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Determination of the Chemical Composition of *Eucalyptus* spp. for Cellulosic Pulp Production

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Abstract: The chemical composition of wood is important to assess the quality of this raw material for the industry of cellulosic pulp production. The purpose of this work was to determine the chemical composition of *Eucalyptus* spp. grown for cellulosic pulp production. Ten *Eucalyptus* spp. clones with six years of age, located in the municipality of Itamarandiba, Minas Gerais, Brazil, were used. Quantification was obtained for extractives, monosaccharides, uronic acids, acetates, lignin, ash and the phenolic composition of the extracts. In average, clones showed around 2.7% extractives, with a predominance of polar compounds soluble in ethanol and water; 27.7% lignin and 0.3% ash. Glucose was the main sugar detected (64.2%), followed by xylose (19.3%). The main components of the extractives were steroids, fatty acids and aromatic acids, followed by smaller amounts of substituted alkanolic acids, fatty alcohols, glycerol derivatives and triterpenes. The ethanol–water extracts presented total phenol contents ranging from 321.4 to 586.6 mg EAG/g of extract, tannins from 28.1 to 65.1 mg catechin/g of extract and flavonoids from 73.6 to 256.9 mg catechin/g of extract. Clones with a higher holocellulose amount and a lower lignin content showed a higher potential for cellulosic pulp production. These findings are important for the development of high-quality wood based on important traits for the pulp and paper sector.

Keywords: *Eucalyptus* spp.; summative chemical composition; wood; extractives; phenolic compounds; monosaccharides; cellulose

1. Introduction

The wood's characteristics vary, depending on genetic and environmental variations, influencing its potential for different uses [1–3]. Wood is a biological, heterogeneous, complex material, with variations between species, individuals of the same species and parts of the same individual [4–6].

The *Eucalyptus* genus is an important raw material for several industries, such as steel, furniture, cellulosic pulp and paper, among others [7,8]. Investments in research and development, together with edaphoclimatic conditions, assure that the planted forests of Brazil are the most productive in the world, with an average of 35 m³/ha.year. This wood

is widely used to produce cellulosic pulp, making Brazil the second largest producer of this product and the eighth largest producer of paper in the world [9]. Therefore, it is of extreme importance to study wood's chemistry [10,11]. *Eucalyptus* wood clones destined for cellulosic pulp production are constantly changing, due to several factors, such as growth, wood quality, resistance to pests, diseases, lack of water and the adaptation to climate and soil, among others. Thus, their characterization needs to be constantly monitored.

Wood's chemical composition and structure consists in cellulose, hemicelluloses, lignin and, in small proportions, ash and extractives. The latter include terpenes, terpenoids, flavonoids, quinones, tannins, stilbenes, simple phenols, oils, fats and waxes [12–14].

The growing demand for cellulose pulp and paper requires a high-quality raw material, stimulating the control of the production chain and the selection of potential clones with high yields of cellulosic pulp, based mainly on productivity and wood quality [15,16]. However, specific characteristics important for further pulp and paper production are usually disregarded in tree breeding programs.

Regarding the chemical characterization of wood destined for the production of cellulosic pulp, low levels of extractives, lignins and ash are desired, as well as high levels of cellulose and hemicellulose [17]. However, each of these chemical components show variations in quality and composition, and this also affects their potential for cellulosic pulp production, which is necessary to perform a deep chemical analysis [18,19].

Thus, the purpose of this paper is to perform a broad chemical characterization of the wood of *Eucalyptus* spp., evaluating the polar and non-polar extractives, lignin and ash, as well as acetates, uronic acids and monosaccharides, aiming at the production of cellulosic pulp.

2. Materials and Methods

2.1. Description of the Material and Sample Preparation

Ten clones of hybrids of *Eucalyptus urophylla* (Table 1), harvested at 6 years of age (the common cutting age in Brazil), located in the municipality of Itamarandiba, in the state of Minas Gerais, Brazil (latitude 17°51'25" S 17.86° S and longitude 42°51'32" W), were used.

Table 1. List of clones of the hybrids of *Eucalyptus urophylla* used in this work.

Clone	Crossing	
1	<i>E. camaldulensis</i> × <i>E. grandis</i>	<i>E. urophylla</i> × <i>E. grandis</i>
2	<i>E. urophylla</i> × <i>E. grandis</i>	<i>E. camaldulensis</i> × <i>E. grandis</i>
3	<i>E. camaldulensis</i> × <i>E. grandis</i>	<i>E. urophylla</i> × <i>E. grandis</i>
4	<i>E. urophylla</i> × <i>E. grandis</i>	<i>E. camaldulensis</i> × <i>E. grandis</i>
5	<i>E. urophylla</i> × <i>E. grandis</i>	<i>E. camaldulensis</i> × <i>E. grandis</i>
6	<i>E. urophylla</i> × <i>E. grandis</i>	<i>E. pelita</i>
7	<i>E. urophylla</i> × <i>E. grandis</i>	<i>E. camaldulensis</i> v <i>E. grandis</i>

A total of five trees per clone were selected from the inner portion of the plantation, with a height and diameter close to the average of the population, without signs of attacks by diseases or pests. Once the trees were cut, seven discs of approximately 2.5 cm thick were removed from the longitudinal positions of 0%, 2%, 10%, 30%, 50%, 70% and 100% of the commercial height (defined up to the circumference of 9.4 cm), as shown in Figure 1.

The discs were sectioned into four wedges, passing by the center (Figure 1), and two of the opposing wedges were air dried and grounded into powder. The grounded material was sieved, first using a 60 mesh sieve, and the retained fraction was submitted to a new sieving using a 40 mesh sieve. This last fraction was used for the chemical characterization of the wood of the clones of *Eucalyptus* spp. (Figure 1).

