6.5	6.5	7.25	7.33	6.75	6.58	6.5	6.42	6.92	5.92	6.58	7.17	5.58
Overall negative odor	25	3.0	2.6	3.1	2.3	3.0	4.17	1.5	1.75	1.58	3.5	4.58	3.08	3.5	3.92	2.33	1.92	2.75	3.33	3.42	3.0	3.17	1.92	2.33	3.75	1.75	2.42	3.17	2.25	2.33	2.33	2.33	3.42
Appareance	8	6.1	6.9	6.0	6.9	6.5	6.1	5.9	5.7	6.2	5.9	6.0	5.8	5.7	6.7	6.3	6.4	5.9	5.6	6.1	7.2	7.1	7.1	6.8	6.9	6.5	6.6	7.0	7.1	6.7	6.7	6.9	6.5
Taste	9	5.4	6.3	5.4	6.3	5.0	5.4	5.9	5.2	5.8	4.6	5.1	5.3	5.3	6.0	5.5	5.8	5.5	4.9	5.5	6.3	5.8	6.4	6.6	6.2	6.0	6.2	6.5	6.8	6.0	6.5	6.1	6.3
Aroma	10	4.7	5.8	4.5	5.8	4.5	4.3	5.4	4.3	5.5	3.8	4.4	4.4	5.1	5.1	4.5	5.2	4.5	4.8	5.3	5.6	5.5	5.8	6.2	5.7	5.8	6.0	6.2	6.0	5.8	5.9	5.7	5.1

Table 2. ANOVA (*F*-test) and concentration of chemicals (mg L^{-1})

