Lignin-derived phenolic compounds in cachaça aged in barrels from tropical wood species

Mariana C. Castro[1], Giovanni C. Silvello[1], and André R. Alcarde[1*]

[1] Escola Superior de Agricultura "Luiz de Queiroz", Universidade de São Paulo, Av. Pádua Dias 11, CP 9, 13418-900, Piracicaba, SP, Brazil

This study investigated the lignin-derived phenolic compounds in cachaça aged in barrels made from tropical woods. Cachaça was aged for 36 months in toasted new wooden barrels made from amburana (*Amburana cearensis*), cabreúva (*Myrocarpus frondosus*) and castanheira (*Bertholletia excelsa*). New barrels made from European oak (*Quercus petraea*) and American oak (*Quercus alba*) were also employed. Cinnamic aldehydes, benzoic aldehydes and benzoic acids were analysed at the end of the ageing time. A significant effect of wood species was observed on all the studied phenolic compounds. Syringaldehyde and the benzoic acids were the main low-molecular-weight compounds in aged cachaça. All the phenolic families under study were at higher concentrations in cachaça aged in amburana barrels. Cachaça aged in castanheira barrels displayed the highest ratio of gallic acid to vanillin, whereas that aged in cabreúva barrels exhibited the highest ratio of syringaldehyde to vanillin. Cachaça aged in barrels made from amburana had the highest sum of lignin-derived phenolic compounds, followed by cachaça matured in American oak and cabreúva barrels. Amburana showed a great potential to provide lignin-derived phenolic compounds to cachaça during ageing. Cachaça aged in oak barrels exhibited the highest contents of ethyl acetate and acetic acid, whereas the samples aged in European and American oak and amburana barrels reached the highest total score in sensory evaluation. The ageing process in new tropical wood barrels, singly or complementarily to oak, enhanced the flavour complexity of aged cachaça and broadened and diversified its taste and aroma profiles.

KEYWORDS
sugarcane spirit
ageing
tropical woods
lignin
phenolic compounds

RECEIVED: June 15, 2021
ACCEPTED: August 12, 2021

* CORRESPONDING AUTHOR:
André R. Alcarde
E-MAIL: andre.alcarde@usp.br

INTRODUCTION

Cachaça is a typical and exclusive sugar cane spirit of Brazil, containing 38–48% ethanol by volume, obtained by the distillation of fermented sugarcane juice [1]. Although ageing is not mandatory for this distilled spirit, the ageing practices conducted on sugar cane spirit in Brazil are of fundamental importance, inasmuch as ageing in wooden barrels (usually from one to three years) improves cachaça sensory profile.

The effects of the ageing process are primarily influenced by the wood species used for making the barrel [2]. American oak (*Quercus alba*) and European oak (*Quercus petraea*) are the most commonly used species to make barrels for ageing distillates [3]. *Quercus robur* and *Quercus petraea* are the European oak species most commonly used in tight cooperage [4].

The availability and extractability of ellagitannins, phenolic and volatile compounds, as well as the water tightness of oak tyloses are the main features that make certain oak species the favourite wood type to produce barrels for wine and distilled beverages [5]. However, tropical woods can be a viable option for ageing cachaça in Brazil, where a vast, diverse flora grows. Some species that have been reported as showing potential for this purpose such as amendoim (*Pterogyne nitens*), araruva (*Centrolobium tomentosum*), bálsamo (*Myroxylon peruiferum*), cabreúva (*Myrocarpus frondosus*), amburana (*Amburana cearensis*), grápia (*Apuleia leiocarpa*), jatobá (*Hymenaeae carbouril*), ipê roxo (*Tabebuia heptaphylla*), jequitibá (*Cariniana estrellensis*), jequitibá rosa (*Cariniana legalis*), pereira (*Platycyamus regnellii*) and peroba (*Paratecoma peroba*) [1,6–8].

Low molecular weight phenolic compounds extracted from wood are incorporated to distillates during ageing [9,10]. Lignin transformations that occur during the ageing process are among the most important factors that influence the quality of distilled beverages. The level of ageing of Scotch whisky, brandies, grape marc distillate and wine distillates can be designated based on the content of phenolic compounds derived from lignin as well as on their profile [11–13].

Lignin macromolecules have branches of coniferyl (guaiacyl-like compounds) and sinapyl (syringyl-like compounds) alcohols. The former gives rise to coniferaldehyde, which is converted to vanillin and, in turn, oxidized to vanillic acid. The latter generates sinapaldehyde, which is transformed into syringaldehyde and later oxidized to syringic acid [14] (Figure 1).

This study aimed to evaluate the phenolic compounds derived from the degradation of lignin in cachaça aged for 36 months in new barrels made from three tropical wood species (*Amburana cearensis* – amburana, *Myrocarpus frondosus* – cabreúva and *Bertholletia excelsa* – castanheira) and two oak species (*Quercus petraea* – European oak and *Quercus alba* – American oak). Although some tropical species have already been studied for cachaça ageing, including cabreúva and amburana, the novelty of the present work lies in the fact that the ageing process was carried out in new barrels from tropical wood species compared to oak species.

