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# Aging marker profile in *cachaça* is influenced by toasted oak chips

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***Cachaça* is the most important distilled spirit in Brazil and the fourth most consumed in the world. Aging is not mandatory for *cachaça*. When aging is carried out, casks generally do not undergo the final wood toasting. However the level of thermal degradation of wood influences the formation of new chemical compounds, which are released during the aging process and improve the quality of the spirit. The objective of this study was to verify the influence of origin of wood and toasting intensity of oak chips on the profile of aging markers in *cachaça*. Staves of oak wood from the forests of Allier, Vosges and Nièvre (France) were milled and screened at 9 mesh. The chips underwent light, medium and heavy toasting. The toasted chips were added to *cachaça* (1 g/L) and kept in a closed system at room temperature, without agitation, for 15 days. The aging congeners (gallic acid, 5-hydroxymethylfurfural, furfural, vanillin, vanillic acid, syringaldehyde, sinapaldehyde, syringic acid and coniferaldehyde) were analysed using HPLC. The increase in toasting intensity enhanced the content of the aging markers in *cachaça*, especially syringic acid, vanillin, syringaldehyde, coniferaldehyde and sinapaldehyde. The generation of aging marker compounds was influenced only by the toasting intensity and not by the origin of the oak wood. Copyright © 2015 The Institute of Brewing & Distilling**

**Keywords:** sugar cane spirit; aging markers; toasted oak chips

## Introduction

The aging process of distilled spirits is an important step to incorporate new compounds into the beverage, contributing to formation of the aroma *(1)*. However, aging is a complex system that involves numerous reactions, mainly based on the extraction of molecules from the wood, which interact with the distilled spirit *(2)*. Certain procedures during cooperage tend to modulate specific characteristics in the aged beverage. For instance, the final toasting applied to casks can improve the aroma complexity of the beverage and select for the extraction of specific compounds *(3)*.

Wood is a complex biological system, composed of several macromolecules, mainly cellulose, hemicellulose, lignin and secondary components, such as pectins, proteins and inorganic elements. These different compounds do not behave the same way when interacting with a distilled spirit, favouring peculiar reactions in the wood–beverage system *(4)*.

Cellulose is the major component of wood, whose original structure is based on glucose and normally it is not degraded by the thermal treatment of wood during the cask-making process, resisting up to 250°C. Hemicellulose is composed of complex polysaccharides, xylans, xyloglucans, fucogalactoxyloglucans and mannans. Lignin is a polymer composed of three types of phenylpropenoic or monolignol alcohols: paracoumaryl, coniferyl and sinapyl alcohols *(5)*. As a result of the thermal degradation of lignin, which takes place for bending the wooden staves and during the final toasting, monomeric compounds are formed from wood, and aromatic acids and aldehydes are generated by the acid ethanolysis of lignin. Other mechanisms that promote the transformation of these compounds occur as a consequence of reactions of oxidation and the hydrolysis of the ester bonds of lignin, contributing to the formation of aldehydes, which generate their corresponding acids when oxidized. The presence of oxygen inside the cask is allowed by the wood's porosity and the formation of a space between the surface of the beverage and the cask *(6)*.

Lignin is composed of two major monomer species, guaiacyl and syringyl, and generates two different groups of compounds, one including coniferaldehyde, vanillin and vanillic acid, originating from the guaiacyl structure, and the other encompassing sinapaldehyde, syringaldehyde and syringic acid, originating from the syringyl structure *(7)*. The main aging markers generated from lignin are phenolic aldehydes of the hydroxybenzoic series, represented by vanillin and syringaldehyde, hydroxycinnamic aldehydes, represented by coniferaldehyde and sinapaldehyde, and free phenolic acids, represented by vanillic, gallic, ellagic, ferulic and syringic acids *(8)*.

Coopers classify the types of toasting used to produce the casks as light (120°C for 5 min), medium (150°C for 10 min) and heavy (180°C for 15 min), but the parameters can vary according to the producer. Light toast results in a brownish hue, whereas the heavy toast confers on the casks a dark chocolate hue, although not producing coal; medium toast provides an intermediary result, producing a colour that resembles toasted bread *(9)*. Highly toasted casks are characterized as carbonized and various pyrolysis products are formed. Furthermore, some undesirable smoke flavour compounds can be transferred to the beverage. Therefore, carbonized casks are initially used in the wine-aging

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process, so that the smoke aroma is reduced, and after that, they are reutilized to age distilled spirits.

