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CHANGES IN THE CONTENT AND COMPOSITION OF THE EXTRACTIVES IN THERMALLY MODIFIED TROPICAL HARDWOODS

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ABSTRACT

Chemical composition of wood is known to change during thermal treatments. Two species grown in Turkey, afrormosia (*Pericopsis elata*) and duka (*Tapirira guianensis*) were heat treated according to Thermowood® method. Lignin, cellulose, hemicelluloses and extractives in dichloromethane, ethanol and water were determined. Wood extracts were analysed by gas chromatography with mass detection and existing compounds were identified by NIST17 database. Results show that hemicelluloses and cellulose content decreased for both heat-treated woods along the treatment while lignin percentage increased. The analysis of extractives has shown several compounds normally associated to lignin thermal degradation that increased along the treatment. At the same time several compounds associated to carbohydrate thermal degradation were found in all the extracts for both heat-treated woods. These founding have allowed the understanding of the degradation pattern of wood during thermal modification. There was not much difference between afrormosia and duka woods structural compounds behaviour along thermal modification. However, the variation of the amount of extractives along the treatment depended on the species.

Keywords: Afrormosia, chemical changes, duka, extractives, heat treatment, *Pericopsis elata, Tapirira guianensis.*

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INTRODUCTION

Understanding the chemical transformations that occur during thermal modification allows us to understand the reason for improving material properties. During thermal modification, structural and non-structural wood compounds are affected by high temperatures. In addition to temperature, also the treatment time influences the variation of the chemical composition of wood (Bourgois *et al.* 1989). Hemicelluloses are the first compounds to be affected by the thermal modification due to their amorphous nature, low molecular weight and branched structure. Nevertheless, hemicelluloses are not all affected in the same way since they have different chemical compositions. One of the main reactions occurring during thermal modification is the cleavage of the acetyl groups of hemicelluloses producing acetic acid (Hofmann *et al.* 2013, Nuopponen *et al.* 2005, Sivonen *et al.* 2002, Tjeerdsma *et al.* 1998). Therefore, acetylated hemicelluloses are the most affected compounds. In hardwoods acetyl radicals are present, linked to xylose in glucuronoxylan (Sundqvist *et al.* 2006) while in softwoods can be found in glucomannan. Consequently, the amount of acetic acid released during the treatment depends on the species. Since acetic acid acts as a catalyst in polysaccharide depolymerization the different amount of acetic acid will surely affect the extent of wood thermal degradation. At the same time, dehydration reactions occur with furfural formation in pentose and hydroxymethylfurfural in hexoses (Tjeerdsma *et al.* 1998). Although cellulose is more resistant than hemicelluloses, there is a degradation of amorphous cellulose and consequently an increase in its crystallinity (Kamperidou 2021, Wang *et al*. 2018). This increase in the crystallinity of cellulose leads to a greater inaccessibility of hydroxyl groups to water molecules, which contributes, together with the degradation of hemicelluloses and lignin condensation to a decrease in the equilibrium moisture content (Boonstra and Tjeerdsma 2006, Wikberg and Maunu 2004).

Even though, lignin is affected by the thermal modification, its degradation is slower than that of carbohydrates, which leads to a percentage increase with treatment. In addition, several studies show that several condensation reactions occur between lignin and other products of degradation reactions, which in turn also contribute to a percentage increase of lignin (Diouf *et al.* 2011, Esteves *et al.* 2008, Windeisen *et al.* 2007).

Lignin degradation occurs through the cleavage of ether bonds, essentially β-O-4 bonds, which leads to new phenolic hydroxyl groups and α- and β-carbon groups that are responsible for cross-links through the formation of methylene bridges (Aydemir *et al.* 2011, Nuopponen *et al.* 2005, Tjeerdsma *et al.* 1998, Tjeerdsma and Militz 2005). Similarly, Brosse *et al.* (2010), through spectroscopic analysis of Milled Wood Lignin (MWL), indicated that recondensation reactions mainly involved guaiacyl units through the formation of diphenolic structures with 5-5 binding.

With heat, the original extractives are degraded or leave the wood. The most volatile compounds are released in the beginning of the treatment while others are degraded. For instance, fats and waxes in the wood are known to move along the axial parenchyma cells towards the surface of the wood, being eventually degraded. According to Nuopponen *et al.* (2005), above 180 ºC these compounds are no longer detected in wood. The ratio between initial extractives degradation and formation of new extractable compounds for mild treatments is favorable for the appearance of new compounds leading to the increase in extractive content. The largest increase is due to extractives in water and ethanol that is where most polysaccharide degradation products are located (Esteves *et al.* 2010, Esteves *et al.* 2008). With the prolongation of the treatment some of the recently produced compounds are also degraded and most of the volatile compounds like furfural and hydroxymethylfurfural are also released from wood leading to a decrease in the amount of extractives. Some of the most volatile compounds produced during thermal modification of wood are released but the other remain in wood and can be extracted by several solvents. The new compounds that are produced during thermal modification are, in accordance to Esteves *et al*. (2010), compounds from polysaccharides degradation and dehydration extracted with nonpolar solvents, like galactosan, mannosan, levoglucosan and arabinofuranose, and compounds found in polar extracts, such as arabinopyranose, arabinose, xylopyranose, xylofuranose and xylose. There are also some phenolic compounds that appear or increase with thermal modification like catechol, vanillin, vanillic acid, 3-vanillyl propanol and coniferyl aldehyde, probably resulting from lignin or phenolic extractives, since these compounds are found in lignin pyrolysis (Faix *et al.* 1990) but not in polysaccharide pyrolysis (Faix *et al.* 1991). In more severe treatments compounds like syringaldehyde, syringic acid and synapaldehyde are also found (Esteves *et al.* 2010).