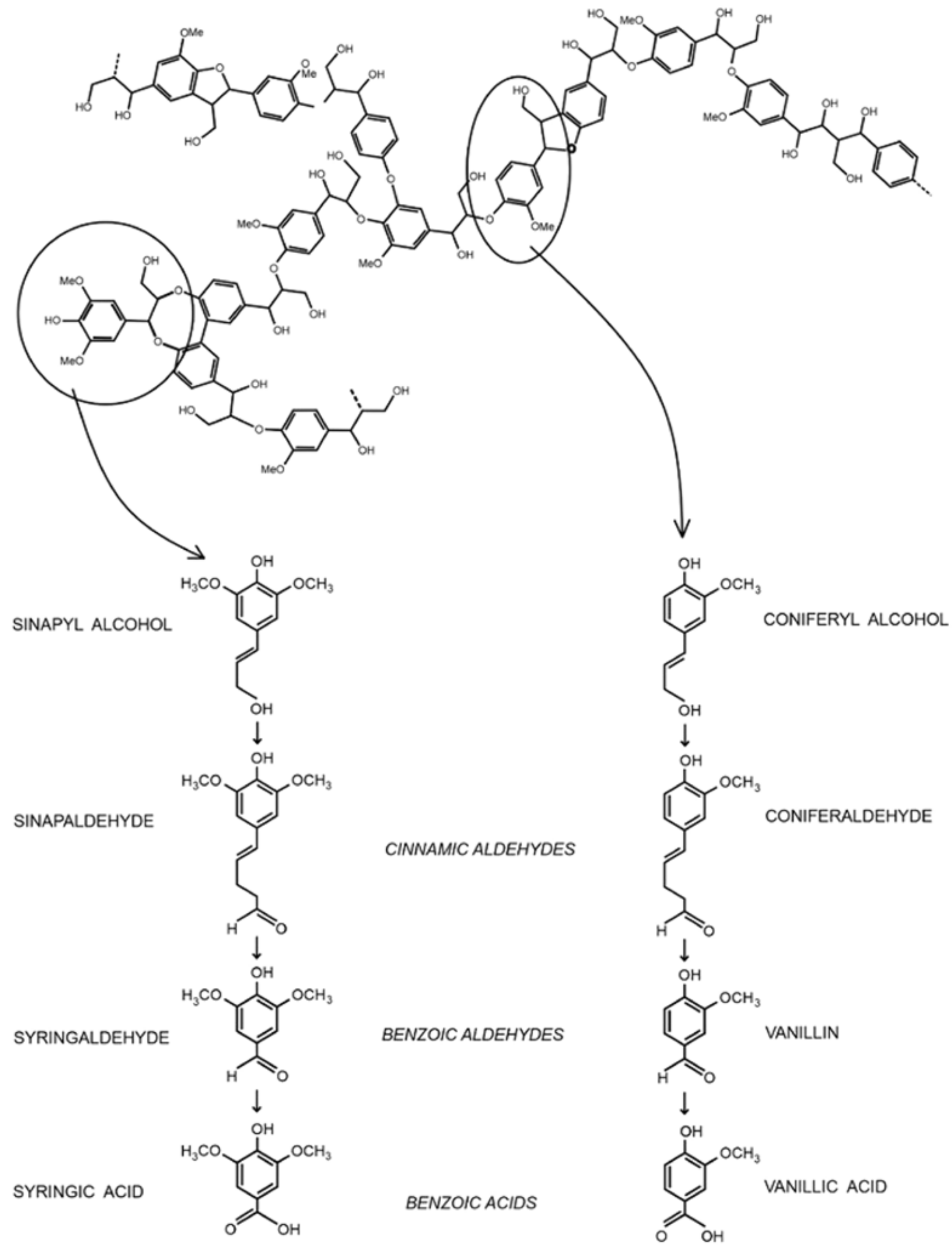

FIGURE 1 Transformations of lignin-derived aromatic compounds during the ageing process of distilled spirits in new wooden barrels.

MATERIALS AND METHODS

The sugarcane spirit used in this study was produced in 2017 in the distillery of the Department of Agri-Food Industry, Foods and Nutrition, Escola Superior de Agricultura "Luiz de Queiroz", Universidade de São Paulo, as previously described [15]. After extraction in a Maqtron M-730 stainless steel presser (Joaçaba, SC, Brazil) the sugarcane juice from variety SP 81-3250 was diluted to 18 °Bx using potable water. Fermentation was carried out in 1,500-L stainless steel tanks (Alambiques Santa Efigênia, Itaverava, MG, Brazil) for 24 h at 30 °C using *Saccharomyces cerevisiae* strain CA-11 (LNF Latino Americana, Bento Gonçalves, RS, Brazil). Fermentation was considered finished when all fermentable sugars were consumed by yeast (Brix stable). The fermented must contain 10.1% ethanol by volume.

Double distillation was carried out in a 1,000L copper pot still (Alambiques Santa Efigênia, Itaverava, MG, Brazil) [16]. The first distillation resulted in a distillate known as phlegma, containing 29.9% ethanol by volume. The phlegma was subjected to the second distillation, in which the "heads" and "tails" fractions were withdrawn. The "heart" fraction characterises the double-distilled cachaça, containing 63.5% ethanol by volume.

The wooden barrels (225L) used for cachaça ageing were made from tropical species: amburana (*Amburana cearensis*), cabreúva (*Myrocarpus frondosus*) and castanheira (*Bertholletia excelsa*), medium toasted (240 °C for 12 min) (Tanoaria Mesacaza, Monte Belo do Sul, RS, Brazil). The oak barrels (225 L) were made from European oak (*Quercus petraea*) and American oak (*Quercus alba*), medium toasted (240 °C for 12 min) (Tonelleries de Bourgogne, Meursault, France). These tropical species were chosen because they are the most used wood species in Brazil for cachaça ageing and medium toasting is usually applied to the internal charring of the barrels.

Double-distilled sugarcane spirit was aged for 36 months at room temperature (22 ± 3 °C), 55 ± 10% relative humidity and protected from vibrations. Samples of 25 mL were collected at the same level from the centre of the barrels at the end of the ageing period (36 months) for analyses of maturation-related congeners. Non-aged double-distilled cachaça was used as control in this study.

Ageing congeners were analysed using high-performance liquid chromatography (HPLC) in a Shimadzu equipment, model LC-10 AD (Tokyo, Japan), with two Shimadzu LC-20 AD pumps, an ultraviolet (UV)–visible detector Shimadzu SPD-20A, a system controller CBM-20A and an automated injection system (20 µL) with gradient elution [1]. The standards employed in this research were vanillin, vanillic acid, syringaldehyde, sinapaldehyde, syringic acid and coniferaldehyde, all purchased from Sigma-Aldrich (St. Louis, MO, USA), purity > 99 %. To obtain the calibration curves for standard mixtures (Table 1), their concentrations ranged from 0.5 to 30.0 mg/L for phenolic aldehydes and from 0.5 to 20.0 mg/L for phenolic acids. Analyses using HPLC had two mobile phases composed of water/acetic acid (98/2, by volume) and methanol/water/acetic acid (70/28/2, by volume) at a flow rate of 1.25 mL/min. A pre-column Shimadzu VP-ODS (1 cm × 4.6 µm) and a C18 reversed-phase column model Shimpack VP-ODS (4.6 mm, 25 cm × 5 µm) thermostabilised at 40 °C were used. The UV detector was programmed to operate at variable wavelengths. The samples were filtered through a Millex-HV filter with polyvinylidene difluoride membrane (13 mm diameter, 0.45 µm pore size) prior to analysis.