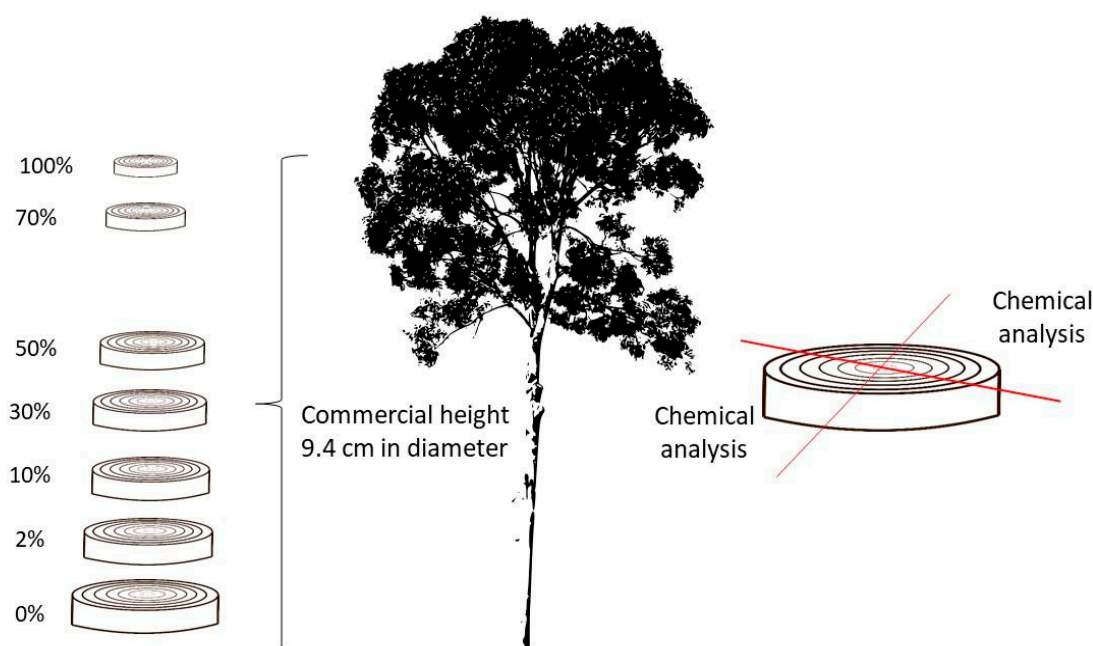


Figure 1. Removal of wood sample discs from different axial positions (at 0%, 2%, 10%, 30%, 50%, 70% and 100% of the commercial height) of the *Eucalyptus* trees for chemical characterization.

2.2. Determination of the Amount of Ashes, Extractives and Lignin

The ash content was determined according to the TAPPI T 211 om-12 (2012) test method [20]. The fraction of extractives was obtained through successive Soxhlet extractions, with dichloromethane (CH_2Cl_2), ethanol ($\text{C}_2\text{H}_5\text{OH}$) and water (H_2O). The solvents were recovered at the end of the process, and the extractive contents were gravimetrically quantified from the mass of residue after drying at $105\text{ }^\circ\text{C}$, and reported as the percentage of the original samples, adapting the procedure described at the Tappi 207 om-93 test method (1994) [21].

The lignin content was expressed by the Klason lignin, acid-soluble lignin and total lignin contents. The Klason lignin content was determined according to the standard test method TAPPI 222 om-02 (2011) [22]; the acid-soluble lignin following the TAPPI UM 250 (1991) [23]; and the total lignin as the sum of the two. The remaining acid solution was kept for sugar analysis.

2.3. Composition of Monosaccharides, Uronic Acids and Acetates

The contents of neutral monosaccharides (rhamnose, arabinose, xylose, galactose, mannose, glucose) were determined by high-performance liquid chromatography (HPLC), using the test method TAPPI T 249 cm-09 (2009) [24]. Uronic acids (galacturonic acid and glucuronic acid) and acetates were quantified by high-performance ion chromatography with pulsed amperometric detection (HPLC-PAD).

2.4. Phenolic Content in Polar Extracts

The determination of bioactive compounds (total phenols, flavonoids and tannins) was performed in the extracts that were soluble in ethanol:water (50:50), obtained from samples composed of five trees per clone.

The total phenol content was determined by the Folin–Ciocalteu method. The calibration curve was prepared using gallic acid as a standard ($0\text{--}150\text{ mg mL}^{-1}$). The total phenol content was expressed in milligrams of gallic acid equivalents (EAG)/100 g of extract [25,26].

The flavonoid content was determined by a colorimetric assay with aluminum chloride, and the tannin content was obtained by the vanillin method- H_2SO_4 [26,27]. The

absorbance of samples was determined for both analyses, and the results were expressed in milligrams of catechin/100 g of dry material extract [26,28].

2.5. Lipophilic Composition of Extractives

The lipophilic extracts of the wood clone solubilized in dichloromethane were recovered as a solid residue after solvent evaporation and vacuum-dried, overnight, at room temperature. Aliquots (2 mg) of each sample were used, which were derivatized. To assess the presence of esterified structures, 2 mg of dichloromethane extracts were dissolved in 0.5 mol L⁻¹ NaOH in methanol:water (50%) and heated to 100 °C, under a nitrogen atmosphere, for 1 h. The reaction mixture was cooled, acidified with 1 mol L⁻¹ HCl to pH 2 and extracted three times with dichloromethane, and then the solvent was evaporated to dryness.

