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Comparison and Quantification of the Development of Phenolic Compounds during the Aging of Cachaça in Oak (*Quercus* sp) and Amburana (*Amburana cearensis*) Barrels

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Abstract

Aging is a stage of the cachaça production process in which several chemical reactions occur between compounds extracted from the wood and other compounds present on the beverage. In an attempt to establish a profile regarding the chemical characterization of aged cachaças, phenolic compounds have been studied because of the specific characteristics of each wood species and their known antioxidant properties. This work sought to assess and compare the development of 12 phenolic compounds in cachaças aged in oak (*Quercus* sp) and amburana (*Amburana cearenses*) barrels during a period of 12 months. There was a progressive increase in the concentration of phenolic compounds in the beverage for both of the types of wood. The principal compounds encountered in the cachaça aged in oak barrels were gallic acid, syringaldehyde and syringic acid, while vanillic acid, syringaldehyde, sinapic acid and gallic acid were isolated from that aged in amburana barrels.

Keywords

Beverage, Aging, Phenolic Compounds, Liquid Chromatography

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1. Introduction

Aging of alcoholic beverages is a common practice among producers that try to increase the value to their products, making them more competitive in the market [1]. Aging is responsible for improving organoleptic characteristics of cachaça, making its flavor more pleasant and mild. Some substances from the wood are incorporated into the beverage during aging [2]. In Brazil, most of the cachaça producers are small-scale producers, and a great variety of wood species may be used for aging [3].

Although oak (*Quercus* sp) is the wood traditionally used for aging alcoholic beverages, several other types of native Brazilian wood species have been employed in the manufacture of barrels for aging cachaça, such as peanut (*Plerogyne nitens*), amburana (*Amburana cearensis*), cedar (*Cedrela fissilis*), jatobá (*Hymenaeae carbouril*), ipê (*Tabebuia* sp), freijó (*Cordia goeldiana*), garapa (*Apuleia leiocarpa*), balm (*Myroxylon peruiferum*), yellow mahogany (*Plathynemia foliosa*) and jequitibá (*Carinian legalis*) [4]. This practice has developed because of the high cost of oak, which is a wood typical of the Northern hemisphere [3] [5] [6].

Among the several types of native Brazilian wood species, a species that has been studied with respect to the aging of cachaça is amburana (*Amburana cearensis*), which belongs to the Leguminoseae Papilonoideae (Fabaceae) family and is commonly known as amburana, imburana-de-cheiro and cumaru [7]. Although it is considered to be a native of the northeastern backlands, the occurrence of *A. cearenses* may be observed in nearly all of South America (from Peru to Argentina). It is a leafy tree that may attain a height of 15 m, with white flowers, flattened pod and brownish-red bark. It has a pleasant odor that is conferred by the presence of coumarins [8].

The main reactions that occur during the aging process are reactions among secondary compounds obtained from distillation, direct extraction of wood components, decomposition of the wood macromolecules (cellulose, hemicellulose and lignin) and the subsequent incorporation of these compounds into the beverage. Furthermore, reactions may occur among the wood compounds and the original compounds of the distilled beverage [9] [10].

The main compounds extracted from wood by the distillates are volatile oils, phenolic compounds, tannic substances, sugars, glycerol and non-volatile organic acids. Among them, the importance of studying phenolic compounds in aged cachaças because of the value of antioxidant compounds for human health should be highlighted [11] [12].

Several studies have assessed the chemical and sensorial quality of aged beverages. Many aldehydes and phenolic acids have been found in distilled alcoholic beverages aged in oak barrels, such as vanillin, syringaldehyde, coniferaldehyde and sinapaldehyde, which were apparently formed by the acid alcoholysis of lignin. Other phenolic acids that have been identified are gallic acid, *p*-hydroxybenzoic acid, *p*-coumaric acid, cinnamic acid, vanillic acid and syringic acid [13].

High-performance liquid chromatography with UV-Vis detectors is widely cited in the literature for the detection of phenolic compounds in beverages [14]-[17]. In addition to HPLC, other techniques are used, such as gas chromatography, capillary electrophoresis (CE), ultraviolet detection, electrochemistry, and fluorescent and mass spectrometries [18]. This work sought to compare the development of 12 phenolic compounds in cachaças aged during a period of 12 months in oak (*Quercus* sp) and amburana (*Amburana cearensis*) barrels using HPLC with UV-Vis detection.