The kind of thermal modification used is known to alter the extractives. According to Esteves *et al.* (2010), that studied two different thermal modification methods, one using a mixture of superheated and supersaturated steam and other with dried air without any shielding gas, different compounds can be obtained. For instance, some aldonic acids, perfuranuronic acids, and deoxyhexoses could only be found on the treatment without shielding gas. Similarly, Poncsak *et al*. (2009) also found that the presence of water vapor increases the portion

of polar extractives in wood. Although there are several papers about the chemical degradation of heat-treated wood, the study of the newly created extractives that remain in wood is almost inexistent. Are these compounds the same for all the species? Do they differ? This work intends to give new information about this subject.

MATERIAL AND METHODS

Material

Boards of two species, commonly used in Turkey by flooring companies afrormosia (*Pericopsis elata*) and duka (*Tapirira guianensis*) with dimensions of approximately 150 mm x 50 mm x 10 mm were purchased in a lumber mill from Düzce industrial zone, Turkey. Both samples came from heartwood of mature trees.

The samples were heat treated according to Thermowood® method in a thermal modification facility in Turkey (Novawood Factory, Gerede, Bolu, Turkey). The treatment temperature was 212 ºC and two different treatment times were used, 1 h and 2 h (Figure 1). Afterwards untreated and treated wood samples were milled in a Retsch SMI mill (Haan, Germany), followed by sifting in a Retsch AS200 (Haan, Germany) sifter during 20 min at 0,83 Hz. The 40-60 mesh fraction was used for chemical analysis, in accordance with TAPPI T 204 (2007).

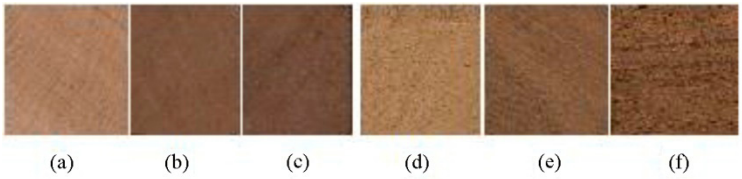

Figure 1: Duka: (a) control, (b) 212ºC/1 h, (c) 212ºC/2 h and afrormosia: (d) control, (e) 212ºC/1 h, (f) 212ºC/2 h.

Extractive content

The extractive content was determined by successive Soxhlet extraction of about 3 g of each sample using dichloromethane, ethanol and water. Extractions were made in 250 mL soxhlets using 150 mL of solvent. The extractions were made during 8 h for dichloromethane and 16 h for both ethanol and water solvents. The extract was concentrated to 100 mL and divided in two 50 mL samples. The first sample was used to quantify the extractives and the other half was used for the determination of extractive composition by GC-MS (Gas chromatography-mass spectrometry). Quantification was made by concentrating the extract in a rotary evaporator transferred to a pre-weighed glass. Dichloromethane extract was air dried in a fume while ethanol and water extracts were dried in an oven at 40 ºC, followed by 1 hour at 100 ºC.

The percentage of extractives in each solvent was determined gravimetrically in relation to initial dry mass according to TAPPI T 204 (2007).

Extractive chemical analysis

After the quantification of the extractives in dichloromethane, ethanol and water, the amount necessary to contain about 3 mg of solid extract was evaporated in a rotary evaporator under vacuum until a volume of about 1 mL was reached. The evaporation was made with bath temperature 40 ºC, using a 6,5 x 10^{-3} MPa vacuum for water, 17,5 x 10^{-3} MPa for ethanol and 90 x 10^{-3} MPa for dichloromethane. The sample were transferred to pre-weighed vial and dried under a nitrogen flow. After that the vials were kept overnight in an oven at 40 ºC with a Petri dish containing P_2O_5, cooled in a desiccator and weighed in an analytical balance, with a precision of ± 0,0001g.

Samples were derivatized with 10 µL of pyridine and 10 µL of BSTFA for each mg of dry extract in accordance to Esteves *et al.* (2010). The vials were closed and kept for 20 min in an oven at 60 ºC, cooled down and injected in a chromatograph HP 6890 Series gas chromatograph from Agilent (Santa Clara, CA, USA) equipped with an Agilent DB-5ms column (30 m × 0,25 mm × 0,25 µm) (Avondale, PA, USA and a mass detector 5973 N Agilent Series (Santa Clara, CA, USA) in scan mode). The data acquisition ranged from 15,0 to 500 amu (atomic mass unit). The interface temperature was 160 °C and the ion source (electron ionization) was set at 230 °C with electron energy of 70 eV, whilst the quadrupole mass filter was kept at 150 °C. The

temperature of the injector and detector were 320 ºC and 325 ºC respectively. The injection of 1 µL was made in splitless mode and the column gas flow was Helium (99,9999 % purity) at 1 mL/min. To achieve the compounds separation, the GC-MS oven temperature started at 100 ºC, keeping it for 5 min, followed by an increase of 5 ºC/min until 310 ºC, maintaining this temperature for 15 min. Extractive compounds were identified by comparing their EI (Electron-Ionization) mass spectra with NIST17 library. Extractive composition was determined by peak area integration with no further correction for eventual differences in their response factors.