The derivatization of samples after hydrolysis was carried out before the analysis. The extracts were dissolved in 100 µL of pyridine, and the compounds with hydroxyl and carboxyl groups were trimethylsilylated in trimethylsilyl (TMS), ethers and esters, respectively, by adding 100 µL of bis(trimethylsilyl) trifluoroacetamide chloride (BSTFA). The mixture was heated at 60 °C for 30 min in an oven. The extracts were derivatized and immediately analyzed by GC-MS (GC-MS Agilent 5973 MSD).

The compounds were identified as TMS derivatives by comparing their mass spectra to the data from a GC-MS spectral library (Wiley, NIST), and by comparing their fragmentation profiles with the published data, reference compounds, ionic fragmentation patterns and/or retention times [29,30]. A complete verification of the chromatogram was carried out in order to find all possible compounds. For the semiquantitative analysis, the peak areas of the total ion chromatograms obtained by the GC-MS analysis were integrated, and their relative proportions were expressed as a percentage of the total chromatogram area. Each aliquot was injected in triplicate, and an average of the obtained values was reported as the result.

3. Results

3.1. Ash, Extractive and Lignin Contents

The contents of ash and extractives (extracted with dichloromethane, ethanol and water) varied between clones, as shown in Figure 2.

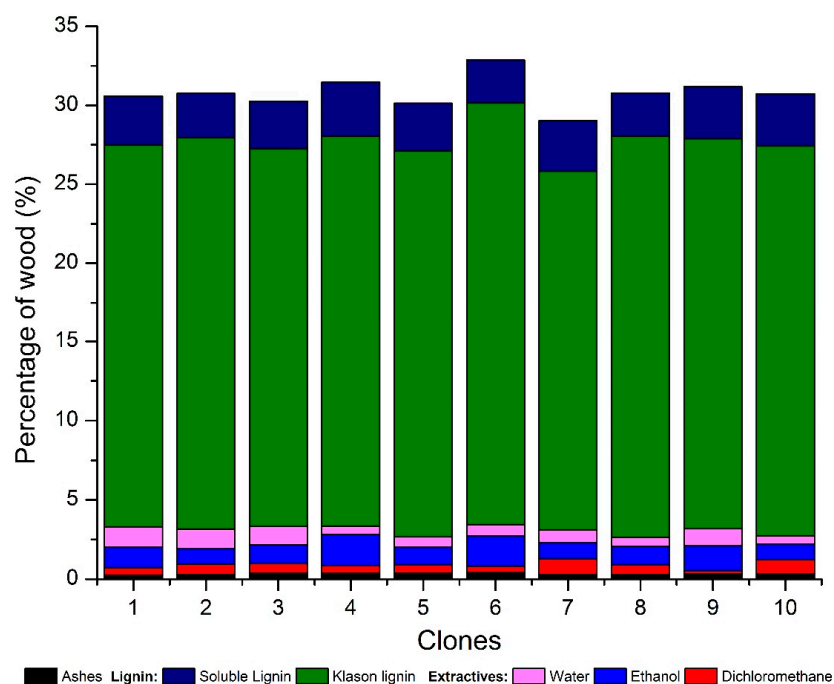


Figure 2. Ash, extractive and lignin contents of the clones of *Eucalyptus* spp.

The ash content of *Eucalyptus* spp. varied between 0.3% (Clone 1) and 0.4%. The content of extractives obtained by the extraction with polar solvents ranged from 2.3% (Clone 5) to 3.0% (Clone 6).

The largest percentage of extractives, ranging from 1 to 1.9%, was obtained when ethanol was used as solvent. The values obtained for the extractions with water and dichloromethane varied from 0.5 to 1.3% and 0.1 to 1%, respectively.

The content of extractives obtained using polar solvents ranged from 2.3% (Clone 5) to 3.0% (Clone 6). The highest percentage of extractives was obtained with ethanol, varying from 1 to 1.9%. The extraction with water and dichloromethane varied from 0.5 to 1.3% and 0.2 to 1%, respectively.

The total lignin ranged from 25.9% (Clone 7) to 29.4% (Clone 6), and Klason lignin varied from 22.7% (Clone 7) to 26.7% (Clone 6), while acid-soluble lignin ranged from 2.7% (Clones 6 and 8) to 3.4% (Clone 4), representing, on average, 11.0% of the total lignin present in the extractive-free wood.

3.2. Composition of Monosaccharides, Uronic Acids and Acetates

Glucose was the main monosaccharide found in wood, with values between 59.1% and 70.7%, while the contents of rhamnose and arabinose were below 1.0%. The amount of uronic acid ranged between 2.6% and 3.4%, while the acetates were between 2.2 and 4.6% (Figure 3).

