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Kinetics of volatile aromatic compound production during the aging of cachaça in different types of wood

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Abstract

This study evaluated cachaças aged up to 48 months in four types of wood (oak, amburana, balsam, and chestnut), with analyses performed every four months, totaling 48 samples per type of wood. Compounds such as ethyl acetate, ethyl lactate, and aldehydes were identified and quantified by gas chromatography and were kinetically modeled by the Peleg model. The results demonstrated that the model presented an excellent fit to the experimental data ($R^2 > 0.94$), indicating that the production of volatile compounds follows second-order kinetics. The initial production rate was higher in the first 24 months, with stabilization observed after this period. Tropical woods, like amburana, balsam, oak, and chestnut, presented a higher initial production rate than oak, demonstrating a slower but constant evolution throughout aging. Light and volatile compounds, such as acetaldehyde and ethyl acetate, predominated initially, contributing to fresh and fruity aromatic profiles. Compounds with a higher molecular weight, as ethyl palmitate and phenols, became more evident in the final stages and were associated with denser and more complex sensory notes. This study highlights the significant impact of wood type and aging time on the chemical and sensory profile of cachaça, providing valuable information for optimizing the aging process and developing beverages with unique aromatic characteristics.

Keywords: spirit drink; fermentation; maturation.

Practical Application: Helps producers optimize aging processes, enhancing the profile of aromatic compounds and the quality of cachaça.

1 INTRODUCTION

Cachaça is the typical and exclusive name for sugarcane distillates produced in Brazil, which can reach 38–48% alcohol content at 20°C, obtained by distilling the fermented must of sugarcane juice. In 2022, the Brazilian Ministry of Agriculture, Livestock and Food Supply (MAPA) published a series of guidelines to establish limits on a range of components within cachaça (MAPA, 2022). Cachaça is Brazil's second most consumed beverage and the third most economically important globally. Currently, 1.3 billion liters are produced in Brazil (Oliveira & Ferrarezi Junior, 2022), with 7,221,219 liters exported, generating a value of US$ 13,178,050 (MAPA, 2022).

Cachaça production varies according to the region. It is influenced by each producer's cultural knowledge and specific practices, with each producer having a specific form that ranges from slight modifications in the activation of commercial yeasts to artisanal starters composed of indigenous yeasts. However, according to Medeiros et al. (2017), production generally begins with the reception and grinding of sugarcane to extract the juice, which is filtered to remove solids. The juice is then diluted and fermented with yeasts. The fermentation product is distilled and separated into three fractions: head, heart, and tail (Serafim & Lanças, 2019). The heart fraction results in cachaça, and can be stored or aged in wooden barrels to improve its aroma and flavor.

During the fermentation process, in addition to ethanol, different low-boiling compounds are generated, including acetaldehyde, ethyl acetate, and methanol, which are concentrated and separated in the initial phase of distillation (Portugal et al., 2017). The production of ethyl lactate and ethyl acetate in alcoholic beverages can significantly influence their organoleptic characteristics (Buglass, 2010). Acetaldehyde is often confused with ethyl acetate, a volatile acidity component. Ethyl acetate has a fruity aroma at low concentrations, and at high concentrations, it becomes pungent and vinegary, adding complexity to beverages. At low concentrations, it is not considered a defect in beverages until levels become detectable (approximately 100–125 mg/l) (Francis & Newton, 2005).

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Additionally, the generation of these compounds may be related to the presence of bacteria, molds, and yeasts, among which those of the genus *Acetobacter* can be mentioned (Ribéreau-Gayon et al., 2006). Acetic bacteria can also generate acid in the presence of oxygen, esterifying acetic acid and ethanol to form ethyl acetate, which produces unpleasant organoleptic characteristics at high concentrations.

In the context of cachaça, the analysis of ethyl esters in different samples distilled in copper stills, mixed copper/stainless steel stills, or stainless-steel columns revealed that ethyl acetate and ethyl lactate are the most abundant (Nascimento et al., 2008). High levels of ethyl lactate in cachaça, compared to whiskies, were suggested to be a result of more excellent *Lactobacillus* activity during fermentation, which occurs spontaneously at high pH temperatures of approximately 45°C, as opposed to the controlled fermentation by yeast cultures at lower temperatures and controlled pH used in whisky production.

Yeasts, such as *Kloeckera apiculata* and *Metschnikowia pulcherrima*, produce acetic acid, ethyl acetate, and diacetyl (Jackson, 2008). Under oxidative conditions, these yeasts also produce ethanol, glycerol, and organic acids, resulting in volatile compounds such as acetic acid, ethyl acetate, and 2-phenylethanol. Malolactic fermentation can also produce transformation of aroma compounds and reduce astringency by decreasing acidity and accelerating polymerization reactions that soften tannins. Although aldehydes, including acetaldehyde, cause undesirable herbal and vegetal aromas, the presence of specific lactic acid bacteria, like the *Oenococcus oeni*, can catabolize acetaldehyde, converting it to ethanol and acetate, thereby improving product quality (Liu, 2002).

Cachaça aging involves storage in wooden barrels for a period that may vary, influencing the sensory characteristics of the beverage (Bortoletto, 2023). Aging cachaça in wooden barrels improves the overall quality of the product (Lima et al., 2022). Due to their sensory characteristics, oak barrels have been widely used in the aging process of sugarcane spirits. However, in Brazil, many native species of flora have also been used to produce barrels. Barrels of different wood species add various sensory properties to sugarcane spirits (Serafim & Lanças, 2019).