2. Material and Methods

2.1. Sample Collection

The samples were produced in a commercial alembic located in the municipality of Perdões, Minas Gerais, Brazil during the harvest of 2011. Distillation was performed in a copper alembic. The cachaça was aged in oak (*Quercus* sp) and amburana (*Amburana cearensis*) barrels, both having a capacity of 200 L, and 130 L of beverage was stored in each barrel. The barrels were kept in closed sheds with controlled temperature and air humidity. They were positioned horizontally to provide a greater contact between the beverage and the wood, and the barrels were distanced from one another to avoid gas exchange. Two-liter aliquots were collected each month during 12 months and sent for the analyses of phenolic compounds. The analyses were performed at the Laboratório de Qualidade de Aguardentes, Departamento de Química (DQI), Universidade Federal de Lavras (UFLA).

2.2. Chromatographic Analysis

Chromatographic analyses were performed on a Shimadzu HPLC equipped with two model SPD-M20A high-

pressure pumps, a model DGU-20A3 degasser, a model CBM-20A interface, a model SIL-10AF automatic injector and a diode array detector (DAD). The column employed was an Agilent-Zorbax Eclipse XDB-C18 (4.6 × 250 mm, 5 µm) connected to an Agilent-Zorbax Eclipse XDB-C18 4-Pack (4.6 × 12.5 mm, 5 µm) pre-column.

The 12 phenolic compounds in cachaças aged in oak and amburana barrels were analyzed according to the method proposed by Anjos [2]. The phenolic compounds were gallic acid, catechin, vanillic acid, phenol, syringic acid, vanillin, syringaldehyde, *p*-coumaric acid, sinapic acid, coumarin, 4-methylumbelliferone and *o*-coumaric acid. The standards for these compounds were acquired from Sigma-Aldrich or Acros Organics. The solvents employed in the mobile phase were HPLC grade: methanol (Merck) and glacial acetic acid (J. T. Baker) and water type I obtained from a Milli-Q system.

External standardization was used for quantification. To construct the analytical curves, dilutions were performed with an intermediate solution containing a mixture of all the standards, which was obtained by means of the dilution of previously prepared stock solutions. This intermediate solution contained the following concentrations of the standards: gallic acid (6.80 mg·L^{-1}), catechin (11.61 mg·L^{-1}), vanillic acid (6.73 mg·L^{-1}), phenol (3.76 mg·L^{-1}), syringic acid (7.93 mg·L^{-1}), vanillin (6.08 mg·L^{-1}), syringaldehyde (7.29 mg·L^{-1}), *p*-coumaric acid (6.56 mg·L^{-1}), sinapic acid (8.97 mg·L^{-1}), coumarin (5.85 mg·L^{-1}), 4-methylumbelliferone (7.05 mg·L^{-1}) and *o*-coumaric acid (6.56 mg·L^{-1}).

The solutions of 2% acetic acid in water (Solvent A) and methanol: water: acetic acid (70:28:2% v/v) (Solvent B) were used as the mobile phase for eluting the compounds. Samples and standards were eluted using the following gradients: from 0 to 25 min (0% - 40% B); 25 - 40 min (40% - 55% B); 40 - 50 min (55% - 100% B); 50 - 60 min (100% - 0% B). The wavelength employed was 280 nm, the flow rate was 0.8 mg·L^{-1}, and the volume injected was 20 µL.

Samples and standards were filtered through a 0.45-µm polyethylene membrane (Millipore) and injected directly into the chromatographic system. Injections of standards and samples were performed in triplicates. The identities of the analytes were confirmed using the retention times, and the profiles of sample peaks were compared with those of the standards.

To guarantee the analytical quality of the results, procedures were performed to validate the method, which was assessed according to the following parameters: selectivity, linearity, limit of detection, limit of quantification and accuracy [2]-[19]. The selectivity was determined through the use of a fresh cachaça (without contact with wood). Initially, an analysis of this cachaça, to which the standards were added, was performed. The mathematical relationship between the sign and the concentration of the species of interest was expressed by means of the line equations (analytical curves) and their respective determination coefficients (R^2).