According to Brazilian law, *cachaça* must be aged only in wooden casks. The use of chips is forbidden for this purpose. However, the high cost of wood and the large number of casks required for aging have led to a search for alternative techniques to allow for faster maturation of beverages and with less investment. In 2006 the European Union approved the use of fragments of wood to age wine *(10)*.

The use of fragments of wood, especially toasted, is considered to be an accelerator of beverage aging *(11)*. The factors that may influence the characteristics of wines undergoing maturation using fragments of oak are geographical origin and the botanical species of wood, level of heat treatment, size and concentration of the fragments, period of maceration and addition of oxygen during the process *(12)*.

*Cachaça*, a typical Brazilian spirit produced by the distillation of fermented sugar cane juice, reaches 38–48% ethanol by volume at 20°C *(13)*, and its total annual production is nearly 1.4 billion L. Aging is not mandatory for *cachaça*. When *cachaça* undergoes aging, the casks are usually non-toasted. However, this technique, which modulates the profile of the aging markers by the toasting intensity applied to the wood, is employed in the production of other distilled spirits widely consumed throughout the world to improve the quality of the final product.

Using chemometric techniques, Granato *et al. (14)* did not find any significant differences in the chemical markers [benzo(a) pyrene, methanol, 2, 3-methyl-1-butanol, acetaldehyde, isobutyl alcohol, *n*-propanol, density, alcoholic strength and higher alcohols] in Brazilian aged and non-aged commercial *cachaças*. Nevertheless, regarding compounds coming from the wood, the main aging markers of *cachaça* traditionally aged in non-toasted oak casks are gallic acid, syringaldehyde, vanillin and syringic acid *(15)*.

The objective of the present study was to assess how the toasting intensity of oak chips influences the profile of the aging markers in *cachaça*. The influence of the origin of the wood on the chemical composition of aged *cachaça* was also examined.

## Materials and methods

The wort was prepared using sugar cane stalks from variety SP 83-2847. The sugar cane juice was extracted using a stainless steel presser. It then underwent a thermal treatment (105°C) to eliminate contaminating 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 *cachaça* so obtained was stored in a 5 $m^3$ stainless steel container until further use. The oak wood samples, collected from the forests Allier, Vosges and Nièvre, in France, were kindly supplied by Tonnellerie Damy from Burgundy, France. The staves of woods were processed in a knife mill (model 40229, Máquinas Piratininga S.A., São Paulo, SP, Brazil), check screened in a vibrating sieve set (USB Granutest, 35 mm, Telastem, São Paulo, SP, Brazil) at 9 mesh/tyler (8 × 2 inches). The milled woods (chips) were toasted at light (100°C for 60 min), medium (150°C for 60 min) and heavy toasting (180°C for 60 min) in a laboratory oven (model EL 1.6, Odontobrás, Riberão Preto, SP, Brazil) in order to simulate the toasting process employed by the cooper. The toasted chips were added to *cachaça* (40% ABV) in brown glass flasks at a concentration of 1 g/L. The flasks were kept in a closed system at room temperature, without agitation, for 15 days. After this period, the samples were filtered and stored in brown glass flasks until further use. A sample of *cachaça* that did not interact with oak chips was used as the control.

### Gas chromatography with flame ionization detection

The volatile congeners, such as aldehydes, esters, methanol, *sec*-butanol, *n*-butanol and higher alcohols (*n*-propyl, isobutyl and isoamyl), were determined. Aliquots of 1.0 μL were automatically injected into a gas chromatographic system (Shimadzu QP-2010 PLUS) using a flame ionization detector and a Stabilwax-DA column (crossbond carbowax polyethylene glycol, 30 m × 0.18 mm × 0.18 μm film thickness). The analyses were performed at a 1:25 split ratio, in triplicate. Nitrogen was used as the carrier gas, at 31.8 cm/s. 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 *(15)*.

