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Thermal modification and its influence on the chemical composition of *Daniellia oliveri* (Rolfe) Hutch & Dalziel wood from Ghana

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Thermal modification of wood is a sustainable treatment process that enhances its durability, dimensional stability, and resistance to biological degradation. This study investigates the chemical transformations of the wood of *Daniellia oliveri*, a lesser-utilized species, subjected to thermal modification at 160 °C, 180 °C, and 200 °C. Based on standards set by the Technical Association of Pulp and Paper Industry (TAPPI), the chemical composition of sapwood and heartwood was analyzed. The results reveal that hemicellulose content declined significantly with increasing treatment temperature, with reductions of up to 34.94% in sapwood and 30.77% in heartwood. Lignin content increased proportionally, reflecting the thermal degradation of hemicelluloses and cellulose and the relative enrichment of lignin. Similarly, extractive content, measured using acetone and ethanol, increased markedly, with the highest values observed after modification at 200 °C, indicating enhanced migration and formation of extractable compounds. Cellulose content was relatively stable, with modest increases, while holocellulose content exhibited a progressive decline due to hemicellulose degradation. These findings underscore the potential of thermal modification to enhance the performance of *Daniellia oliveri* wood, particularly its resistance to biodegradation and moisture. By improving its chemical properties, thermal treatment positions this species as a viable alternative to more durable yet overexploited tropical hardwoods, supporting sustainable forestry and expanding its market potential. The study concludes that thermal modification offers an environmentally friendly and economically advantageous approach to enhancing the utility of lesser-utilized wood species for high-value applications.

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Introduction

Thermal modification of wood is an innovative technique that changes its chemical properties to enhance durability, dimensional stability, and resistance to

biological degradation. This process involves applying elevated temperatures, typically ranging from 160 °C to 250 °C, in an oxygen-controlled or oxygen-depleted environment to prevent combustion (Sikora et al., 2018). Among the primary chemical transformations during

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thermal modification are changes in the wood's polymeric structure, including modifications to cellulose, hemicelluloses, and lignin, as well as the formation of extractives. These changes contribute to the improved properties of thermally modified wood, making it a sustainable and environmentally friendly alternative to chemically treated wood (Hill et al., 2021).

Daniellia oliveri, commonly referred to as African copaiba or *kanchil*, as it is known in the local dialect of the Sissala ethnic group in Ghana, is a Lesser-Utilized Species (Chakurah et al., 2024). It is a multipurpose hardwood species prevalent in sub-Saharan Africa. While there is limited information on its status in Ghanaian forests, it is considered a species of least concern by the International Union for Conservation of Nature (IUCN) (Arévalo et al., 2020) and is not restricted by the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES) (Adutwum et al., 2019). Due to a lack of fundamental knowledge regarding the wood's characteristics, *Daniellia oliveri* has not been widely used in Ghana and is underutilized in the global timber market.

Daniellia oliveri is a tropical deciduous hardwood with a grayish-white color. It features a flattened top and a dense, spreading crown. The average tree height is 25 meters, but some specimens reach heights of 45 meters and diameters of 1.5 to 2 meters. This species is widely dispersed across East, Central, and West Africa (Schmelzer & Louppe, 2012). Though valued for its durable heartwood, medicinal properties, and ecological significance, untreated *Daniellia oliveri* wood is susceptible to biodegradation, dimensional instability, and moisture absorption. Thermal modification offers a promising approach to addressing these challenges in order to expand the utilization potential of this wood species for construction, furniture, and outdoor applications (Goli et al., 2022).

The thermal modification process induces significant chemical transformations in wood, primarily targeting its major components: cellulose, hemicelluloses, lignin, and extractives. Hemicelluloses, which are heterogeneous polymers composed of various sugar units, are the most thermally labile component of wood, degrading significantly at elevated temperatures (Wang et al., 2020). This degradation reduces hemicellulose content, lowering the wood's equilibrium moisture content and enhancing dimensional stability and resistance to microbial attack (Boonstra & Tjeerdsma, 2006). Holocellulose, which encompasses both cellulose and hemicelluloses, undergoes a reduction, with hemicelluloses contributing predominantly to the mass loss.