During the aging process, compounds found in the barrel wood migrate to the cachaça, the most relevant being volatile compounds, phenolic compounds, sugars, glycerol, non-volatile organic acids, and tannic substances that modify the flavor, aroma, and color of the drink. The aging process causes a significant increase in the dry extract content of the product due to the migration of non-volatile compounds from the wood to the liquid. Volatile acidity and aldehyde concentration also increase due to ethanol and acetaldehyde oxidation. The esterification of alcohols and acids produces esters responsible for the pleasant odor of aged drinks (Rodrigues et al., 2014).

Despite the growing interest in the quality and production processes of cachaça, few scientific studies have focused on the kinetic analysis of the evolution of volatile compounds during the aging of the beverage. Detailed research on the formation and degradation of compounds such as acetaldehyde, ethyl acetate, and ethyl lactate over time is scarce. However, these compounds play a crucial role in the organoleptic characteristics of cachaça. Understanding the variations in the concentration of these components during aging is essential to optimize the production process and improve the quality of the final product.

The lack of robust kinetic data limits producers' ability to predict and control the sensory profile of aged cachaça. Existing studies focus more on the initial characterization of volatile compounds present in the fresh distillate or after specific aging periods without considering the interactions and transformations that occur over time. In this sense, this article aimed to determine the effect of the aging process of cachaças in different types of wooden barrels (amburana, oak, chestnut, and balsam) on the kinetic profile of volatile compounds produced during storage.

1.1 Relevance of the work

The relevance of this work lies in the exploration of the kinetics involved in the production of volatile aromatic compounds during the aging process of cachaça in various types of wood. By employing mathematical models, it is possible to obtain information about the production and stabilization rates of key compounds, including ethyl acetate, ethyl lactate, and aldehydes, over different time periods. Furthermore, this research highlights the impact of tropical woods and oak on the cachaça aging process.

2 MATERIALS AND METHODS

2.1 Aging of cachaças

Cachaça samples produced by a company from the Alexânia region, Goiás, Brazil, were analyzed after 48 months of aging in amburana (*Amburana cearensis*), oak (*Quercus spp*), Brazil nut (*Bertholletia excelsa*), and balsam (*Myroxylon balsamum*) barrels. The total aging time was 48 months, and physical-chemical analyses were performed every four months (4, 8, 12, 16, 20, 24, 28, 32, 36, 40, 44, 48). All samples evaluated were from four barrels of each type of wood. Thus, the total number of samples to be analyzed is 48 samples per type of wood.

2.2 Determination of esters and aldehydes

The concentrations of aldehydes, ethyl acetate, and ethyl lactate were determined on a gas chromatograph (Shimadzu GC-17A) equipped with automatic injection, flame ionization detector, and a DB-VAX capillary column (30 m × 0.25 mm × 0.25 μm). The samples were analyzed undiluted at an injector temperature of 180°C and detector temperature of 190°C; injection split 1:15; column temperature program of 40°C (4 min), 40–120°C at 32°C/min, and 120–180°C at 25°C/min. The concentrations of the compounds were determined by comparing their areas with those of external standards.

2.3 Kinetic study

The Peleg model was used to study the production process of volatile compounds (aldehydes, ethyl acetate, and ethyl lactate) from distillates during aging according to the methodology reported by Delgado-González et al. (2021). Equation 1 presents Peleg's empirical hyperbolic model (Peleg, 1988) for describing volatile compound production curves:

$$\boldsymbol{Y(t)} = \frac{\boldsymbol{t}}{\boldsymbol{K_1 + K_2 . t}} \quad (1)$$

Where: $Y_{(t)}$ is the concentration of each compound monitored at time t, and K_1 and K_2 are two constants that are related to the initial rate (V_0) and the theoretical yield of the compounds at equilibrium (Y_{eq}) according to Equations 2 and 3:

$$\boldsymbol{V_O} = \frac{\boldsymbol{1}}{\boldsymbol{K_1}} \quad (2)$$

$$\boldsymbol{Y_{eq}} = \frac{\boldsymbol{1}}{\boldsymbol{K_2}} \quad (3)$$

2.4 Volatile aromatic compound analysis

The analysis of volatile aromatic compounds was performed on a Shimadzu Nexis GC2030 gas chromatograph (Kyoto, Japan) coupled to a mass spectrometer with an automatic AOC injector and equipped with an SH-Stabilwax-MS column (30 m × 250 µm × 0.25 µm). The samples were placed in a vial for liquid injection. The oven temperature scale was initially maintained at 40°C for 5 min, then increased to 160°C at a heating rate of 5°C/min until 160°C, and finally increased to 250°C at a rate of 10°C/min, where it remained for 20 min. The analysis time was 55 min. The injection volume was 1 µL in 1:10 split mode, and the helium carrier gas was adjusted to a constant flow rate of 1.56 mL/min and linear velocity of 45.0 cm/s. The injector, interface, and ion source temperatures were maintained at 250°C. Electron ionization was applied at 70 eV, and full-scan spectra were acquired from 40–400 m/z with a scan time of 150 ms and were compared with reference compounds from the NIST 17 library.