Sample	*F*-test value	D3	D4	D5	D6	D7	D8	D9	D11	D12	E1	E7	E8	E24	E18	E22	E10	E11	E13	E14	E15	E6	E21	E23	E28	E29	E31	E3	E4
Classification		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2
Hedonic Index		5.3	5.3	5.7	5	5.8	4.8	5.1	5.2	5.4	5.9	5.4	5.8	5.3	5.1	5.6	6.4	6.1	6.4	6.5	6.2	6.1	6.3	6.6	6.6	6.2	6.3	6.2	6
% Vol.	26	41.3	41.7	41.9	35.4	41.3	40.3	38.7	41	38.7	38.6	41.4	38.7	39.6	45.3	41	42.5	39.2	43.4	40.6	37.4	39.2	40.3	40.5	43.8	36.8	42.1	38.2	38.2
Methanol / (mg L^{-1})	25	7.85	14.6	21.1	14.5	15.6	66	17.2	21.7	50.9	100	7.00	23	57.4	7.82	35	32.3	17.6	27.3	23.5	21.6	10.8	42	72	34.2	97.4	67.5	28.5	23.6
Propanol / (mg L^{-1})	26	329	126	215	124	232	157	140	118	185	22	168	120	409	268	73	142	256	151	156	176	270	156	330	95.4	198	163	154	195
Isobutanol / (mg L^{-1})	23	171	189	196	111	187	256	249	234	219	145	119	113	267	193	290	283	169	251	286	141	107	219	211	237	116	204	182	183
Isoamyl alcohol / (mg L^{-1})	26	462	827	779	780	368	642	754	937	549	471	523	450	665	721	482	1150	620	1210	1250	770	514	547	481	1290	516	1000	669	512
1-Butanol / (mg L^{-1})	26	10.3	< LOD	4.26	4.26	4.64	4.12	4.54	< LOD	< LOD	< LOD	7.3	< LOD	4.27	4.43	4.05	< LOD	5.14	4.79	< LOD	9.0	3.7	4.19	4.23	< LOD	< LOD	< LOD	7.32	4.3
2-Butanol / (mg L^{-1})	25	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	78.2	269	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	11.6	11.5	6.87	< LOD	< LOD	< LOD	7.95	< LOD	< LOD	< LOD	< LOD	< LOD
Hexanol / (mg L^{-1})	23	3.0	9.3	0.6	3.1	5.5	< LOD	9.3	4.7	4.1	12.4	6.9	6.5	2.3	6.0	9.8	5.1	3.3	3.7	7.9	2.0	0.73	7.3	2.7	3.2	5.2	18.1	< LOD	11.8
Acetaldehyde / (mg L^{-1})	16	200	123	98.5	100	123	127	101	45.2	89.5	100	168	162	180	143	147	220	154	246	328	439	222	135	154	353	168	208	212	180
Benzaldehyde / (mg L^{-1})	19	1.89	5.71	8.57	1.72	1.9	2.3	2.1	2.1	3.9	3.72	1.78	1.89	6.26	1.77	3.96	8.61	8.26	7.65	5.84	2.71	5.02	3.1	5.83	3.18	5.02	5.55	5.47	6.75
Butyraldehyde / (mg L^{-1})	25	< LOD	0.456	0.74	0.61	< LOD	< LOD	< LOD	22	4.78	0.25	0.35	0.27	1.34	< LOD	0.42	0.26	0.42	0.37	1.33	< LOD	0.35	< LOD	1.06	0.55	0.61	1.1	0.41	< LOD
Formaldehyde / (mg L^{-1})	19	20.4	1.16	1.21	1.33	3.46	2.9	3.5	1.3	1.5	3.34	3.42	2.25	2.04	6.27	2.74	12	9.3	15.7	7.8	10	4.31	5.49	3.19	16.7	4.73	6.39	14	16.2
Hexanaldehyde / (mg L^{-1})	21	< LOD	< LOD	< LOD	< LOD	0.77	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.19	0.13	0.16	0.24	0.83	0.23	0.37	< LOD	0.16	0.09	0.94	0.11	0.31	0.55	0.13
5-HMF / (mg L^{-1})	23	1.92	1.08	0.28	0.78	0.109	0.9	1.6	0.5	0.3	1.02	4.5	3.49	4.04	0.81	1.01	0.80	2.84	1.51	3.55	7.48	19.4	2.1	4.17	2.78	1.48	0.82	2.43	2.4
Proprionaldehyde / (mg L^{-1})	25	0.07	0.045	< LOD	0.06	0.1	< LOD	< LOD	< LOD	< LOD	< LOD	0.15	0.09	0.23	0.16	1.35	0.16	0.72	0.37	0.09	0.58	0.11	0.92	< LOD	< LOD	< LOD	< LOD	0.65	0.39
Acrolein / (mg L^{-1})	23	0.218	< LOD	0.187	0.258	< LOD	< LOD	0.49	< LOD	< LOD	0.33	0.25	0.22	< LOD	< LOD	< LOD	0.21	0.3	0.3	0.16	0.36	0.28	< LOD	< LOD	< LOD	< LOD	< LOD	0.34	< LOD
Acetone / (mg L^{-1})	19	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	6.50	< LOD	6.40	< LOD	6.40	< LOD	< LOD	< LOD	6.90	< LOD	< LOD	< LOD	6.70