Aldehydes, esters, methanol, acetic acid and higher alcohols (1-propanol, 2-methyl-1-propanol and 3-methyl-1-butanol) were analysed using gas chromatography with a flame ionisation detector (GC-FID) [1]. Aliquots of 1.0 µL were automatically injected into the 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). The analyses were performed at a 1:20 split ratio. Nitrogen was used as the carrier gas (flow rate of 1.5 mL/min, total flow of 27 mL/min and pressure of 252.4 kPa). The temperatures of both the injector and the detector were set at 240 °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.

The determination of the colour intensity was carried out at 420 nm [17], in a Spekol 1300 UV-Vis single beam spectrophotometer (Analytik Jena GmbH, Jena, Germany) using quartz cuvettes.

Sensory assessment of sugar cane spirits was carried out using the Buxbaum model of positive ranking [18,19]. Aged cachaça samples and control were diluted to 40% (by volume) before sensory analysis.

Statistical analyses were performed applying analysis of variance (ANOVA) and the Statistical Analysis System, version 9.3. The means of the results obtained from triplicate analyses were compared using the Tukey's test ($p \geq 0.05$).

TABLE 1 Retention time (RT), limit of detection (LOD) and limit of quantification (LOQ) of ageing-marker compounds and correlation coefficients (a, b, r^2) of the calibration curves for cachaça aged for 36 months in new barrels made from tropical wood and oak.

AGEING-MARKER COMPOUND	RT (min)	LOD (mg/L)	LOQ (mg/L)	a	b	r^2
Gallic acid	6.37	0.03	0.10	1821.48	55.92	0.991
Vanillic acid	24.01	0.04	0.17	1263.18	256.33	0.997
Syringic acid	26.62	0.03	0.11	2428.26	-102.89	0.998
Vanillin	27.08	0.03	0.08	3110.11	-87.12	0.998
Syringaldehyde	29.15	0.05	0.16	1079.89	341.11	0.997
Coniferaldehyde	34.83	0.03	0.07	4548.14	146.96	0.997
Synapaldehyde	35.85	0.03	0.10	3217.87	102.27	0.996

RESULTS AND DISCUSSION

PHENOLIC COMPOUNDS

A significant effect of wood species was observed on all the studied phenolic compounds. Syringaldehyde and benzoic acids were the main low molecular weight compounds in aged cachaça (Table 2).

Coniferaldehyde was found at low concentrations in cachaça aged in castanheira and European oak barrels and at the highest contents in the beverage matured in barrels made from amburana and cabreúva. Cachaça aged in castanheira and cabreúva barrels exhibited the lowest concentrations of sinapaldehyde, whereas the one aged in amburana barrels had the highest content of this compound, as well as the highest concentration of both cinnamic aldehydes added together.

The highest content of vanillin was registered in the distilled spirits aged in barrels made from amburana and both oak species. Syringaldehyde was found at the lowest concentration in cachaça aged in castanheira barrels and at the highest content in that matured in amburana barrels. Cachaça aged in barrels made from American oak exhibited the second highest concentration of syringaldehyde. The beverages aged in barrels made from cabreúva and castanheira displayed the lowest concentration of both benzoic aldehydes added together.

The analysis of vanillic acid revealed the lowest concentrations in cachaça aged in European oak barrels, approximately half of the content found in the one aged in barrels made from all the other wood species. The content of syringic acid in cachaça aged in amburana barrels was the highest, whereas the distilled spirits aged in barrels made from castanheira and European oak exhibited the lowest content of this benzoic acid.

Some studies have reported the predominance of vanillin, syringaldehyde, vanillic acid and syringic acid in cachaça aged in oak barrels [17,20,21]. Cachaça aged in amburana barrels exhibited high contents of sinapaldehyde and vanillic acid. Cabreúva barrels imparted high contents of syringaldehyde and syringic acid to aged cachaça [1,8,17,22,23].

The results of low-molecular lignin-derived phenolic compounds obtained for cachaça aged in European oak barrels (Table 2) are in reasonable agreement with those

TABLE 2 Colour (%T at 420 nm) and content (mg/L) of ageing-marker compounds derived from lignin and some ratios among them in cachaça aged for 36 months in new barrels from tropical wood and oak.

AGEING-MARKER COMPOUND		CONTROL (non-aged cachaça)	AGED CACHAÇA				
			AMBURANA (*Amburana cearensis*)	CABREÚVA (*Myrocarpus frondosus*)	CASTANHEIRA (*Bertholletia excelsa*)	EUROPEAN OAK (*Quercus petraea*)	AMERICAN OAK (*Quercus alba*)
Cinnamic aldehydes	Coniferaldehyde	< LOD[1]	4.60±0.13^{a}	5.29±0.12^{a}	1.39±0.05^{c}	1.29±0.03^{c}	2.16±0.05^{b}
	Sinapaldehyde	< LOD[1]	12.15±0.33^{a}	1.66±0.04^{c}	0.95±0.02^{c}	2.37±0.08^{b}	3.71±0.10^{b}
	Total		16.75±0.46^{a}	6.95±0.16^{b}	2.33±0.07^{c}	3.66±0.11^{c}	5.87±0.15^{b}
Benzoic aldehydes	Vanillin	< LOD[1]	7.60±0.18^{a}	2.16±0.07^{b}	1.93±0.07^{b}	6.14±0.12^{a}	6.12±0.14^{a}
	Syringaldehyde	< LOD[1]	41.27±1.51^{a}	17.36±0.43^{c}	6.20±0.16^{e}	11.81±0.29^{d}	29.95±0.67^{b}
	Total		48.87±1.69^{a}	19.52±0.50^{c}	8.13±0.23^{d}	17.95±0.41^{c}	36.07±0.81^{b}
Benzoic acids	Vanillic acid	< LOD[1]	12.45±0.29^{a}	14.32±0.31^{a}	14.10±0.33^{a}	6.34±0.15^{b}	13.89±0.39^{a}
	Syringic acid	< LOD[1]	33.25±0.60^{a}	8.89±0.21^{b}	4.66±0.11^{c}	6.33±0.11^{c}	10.64±0.33^{b}
	Total		45.70±0.89^{a}	23.21±0.52^{b}	18.76±0.44^{bc}	12.67±0.26^{c}	24.53±0.72^{b}
	Gallic acid	< LOD[1]	6.60±0.19^{c}	3.23±0.09^{d}	40.61±0.79^{a}	22.82±0.48^{b}	8.00±0.21^{c}
Gallic acid/Vanillin			0.87^{c}	1.49^{c}	21.04^{a}	3.72^{b}	1.31^{c}
Syringaldehyde/Vanillin		–	5.43^{b}	8.04^{a}	3.21^{c}	1.92^{d}	4.89^{b}
Guaiacyl-type compounds		–	24.65±0.60^{a}	21.77^{ab}	17.42^{b}	13.77^{c}	22.17^{a}
Syringyl-type compounds		–	86.67±2.44^{a}	27.91^{cd}	11.81^{e}	20.51^{d}	44.30^{b}
Colour		99.8±0.1^{a}	74.6±0.7^{c}	62.4±0.6^{d}	81.2±0.8^{b}	73.5±0.8^{c}	74.9±0.7^{c}

