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Comparison between Cachaça and Rum Using Pattern Recognition Methods

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The differentiation between cachaça and rum using analytical data referred to alcohols (methanol, propanol, isobutanol, and isopentanol), acetaldehyde, ethyl acetate, organic acids (octanoic acid, decanoic acid, and dodecanoic acid), metals (Al, Ca, Co, Cu, Cr, Fe, Mg, Mn, Ni, Na, and Zn), and polyphenols (protocatechuic acid, sinapaldehyde, syringaldehyde, ellagic acid, syringic acid, gallic acid, (−)-epicatechin, vanillic acid, vanillin, *p*-coumaric acid, coniferaldehyde, coniferyl alcohol, kaempferol, and quercetin) is described. The organic and metal analyte contents were determined in 18 cachaça and 21 rum samples using chromatographic methods (GC-MS, GC-FID, and HPLC-UV−vis) and inductively coupled plasma atomic emission spectrometry, respectively. The analytical data of the above compounds, when treated by principal component analysis, hierarchical cluster analysis, discriminant analysis, and *K*-nearest neighbor analysis, provide a very good discrimination between the two classes of beverages.

KEYWORDS: Cachaça; rum; mean volatiles; metals; principal component analysis; KNN; PLS-DA

INTRODUCTION

The production of Brazilian sugar cane spirit, which has been popularized as cachaça, is around two billion liters per year, from which <1% is exported (*1*). A great deal of effort has been dedicated to increase the exportation volume and qualify cachaça as an international beverage typical of Brazil (*2*). Great improvements were made regarding the knowledge of cachaça's chemical composition in the past decade (*3*−*7*). Consequently, quality control has been improved, and its chemical composition and sensory profile are now being drawn.

Due to the internationalization of cachaça, some confusion over rum and cachaça identities has arisen. Cachaça is the denomination of the typical Brazilian spirit produced from the distillation of fermented sugar cane juice (*2*), whereas rum, traditionally produced in Caribbean countries, is a sugar cane spirit obtained by the distillation of cooked fermented sugar cane juice and molasses (*8*).

A distinction between molasses and sugar cane juice based on their respective chemical profiles cannot be drawn at the moment. However, both beverages are expected to exhibit differences in the chemical composition of the must, as well as a variation in their organic composition fraction. Moreover, the metal contents are influenced by the distillation equipment (pot-still or column), the SO_2 content of the fermented must, and the water used for the final dilution.

Several examples can be found in the literature of the metal and secondary compound profiles being used to differentiate beverages (*9*−*20*). For instance, the content of higher alcohol has been used to certify Irish whiskey authenticity (*17*) and differentiate Chivas Regal from non-Chivas Regal whiskey samples (*18*); the content of organic acids and esters has been used to differentiate between expensive and cheap rums (*19*), and the concentrations of alcohol, esters, and fatty acids can classify and differentiate the origin of a variety of wines (*20*). The content of metals can also distinguish different types of teas, beers, and wines as well as identify the geographical origin and authenticity of beverages (*9*−*11*). Isotopic analysis (^{14}C, $^{2}H/^{1}H$) has been also widely used for beverage differentiation and even for geographical origin classification (*21*). Some molasses from Brazilian sugar cane produced in northwestern Brazil have been exported to countries of Central America; therefore, precluding the use of this approach to differentiate between cachaça and rum must be very difficult.

With the aim of differentiating between rum and cachaça, this paper reports the analytical data of the alcohols (methanol,

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propanol, isobutanol, and isopentanol), ethyl acetate, acetaldehyde, organic acids (octanoic acid, decanoic acid, and dodecanoic acid), polyphenols (gallic acid, protocatechuic acid, (−)-epicatechin, vanillic acid, syringic acid, syringaldehyde, vanillin, *p*-coumaric acid, coniferaldehyde, sinapaldehyde, ellagic acid, coniferyl alcohol, kaempferol, and quercetin) and the metal fraction (aluminum, calcium, cobalt, copper, chromium, iron, manganese, magnesium, nickel, sodium, and zinc). These analytical data were treated by means of the multivariate statistical methods principal component analysis (PCA), hierarchical cluster analysis (HCA), *K*-nearest neighbor analysis (KNN) (*22*, *23*), and discriminate analysis (PLS-DA) (*24*) to differentiate samples of rum and cachaça.

