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Congeners in sugar cane spirits aged in casks of different woods

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ABSTRACT

The profile of volatile compounds and aging markers in sugar cane spirits aged for 36 months in casks made of 10 types of wood were studied. The ethanol content, volatile acidity, aldehydes, esters, higher alcohols, and methanol were determined. In addition, gallic, vanilic and syringic acids, siringaldehyde, coniferaldehyde, sinapaldehyde, vanillin, 5-hydroxymethylfurfural and furfural were identified and quantified. The profile of volatile compounds characterised aging in each type of wood. The beverage aged in oak cask achieved the highest contents of maturation-related congeners. The Brazilian woods, similar to oak, were jequitibá rosa and cerejeira, which presented the highest contents of some maturation-related compounds, such as vanillin, vanilic acid, syringaldehyde and sinapaldehyde. Although oak wood conferred more chemical complexity to the beverage, Brazilian woods, singly or complementarily, present potential for spirit characterisation and for improving the quality of sugar cane spirits.

1. Introduction

According to the Brazilian law that regulates the identity and quality standards of sugar cane spirits, *cachaça* is considered a typical and exclusive sugar cane spirit of Brazil. It is produced by the distillation of fermented sugar cane juice, reaching 38–48% ethanol by volume at 20 °C and presenting peculiar sensory features (Brasil, 2005a). Sugar cane spirit production involves the extraction of sugar cane juice, fermentation and distillation. After these processes, aging is of fundamental importance and it is generally carried out in appropriate wooden casks, where *cachaça* is kept for a certain period of time aiming to refine its sensory profile and improve its chemical quality.

Unfortunately aging is not a mandatory step for *cachaça*. The Brazilian law establishes that aged *cachaça* should contain at least 50% of the spirit matured in appropriate wooden casks (maximum capacity of 700 L) for a period of not less than 1 year. Premium and extra premium *cachaças* are spirits that were whole aged for 1 year and 3 years, respectively (Brasil, 2005a).

The maturation of distilled beverages in wooden casks is an important step of the production process. A fresh spirit presents aggressive sensory features and strong alcoholic flavour. These negative characteristics can be attenuated by aging. Numerous physicochemical interactions occur between the wood and the spirit during aging. Several phenomena of migration of volatile and non-volatile compounds of wood to spirit take place. Along maturation, the evolution of phenolic compounds, beverage oxidation, stabilisation of colour and flavour, and development of notes of wood contribute to the richness and complexity of distilled beverages aroma (Ramirez-Ramirez, 2002).

The effects of maturation are mainly influenced by the type of cask wood (Mosedale & Puech, 1998). The mechanism of spirit maturation is based on the exchange of compounds present in wood and beverage, which can be classified in seven categories: direct extraction of wood compounds; decomposition of macromolecules; reaction between wood compounds and the compounds present in the freshly distilled spirit; interactions specifically involving the wood extract; reactions involving only the compounds present in the distilled beverage; evaporation of volatile compounds through the cask surface; and formation of stable molecules (Piggott & Conner, 2003).

Oak is the principal wood used for spirits aging worldwide because it actively participates in the beverage flavour due to the extraction of aromatic molecules from the wood (Ramirez-Ramirez, 2002). However, in Brazil, oak is not a native wood and it is necessary to import it from Europe or North America. Native Brazilian woods can be a viable option for sugar cane spirit producers, since they are easily found and peculiar compounds from each different type of wood may be transferred to the beverage allowing the characterisation of the spirit.

As Brazil has a vast diversity of flora, it is very interesting to study the chemical profiles of sugar cane spirits aged in casks made of different Brazilian woods and compare them with those obtained in oak casks. Although several physical and chemical properties of wood may influence the maturation process of alcoholic beverages, a number of studies report direct and indirect effects

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of the wood, such as species, methods used to treat the wood and make the casks, thermal treatment and final cooperage operations (Mosedale, 1995).

Sensory and physicochemical analyses show important differences among wood species from different geographical regions, which typify the notes of wood developed in the spirit due to the extraction of peculiar compounds. Therefore, wood species, its geographical region, wood age and forest management are relevant parameters when choosing the cask, since they interact to define wood quality and, consequently, the sensory and chemical profile of the resulting aged spirit (Chatonnet, 2003).

This research aimed to study the profile of volatile compounds and specific aging markers in sugar cane spirits aged for 36 months in casks made of 10 types of wood, namely: amendoim (*Pterogyne nitens* Tul.), araruva (*Centrolobium tomentosum* Guillem. ex. Benth.), cabreúva (*Myrocarpus frondosus* Allemão), cerejeira [*Amburana cearensis* (Fr. Allem.) Smith], grápia [*Apuleia leiocarpa* (Vogel) J.F. Macbr.], ipê roxo [*Tabebuia heptaphylla* (Vell.) Toledo], jequitibá [*Cariniana estrellensis* (Raddi) Kuntze], jequitibá rosa [*Cariniana legalis* (Mart.) Kuntze], oak (*Quercus sessilis* Ehrh. ex Schur.) and pereira (*Platycyamus regnellii* Benth.).

2. Materials and methods

2.1. Construction of wooden casks, production of sugar cane spirit and aging in wooden casks

The casks were constructed in the shape of frustum of cone with inner diameter of the base of 66 cm, height of 86 cm and inner diameter of the lid of 54 cm, resulting in an average cask volume of 245 L, an internal contact area with the sugar cane spirit of 196 dm^2 (excluding the lid) and, consequently, a volume/surface area ratio of 1.25 L/dm. The casks were not charred after construction. Before the experiment, the casks were washed with steam, hot water and cold water, filled with sugar cane spirit and stored for 24 months. After that, they were exhausted and washed with cold water to be ready for the aging process.