### HPLC

The aging congeners were analysed using high-performance liquid chromatography (HPLC; Shimadzu, model LC-10AD), with two Shimadzu LC-20AD pumps, a UV–vis detector Shimadzu SPD-20A, a system controller CBM-20A and an automated injection system with gradient elution. The standards used in this study were gallic acid, 5-hydroxymethylfurfural, furfural, vanillin, vanillic acid, syringaldehyde, sinapaldehyde, syringic acid and coniferaldehyde, all produced by Sigma-Aldrich (St Louis, MO, USA), purity >99%. The HPLC method employed in this study had two mobile phases composed of water–acetic acid, 98:2 (v/v) and methanol–water–acetic acid, 70:28:2 (v/v/v), total flow of 1.25 mL/min and volume of injection 20 μL. A pre-column Shimadzu VP-ODS (1 cm × 4.6 μm) and a $C_{18}$ reversed-phase column model, Shim-pack VP-ODS (4.6 mm × 25 cm × 5 μm), both thermostatized at 40°C, were used. The UV detector was programmed at variable wavelengths *(15)*. The samples analysed were previously filtered using Millex-HV filter with PVDF membrane (diameter 13 mm, pore size 0.45 μm).

The quantification of the compounds was performed based on external calibration curves of six standard concentration points. The concentration range and correlation coefficients ($a$, $b$, $r^2$), as well as retention indices (RI), detection limit (DL) and quantification limit (QL) of volatile and maturation-related compounds, are shown in Table 1. The DL and QL were calculated based on chromatographs baseline noise *(16)*.

### Statistical analysis

The statistical analyses were performed using analysis of variance (one-way ANOVA) and the Tukey test with an ANOVA $p$-value $< 0.05$ *(17)*.

## Results and discussion

All of the volatile congeners present in samples were within the limits established by the Brazilian Standard of Identity and Quality for *cachaça* (Table 2). The different toasting intensities did not influence the content of the volatile congeners in the *cachaça*

**Table 1.** Retention indices (RI), detection limit (DL) and quantification limit (QL) of volatile, contaminant and maturation-related congeners and concentration range and correlation coefficients ($a$, $b$, $r^2$) of the calibration curves in alcoholic solutions (40% ABV) for quantification of the compounds in *cachaças* matured in toasted oak chips

| Compound | RI (min) | DL (mg/100 mL AE)[a] | QL (mg/100 mL AE) | Concentration range (mg/100mL AE) | $a$ | $b$ | $r^2$ |
|---|---|---|---|---|---|---|---|
| *Volatile congeners* | | | | | | | |
| Acetaldehyde | 0.29 | 0.081 | 0.251 | 7.5–37.5 | 0.8096 | −0.0652 | 0.998 |
| Ethyl acetate | 1.41 | 0.043 | 0.132 | 12.5–62.5 | 0.0372 | 0.0905 | 0.994 |
| *n*-Propyl alcohol | 4.43 | 0.056 | 0.186 | 37.5–187.5 | 0.2317 | 0.0099 | 0.999 |
| Isobutyl alcohol | 5.22 | 0.026 | 0.094 | 12.5–62.5 | 0.0206 | 0.0037 | 0.999 |
| Isoamyl alcohol | 6.72 | 0.017 | 0.041 | 50–250 | 0.1766 | 0.0145 | 0.999 |
| Acetic acid | 9.15 | 0.490 | 1.721 | 37.5–187.5 | 0.6238 | 0.1111 | 0.994 |
| *Contaminant congeners* | | | | | | | |
| Methanol | 1.62 | 0.161 | 0.544 | 5–25 | 0.7847 | 0.0486 | 0.965 |
| *n*-Butyl alcohol | 5.99 | 0.061 | 0.200 | 0.75–3.75 | 0.2036 | 0.1331 | 0.997 |
| *sec*-Butyl alcohol | 4.02 | 0.215 | 0.710 | 2.5–12.5 | 0.2667 | 0.0024 | 0.999 |
| *Maturation congeners* | | | | | | | |
| Gallic acid | 3.98 | 0.031 | 0.096 | 2.5–12.5 | 1821.48 | 55.92 | 0.991 |
| 5-Hydroxymethylfurfural | 9.52 | 0.017 | 0.046 | 2.5–12.5 | 6071.74 | 89.23 | 0.997 |
| Furfural | 11.70 | 0.010 | 0.046 | 2.5–12.5 | 5780.22 | 1,032.35 | 0.997 |
| Coniferaldehyde | 32.39 | 0.022 | 0.066 | 7.5–75 | 4545.65 | 148.97 | 0.998 |
| Vanillin | 24.68 | 0.026 | 0.067 | 2.5–12.5 | 3108.58 | −87.67 | 0.999 |
| Vanillic acid | 21.62 | 0.048 | 0.158 | 5–25 | 1260.59 | 258.17 | 0.998 |
| Synapaldehyde | 33.45 | 0.030 | 0.094 | 5–50 | 3218.26 | 102.24 | 0.993 |
| Syringaldehyde | 26.76 | 0.054 | 0.166 | 5–25 | 1080.26 | 342.27 | 0.994 |
| Syringic acid | 24.20 | 0.029 | 0.096 | 2.5–12.5 | 2429.59 | −104.75 | 0.998 |

[a] AE, Anhydrous ethanol.

matured with toasted oak chips. The contents of *sec*-butanol and *n*-butanol in all of the samples were below the detection limit defined by the method used.