MATERIALS AND METHODS

Samples. Fourteen cachaça samples were supplied by ABRABE (Associação Brasileira de Bebidas), and four others were supplied directly by producers from different states of Brazil. Four rum samples were purchased in U.S. and Canadian liquor stores, and 17 rum samples were supplied by ABRABE. Identification codes (C and R) were assigned for each cachaça and rum, respectively.

Cachaça samples included C01 (São Paulo), C02 (São Paulo), C03 (São Paulo), C04 (São Paulo), C05 (Pernambuco), C06 (Rio Grande do Sul), C07 (São Paulo), C08 (Rio de Janeiro), C09 (Ceará), C10 (São Paulo), C11 (Ceará), C12 (Ceará), C13 (Pernambuco), C14 (São Paulo), C15 (São Paulo), C16 (Rio de Janeiro), C17 (São Paulo), and C18 (Ceará). The names in parentheses define the Brazilian states where the cachaça samples were produced.

Rum samples included R01 (Venezuela), R02 (Jamaica), R03 (Brazil), R04 (Brazil), R05 (Brazil), R06 (Mexico), R07 (Canada), R08 (Canada), R09 (Guyana), R10 (Cuba), R11 (Cuba), R12 (Cuba), R13 (Brazil), R14 (Brazil), R15 (Jamaica-USA), R16 (France), R17 (France), R18 (France), R19 (Venezuela), R20 (France), and R21 (Mexico).

Materials. Ethanol, methanol, acetonitrile, acetaldehyde, ethyl acetate, propanol, isobutanol, isopentanol, hexanol, and dicloromethane (HPLC grade) were purchased from Mallinckrodt (Xalostoc, Mexico). All acid standards (octanoic acid, nonanoic acid, decanoic acid, and dodecanoic acid), HNO_3, H_3PO_4, and HCl were of analytical grade from Mallinckrodt. The polyphenols (gallic acid, protocatechuic acid, epicatechin, vanillic acid, syringic acid, syringaldehyde, vanillin, *p*-coumaric acid, coniferyl aldehyde, sinapaldehyde, ellagic acid, coniferyl alchool, kaempferol, and quercetin) were obtained from Aldrich (Steinheim, Germany). The metal standard solutions (Al, Ca, Co, Cu, Cr, Fe, Mg, Mn, Ni, Na, and Zn) were obtained by the dilution of a multielement standard purchased from Carlo Erba (Milano, Italy), and previously distilled water was deionized using a Milli-Q system (Molsheim, France). The solid phase extraction was performed using a Supelclean ENVI-18 cartridge packaged with 1.00 g of octadecylsilane (C18) by Supelco (Bellefonte, PA). All of the standards after a previous HPLC-UV−vis/GC-MS analysis proved to have analytical grade and therefore could be used as purchased.

Analytical Procedure. *Organic Acid.* Samples of cachaça and rum were previously preconcentrated by solid phase extraction using C18 cartridges. Each cartridge was first washed with 4.0 mL of methanol and then with 2.0 mL of water/ethanol (60:40 v/v) with pH adjusted to 4.0 using 0.01 mol L^{-1} HCl. A sample containing 50.0 mL of cachaça and 1.0 mL of the internal standard (100 mg L^{-1} of nonanoic acid) was transferred into a reservoir and eluted through the cartridge under negative pressure (flow rate of 5 mL min^{-1}). The analyte was eluted from the cartridge with 2.0 mL of dicloromethane. Aliquots of 1.0 μL were injected into the gas chromatograph (Shimadzu GC17A) coupled to a mass selective detector (Shimadzu QP5050A) using an HP-FFAP (Hellma, Brazil) column (cross-linked polyethylene glycol esterified, 50 m × 0.20 mm, 0.33 μm film thickness).

The analyses were performed at a split of 1:20. Helium was used as carrier gas (flow rate of 0.7 mL min^{-1}). The temperatures of both injector and interface were set at 240 °C. The oven temperature program was 60 °C for 1 min, followed by an increase to 190 °C at 10 °C min^{-1} kept for 5 min, and then up to 220 °C at 10 °C min^{-1}, after which the temperature was kept constant for 15 min. The mass selective detector was set to operate at SIM mode (*m*/*z* 73, 144, 172, and 200).