Lignin, an aromatic polymer responsible for the rigidity and hydrophobicity of wood, undergoes structural modifications during thermal treatment. The representation of the fundamental structural elements, including cellulose, hemicelluloses, and lignin, along

with the slight variation between the unmodified and modified samples, provides support to the claim that even the mildest heat treatments influence the amounts of wood components (Kamperidou, 2021). Consequently, the spectral lines in the regions of the wood components exhibit minor modifications and shifts as a result of all treatments.

The relative lignin content increases due to the degradation of hemicelluloses and condensation reactions at high temperatures (Zhao et al., 2022). This increase enhances decay resistance and reduces hygroscopicity. Lignin's depolymerization and condensation entail the formation of new cross-links, further increasing its hydrophobicity and reducing water absorption (Komatsu & Yokoyama, 2022; Li et al., 2018).

Cellulose, a crystalline polymer that provides structural strength to wood, is more thermally stable than hemicelluloses. However, prolonged exposure to high temperatures can cause depolymerization and changes in crystallinity, which may influence the mechanical properties of thermally modified wood (Hill, 2006). Acid-catalyzed reactions at higher temperatures can reduce the degree of polymerization, affecting the wood's mechanical properties (Luo et al., 2022).

The formation of extractives, including phenolic compounds and other low-molecular-weight substances, is another critical aspect of thermal modification. These substances can enhance the wood's resistance to fungal and insect attacks (Candelier et al., 2020). Elevated temperatures promote the production of these extractives, which also impart a darker coloration to the wood, an attribute valued in aesthetic applications.

Hemicellulose degradation occurs primarily through hydrolysis of acetyl groups, releasing acetic acid, which acts as a catalyst for further degradation. This breakdown generates furfural and other volatile compounds, leading to mass loss and the formation of extractives (Militz & Altgen, 2014).

Lignin undergoes depolymerization and condensation, forming new cross-links and increasing its relative content. This process enhances the hydrophobicity of the wood, reducing its water absorption capacity.

Cellulose, while more thermally stable, is susceptible to acid-catalyzed depolymerization at higher temperatures. The reduction in the degree of polymerization of cellulose can alter the mechanical properties of thermally modified wood.

The thermal modification process promotes the formation of extractives, including phenolic compounds and other secondary metabolites, which act as natural preservatives and enhance the wood's resistance to fungal and insect attacks (Candelier et al., 2020). Thermal modification is an environmentally friendly wood treatment method, as it does not involve toxic chemicals (Chakurah et al., 2024). By relying solely on heat, steam, or inert

gases, this process has minimal environmental impact. Enhancing the durability and performance of less durable wood species such as *Daniellia oliveri* reduces the demand for naturally durable tropical hardwoods, many of which are overexploited and endangered. This contributes to sustainable forestry practices and promotes the use of renewable resources. Economically, thermal modification adds value to *Daniellia oliveri* by improving its properties and expanding its market potential. This enables its utilization in high-value applications, creating opportunities for income generation and economic development in regions where the species is abundant. Additionally, the enhanced durability of thermally modified wood reduces maintenance costs and extends the service life of wood products, providing long-term economic benefits (Búryová & Sedlák, 2021).

The thermal modification of *Daniellia oliveri* wood at temperatures of 160 °C, 180 °C, and 200 °C represents a novel approach to improving the properties of this species. Understanding the chemical transformations taking place during this process is essential for optimizing treatment conditions and maximizing benefits. This research investigates the effects of thermal modification on the chemical composition of *Daniellia oliveri* wood. It will evaluate changes in the content of lignin, cellulose, hemicelluloses, and extractives at different treatment temperatures. This study thus seeks to contribute to the growing body of knowledge on thermally modified wood and support the sustainable utilization of *Daniellia oliveri* as a valuable timber resource.

Material and methods

Specimen preparation

Five defect-free mature *Daniellia oliveri* trees, measuring 60 to 80 cm in diameter, were purposively selected from the natural woodlands in the Du-west community, in view of their availability and prominence there. The sizes of the five trees were specifically chosen, and the straightness of their trunks and their lack of defects were confirmed before harvesting. Following the selection of trees, the base of each tree, measuring about one meter, was extracted and further processed and treated. The treated specimens were then analyzed to ascertain their chemical makeup at the chemical laboratory of the Forestry Research Institute of Ghana.