The low-molecular-weight phenolic compounds, considered aging markers and therefore indicators of quality in aged distilled spirits *(18)*, increased significantly following an increase in toasting intensity. The use of higher temperatures in oak wood treatment is associated with a decrease in the production of hemicellulose derivatives and an increase in furfural derivatives, except when the temperature is very high, which can cause polymerization of furfural.

Toasting types and intensities are not standardized and the process depends on the specific techniques used by each cooper. Consequently, when comparing casks from different coopers, this specificity should be taken into account. The intensity of thermal degradation influences the physical characteristics of wood owing to an increase in porosity and surface, and also modifies the chemical characteristics, generating new compounds and making their extraction by the beverage easier. Because of the interaction with the wood, the distilled spirit has its sensory features transformed, increasing the complexity of the aroma *(19)*.

The profile of aging markers in *cachaças* aged by toasted chips from oak coming from the different French forests (Fig. 1) showed that syringic acid, vanillin, syringaldehyde, coniferaldehyde and sinapaldehyde increased in all of the *cachaças* matured in heavily toasted oak chips. However, the toasting intensities of the oak wood did not show significant differences amongst the forests, suggesting that the generation of these compounds was influenced only by toasting intensity and not by the origin of the oak wood. However, variations in flavour and compounds extractable from wood originating from different forests may be relevant to the maturation of alcoholic beverages. Mosedale *et al. (20)* assessed the content of maturation congeners in hydroalcoholic extracts of oak wood from two French forests, Tronçais and Limousin. The thermal treatment of these types of wood permitted differentiation according to the quantity of elagitannins found in the samples. The colour observed for oak wood from Tronçais was lighter than that registered for oak wood from Limousin, and the former also presented a lower content of compounds derived from lignin. Their study showed that different oak woods may influence the content of extractable compounds derived from lignin in a number of ways, even when submitted to identical thermal treatments.

The highest content of gallic acid was observed in the *cachaças* matured in heavily toasted Allier oak chips (0.34 mg/L), medium-toasted Nièvre oak chips (0.32 mg/L) and medium and lightly toasted Allier oak chips (0.29 mg/L and 0.28 mg/L). The lowest content of gallic acid was registered for the *cachaças* matured in Vosges oak chips (Table 3).

The highest content of 5-hydroxymethylfurfural was found in *cachaças* matured in Nièvre and Allier oak chips. Toasting intensity had no influence on this parameter in samples matured in Allier oak chips.

The highest content of furfural was registered for the *cachaças* matured in medium-toasted Allier and Nièvre oak chips. All *cachaças* matured in heavily toasted oak chips presented almost the same content of furfural regardless of the origin of the oak wood. The lowest content of this compound was observed in the *cachaças* matured in Vosges oak chips, regardless of toasting intensity.

**Table 2.** Volatile congeners ± standard deviation in *cachaças* matured in toasted oak chips from different forests (Allier, Vosges and Nièvre, in France) submitted to different toasting intensities (L, light; M, medium; H, heavy)