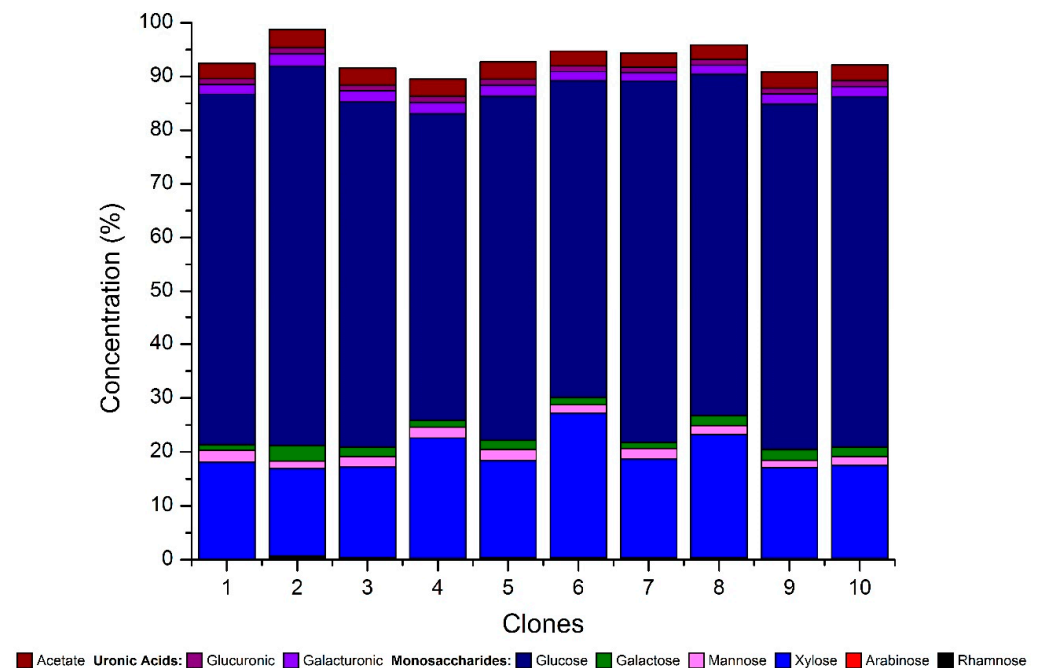


Figure 3. Chemical composition of monosaccharides, uronic acids and acetate of *Eucalyptus* spp. clones.

3.3. Composition of Extractives

The average values of the phenolic content of the polar extracts of *Eucalyptus* spp., namely, extraction yield, total phenols, flavonoids and tannins, are shown in Table 2. The extraction yield varied from 1.5% (Clone 10) to 2.7% (Clone 9), while the phenolic content ranged from 321.4 mg EAG/g of extract (Clone 9) to 586.6 mg EAG/g of extract. Concerning the concentration of flavonoids and tannins, it was possible to observe a variation from 73.6 mg (Clone 9) to 256.8 mg catechin/g of extract (Clone 3) and 28.1 (Clone 9) to 65.1 mg catechin/g of extract (Clone 6), respectively. Lower values observed for phenols, tannins and flavonoids are more favorable for the production of cellulosic pulp, since during the

pulping process these chemical substances are undesirable and must be extracted, in order to reduce the consumption of reagents and increase the efficiency of the process.

Table 2. Average values of extraction yield, phenols, tannins and wood flavonoids of ten *Eucalyptus* spp. clones.

Clones	Extraction Yield ¹	Total Phenolic Content ²	Flavonoids ³	Tannins ³
1	2.6	471.6	118.5	33
2	2.2	367.6	175.7	56.9
3	2.3	423.8	256.8	33.7
4	2.5	379.3	148.2	28.9
5	1.8	349	143.8	40.3
6	2.6	360.2	221.7	65.1
7	1.9	447.4	110.5	37.4
8	1.7	586.6	236.5	60.6
9	2.7	321.4	73.6	28.1
10	1.5	541.4	112	53.8

¹ % of wood; ² mg EAG/g of extract; ³ mg catechin/g of extract.

The analysis of the lipophilic extracts shows that the studied clones mainly contain steroids, fatty acids and aromatics, varying from 0.0% (Clones 3 and 8) to 58.4% (Clone 4) for steroids, from 19.1% (Clone 2) to 29.0% (Clone 7) for fatty acids and 0.0% (Clones 3 and 8) to 25.4% (Clone 10) for aromatics (Figures 4–6).

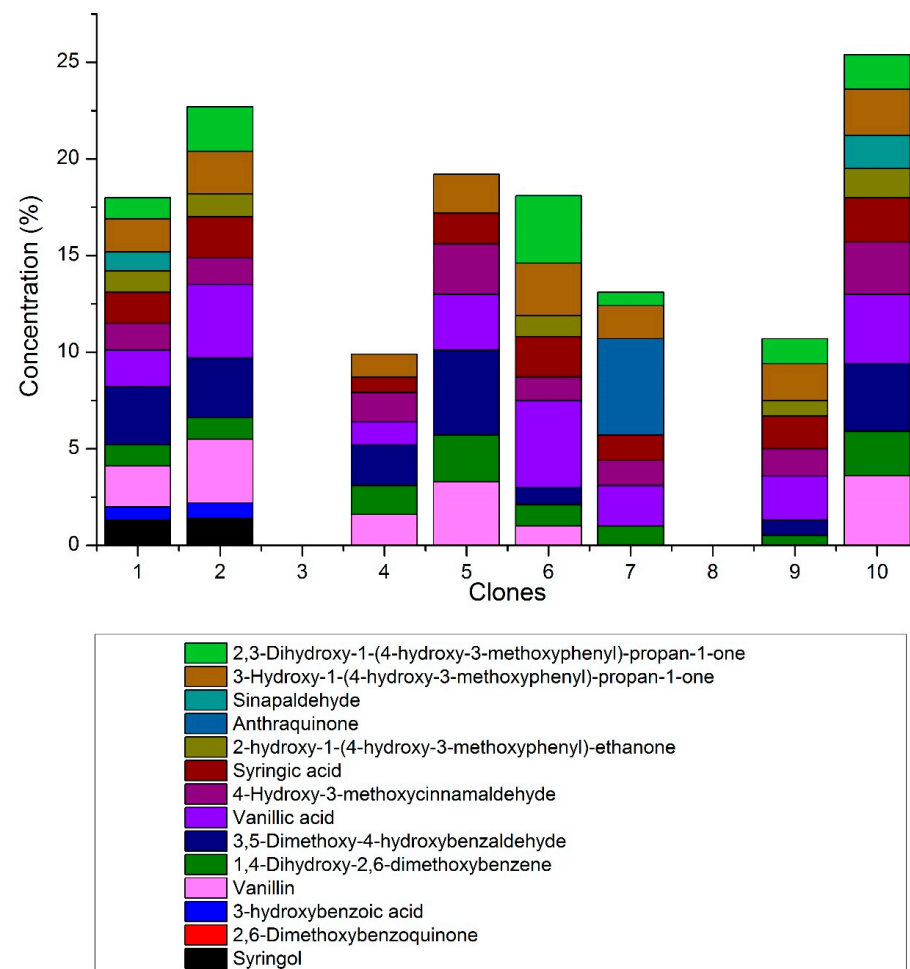


Figure 4. Aromatic constituents of *Eucalyptus* spp. identified in lipophilic extracts obtained with dichloromethane.