The billets obtained from the felled trees were sawn to dimensions of 50 mm x 50 mm x 150 mm using the quarter-sawing technique, which decreased warping and made it simpler to separate sapwood and heartwood in order to ascertain radial variation in chemical compositional properties. The oven-dry densities of the specimens used for the study were 544.72 kg/m³ and 518.56 kg/m³ for heartwood and sapwood respectively.

The wood workshop/laboratory at the Akenten Appiah Menka University of Skills Training and Entrepreneurial Development-Kumasi campus was used in preparing wood samples with the required dimensions. In accordance with the TAPPI standards, the specimens were cut into lengths appropriate for the chemical determination. This was done from prepared stacks of sawn timber free of defects such as knots, waness, and other biological features that lower wood performance.

Thermal modification process

Six sets of sapwood and heartwood were heat-treated for three hours at temperatures of 160 °C, 180 °C and 200 °C using a muffle furnace at Kwame Nkrumah University of Science and Technology chemical engineering laboratory. The control group (untreated) consisted of ten replicates of sapwood and heartwood. To prevent heat loss during the treatment process, the specimens were placed in an oven with a door that was securely closed. The oven was set to the selected temperatures ranges before the various heat treatments were performed. Following each treatment period, the samples were removed from the oven and placed in a desiccator containing silica gel to cool.

Determination of chemical composition of thermally modified *Daniellia oliveri* wood

The chemical laboratory of the Council for Scientific and Industrial Research – Forestry Research Institute of Ghana (CSIR-FORIG) was used to perform chemical analysis of the wood. The Technical Association of Pulp and Paper Industry (TAPPI) Test Methods were followed in determining the chemical composition of specimens at 12% moisture content. A Willy mill was used to chip and grind wood samples from the sapwood and heartwood sections of the quarter-sawn specimens. Following about four weeks of air drying, the ground samples were sieved through 40–60 mesh screens to extract particles that were retained on the 60 mesh but passed through the 40 mesh. For the chemical analysis, 20 g of each sample was weighed, transferred to an appropriately labeled container, covered, and kept at room temperature (Fig. 1).

Determination of extractive content

According to the TAPPI standard T 204 cm-97 test technique, the extractive contents of the samples were ascertained using a Soxhlet extractor (Technical Association of Pulp and Paper Industry, 2007). Extraneous elements were extracted using acetone and alcohol as solvents. A cellulose thimble was filled with 1 g of the air-dried wood sample. The extraction thimble and its contents were placed in a Soxhlet device (Fig. 2), and



Fig. 1. Milled control sapwood specimen being weighed on a scale before determination of chemical components



Fig. 2. Determination of extractive content of control and thermally modified specimen using Soxhlet apparatus

the solvent was extracted for four hours. The extractive content of the wood samples was determined by evaporating the residual solvent after each extraction procedure at a lower pressure. The weight of the dried extract was represented as a percentage of the sample.

Acetone extractives

$$\% \text{Acetone} = \frac{A}{B} \times 100 \quad (1)$$

where A is the weight of the residue after drying and B is the weight of the initial sample.

Ethanol extractives

$$\% \text{Ethanol} = \frac{A}{B} \times 100 \quad (2)$$

where A is the weight of the residue after drying and B is the weight of the initial sample.

Determination of lignin content

The TAPPI standard method T 222 cm 88 was used to quantify the lignin concentration of control and modified specimens of *Daniellia oliveri*. First, 1 g of the

extractive-free sample was weighed into a conical flask. With careful swirling, 15 ml of cold sulfuric acid was gradually added to the sample and thoroughly mixed. With frequent stirring, the reaction persisted at room temperature for two hours. A 1-liter flask was then filled with the contents of the beaker. The mixture was heated for four hours on a water bath after being diluted with distilled water. The mixture was filtered after it had cooled to room temperature. After being cleaned with distilled water, the residue was dried in an electric oven set at 105 °C until it reached a stable weight. The lignin content was expressed as a percentage of the extracted oven-dried wood:

$$\% \text{Lignin} = (A/B * (1 - \text{ext}/100)) * 100 \quad (3)$$

where:

A = weight of lignin,

B = weight of extractive-free sample,

ext. = sum of ethanol and acetone extractives.