Quantitative analyses were realized using the internal standard method and performed in duplicate.

Alcohols, Acetaldehyde, and Ethyl Acetate. Samples of cachaça and rum were spiked with internal standard (*n*-hexanol, 250 mg L^{-1}). Aliquots of 1.0 μL were injected into the gas chromatograph system (HP 5890 series II) using a flame ionization detector (FID) and an HP-FFAP (Hellma, Brazil) column (cross-linked polyethylene glycol esterified, 50 m × 0.20 mm, 0.33 μm film thickness).

The analyses were performed at a 1:10 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 55 °C for 5 min, followed by an increase to 100 °C at 2 °C min^{-1} kept for 3 min and then up to 190 °C at 5 °C min^{-1} kept for 15 min.

Quantitative analyses were realized using the internal standard method and performed in duplicate.

Polyphenols. Samples of nonaged cachaças and rums (60.0 mL) were previously rotoevaporated at 40 °C until dryness and then dissolved with 5.0 mL of ethanol. The resulting residue was totally dissolved in ethanol. The ethanol solution was transferred to a reservoir and eluted through the solid phase cartridge (C18) under negative pressure (flow rate of 5 mL min^{-1}). The solid phase cartridge had been previously washed with 4.0 mL of methanol and then with 2.0 mL of ethanol. The analyte was eluted from the cartridge with 2.0 mL of methanol. Aliquots of 25.0 μL were injected into the liquid chromatographic system (Shimadzu LC10AD) coupled to an SPD-M6A diode array detector (Shimadzu). The separation was performed using a Resolve column (30.0 cm × 4.0 mm i.d., 5.0 μm) (Waters Co.) with the following mobile phases: solvent A, methanol/acetonitrile/tetrahydrofuran (97:0.3:0.01 v/v/v); solvent B, water/H_3PO_4 (99:1 v/v). The gradient profile at a flow rate of 1 mL min^{-1} was as follows: solvent A, 37% isocratic for 2 min, from 37 to 47% A in 2 min, from 47 to 57% A in 2 min, from 57 to 67% A in 2 min, from 67 to 77% A in 2 min, from 77 to 87% A in 2 min, and then from 87 to 37% A in 2 min. The detections were carried out at 280 nm.

Samples of aged cachaça and rum (40.0 mL) were extracted using the solid phase extraction methodology described above and injected into an HPLC-UV−vis system using the same conditions.

Quantitative analyses were realized using the external standard method and performed in duplicate.

Metals. The sample (50.0 mL) was placed into an open 250.0 mL beaker and then digested with 5.0 mL of HNO_3 under controlled heat until 5.0 mL of sample volume. After cooling at room temperature, the treated sample was transferred to a 25.0 mL volumetric flask, diluted to volume with 5% nitric acid solution, and then analyzed.

The analyses were performed by ICP-AES (Optima 3000 dual view, Perkin-Elmer). The instrumental conditions and analytical lines for each

Table 1. Operating Parameters for Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

operating power (W)	1300
coolant Ar flow rate (L min^{-1})	0.5
plasma Ar flow rate (L min^{-1})	15
nebulizer type	Meinhard
sample flow rate (mL min^{-1})	1.0

element	λ (nm)
Al	302.2
Ca	317.9
Co	228.6
Cu	324.8
Cr	205.6
Fe	238.2
Mg	279.1
Mn	257.6
Ni	232.0
Na	330.2
Zn	213.9