The limits of detection and quantification of the methods were estimated using the parameters of the analytical curve according to the mathematical equations: LD = 3 × (s/S) and LQ = 10 × (s/S), in which s is the estimate of the standard deviation of the equation for the regression line, and S is the angular coefficient of the analytical curve. The accuracy was assessed by means of recovery assays using three randomly chosen samples that were fortified with analyte standards at three different concentrations. The recovery was determined by considering the results obtained for each analyte using the following mathematical equation: %Recovery = [(measured concentration)/(expected concentration)] × 100 [19].

2.3. Statistical Analysis

A completely randomized design (CRD) was used in a scheme of fractions subdivided in the space. The data were submitted to analysis of variance, and the means were compared by the Scott-Knott test at 95% of confidence using the statistical software SISVAR [20]. A principal component analysis (PCA) was performed to verify possible similarities between the types of wood with respect to the concentrations of phenolic compounds. Results were centered on the mean for posterior analysis, which was accomplished using the CHEMOFACE software [21].

3. Results and Discussion

The chromatogram of the standard solution of the 12 phenolic compounds obtained through spectrophotometric detection after analysis of 20 µL by HPLC is presented in **Figure 1**. The compounds were well separated under the chromatographic conditions employed.

The mean retention time observed for each compound was: 1) gallic acid (8.754 ± 0.433 min); 2) catechin
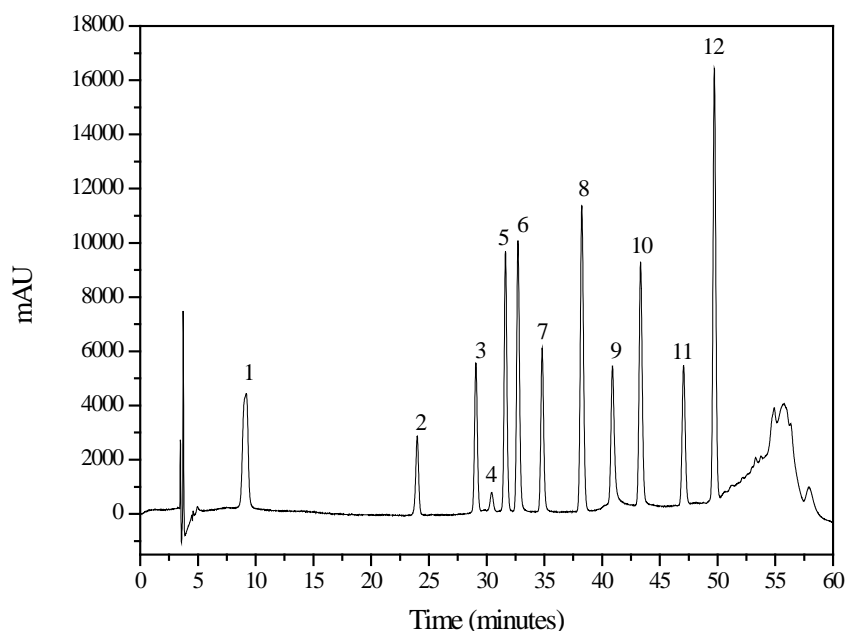
Figure 1. Chromatogram of the standard solution of phenolic compounds with spectrophotometric detection. Concentration of each standard: 1.161×10^{-5} mg·L^{-1}.

(23.961 ± 0.107 min); 3) vanillic acid (29.021 ± 0.119 min); 4) phenol (29.607 ± 0.457 min); 5) syringic acid (31.571 ± 0.105 min); 6) vanillin (32.647 ± 0.104 min); 7) syringaldehyde (34.721 ± 0.135 min); 8) *p*-coumaric acid (38.085 ± 0.349 min); 9) sinapic acid (40.743 ± 0.212 min); 10) coumarin (42.294 ± 0.962 min); 11) 4-methylumbelliferone (46.843 ± 0.126 min); and 12) *o*-coumaric acid (49.501 ± 0.128 min), values that corroborate with those found by Anjos [2]. In the end of the run, an increase was observed in the base line that may be explained by the presence of oligomers and polymers. In the literature, studies that correlate the phenol contents with the use of reversed-phase liquid chromatography relate that the presence of many oligomers and polymers of flavan-3-ol results in alterations in the base line of the chromatograms [22] [23].