2.5 Statistical analysis

The parameters of this study's Peleg model were calculated by adjusting the experimental data through nonlinear regression using the Levenberg-Marquardt method (Marquardt, 1963) and the Statistica 14.0 software. The agreement between the experimental data and the calculated values was assessed using the coefficient of determination (R^2 adj) and the root mean square error (RMSD) as reported by Colivet et al. (2016), according to Equation 4.

$$RMSD = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(experimental - calculated)^2} \quad (4)$$

The analyses of volatile aromatic compounds were performed using Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) through R-Studio software (2024). The data were projected in PCA using linear combinations of the original variables (volatile aromatic compounds), forming the Principal Components (PCs). Score and loading graphs were generated, representing, respectively, the distribution of the samples according to the PCs and the importance of the variables. Based on the median values of each attribute evaluated in gas chromatography, HCA was used to verify the relative similarities between the samples (Euclidean distance). The HCA results were represented in the form of a two-dimensional dendrogram.

3 RESULTS AND DISCUSSION

3.1 Aging kinetics of cachaça

The total aldehyde content was monitored over 48 months in cachaças aged in different types of wood. Figure 1 shows that, regardless of the type of wood, the acetaldehyde content increased significantly in the first 10 months. However, cachaças aged in oak barrels presented lower values. Figure 1A (0–25 months) shows that the aldehyde concentration in balsam wood reached a sharp peak around the first 10 months, and then there was a reduction, while cachaças aged in oak and amburana showed smaller peaks than the other works. Chestnut wood, on the other hand, presented stable and lower concentrations. In Figure 1B (25–48 months), balsam wood revealed the highest concentration values, slightly decreasing over time. Oak and amburana showed a more constant behavior, with slight increases, while chestnut remained at lower levels. This behavior may be associated with the composition of the woods and their ability to interact with beverages during storage.

Valcárcel-Muñoz et al. (2022) determined that the aldehyde content in brandy from Jerez fluctuates during aging in cherry barrels; this behavior is associated with the oxidation of ethanol during storage and the high volatility of the aldehyde. About cachaças, this fluctuation can be observed during the 48 months of storage and is quite pronounced. In this sense, acetaldehyde is formed biologically by yeast metabolism through the decarboxylation of pyruvate (an intermediate of the glycolytic pathway) during the initial phase of alcoholic fermentation and chemically by the oxidation of ethanol by alcohol dehydrogenase (Shin & Lee, 2019).

Figures 1A and B also show that the highest concentration of aldehyde was found in cachaça aged in chestnut barrels, which may be correlated with the strong, astringent flavor of these beverages. Geroyiannaki et al. (2007) reported that acetaldehyde is a potent flavor compound found in many alcoholic beverages and foods, such as apple juice, spirits, and beer.

All aged cachaças showed an exponential increase in ethyl acetate content during the first 24 months, which was more pronounced in cachaças aged in chestnut and oak barrels. However, from month 26 onwards, the ethyl acetate content began to stabilize for cachaças aged in amburana, chestnut, and balsam barrels until month 48, except for those aged in oak, which continued to show an increasing trend in this parameter during storage.

Yu et al. (2023) reported that the amounts of ethyl acetate are closely linked to the flavor and quality of distilled alcoholic beverages. Ethyl acetate is an aromatic component that produces an elegant, smooth, fragrant, and pure flavor, enhancing the liquor's

