

Characterization of Cachaça and Rum Aroma

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Cachaça, the most popular alcoholic beverage in Brazil, is a sugar cane spirit similar to rum. Its production is around 2 billion liters per year, of which <1% is exported. Although rum is similar to cachaça its flavor difference is easily recognizable. Using gas chromatography–olfactometry (GCO) to separate and characterize the odorants present in cachaça and rum, these two sugar cane products were compared and standards identified to use in a descriptive sensory analysis (DSA). In the DSA cachaça was more intense in the grassy, spicy, sulfury, and vinegar descriptors, whereas apple and caramel were the same in both rum and cachaça. The GCO data for the apple-smelling compounds β -damascenone along with ethyl butyrate, isobutyrate, and 2-methylbutyrate were at the same potency in both cachaça and rum, whereas the spicy-smelling eugenol, 4-ethylguaiaicol, and 2,4-nonadienal were much more potent in cachaça.

KEYWORDS: Brazilian sugar cane spirit; rum; aroma; descriptive analysis; gas chromatography–olfactometry

INTRODUCTION

Cachaça is the typical Brazilian spirit produced from the distillation of fermented raw sugar cane juice (1), whereas rum, traditionally produced in Caribbean countries, is a spirit obtained by fermenting cooked sugar cane juice and molasses (2). The production of cachaça is nearly 2 billion liters per year, of which <1% is exported (3). Efforts to increase the exportation of cachaça (1) can be aided by a knowledge of cachaça's chemical and sensory properties, especially as they compare to those of rum. The use of cooked cane juice during rum production should give it an aroma different from that of cachaça which is based on the fermentation of raw ingredients. In this study the most potent odorants extracted from cachaça and rum were detected by gas chromatography–olfactometry (GCO) and the results compared with the results of a descriptive sensory analysis (DSA). Authentic standards of some of the odorants detected by GCO were used to train the DSA panel to help in comparing the results of the two products. The purpose of this study was to compare the sensory descriptive properties and the odorant potencies of cachaça with those of rum to determine their major differences in flavor chemistry.

MATERIALS AND METHODS

Samples. Aged and unaged cachaça beverages were obtained from a medium-sized producer in Brazil. Although there are many smaller cachaça producers whose products vary in quality, the brand chosen

(João Mendes, Pedrões, Brazil) was both available and representative of cachaça flavor. Rum from the largest producer in Puerto Rico (Bacardi, San Juan, Puerto Rico) is the most prevalent in the export market. The samples were stored at ambient temperature and diluted with deionized water to the same alcohol content (11%). Cachaça is usually consumed diluted with other beverages to an alcohol concentration of ~10%. Because aged cachaça is often marketed in Brazil at a premium price, samples of aged and unaged product from the same producer were compared by sensory difference testing.

Standards. Authentic standards were obtained from the following sources: isobutanol, propanol, isoamyl alcohol, formic acid, 2-methylpropan-1-ol, eugenol, ethyl laurate, guaiacol, 2-phenylethanol, and ethyl octanoate from Sigma, St. Louis, MO; 2,4,6-trichloroanisole, isoamyl acetate, ethyl vanillin, *cis*-3-hexen-1-ol, dimethyl sulfide, thymol, and acetic acid from Aldrich Chemical Co., Milwaukee, WI; dimethylheptanal from Bedoukian Research Inc., Danbury, CT; ethyl hexanoate and diacetyl from Mil-Spec Industries Corp., Roslyn Heights, NY; citrus oil from Fritz Brothers Inc., New York City; heptanal from Eastman Organic Chemical Kodak, Rochester, NY; maltol from K & K Laboratories Inc., Plainview, NY; almond extract from McCormick & Co. Inc., Hunt Valley, MD. Each standard was prepared in Freon 113 at 0.01% v/v and chromatographed separately under the same conditions as the GCO-MS for identification purposes.

Sensory Tests. A panel of 12 people (6 women and 6 men, staff and graduate students from the New York Agriculture Experiment Station) between the ages of 24 and 66, all with previous experience serving on sensory panels, was used for all sensory testing. Panelists tasted between 11:30 a.m. and 12:30 p.m.