The selectivity of the methods employed was assessed through the comparison between the matrix lacking the substances of interest (phenolic compounds) and the matrix with the analyte standards (**Figure 2**). A positive selectivity was observed, because the chromatogram presented a satisfactory separation of the compounds.

The correlation coefficients ranged from 0.9994 to 0.9999, thus showing a strong linear correlation between the concentrations of the analyzed compounds and the area of the peaks, as recommended in the literature [24] [25]. The correlation coefficients, limits of detection and limits of quantification obtained are presented on **Table 1**.

The limits of detection and quantification found for the phenolic compounds ranged from 0.025 to 0.057 mg·L^{-1} and from 0.084 to 0.190 mg·L^{-1}, respectively. These values were inferior to those found by Aquino and Santiago [6]-[17], and were close to those obtained by Anjos and Zacaroni [2]-[13]. Anjos [2] found values between 0.016 and 0.131 mg·L^{-1} and ranging from 0.055 to 0.437 mg·L^{-1} for the limits of detection and quantification, respectively. Santiago [17] found limits of detection and quantification ranging from 0.031 to 0.168 mg·L^{-1} and 0.104 to 0.677 mg·L^{-1}, respectively.

The method employed for the analysis of phenolic compounds in cachaça aged in wood barrels was shown to be highly sensitive. The differences may be explained by differences in chromatographic conditions, such as the equipment and/or methods adopted for quantifying the compounds [19]-[26].

The accuracy of the analytical method was assessed by means of recovery assays in which the concentration of phenolic compounds was calculated through the increase of peak areas obtained after the addition of a known amount of standard to three randomly chosen samples [2]. The mean results for the percentage of recovery were 92% for gallic acid, 82% for catechin, 95% for vanillic acid, 90% for phenol, 92% for syringic acid, 96% for vanillin, 93% for syringaldehyde, 94% for *p*-coumaric acid, 91% for sinapic acid, 95% for coumarin, 96% for 4-methylumbelliferone and 86% for *o*-coumaric acid.
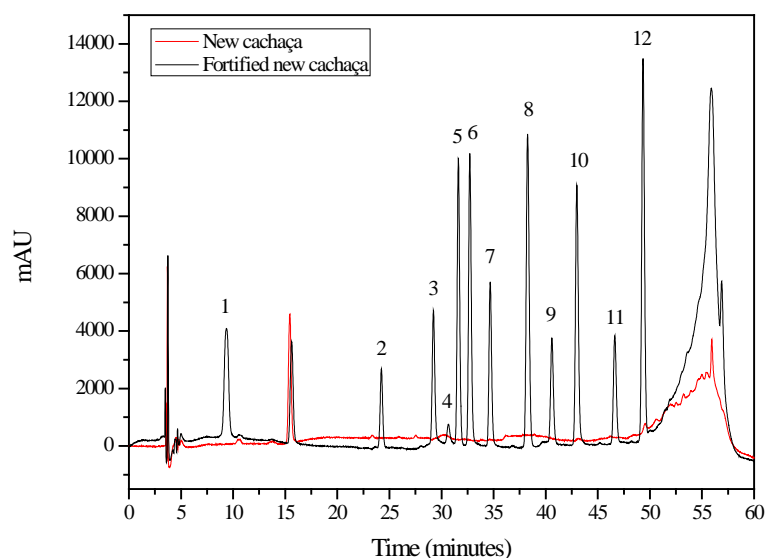
Figure 2. Chromatogram of the fresh cachaça and that fortified with standards of phenolic compounds at the 1.04×10^{-5} mol·L^{-1} concentration. Identification of peaks: (1) gallic acid; (2) catechin; (3) vanillic acid; (4) phenol; (5) syringic acid; (6) vanillin; (7) syringaldehyde; (8) *p*-coumaric acid; (9) sinapic acid; (10) coumarin; (11) 4-methylumbelliferone; and (12) *o*-coumaric acid.

Table 1. Parameters, correlation coefficients (r^2) for the analytical curves, and limits of detection (LD) and quantification (LQ)[*] obtained by the analytical method employed.

