# **CHEMISTRY**

# Cachaça without any mystery

Compared to whiskies, the Brazilian drink has fewer aldehydes, substances that are responsible for hangovers

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genuine Brazilian drink, cachaça is the spirit most consumed in the country and the third in the world. The caipirinha drink (cachaça, sugar, lime and ice) is on the menu of bars and restaurants of several countries. In Brazil, over the last ten years, this spirit made from sugarcane juice has ceased to be just a drink only for the bars of the poorer classes and has started to be consumed in sophisticated environments. In spite of its longevity in the nation's culture and its recent commercial success, cachaça has spent a long time as a great unknown to science, which has, for example, prevented one from knowing that the concentration of aldehydes in this spirit is, on average, lower than in some imported whiskies. Fruit of recent research, this is an important result, as aldehydes are regarded as substances partly responsible for hangovers.

Carried out at the Cane Spirit Chemistry Development Laboratory (LDQA) of the São Carlos Chemistry Institute (IQSC) of the University of São Paulo (USP) - the studies have resulted in a considerable advance in the chemical characterization of this drink. This is going to serve not only to bring more quality to the cachaça produced - 1.5 billion liters and US\$ 500 million dollars a year – but also to open up the market of the greatest economy in the world, the United States. This is due to the misunderstanding that the American customs authorities have between rum and cachaça. To enter the country, Brazilian cane spirit must have written on the label that cachaca is a kind of Brazilian rum. "The differences between the two spirits start with the manufacturing process. While cachaça is a product of the distillation of fermented sugarcane juice, rum is distilled from the product of the fermentation of cooked

sugarcane juice or of molasses, a byproduct of the production of sugar", explains Professor Douglas Franco, the coordinator of the laboratory and director of the IQSC.

The work started ten years ago focused first on the chemical characterization of Brazilian cachaca. "Our studies show an average quantitative and qualitative chemical profile of the cane spirit manufactured in the country. This is a pioneer and landmark research project that contributes towards knowing the composition and the chemical reactions that take place in sugarcane spirit. Besides water and ethanol, which correspond to over 98% of the composition of the drink, we have identified a large number of secondary chemical compounds. These are the substances, found in a lower concentration, that give cane spirit its organoleptic properties (connected with the sense organs), like color, flavor and



Over 150 samples of cachaça collected for analysis in all the producing regions of the country

can give cachaça a disagreeable odor, the solution to reducing the problem lies in the adoption of metallic copper in the construction of the still.

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has to be controlled with chemical tests. With regard to the sulphurated compounds, in particular dimethylsulphide, that

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n the first case, the solution is to control the production process better. In the second, all that is needed is not to burn the sugarcane before harvesting. Another substance that is harmful for cachaça, ethyl carbamate, regarded as a carcinogenic agent, has various sources of origin. It can either be formed during the process of fermentation, in a distillation that is badly managed, or by chemical reactions during the storage of the beverage. "We found that ions of copper, iron and cyanide present in the final product have a much more important role in the formation of carbamates in cachaça than in other spirits", Franco explains. To avoid contaminating the cachaça with carbamates, there has to be a more rigid control over the concentrations of these ions. In the samples studied at the IQSC, only 21% showed a concentration equal to or lower than what is established by Canadian law for distilled drinks. This parameter was taken into consideration because Brazilian legislation is remiss in not setting maximum limits for concentrations of impurities.

According to Franco, a proviso has to be made with regard to the flaws found in the Brazilian spirit. "These defects are common in all the drinks in the world. The problem is regulating and controlling the concentration of the unwanted substances". The researcher also advises that, besides the defects already mentioned, many Brazilian producers do not carry out a proper control over the distilling process, which jeopardizes the final quality of the pro-

smell", explains Franco. "We tried to understand the chemistry of the cachaça with a view to protecting the health of the consumer, to adding value to the product, to improving the training of the manufacturers and to stimulating agribusiness."

Over 150 samples of cachaça from the main producing regions in the country were studied. The purpose was to draw up a diagnosis of the presence of various substances, such as alcohols, carboxylic acids, esters, ketones, aldehydes, phenols, polyphenols, amino acids, dextrans, carbamates, aromatic polycyclical hydrocarbons (benzene derivatives) and sulphurated compounds in cachaça, among others. "We investigated the presence of over 300 different substances, and have now identified over 100 secondary compounds that go into Brazilian cachaça", Franco says.