The sugar cane spirit used in this study was produced in 2008 in the distillery of the Agro-food Industry and Nutrition Department of the College of Agriculture "Luiz de Queiroz" of the University of São Paulo. The wort was prepared using sugar cane variety SP 83-2847. The sugar cane juice was extracted using a stainless steel presser, underwent a thermal treatment (105 °C) to eliminate contaminant microorganisms and a decantation for 2 h for colloidal precipitation. Fermentation was performed in 4-m^3 tanks using *Saccharomyces cerevisiae* strain CA-11 (LNF Latinoamericana, Bento Gonçalves-RS, Brazil) and distillation was carried out in columns.

The volume of the sugar cane spirit necessary to conduct this study was homogenized and distributed in casks made of 10 types of wood: amendoim, araruva, cabreúva, cerejeira, grápia, ipê roxo, jequitibá, jequitibá rosa, European oak and pereira. The sugar cane spirit (61% ethanol, v/v) was aged in the wooden casks for three years, in triplicate, at room temperature (22 ± 5 °C), relative humidity of 55 ± 10% and protected from vibrations. The remaining volume of sugar cane spirit was stored in a 50-m^3 cask made of amendoim and it was considered the sugar cane spirit control.

2.2. Physicochemical and chromatographic analyses

2.2.1. Alcohol content, volatile acidity, colour, and phenolic compounds

Sugar cane spirit diluted with potable water to 41% ethanol (v/v) was analysed to assess the alcoholic content and volatile acidity (Brasil. Ministério da Agricultura, 2005b). The intensity of the spirits colour was determined by transmittance at 420 nm. The content of total phenolic compounds was determined by spectrophotometry at 765 nm using the Folin–Ciocalteu reagent (Amerine & Ough, 1980).

Table 1
Parameters used in high performance liquid chromatography (HPLC) analysis.

Time (min)	Solvent A[a] (% v/v)	Solvent B[b] (% v/v)	Wavelength (nm)
0	100	0	271
6	100	0	280
25	60	40	276
34	60	40	276
37	60	40	320

[a] Solvent A: water:acetic acid 98:2 (% v/v).
[b] Solvent B: methanol:water:acetic acid 70:28:2 (% v/v).

2.2.2. Gas chromatography

The contents of aldehydes, esters, methanol and higher alcohols (*n*-propyl, isobutyl and isoamyl) were determined using gas chromatography. Samples were spiked with the internal standard (4-methyl-2-pentanol). Aliquots of 1.0 μL were automatically injected into the gas chromatographic system (Shimadzu, QP-2010 PLUS, Tokyo, Japan) equipped with a Stabilwax-DA column (crossbond carbowax polyethylene glycol, 30 m × 0.18 mm × 0.18 μm film thickness) and a flame ionisation detector (FID). The analyses were performed at a 1:25 split ratio, in triplicate. Nitrogen was used as the carrier gas (flow rate of 1.5 mL/min, total flow of 27 mL/min and pressure of 252.3 kPa). The temperatures of both the injector and the detector were set at 250 °C. The oven temperature program was 40 °C for 4 min, followed by an increase to 120 °C at 20 °C/min, kept for 1 min, and then up to 180 °C at 30 °C/min, and maintained for 4 min.

2.2.3. High performance liquid chromatography (HPLC)

The aging congeners were analysed using HPLC (Shimadzu, model LC-10AD, Kyoto, Japan), with two Shimadzu LC-20AD pumps, UV–VIS detector Shimadzu SPD-20A, system controller CBM-20A and an automated injection system (20 μL) with gradient elution. The standards used in this study were gallic acid, 5-hydroxymethylfurfural (HMF), furfural, vanillin, vanillic acid, syringaldehyde, sinapaldehyde, syringic acid and coniferaldehyde, all from Sigma–Aldrich (St. Louis, MO, USA), purity >99%. The HPLC method had two mobile phases composed of water/acetic acid (98:2, v/v) and methanol/water/acetic acid (70:28:2, v/v/v) at a flow of 1.25 mL/min (Aquino, Rodrigues, Nascimento, & Casimiro, 2006). A pre-column Shimadzu VP-ODS (1 cm × 4.6 μm) and a C18 reversed phase column model Shim-pack VP-ODS (4.6 mm, 25 cm × 5 μm) thermostabilized at 40 °C were used. The UV detector was programmed to operate at variable wavelengths, according to the sequence shown in Table 1. The samples were previously filtered using Millex-HV filter with PVDF membrane (diameter 13 mm, pore size 0.45 μm).

3. Results and discussion

Regardless of the wood type, all the aged spirits were darker than the control (Table 2). Only five types of wood had more intense colour than the average of aged spirits, namely grápia, pereira, cabreúva, ipê roxo and oak. Sugar cane spirit aged in grápia casks presented the most intense colour. The colour of the spirits aged in amendoim, jequitibá and araruva casks was similar to the control, indicating low extraction of colour compounds.

Sugar cane spirits with the highest contents of total phenolic compounds were aged in cerejeira, oak and grápia casks (Table 2). In addition to these woods, only the spirit aged in cabreúva presented total phenolic content above the mean value. No correlation was observed between the values found for colour and total

Table 2
Colour and total phenolic content[a] in sugar cane spirits aged for 36 months in casks made of different types of wood.