Determination of cellulose content

A small glass watch cover was used to weigh 1.5 g of the holocellulose into a 250 ml Erlenmeyer flask in order to calculate the cellulose content. 100 milliliters

of NaOH solution were added to the flask while it was being thoroughly stirred in a water bath set at 25 °C. Following 30 minutes of stirring, 100 ml of water was added, and for an additional 30 minutes the mixture was constantly stirred. After taking out the Erlenmeyer flask, the contents were filtered using a known-weight fried-glass crucible. 25 milliliters of NaOH solution, 40 milliliters of acetic acid, and distillation water were used to wash the residue clean. After being oven-dried at 105 °C, it was cooled in a desiccator and weighed until it reached a consistent weight.

$$\% \text{Cellulose} = \frac{A}{B} \times 100 \quad (4)$$

where:

A = weight of cellulose,

B = weight of extractive-free wood sample.

Determination of hemicelluloses

Both the modified and control sample specimens were collected and milled into fine powder. To improve hemicellulose measurement, the samples were hydrolyzed with 72% sulfuric acid to eliminate the lignin. The carbohydrate component was then hydrolyzed with sulfuric acid to convert hemicelluloses into monomeric sugars. After that, the hydrolyzed solution was filtered and neutralized, and a high-performance liquid chromatography apparatus was used to evaluate the resultant sugars. Equation 5 was used to calculate the hemicellulose content:

$$\begin{aligned} \text{Hemicelluloses} &= \text{Holocellulose} - \text{Cellulose} \\ \% \text{Hemicelluloses} &= 100 - \% \text{Cellulose} \end{aligned} \quad (5)$$

Statistical analysis

Statistical Package for Social Sciences (SPSS) version 23.0 was used to statistically analyze and assess the chemical differences between the experimental groups. Two-way analysis of variance (ANOVA) with a standard alpha value ($p < 0.05$) was used to determine statistical significance.

Results and discussion

Chemical properties

To investigate the chemical composition of thermally modified *Daniellia oliveri*, the TAPPI (2007) standard was followed. The thermal modification of *Daniellia oliveri* wood at temperatures of 160 °C, 180 °C, and 200 °C provides a gradient of changes in its chemical composition and properties. As indicated in Table 1, which shows a comparison of thermally modified specimens with the control specimens, the content

of hemicelluloses and holocellulose of modified specimens decreased, while lignin, extractives and cellulose content increased. As the modification temperature increased, the relative hemicellulose content exhibited a decreasing trend. This outcome was consistent with the changes in mass loss of the modified specimens. The hemicellulose content was 30.77% and 34.94% for the control heartwood and sapwood portions respectively, higher than in the modified specimens. After modification for 3 h at 200 °C, the hemicellulose content was 1.78% in heartwood and 4.17% in sapwood (Table 1). This suggests that thermal modification caused the degradation of hemicelluloses in *Daniellia oliveri* wood.

Extractive content

Fig. 3 provides a graphical representation of the content of extractives in thermally modified *Daniellia oliveri* specimens. In general, there was an increase in extractive content for both heartwood and sapwood as the modification temperature rose. For the untreated specimens, the acetone extractive content was 2.27% for heartwood and 1.79% for sapwood, while ethanol extractives amounted to 0.52% for sapwood and 1.28% for heartwood. These values rose as the modification temperature increased (Fig. 3). The highest acetone extractive content (11.79%) was recorded with a modification temperature of 200 °C. Similar results were obtained by Sharma et al. (2022), who reported that with different modification temperatures, the maximum alcohol benzene extractive content (13.13%) was obtained for a temperature of 200 °C, and the minimum (8.03%) for the control, concluding that as temperature increases the extractive content also increases.

Bi et al. (2024) also observed a significant rise in extractive content with increasing modification temperatures. According to Esteves et al. (2022), even while extractive content normally rises with higher modification temperatures, it may rise further in response to newly released extractable components such as ethanol and water that are produced at specific temperatures during polysaccharide degradation. According to Esteves et al. (2008), when the original extractives disintegrated and were replaced by fresh compounds, the extractives composition shifted. Outcomes of polysaccharide or hemicellulose breakdown at 200 °C may have contributed to the increase in extractive content at high temperature.