Ethyl acetate / (mg L^{-1})	20	189	161	80.8	68.4	95.5	63.4	513	50.9	99.1	376	164	461	229	171	700	479	248	1160	1330	295	515	486	310	867	92.5	248	323	484
Ethyl butyrate / (mg L^{-1})	25	< LOD	< LOD	0.44	< LOD	< LOD	0.55	0.61	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.61	0.429	1.3	0.52	1.08	< LOD	106	< LOD	3.2	< LOD	< LOD	< LOD	0.62
Ethyl hexanoate / (mg L^{-1})	20	0.634	0.56	0.62	0.58	< LOD	1.29	0.76	< LOD	< LOD	0.61	0.55	0.74	0.87	0.66	0.75	0.83	0.74	1.2	1.25	2.0	0.77	0.95	0.58	1.6	< LOD	0.86	1.29	0.93
Ethyl lactate / (mg L^{-1})	26	32	75.9	11.6	26.2	41.2	< LOD	64.4	32.4	26.4	110	64.4	60.4	21.2	35.7	73.2	44.8	28.6	30	57.3	19.7	16.2	49.3	19.9	18	38.8	120	3.71	96.5
Dimethylsulphide / (mg L^{-1})	24	0.6	4.5	0.23	1.9	1.6	0.42	14	1.13	0.18	0.01	0.04	0.03	0.10	0.59	0.02	0.03	0.07	0.04	0.04	0.05	0.07	0.04	0.08	0.02	0.05	0.04	0.04	0.05
Ethyl carbamate / (μg L^{-1})	26	50	70	40	< LOD	< LOD	200	< LOD	< LOD	< LOD	52.6	56.7	77.5	46	< LOD	47.8	136	60.2	87.4	< LOD	< LOD	78.1	55.6	45.7	49.1	121	84.8	< LOD	138
Copper / (mg L^{-1})	26	4.3	0.4	0.4	0.4	1.5	0.4	6.8	0.2	1.2	6.4	0.13	0.13	3.5	1.7	3.5	3.5	1.1	1.6	2.1	0.3	1.7	3.1	3.2	1.7	1.7	1.5	2.3	1.2
Iron / (mg L^{-1})	26	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	2.2	< LOD	< LOD	3.4	< LOD	< LOD	< LOD	< LOD	< LOD	2.0	0.1	0.5	< LOD	0.3	< LOD	0.5	< LOD	0.3	0.1	< LOD	0.3	3.6
Lead / (mg L^{-1})	26	0.04	0.02	< LOD	0.06	0.03	0.02	0.06	< LOD	0.24	0.07	0.01	0.03	< LOD	0.04	0.06	0.06	0.02	0.01	0.01	0.09	< LOD	0.02	0.02	< LOD	< LOD	< LOD	0.19	0.02
Acetic acid / (mg L^{-1})	23	171	136	100	67	129	14.6	1211	86.9	44.4	405	125	127	285	614	646	418	307	775	417	380	268	848	544	759	159	259	370	782
Latic acid / (mg L^{-1})	22	71.3	883	0.32	596	135	174	332	214	2.14	42.2	13.5	23	15.9	21.4	64.5	37.7	25.1	14.9	41.7	22.9	10.6	34.1	28.8	29.1	43.5	54.8	4.89	24
Glicolic acid / (mg L^{-1})	23	< LOD	< LOD	< LOD	< LOD	0.13	< LOD	0.16	< LOD	< LOD	0.01	< LOD	< LOD	< LOD	0.62	0.15	1.16	0.73	6.71	0.37	0.76	0.2	0.39	0.31	0.73	0.6	0.5	< LOD	< LOD
Piruvic acid / (mg L^{-1})	25	< LOD	< LOD	< LOD	< LOD	0.4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.72	< LOD	< LOD	< LOD	3.91	0.78	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Succinic acid / (mg L^{-1})	23	0.03	< LOD	< LOD	< LOD	0.03	< LOD	0.05	0.02	< LOD	0.02	< LOD	< LOD	0.6	0.03	< LOD	0.21	0.36	0.18	0.06	0.26	0.05	0.6	0.12	< LOD	< LOD	< LOD	0.14	0.22
Citramalic acid / (mg L^{-1})	20	0.05	< LOD	< LOD	0.05	< LOD	< LOD	0.04	0.1	< LOD	0.04	< LOD	< LOD	< LOD	0.05	0.06	0.11	< LOD	0.29	0.36	0.32	0.06	0.8	< LOD	0.33	0.12	0.08	< LOD	0.03
Capric acid / (mg L^{-1})	21	0.11	< LOD	< LOD	< LOD	0.69	0.91	< LOD	0.13	< LOD	0.96	0.5	0.17	< LOD	1.16	0.2	1.06	< LOD	4.34	1.31	1.32	1.47	1.05	1.68	0.2	0.182	0.13	0.31	1.31
Lauric acid / (mg L^{-1})	13	0.06	0.15	0.05	0.02	0.48	0.23	0.32	0.09	0.06	0.2	0.14	0.11	0.21	0.44	0.22	0.94	0.88	2.44	0.83	1.2	0.57	0.67	1.09	2.94	0.87	1.01	0.93	0.38
Miristic acid / (mg L^{-1})	19	0.37	0.11	0.06	0.09	0.11	0.01	0.21	0.28	0.05	0.13	< LOD	0.02	0.7	0.42	0.07	1.45	0.8	3.33	0.08	1.34	0.68	0.3	0.41	5.16	0.71	2.33	0.51	0.49
Palmitic acid / (mg L^{-1})	18	0.21	0.73	0.5	0.58	0.17	0.03	0.31	0.16	0.11	0.23	0.1	0.11	0.29	0.52	0.48	1.38	0.3	1.44	0.42	0.74	0.44	0.74	0.87	1.23	0.38	0.39	0.52	0.48