Spirit	Colour (% T at 420 nm)	Total phenolic content (mg/100 mL anhydrous ethanol, gallic acid equivalents)
Control	94.8 ± 1.2	0.26 ± 0.07
Amendoim (*Pterogyne nitens*)	92.0 ± 0.1	1.37 ± 0.03
Araruva (*Centrolobium tomentosum*)	89.0 ± 0.1	2.17 ± 0.08
Cabreúva (*Myrocarpus frondosus*)	62.4 ± 1.0	3.56 ± 0.10
Cerejeira (*Amburana cearensis*)	74.6 ± 2.6	5.49 ± 0.37
European oak (*Quercus sessilis*)	63.5 ± 1.2	4.87 ± 0.27
Grápia (*Apuleia leiocarpa*)	39.7 ± 0.8	4.85 ± 0.98
Ipê roxo (*Tabebuia heptaphylla*)	63.4 ± 1.5	2.08 ± 0.79
Jequitibá (*Cariniana estrellensis*)	90.7 ± 0.2	0.70 ± 0.65
Jequitibá rosa (*Cariniana legalis*)	79.6 ± 2.7	1.94 ± 0.78
Pereira (*Platycyamus regnellii*)	60.9 ± 0.5	1.65 ± 0.65
Mean	73.7	2.63

[a] Average of triplicates ± standard deviation.

phenolic compounds. The spirit aged in cerejeira presented high content of total phenolic compounds and mean colour value. On the other hand, sugar cane spirits aged in pereira and ipê roxo casks presented intense colour and low content of total phenolic compounds. The control presented the lowest colour and total phenolic compound values. These results are in accordance with the findings of another study that compared these features present in sugar cane spirits aged in different types of Brazilian wood (Alcarde, Souza, & Belluco, 2010).

Sugar cane spirits aged in different Brazilian woods (cerejeira, bálsamo – *Myroxylon peruiferum* L.F., jequitibá, jatobá [*Hymenaea* stigonocarpa Mart. ex Hayne] and ipê) presented similar phenolic compounds to those found in distilled spirits aged in oak casks (Dias, Maia, & Nelson, 1998). Faria, Cardello, Boscolo, Isique, Odello, and Franco (2003) observed that pau d'arco [(*Tabebuia impetiginosa* (Mart. ex DC.)], amendoim, amarelo (*Plathymenia reticulata* Benth.) and louro [(*Aniba parviflora* (Meisn.) Mez.] transferred similar or higher contents of total phenolic compounds to sugar cane spirits compared to oak wood. Based on sensory results, the spirits aged in amendoim, pereiro (*Aspidosperma pyrifolium* Mart.) and jatobá presented a qualitative profile of attributes similar to oak, being considered good alternatives to build casks to age *cachaça*.

The principal contribution of wood to aging distilled beverages is related to the extraction of compounds from the wood and the formation of new aromatic molecules as a result of hydrolysis, oxidation and reaction of these compounds with the spirit. The aromatic profile of the aged spirit depends on several factors, such as wood genus and species, geographical region of the wood, cooperage operations (wood cut, aging and thermal treatment), aging time and warehouse (Conner, Reid, & Jack, 2003).

Numerous chemical transformations are associated to maturation of spirits, such as the oxidation of alcohols to aldehydes, the oxidation of aldehydes to acids, the degradation of lignin through ethanolysis forming aromatic aldehydes and the esterification reaction between acids and alcohols forming esters (Reazin, 1981). These compounds are responsible for the characterisation of aged spirits. In the aging process of distilled beverages there is a decrease in pH and in the contents of copper, methanol and ethanol, and an increase in acidity and in the contents of esters, aldehydes, furfural, higher alcohols, congeners and phenolic compounds (Parazzi, Arthur, Correa Lopes, & Borges, 2008). In this study, the contents of aldehydes, esters, methanol, higher alcohols, volatile acidity, furfural and congeners in all aged sugar cane spirits were within the limits established by the Brazilian law (Table 3) (Brasil, 2005a).

The sugar cane spirit aged in the oak cask presented the highest content of aldehydes. Oak extract favours the oxidation of spirits, forming acetaldehyde from ethanol (Dias, 2009). Aldehydes containing up to 8 carbon atoms have disagreeable aroma and those containing more than 10 carbon atoms confer agreeable taste and aroma to beverages (Braga, 2006). Also, high contents of aldehydes generally hinder the quality of spirits. The balance between free aldehydes, hemiacetal and acetal in the spirit is influenced by pH and the content of ethanol (Piggott & Conner, 2003) as well as by the type of wood used in the cask (Miranda, Martins, Belluco, Horii, & Alcarde, 2008).

Ester formation occurs during fermentation and the aging process mainly due to esterification reactions between acids and alcohols of the spirit (Masson, Cardoso, Vilela, Pimentel, Morais, & Anjos, 2007). Ethanol can react with the acids derived from pyruvic acid, such as lactic and acetic acids, and also with other organic acids, such as butyric, caproic, capric and lauric acids. Ethyl acetate is generally the predominant ester in sugar cane spirits, corresponding to approximately 80% of total esters in this beverage. It originates from the esterification reaction between ethanol and acetic acid in the maturation period and its amount depends on the relative abundance of the corresponding alcohols and the acyl-coA radicals involved in yeast metabolism (Janzantti, 2004). In the present study, the spirits aged in araruva, grápia and oak casks presented the highest content of esters, whereas the control presented the lowest.

The presence of methanol in distilled spirits is undesirable because of its toxicity. This compound results from the degradation of pectin, a polysaccharide formed through the association of several molecules of galacturonic acid, which have methanol in their structure. During wort fermentation, the hydrolysis of galacturonic acid releases methanol (Masson et al., 2007). In sugar cane spirits, methanol is formed mainly from sugarcane bagasse particles, a type of fiber that contains pectin, which remains in the juice after filtration (Bogusz, Ketzer, Gubert, Andrades, & Gobo, 2006). The aged sugar cane spirits study presented an average of 8.13 mg methanol per 100 mL anhydrous ethanol, and low variation between the different types of wood. This amount is inferior to the limit established by the Brazilian law, 20 mg/100 mL anhydrous ethanol (Brasil, 2005a). In sugar cane spirits, the concentration of methanol is generally low, since the content of pectin in sugar cane is lower than that found in other raw materials used to produce distilled beverages.