| Sample | Toast | Volatile congener ± standard deviation (mg/100 mL anhydrous ethanol) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Acetaldehyde | Ethyl acetate | *n*-Propanol | Isobutanol | Isoamyl alcohol | Superior alcohols[a] | Volatile acidity (acetic acid) | Furfural + 5-HMF[b] | Total volatile congeners[c] | Methanol |
| Control | | 13.78 ± 0.67 | 13.20 ± 0.15 | 44.20 ± 7.46 | 64.99 ± 5.57 | 182.18 ± 22.36 | 291.36 ± 35.38 | 45.91 ± 0.80 | <DL[d] | 363.50 ± 32.62 | 1.70 ± 0.19 |
| Allier | L | 13.87 ± 0.13 | 13.83 ± 0.50 | 47.88 ± 2.67 | 62.78 ± 1.81 | 178.74 ± 2.12 | 289.40 ± 5.71 | 45.19 ± 2.02 | 0.34 | 360.79 ± 6.11 | 1.84 ± 0.26 |
| | M | 13.48 ± 0.51 | 12.70 ± 0.81 | 47.81 ± 1.43 | 63.40 ± 1.48 | 176.83 ± 5.41 | 288.04 ± 8.18 | 45.50 ± 1.35 | 0.48 | 360.62 ± 7.63 | 1.58 ± 0.57 |
| | H | 13.46 ± 0.28 | 13.38 ± 0.39 | 46.08 ± 0.70 | 62.81 ± 1.95 | 173.73 ± 5.91 | 282.63 ± 4.16 | 44.15 ± 0.74 | 0.30 | 352.07 ± 4.54 | 1.83 ± 0.14 |
| Vosges | L | 13.19 ± 1.85 | 13.60 ± 2.65 | 45.96 ± 0.53 | 62.74 ± 1.19 | 172.52 ± 1.67 | 281.22 ± 2.58 | 45.97 ± 0.94 | 0.16 | 351.45 ± 3.83 | 1.69 ± 0.17 |
| | M | 13.42 ± 0.07 | 14.60 ± 0.13 | 44.98 ± 0.48 | 64.03 ± 0.94 | 171.33 ± 4.82 | 280.34 ± 3.94 | 47.84 ± 1.38 | 0.16 | 354.40 ± 4.51 | 1.90 ± 0.10 |
| | H | 12.90 ± 0.45 | 14.58 ± 0.25 | 44.67 ± 1.23 | 62.82 ± 1.46 | 173.10 ± 4.13 | 280.59 ± 3.77 | 45.69 ± 0.63 | 0.26 | 352.19 ± 4.42 | 1.81 ± 0.41 |
| Nièvre | L | 13.04 ± 0.57 | 13.98 ± 0.91 | 45.58 ± 2.78 | 62.69 ± 0.72 | 172.54 ± 3.19 | 280.81 ± 6.37 | 45.69 ± 0.60 | 0.26 | 355.82 ± 6.49 | 1.88 ± 0.35 |
| | M | 12.52 ± 1.32 | 13.30 ± 2.47 | 45.46 ± 2.36 | 61.06 ± 2.74 | 171.67 ± 3.45 | 278.19 ± 1.50 | 47.23 ± 0.69 | 0.44 | 349.72 ± 2.63 | 1.98 ± 0.13 |
| | H | 13.27 ± 0.19 | 14.33 ± 0.56 | 47.31 ± 0.68 | 63.04 ± 0.91 | 172.19 ± 3.55 | 282.54 ± 4.68 | 46.80 ± 1.81 | 0.32 | 355.19 ± 2.52 | 2.01 ± 0.13 |

[a] Superior alcohols: *n*-propyl alcohol + isobutyl alcohol + isoamyl alcohol.

[b] Furfural + 5-hydroxymethylfurfural determined by high-performance liquid chromatography (HPLC).

[c] Total volatile congeners: acetaldehyde + ethyl acetate + superior alcohols + volatile acidity + furfural + 5-hydroxymethylfurfural.

[d] DL, Detection limit.

All the results in the same column did not present a difference ($p$-value $\geq 0.05$ according to one-way ANOVA).