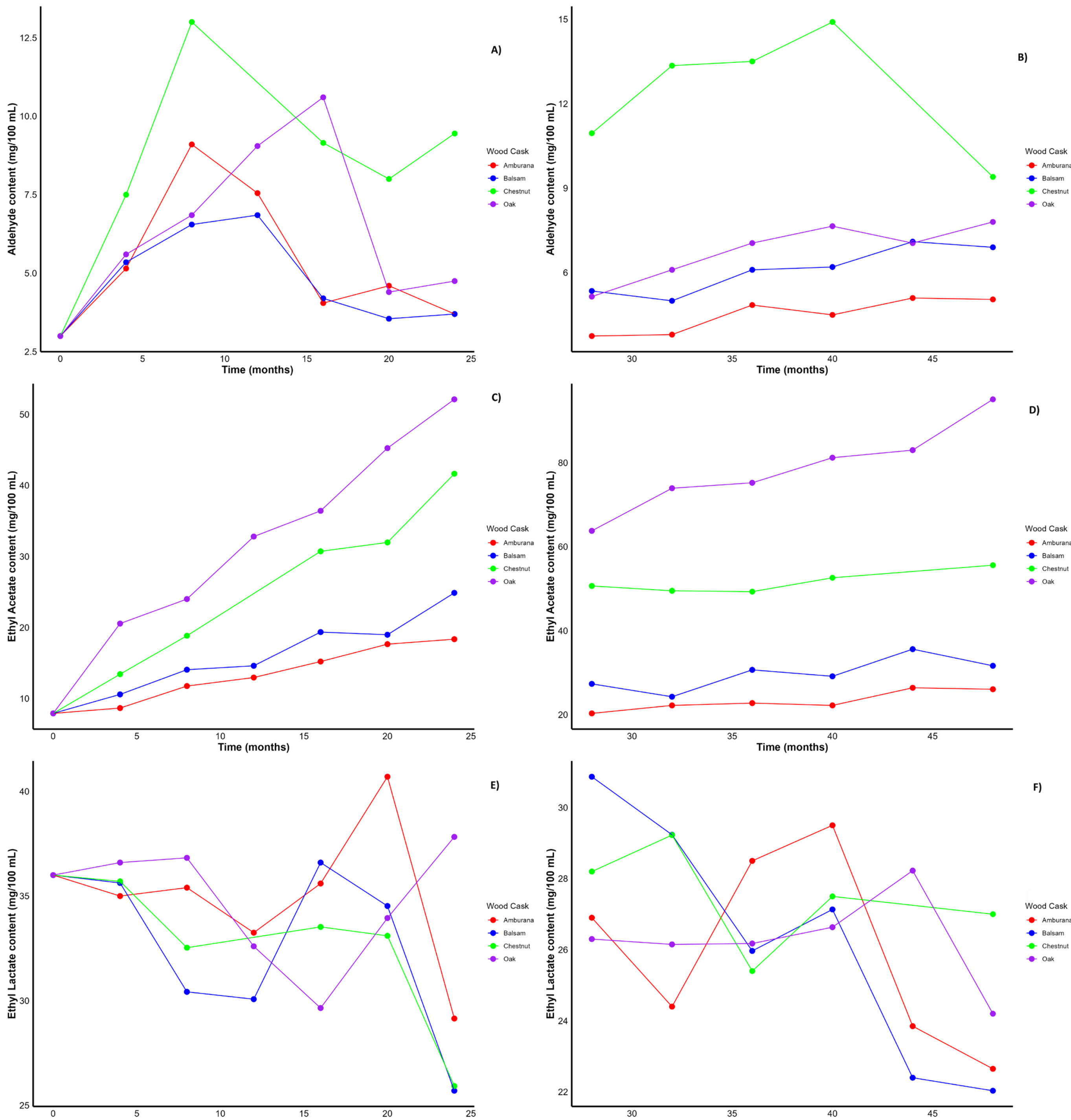

Figure 1. Effect of storage of aged cachaças in different types of wood on the content of aldehydes (**A** and **B**), ethyl acetate (**C** and **D**), and ethyl lactate (**E** and **F**).

aroma and richness. On the other hand, Srdjenović-Čonić et al. (2022) reported that ethyl acetate is commonly found in distilled beverages and can originate from fermentation or be created during barrel aging and that the longer a beverage is aged, the more likely it is to contain ethyl acetate. Ethyl acetate is widely used as a flavor enhancer in distilled beverages due to its floral and fruity flavor (Acosta-Salazar et al., 2021; Srdjenović-Čonić et al., 2022). In this sense, it can be deduced that cachaças aged in chestnut and oak barrels have more fruity flavors than those cachaças aged in other woods.

Concerning the ethyl lactate content, it was observed that regardless of the type of wood used in the aging of the cachaça, there was a reduction during storage, starting with values around 36 mg/L and ending with values below 24 mg/L, except cachaças aged in chestnut barrels, which presented values close to 26 mg/L. This behavior may be associated with the fact that during aging, ethyl lactate is transformed into ethyl acetate (a fact observed in this study). Ethyl acetate, ethyl lactate, and higher alcohols are produced mainly in the initial fermentation phase, and their concentrations increase substantially after distillation (Yu et al., 2023). In this sense, Serafim and Franco (2015) reported that cachaças obtained from natural yeasts presented higher total concentrations of esters, predominating ethyl lactate and ethyl acetate. Ethyl lactate is produced by the esterification between ethanol and lactic acid (Pereira & Rodrigues, 2014). During the aging of distilled beverages, ethyl lactate is one of the first esters to form, reaching a relatively stable level after 6–12 months of storage (Shinohara & Shimizu, 1981). However, this study showed a slight stabilization in the first 24 months, with a substantial decrease at 48 months.

According to Stanojević et al. (2024), high levels of ethyl lactate can be considered responsible for giving distillates a buttery flavor and a rancid butter smell. Its presence is associated with malolactic fermentation and is treated as an indication of deterioration. Thus, in this study, it can be inferred that the aging process contributes to reducing this compound, improving the sensory characteristics of cachaça.

3.2 Mathematical models

The predictive analyses showed that the Peleg model adjusted to the experimental data for all the woods used regarding ethyl acetate and ethyl lactate ($R^2 > 0.94$). However, the adjustment was worse when the aldehyde content was analyzed in the first 24 months. At the same time, when the residual value (RMSD) between the experimental and predicted values was analyzed, relatively low values were also obtained (Table 1).

Regarding the kinetic study of all the compounds (ethyl acetate, ethyl lactate, and aldehyde), it was observed that the production rate (K_1) was higher during the first 24 months compared to the rate of 25–48 months, regardless of the type of wood. This behavior shows that a balance can be achieved from month 24 onwards. In this sense, when comparing the speed of ethyl acetate production, it is clear that cachaças aged in tropical woods (balsam, chestnut, and amburana) presented a higher speed of production of these compounds than cachaça aged in oak barrels in the first 24 months. However, from months 25–48, this speed was similar regardless of the type of wood.