Higher alcohols refer to the sum of isobutyl, propyl and isoamyl alcohols (Brasil, 2005a). Sugar cane spirit aged in jequitibá rosa cask presented the highest content of higher alcohols, followed by the spirits aged in jequitibá and amendoim casks. The spirit aged in grápia cask presented the lowest content. Higher alcohols contain more than two carbon atoms and originate from the metabolism of nitrogen-containing compounds by yeast. The alcohols containing up to 5 carbon atoms, such as amyl and propyl alcohols and their isomers, contribute to the formation of the aromatic bouquet. Nevertheless, the excess of higher alcohols interferes negatively both in the commercial value and in the quality of sugar cane spirits.

The volatile acidity of sugar cane spirits gradually increases during aging (Miranda et al., 2008). One of the factors that confer high acidity to spirits is the oxidation of ethanol, which forms acetaldehyde and, subsequently, acetic acid. Sugar cane spirits aged in araruva and amendoim casks were more acid than the others, reaching 143 mg acetic acid/100 mL anhydrous ethanol. The porosity of these two types of wood, resulting from the natural structure of the fibres, might have allowed a higher oxidation of the spirits and, consequently, an increase in its volatile acidity.

The sugar cane spirit aged in oak cask presented 120 mg acetic acid/100 mL anhydrous ethanol. The acidity detected in alcoholic beverages aged in oak casks can also be originated from the wood extract, which presents considerable amounts of phenolic acids

Table 3
Content of volatile congeners[a] (mg/100 ml anhydrous ethanol) in sugar cane spirits aged for 36 months in casks made of different types of wood.

Spirit	Aldehydes (acetic aldehyde)	Esters (ethyl acetate)	Methanol	Propanol	Isobutanol	Isoamyl alcohol	Superior alcohols[b]	Volatile acidity	Furfural + HMF[c]	Total volatile congeners[d]
Control	10.31 ± 0.55	15.51 ± 0.22	7.43 ± 0.19	51.56 ± 2.45	55.12 ± 1.91	164.43 ± 21.84	271.11 ± 23.58	60.95 ± 1.96	0.59 ± 0.02	358.47 ± 5.82
Amendoim (*P. nitens*)	12.04 ± 0.47	18.15 ± 0.41	7.52 ± 0.11	59.90 ± 2.91	50.90 ± 2.54	161.23 ± 12.64	272.02 ± 21.61	143.70 ± 3.21	0.34 ± 0.03	446.25 ± 5.91
Araruva (*C. tomentosum*)	9.50 ± 0.51	40.00 ± 0.58	7.59 ± 0.15	55.80 ± 2.16	38.41 ± 1.83	120.90 ± 18.83	215.11 ± 19.50	143.97 ± 1.44	0.68 ± 0.01	409.26 ± 5.57
Cabreúva (*M. frondosus*)	10.30 ± 0.58	21.81 ± 0.66	8.82 ± 0.21	48.48 ± 3.85	47.09 ± 0.94	155.22 ± 19.53	250.79 ± 21.42	93.26 ± 1.51	1.40 ± 0.02	377.56 ± 6.17
Cerejeira (*A. cearensis*)	8.73 ± 0.32	15.59 ± 0.13	6.98 ± 0.09	50.07 ± 4.21	54.37 ± 2.73	161.41 ± 19.84	265.85 ± 16.92	70.92 ± 1.95	0.16 ± 0.04	361.25 ± 7.21
European oak (*Q. sessilis*)	13.38 ± 0.64	32.72 ± 0.47	9.30 ± 0.17	50.81 ± 2.73	45.98 ± 2.65	140.69 ± 15.43	237.48 ± 25.74	120.31 ± 3.17	1.70 ± 0.01	405.59 ± 6.92
Grápia (*A. leiocarpa*)	11.24 ± 0.59	36.77 ± 0.53	8.54 ± 0.27	45.73 ± 2.92	26.66 ± 2.52	118.56 ± 22.65	190.96 ± 22.58	85.73 ± 1.94	0.64 ± 0.02	325.34 ± 5.16
Ipê roxo (*T. heptaphylla*)	11.55 ± 0.51	20.18 ± 0.51	7.76 ± 0.25	49.16 ± 4.19	47.07 ± 1.34	148.31 ± 18.55	244.54 ± 21.43	80.26 ± 0.92	0.87 ± 0.02	357.40 ± 8.25
Jequitibá (*C. estrellensis*)	10.14 ± 0.88	19.39 ± 0.75	8.00 ± 0.10	52.31 ± 6.01	55.59 ± 1.73	184.56 ± 16.30	292.45 ± 29.48	117.16 ± 1.33	1.06 ± 0.05	440.20 ± 6.35
Jequitibá rosa (*C. legalis*)	9.42 ± 0.47	17.60 ± 0.63	8.25 ± 0.26	52.21 ± 2.05	67.51 ± 2.93	202.73 ± 23.66	322.45 ± 21.48	62.42 ± 1.49	0.72 ± 0.05	412.61 ± 5.27
Pereira (*P. regnellii*)	10.34 ± 0.29	18.23 ± 0.15	7.98 ± 0.34	50.19 ± 3.72	50.53 ± 2.75	164.17 ± 17.04	264.88 ± 25.58	70.83 ± 1.85	0.64 ± 0.03	364.92 ± 7.93
Mean	10.63	23.27	8.02	51.47	49.02	156.56	257.06	95.41	0.80	387.17
Brazilian law[e]	Max 30	Max 200	Max 20	–	–	–	Max 360	Max 150	Max 5	200–650

[a] Average of triplicates ± standard deviation.
[b] Propanol + isobutanol + isoamyl alcohol.
[c] HMF: hydroxymethylfurfural.
[d] Sum of aldehydes, esters, high alcohols, volatile acidity, furfural and HMF.
[e] Source: Brasil, 2005a.

(gallic, tannic, ferulic, syringic and vanillic). Considering the sum of the contents of syringic, vanillic and gallic acids (Table 4), the spirit aged in oak cask presented higher results compared to the others, contributing to the acidity found in the spirit aged in oak.