Difference Test. A triangle test was used to determine if the panel could detect differences between unaged and aged cachaça and between unaged cachaça and rum aroma. For the triangle test, three samples were presented simultaneously to the panelists; two samples were the same, and one was different. The samples, 30 mL per glass, were served

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Table 1. Standard Odorants Used to Train the DSA Panel

descriptor	reference standard	amount ($\mu\text{g/mL}$)
alcohol	equimolar of isobutanol, propanol, and isoamyl alcohol	100
pungent solvent	formic acid	10,000
spicy	2-methylpropan-1-ol	1,000
malt	eugenol	1
mold	malt extract	400
fruity (ester)	2,4,6-trichloroanisole	1
fruity (others)	isoamyl acetate	10
apple	ethyl octanoate	10
melon	ethyl hexanoate	10
citrus	dimethylheptanal	20
floral	citrus oil	100
vanilla	2-phenylethanol	100
buttery	ethyl vanillin	10
grassy	diacetyl	1
oily	<i>cis</i> -3 hexen-1-ol	1000
woody	heptanal	1
sulfury	oak extract	1000
medicine	dimethyl sulfide	1
caramel	thymol	120
soapy	maltol	1135
vinegar	ethyl laurate	12
smoky	acetic acid	5322
almond	guaiacol	27
	almond extract	2500

Table 2. Most Potent Odorants Found in Cachaça Using GCO

compound	RI ^a	descriptor	Charm	OSV ^b
β -damascenone	1383	floral/fruity	60974	100
eugenol	1368	spicy	6625	33
diethyl acetal	730	fruity	5009	29
phenyl ethyl alcohol	1111	floral	3705	25
ethyl isobutyrate	758	melon	1806	17
unknown 1	1174	cereal	1327	15
ethyl 2-methylbutyrate	850	apple	1120	14
2-phenylethyl acetate	1255	floral	768	11
ethyl phenyl acetate	1243	fruity	702	11
2,4-nonadienal	1214	floral	675	11
4-ethylguaiacol	1279	spicy	581	10
unknown 4	1066	other	376	8
unknown 5	866	cereal	340	7
diacetyl	645	butter	254	6
guaiacol	1088	medicine	252	6
unknown 6	1204	other	232	6
ethyl acrylate	702	plastic	231	6
4-vinyl-2-methoxyphenol	1316	spicy	220	6
heptanal	901	solvent	178	5
unknown 7	1045	floral	143	5
isoamyl acetate	877	fruity	117	4
ethyl butyrate	803	apple	113	4
1-octen-3-one	978	mushroom	91	4
<i>E</i> -2-nonenal	1159	grassy	75	4
vanillin	1407	vanilla	3	1

^a Retention index on DB5. ^b Transformed Charm values using Steven's law (exponent = 0.5) (16).

at ambient temperature (20 °C) in clear wine glasses covered by watch glasses in individual tasting booths. Red lighting was used to reduce the effect of variations in the color of the samples (4). The panelist was asked to smell the samples and indicate the odd sample by its three-digit code. No special training preceded the test.

Descriptive Sensory Analysis. For one month, the sensory panel met twice a week for 60 min to develop a vocabulary suitable for describing the aromas of cachaça and rum. During these sessions, the panelists generated, discussed, and modified descriptive terms using the cachaça and rum samples (5, 6). Twenty-five standards (Table 1) prepared from the lists of GCO descriptors (Tables 2 and 3) were used to help the group reach a consensus on the 10 descriptors used in the

Table 3. Most Potent Odorants Found in Rum Using GCO

odorant	RI ^a	descriptor	Charm	OSV ^b
β -damascenone ^c	1383	floral/fruity	15467	100
diethyl acetal	730	fruity	1035	26
unknown 2	866	cereal	791	20
ethyl 2-methylbutyrate	850	apple	633	16
ethyl isobutyrate	758	melon	299	14
β -methyl- γ -octalactone	1204	musty	150	6
vanillin ^c	1407	vanilla	134	9
ethyl butyrate	803	apple	113	9
phenyl ethyl alcohol ^c	1111	floral	93	8
1-octen-3-one	978	mushroom	91	8
2-phenylethyl acetate ^c	1255	floral	75	7
guaiacol ^c	1088	medicine	54	6
heptanal	901	solvent	37	5
<i>E</i> -2-nonenal	1159	grassy	15	3
2,4-nonadienal	1214	oil	10	3
phenyl ethyl acetate ^c	1243	fruity	10	3
eugenol ^c	1368	spicy	10	3
unknown 1	1174	Band-aid	6	2
diacetyl	644	butter	1	1
4-ethylguaiacol	1279	spicy	1	1