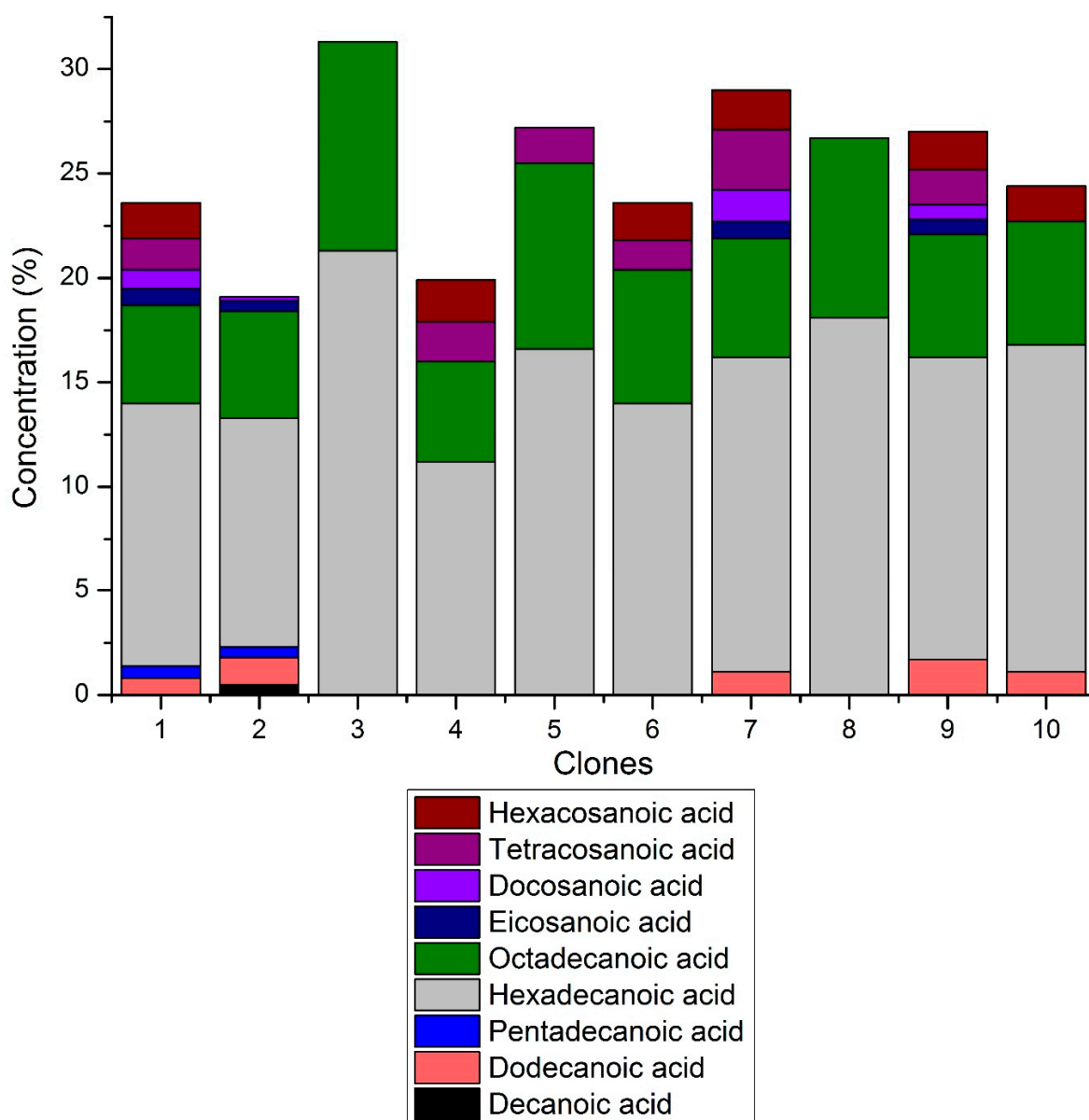


Figure 5. Fatty acid contents of *Eucalyptus* spp. identified in lipophilic dichloromethane extracts.

The values determined for fatty alcohols, steroids, glycerol derivatives and triterpenes are shown in Figure 6. Variations from 0.0% (Clones 3, 4, 6, 7, 8, 9, 10) to 3.5% (Clone 1) were found for fatty alcohols, and from 0.0% (Clones 3, 4, 5, 7 and 9) to 10.5% (Clone 8) for glycerol derivatives. The occurrence of triterpenes was identified only in Clone 9 (1.8%).

Substituted alkanolic acids were identified in the lipophilic extracts, with an average content of 9.9% among the evaluated clones. *Trans*-9-octadecanoic acid and 9,12-octadecanoic acid were also identified (Figure 7).