Total volatile congeners of aged sugar cane spirits is the sum of the contents of aldehydes, esters, higher alcohols, acidity, furfural and 5-HMF. The Brazilian law established that it might range from 200 to 650 mg/100 mL anhydrous ethanol (Brasil, 2005a). All the sugar cane spirits analysed in this study presented volatile congeners within these limits. Sugar cane spirits aged in amendoim and jequitibá casks presented the highest values, due to their high volatile acidity and high content of higher alcohols.

The volatile congeners found in sugar cane spirits aged in cerejeira, cabreúva, pereira, ipê roxo and grápia casks were below the mean value obtained for all types of wood. Miranda, Horii, and Alcarde (2006) found 583.02 mg congeners per 100 mL anhydrous ethanol in sugar cane spirit aged in oak casks. Alcarde et al. (2010) compared sugar cane spirits aged in casks made of different types of wood and registered the highest coefficient of congeners (373.84 mg/100 mL anhydrous ethanol) for grápia casks and the lowest (298.07 mg/100 mL anhydrous ethanol) for cabreúva casks. Miranda, Martins, Belluco, Horii, and Alcarde (2007) analysed volatile compounds in 94 samples of commercial sugar cane spirits and the mean result found was 400.46 mg/100 mL anhydrous ethanol. Parazzi et al. (2008) reported that the sum of volatile congeners in sugar cane spirits increased over time during the 36 months of aging in oak casks.

Analyses of ethanol, dry extract, acetic acidity, aroma, colour and taste in sugar cane spirits aged in casks of different Brazilian woods (amendoim, jequitibá, ipê roxo, araruva, cabreúva and pereira) showed that except for jequitibá all types of wood conferred good sensory quality to the spirit (Delgado, Marques, & Almeida, 1996).

Alcarde et al. (2010) assessed some aspects of chemical composition and sensory acceptance of sugar cane spirit aged for three years in casks of different types of wood (amendoim, araruva, cabreúva, European oak, cerejeira, grápia, jequitibá, ipê roxo and pereira). The global physicochemical composition indicated similarities among them, which were classified according to the type of wood into: group 1 – amendoim, araruva and jequitibá; group 2 – cabreúva and pereira; group 3 – European oak cerejeira, grápia, and ipê roxo.

We identified the low molecular weight phenolic compounds indicated as maturation-related congeners and aging markers in alcoholic beverages (Table 4). These compounds, derived from the wood macromolecules, impart typical taste and aroma to aged alcoholic beverages.

The natural structure of wood is heterogenous (Barrera Garcia, 2007). The oldest zone is located in the inner part of the trunk and the regions nearer its outermost layer are younger. Therefore, wood is a complex system, composed mainly of cellulose (45%), hemicellulose (20%) and lignin (25%). These different polymers do not interact the same way with the distillates (Masson, Puech, & Moutounet, 1996).

The heating treatment applied to cask staves aggregates important characteristics to the wood that should be taken into consideration for aging spirits. This thermal treatment is necessary to bend the staves to the correct shape when constructing the casks, as well as to modify the wood molecular structure so that the wood compounds can be better extracted by the spirits in the aging process. The heating treatment causes the degradation of wood polymers, allowing the formation of new aromatic compounds, which confer a distinct taste to the product. Additionally, the level of thermal degradation has influence both on the physical properties of wood, since it increases its porosity and contact surface, and on its chemical properties, because it facilitates the extraction of

Table 4
Composition of maturation markers[a] (mg/100 ml anhydrous ethanol) in sugar cane spirits aged for 36 months in casks made of different types of wood.

Spirit	Gallic acid	5-HMF[b]	Furfural	Coniferaldehyde	Vanillin	Vanillic acid	Synapaldehyde	Syringaldehyde	Syringic acid	Total maturation congeners[c]
Control	<DL[d]	<DL	0.59 ± 0.03	<DL	0.64 ± 0.02	1.00 ± 0.01	<DL	<DL	0.51 ± 0.04	2.15
Amendoim (*P. nitens*)	<DL	<DL	0.34 ± 0.02	<DL	1.34 ± 0.01	1.13 ± 0.05	<DL	<DL	1.40 ± 0.02	3.87
Araruva (*C. tomentosum*)	<DL	<DL	0.68 ± 0.02	0.34 ± 0.02	1.54 ± 0.10	1.91 ± 0.04	<DL	0.75 ± 0.01	1.95 ± 0.01	6.47
Cabreúva (*M. frondosus*)	<DL	0.21 ± 0.00	1.19 ± 0.00	<DL	1.04 ± 0.13	0.92 ± 0.03	<DL	3.56 ± 0.02	3.39 ± 0.59	8.91
Cerejeira (*A. cearensis*)	<DL	<DL	0.16 ± 0.02	0.27 ± 0.07	0.87 ± 0.03	6.19 ± 0.21	5.91 ± 0.31	<DL	0.90 ± 0.08	14.15
European oak (*Q. sessilis*)	8.32 ± 0.07	0.26 ± 0.02	1.44 ± 0.02	0.34 ± 0.01	2.21 ± 0.03	2.05 ± 0.08	1.06 ± 0.19	11.26 ± 0.11	4.70 ± 0.21	21.63
Grápia (*A. leiocarpa*)	<DL	0.14 ± 0.00	0.48 ± 0.00	0.20 ± 0.00	0.47 ± 0.02	2.33 ± 0.11	<DL	3.00 ± 0.64	1.34 ± 0.024	7.34
Ipê roxo (*T. heptaphylla*)	<DL	<DL	0.87 ± 0.00	<DL	0.49 ± 0.08	1.30 ± 0.42	<DL	0.54 ± 0.05	0.30 ± 0.18	2.63
Jequitibá (*C. estrellensis*)	<DL	<DL	1.06 ± 0.02	<DL	1.57 ± 0.05	1.56 ± 0.03	<DL	<DL	1.19 ± 0.00	4.32
Jequitibá rosa (*C. legalis*)	0.91 ± 0.05	0.12 ± 0.00	0.59 ± 0.02	0.77 ± 0.01	4.20 ± 0.03	3.77 ± 0.02	0.57 ± 0.01	5.39 ± 0.11	2.61 ± 0.12	17.32
Pereira (*P. regnellii*)	<DL	<DL	0.64 ± 0.00	<DL	0.61 ± 0.10	0.96 ± 0.02	0.30 ± 0.02	<DL	0.90 ± 0.05	2.77
Mean	4.62	0.18	0.73	0.38	1.36	2.10	1.96	4.08	1.74	8.32