^a Retention index on DB5. ^b Normalized and transformed Charm values using average Steven's law exponent (0.5) (16). ^c Previously reported in rum (6).

DSA: apple, caramel, vanilla, melon, alcohol, citrus, spicy, vinegar, sulfury, and grassy. The sugar cane spirits were evaluated for the intensity of these aromas in individual booths in an enclosed room (5). The samples, 30 mL per glass, were served randomly, at ambient temperature (20 °C), in clear wine glasses covered by watch glasses. Each sample was coded with a three-digit random number (samples were evaluated twice per panelist). The intensity of each aroma attribute was rated on a structured category (15 points) scale using a flat database computer program (File Marker Pro 5 software, Santa Clara, CA). Six ballot screens, one for each attribute, consisting of four scales, one for each sample tested, were presented in succession.

Sample Extraction. The beverage samples (50 mL) were placed in a 100 mL extraction flask together with 15 mL of Freon-113 and then sonicated at 40 kHz and 20 °C for 10 min. The liquid phases were separated in a 250 mL separation funnel. The lower phase (Freon) was collected, and the upper phase was rinsed with an additional 5 mL and sonicated as described previously. This extraction procedure was repeated for a third time with a total of 15 mL of Freon. The extracts were dried with anhydrous magnesium sulfate. The extracts were concentrated to 1 mL under reduced pressure (0.5 atm) using a rotary evaporator and water bath (30 °C) (7).

Gas Chromatography–Olfactometry. CharmAnalysis was used to quantify the odor activity in the unaged cachaça and rum extracts (8). One microliter of each concentration was injected into the GCO in splitless mode, a modified Hewlett-Packard 5890 gas chromatograph equipped with a 0.32 mm \times 13.5 m fused silica capillary column (DB-5) and a high-resolution olfactometer system that mixed the GC effluent with a stream of humidified air (20 L/min) (9). This air stream passed through a 10 mm diameter stainless steel tube and was sniffed by a person (the sniffer) after the solvents were eluted. The injector was held at 200 °C, and the GC was held at 35 °C for 3 minutes following sample injection and programmed at 6 °C/min to 225 °C; He at 2 mL/min was used as a carrier gas. All extractions were sniffed twice (repeated measure) until no odor was detected (successive 3-fold dilutions until 1:729), and the retention time of each odorant was converted to retention indices by adjusting to a series of 7–18 carbon *n*-paraffins run under identical conditions but detected with a flame ionization detector (10). The raw data were used to calculate Charm values (peak areas in Charm chromatograms) according to the procedures of Acree et al., and least detectable values of 10 were used for the estimation of Charm ratios (11).

Gas Chromatography–Mass Spectrometry (GC-MS). Mass spectrometric characterizations of the aroma extracts were performed using a Hewlett-Packard 5890 GC attached to a 5970 mass selective detector (MSD). One microliter of each 243-fold concentrated extract was

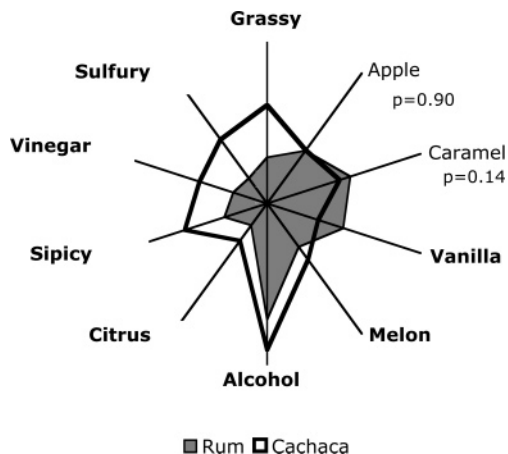


Figure 1. Spider plot of the unaged cachaça and rum. Distance from the origin is proportional to the mean. All p values were <0.001 except those for caramel and apple.