Compound	b	a	r^2	LD (mg·L^{-1})	LQ (mg·L^{-1})
Gallic acid	68463.23	−3035.01	0.9998	0.044	0.146
Catechin	16893.41	−671.57	0.9999	0.057	0.190
Vanillic acid	44512.01	−1041.40	0.9995	0.035	0.116
Phenol	12042.23	−403.83	0.9994	0.032	0.107
Syringic acid	74757.71	−1607.86	0.9997	0.035	0.117
Vanillin	96068.54	−2649.16	0.9996	0.027	0.091
Syringaldehyde	49814.62	−2113.48	0.9998	0.034	0.116
p-Coumaric acid	116451.88	−1282.22	0.9994	0.025	0.084
Sinapic acid	31456.89	−2638.53	0.9996	0.046	0.155
Coumarin	108863.21	−2863.04	0.9998	0.026	0.087
4-Methylumbelliferone	32840.07	1089.44	0.9996	0.043	0.147
o-Coumaric acid	149391.38	−3430.66	0.9997	0.033	0.113

[*]Linear regression: y = bx + a.

According to Ribani and Collins [19]-[26], the acceptable values of recovery for analyses are between 70 and 120%, with an accuracy of ±20%. However, depending on the analytical complexity of the sample, this value may vary from 50% to 120%, with an accuracy of ±15%. Thus, according to the results found in the present work for the 12 phenolic compounds studied, the method presented a high recovery, with the mean values ranging from 82% to 96%. There are studies in the literature reporting recoveries close to those observed in the current work [2]-[13]. The results obtained for the quantification of 12 phenolic compounds during the aging of cachaça in oak and amburana barrels are presented on **Table 2** and **Table 3**, respectively.

Table 2. Concentrations of 12 phenolic compounds (mg·L^{-1}) observed during the aging of cachaça in oak barrels.

Aging time (months)	0	1	2	3	4	5	6
Compounds							
Gallic acid	ND	0.213 ± 0.001	0.269 ± 0.003	0.317 ± 0.003	0.367 ± 0.004	0.417 ± 0.001	0.477 ± 0.003
Catechin	ND	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
Vanillic acid	ND	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
Phenol	ND	ND	ND	ND	ND	ND	ND
Syringic acid	ND	<LQ	<LQ	0.138 ± 0.001	0.169 ± 0.001	0.190 ± 0.001	0.221 ± 0.001
Vanillin	ND	<LQ	<LQ	0.097 ± 0.001	0.113 ± 0.001	0.119 ± 0.006	0.134 ± 0.002
Syringaldehyde	ND	0.118 ± 0.002	0.135 ± 0.002	<LQ	0.177 ± 0.005	0.210 ± 0.006	0.231 ± 0.004
p-Coumaric acid	ND	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
Sinapic acid	ND	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
Coumarin	ND	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
4-Methylumbelliferone	ND	ND	ND	ND	ND	ND	ND
o-Coumaric acid	ND	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
Sum of each phenolic compound (on each month)	ND	0.331	0.404	0.552	0.826	0.936	1.063

Aging time (months)	7	8	9	10	11	12	Evolution/ Times
Compounds							
Gallic acid	0.522 ± 0.004	0.567 ± 0.001	0.606 ± 0.001	0.652 ± 0.007	0.691 ± 0.003	0.720 ± 0.003	3.380
Catechin	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	-
Vanillic acid	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	-
Phenol	ND	ND	ND	ND	ND	ND	-
Syringic acid	0.245 ± 0.001	0.272 ± 0.003	0.294 ± 0.001	0.315 ± 0.001	0.332 ± 0.001	0.346 ± 0.009	2.507
Vanillin	0.142 ± 0.003	0.153 ± 0.001	0.158 ± 0.001	0.174 ± 0.007	0.194 ± 0.002	0.201 ± 0.004	2.072
Syringaldehyde	0.250 ± 0.001	0.279 ± 0.002	0.301 ± 0.001	0.323 ± 0.001	0.334 ± 0.001	0.346 ± 0.012	2.932
p-Coumaric acid	<LQ	<LQ	<LQ	0.045 ± 0.003	0.048 ± 0.009	<LQ	1.066
Sinapic acid	<LQ	<LQ	<LQ	0.157 ± 0.003	0.157 ± 0.009	0.157 ± 0.015	1.000
Coumarin	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	-
4-Methylumbelliferone	ND	ND	ND	ND	ND	ND	-
o-Coumaric acid	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	-
Sum of each phenolic compound (on each month)	1.159	1.271	1.359	1.666	1.747	1.770	-

ND = non-detected; <LD = lower than the limit of detection; <LQ = lower than the limit of quantification.