higher average value was observed for the aged *cachaças* (60.0 μg L^{-1}), which could be consistent with the increase on the concentration of the non-volatile compounds during storage.[40] Similar to lead and iron, ethyl carbamate does not exhibit sensory properties, but it is important as a chemical descriptor just like these metal ions. Copper by itself was not detected by sensory tests, but its presence could be correlated to aldehyde content.

Descriptive sensory evaluation

The results of the descriptive sensory evaluations of the *cachaça* samples are given in Table 1. They correspond to average notes given by the assessors for the sensory descriptors. The ANOVA results showed that *cachaças* were significantly different ($p < 0.05$) regarding the descriptors: taste, aroma, intensity of yellow color, burnt, floral, fruity, spicy, woody, vegetable, overall positive odor, biochemistry/chemistry, bitterness and overall negative odor.

Consumer hedonic measurement

According to the ANOVA test, significant differences ($p < 0.05$) were found in the *cachaça* hedonic (HI) data for appearance, taste and aroma (Table 1). Samples E23 and E28, which were aged in oak barrels, exhibit the higher hedonic index (HI = 6.6). The worst performance was observed for sample D8 (HI = 4.8), which was stored in a stainless steel container. According to with previous work, in general, the aged *cachaças* showed the best hedonic evaluation for appearance, aroma and taste.[15,41]

Multivariate analysis

PCA was applied to the data base in Tables 1 and 2 to observe sensory similarities based on the descriptive sensory and chemical data, respectively. In the score plot (Figure 1a), it can be observed a tendency of the sample separation in two clusters of *cachaças* with HI < 6 and HI > 6, respectively.

The loading plot (Figure 1b) shows the sensory descriptors that influenced this separation. The three first components, PC1 (37.4%), PC2 (22.2%) and PC3 (12.6%) account for 72.2% of the total variance data for the nine descriptors. The first component (PC1) showed the highest scores regarding the overall positive odor, spicy, burnt, woody, fruity and floral attributes, whereas the biochemistry/chemistry, bitterness and vegetable descriptors are more related to the second component (PC2).

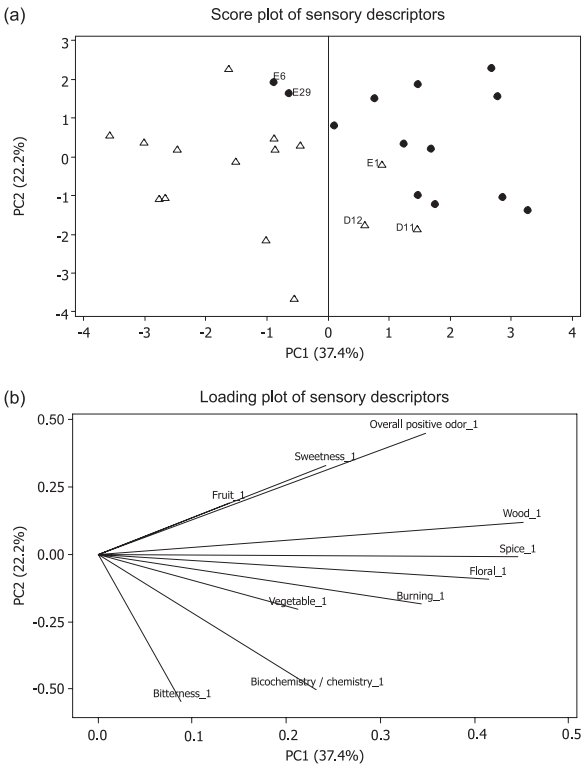

Figure 1. PCA of the sensory descriptors data, (a) score plot (△) HI < 6 and (●) HI > 6, and (b) loading plot.

Three samples with HI < 6 (D11, D12 and E1) can be observed into the better ranked cluster (HI > 6). It can be explained by analyzing the hedonic evaluation of the consumers and of the trained panel. In this case, only taste and aroma were considered since the appearance did not correlate well with the chemical and the other sensory descriptive variables. These samples, which were misplaced in the HI > 6 cluster exhibit smaller values for aroma (consumers) in comparison to the same attribute of the samples with HI > 6. However, the trained panel well recognized their floral and fruity attributes. This would suggest the poorer consumer abilities with respect to the trained panelist group on recognizing the aroma of *cachaças*. The same was observed regarding the burnt descriptor. The relative woody, floral, burnt and fruity low scores, attributed by the trained panelist group, would explain the presence of the two misplaced samples (E6 and E29) in the cluster of HI < 6.

PCA was applied to the chemical database in Table 2 to observe chemical similarities among the *cachaças*. In the score plot (Figure 2a), the tendency of two clusters formation was also observed. Again, one composed mostly of *cachaças* with HI < 6 and the other mainly of samples with HI > 6.