injected into the gas chromatograph equipped with an HP5-MS capillary column (0.20 i.d., 30 m) and He at 2 mL/min as a carrier gas. The GC was held at 35 °C for 3 min following sample injection and programmed at 4 °C/min to 225 °C. The injector was held at 200 °C. The compounds eluted from the column were ionized with electrons at 70 eV. Spectra of compounds eluting ± 5 RI of the odor-active compounds detected in the GCO were investigated. All other spectra were ignored. An identification was reported only when the spectra, retention time, and odor character matched those of an authentic standard (12).

Statistical Analysis—Sensory Analysis. Two-way analysis was used to study the variance (ANOVA) for each beverage for each attribute with the EXCEL program for p values of <0.001 (13).

Statistical Analysis—GCO. GCO produced chromatograms and tables listing indices, odor characters, and peak areas (Charm values). The Charm values could be compared by normalizing the data to produce an odor spectrum (14). An odor spectrum is based on the idea of Steven's law, $\Psi = k\Phi^n$, where Ψ is the perceived intensity of a stimulant, k is a constant, Φ is the stimulus level, and n is an exponent between 0.3 and 0.8 for odor (15). The median value of $n = 0.5$ was used. The odor spectrum, a plot of odor spectrum values against retention indices, shows the pattern of relative potency independent of concentrations (7). The Charm values of the ratio of unaged cachaça/rum was calculated to determine the major differences in odorant potencies between these spirits. To meaningfully calculate ratios, a least detectable response of 10 was used for all responses of <10 (11).

RESULTS AND DISCUSSION

Sensory Analysis. All 12 judges could distinguish the unaged cachaça from rum and the aged cachaça from rum, but they could not find differences between unaged cachaça and aged cachaça in the triangle test for a $p < 0.05$ significance level. For this reason, the descriptive analysis was conducted to determine only the differences between unaged cachaça and rum. **Figure 1** shows the mean intensity ratings for the unaged cachaça and rum plotted on a spider graph using 10 descriptors. In this diagram, the center of the figure represents low intensity with respect to each descriptor, increasing to an intensity of 15 at the ends of the axes. ANOVA of these results showed that unaged cachaça and rum were different in their alcohol, vinegar, vanilla, citrus, melon, spicy, sulfury, and grassy aroma attributes. Scores for the caramel and apple attributes showed no significant differences between unaged cachaça and rum.

GCO Analysis. The GCO analysis detected 24 odor active volatiles in unaged cachaça Freon extracts. **Table 2** shows the odorants, Charm values (14), and odor spectrum values (OSV) (7) that were detected in the unaged cachaça by GCO analysis. A Charm value, the area of a peak in the Charm chromatogram,

Table 4. Potency Ratios of the Odorants Common to Rum and Cachaça

odorant	potency (Charm)		odor	ratio C/R
	cachaça	rum ^a		
eugenol	6625	10	spicy	663:1
unknown 1	1327	10	cereal	133:1
ethyl phenyl acetate	702	10	fruity	70:1
2,4-nonadienal	675	10	floral	68:1
4-ethylguaiaicol	581	10	spicy	58:1
phenyl ethyl alcohol	3705	83	floral	45:1
2-phenylethyl acetate	768	75	floral	10:1
ethyl isobutyrate	1806	192	melon	9:1
diethyl acetal	5009	1035	fruity	5:1
β -damascenone	60974	15467	fruity/floral	4:1
ethyl 2-methylbutyrate	1120	633	apple	2:1
ethyl butyrate	113	192	apple	1:1
vanillin	10	134	vanilla	1:13
β -methyl- γ -octalactone	10	140	mould	1:14
unknown 2	10	791	solvent	1:79

^a Values of <10 were rounded up to 10 (a least detectable potency).