Following this detailed study, it was possible to enumerate the main defects

in some samples of the national spirit, such as sulphurated compounds, flakes, aromatic hydrocarbons and carbamates. The study revealed the cause of the defects and what can be done to avoid them. The flakes, for example, are nonpoisonous deposits made up of substances added to the cachaça - like the sugar that masks the acidity – which are joined together, originating a solid and insoluble material. "The sugar may be contaminated with a substance called dextran (an impurity formed by the Leuconostoc mesenteroides bacterium when the cane is cut and stored) that, when associated with amino acids and polyphenols present in the drink, form deposits on the bottom of the bottle.

**Metallic copper -** The cachaça, which used to be transparent, now comes to show an undesirable visual pollution", says the researcher. To avoid the formation of flakes, the action of these vectors

# From the slave quarters to the national drink

Danadinha [meanie], garapa-doida [crazy juice], esquenta-aqui-dentro [warms you up inside], dengosa [coy], ximbira, venenosa [poisonous], limpa-goela [throat clearer], bafo-de-tigre [tiger's breath], lindinha [pretty], tome-juízo [use your head], desmancha-samba [break up the samba] and zuninga [humdinger]. These are just 12 of the names by which cachaca is known in the four corners of Brazil. In the Novo Dicionário Aurélio da Língua Portuguesa [New Aurélio Dictionary of the Portuguese Language] some 150 denominations are to be found, but it is estimated that there are many others that have not been cataloged and that, in total "água ardente", or burning water, may have 500 different names. The *Dicionário Houaiss* [Houaiss Dictionary], in turn, clarifies that the beverage has been present in Brazilian life ever since the days of Colonial Brazil. In the definition under this heading, the dictionary explains that it is "a fermented beverage made from lees of sugarcane juice or from raw molasses served to the animals and the slaves of the old sugar mills".

According to the history books, cachaça arose in the sugarcane mills of the captaincy of São Vicente around 1540. The drink was produced using waste from the manufacture of sugar candy and was given the name of sour juice. Regarded as a secondary product of the

sugar industry, it did not have, in its primordial days, any alcoholic content, and it used to be served as a food supplement for sheep and goats. In the sugar mills of the northeast, the juice was also given to slaves with their first meal of the day, for them to bear up to the hard work in the sugarcane plantations.

In the second half of the 16<sup>th</sup> century, the beverage started to be produced in clay stills and, later, in copper stills, and was given the name of 'aguardente' [firewater]. In those days, it was even used as a currency for the purchase of slaves in Africa. The techniques for making it went on improving, and its improved quality made consumption grow rapidly. With time, the drink left the

duct. "In spite of the existence of good professionals in this area, the process of distilling is still very faulty, because the producers do not follow the specifications recommended by the makers of the equipment", says Franco.

One of the discoveries at the LDOA, which is also made up of Professors Benedito dos Santos Lima Neto and Ubirajara Pereira Rodrigues Filho, in collaboration with researchers from the Faculty of Food Engineering (FEA) of the State University of Campinas (Unicamp) and the Faculty of Pharmaceutical Sciences (FCF) of the São Paulo State University (Unesp), concerns the use of woods alternative to oak in the making of barrels for aging the drink. "The traditional oak is not part of the Brazilian flora. Our research showed that viraro (Pterogyne nitens), found in several regions of the country, is highly recommended for replacing it in barrel making", explains Franco.

Besides the project for the chemical characterization of Brazilian cachaça, financed by FAPESP, the LDQA's coordinator has another project with the Foundation, which is included under the heading of public policies, in partnership with the Municipal Secretariat for Science, Technology and Economic Development of São Carlos. The objective is to do a survey of the qualities and defects of the cachaça produced by

small producers from São Paulo (up to 200,000 liters a year) and to propose measures for the improvement of the product. "We are analyzing 104 samples of cachaça coming from distilleries and stills in the state of São Paulo. In the first stage, we collected the samples. We are now carrying out a chemical analysis of the drinks. Besides identifying defects and qualities, we want to use this data to define chemical discriminators (substances that permit differentiation between two or more products) that associate cachaca with the region of origin. Accordingly, São Paulo cachaça, and later, from the rest of Brazil, will be able to have a regional deno-

mination, in a similar way to French and Italian wines.

Millionaire market - The effort to understand the chemistry of cachaça has its raison d'être. The product drives a millionaire market. According to data from the Brazilian Institute of Cachaça from the Still (IBCA), of the 1.5 billion liters a year of cachaça produced in the country, 1,050 billion is industrial cane spirit, produced in distilleries, and 450 million is homemade cachaça, made in small stills. The sector covers some 30,000 producers, who pour onto the market 5,000 brands. There are roughly 400,000 direct jobs.