[a] average of triplicates ± standard deviation.
[b] HMF: hydroxymethylfurfural.
[c] Sum of conyferaldehyde, vanillin, vanillic acid, synapaldehyde, syringaldehyde, and syringic acid.
[d] DL: Detection Limit.

wood compounds. Consequently, the spirits that interact with the wood have their organoleptic characteristics transformed, enhancing their aromatic complexity (Chatonnet & Boidron, 1989).

Furfural can be formed by pyrogenation of organic matter during distillation in pot stills (Masson et al., 2007) contributing to the burning taste of sugar cane spirits. When the staves are heated to construct the casks, hemicelluloses breaks down into sugars which rapidly break down further into caramelisation products by dehydration and Maillard reaction (Chatonnet & Boidron, 1989), forming compounds which are relevant to the aromatic bouquet and the typical colour of aged spirits. Pentoses form furfural as their main degradation product, whereas hexoses form 5-HMF and other compounds, such as 2-hydroxyacetylfuran and isoformaldehyde. The fragmentation of the carbon chain of these primary products forms other compounds, such as levulinic, formic, lactic, pyruvic and acetic acids, acetol, acetoin, and diacethyl.

Lignin is the principal wood macromolecule which influences distilled beverages in the maturation process. The thermal degradation of lignin occurs when the staves are heated to construct the casks and in the final toasting. These procedures contribute to extract monomeric compounds from the wood, followed by the generation of aromatic acids and aldehydes as a result of the acid ethanolysis of lignin. The oxidation and hydrolysis of the ester linkages of lignin also may contribute to formation of aldehydes, which generate their corresponding acids when oxidised. The presence of oxygen inside the cask is allowed by wood porosity and the headspace between the liquid and the lid of the cask (Conner et al., 2003).

Lignin presents a structure composed of two major monomer species, named guaiacyl (1-hydroxy-3-methoxyphenyl) and syringyl (3,5-dimethoxy-4-hydroxyphenyl) (Masson et al., 1996). In matured beverages, guaiacyl generates coniferaldehyde, vanillin and vanillic acid, whereas syringyl generates sinapaldehyde, syringaldehyde and syringic acid. Two possible pathways have been proposed to explain the mechanisms involved in the extraction of these maturation-related congeners from lignin: the first is the simple extraction of phenolic compounds present in the wood, which are then incorporated to the spirit; the second is the action of ethanol, forming an ethanol-lignin complex, which is then broken down into simple phenolic compounds (Puech, 1981). The main aging markers are considered to be cinnamic aldehydes (coniferaldehyde and sinapaldehyde), benzoic aldehydes (vanillin and syringaldehyde) and benzoic acids (vanillic and syringic acids) (Aylott & W. M. MacKenzie., 2010). The oxidation of sinapaldehyde generates syringaldehyde, which may be oxidised into syringic acid. The oxidation of coniferaldehyde forms vanillin, which may be oxidised into vanillic acid (Puech, Jouret, & Goffinet, 1985).

Based on the sum of the maturation-related congeners (sinapaldehyde, syringaldehyde, syringic acid, coniferaldehyde, vanillin, vanillic acid, 5-HMF, furfural and gallic acid), the highest value was registered for the spirit aged in oak cask, in which we detected the presence of all compounds analysed by the methodology employed. Among the different types of Brazilian wood, the spirit aged in jequitibá rosa cask presented all the maturation-related congeners in concentrations above the Detection Limit (DL) (Table 5). The spirit in jequitibá rosa also presented the highest sum of maturation-related congeners, followed by cerejeira, in which gallic acid was the only compound not quantified. Furfural, vanillic acid, vanillin and syringic acid were detected in all aged sugar cane spirits. The control spirit presented exclusively these compounds, as well as the spirit aged in amendoim cask.

Oak cask imparted the highest contents of gallic acid, syringaldehyde and syringic acid to spirits. The sugar cane spirit matured in jequitibá rosa cask presented the highest content of vanillin. Cerejeira cask imparted the highest contents of vanillic acid and

Table 5
Retention Time (RT), detection limit (DL), and quantification limit (QL) of volatile and maturation-related compounds and correlation coefficients (a, b, r^2) of the calibration curves in sugar cane spirits aged for 36 months in casks made of different types of wood.