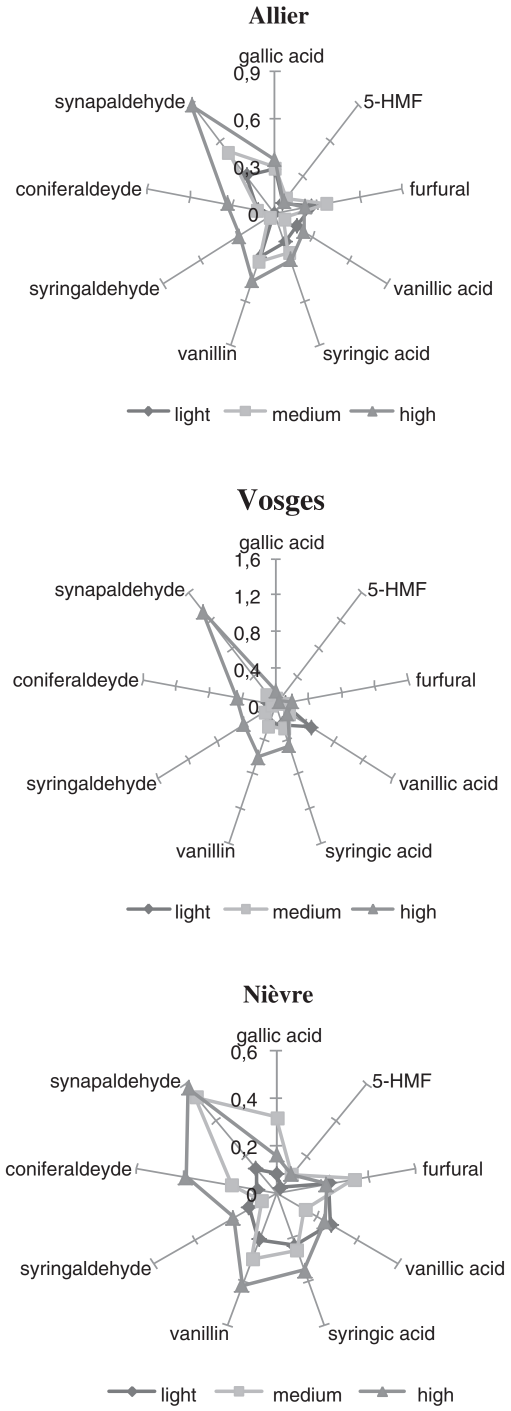

**Figure 1**. Aging marker profiles in *cachaça* matured in toasted oak chips from different forests (Allier, Vosges and Nièvre) that had undergone different toasting intensities (light, medium and heavy).

Heavy toasting was related to an increase in the content of vanillic acid only in the *cachaças* matured in Allier oak chips. In the *cachaças* matured in Vosges and Nièvre oak chips, no difference was observed for this parameter.

Syringic acid was found in the highest levels in the *cachaça* matured in heavily toasted Vosges oak chips (0.47 mg/L). The effect of heavy toast on the content of this compound was important compared with medium and light toasts. In all samples of the *cachaça* matured in medium and lightly toasted oak chips, the content of syringic acid was similar, and those matured in heavily toasted oak chips presented an increase in this compound.

The highest content of vanillin was observed in the *cachaça* matured in heavily toasted Vosges oak chips. All samples of the *cachaça* matured in heavily toasted oak chips presented a significant increase in this compound. Only in the sample of *cachaça* matured in lightly toasted Nièvre oak chips was the content of vanillin lower than that observed for the medium toast. The content of this compound in *cachaça* matured in oak chips of other origins did not present significant differences between a light and medium toast.

Highly toasted Vosges oak chips conferred the highest content of syringaldehyde to *cachaça* (0.43 mg/L). The effect of heavy toast was observed in the samples of *cachaça* matured in Allier and Vosges oak chips, whereas for those matured in Nièvre oak chips, toasting intensity did not cause a statistically significant effect.

The sample of *cachaça* matured in heavily toasted Vosges oak chips presented the highest content of coniferaldehyde. The effect of heavy toast was important in increasing the content of this compound in oak wood of all origins. No difference was observed for the content of coniferaldehyde in the samples of *cachaça* matured in medium and lightly toasted Allier and Vosges oak chips. The content of coniferaldehyde gradually increased in the *cachaças* matured in Nièvre oak chips as toasting intensity increased.

The highest content of sinapaldehyde was also observed in the *cachaça* matured in heavily toasted Vosges oak chips. Heavy toasting increased the content of sinapaldehyde in *cachaças* matured in oak wood from all origins.

Heavy toasting significantly increased the sum of all maturation congeners, principally in the samples of *cachaça* matured in Allier and Vosges oak chips (Fig. 1). The total content of these congeners gradually increased in the *cachaças* matured in heavily toasted Allier oak chips. In the samples of *cachaça* matured in Vosges oak chips, the highest result was registered for heavy toast, although similar results were observed for light and medium toast. The highest content of the maturation congeners in the *cachaças* matured in Nièvre oak chips were found for medium and heavy toast. However, the means of each forest did not show a difference for this parameter.

The highest contents of syringic acid, vanillin, syringaldehyde, coniferaldehyde and sinapaldehyde were registered for the *cachaças* matured in heavily toasted oak chips (Fig. 1), indicating that, the more intense the thermal treatment, the higher the extraction of maturation congeners by the beverage.