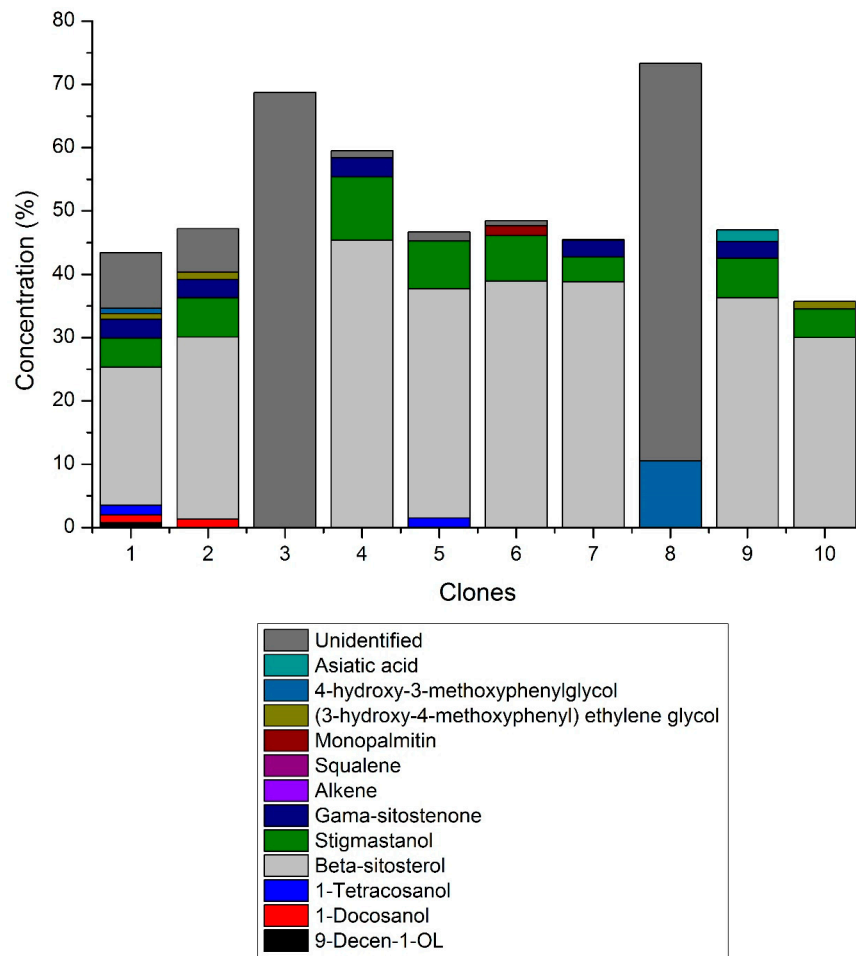


Figure 6. Fatty alcohol concentration (9-decen-1-ol, 1-docosanol, 1-tetracosanol); steroids (β -sitosterol, stigmastanol, γ -sitostenone, alkene, squalene); glycerol derivatives (monopalmitin, 3-hydroxy-4-methoxyphenyl ethylene glycol, 4-hydroxy-3-methoxyphenylglycol) and triterpenes (Asian acid) identified in the lipophilic fraction of *Eucalyptus* spp. clones extracted with dichloromethane.

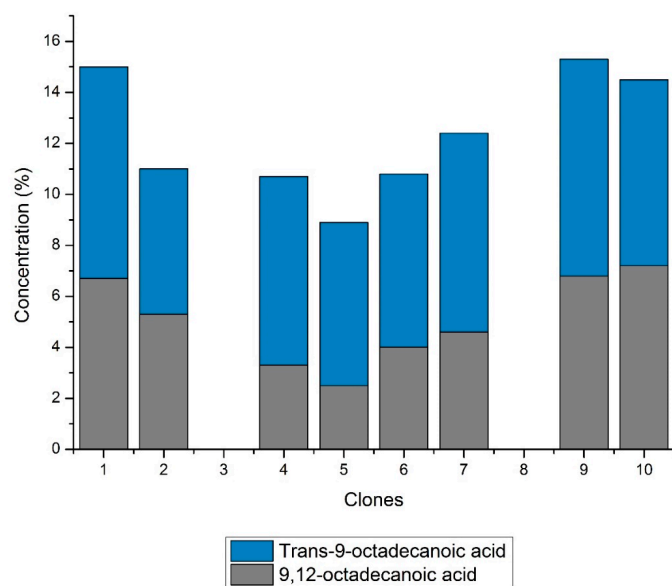


Figure 7. Substituted alkanolic acid content of *Eucalyptus* spp. identified in lipophilic dichloromethane extracts.

4. Discussion

4.1. Ash, Extractive and Lignin Contents

Clones 1 and 6 showed the lowest and highest amounts of ashes, respectively. The observed values are within the range reported by Nosek & Jandacka (2016) and Oliveira (2018) [31,32]. Ashes are minerals found in wood. Being non-fibrous, they cannot be converted into cellulosic pulp; in addition, they cause incrustations on equipments, increasing the consumption of reagents and reducing the pulp quality [33,34]. Therefore, they are undesired in the cellulosic pulp production process.

The total of extractives varied according to the solvent used, demonstrating that using only one solvent is not enough to study the chemical composition, since polarities may not be compatible with the type of extractives [35–37]. The mean (average) values found in this work are consistent with the range reported in literature. Herrera et al. (2018) [38] found a variation of Klason lignin from 22.4% to 22.9%; Zaniccio and Colodette (2011) [16] observed soluble lignin contents ranging from 2.9% to 4.3%, a range similar to the values found in the present study. Extractives are non-fibrous parts of the wood that are not converted into cellulosic pulp, thus being undesired in the process.