[1]LOD: limit of detection

Means (x±standard deviation) in rows with different superscript lowercase letters are significantly different ($p < 0.05$) as analysed by ANOVA and the Tukey's test.

observed in commercial extra old wine distillates: 2.4 mg/L coniferaldehyde, 1.6 mg/L sinapaldehyde, 16.7 mg/L vanillin, 27.8 mg/L syringaldehyde, 4.5 mg/L vanillic acid and 8.3 mg/L syringic acid [13]. The following concentrations of the studied phenolics were found in five to six year old commercial grape mark distillates aged in 225L barrels made from European oak: 9.1 mg/L coniferaldehyde, 6.3 mg/L sinapaldehyde, 3.8 mg/L vanillin, 8.2 mg/L syringaldehyde, 2.4 vanillic acid and 3.6 mg/L syringic acid. In contrast, for the commercial grape mark distillates matured in American oak 225-L barrels for 6 years, the values were: 2.0 mg/L coniferaldehyde, 4.2 mg/L sinapaldehyde, 3.8 mg/L vanillin, 8.2 mg/L syringaldehyde, 2.1 vanillic acid and 3.1 mg/L syringic acid [12].

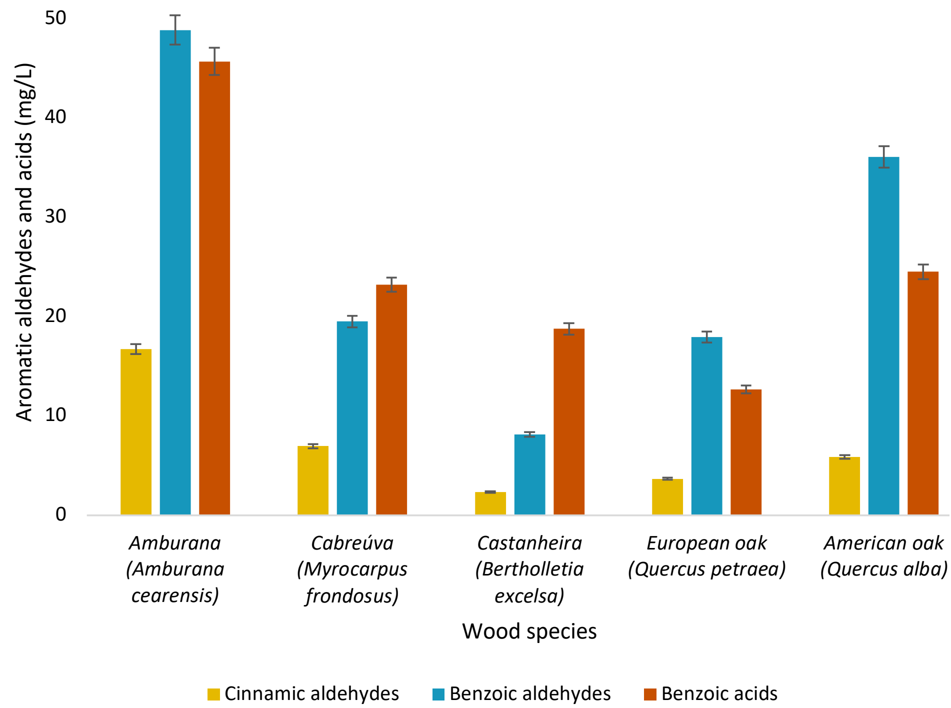

FIGURE 2 Cinnamic aldehydes (coniferaldehyde and sinapaldehyde), benzoic aldehydes (vanillin and syringaldehyde) and benzoic acids (vanillic and syringic acids) contents in cachaça aged for 36 months in new barrels made from tropical wood and oak.

All the phenolic families under study were measured at higher concentrations in cachaça aged in amburana barrels (Figure 2). Cachaça aged in barrels made from American oak showed the second highest contents of benzoic aldehydes and benzoic acids, while the beverage matured in cabreúva barrels exhibited the second highest contents of cinnamic aldehydes. The distilled spirits aged in castanheira barrels had the lowest contents of cinnamic and benzoic aldehydes. Cachaça aged in barrels made from European oak exhibited the lowest contents of benzoic acids.

The ratio of gallic acid to vanillin is influenced by the species of wood [24] and a higher ratio may contribute to high quality brandy [25]. In the present study, this ratio was significantly higher in cachaça aged in castanheira barrels (21.0) compared to the distilled spirits matured in barrels made from all the other wood species (Table 2). Cachaça aged in European oak barrels exhibited the second highest gallic acid/vanillin (3.1), while in the distilled beverages aged in barrels made from all the other wood species this ratio was near one.

The ratio of syringaldehyde to vanillin may indicate the level of maturation of aged distillates [24,26], and for most of those aged in oak barrels it is near two, ranging from 1.4 to 2.5 [12,13,27-29]. In this study, this ratio was 1.92 and 4.89 for cachaça aged in European oak and American oak barrels, respectively. Among the tropical woods, cachaça aged in barrels made from cabreúva exhibited the highest ratio of syringaldehyde to vanillin (8.04), whereas in the distilled spirits aged in amburana and castanheira barrels this ratio was 5.43 and 3.21, respectively.