Lignin content

Table 1 shows a statistically significant difference and consistent increasing trend for lignin content, from 17.43% for untreated wood to 29.73% for wood modified at 200 °C. As the temperature increased the lignin

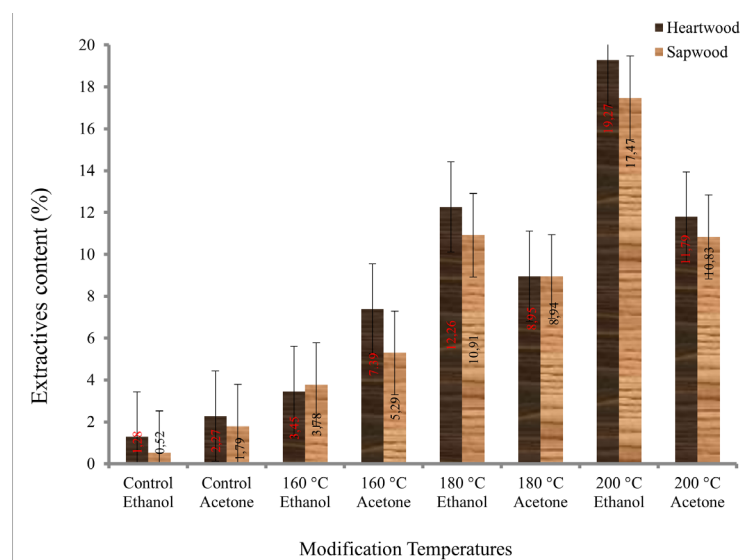


Fig. 3. Extractive content of thermally modified wood of *Daniellia oliveri* (Rolfe) Hutch & Dalziel

content also increased. The temperature at which wood is treated determines what chemical changes occur, with temperature being the primary determinant. Due to lignin's strong thermal resilience and the breakdown of hemicelluloses, heat-treated *Daniellia oliveri* wood had a higher relative lignin content than the control specimen (Barlović et al., 2022; Gupta et al., 2023; Sharma et al., 2022).

Simultaneously, the lignin condensation reaction that occurred during the heat treatment and the subsequent formation of the lignin crosslinking network were linked to the rise in lignin content (Boonstra & Tjeerdsma, 2006). Similar results were obtained by Yalcin & Sahin (2015). In their study of changes in the chemical structure and decay resistance of heat-treated narrow-leaved ash wood, they found that the amount of lignin in narrow-leaved ash wood rises with modification temperature; the maximum temperature of 220 °C gave the highest lignin content of 41.15%, and the minimum lignin content (19.89%) was obtained for 140 °C. According to some studies, lignin polycondensation interactions with other cell wall components may be the cause of an increase in lignin concentration following thermal modification (Boonstra & Tjeerdsma, 2006; Gaff et al., 2023; Gupta et al., 2023).

Cellulose content

When modification was performed at comparatively low temperature of 160 °C, the cellulose content of control sapwood was 47.13%, and that of the control heartwood was slightly higher at 48.06%. The change in cellulose content was comparatively stable between radial sections. The cellulose content of the specimens rose as the modification temperature increased, for all

of the thermal modification temperatures applied. The primary reason for the continuous increase in cellulose content was the disintegration of the amorphous region of cellulose in an acidic environment, brought on by the significant amount of acetic acid created by the thermal breakdown of hemicelluloses (Dubey, 2010).

A similar study was carried out by Fengel and Wegener (1984), who explained the increase in cellulose content in samples treated at 160 °C compared with the control group by pointing to cellulose's stronger cohesive bonding during hydrolysis, which makes it more thermally stable. Moreover, compared with hemicelluloses, cellulose offers limited accessibility to its glucosidal linkages, which are susceptible to degradation by the release of acids (Boonstra & Tjeerdsma, 2006). Additionally, the degradation of hemicelluloses has been found to increase with the duration of heat modification, to a point where the relative content of cellulose trended upward (Wang et al., 2020).

Hemicellulose content

The hemicellulose content decreased significantly from 30.77% and 34.94% for unmodified heartwood and sapwood respectively to 1.78% and 4.17% for heartwood and sapwood modified at 200 °C (Table 1). This result is comparable to that of Wang et al. (2021), who stated that hemicelluloses are the first structural element of wood to be impacted by heat modification. In line with the findings of this study, they noted that deacetylation and the liberated acetic acid function as a depolymerization catalyst that further promotes polysaccharide degradation (Gašparík et al., 2024). As the modification temperature rose, the content of hemicelluloses decreased, with the greatest reduction occurring at 200 °C.