Klason lignin determination

The samples for lignin determination were kept in an oven at 60 ºC overnight, followed by 1 hour at 100 ºC. Klason and acid-soluble lignin contents were determined on 350 mg of extracted samples. Sulfuric acid (72 %, 3,0 mL) was added to the sample and the mixture placed in a water bath at 30 ºC for 1 h, mixing every 10 minutes. The samples were transferred to 100 mL Schott flasks and 84 mL of distilled water was added after which the samples were autoclaved during one hour at 120 ºC. After that the samples were cooled with ice, vacuum-filtered through a crucible nº 4 and washed with boiling purified water. Klason lignin was determined as the mass of the solid residue after drying at 105 ºC. Acid- soluble lignin was determined by removing 2 mL of the filtered solution, diluting to 20 mL and measuring the absorbance at 205 nm using a UV/VIS spectrophotometer in accordance with TAPPI UM 250-00 (2000). Klason lignin and acid-soluble lignin were reported as percentage of the original sample and combined to give the total lignin content. The analyses were made in duplicate.

Holocellulose and Alpha-Cellulose determination

The holocellulose and α-cellulose content of extractive-free samples was determined by the chlorite method and by Test Method T 429 cm-10, both described in Domingos *et al.* (2020). The percentage of holocellulose and α-cellulose were determined in relation to the dry mass of wood. Hemicelluloses content was determined by difference.

Statistical analysis

Statistical analysis was performed using Statistics (2019). A two-way ANOVA was made to test if there was a difference between heat treatment and kind of wood for Dichloromethane, ethanol and water extractives, lignin, cellulose and hemicelluloses. One-way ANOVA was done for each wood along heat treatment.

RESULTS AND DISCUSSION

Table 1 presents the chemical composition of untreated and heat treated duka, and afrormosia woods. Duka wood has a high amount of extractives mainly soluble in ethanol with 9,4 %, followed by water (4,1 %) and dichloromethane (0,9 %) totalizing 14,4 %. Duka has a higher amount of extractives than afrormosia (12,5 %) that has about 5,4 % of ethanol extractives, 4,6 % water extractives and 2,5 % of dichloromethane extractives. Regarding macromolecular compounds, it is also some difference between both woods. Lignin of untreated afrormosia wood has the highest amount with 30,2 % significantly more than duka with 23,5 %. Relating to cellulose, duka wood has 42,0 % and afrormosia 37,3 %, while the hemicelluloses content is similar for duka with 20,1 % and afrormosia with 20,0%.

Table 1: Chemical composition of untreated and heat treated duka, and afrormosia woods.

	Sample	Extractives (%)				Lignin (%)	Cellulose (%)	Hemic (%)
		Dic	Ethanol	Water	Total			
Duka	Unmodified	0,92	9,42	4,07	14,40	23,51	42,04	20,05
	Heat treated (212 °C/1 h)	2,41	7,76	7,63	17,80	30,51	40,65	11,04
	Heat treated (212 °C/2 h)	2,68	7,35	5,14	15,16	33,17	41,33	10,33
Afrormosia	Unmodified	2,53	5,39	4,60	12,52	30,18	37,33	19,98
	Heat treated (212 °C/1 h)	4,54	4,46	7,72	16,72	36,16	35,81	11,31
	Heat treated (212 °C/2 h)	4,69	5,23	12,38	22,31	33,61	33,25	10,84

The structural compounds most affected by the thermal modification were the hemicelluloses as reported by other authors (Esteves *et al.* 2010, Esteves *et al.* 2008, Sivonen *et al.* 2002, Tjeerdsma *et al.* 1998). With 1 h treatment at 212 ºC, duka's hemicelluloses decrease almost 50 %, from 20,1 % to 11,0 %, similarly to afrormosia where hemicelluloses decreased from 20,0 % to 11,3 %. The decrease was higher for both samples heat-treated for 2 h, nevertheless the biggest differences are observed between untreated and heat-treated wood during 1 h.

Cellulose content also decreases with thermal modification for both duka and afrormosia woods: from 42,0 % to 40,7 % and from 37,3 % to 35,8 %, respectively. This is probably due to the degradation of amorphous cellulose leading to an increase in its crystallinity (Bhuiyan *et al.* 2001, Wikberg and Maunu 2004).

Contrary to the other structural compounds, the percentage of lignin increases with 1 h treatment from 23,5 % to 30,5 % and from 30,2 % to 36,2 % for duka and afrormosia woods respectively. This percentage increase does not mean, however, that there is no lignin degradation but only that the rate of lignin degradation is lower than that of polysaccharide compounds. There is also feasible that the condensation reactions that are known to occur between lignin and degradation compounds might increase the amount of lignin (Esteves *et al.* 2008). This is also supported by the amount of phenolic compounds found in the extracts although some might come from the degradation of other phenolic extractives found in untreated wood. The increase in heat treated wood lignin and decrease in polysaccharide content has been reported before by several authors (Boonstra and Tjeerdsma 2006, Ding *et al.* 2011, Tjeerdsma and Militz 2005).