Non-polar compounds solubilized in dichloromethane are the smallest fraction of the total extractives. Hardwoods have a higher proportion of polyphenolic compounds removable with polar solvents [39], in contrast with conifers that have a higher proportion of non-polar extractives due to the presence of resins [36,37]. The extractive content of *Eucalyptus* spp. ranged from 2.3% to 3.0%, which confirms the findings of Arantes et al. (2011) [40]. Gomide et al. (2010) [41] observed a variation from 1.2% to 7.3% in 75 clones of *Eucalyptus* spp. for total extractives; while for alcohol/toluene soluble extractives, the variation was from 1.8% to 4.1%, values similar to those obtained in the present work. Non-polar extractives are difficult to remove, and their presence consumes reagents and causes wear in machinery and pitch.

Based on the extractives content, Clones 5, 8 and 10 showed a larger potential for the production of cellulosic pulp, while Clones 1, 2, 3, 4, 6, 7 and 9 demonstrated less capacity. Extractives are undesired in the production of cellulosic pulp, as they hinder the penetration of reagents, thus increasing their consumption, decreasing the pulping yield, increasing bleaching costs and causing impregnations in the equipment and in the cellulosic pulp [42–44]. However, the nature of these compounds can have an influence in different ways. The non-polar extractives, especially fatty acids, are difficult to remove, and it is also difficult to increase the consumption of reagents and, consequently, enlarge the production costs. They can also get impregnated into the equipment during the pulping process, which also increases the maintenance costs. In cellulosic pulp, it can also form the pitch, which can even hinder the commercialization of the product [45,46].

The clones evaluated had total lignin contents between 25.9% and 29.4%. The lower values found for Clones 3 and 7 are more suitable for cellulosic pulp production. Lignins are unwanted because they contain a large part of the chromophore groups of the cellulosic pulp and must be removed to increase the product's whiteness [47,48]. The removal of these compounds in the pulping and bleaching stage represents a large part of the production costs, due to the increase in the consumption of reagents, a drop in yield and an increase in the consumption of water and the generation of effluents. In the kraft pulping process, where the main objective is to separate the cellulose fibers by removing the lignin, the amount of lignin interferes with the pulping dynamics and efficiency, but it also influences the degree of delignification and/or the process' economy. Woods with lower lignin contents increase the pulping yield and may require a decrease in active alkali in the cooking liquor, reducing the reagent costs. In fact, small reductions in the lignin content of wood can represent large savings in the industrial production, along with gains in yield, as studied by Silva et al. (2017) [49].

4.2. Monosaccharides

Glucose was the main carbohydrate found in wood, around 64.2% in average, and a variation of 59.1% to 70.7%, being more expressive in Clone 2. Glucose is the cellulose monomer, the most abundant component in wood, which explains the high values found, being desirable in the production of cellulosic pulp. Xylose represents the main hemicellulose of hardwood, with values between 16.2% (Clone 2) and 26.7% (Clone 6). Other sugars, including rhamnose, arabinose, mannose and galactose, are the minor constituents, with average values of 0.2%, 0.15%, 1.8% and 1.7%, respectively.

Cellulose is the main component of the cellulosic pulp, so its content must be high in order to maximize the yield of the process [50]. Cellulose has a high degree of polymerization, being responsible for the mechanical strength of the pulp.

Hemicelluloses must be kept in the cellulosic pulp, as they only have amorphous regions with a low degree of polymerization and an irregular structure, and high hygroscopicity (this fact is important to reduce the time and energy required for refining the cellulosic pulp and increasing the specific or binding area of the fibers) [51]. The reduction of the hemicellulose content decreases fiber accessibility and increases fiber flattening during drying, leading to an improved sheet density and higher hornification [52].

The values obtained in this study for the monomeric composition of the sugars are in agreement with others found in the literature for woods of the *Eucalyptus* genus [53–55].

Clones 2 and 9 show the lowest and highest uronic acid contents, respectively. These acids are mainly constituted by 4-methylglucuronic and galacturonic acids, which make up around 3–5% of the wood mass. The glucuronic acid units are found predominantly in the xylans, while the galacturonic acid units are constituents of pectins [56]. The uronic acid content varied from 2.6% (Clone 7) to 3.4% (Clone 2). This result was similar to the observations of Gomide et al. (2005) [57], who evaluated wood from different clones of *Eucalyptus* spp. and found values ranging from 3.2% to 4.7%, and by Gomes et al. (2015) [58], who found uronic acid values between 3.0% and 4.1%. The 4-0-methylglucuronic acids (MeGlcA's) are converted into hexenuronic acids during the pulping process and must be removed during bleaching through an acid stage, as they are leukochromophores [59,60]. Therefore, their presence is unwanted in the production of cellulosic pulp, and their quantification is necessary.

Acetates are also part of hemicelluloses, as they are connected to the xylan chain. The acetate contents ranged from 2.2% (Clone 2) to 5.3% (Clone 4). This result was similar to the values obtained by Gomes et al. (2015) [58] who reported variations from 1.6% to 3.0% for *Eucalyptus* spp., while Gomide et al. (2010) [41] found acetate contents between 2.6% and 3.1% for commercial clones of *Eucalyptus* spp.

4.3. Composition of Wood Extractives

The wood extract obtained with ethanol:water (50% v/v) showed an average value of 2.2% of extraction yield among the evaluated clones, being within the values (2.1% to 3.4%) determined by Carvalho et al. (2014) [61].

The phenolic compounds found in extracts of *Eucalyptus* spp. clones are of large interest to the industry, being used as a base for paints, surfactants, textiles, rubbers, plastics, packaging, pharmaceutical applications and the food industry [62]. Therefore, a better knowledge and quantification of these compounds is extremely important, given the lack of research in the literature addressing the phenolic content in wood of species of the *Eucalyptus* genus. Most researchers studied the phenolic contents present only in the bark and not in the (inside) wood [63–65].