Holocellulose content

The holocellulose in the woody material consists of both α -cellulose and hemicelluloses (Dieguez-Alonso et al., 2015). As shown in Table 1, the maximum holocellulose content (82.07%) was recorded for the control sapwood, while 79.01% was recorded for the control heartwood; the minimum values (58.35% for heartwood and 59.58% for sapwood) were recorded following modification at 200 °C. The higher holocellulose content of the unmodified sapwood compared with unmodified heartwood may be attributed to the larger amount of parenchyma cells. According to Zimmer and Treu (2021), long parenchyma cells, with thickened polylamella and lignified walls, usually contain starch granules, and the starch content of oblong parenchyma cells in lignocellulosic materials causes them to have higher holocellulose content than the heartwood.

According to Rowell (2014), holocellulose makes up 65% to 70% of the dry weight of wood, which is mostly composed of the combination of hemicelluloses and cellulose. A study by Sikora et al. (2018) revealed that hemicelluloses are the least stable part of wood after heat treatment, because they become less prevalent in thermally altered wood. In turn, Gupta (2019) reported that the concentration of holocellulose decreases as the modification temperature rises. The present findings for thermally modified *D. oliveri* wood are in line with those of the aforementioned researchers. The high holocellulose content in unmodified specimens indicates that they had a higher carbohydrate content than the modified specimens, which may make them more vulnerable to attacks by biodegrading agents such as termites, fungi, and borers (Jenoh et al., 2021). Research has revealed that lignin from phenylpropane and simple sugars of monomers constitute the carbohydrate polymers that make up hemicelluloses

and cellulose (Browning, 1975). This may eventually compromise the wood's inherent resilience, resulting in a shorter service life than that of specimens that have been modified (Chavan & Attar, 2013; Liese & Kumar, 2003).

Conclusion

The untreated heartwood had a higher extractive content than the untreated sapwood, and both acetone and ethanol extractives increased significantly with rising modification temperature. The highest values were recorded after modification at 200 °C for both heartwood and sapwood. This suggests that thermal treatment enhances the migration and formation of extractable compounds.

Lignin content increased with temperature for both heartwood and sapwood, indicating thermal degradation of hemicelluloses and cellulose, which likely leads to the relative enrichment of lignin.

Cellulose content showed a slight increase with temperature, with the highest values recorded at 200 °C. This suggests that cellulose remains relatively stable during thermal modification, even at elevated temperatures.

Hemicellulose content decreased significantly as the temperature increased, particularly for a modification temperature of 200 °C, where the values were markedly lower. This demonstrates the susceptibility of hemicelluloses to thermal degradation.

Holocellulose content decreased progressively with increasing modification temperature. The decline reflects the combined loss of hemicelluloses and the relatively stable cellulose fraction.

The p-values indicate that the observed changes in chemical composition were statistically significant for both radial sections, confirming the impact of thermal modification.

Table 1. ANOVA for chemical composition of thermally modified *Daniellia oliveri* wood

Chemical composition	Radial section	Control	Temperatures			P-value
			Modification @160 °C	Modification @180 °C	Modification @200 °C	
Lignin (%)	Heartwood	18.72±2.24**	26.79±2.78 ^a	28.84±1.88**	29.86±1.97**	0.01
	Sapwood	16.14±1.87**	21.30±2.83**	28.81±2.53**	29.59±2.28**	0.02
Cellulose (%)	Heartwood	48.06±1.43**	49.41±2.64**	51.76±3.21**	56.57±2.79**	0.00
	Sapwood	47.13±2.33**	48.33±2.75**	50.16±2.52**	55.41±3.20**	0.00
Hemicelluloses (%)	Heartwood	30.77±3.27**	16.41±5.27**	10.45±5.94**	1.78±2.58**	0.01
	Sapwood	34.94±2.43**	25.16±4.11**	12.09±3.73**	4.17±3.56**	0.00
Holocellulose (%)	Heartwood	79.01±3.66**	65.82±7.11**	62.21±3.33**	58.35±3.27**	0.04
	Sapwood	82.07±4.27**	73.49±3.63**	62.25±4.31**	59.58±2.61**	0.02

± = Standard deviation; means in a column marked ** are statistically significantly different ($p < 0.05$)

Authors' contributions:

All authors participated from conception to the conclusion of this research.

Conflict of interest

The author(s) declare(s) that there is no conflict of interest concerning the publication of this article.

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