Table 1 presents the percentage of extractive for untreated, and heat treated afrormosia and duka woods. Thermal modification increases the amount of extractives essentially for mild treatments (1 h) has can be seen in Table 1. This increase is mostly due to water and ethanol extractives as stated before by Esteves *et al.* (2010). The increase or decrease depends on the equilibrium between the degradation of initial extractives and the appearance of new ones originated by the degradation of structural compounds. This is probably why the variation in extractive content along thermal modification depends on the species. While the amount of extractives increased along the treatment for afrormosia, in duka wood there is an initial increase followed by a decrease (Table 1). One of the feasible explanations for the higher amount of extractives produced from thermal degradation of afrormosia wood might be the higher decrease in cellulose content. This is in accordance with the increase found in the water extract of treated afrormosia wood since most of the compounds released by cellulose thermal degradation are water soluble. Also the higher increase in lignin percentage of duka wood might suggest that there was a higher condensation between lignin and derivatives from polysaccharide thermal degradation.

Dichloromethane extractives increased with the treatment for both woods, however this extract still represents the minority extract even for heat-treated wood. Ethanol extractives decreased along the treatment for duka wood. This is most likely due to the high amount of ethanol extractives in initial wood (10,9 %) that are degraded of volatilized along the thermal modification. Regarding afrormosia there is a decrease followed by an increase for the 2 h treatment. The highest increase in afrormosia wood was in water extractives from 4,53 % to 12,02 %, while for Duka wood there is an increase followed by a decrease. If there is a significant decrease in wood polysaccharides, mainly in hemicelluloses but also in cellulose to some extent, it is expected that most of the newly formed extractives are sugars that can mainly be found in water and somewhat in ethanol extracts. Extractive composition is very difficult to determine since there isn´t a single equipment able to identify all the extractives found on wood. GC-MS was used to identify compounds that are already volatile or that can be made volatile by the derivatization process. Dichloromethane extracts are mainly composed of the less polar compounds like fatty acids, alkanes, waxes, terpenes and terpenoids, although some other compounds can also be extracted like several phenolic compounds. Usually, when extraction is made by soxhlet the most volatile compounds like monoterpenes (two isoprene units) and sesquiterpenes (three isoprene units) are not found in the extract and only higher terpenes and terpenoids such as resin acids (diterpenes) and phytosterols (triterpenes) are found.

Table 2 presents the results for an analysis of variance (ANOVA) of extractives, lignin, cellulose and hemicelluloses with heat treatment and wood fixed factors (only interaction significance level is presented). Results show that interaction between treatment and wood factors is significant for most of all chemical compounds except for dichloromethane extractives and hemicelluloses. The non-significance of hemicelluloses is apparently due to this compound being determined by difference. Therefore, and because there was a high significance level for the cross-effects (heat treatment x wood), single effects must be evaluated. These effects are presented in Table 3.

Table 2: Interaction significance level for Two-way ANOVA for chemical compounds with heat treatment and wood fixed factors for afrormosia and duka woods.

Chemical compound	Significance (P value)
Dichloromethane Extractives	0,258
Ethanol Extractives	0,035
Water Extractives	0,000
Total Extractives	0,001
Lignin	0,000
Cellulose	0,010
Hemicelluloses	0,974

One-way analysis of variance (ANOVA) was used to study the effects of the heat treatment on the amount of each chemical compound. Results showed that there was a statistically significant difference along the heat treatment for all chemical compounds with the exception of ethanol extractives and cellulose for duka wood. This strengthens the results presented before.

Table 3: P value for One-way ANOVA of chemical compounds with heat treatment for afrormosia and duka woods.

	Significance (P value)	
	Afrormosia	Duka
Dichloromethane Extractives	0,003	0,007
Ethanol Extractives	0,029	0,053
Water Extractives	0,001	0,008
Total Extractives	0,003	0,075
Lignin	0,001	0,001
Cellulose	0,013	0,207
Hemicelluloses	0,019	0,030

There is an increase in dichloromethane extractives and this increase is seen in both woods. The extractive composition of untreated and heat-treated wood can give us some notion of what is happening with wood compounds along the thermal modification. It is known that wood degradation starts with the hemicelluloses that decrease along the treatment as stated before. It is expected that furfural and hydroxymethyl-furfural arise from the degradation of pentose and hexose, respectively (Tjeerdsma and Militz 2005). Nevertheless, since these compounds are very volatile, they generally cannot be found in the extracts of treated wood and therefore none of such compounds could be found in the analysed extracts. On the other hand, only a fraction of the new compounds that are formed can be determined from GC-MS analyses, probably because the remaining extractives have high molecular masses and high boiling points and are difficult to be volatilized. This is seen mainly in ethanol and water extracts that after derivatization still have some undissolved compounds.

Table 4, Table 5, Table 6 and Table 7 present the retention time (RT) and the amount of the most important extractives in dichloromethane and ethanol of afrormosia and duka woods. Dichloromethane extract of untreated afrormosia wood (Table 4) is dominated by the high amount of β-Sitosterol which is one of the most common phytosterol in wood that accounts for more than 50 % of the extract. For example, Kilic and Niemz (2012) studied the extractives of eleven tropical woods and in all the tested woods β-sitosterol was found. Also, some other phytosterols could be found in the extract like campesterol and stigmasterol. Both these compounds were also found in the extracts of several tropical woods by Kilic and Niemz (2012). Some resin acids (diterpenes) dehydroabietic, fatty acids like stearic and palmitic, some glycols like glycerol and diethylene glycol and some phenolic compounds like vanillin, 2,4- dihydroxybenzaldehyde or 2,6 dimethoxyhydroquinone were also found.