As mentioned, ethyl acetate can be produced by esterifying acetic acid and ethanol. However, this rate of ethyl acetate production does not mean that the content of this compound is higher in cachaças produced with tropical woods, but rather that they may present slower production during maturation and the production rate increases significantly in the subsequent months up to the first 24 months. The constant of the initial production rate (B_0) of ethyl acetate was observed for more exhaustive analyses. In this case, it was found that when the cachaça is stored in oak barrels, production is faster in t→0 months. Furthermore, after 25 months of aging, the B_0 values were relatively equal, slightly higher in cachaças aged in balsam and oak barrels. At the same time, when interpreting the ethyl

Table 1. Peleg model parameters for different woods used in the aging of cachaça over 48 months.

Wook cask	Compounds	Time (months)	K_1 (months 100 mL/mg	K_2 (months 100 mL/mg	B_0	C_{sp} (mg/100mL)	R^2	RMSD
Amburana	Ethyl acetate	0–24	0.381	0.040	2.621	25.156	0.945	3.239
	Ethyl acetate	25–48	0.861	0.003	1.161	301.130	0.931	9.853
	Ethyl lactate	0–24	0.032	0.036	31.210	27.469	0.685	21.064
	Ethyl lactate	25–48	0.167	0.032	5.980	30.834	0.996	1.905
	Aldehydes	0–24	0.362	0.087	2.765	11.390	0.910	2.000
	Aldehydes	25–48	3.892	0.118	0.256	8.460	0.977	0.699
Chestnut	Ethyl acetate	0–24	0.381	0.007	2.627	140.845	0.829	12.430
	Ethyl acetate	25–48	0.099	0.016	10.093	60.076	0.990	5.739
	Ethyl lactate	0–24	0.001	0.028	725.240	35.445	0.714	0.685
	Ethyl lactate	25–48	−0.139	0.039	−7.194	25.090	0.991	2.856
	Aldehydes	0–24	0.361	0.087	2.765	11.390	0.910	2.009
	Aldehydes	25–48	0.122	0.078	8.171	12.792	0.979	1.967
Balsam	Ethyl acetate	0–24	0.350	0.030	2.864	33.618	0.951	3.874
	Ethyl acetate	25–48	0.567	0.018	1.762	53.669	0.985	3.878
	Ethyl lactate	0–24	0.038	0.037	26.315	27.027	0.684	21.036
	Ethyl lactate	25–48	−0.674	0.056	−1.482	17.782	0.998	1.538
	Aldehydes	0–24	0.283	0.117	3.528	8.486	0.897	1.896
	Aldehydes	25–48	4.076	0.065	0.245	15.474	0.980	0.857
Oak	Ethyl acetate	0–24	0.212	0.012	4.711	83.975	0.820	5.670
	Ethyl acetate	25–48	0.238	0.007	4.193	14.832	0.980	10.920
	Ethyl lactate	0–24	0.001	0.027	74.877	37.052	0.734	20.801
	Ethyl lactate	25–48	−0.082	0.041	−12.206	24.447	0.990	2.779
	Aldehydes	0–24	0.088	0.161	11.289	6.198	0.815	2.531
	Aldehydes	25–48	5.319	0.000	0.188	32.761	0.986	0.795

K1: constant of the Peleg model; K2: constant capacity of the Peleg model; B_0: initial production rate; C_{sp}: production capacity; R2: coefficient of determination; RMSD: root mean square error.

acetate production capacity (C_{sp}) in different types of wood, it is evident that regardless of the type of wood, there was an increase in the ethyl acetate production capacity except for chestnut wood, which obtained lower values after 25 months of aging.

Regarding the kinetic parameters obtained for ethyl lactate, it was observed that B_0 was higher in cachaças aged in oak and chestnut barrels than those aged in amburana during the 48 months of maturation. At the same time, it is evident that there is a significant reduction in B_0 values after 24 months of aging, with the same behavior found in the production capacity (C_{sp}). However, for these parameters, the Peleg model presented the worst fit. The kinetic parameters B_0 and C_{sp} for aldehydes also decreased from month 25 onwards, which may be associated with the degradation and/or transformation of different compounds during aging.

3.3 Volatile aromatic compounds

Table 2 presents a profile of the volatile aromatic compounds found in cachaças aged in different types of wood, revealing heterogeneous volatile compounds that may contribute to the aromatic profile of the beverages. More volatile compounds, such as acetaldehyde and ethyl acetate, have low molecular weights and are associated with pungent, ethereal, and sweet aromas (Nóbrega, 2003). In contrast, less volatile compounds like ethyl palmitate and caprylic acid have higher molecular weights and retention times more significant than 32 minutes, with denser and waxy odors (Zheng et al., 2014). According to Lončarić et al. (2022), ethyl palmitate in brandy-type beverages is common in distilled beverages, reflected in the aromatic compound profile of these beverages. On the other hand, Guerrero-Chanivet et al. (2020) indicate that compounds such as caprylic acid and ethyl palmitate are naturally present in wood, which, during the aging process, can cause migration and contribute to the aromatic profile of this type of beverage.

The aromatic compounds of beverages range from compounds related to alcoholic and floral odors, such as phenylethyl alcohol, to aromatic compounds related to medicinal and smoky aromas, as phenol. Woody and fresh profiles are represented by compounds like nerolidol and farnesol. Slaghenaufi & Ugliano (2018) reported having found these compounds during the aging of wine in different types of wood. They can contribute to the sensory profile of these beverages, increasing significantly during storage. In addition, compounds such as acetic acid also present acidic notes, while 2,3-butanediol offers a sweet, buttery aroma. According to Alvarenga et al. (2023), acetic acid may be associated with acetic bacteria during the fermentation process, directly impacting the quality of cachaça.