The polyphenolic nature of the extract is shown by the contents of phenolic compounds, flavonoids and tannins. The total phenols ranged from 321.4 mg EAG/g of extract (Clone 9) to 586.6 mg EAG/g of extract (Clone 8); flavonoids from 73.6 mg catechin/g of extract (Clone 9) to 256.8 mg catechin/g of extract (Clone 3); tannins from 28.9 mg catechin/g of extract (Clone 4) to 65.1 mg catechin/g of extract (Clone 6). The values found in this study are in agreement with those obtained by Santos et al. (2011) [66], for total

phenols in methanol extracts:water from *Eucalyptus globulus* bark, 413.8 mg of EAG/g of extract. Vázquez et al. (2008) [67], determined 223 mg EAG/g of extract and 201 mg EAG/g extract for *Eucalyptus globulus* bark extracted with ethanol:water 50:50 (v/v) and methanol:water 50:50 (v/v), respectively. Sartori et al. (2018) [65] found yields of 360.5 and 401.2 mg EAG/g for the extract in ethanol:water (50% v/v) for the bark of two *E. urophylla* hybrids. Lima et al. (2007) [1] reported a total phenol content of 0.93 mg/g of wood in methanol:water extracts of *Candeia* (*Moquinia polymorpha* (LESS.) DC.) wood.

The average value of the flavonoid concentration was 159.7 mg catechin/g of extract. Puttaswamy et al. (2014) [68] reported similar values in ethanol extracts of *E. tereticornis* bark (160 µg rutin/mg of extract). Sartori et al. (2018) [65] observed yields of 152.8 and 204.0 mg catechin/g for the extract in ethanol:water (50% v/v) of the bark of two *E. urophylla* hybrids.

The average tannin content observed in the wood extracts of *Eucalyptus* spp. was 43.8 mg catechin/g of extract. The value found in the literature for bark extracts of *Eucalyptus* species is 40.0 mg EAG/g of extract in ethanol:water (75:25) for *E. globulus* bark [69]. A value of 103 µg of tannic acid/mg for methanol:water extract of *E. tereticornis* barks was observed by Puttaswamy et al. (2014) [68] and of 67.7 mg catechin/g ethanol extract: water (50% v/v) in barks of two *E. urophylla* hybrids by Sartori et al. (2018) [65]. Lima et al. (2007) [1] reported an average tannin content in methanol:water extracts from woods of *Candeia* around 0.29 mg/g.

The analysis of lipophilic extracts shows that the studied clones are mainly constituted by steroids, fatty acids and aromatics, which is corroborated by the studies carried out by Cruz et al. (2006) [70] who evaluated the wood of *Eucalyptus* species, and by Schlemmer et al. (2020) [43] using two species of conifers.

The extracted aromatic compounds are equivalent to 15.9% of the total identified substances. Out of the aromatic compounds identified, synapaldehyde and vanillic, syringic and benzoic acids were already identified in *E. globulus* by Freire et al. (2002) [63].

Data from Figures 3, 4 and 6 show the predominance of steroids in the extracts, in relation to the other components. In dichloromethane extract, steroids accounted for 40.2% of the total identified compounds. As noted by Freire et al. (2002) [63] β-sitosterol was the predominant steroid in the extractives of *E. globulus*, but the steroids stigmastanol, γ-sitostenone, alkene and squalene were also found in the study.

Fatty acids were also identified in expressive amounts in the extracts, making up 29.6% of the total identified substances. Hexadecanoic acid was the main compound, with an average content of 15% in the studied clones, followed by octadecanoic, tetracosanoic, hexacosanoic, dodecanoic, eicosanoic, docosanoic, decanoic and pentadecanoic acids. Similar results were obtained by Dunlop-Jones et al. (1991) [71] and Cruz et al. (2006) [70] for extracts of *E. globulus*, in which hexadecanoic and octadecanoic acids were also the most frequent fatty acids.

Fatty alcohols, substituted alkanic acids, glycerol derivatives and triterpenes were present in low amounts. Glycerol derivatives were also identified for Clones 1, 2, 6, 8 and 10. Clone 8 stands out for having the highest amount of glycerol derivatives, 10.5%.

Extractives are undesirable in the production of cellulosic pulp, as they reduce process yield and increase the consumption of pulping and bleaching reagents, as well as the effluent load. However, different types of extractives hinder the cellulosic pulp production in different intensities. Polar extractives are easier to remove, but non-polar extractives lead to higher removal costs [72–75]. Therefore, the focus of clone selection for the production of cellulosic pulp must be taken into account for woods that have lower concentrations of extractives.

5. Conclusions

This study analyzed the chemical composition of ten clones of *Eucalyptus* spp., showing that glucose and xylose were the main wood monosaccharides present in the biomass.

The value of glucose content observed for Clone 2, above 70%, is noteworthy, indicating that this genetic material has a high potential for cellulosic pulp production.

The amounts of lipophilic extractives obtained by direct extraction with dichloromethane were relevant for the chemical characterization of wood. The extractives from these clones showed quantitative differences, despite being qualitatively very similar. Steroids, fatty acids and aromatics were the most abundant compounds in all clones, followed by smaller amounts of substituted alkanolic acids, fatty alcohols, glycerol derivatives and triterpenes.

The lignin contents ranged from 25.9% to 29.4%, being unwanted in the cellulosic pulp production. Clones 3 and 7 showed lower values.

The results obtained show the suitability of the different clones for the production of cellulosic pulp. Clone 2 showed a higher potential due to the higher holocellulose content, and Clones 3 and 7 due to their lower lignin content.

These findings can aid in the development of further improvement programs to develop high-quality wood, based on growth and physiological traits important to the pulp industry.

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