With thermal modification the main changes observed in the dichloromethane extract of afrormosia wood is the disappearance or decrease of the initial extractives and the increase of new compounds. From the initial

extractives there is a high decrease of β-sitosterol, campesterol and pimaric acid. The appearance of a different sterol stigmasta-3,5 diene might be due to structural changes of the initial sterols. The new formed compounds that increased along the thermal modification are namely vanillin, syringaldehyde, vanilic acid and syringic acid. For the most severe treatment (2 h), coniferaldehyde, sinapaldehyde and acetovanillone were also detected.

Table 4: Dichloromethane extractives of untreated and heat treated afrormosia wood.

RT	Identification	Unmodified	212 °C/1 h	212 °C/2 h
5,12	2-Hydroxybutyric acid, 2TMS derivative	-	-	0,319
8,25	Guaiacol-TMS	0,428	-	-
8,56	Diethylene glycol, 2TMS derivative	0,618	15,476	-
8,93	Benzoic Acid, TMS derivative	-	1,215	-
9,29	Glycerol, 3TMS derivative	2,931	1,942	0,442
12,55	4-Hydroxybenzaldehyde, TMS derivative	0,563	-	0,207
12,97	Hydroquinone, 2TMS derivative	0,385	-	0,163
13,08	Syringol, TMS derivative	-	-	0,582
14,84	Ethyltriethylene glycol, TMS derivative	-	1,826	-
16,26	4-Trimethylsiloxy(trimethylsilyl)valerate	-	0,720	-
16,44	2,4-Di-tert-butylphenoxytrimethylsilane	0,811	-	0,445
16,71	Vanillin, TMS derivative	0,478	16,792	12,036
17,29	Tyrosol, 2TMS derivative	-	-	0,173
18,75	Acetovanillone, TMS derivative	-	-	0,280
19,28	2,4-Dihydroxybenzaldehyde, 2TMS derivative	0,874	-	-
19,83	2,6-Dimethoxyhydroquinone, 2O-TMS	1,236	-	1,511
19,94	2,4-Dihydroxybenzaldehyde, 2TMS derivative	1,864	2,875	1,331
20,59	Syringaldehyde, TMS derivative	0,939	7,680	25,146
21,76	Vanillic Acid, 2TMS derivative	0,427	4,813	2,614
23,72	Coniferyl aldehyde, TMS derivative	-	-	3,161
24,01	Nonaethylene glycol, 2TMS derivative	-	0,445	-
24,54	Syringic acid, 2TMS derivative	-	2,759	3,558
26,88	Sinapaldehyde, TMS derivative	-	-	6,961
27,32	Palmitic Acid, TMS derivative	9,167	9,711	2,848
30,43	3,4'-Isopropylidenediphenol, bis(trimethylsilyl) ether	-	-	0,535
30,82	Stearic acid, TMS derivative	1,005	2,983	0,611
33,36	Dehydroabietic acid, TMS derivative	0,901	1,815	-
38,72	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	3,691	-	1,691
43,45	Stigmasta-3,5-diene	-	0,940	-
45,20	Campesterol, TMS derivative	6,517	3,099	2,202
45,48	Stigmasterol, TMS derivative	1,100	1,165	-
46,25	β-Sitosterol, TMS derivative	66,066	23,744	33,183

These compounds are most certainly derived from lignin degradation although they can also result from the degradation of some other phenolic compounds. These compounds have been reported to be the result of heating or alcoholic hydrolysis of lignin (Moreno and Peinado 2012). In accordance to these authors, the degradation of lignin creates several aldehydes, such as syringaldehyde, sinapaldehyde, vanillin and

coniferaldehyde that further degrade into phenolic acids due to oxidation reactions, syringaldehyde leads to syringic acid, sinapaldehyde to sinapic acid, vanillin to vanillic acid and coniferaldehyde to ferulic acid. Also, acetovanillone has been reported to appear resulting from lignin degradation.

A high amount of diethyleneglycol was found for the 1 h treatment but, even though this compound can be found in wood extracts, this high amount suggests a possible contamination in the analysis. A phthalate peak was also found in the extracts but was most likely due to some plastic contamination.

The extractives in dichloromethane of untreated duka are not much different from those existing in afrormosia wood. Nevertheless, there were several compounds in untreated duka wood that could not be identified. The phytosterols, β-sitosterol, campesterol and stigmasterol were also found in dichloromethane extract of duka wood. Similarly, the diterpene dehydroabietic acid was also present. Three fatty acids were detected, pimaric acid, 11- octadecenoic acid, and stearic acid. A high amount of diethylene-glycol, other polyalcohols like glycerol were also found (Table 5). Similarly to afrormosia, wood the compounds associated with lignin degradation like vanillin, syringaldehyde, vanilic acid and syringic acid were found.

Table 5: Dichloromethane extractives of untreated and heat treated duka wood.