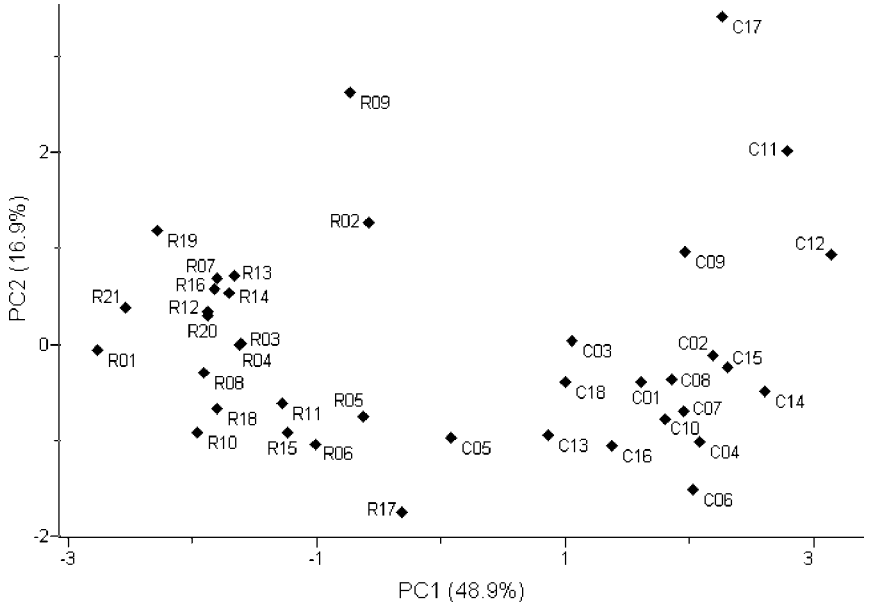

Figure 1. PCA scores plot of cachaça and rum samples using the variables protocatechuic acid, propanol, isobutanol, isopentanol, copper, magnesium, and manganese.

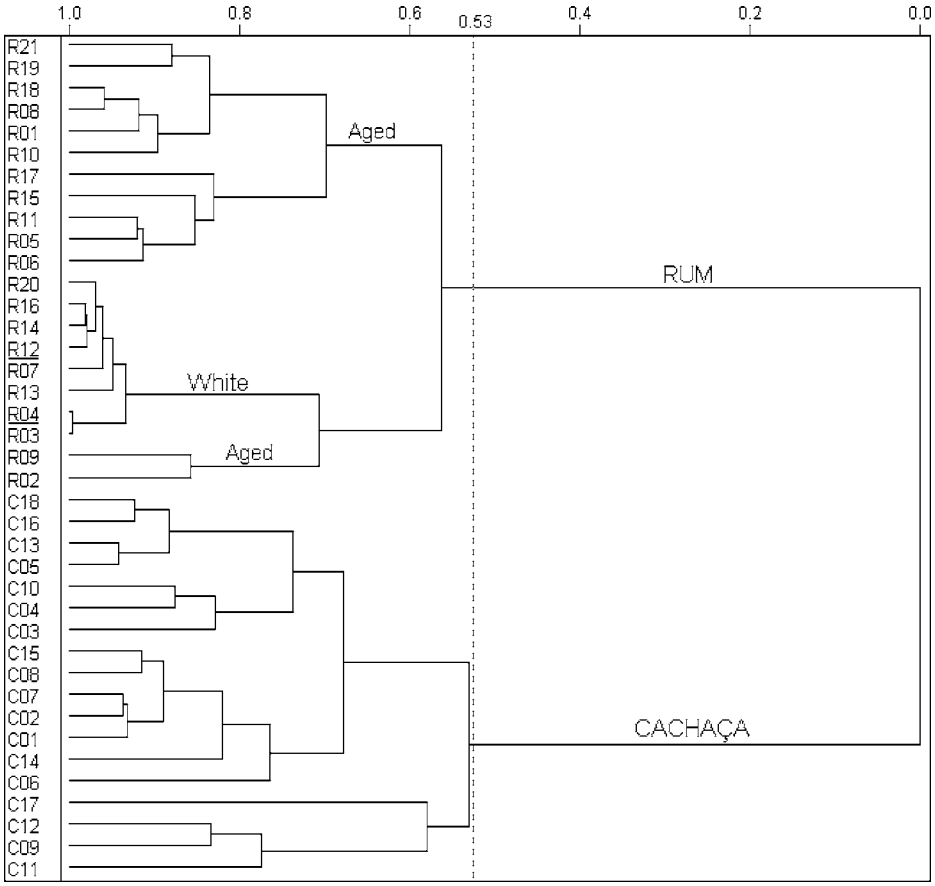

Figure 2. HCA dendogram for cachaça and rum samples: data preprocessing, autoscale; clustering technique, incremental.

element are given in **Table 1**. The calibration curves were constructed by using the external standard method, and all of the analyses were performed in triplicate and checked by standard addition. No matrix effect was detected.