In addition, the relationship between benzoic aldehydes (vanillin and syringaldehyde) and cinnamic aldehydes (coniferaldehyde and sinapaldehyde) allowed differentiating the type of wood (chestnut or oak) used in the ageing process of wine brandies [28]. Orujo aged in American oak barrels had the highest ratio of benzoic aldehydes to cinnamic aldehydes (1.95), whereas orujo aged in European oak barrels this ratio was 0.79. Similar values were observed in orujos aged in barrels made from French oak of different origins, ranging from 0.84 to 1.07 [12]. In the present study, the relationship between both aldehyde families was higher for cachaça aged in American oak barrels (6.14), as shown in Table 2. Cachaça aged in cabreúva and amburana barrels displayed the lowest ratio of benzoic aldehydes to cinnamic aldehydes, 2.81 and 2.92, respectively. In the distilled spirits matured in castanheira and European oak barrels this ratio was 3.49 and 4.90, respectively.

Phenolic acids have been considered the main quality markers for aged wine distillates [13]. In wine distillates aged for more than 20 years, the concentration of benzoic acids increased continuously, reaching concentrations of 8.3 mg/L syringic acid and 4.5 mg/L vanillic acid, totalizing 12.8 mg/L benzoic acids [13]. Similar values of total benzoic acids were found in cachaça aged in barrels made from

European oak in the present study (12.67 mg/L), and the highest content of these compounds was found in cachaça aged in amburana barrels, 45.70 mg/L. Cachaça matured in castanheira barrels exhibited 18.76 mg/L benzoic acids, while in that aged in cabreúva and American oak barrels the content of these compounds was near 24 mg/L.

The ratio of syringic acid to vanillic acid can be taken into consideration for characterising the age of distillates. Cognacs aged for up to two years in used six-year-old European oak barrels (350L) displayed a prevalence of vanillic acid (syringic acid/vanillic acid from 0.67 to 0.89). Conversely, cognacs aged for 10 to 30 years at the same conditions exhibited higher content of syringic than vanillic acid (syringic acid/vanillic acid between 1.19 and 1.40) [30]. This ratio was 1.50 in commercial grape marc distillates aged for four years in 225L barrels made from European oak [12]. In this study, cachaça aged in American oak, cabreúva and castanheira barrels exhibited higher concentration of vanillic than syringic acid (syringic acid/vanillic acid from 0.33 to 0.77). In cachaça aged in barrels made from European oak, this ratio was near 1.0, while that matured in amburana barrels had a prevalence of syringic over vanillic acid (syringic acid/vanillic acid 2.67).

The highest concentration of syringyl-type compounds was found in cachaça aged in amburana barrels, followed by the beverages matured in barrels made from American oak, cabreúva and European oak. Cachaça aged in castanheira barrels displayed the lowest content of syringyl-type compounds (Figure 3).

Furthermore, cachaça matured in amburana barrels also exhibited the highest concentration of guaiacyl-type compounds, followed by the distilled spirits aged in barrels made from American oak, cabreúva and castanheira. Cachaça aged in European oak barrels had the lowest content of guaiacyl-type compounds.

Toasted powder extracts from Imburana (*Amburana cearensis*), oak (*Quercus alba*) and Balm (*Myrocarpus frondosus*) were obtained by solvent reflux (1.5 g of powder extracts in 50 mL of 50% (v/v) ethanol/water solution). The extract from Imburana exhibited the highest concentration of syringyl-type compounds compared to powder extracts from the woods balm and oak [31].

Except for cachaça matured in castanheira barrels, the distilled spirits aged in barrels made from all the other wood species showed higher contents of syringyl-type compounds than guaiacyl-type compounds (syringyl-type compounds/guaiacyl-type compounds ranging from 1.28 to 3.52).

A prevalence of syringyl-type compounds over guaiacyl-type compounds was observed in wine distillates aged for up to 50 years (syringyl-type compounds/guaiacyl-type compounds ranging from 1.60 to 2.09) [13]. Similarly, the contents of syringyl-type compounds were higher than those of guaiacyl-type compounds in grape mark distillates aged for 5–6 years in European oak and in American oak barrels, since the ratios of syringyl-type to guaiacyl-type compounds were 1.18 and 1.96, respectively [12].

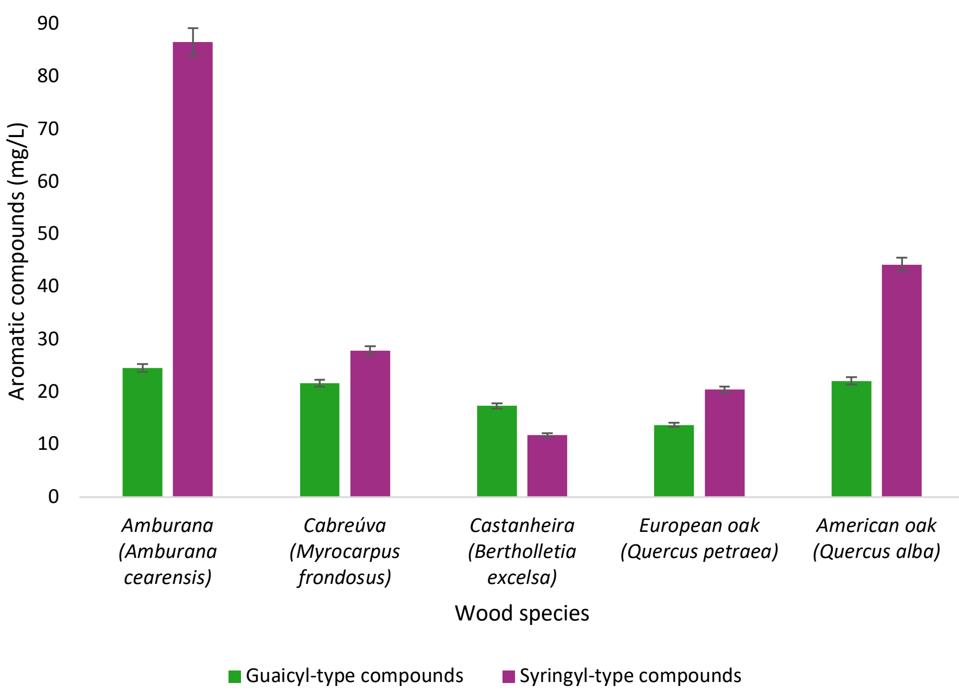

FIGURE 3 Total content of guaiacol-type compounds (coniferaldehyde, vanillin and vanillic acid) and syringol-type compounds (sinapaldehyde, syringaldehyde and syringic acid) in cachaça aged for 36 months in new barrels made from tropical wood and oak.