Volatile congener	RT (min)	DL (mg/100 mL anhydrous ethanol)	QL (mg/100 mL anhydrous ethanol)	a	b	r^2
Acetaldehyde	1.61	0.080	0.266	0.8096	-0.0652	0.9984
Ethyl acetate	2.73	0.044	0.144	0.0372	0.0905	0.9936
Methanol	2.94	0.159	0.534	0.7847	0.0486	0.9652
Propanol	5.75	0.054	0.176	0.2317	0.0099	0.9991
Isobutanol	6.54	0.029	0.098	0.0206	0.0037	0.9995
Isoamyl alcohol	8.04	0.015	0.044	0.1766	0.0145	0.9991
Maturation congener	RT (min)	DL (mg/100 mL anhydrous ethanol)	QL (mg/100 mL anhydrous ethanol)	a	b	r^2
Gallic acid	6.37	0.032	0.098	1821.48	55.92	0.9906
5-HMF[a]	11.91	0.015	0.049	6071.74	89.23	0.9972
Furfural	14.09	0.012	0.041	5780.22	1032.35	0.9972
Vanillic acid	24.01	0.051	0.171	1260.59	258.17	0.998
Syringic acid	26.59	0.027	0.090	2429.59	−104.75	0.9984
Vanillin	27.07	0.022	0.073	3108.58	−87.67	0.9992
Syringaldehyde	29.15	0.051	0.171	1080.26	342.27	0.9936
Coniferaldehyde	34.78	0.020	0.068	4545.65	148.97	0.9976
Synapaldehyde	35.84	0.029	0.098	3218.26	102.24	0.9931

[a] HMF: hydroxymethylfurfural.

sinapaldehyde to spirits, five times higher than the oak cask. Oak, cabreúva and jequitibá rosa casks transferred the highest amounts of syringic acid to spirits. The highest contents of vanillin were found in the spirits matured in jequitibá rosa and oak. Vanillic acid was also the predominant compound in the spirits matured in jequitibá rosa and grápia. Syringaldehyde was the predominant compound in the spirit matured in oak cask. Among the different types of Brazilian wood, the highest amount of syringaldehyde was detected in the spirits aged in jequitibá rosa and grápia. Coniferaldehyde was present in low contents in all spirits, and the highest content of this compound was found in the spirit matured in jequitibá rosa (Table 6).

Dias et al. (1998) studied the extraction of maturation-related compounds in sugar cane spirits aged for 6 months in casks made of several types of wood and reported the predominance of vanillic acid and sinapaldehyde for cerejeira, syringic acid and coniferaldehyde for ipê, gallic acid for jequitibá and vanillin for cabreúva. In our study, the sugar cane spirit aged in oak presented the highest amount of aging-marker congeners, such as gallic acid, syringaldehyde and syringic acid. The spirit aged in jequitibá rosa presented the highest contents of coniferaldehyde and vanillin. The spirit aged in cerejeira presented the predominance of vanillic acid and sinapaldehyde. The spirits matured in amendoim, jequitibá, araruva, pereira and ipê roxo were not distinguished by any maturation-related congeners. Cabreúva and grápia presented medium potential to supply maturation-related congeners to the spirit during aging. Delgado et al. (1996) reported that amendoim, araruva, ipê roxo, cabreúva and pereira were suitable for the aging of sugar cane spirit because they had positive effects on the sensory quality of the beverage.

Table 6
Predominant maturation-related congeners in sugar cane spirits aged for 36 months in casks made of different types of wood.

Wood	Predominant maturation-related congeners	Content (mg/100 mL anhydrous ethanol)
European oak (*Q. sessilis*)	Gallic acid	8.32
	Vanillin	2.21
	Syringaldehyde	11.26
	Syringic acid	4.70
Jequitibá rosa (*C. legalis*)	Vanillin	4.20
	Vanillic acid	3.77
	Syringaldehyde	5.39
	Syringic acid	2.61
Cerejeira (*A. cearensis*)	Vanillic acid	6.19
	Sinapaldehyde	5.91
Cabreúva (*M. frondosus*)	Syringaldehyde	3.56
	Syringic acid	3.39
Grápia (*A. leiocarpa*)	Vanillic acid	2.33
	Syringaldehyde	3.00

Among the Brazilian types of wood, jequitibá rosa was the most similar to European oak because it presented all maturation-related congeners above the DL and also the highest value for vanillin. Oak wood was superior to jequitibá rosa in the contents of syringaldehyde and gallic acid. Cerejeira presented the highest contents of synapaldehyde and vanillic acid.

According to the chemical profile of the aged spirits, the different types of wood could reduce the content of peculiar compounds that affect its quality, mainly related to pungent taste and off flavour. The aged spirits presented maturation-related congeners which favour the generation and enhancement of flavour and agreeable aromas, attributes of qualitative sensory characteristics.

4. Conclusion

Oak cask presented the highest potential to generate aging-marker compounds. Among the different types of Brazilian wood, jequitibá rosa was the most similar to oak because it supplied higher vanillin and vanillic acid contents to the spirit. Cerejeira also showed high potential to be used for aging because of the contents of vanillic acid and sinapaldehyde of the aged spirits, as well as the sum of aging markers. Grápia and cabreúva presented only medium potential to be used in maturation of sugar cane spirits because some of the congeners assessed in our study were not found in the spirits aged in the casks of these types of wood.

The influence of different types of wood on the chemical composition of aged sugar cane spirits was demonstrated. Therefore, this study indicates the possibility of characterising the final product based on certain attributes that can specify a type of wood.

In spite of the evidence that oak confers more complexity and chemical quality to sugar cane spirits, different types of Brazilian wood may also be used to produce casks aiming to broaden and diversify the taste and aroma of this distilled beverage, with comparable or even complementary results, aiming to characterise the product and improve the quality of Brazilian *cachaça*.

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References

Alcarde, A. R., Souza, P. A., & Belluco, A. E. (2010). Aspects of the chemical composition and sensorial acceptance of sugar cane spirit aged in casks of different types of woods. *Ciencia e Tecnologia de Alimentos, 30*, 226–232.

Amerine, M. A., & Ough, C. S. (1980). *Methods for analysis of musts and wines*. New York, USA: John Wiley & Sons.

Aquino, F. W. B., Rodrigues, S., Nascimento, R. F., & Casimiro, A. R. S. (2006). Simultaneous determination of aging markers in sugar cane spirits. *Food Chemistry, 98*(3), 569–574.

Aylott, R. I., & MacKenzie, W. M. (2010). Analytical strategies to confirm the generic authenticity of scotch whisky. *Journal of the Institute of Brewing, 116*(3), 215–229.