According to Hale *et al.* *(21)*, high contents of compounds derived from wood macromolecules are mainly provided by medium toasting. They also reported that high temperatures applied to the wood destroy parts of these compounds, whereas temperatures below 200°C do not cause a great loss. Therefore, it is possible to infer that in their study the medium toast was obtained at temperatures below 200°C. Sarni *et al.* *(22)* observed that in the extracts of French oak matured for 36 months, guaiacyl (G) structures presented lower thermal stability than syringyl (S) structures, and the ratio G:S increased at temperatures below 190°C.

Vanillic acid is normally present in aged alcoholic beverages and is produced by the oxidation of vanillin. Vanillin is formed during toasting as a result of an oxidation process related to

**Table 3.** Aging congeners ± standard deviation in *cachaça* matured in toasted oak chips from different forests (Allier, Vosges and Nièvre, in France) submitted to different toasting intensities (L: light; M: medium; H: high) in comparison to cachaça aged in cask

| Sample | Toast | Aging congeners ± standard deviation (mg/L)[a] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | GA | 5-HMF | F | CN | V | VA | SP | SG | SA | Total[b] |
| Control | | ND[c] | <DL[d] | <DL | ND | ND | ND | ND | ND | ND | <DL |
| Allier | L | 0.28a[e] ± 0.01 | 0.09a ± 0.03 | 0.26b ± 0.02 | 0.12b ± 0.03 | 0.30b ± 0.03 | 0.17ab ± 0.08 | 0.31c ± 0.04 | 0.03b ± 0.01 | 0.20b ± 0.07 | 1.76c |
| | M | 0.29a ± 0.04 | 0.10a ± 0.04 | 0.36a ± 0.03 | 0.13b ± 0.02 | 0.33b ± 0.02 | 0.07b ± 0.04 | 0.51b ± 0.04 | 0.03b ± 0.05 | 0.27ab ± 0.01 | 2.09b |
| | H | 0.34a ± 0.02 | 0.11a ± 0.05 | 0.21c ± 0.01 | 0.34a ± 0.01 | 0.46a ± 0.03 | 0.26a ± 0.09 | 0.90a ± 0.05 | 0.29a ± 0.05 | 0.32a ± 0.01 | 3.23a |
| Vosges | L | 0.07a ± 0.01 | 0.05a ± 0.03 | 0.12b ± 0.02 | 0.10b ± 0.03 | 0.21b ± 0.01 | 0.23a ± 0.04 | 0.10b ± 0.03 | 0.15b ± 0.05 | 0.23b ± 0.04 | 1.26b |
| | M | 0.10a ± 0.03 | 0.05a ± 0.02 | 0.13b ± 0.02 | 0.08b ± 0.04 | 0.25b ± 0.02 | 0.18a ± 0.07 | 0.16b ± 0.02 | 0.14b ± 0.03 | 0.27b ± 0.02 | 1.36b |
| | H | 0.16a ± 0.04 | 0.06a ± 0.02 | 0.20a ± 0.04 | 0.47a ± 0.05 | 0.60a ± 0.03 | 0.17a ± 0.04 | 1.34a ± 0.06 | 0.43a ± 0.04 | 0.47a ± 0.01 | 3.90a |
| Nièvre | L | 0.08b ± 0.03 | 0.03b ± 0.02 | 0.28a ± 0.09 | 0.08c ± 0.02 | 0.21c ± 0.02 | 0.32a ± 0.13 | 0.13b ± 0.01 | 0.13a ± 0.08 | 0.24b ± 0.04 | 1.50b |
| | M | 0.32a ± 0.06 | 0.10a ± 0.03 | 0.34a ± 0.04 | 0.19b ± 0.02 | 0.30b ± 0.05 | 0.24a ± 0.08 | 0.53a ± 0.05 | 0.07a ± 0.02 | 0.26b ± 0.0 | 2.35a |
| | H | 0.16b ± 0.03 | 0.12a ± 0.03 | 0.22a ± 0.07 | 0.39a ± 0.02 | 0.42a ± 0.02 | 0.13a ± 0.03 | 0.58a ± 0.02 | 0.21a ± 0.02 | 0.35a ± 0.02 | 2.58a |
| *Cachaça* aged in oak casks[f] | | 0.32 ± 0.05 | 0.17 ± 0.03 | 0.30 ± 0.05 | 0.23 ± 0.02 | 0.11 ± 0.01 | 0,08 ± 0.01 | 0.60 ± 0.08 | 0.18 ± 0.02 | 0.06 ± 0.00 | 2.05 |

[a] GA, gallic acid; 5-HMF, 5-hydroxymethylfurfural; F, furfural; CN, coniferaldehyde; V, vanillin; VA, vanillic acid; SP, sinapaldehyde; SG, syringaldehyde; SA, syringic acid.