Statistical Data Treatment. The results from the chemical analyses of 39 samples were organized in a matrix form and autoscaled prior to the data analysis. In this paper, the pattern recognition procedures applied were principal component analysis (PCA), hierarchical cluster analysis (HCA), discriminant analysis (PLS-DA), and *K*-nearest neighbor analysis (KNN). The data analyses were performed using Pirouette 2.2 software (Informetrix, Seattle, WA).

The classification with KNN is based on distance (multivariate Euclidean distance) comparison among samples. The distance between every pair of samples is calculated. The predicted class of a test compound is determined on the basis of the distance of this sample with respect to the closest *K* samples in the set. Each of the *K*-nearest

samples is chosen to "vote" once for its class. The class receiving the highest number of votes is assigned to that sample. An implementation of discriminant analysis (DA) is applied here, based upon partial least-squares regression (PLS-DA), a multivariate regression technique widely used in the chemical sciences (*24*). The data matrix *X* is related to a set of class variables, *Y*, consisting of dummy variables used to indicate class membership.

RESULTS AND DISCUSSION

The analytical data of each group of compounds were analyzed by the PCA method. The PCA scores plots for alcohols showed that propanol, isobutanol, and isopentanol tended to differentiate cachaça from rum. For the 11 metals analyzed only copper, manganese, and magnesium leaned to distinction; for the polyphenols only protocatechuic acid favored separation. The PCA scores plots for octanoic acid, decanoic acid, and dodecanoic acid did not allow a distinction between rum and cachaça. Thus, a PCA was performed only with the compounds that tended to separation, that is, protocatechuic acid, propanol, isobutanol, isopentanol, copper, manganese, and magnesium, considering them possible chemical discriminators. **Table 2** shows the concentrations of these compounds in cachaça and rum samples.

The PCA method was applied using the analytical data for the chemical descriptors previously cited. From the scores plot in **Figure 1**, with three PCs accounting for 77.7% of the total variance of the original data, a clear separation between cachaça and rum can be verified (PC1 versus PC2), indicating that the above selected compounds are promising descriptors to distinguish cachaça from rum.

Examination of the PC loadings (**Table 3**) shows that PC1 (48.9% of original information) was strongly correlated with the alcohols and copper, whereas manganese and magnesium were the main contributors to PC2 (16.9% of total variance). PC3 (11.9% of total variance) describes isobutanol, manganese, and protocatechuic acid.

To assess this statement, the HCA of the selected variables produced the grouping revealed in the dendogram (**Figure 2**). Two clusters were found at a similarity level of 0.53, where the first cluster includes rum samples and the second one includes cachaça samples. The rum cluster presents three subclusters. The top one contains only aged rum, the midle subcluster contains white rum and two aged samples (underlined in **Figure 2**), and in the small subcluster are two aged rum samples. Unfortunately, for the cachaça cluster no trends are observed for aged and nonaged samples in the subclusters.

The reliability of the use of these seven discriminators to distinguish cachaça from rum was assessed by the KNN (*22*, *23*) with three nearest neighbors, using an external set of six new samples, listed at the end of **Table 2**. **Table 4** contains the predicted results, where four of them are cachaça and the two others are rum. The very same results were obtained by the discriminant method PLS-DA with one factor for each class (**Table 4**). Remarkably, the use of these seven chemicals could ascribe 100% certainty to the nature of these samples.

Although a large number of discriminators were analyzed, others could certainly be defined. However, according to the present data, the method described in this paper has shown to be useful to accurately determine whether the sample is either cachaça or rum in a short period of time, which is of prime economic importance to countries and distillers. Furthermore, it provides the consumer with the correct product. Therefore, the analyses of seven chemical descriptors together by PCA, HCA, PLS-DA, and KNN is quite appropriate to distinguish cachaça and rum. This procedure can be recommended as a routine method for forensic purposes.