RT	Identification	Unmodified	212 °C/1 h	212 °C/2 h
5,58	2-Hydroxy-2-methylbutyric acid, 2TMS derivative	-	3,398	4,556
8,59	Diethylene glycol, 2TMS derivative	18,016	4,494	8,632
9,35	Glycerol, 3TMS derivative	7,148	0,375	-
14,78	Carbitol, TMS derivative	8,217	2,430	2,858
16,20	4-Hydroxybutanoic acid, 2TMS derivative	-	3,637	8,180
16,74	Vanillin, TMS derivative	2,010	11,009	7,320
18,63	Triethanolamine, 3TMS derivative	2,623	-	-
19,39	β-Arabinopyranose, 4MS derivative	-	0,728	1,363
19,88	2,6-Dimethoxyhydroquinone, 2O-TMS	-	0,952	0,782
20,57	Syringaldehyde, TMS derivative	-	28,306	19,856
21,80	Vanillic Acid, 2TMS derivative	2,138	3,128	2,412
23,57	Octaethylene glycol, 2TMS derivative	1,639	-	-
24,01	Decaethylene glycol, 2TMS derivative	2,281	-	-
24,57	Syringic acid, 2TMS derivative	-	4,926	4,365
27,37	Palmitic Acid, TMS derivative	10,219	3,953	5,401
30,42	11-Octadecenoic acid, (Z)-, TMS derivative	2,986	-	-
30,89	Stearic acid, TMS derivative	3,378	0,880	-
33,36	Dehydroabietic acid, TMS derivative	3,250	2,726	-
34,03	Undecaethylene glycol, 2TMS derivative	1,019	-	-
34,26	Hexaethylene glycol, 2TMS derivative	2,665	-	-
42,67	Stigmastan-3,5,22-trien	-	0,700	1,240
43,00	Stigmasta-3,5-diene	-	0,619	0,955
43,45	β-Sitosterol, propionate	-	2,794	5,122
45,22	Campesterol, TMS derivative	1,675	2,413	2,873
45,50	Stigmasterol, TMS derivative	8,302	5,295	4,638
46,24	β-Sitosterol, TMS derivative	22,434	17,238	19,447

The ethanol extracts of both woods are much more complex than the extracts in dichloromethane. Afrormosia ethanol extract (Table 6) is composed of glycerol, which is one of the most common extractable compounds in wood, several phenolic compounds like Resorcinol, 2,4-dihydroxybenzaldehyde, 2,4-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, trans-coniferryl alchool, 1-(3-hydroxyphenyl) ethane-1,2-diol, hydrobenzoin, gallic acid and others. Some monosaccharides (sugars), like D-sorbitol, xylitol, scyllo-inositol, myo-inositol and disaccharides, identified as sucrose or lactose were detected. Nevertheless, GC-MS spectra of these compounds are very similar and can be easily wrongly identified. Several lignans like isolaricresinol, medioresinol and syringaresinol were also found. A flavonoid taxifolin, a stilbene, pynosilvin and a sulphur-based compound were also identified (3-methyl-5-octadecyl-2-tridecyl-thiophene). With thermal modification, most of the initial compounds are not detected in ethanol extract with the exception of the initial steroids that are still found and still represent a high amount of the chromatogram. Probably because these compounds are more heat resistant than others. Nevertheless, this can also happen because there are less volatile or volatilized compounds in ethanol extract of heat-treated wood.

There are many new compounds that appear in ethanol extract but some of them could not be identified, probably because they have a very close retention time using this GC column and for higher oven temperatures there are often mixtures between these compounds and siloxane peaks from the column. Nonetheless, several hydroxy acids could be found like 2-hydroxybutyric acid, 2-hydroxyhexanoic acid, 4-hydroxybutanoic acid or dimethylolpropionic acid. These compounds are usually resultant from sugar degradation in acid media and it is known that wood pH decreases with thermal modification (Dzurenda *et al.* 2020). Also, some deoxy pentonic acids like 3-deoxy-erythro-pentonic acid and 3-deoxy 2,4,5 hydroxy-pentanoic acid, resulting from the degradation of pentose structures were detected in the extract. Levoglucosan increased along the thermal modification. This compound is a six-carbon ring structure known to be formed from the pyrolysis of hexoses, specially from glucose (Faix *et al.* 1991). The appearance of these compounds can enlighten the pathway of carbohydrates degradation by heat-treatment and show that both hemicelluloses and cellulose are being affected by the treatment. In accordance to Luijkx *et al.* (1995) hydrothermolysis of D-glucose leads to the formation of small amounts of 3-deoxyhexonic acids. Several phenolic compounds, associated to lignin or phenolic extractives degradation already identified in the dichloromethane extract, are still found in ethanol extract and represent a high amount, like syringaldehyde, vanillic acid, syringic acid and sinapaldehyde. A different compound, not found in dichloromethane extract, trans-sinapyl alcohol was found here. There is a compound appearing at 39,95 min that is identified as alizarin yellow GG, O,O'-di(trimethylsilyl) but is certainly a different compound with a similar mass spectra. There is a clear increase of this compound with the thermal modification and even though the peak is well resolved no better identification was obtained in NIST GC-MS database, probably because it is a high mass compound that has not yet been identified.

Ethanol extract from duka wood (Table 7) proved to be more difficult to analyse. It is mostly composed of di and triterpenoids structures like phytosterols but most of them could not be completely identified. The ones that are identified were 2-methoxyestrone and betulin and even about these two some doubts remain since 2-methoxyestrone is not commonly associated with wood and betulin is normally associated with *Betula spp*.

Table 6: Ethanol extractives of untreated and heat treated afrormosia wood.