MAJOR VOLATILE COMPOUNDS

The major volatile compounds in aged cachaça were 3-methyl-1-butanol and isoamyl alcohol (~160 mg/100 mL anhydrous ethanol, AE), followed by acetic acid (Table 3). Isoamyl alcohol was the most abundant higher alcohol present in cachaça [32], approximately 193 mg/100 mL AE. The contents of the two other higher alcohols, 1-propanol and 2-methyl-1-propanol (isobutanol), were similar in all aged spirits (~50 mg/100 mL alcohol). Higher alcohols, such as propanol, isobutanol and isoamyl alcohol, are related to yeast metabolism of sugars and amino acids during ethanolic fermentation [33]. Specific contents

TABLE 3 Major volatile compounds (mg/100 mL anhydrous ethanol) in cachaça aged for 36 months in new barrels from tropical wood and oak.

AGEING-MARKER COMPOUND	CONTROL (non-aged cachaça)	AGED CACHAÇA				
		AMBURANA (*Amburana cearensis*)	CABREÚVA (*Myrocarpus frondosus*)	CASTANHEIRA (*Bertholletia excelsa*)	EUROPEAN OAK (*Quercus petraea*)	AMERICAN OAK (*Quercus alba*)
Acetaldehyde	10.31±0.55[a]	10.13±0.32[a]	10.30±0.58[a]	10.37±0.55[a]	10.38±0.64[a]	10.47±0.27[a]
Ethyl acetate	15.51±0.22[d]	15.59±0.13[d]	21.81±0.66[c]	23.51±0.72[c]	32.72±0.47[b]	47.22±1.92[a]
1-Propanol	51.56±2.45[a]	50.07±4.21[a]	48.48±3.85[a]	49.41±2,56[a]	50.81±2.53[a]	59.39±2.92[a]
2-Methyl-1-propanol	55.12±1.91[a]	54.37±2.73[a]	47.09±0.94[a]	49.51±2.66[a]	45.98±2.65[a]	56.62±3.54[a]
3-Methyl-1-butanol	164.43±21.80[a]	161.41±19.80[a]	155.22±19.50[a]	159.40±17.05[a]	160.69±15.40[a]	165.42±14.19[a]
Acetic acid	60.95±1.96[d]	70.92±1.95[c]	93.26±1.51[b]	51.01±0.99[e]	120.31±3.17[a]	110.25±1.86[a]
Methanol	7.43±0.19[a]	7.08±0.09[a]	7.79±0.21[a]	7.07±0.11[a]	7.30±0.17[a]	7.70±0.11[a]
Higher alcohols	271.11±23.50[a]	265.85±16.90[a]	250.79±21.40[a]	258.32±21.66[a]	257.48±25.70[a]	281.43±10.69[a]

Means (x±standard deviation) in rows with different superscript lowercase letters are significantly different ($p < 0.05$) as analysed by ANOVA and the Tukey's test.

and proportions of higher alcohols positively influence the aroma of distillates. Conversely, when present in concentrations higher than 350 mg/100 mL AE, higher alcohols are often associated with poor quality distillates [33]. The contents of higher alcohol in aged cachaça ranged from 257 to 281 mg/100 mL AE.

Similarly to what was observed for higher alcohols (1-propanol, 2-methyl-1-propanol and 3-methyl-1-butanol), negligible variations were also found for acetaldehyde (± 1.7% between the control and any of the aged spirits) and methanol (± 4.9% between the control and any of the aged spirits). In contrast, ethyl acetate was present at markedly higher levels (compared to the control) in cachaça aged in oak barrels (Table 3), with a 3-fold average increase for American oak and a 2-fold average increase for European oak. Cachaça aged in cabreúva and castanheira exhibited an average increase over 50% in ethyl acetate content. The content of ethyl acetate in cachaça aged in amburana was similar to the control. Ethyl-acetate is the most common ester in cachaça [32]. Since the cachaça used as control in this study was produced using double distillation, it contained only 15.5 mg/100 mL AE ethyl-acetate, lower than the average of Brazilian sugar cane spirits (88 mg/100 mL AE) [32]. A significant increase in acetic acid content was observed in cachaça aged in oak barrels (+100% for European oak and +80% for American oak). Although cachaça aged in cabreúva and amburana barrels also had a significant increase in acetic acid content, it was smaller than that found in the cachaça aged in oak barrels, +50% and +16%, respectively. In contrast, cachaça aged in castanheira barrels showed a decrease by 16% in acetic acid content.

SENSORY EVALUATION

The differences in chemical composition of aged cachaça resulted in statistically significant differences ($p < 0.05$) in the sensory assessment (Table 4). Cachaça aged in

TABLE 4 Sensory assessment of cachaça aged for 36 months in new barrels from tropical wood and oak.

AGEING-MARKER COMPOUND	CONTROL (non-aged cachaça)	AGED CACHAÇA				
		AMBURANA (*Amburana cearensis*)	CABREÚVA (*Myrocarpus frondosus*)	CASTANHEIRA (*Bertholletia excelsa*)	EUROPEAN OAK (*Quercus petraea*)	AMERICAN OAK (*Quercus alba*)
Colour (max 2 points)	1.5±0.2[b]	2.0±0.0[a]	1.6±0.1[b]	2.0±0.0[a]	2.0±0.0[a]	2.0±0.0[a]
Clearness (max 2 points)	2.0±0.0[a]	2.0±0.0[a]	2.0±0.0[a]	2.0±0.0[a]	2.0±0.0[a]	2.0±0.0[a]
Odour (max 4 points)	2.5±0.7[c]	3.8±0.1[a]	2.8±0.4[bc]	3.2±0.2[b]	3.5±0.3[a]	3.6±0.2[a]
Taste (max 12 points)	7.0±0.5[d]	11.5±0.4[a]	8.5±0.4[c]	9.8±0.5[b]	11.1±0.3[a]	10.8±0.4[a]
Total (max 20 points)	13.0±0.4[c]	19.3±0.3[a]	14.9±0.4[c]	17.0±0.2[b]	18.6±0.2[a]	18.3±0.2[a]

Means (x±standard deviation) in rows with different superscript lowercase letters are significantly different ($p < 0.05$) as analysed by ANOVA and the Tukey's test.