Table 3. Concentrations of 12 phenolic compounds (mg·L^{-1}) observed during the aging of cachaça in amburana barrels.

Aging time (months)	0	1	2	3	4	5	6
Compounds							
Gallic acid	ND	0.326 ± 0.006	0.405 ± 0.004	0.510 ± 0.006	0.646 ± 0.006	0.829 ± 0.002	1.007 ± 0.008
Catechin	ND	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
Vanillic acid	ND	1.095 ± 0.009**	2.975 ± 0.006**	4.089 ± 0.004**	4.741 ± 0.007**	5.451± 0.050**	6.101 ± 0.009**
Phenol	ND	0.112 ± 0.004	0.226 ± 0.003	0.255 ± 0.012	0.333 ± 0.001	0.389 ± 0.014	0.451 ± 0.002
Syringic acid	ND	0.869 ± 0.011	0.789 ± 0.002	0.790 ± 0.002	0.846 ± 0.001	0.921 ± 0.007	0.988 ± 0.016
Vanillin	ND	0.098 ± 0.001	0.090 ± 0.006	0.084 ± 0.003	0.081 ± 0.001	0.103 ± 0.003	0.113 ± 0.002
Syringaldehyde	ND	0.805 ± 0.004	0.744 ± 0.002	0.806 ± 0.005	0.927 ± 0.005	1.092 ± 0.002	1.304 ± 0.006
p-Coumaric acid	ND	0.119 ± 0.007	0.147 ± 0.001	0.166 ± 0.001	0.183 ± 0.023	0.350 ± 0.001	0.393 ± 0.003
Sinapic acid	ND	0.255 ± 0.001	0.634 ± 0.004	0.881 ± 0.003	0.947 ± 0.052	1.088 ± 0.015	1.206 ± 0.040
Coumarin	ND	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
4-Methylumbelliferone	ND	<LQ	<LQ	0.254 ± 0.015	0.334 ± 0.012	0.503 ± 0.005	0.511 ± 0.019
o-Coumaric acid	ND	<LQ	0.145 ± 0.015	0.167 ± 0.003	0.172 ± 0.006	0.173 ± 0.001	0.180 ± 0.007
Sum of each phenolic compound (on each month)	ND	3.679	6.155	8.002	9.210	10.899	12.324

Aging time (months)	7	8	9	10	11	12	Evolution/ Times
Compounds							
Gallic acid	1.188 ± 0.004	1.372 ± 0.005	1.528 ± 0.002	1.661 ± 0.008**	1.757 ± 0.002**	1.865 ± 0.005**	5.721
Catechin	0.209 ± 0.010	0.217 ± 0.004	0.231 ± 0.003	0.229 ± 0.003	0.230 ± 0.010	0.244 ± 0.010	1.167
Vanillic acid	6.574 ± 0.046**	7.111 ± 0.068**	7.512 ± 0.028**	7.857 ± 0.023**	8.023 ± 0.002**	8.355 ± 0.032**	7.630
Phenol	0.470 ± 0.015	0.462 ± 0.001	0.493 ± 0.003	0.489 ± 0.013	0.550 ± 0.034	0.785 ± 0.078	7.008
Syringic acid	1.042 ± 0.001	1.092 ± 0.001	1.118 ± 0.006	1.135 ± 0.006	1.159 ± 0.013	1.254 ± 0.005	1.443
Vanillin	0.125 ± 0.002	0.140 ± 0.005	0.147 ± 0.001	0.155 ± 0.001	0.157 ± 0.001	0.156 ± 0.004	1.592
Syringaldehyde	1.490 ± 0.018	1.667 ± 0.015	1.799 ± 0.040	1.957 ± 0.003**	2.024 ± 0.020**	2.226 ± 0.002**	2.765
p-Coumaric acid	0.433 ± 0.001	0.470 ± 0.004	0.508 ± 0.001	0.525 ± 0.005	0.556 ± 0.006	0.601 ± 0.003	5.050
Sinapic acid	1.262 ± 0.036	1.384 ± 0.029	1.498 ± 0.034	1.806 ± 0.026	1.761 ± 0.050	2.577 ± 0.040**	10.105
Coumarin	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	-
4-Methylumbelliferone	0.707 ± 0.059	1.076 ± 0.010	1.263 ± 0.002	1.363 ± 0.025	1.566± 0.020	1.727± 0.018	6.799
o-Coumaric acid	0.185 ± 0.006	0.203 ± 0.003	0.229 ± 0.010	0.238 ± 0.008	0.267± 0.002	0.256± 0.017	1.765
Sum of each phenolic compound (on each month)	13.685	15.194	16.326	17.415	18.050	20.049	-