RT	Identification	Unmodified	212 °C/1 h	212 °C/2 h
5,33	2-Hydroxybutyric acid, 2TMS	-	5,797	2,317
9,36	Glycerol, 3TMS derivative	11,942	3,584	3,212
10,69	Butanedioic acid, 2TMS derivative	-	2,781	1,258
11,00	Glyceric acid, 3TMS derivative	-	0,465	-
11,19	2-Hydroxyhexanoic acid di-TMS	-	0,964	0,976
12,56	Resorcinol, 2TMS derivative	1,389	0,355	-
13,24	Pentanedioic acid, 2TMS derivative	-	0,413	-
15,65	4-Hydroxybutanoic acid, 2TMS	-	1,517	1,676
15,73	Dimethylolpropionic acid, 3TMS	-	2,690	-
16,01	4-	-	1,592	7,182
16,31	Benzoic acid, 2-(dimethylamino)-3-	0,850	-	-
16,71	1,5-Pentanediol, 2TMS derivative	-	0,380	-
16,79	Vanillin, TMS derivative	-	1,724	-
18,21	Methyl isovanillate, TMS derivative	0,322	-	-
18,65	3,4-Dihydroxybenzaldehyde,	0,337	0,258	-
18,74	4-Hydroxybenzoic acid, 2TMS	0,905	1,005	0,998
19,04	Pentonic acid, 3-deoxy-2,4,5-tris-O-(trimethylsilyl)-, trimethylsilyl ester	-	-	0,690
19,38	β-Arabinopyranose, 4MS derivative	-	2,077	1,860
19,87	2,6-Dimethoxyhydroquinone, 2O-TMS	-	2,944	3,883
19,99	2,4-Dihydroxybenzaldehyde, 2TMS	10,819	1,762	1,504
20,26	3-Deoxy-erythro-pentonic acid,	-	1,029	1,443
20,35	Levoglucosan, 3TMS derivative	-	1,652	2,411
20,54	Xylitol, 5TMS derivative	1,432	-	0,136
20,58	Syringaldehyde, TMS derivative	-	9,693	9,723
21,79	Vanillic Acid, 2TMS derivative	2,060	14,096	14,847
22,73	2,4-Dihydroxybenzoic acid, 3TMS	6,571	0,820	0,899
22,86	Protocatechoic acid, 3TMS derivative	-	1,042	1,024
22,92	3,5-Dihydroxybenzoic acid, 3TMS	1,689	-	-
24,01	2,5-Dihydroxybenzoic acid, 3TMS	0,610	0,467	-
24,48	Taxifolin, 5O-TMS	0,398	-	-
24,56	Syringic acid, 2TMS derivative	1,268	12,649	17,022
24,72	Pinosylvin, bis(trimethylsilyl) ether	0,484	0,856	-
24,78	D-Sorbitol, 6TMS derivative	1,445	-	-
25,29	4,4'-Methylenedi-2,6-xylenol,	-	1,507	1,671
25,30	Scyllo-Inositol, 6TMS derivative	0,525	-	-
25,41	trans-Coniferryl alchool, 2O-TMS	4,470	0,969	1,588
26,94	Sinapaldehyde, TMS derivative	-	1,746	2,137
27,40	Palmitic Acid, TMS derivative	1,211	0,850	-
27,84	Myo-Inositol, 6TMS derivative	0,413	-	0,411
28,14	trans-Sinapyl alcohol, 2O-TMS	-	1,387	2,164
29,98	Hydrobenzoin, 2TMS derivative	7,300	-	-
32,77	2,5-Dihydroxybenzaldehyde, 2TMS	8,090	-	-
33,35	Dehydroabietic acid, TMS derivative	-	1,012	-
33,69	(S,S)-(-)-Hydrobenzoin,	2,385	-	-
35,73	1,2-Benzenedicarboxylic acid, bis(2-	2,524	-	0,353
35,87	1-(3-Hydroxyphenyl)ethane-1,2-diol	8,059	-	-
36,28	1-Monopalmitin, 2TMS derivative	-	-	0,439
36,65	Sucrose, 8TMS derivative	0,423	-	-
38,16	Lactose, 8TMS derivative	1,874	-	-
38,30	cis-Resveratrol, 3TMS	0,306	-	-
38,64	Maltose 8TMS	-	0,660	1,010
38,78	Gallic acid, 4TMS derivative	5,077	-	-
39,04	Glycerol monostearate, 2TMS	0,304	-	0,722
39,90	Thiophene, 3-methyl-5-octadecyl-2-	6,737	-	-
39,95	Alizarin Yellow GG, O,O'-	-	5,837	6,791
41,46	Isolariciresinol, 4O-TMS	-	0,806	-
42,10	3-(3',4'-Dimethoxyphenyl)-7-hydroxy-4-phenylcoumarin, TMS	-	1,234	1,437
42,66	2,2-Bis(3-allyl-4-hydroxyphenyl)propane, bis(trimethylsilyl) ether	0,817	-	-
46,23	β-Sitosterol, TMS derivative	2,573	2,445	3,057
47,82	Medioresinol, 2-O-TMS	1,923	1,685	1,852
49,55	Syringaresinol, 2TMS	2,467	7,247	8,881

There are several compounds that appear in the zone normally identified as the phytosterols zone of the GC-MS Chromatogram that are identified as methylglycocholate which is a common compound in bile acids and therefore not probable to exist in wood extracts. Nevertheless, this compound was reported as been present in coffee extracts by Masek *et al.* (2020).

Table 7: Ethanol extractives of untreated and heat treated duka wood.