European and American oak and amburana barrels obtained the highest total score and were characterized as smooth and pleasant in aroma and taste. Cachaça aged in castanheira barrels was also considered pleasant and the taste and smell were acceptable. Cachaça aged in cabreúva barrels received the lowest total score, similar to the control (non-aged cachaça), and the panelists described its aroma and taste as sharp, acid, pungent and burning. The common sensory descriptors associated with the cachaças aged in the different woods species were: European oak (roasted almonds, ripe fruits and spices), American oak (vanilla, coconut and caramel), amburana (vanilla, sweet and spices), castanheira (vanilla, chocolate, caramel and chestnuts), cabreúva (herbaceous, bitter and astringent).

CONCLUSION

The results obtained in this study contributed to the knowledge of phenolic composition of cachaça aged in new barrels made from tropical wood species. Amburana showed great potential to provide lignin-derived phenolic compounds to cachaça during the ageing process. Cachaça samples aged in oak and amburana barrels received the highest scores in the sensory assessment. Tropical wood species, singly or complementarily to oak, enhanced flavour complexity of aged cachaça and simultaneously broadened and diversified its taste and aroma profiles.

FUNDING STATEMENT

The present study is part of the project 'Characterization of the level of maturation of aged sugar cane spirit (cachaça): evaluation of maturation-related phenolic compounds', Grant 2016/23211-5, funded by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), São Paulo, SP, Brazil and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) - Finance Code 001, Brasília, DF, Brazil.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

ORCID IDs

M.C. Castro https://orcid.org/0000-0002-4159-0727
G.C. Silvello https://orcid.org/0000-0002-4672-4800
A.R. Alcarde https://orcid.org/0000-0002-9319-7847

CRediT CONTRIBUTOR

ARA conceived the idea and the design of the work. MCC performed the analysis. GCS carried out data analysis and interpretation. ARA and MCC drafted the article. ARA critically revised the article. All authors approved the final version of the manuscript for publication and have agreed to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

REFERENCES

[1] Bortoletto, A.M.; Alcarde, A.R. Congeners in Sugar Cane Spirits Aged in Casks of Different Woods. Food Chem. **2013**,139, 695–701. doi: 10.1016/j.foodchem.2012.12.053.

[2] Mosedale, J.R.; Puech, J.L. Wood Maturation of Distilled Beverages. Trends Food Sci. Technol. **1998**, 9, 95–101. doi: 10.1016/S0924-2244(98)00024-7.

[3] Chatonnet, P.; Dubourdieu, D. Comparative Study of the Characteristics of American White Oak (*Quercus alba*) and European Oak (*Quercus petraea* and *Q. robur*) for Production of Barrels Used in Barrel Aging of Wines. Am. J. Enol. Viticult. **1998**, 49, 79–85.

[4] Alañón, M.E.; Castro-Vázquez, L.; Díaz-Maroto, M.C.; Hermosín-Gutiérrez, I.; Gordon, M.H.; Pérez-Coello, M.S. Antioxidant Capacity and Phenolic Composition of Different Woods Used in Cooperage. Food Chem. **2011**, 129, 1584–1590. doi: 10.1016/j.foodchem.2011.06.013.

[5] De Rosso, M.; Cancian, D.; Panighel, A.; Vedova, A.D.; Flamini, R. Chemical Compounds Released from Five Different Woods Used to Make Barrels for Aging Wines and Spirits: Volatile Compounds and Polyphenols. Wood Sci. Technol. **2009**, 43, 375–385. doi: 10.1007/s00226-008-0211-8.

[6] Faria, J.B.; Cardello, H.; Boscolo, M.; Isique, W.D.; Odello, L.; Franco, D.W. Evaluation of Brazilian Woods as an Alternative to Oak for Cachacas Aging. Eur. Food Res. Technol. **2003**, 218, 83–87. doi: 10.1007/s00217-003-0795-z.

[7] Alcarde, A.R.; Souza, P.A.; Belluco, A.E. Aspects of the Chemical Composition and Sensorial Acceptance of Sugar Cane Spirit Aged in Casks of Different Types of Woods. Ciênc. Tecnol. Aliment. **2010**, 30, 226–232 (in Portuguese). doi: 10.1590/S0101-20612010000500035.

[8] Santiago, W.D.; Cardoso, M.G.; Nelson, D.L. Cachaça Stored in Casks Newly Constructed of Oak (*Quercus* sp.), Amburana (*Amburana cearensis*), Jatoba (*Hymenaeae carbouril*), Balsam (*Myroxylon peruiferum*) and Peroba (*Paratecoma peroba*): Alcohol Content, Phenol Composition, Colour Intensity and Dry Extract. J. Inst. Brew. **2017**, 123, 232–241. doi: 10.1002/jib.414.

[9] Goldberg, D.M.; Hoffman, B.; Yang, J.; Soleas, G.J. Phenolic Constituents, Furans, and Total Antioxidant Status of Distilled Spirits. J. Agric. Food Chem. **1999**, 47, 3978–3985. doi: 10.1021/jf9811626.

[10] Canas, S.; Casanova, V.; Belchior, A.P. Antioxidant Activity and Phenolic Content of Portuguese Wine Age Brandies. J. Food Compos. Anal. **2008**, 21, 626–633. doi: 10.1016/j.jfca.2008.07.001.

[11] Aylott, R.I.; MacKenzie, W.M. Analytical Strategies to Confirm the Generic Authenticity of Scotch Whisky. J. Inst. Brew. **2010**, 116, 215–229. doi: 10.1002/j.2050-0416.2010.tb00424.x.

[12] Rodríguez-Solana, R.; Salgado, J.M.; Domínguez, J.M.; Cortés-Diéguez, S. First Approach to the Analytical Characterization of Barrel-Aged Grape Marc Distillates Using Phenolic Compounds and Colour Parameters. Food Technol. Biotechnol. **2014**, 52, 391–402. doi: 10.17113/ftb.52.04.14.3627.

[13] Cernîşev, S. Analysis of Lignin-Derived Phenolic Compounds and their Transformations in Aged Wine Distillates. Food Control. **2017**, 73, 281–290. doi: 10.1016/j.foodcont.2016.08.015.

[14] Puech, J.L. Extraction and Evolution of Lignin Products in Armagnac Matured in Oak. Am. J. Enol. Viticult. **1981**, 32, 111–114.