ND = non-detected; <LD = lower than the limit of detection; <LQ = lower than the limit of quantification; **Sample diluted (10 times) in 40% ethyl alcohol for the quantification.

A progressive increase in the concentration of phenolic compounds for each species of wood analyzed was observed. The concentration ranged from 0.331 to 1.770 mg·L^{-1} (for cachaça aged for 1 to 12 months in oak barrels) and from 3.679 to 20.049 mg·L^{-1} (for cachaça aged for 1 to 12 months in amburana barrels). It was evident that cachaça aged in amburana barrels contained higher concentrations of phenolic compounds. Such high concentrations may be explained by morphological differences, time of use and type of pre-treatment of the barrel [10]-[27].

The cachaça aged in oak barrels contained a predominance of gallic acid, syringic acid and syringaldehyde, results that corroborate those of Anjos and Zacaroni [2]-[13]. The cachaça aged in amburana barrels contained predomnately gallic acid, vanillic acid, syringaldehyde and sinapic acid. This result differs from that of Santiago [17], who assessed cachaça stored in amburana barrels during four months and observed a predominance of catechin, syringaldehyde and 4-methylumbelliferone. Generally, there is a progressive increase in the concentration of phenolic compounds in cachaças stored in different barrels. Despite the complexity of the process, the mechanism of the gradual increase in the content of acids and aldehydes seems to follow the scheme: cinnamic aldehydes (coniferaldehyde and sinapaldeído), benzoic aldehydes (vanillin and syringaldehyde) and benzoic acids (vanillic acid and syringic acid) [2]-[5]. The differences in the composition of phenols were observed in the chromatograms (**Figure 3** and **Figure 4**) of the cachaças aged in oak and amburana barrels.

The PC1 × PC2 biplot of loadings and scores in which phenolic compounds of aged cachaças were related with the types of wood studied is presented in **Figure 5**. The PCA showed that it was possible to describe 99.49% of the data with the first and second principal components, from which 98.61% of the total variance was described by the first component. According to this analysis, all the samples differed with respect to the phenolic compounds throughout the different months of aging and the type of wood used in the process.

4. Conclusion

The chromatographic method proposed for the determination of 12 phenolic compounds presented acceptable values for all the validation parameters analyzed. A progressive increase was observed with respect to the incorporation of phenolic compounds during the aging of cachaça in barrels constructed from both species of wood. The main compounds quantified in the cachaça aged in the oak barrel were gallic acid, syringaldehyde and syringic acid, and those observed in the cachaça aged in the amburana barrel were vanillic acid, syringaldehyde, sinapic acid and gallic acid.
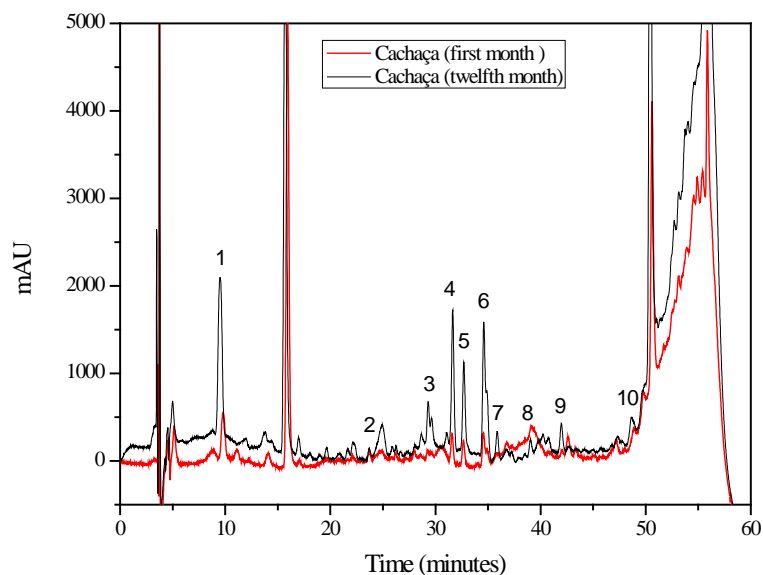