3.3.1 Principal component analysis and hierarchical cluster analysis

HCA was performed using the squared cluster linkage method. Euclidean distance was applied to measure the cluster homogeneity among the aged cachaça samples based on different storage times (Figure 2). A heatmap was also created using the merged volatile aromatic compound profile dataset. The clustering results were similar to those observed in the

Table 2. Profile of the main volatile aromatic compounds of cachaças aged in different types of wood.

Compound code	Compound name	IUPAC name	MW (g/mol)	Retention time (min)	Odor
C1	Acetaldehyde	Acetaldehyde	44.05	1.42	Pungent, Ethereal
C2	Ethyl Acetate	Ethyl Acetate	88.11	2.19	Fruity, Sweet
C3	Propanol	propan-1-ol	60.1	4.92	Alcoholic, Slightly Sweet
C4	Isobutanol	2-methylpropan-1-ol	74.12	6.81	Whiskey-like, Pungent
C5	Isoamyl alcohol	3-methylbutan-1-ol	88.15	10.43	Fusel Oil, Fruity
C6	Ethyl lactate	ethyl 2-hydroxypropanoat	118.13	14.25	Sweet, Fruity
C7	Decanoic acid, ethyl ester	ethyl decanoate	200.32	21.65	Floral, Sweet
C8	Phenylethyl alcohol	2-phenylethanol	122.16	27.72	Rose, Floral
C9	Ethyl palmitate	ethyl hexadecanoate	284.5	32.46	Waxy, fatty, and slightly fruity odor.
C10	Acetic acid	Acetic acid	60.05	17.28	Acid, vinegar
C11	o-Coumaric acid	(E)-3-(2-hydroxyphenyl) prop-2-enoic acid	164.16	34.14	Mild, sweet, and slightly balsamic odor
C12	2,3-Butanediol	(2R,3R)-butane-2,3-diol	90.12	19.78	Sweet, Buttery
C13	Phenol	Phenol	94.11	29.64	Medicinal, Smoky
C14	Guaiacol	2-methoxyphenol	124.14	26.71	Spicy, Sweet
C15	Capric acid	decanoic acid	172.26	32.60	Waxy, Fatty
C16	Hydrocoumarin	3,4-dihydrochromen-2-one	148.16	32.73	Sweet, Hay-like
C17	2-Butanol	butan-2-ol	74.12	45.21	Slightly Alcoholic
C18	Farnesol	(2E,6E)-3,7,11-trimethyldodeca-2,6,10-trien-1-ol	222.37	31.30	Woody, Floral
C19	Catechol	benzene-1,2-diol	110.11	35.59	Phenolic, Medicinal
C20	Nerolidol	(6E)-3,7,11-trimethyldodeca-1,6,10-trien-3-ol	222.37	28.93	Woody, Fresh
C21	Glycerin	propane-1,2,3-triol	92.09	32.96	Odorless

IUPAC: International Union of Pure and Applied Chemistry; MW: molecular weight.