[15] Bortoletto, A.M.; Correa, A.C.; Alcarde, A.R. Aging Practices Influence Chemical and Sensory Quality of Cachaça. Food Res. Int. **2016**, 86, 46–53. doi: 10.1016/j.foodres.2016.05.003.

[16] Alcarde, A.R.; Souza, L.M.; Bortoletto, A.M. Ethyl Carbamate Kinetics in Double Distillation of Sugar Cane Spirit. J. Inst. Brew. **2012**, 118, 27–31. doi: 10.1002/jib.14.

[17] Anjos, J.P.; Cardoso, M.G.; Saczk, A.A.; Dórea, H.S.; Santiago, W.D.; Machado, A.M.R.; Zacaroni, L.M.; Nelson, D.L. Evolution of the Concentration of Phenolic Compounds in Cachaça During Aging in an Oak (*Quercus* sp.) Barrel. J. Braz. Chem. Soc. **2011**, 22, 1307–14. doi: 10.1590/S0103-50532011000700016.

[18] Tešević, V.; Nikićević, N.; Jovanović, A.; Djoković, D.; Vujisić, L.; Vučković, I.; Bonić, M. Volatile Components from Old Plum Brandies. Food Technol. Biotechnol. **2005**, 43, 367–372.

[19] Pielech-Przybylska, K.; Balcerek, M.; Nowak, A.; Patelski, P.; Dziekońska-Kubczak, U. Influence of Yeast on the Yield of Fermentation and Volatile Profile of 'Węgierka Zwykła' Plum Distillates. J. Inst. Brew. **2016**, 122, 612–623. doi: 10.1002/jib.374.

[20] Castro, M.C.; Bortoletto, A.M.; Silvello, G.C.; Alcarde, A.R. Maturation Related Phenolic Compounds in Cachaça Aged in New Oak Barrels. J. Inst. Brew. **2021**, 127, 70–77. doi: 10.1002/jib.629.

[21] Silvello, G.C.; Bortoletto, A.M.; Castro, M.C.; Alcarde, A.R. New Approach for Barrel-Aged Distillates Classification Based on Maturation Level and Machine Learning: A Study of Cachaça. LWT. **2021**, 140, 110836. doi: 10.1016/j.lwt.2020.110836.

[22] Zacaroni, L.M.; Cardoso, M.G.; Saczk, A.A.; Moraes, A.R.; Anjos, J.P.; Machado, A.M.R.; Nelson, D.L. Determination of Phenolic Compounds and Coumarins in Sugar Cane Spirit Aged in Different Species of Wood. Anal. Lett. **2011**, 44, 2061–2073. doi: 10.1080/00032719.2010.546017.

[23] Santiago, W.D.; Cardoso, M.G.; Santiago, J.A.; Gomes, M.S.; Rodrigues, L.M.A.; Brandão, R.M.; Cardoso, R.R.; d'Avila, G.B.; Silva, B.L.; Caetano, A.R.S. Comparison and Quantification of the Development of Phenolic Compounds During the Aging of Cachaça in Oak (*Quercus* sp) and Amburana (*Amburana cearensis*) Barrels. Am. J. Plant. Sci. **2014**, 5, 3140–50. doi: 10.4236/ajps.2014.521330.

[24] Gimenez-Martínez, R.; López-García de la Serrana, H.; Villalón-Mir, M.; Navaro-Alarcón, M.; Olalla-Herrera, M.; Cabrera-Vique, C.; López-Martínez, M.C. Study of vanillin, Syringaldehyde and Gallic Acid Content in Oak Wood and Wine Spirits Mixtures: Influence of Heat Treatment and Chip Size. J. Wine Res. **2001**, 12, 175–182. doi: 10.1080/09571260120106811.

[25] Gómez-Cordovés, C.; Bartolomé, B.; Jimeno, M.L. Identification of 2,3-Dihydroxy-1-Guaiacylpropan-1-one in Brandies. J. Agric. Food Chem. **1997**, 45, 873–876. doi: 10.1021/jf9605613.

[26] Puech, J.L.; Moutounet, M. Phenolic Compounds in an Ethanol-Water Extract of Oak Wood and in a Brandy. Lebensm. Wiss. Technol. **1992**, 25, 350–352.

[27] MacNamara, K.; van Wyk, C.J.; Brunerie, P.; Augustyn, O.P.H.; Rapp, A. Flavour Components of Whiskey. III. Ageing Changes in the Low-Volatility Fraction. S. Afr. J. Enol. Viticult. **2001**, 22, 82–92. doi: 10.21548/22-2-2199.

[28] Canas, S.; Quaresma, H.; Belchior, A.P.; Spranger, M.I.; Bruno-de-Sousa, R. Evaluation of Wine Brandies Authenticity by the Relationships Between Benzoic and Cinnamic Aldehydes and Between Furanic Aldehydes. Cienc. Tec. Vitivinic. **2004**, 19, 13–27.

[29] Canas, S.; Caldeira, I.; Belchior, A.P. Extraction/Oxidation Kinetics of Low Molecular Weight Compounds in Wine Brandy Resulting from Different Ageing Technologies. Food Chem. **2013**, 138, 2460–2467. doi: 10.1016/j.foodchem.2012.12.018.

[30] Viriot, C.; Scalbert, A.; Lapierre, C.; Moutounet, M. Ellagitannins and Lignins in Aging of Spirits in Oak Barrels. J. Agr. Food Chem. **1993**, 41, 1872–1879. doi: 10.1021/jf00035a013.

[31] Aquino, F.W.B.; Rodrigues, S.; Nascimento, F.N.; Casimiro, A.R.S. Phenolic Compounds in Imburana (*Amburana cearensis*) Powder Extracts. Eur. Food Res. Technol. **2005**, 221,739–745. doi: 10.1007/s00217-005-0065-3.

[32] Bortoletto, A.M.; Alcarde, A.R. Assessment of Chemical Quality of Brazilian Sugar Cane Spirits and Cachaças. Food Control. **2015**, 54, 1–6. doi: 10.1016/j.foodcont.2015.01.030.

[33] Rodríguez-Solana, R.; Galego, L.R.; Pérez-Santín, E.; Romano, A. Production Method and Varietal Source Influence the Volatile Profiles of Spirits Prepared from Fig fruits (*Ficus carica* L.). Eur. Food Res. Technol. **2018**, 244, 2213–2229. doi: 10.1007/s00217-018-3131-3.