The loading plot (Figure 2b) illustrates the behavior of the 31 analyzed organic compounds regarding to

the quality of the *cachaças*. The number of variables were not reduced purposely since the goal is to show the correlation between the chemical variables and the hedonic quality of *cachaças*. The first eleven principal components with eigenvalues greater than 1 account for 83.8% of the total variability, suggesting that these principal components adequately explain the data variations.[42]

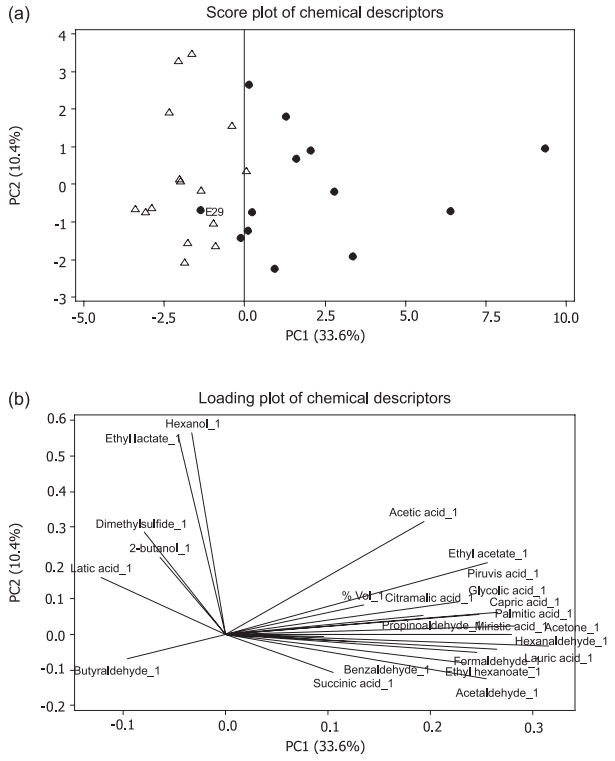

Figure 2. PCA of the chemical data, (a) score plot (△) HI < 6 and (●) HI > 6, and (b) loading plot.

PC1 (33.6%) showed that alcohol content (% vol.), acids (except lactic acid), esters (except ethyl lactate), aldehydes (except butyraldehyde), ethyl carbamate and fatty acids were the most representative variables in defining the cluster of *cachaças* with HI > 6. On other hand, lactic acid, ethyl lactate, 2-butanol, hexanol, butyraldehyde, lead and dimethylsulfide correlated negatively with PC1, which accounts for the clustering of *cachaças* with HI < 6.

One sample with HI > 6 (E29) can be observed in the HI < 6 cluster. It can be explained by analyzing the chemical composition of these samples. This misplaced sample exhibited higher average concentrations for methanol, propanol, and hexanol and lower concentrations for acetaldehyde, benzaldehyde, formaldehyde, propionaldehyde, acetone, ethyl acetate, ethyl butyrate and ethyl hexanoate than the samples with HI > 6.

A variable reduction in PCA was performed considering the load value of each variable in the corresponding principal component (PC1 and PC2) in Figure 2. Through elimination of descriptors, which leads to the same information as in Figure 2, seven variables were then selected from the original database: lactic acid, ethyl lactate, dimethylsulfide, benzaldehyde, acetaldehyde, lauric and acetic acid. This approach leads to a better clustering of *cachaças* than the one observed in Figure 2 without losing the quality of the analytical results. An increase in the variance of 27.1% was observed in the first three PCs (PC1 = 33.8%, PC2 = 23.2% and PC3 = 14.6%) relatively to the previous result.[43] A similar trained panel clustering was reached using only seven chemical variables (Figure S1 in the SI section).

Comparing Figures 1 and 2, a similarity between sensory and chemical descriptors is suggested. A tendency of clustering of two groups is also observed in Figure S2 (in the SI section) which combines both sensory and chemical descriptors. The loading plot of Figure S1b (in the SI section), illustrates the observed correlation between chemical compounds and sensory descriptors. The compounds that mostly correlated with the flavor of sugarcane spirits were acetaldehyde, hexanaldehyde, ethyl esters and acetates (fruity), acetic acid (burnt) and isobutyl alcohol (floral). These correlations between the sensory and chemical descriptors are in agreement with the sensory literature.[44] Woody and vegetable attributes do not correlate with the chemical compounds analyzed. Although compounds as terpenes, lactones, phenols, ketones (except 2-propanone) and other volatiles compounds were not determined, the chemical descriptors here studied would certainly be useful on identify a "good" *cachaça*.