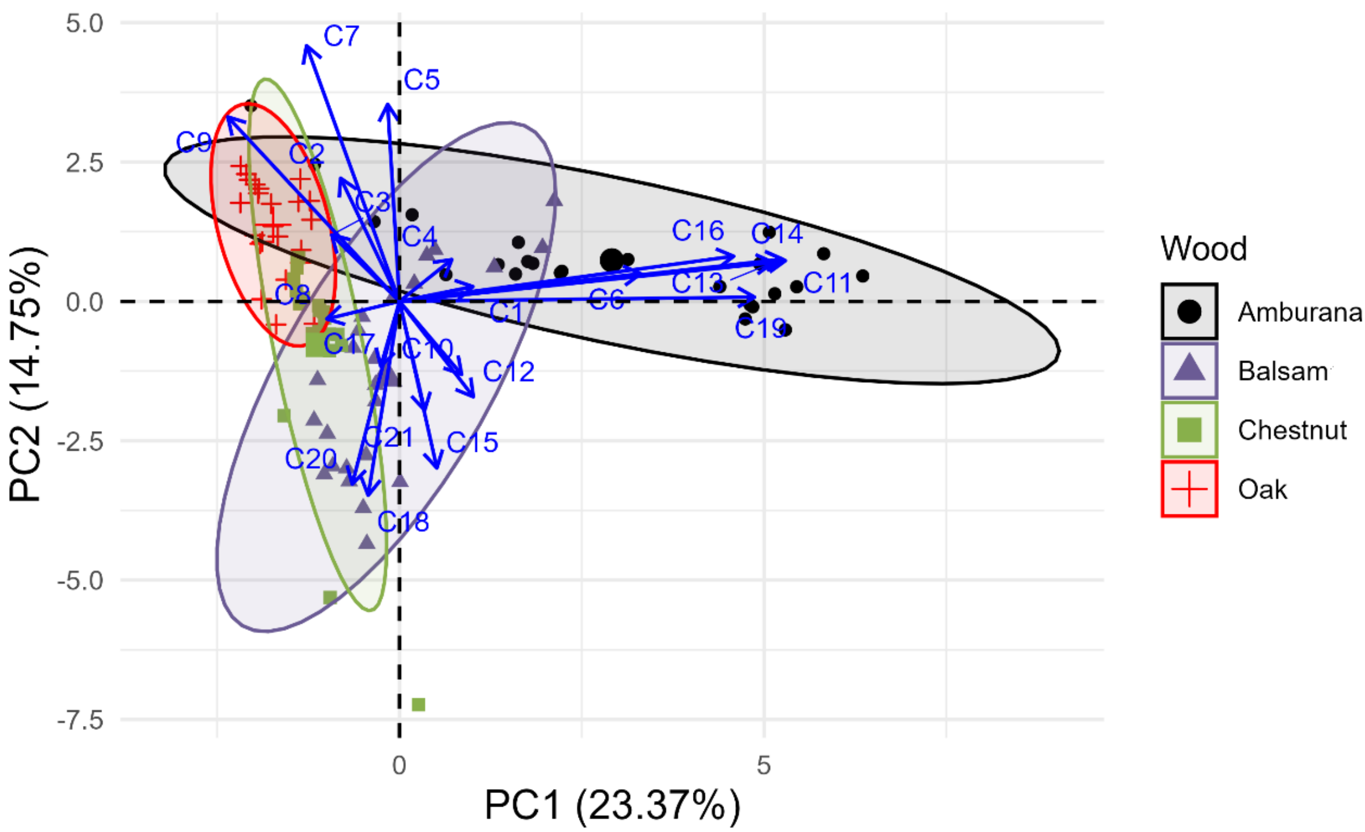

Figure 2. Principal component analysis of aromatic compounds found in cachaças aged in different types of wood.

PCA biplot plotted in Figure 2. As shown in the figure, all the samples were grouped into different clusters, indicating notable differences among the cachaça samples at different aging times.

Figure 2 presents a PCA of the volatile compounds found in cachaças aged in different types of wood, highlighting clusters formed based on their chemical and sensory characteristics. The various clusters are represented by colored ellipses, indicating groups of compounds that share similar properties. The principal axes (PC1 and PC2) explain most of the variability in the data. The blue vectors indicate the contribution and direction of each compound to the analyzed components. The red cluster, located on the left, includes compounds such as decanoic acid, ethyl ester (C7), phenylethyl alcohol (C8), and ethyl palmitate (C9), which have floral and waxy characteristics. In the lower center, the green cluster comprises substances like nerolidol (C20) and 2-butanol (C17), associated with woody and alcoholic notes.

The purple cluster on the right includes compounds such as phenol (C13), guaiacol (C14), and catechol (C19) related to phenolic and medicinal aromas. The vectors indicate the magnitude and direction of the compounds' influence on the main components. In this sense, ethyl palmitate (C9) strongly contributes to the PC1 axis, while phenol (C13) significantly influences the PC2 axis.

The red cluster, located on the left, includes compounds such as decanoic acid, ethyl ester (C7), phenylethyl alcohol (C8), and ethyl palmitate (C9), which have floral and waxy characteristics. In the lower center, the green cluster is composed of substances like nerolidol (C20) and 2-butanol (C17), associated with woody and alcoholic notes. On the other hand, the purple cluster on the right includes compounds such as phenol (C13), guaiacol (C14), and catechol (C19), which are known for their phenolic and medicinal aromas.

The heat map illustrates the HCA of volatile compounds identified during the aging of cachaça in different types of wood stored for 48 months (Figure 3). The compounds from C1 to C21 are represented on the horizontal axis, while the storage times are displayed on the vertical axis. The color scale ranges from blue (low intensity) to red (high intensity), relating them to variations in chemical profiles.

The dendrograms show the formation of clusters for the compounds and aging times. Compounds including phenylethyl alcohol (C8), 2-butanol (C17), and phenol (C13) exhibit higher intensities in the early stages of aging, highlighting their initial sensory contribution. On the other hand, compounds such as ethyl lactate (C6), ethyl palmitate (C9), and decanoic acid, ethyl ester (C7) show higher intensity in the intermediate and final stages, indicating a more relevant role in the advanced phase of maturation. Compounds like acetaldehyde (C1) and farnesol (C18) have intensity patterns that vary over time, while others, such as 2,3-butanediol (C12) and acetic acid (C10), show low contribution in specific periods. This map enhances the dynamics of chemical and sensory evolution throughout the aging of cachaça in balsam, emphasizing the influence of this wood on the development of the volatile compound profile.