[b] Sum of all aging congeners.

[c] ND, Not determined.

[d] DL, Detection limit.

[e] Different letters in the same column within forest represent statistically different results ($p < 0.05$) according to the Tukey test.

[f] *Cachaça* aged in 220 L European medium-toasted oak casks for 15 days.

toasting intensity. Vanillin and syringaldehyde are the most abundant phenolic aldehydes in the structure of lignin *(22)* and, consequently, more abundant than the other compounds in aged beverages.

In the present study, the most abundant compounds in matured *cachaças*, on average, were sinapaldehyde (0.50 mg/L) and vanillin (0.34 mg/L). Vanillin was always among the most abundant compounds in the *cachaças* matured in all oak chips.

Arapitsas *et al. (11)* studied the differences between aging wine in casks and maturing it in oak chips. They analysed the aromatic compounds vanillin, guaiacol, whisky lactone, eugenol, furfural and syringaldehyde. Their work permitted the distinction between these two methods of beverage maturation. The contents of syringaldehyde, vanillin, guaiacol and furfural were higher in the wine samples matured in oak chips than in the wines aged in casks.

Alcarde *et al. (23)* studied the formation of volatile and maturation-related congeners during aging of sugarcane spirit in non-toasted oak barrels. Aged *cachaça* presented alterations in the levels of ethanol, superior alcohol, acid aldehyde, volatile acidity, ethyl acetate, total volatile congeners, isoamyl alcohol, ethyl carbamate and copper. The aging markers (gallic acid, furfural, 5-HMF, vanillic acid, syringic acid, vanillin, syringaldehyde, sinapaldehyde and coniferaldehyde) were compared with the compounds found in whisky, cognac, armagnac, bourbon and brandy. The authors concluded that monitoring the generation and evolution of congeners during the aging process allowed for the characterization of *cachaça* and the identification of product maturity.

In another study, *cachaça* was aged in casks made of different Brazilian woods and oak for 3 years *(15)*. The profile of maturation compounds characterized aging in each type of wood. The spirit aged in oak casks achieved the highest content of the maturation-related congeners. Some Brazilian woods could be considered similar to oak because they present the highest content of some of the maturation-related compounds, such as vanillin, vanillic acid, syringaldehyde and sinapaldehyde. Although oak wood conferred more chemical complexity to the beverage, Brazilian woods, singly or complementarily, present potential for spirit characterization and for improving the quality of sugar cane spirits.

Aquino *et al. (18)* found the following average content (mg/L) of aging markers in 31 samples of aged *cachaças*: 0.63 for gallic acid; 3.11 for 5-HMF; 1.10 for furfural; 0.51 for coniferaldehyde; 1.32 for vanillin; 0.90 for vanillic acid; 1.47 for sinapaldehyde; 5.24 for syringaldehyde; and 2.10 for syringic acid.

Gallic acid is extracted from wood tannins. Furfural and 5-HMF are extracted from cellulose *(2)*. The concentrations of these compounds in *cachaça* stored in oak casks (200 L) for the same aging period (15 days) were similar to those obtained for *cachaças* in medium-toasted oak chips (Table 3). Nevertheless, for the aging markers extracted from lignin (coniferaldehyde, sinapaldehyde vanillin, syringaldehyde, vanillic acid and syringic acid), compounds that strongly characterize the flavour of aged spirits, their concentrations were lower in the *cachaças* aged in casks than in the *cachaças* aged by chips because of the higher relationship of wood surface/spirit volume provided by the chips.

## Conclusions

More intensive toasting increased the content of the aging markers in *cachaça*, especially syringic acid, vanillin, syringaldehyde, coniferaldehyde and sinapaldehyde. The different origins of oak wood did not cause significant effects when compared, showing that the generation of these compounds was influenced only by toasting intensity and not by the origin of the oak wood.

No alterations in the content of the volatile congeners were observed in the samples. Therefore, the results of the present study support the conclusion that the interaction with oak chips does not influence the content of these compounds.

It should be pointed out that the results could have been different if casks had been used to age the *cachaça* instead of chips. The use of oak barrels would certainly modify the profile of the volatile congeners owing to the oxidation processes allowed by the oxygen transfer from wood. Notwithstanding, the present study provides a scientific basis for the use of chips and toasted barrels for aging *cachaça*.

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