Following this reasoning, the data sets in Tables 1 and 2 were analyzed, using linear discriminant analysis (LDA) and ethyl lactate, dimethylsulfide, lactic acid, lauric acid, citramalic acid and glycolic acid as chemical descriptors since they provided the highest scores in PCA (loading plot, Figure 2b) without high correlation. A model was then generated using 28 samples being 16 with HI < 6 and 12 with HI > 6, 80% of the samples were used in the calibration step and the remaining 20% for the model validation, which was preformed following the leave-one-out approach. The calculated model predicted abilities in terms of calibration and validation are 86.4 and 100%, respectively. The model robustness (prevision ability) was also additionally checked using nine new *cachaças* (blind samples) out of to the group considered, but with known sensory and chemical evaluations. The model was able to classify correctly seven out of these samples (Table 3).

Table 3. Classification of Brazilian *cachaças* according to their qualities using linear discriminant analysis (LDA)

Model construction	True group	
	HI < 6	HI > 6
Total number of samples	13	9
Samples with correct classification	11	8
Individual correct percentage	84.6%	88.9%
Number of samples = 22		
Number of samples correct = 19		
Proportion correct = 86.4%		
Model validation ("unknown" samples)	**True group**	
	HI < 6	HI > 6
Total number of samples	3	3
Samples with correct classification	3	3
Individual correct percentage	100%	100%
Number of samples = 6		
Number of samples correct = 6		
Proportion correct = 100 %		
Test of model of *cachaças* with known quality	**True group**	
	HI < 6	HI > 6
Total number of samples	3	6
Samples with correct classification	2	5
Individual correct percentage	66.7%	83.3%
Number of samples = 9		
Number of samples correct = 7		
Proportion correct = 77.8%		

Variables: ethyl lactate, dimethylsulphide, lactic acid, lauric acid, citramalic acid and glycolic acid.

Conclusions

This study deals with the descriptive aspects of sugarcane spirits (*cachaças*) aiming to a better understanding of their sensory and chemical characteristics and their possible correlations. Although HI was arbitrarily selected, the data of both sensory and chemical analyses suggest a good correlation between these descriptors. Even considering the limited number of compounds analyzed and the fact that more than one compound could be responsible for a sensory attribute with a possible synergism between compounds, the results provide a sound model to predict the quality of a beverage based on chemical descriptors. The model can certainly be refined by still more extensive data sets of samples, chemical constituents and tasters. However, the current approach holds undoubtedly promise to evaluate *cachaças* as an alternative to sensory analysis which requires tedious trainings to educate qualified tasters.

Supplementary Information

Complete analytical data and sensory information are available free of charge at http://jbcs.sbq.org.br as PDF file.

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Supplementary Information

Correlation between Chemical Composition and Sensory Properties of Brazilian Sugarcane Spirits (*Cachaças*)

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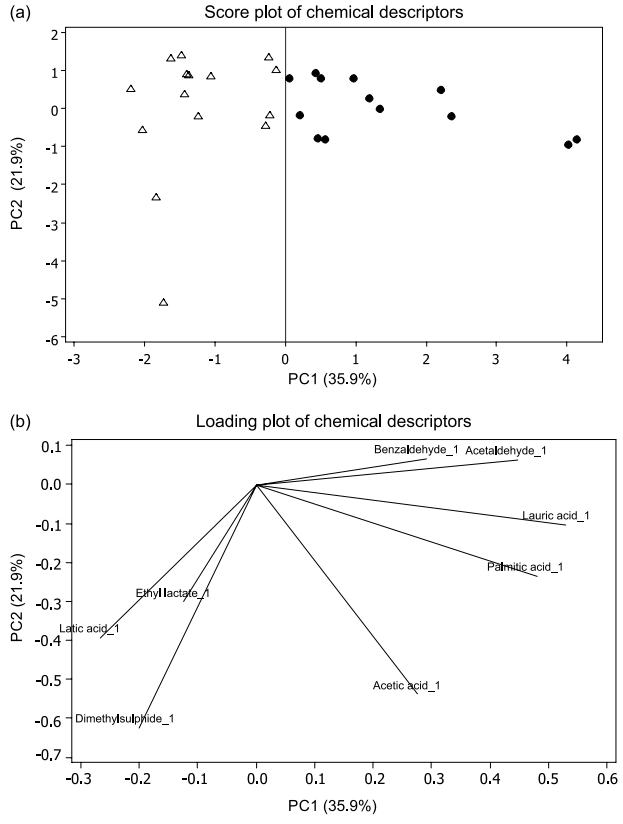

Figure S1. PCA of the chemical data, (a) score plot and (b) loading plot.