Table 2. Concentration of Chemical Descriptor in Cachaça (C) and Rum (R) Samples (Milligrams per Liter)

sample	propanol	iso-butanol	iso-pentanol	Mn	Mg	Cu	protocate-chuic acid
C01	136	181	571	0.80	0.013	3.3	*c*
C02	172	220	572	1.2	0.032	3.1	*c*
C03	309	11.2	559	1.3	0.026	0.021	*c*
C04	247	222	786	1.4	0.002	0.036	*c*
C05	123	133	584	0.035	0.004	0.067	*c*
C06	352	133	485	0.38	0.004	4.0	*c*
C07	198	205	654	0.65	0.028	2.6	*c*
C08	137	250	604	0.38	0.052	2.8	*c*
C09	137	195	549	1.9	0.048	1.4	*c*
C10	319	176	596	0.79	0.043	0.24	*c*
C11	138	*a*	774	2.7	0.034	5.2	*c*
C12	124	221	621	2.4	0.028	4.9	*c*
C13	159	165	669	0.24	0.016	0.68	*c*
C14	175	277	938	0.54	0.072	1.4	*c*
C15	184	187	669	0.48	0.053	4.1	*c*
C16	177	262	588	0.48	0.023	0.59	*c*
C17	126	169	524	1.6	0.21	0.36	*c*
C18	129	194	505	0.60	0.023	1.5	*c*
R01	30.4	12.8	36.6	0.072	0.004	0.050	2.08
R02	104	83.4	156	0.67	0.083	*b*	0.880
R03	47.1	40.9	120	0.020	0.001	0.015	0.190
R04	50.1	37.3	122	0.018	0.002	0.030	0.180
R05	115	111	347	0.035	0.002	0.097	0.300
R06	181	73.1	287	*b*	0.001	*b*	1.04
R07	15.3	21.7	6.86	0.44	0.005	*b*	0.170
R08	74.9	67.1	112	0.23	0.008	0.40	1.87
R09	35.4	9.79	1.35	1.6	0.069	0.066	0.160
R10	69.9	106	293	0.054	0.005	0.15	2.66
R11	74.0	104	259	0.033	0.004	0.30	1.09
R12	24.2	20.9	45.7	0.069	0.005	0.032	0.170
R13	17.4	27.9	73.4	0.12	0.026	0.12	0.200
R14	17.7	24.2	65.5	0.21	0.012	0.17	0.140
R15	40.4	212	207	0.027	0.004	0.075	1.43
R16	28.8	11.3	17.2	0.21	0.019	0.17	0.190
R17	274	149	295	0.11	0.001	0.22	1.42
R18	77.1	79.9	247	0.10	0.002	0.015	1.88
R19	18.8	11.8	19.2	0.47	0.055	*b*	1.94
R20	46.9	13.0	3.84	0.11	0.0020	*b*	0.100
R21	*a*	*a*	*a*	0.10	0.0050	0.24	1.18
A	243	169	678	5.2	0.54	0.43	*c*
B	192	291	1110	1.7	0.071	0.65	*c*
C	292	119	467	*b*	0.53	1.5	*c*
D	178	214	709	0.30	0.011	0.05	2.22
E	33.3	*a*	*a*	0.42	0.014	0.006	1.26
F	65.9	77.2	172	0.12	2.7	1.8	1.30

[a] Not detected, <0.05 mg L^{-1}. [b] Not detected, <0.05 μg L^{-1}. [c] Not detected, <0.08 μg L^{-1}.

Table 3. Loadings for the First Three PCs

	PC1 (48.9%)	PC2 (16.9%)	PC3 (11.9%)
protocatechuic acid	–0.339	–0.157	0.308
propanol	0.385	–0.396	–0.078
isobutanol	0.395	–0.349	0.404
isopentanol	0.496	–0.217	0.092
Mn	0.226	0.615	0.630
Mg	0.364	0.517	–0.219
Cu	0.387	0.045	–0.527

Table 4. KNN Prediction Using Three Nearest Neighbors and One-Factor Model PLS-DA (1 = C; 2 = R)

A	1	C	1	E	2
B	1	D	1	F	2

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Supporting Information Available: Sample list names and complete anaytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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