Figure 3. Chromatogram of aged cachaça on the first and twelfth month of storage in oak barrels. Identification of peaks: (1) gallic acid; (2) catechin; (3) vanillic acid; (4) syringic acid; (5) vanillin; (6) syringaldehyde; (7) *p*-coumaric acid; (8) sinapic acid; (9) coumarin; (10) *o*-coumaric acid.
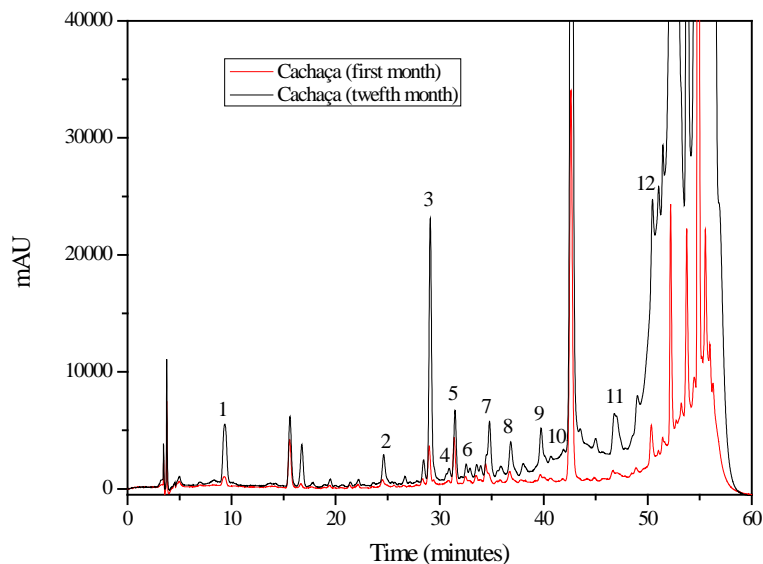
Figure 4. Chromatogram of aged cachaça on the first and twelfth month of storage in amburana barrels. Identification of peaks: (1) gallic acid; (2) catechin; (3) vanillic acid; (4) phenol; (5) syringic acid; (6) vanillin; (7) syringaldehyde; (8) *p*-coumaric acid; (9) acid sinapic; (10) coumarin; (11) 4-methylumbelliferone; (12) *o*-coumaric acid.
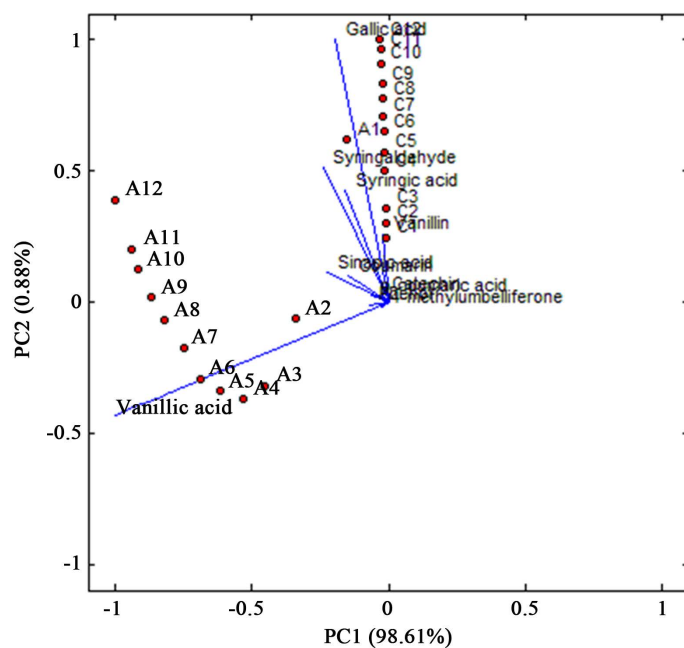

Figure 5. PC1 × PC2 biplot of loadings and scores of cachaças aged in oak and amburana barrels withs respect to the composition of phenolic compounds.

Acknowledgements

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