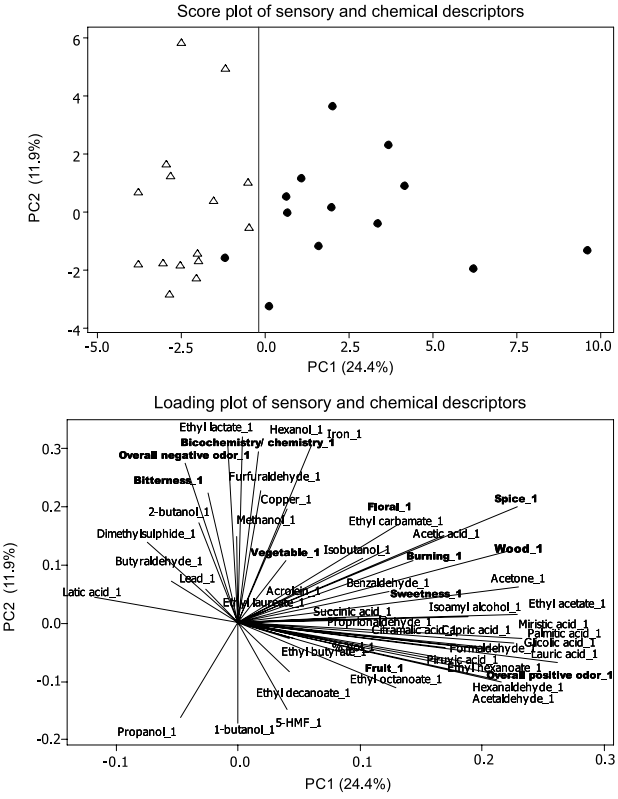

Figure S2. PCA of the sensory and chemical data, (a) score plot and (b) loading plot.

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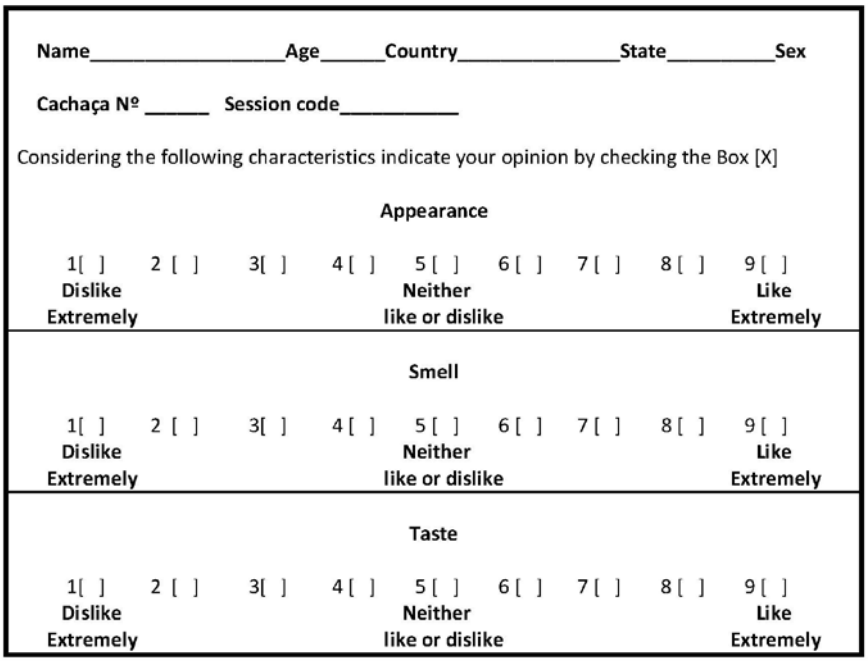

Figure S3. Form used in the consumer hedonic test of *cachaça*.