# THE PROJECTS

On the Presence of Hydrocarbons, Flakes and Carbamates in Cane Spirit, their Quantification, Genesis and Prevention

## MODALITY

Regular line of research grants

#### COORDINATOR

Douglas Wagner Franco — São Carlos Institute of Chemistry of USP

## INVESTMENT

R\$ 62,084.85 and US\$ 149,445.57 Improving the Quality of Cachaça and Proposal of a Standard of Quality

# MODALITY

Research in Public Policies Program

#### COORDINATOR

Douglas Wagner Franco – São Carlos Chemistry Institute of USP

#### INVESTMENT

R\$ 60,000.00 and R\$ 17,100.00 (partnership)

slave quarters and established itself on the table of the lords of the mills and of the Portuguese families who missed their 'bagaceira', the spirit made from grape bagasse. It did not take long for "sour juice" to begin to compete in the market with Portuguese wines and with 'bagaceira' itself. The colonial authorities decided, then, to prohibit the production and marketing of the drink in Brazil, claiming that it was responsible for tumults and commotion. As we know, all this was in vain. Firewater continued to be made and more and more consumed by the population.

In the course of the last five centuries, the drink has been present at the most important moments in the history of Brazil. During the Inconfidência Mineira, at the end of the 18<sup>th</sup> century, cachaça was transformed into a symbol of "Brazilianness" and of resistance to the Portuguese domination. The same happened in the Pernambuco Revolution of 1817. The historians say the Father João Ribeiro Pessoa, one of the leaders of the movement, replaced the Port wine of the mass for genuine cachaça, as a way of showing to the faithful his support for the revolution that had separation

from Portugal as its objective. Years later, Dom Pedro I toasted the independence of Brazil with a glass of cachaça, a gesture that was repeated by former president Fernando Henrique Cardoso during the commemorations of the 500 years of the discovery of Brazil, in 2000. In the two years that followed, the federal government published two decrees (3062/01 and 3072/02) that establish the denomination "cachaça" as official and exclusive for sugarcane spirit produced in Brazil, in an effort to protect the brand and make it popular in the international market.



The São Jorge dos Erasmos sugar mill, in Santos (SP): sugar in the first half of the 16<sup>th</sup> century

São Paulo is the leader in production, with 44%, followed by Pernambuco and Ceará, with 12% each. These states concentrate some of the major manufacturers of industrial cachaça -Pirassununga (SP), Velho Barreiro (SP), Pitú (PE), Ypióca (CE) and Colonial (CE). Minas Gerais, Rio de Janeiro, Goiás and Espírito Santo, each with 8% of the market, make up the list of industrial manufacturers. Analyzing just the figures for homemade cachaça, Minas Gerais is the main center of production. "The state has 8,466 stills that produce 230 million liters a year", says José Lúcio Mendes, the IBCA's director for Promotions.

After its nation-wide success, cachaça is winning over appreciators in other countries. Last year, 14.8 million liters (about 1% of the production) were exported to 70 countries. Exports earn Brazil US\$ 9 million a year, ac-

cording to data from 2001. The target for 2003 is to export 20 million liters, a growth of over 30%. Europe buys around 60% of the cachaça exported, with Germany, the largest importer, taking 30%. It now remains to win over the American market, still immersed in the confusion between cachaça and rum. "We do not accept this classification. Rum is rum, and cachaça is cachaça. To get over this impasse, we agreed with the American authorities that we would do a detailed chemical analysis showing the differences between the two beverages", says Maria José Miranda, the national manager of the Brazilian Program for Developing Cachaça (PBDAC), created by the Brazilian Beverages Association (Abrabe), with the objective of promoting the product on a world-wide scale. USP's laboratory in São Carlos was contracted to do this work.

To lay down the chemical foundations for the differences between the drinks, the team from the LDQA investigated the presence and concentration of 150 compounds in 31 certified samples of rum and cachaça. Chemometrical methods (for a statistical analysis of the results) were applied to the data collected, in which seven chemical discriminators were determined, to allow for an unequivocal distinction between rum and cachaça. These results are going to serve to eliminate the confusion that has arisen in the United States.

In its ten years of activity, the LDQA has established itself as an important center for the production of knowledge on Brazilian cane spirit. In the period, seven masters and five doctors have been trained up until now. Twelve complete articles have been published in international scientific periodicals, eight in specialized Brazilian magazines and another 13 in national promotional magazines. The interchange with foreign institutions has also been important. "We are working in collaboration with several institutions in Denmark, Italy and Belgium. With our researches, we want to take cachaça to the same level of quality as the other distilled beverages marketed all over the world, such as whisky, vodka and rum", says Franco.