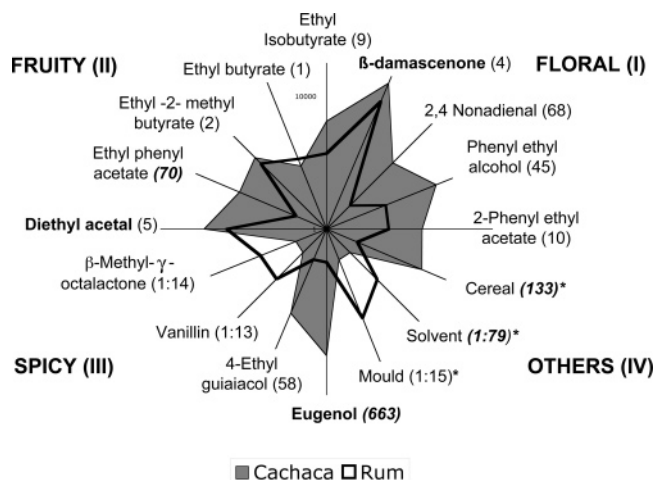


Figure 2. Most potent odorants in unaged cachaça and rum. Charm value ratios of unaged cachaça/rum are given in parentheses. An asterisk indicates major differences between unaged cachaça and rum.

is proportional to the concentration of the component in the extract divided by the gas-phase detection threshold. The OSV is the normalized Charm value modified with an approximate Steven's law exponent (15). OSVs are independent of total concentration and approximate the relative potency of each odorant (15). Among the volatiles detected by GCO, β -damascenone, eugenol, diethyl acetal, phenyl ethyl alcohol, ethyl isobutyrate, unknown 1 (smells like cereal), ethyl 2-methylbutyrate, 2-phenylethyl acetate, ethyl phenyl acetate, 2,4-nonadienal, and 4-ethylguaiaicol were identified as being the most potent odorants in unaged cachaça (**Table 2**). β -Damascenone, with a characteristic floral-fruity aroma, had the largest odor activity in unaged cachaça. It is a potent odorant in many natural products contributing to the odor character of Bulgarian rose oil (16), apple products (17), Satsuma mandarin juice (18), various grapes varieties and wines (19), rum (20), and alcoholic beverages (21). The odor descriptor "spicy" was associated with eugenol and 4-ethylguaiaicol, "melon" with ethyl isobutyrate, and "apple" with ethyl 2-methylbutyrate in the GCO analysis. The GCO analysis detected 16 odor active volatiles in rum Freon extracts. **Table 3** shows the odorants, Charm values, and OSV that were detected in the rum by GCO analysis. Among the volatiles detected by GCO, β -damascenone, diethyl acetal, unknown 1 (solvent), ethyl 2-methylbutyrate, ethyl isobutyrate,

ethyl butyrate, unknown 2 (mold), β -methyl- γ -octalactone, and vanillin were identified as being the most potent odorants in rum. The most potent odorant found in both rum and cachaça was β -damascenone, but the potency of this compound was 4 times less than in cachaça. The aroma descriptors obtained in the descriptive analysis, such as apple, melon, and vanilla were detected as ethyl 2-methylbutyrate and ethyl butyrate (apple), ethyl isobutyrate (melon), and β -methyl- γ -octalactone and vanillin (vanilla) in the GCO. **Table 4** shows the ratio of the Charm values between unaged cachaça and rum. Overall, cachaça contains odorants at a higher potency level than rum, consistent with the higher response of every perception measured in **Figure 1**. The odorants that showed a ratio between 10:1 and 1:10 are among the most potent odorants in both cachaça and rum and represent flavor chemistry that is shared by both products. This is consistent with similar scores given to the apple, melon, and to some extent citrus perceptions measured in both cachaça and rum (**Figures 1** and **2**). The major differences between the two products was a higher potency for eugenol, an unknown cereal-smelling compound, phenyl ethyl alcohol, phenyl ethyl acetate, 2,4-nonadienal, and 4-guaiacol in cachaça. Taken together these compounds seem to explain the much stronger spicy and cereal smells characteristic of cachaça. **Figure 2** shows a plot of both the perceptual data and the potency data simultaneously.

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