Table S1 Aging times and nature of the aging material for the *cachaças*

Cachaça sample	Aging time	Recipient
D3	8 months	Stainless steel
D4	6 months	Freijó (*Cordia goeldiana*)
D5	8 months	Amendoim (*Pterogyne nitens*)
D6	2 months	Amendoim (*Pterogyne nitens*)
D7	6 months	Oak (*Quercus*)
D8	3 years	Stainless steel
D9	6 months	Oak (*Quercus*)
D11	3 months	Jequitibá (*Cariniana estrellensis*)
D12	3 months	Jequitibá (*Cariniana estrellensis*)
E1	1 year	Oliveira (*Olea europaea* L.)
E3	2 years	Oak (*Quercus*)
E4	4years	Oak (*Quercus*)
E6	1 year and 6 months	Oak (*Quercus*)
E7	1 year	Jequitibá (*Cariniana estrellensis*), Grapia (*Apuleia Leiocarpa*)
E8	1 year	Grapia (*Apuleia Leiocarpa*)
E10	4 years	Oak (*Quercus*)
E11	2 years	Oak (*Quercus*)
E13	10 years	Oak (*Quercus*)
E14	2 years	Oak (*Quercus*)
E15	4 years	Oak (*Quercus*)
E18	2 years	Oak (*Quercus*)
E21	2 years	Oak (*Quercus*)
E22	3 years	Oak (*Quercus*)
E23	4 years	Oak (*Quercus*)
E24	2 years	Louro canela (*Lauraceae*)
E28	1 year and 6 months	Oak (*Quercus*)
E29	1 year and 6 months	Oak (*Quercus*)
E31	2 year	Oak (*Quercus*)

Table S2. Descriptive sensory vocabulary for *cachaças*

Aroma	Appearance	Taste
Floral	intensity of the yellow color	burnt
Fruity	transparency	sweetness
Vegetable		bitterness
Spicy		
Biochemistry/Chemistry (fermented, plastic, fusel oil, sulfide, solvent)		
Woody		
Overall positive odor		
Overall negative odor		

Table S3. Median and average concentrations for organic compounds according to the HI values of the *cachaças*

Sample	Average (HI < 6)	Average (HI > 6)	Median (HI < 6)	Median (HI > 6)
Hedonic index	5.38	6.3	5.3	6.3
% vol.	40.3	40.2	41	40.3
Methanol / (mg L^{-1})	31	38	21	29
Propanol / (mg L^{-1})	179	188	157	163
Isobutanol / (mg L^{-1})	196	199	193	204
Isoamyl alcohol / (mg L^{-1})	627	810	642	669
1-Butanol / (mg L^{-1})	3.48	3.3	4.26	4.19
2-Butanol / (mg L^{-1})	25.3	2.9	< LOD	< LOD
Hexanol / (mg L^{-1})	5.6	5.5	5.5	3.7
Acetaldehyde / (mg L^{-1})	127	232	123	212
Benzaldehyde / (mg L^{-1})	3.3	5.6	2.1	5.55
Butyraldehyde / (mg L^{-1})	2.1	0.5	0.35	0.41
Formaldehyde / (mg L^{-1})	3.79	9.7	2.74	9.3
Hexanaldehyde / (mg L^{-1})	0.07	0.3	< LOD	0.23
5-HMF / (mg L^{-1})	1.49	4.0	1.01	2.43
Proprionaldehyde / (mg L^{-1})	0.15	0.3	0.06	0.16
Acetone / (mg L^{-1})	< LOD	2.5	< LOD	< LOD
Ethyl acetate / (mg L^{-1})	228	526	164	479
Ethyl butyrate / (mg L^{-1})	0.11	8.8	< LOD	0.52
Ethyl hexanoate / (mg L^{-1})	0.57	1.0	0.62	0.93
Ethyl lactate / (mg L^{-1})	45.0	41.8	35.7	30
Dimethylsulfide / (mg L^{-1})	1.69	0.0	0.42	0.04
Ethyl carbamate / (mg L^{-1})	43	66	46	60
Copper / (mg L^{-1})	2.1	1.9	1.2	1.7
Iron / (mg L^{-1})	0.4	0.6	< LOD	0.3
Lead / (mg L^{-1})	0.05	< LOD	0.03	0.02
Acetic acid / (mg L^{-1})	277	484	129	417
Latic acid / (mg L^{-1})	173	29	65	29
Glicolic acid / (mg L^{-1})	0.07	1.0	< LOD	0.5
Piruvic acid / (mg L^{-1})	0.07	0.4	< LOD	< LOD
Succinic acid / (mg L^{-1})	0.1	0.2	< LOD	0.14
Citramalic acid / (mg L^{-1})	< LOD	0.2	< LOD	0.11
Capric acid / (mg L^{-1})	0.3	1.1	0.13	1.06
Lauric acid / (mg L^{-1})	0.19	1.1	0.15	0.93
Miristic acid / (mg L^{-1})	0.18	1.4	0.11	0.71
Palmitic acid / (mg L^{-1})	0.30	0.7	0.23	0.52

LOD: limit of detection