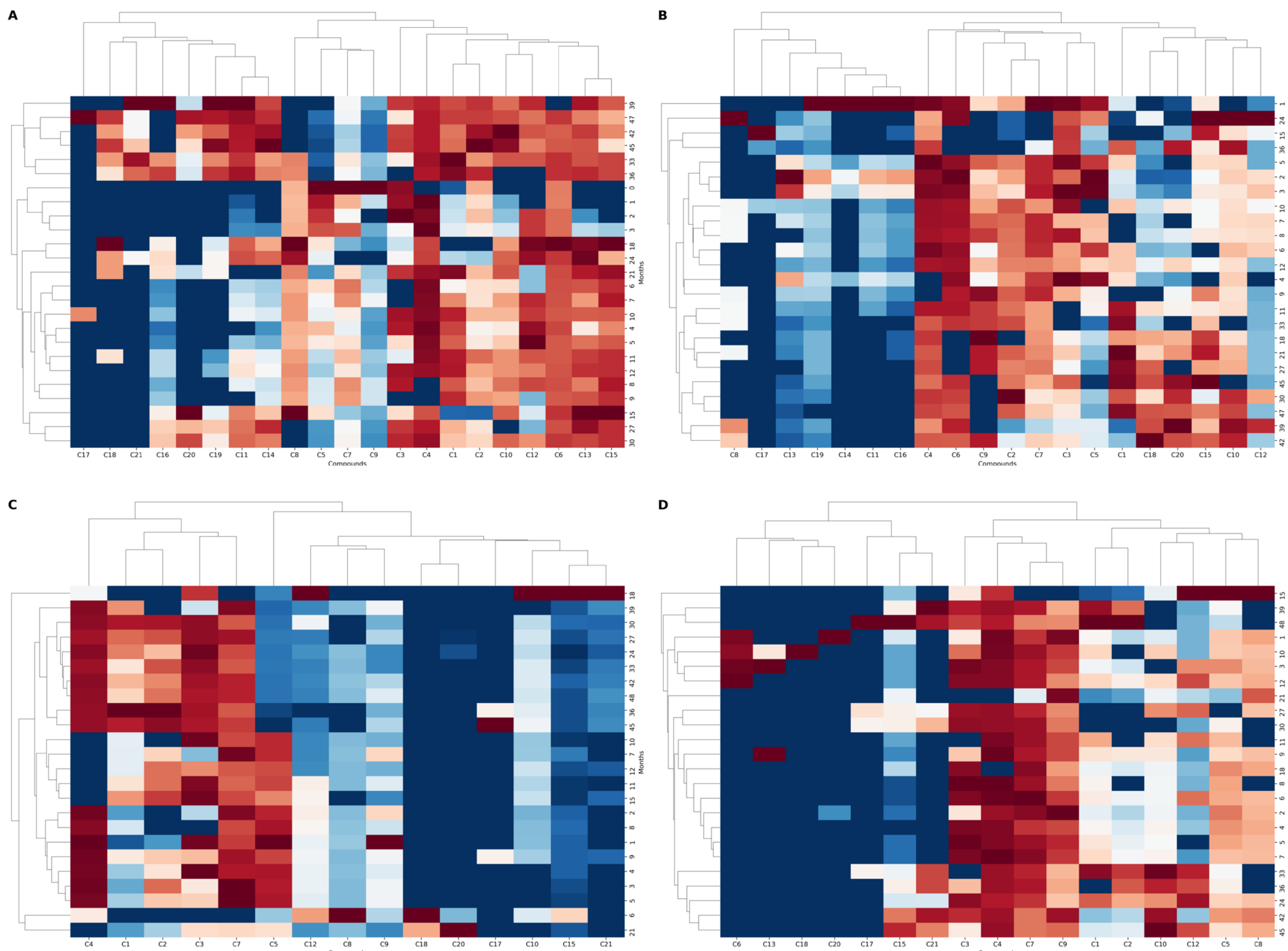

Figure 3. Clustered heatmap of volatile compounds in aged cachaça: amburana **(A)**, balsam **(B)**, chestnut **(C)**, and oak **(D)**.

Compounds with lower molecular weights, such as acetaldehyde (C1), ethyl acetate (C2), and propanol (C3), predominate in the initial stages in all woods due to their high volatility. As aging time progresses, compounds with higher molecular weights, as the phenylethyl alcohol (C8), ethyl palmitate (C9), and decanoic acid, ethyl ester (C7), become more intense, indicating a gradual release or formation during interaction with the wood.

Phenolic compounds, such as phenol (C13) and guaiacol (C14), are more evident in woods like oak and balsam, suggesting a typical sensory contribution of smoky and medicinal notes in these woods. Floral and waxy compounds, like phenylethyl alcohol (C8) and ethyl palmitate (C9), appear more prominently in amburana and chestnut in advanced stages, indicating an association with the sensory profile of these woods. In the first 6 months, light and volatile compounds like acetaldehyde (C1), ethyl acetate (C2), and propanol (C3) predominate, contributing to a fresh and fruity sensory profile. This pattern is consistent in all woods. In the intermediate stages (6–24 months), compounds such as ethyl lactate (C6) and decanoic acid, ethyl ester (C7) become more present, marking the transition to a more complex and floral profile. In the advanced stages (24–48 months), compounds with higher molecular weight predominate, including ethyl palmitate (C9) and phenylethyl alcohol (C8), indicating greater sensory maturity, with dense and complex notes. Phenolic compounds are also more noticeable at this stage, especially in woods like oak and balsam.

4 CONCLUSION

This study demonstrated that the types of wood significantly influence the aging process of cachaça. Peleg's kinetic model showed good adjustment to the production of compounds such as ethyl acetate, ethyl lactate, and aldehydes. Tropical woods, like amburana, balsam, and chestnut, showed a higher initial speed of production of these compounds in the first 24 months, while oak showed a slower stabilization pattern.

Low molecular weight compounds predominated in the initial stages of aging, while higher molecular weight compounds associated with more complex sensory profiles stood out in the advanced stages.

The results of this study provide a basis for carrying out processes to optimize the aging of cachaça and open new horizons in the use of other tropical woods in the aging of these products.

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