Barrera Garcia, D. (2007). Sorption de composés phénoliques du vin par le bois de chêne: Approches macroscopique et moléculaire. Thesis Ph.D., Dijon, França: Université de Bourgogne, 191).

Bogusz, S., Jr., Ketzer, D. C. M., Gubert, R., Andrades, L., & Gobo, A. B. (2006). Composição química da cachaça produzida na região noroeste do Rio Grande do Sul, Brasil. *Ciencia e Tecnologia de Alimentos, 26*, 793–798.

Braga, V. S. A. (2006). *A influência da temperatura na condução de dois processos fermentativos para produção de cachaça, Escola Superior de Agricultura ''Luiz de Queiroz''*. Piracicaba, Brazil: Universidade de São Paulo. 91.

Brasil, (2005a). Ministério da Agricultura, Pecuária e Abastecimento. Instrução Normativa No. 24, Diário Oficial da União.

Brasil, (2005b). Ministério da Agricultura, Pecuária e Abastecimento. Instrução Normativa No. 13, Diário Oficial da União.

Chatonnet, P. (2003). *Maîtrise de l'interaction entre vins et bois par l'appréciation du ≪Potenciel oénoloegique≫ du bois de chêne: Application à la sélection et au contrôle de la qualité des merrains*. Oenologie: Revue Oenologie Technologie Vitivinicole. 25–30.

Chatonnet, P., & Boidron, J. N. (1989). Incidence du traitement thermique du bois de chêne sur sa composition chimique. 1ère Partie: Définition des paramètres thermiques de la chauffe des fûts en tonnellerie. *Journal International des Sciences de la Vigne et du Vin, 23*, 77–87.

Conner, J., Reid, K., & Jack, F. (2003). Maturation and blending. In I. Russell, G. Stewart, & C. Bamforth (Eds.), *Whisky: Technology, production and marketing. Handbook of alcoholic beverages* (pp. 209–240). London: Academic Press.

Delgado, A. A., Almeida, C. L., & Marques, T. A. (1996). Madeiras nacionais para envelhecimento natural de aguardente. *Álcool e Açúcar, 1*, 22–27.

Dias, S. M. B. C. (2009). Fatores que influenciam no processo de envelhecimento da cachaça. *Informe Agropecuário, 1*, 32–40.

Dias, S., Maia, A., & Nelson, D. (1998). Efeito de diferentes madeiras sobre a composição da aguardente de cana envelhecida. *Ciência e Tecnologia de Alimentos, 18*(3), 331–336.

Faria, J. B., Cardello, H., Boscolo, M., Isique, W. D., Odello, L., & Franco, D. W. (2003). Evaluation of Brazilian woods as an alternative to oak for cachacas aging. *European Food Research and Technology, 218*(1), 83–87.

Janzantti, N. S. (2004). Compostos voláteis e qualidade de sabor de cachaça, Thesis Ph.D., Faculdade de Engenharia de Alimentos. Campinas, SP, Brazil: Universidade Estadual de Campinas.

Masson, G., Puech, J. L., & Moutounet, M. (1996). Composition chimique du bois de chêne de tonnellerie. *Bulletin d'O.I.V., 69*, 634–657.

Masson, J., Cardoso, M. G., Vilela, F. J., Pimentel, F. A., Morais, A. R., & Anjos, J. P. (2007). Physicochemical and chromatographic parameters in sugar cane brandies from burnt and non-burnt cane. *Ciencia e Agrotecnologia, 31*(6), 1805–1810.

Miranda, M. B., Horii, J., & Alcarde, A. R. (2006). Estudo do efeito da irradiação gamma (60CO) na qualidade da cachaça e no tonel de envelhecimento. *Ciencia e Tecnologia de Alimentos, 26*(4), 772–778.

Miranda, M. B., Martins, N. G., Souza Belluco, A. E., Horii, J., & Alcarde, A. R. (2007). Chemical quality of brazilian sugarcane spirits. *Ciencia e Tecnologia de Alimentos, 27*(4), 897–901.

Miranda, M. B., Martins, N. G. S., Belluco, A. E. S., Horii, J., & Alcarde, A. R. (2008). Chemical profile of aguardente – Brazilian sugar cane alcoholic drink – aged in oak casks. *Ciencia e Tecnologia de Alimentos, 28*(Suppl.), 84–89.

Mosedale, J. R. (1995). Effects of oak wood on the maturation of alcoholic beverages with particular reference to whiskey. *Forestry, 68*, 203–230.

Mosedale, J. R., & Puech, J. L. (1998). Wood maturation of distilled beverages. *Trends in Food Science & Technology, 9*(3), 95–101.

Parazzi, C., Arthur, C. M., CorreaLopes, J. J., & Borges, M. R. (2008). Determination of the main chemical components in Brazilian sugar cane spirit aged in oak (Quercus sp.) barrels. *Ciencia e Tecnologia de Alimentos, 28*(1), 193–199.

Piggott, J. R., & Conner, J. M. (2003). Whiskies. In A. G. H. Lea & J. R. Piggott (Eds.), *Fermented beverage production* (pp. 239–262). New York: Klumer Academic.

Puech, J. L. (1981). Extraction and evolution of lignin products in armagnac matured in oak. *American Journal of Enology and Viticulture, 32*(2), 111–114.

Puech, J. L., Jouret, C., & Goffinet, B. (1985). Evolution des composes phenoliques du bois de chêne au cours du vieillissement de l'Armagnac. *Sciences des Aliments, 5*(3), 379–392.

Ramirez-Ramirez, G. (2002). Étude de la sorption des composés d'arôme du vin par le bois de chêne en système modèle d'élevage en fûts. Thesis Ph.D., Dijon, França: Université de Bourgogne, 346.

Reazin, G. H. (1981). Chemical mechanisms of whisky maturation. *American Journal of Enology and Viticulture, 32*, 283–289.