RT	Identification	Unmodified	212 °C/1 h	212 °C/2 h
7,72	Catechol, TMS derivative	1,517	-	-
7,95	1-Methyl-1-N-octyloxy-1-silacyclobutane	5,993	-	-
9,05	1-Octen-3-ol, TMS derivative	10,140	-	-
9,36	Glycerol, 3TMS derivative	-	0,981	-
10,73	Butanedioic acid, 2TMS derivative	-	1,073	-
11,2	Hexanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester	-	0,692	-
12,47	2,4-Dimethoxyphenol	-	-	1,077
14,01	4,6-Dioxoheptanoic acid per-tms	24,445	-	-
14,26	Vanillin lactoside	-	-	4,208
14,89	Phenol, 4-methoxy-3-(methoxymethyl)-	-	-	1,422
15,11	1-Tetradecanol, TMS derivative	0,596	-	-
15,67	4-Hydroxybutanoic acid, 2TMS derivative	-	12,118	-
16,79	Vanillin	-	-	7,537
16,83	5,8,11,14-Eicosatetraynoic acid, TMS derivative	2,313	-	-
17,78	Syringaldehyde	-	-	10,116
18,38	3,5,3',5'-Tetramethyl-N4-propyl-biphenyl-4,4'-diamine	5,777	-	-
18,49	3,4-Dihydroxybenzaldehyde, bis(trimethylsilyl) ether	-	1,414	0,666
19,01	2-Hydroxymandelic acid, ethyl ester, di-TMS	8,703	-	-
19,04	Pentonic acid, 3-deoxy-2,4,5-tris-O-(trimethylsilyl)-, trimethylsilyl ester	-	0,355	-
19,39	Arabinofuranose, 1,2,3,5-tetrakis-O-(trimethylsilyl)-	-	5,844	1,906
19,56	Phloroglucinol, O,O'-bis(trimethylsilyl)-	6,417	10,746	-
19,88	2,6-Dimethoxyhydroquinone, 2O-TMS	-	4,901	-
20,13	D-(+)-Talofuranose, pentakis(trimethylsilyl) ether (isomer 2)	-	0,679	-
20,35	Levoglucosan, 3TMS derivative	-	1,633	-
20,58	Syringaldehyde, TMS derivative	-	9,115	37,595
21,79	Vanillic Acid, 2TMS derivative	-	5,353	3,892
22,03	3-Deoxy-ribo-hexonic acid γ-lactone, TMS	-	0,819	0,578
22,35	3-Deoxy-arabino-hexonic acid γ-lactone, TMS	-	4,904	10,545
22,86	Protocatechoic acid, 3TMS derivative	-	5,986	-
24,15	Taxifolin, 5O-TMS	0,178	0,555	-
24,58	Syringic acid, 2TMS derivative	-	16,537	16,503
26,96	Sinapaldehyde, TMS derivative	-	1,044	-
27,85	1,2,3,4,5,6-Hexa-O-trimethelsilyl-myo-inositol	-	1,199	-
28,15	trans-Sinapyl alcohol, 2O-TMS	-	0,391	0,203
35,22	β-D-Xylopyranose, 4TMS derivative	-	0,518	-
35,98	α-D-Glucopyranosiduronic acid, 3-(5-ethylhexahydro-2,4,6-trioxo-5-pyrimidinyl)-1,1-dimethylpropyl 2,3,4-tris-O-(trimethylsilyl)-, methyl ester	-	3,733	-
38,09	Lactulose, octakis(trimethylsilyl) ether, methyloxime (isomer 1)	-	0,401	-
39,95	Alizarin Yellow GG, O,O'-di(trimethylsilyl)-	-	1,511	0,951
42,93	Pinosylvin, bis(trimethylsilyl) ether	4,256	-	0,908
43,23	Ferruginol, trimethylsilyl ether	8,549	-	-
45,23	2-Methoxyestrone, TMS derivative	12,164	-	-
47,15	Betulin	8,480	-	-

This chromatographic methodology could not efficiently separate these compounds probably because they have very similar structures. The initial content of these compounds represented more than 40 % of the extract for untreated wood and was practically inexistent in treated wood extracts (Table 1). Besides these compounds, one meroterpene, ferrufinol, was detected in ethanol extract. A significant amount of a hydroxy acid, 4,6-dioxoheptanoic acid was also detected. There were also some phenols like catechol, 2-hydroxymandelic acid, ethyl ester or phloroglucinol. Other compounds identified in this extract were alcohols like glycerol, 1-octen-3-ol and 1-tetradecanol, one fatty acid, 5,8,11,14- eiocosatetrayonic acid, one flavonoid, taxifolin, one stilbene and pinosylvin.

With thermal modification several compounds could be identified in heat-treated wood extracts, similarly to afrormosia wood. Some hydroxy acids were also found like 2-hydroxyhexanoic acid and 4-hydroxybutanoic acid. Likewise, some deoxy pentonic acids like 3-deoxy-2,4,5-hydroxy-pentanoic acid and two lactones: 3-deoxy-arabino-hexonic acid γ-lactone and 3-deoxy-ribo-hexonic acid γ-lactone. Levoglucosan was also detected. Similar compounds were described as been a result of carbohydrates pyrolysis (Faix *et al.* 1991). Butanedioc acid, a dicarboxylic acid that has been reported before as being a volatile organic compound released from particleboard heated at temperatures 140 ºC and 180 ºC (Liu *et al.* 2010) was also detected in ethanol extract.

Regarding phenolic compounds, syringaldehyde, vanillic acid, syringic acid, sinapaldehyde and trans-sinapyl alcohol, that were identified in both dichloromethane extracts and in afrormosia ethanol extracts, were also present. It was also found some other phenolic structures like 2,6-dimethoxyhydroquinone, protocatechoic acid and 3,4-dihydroxybenzaldehyde. The same compound identified as alizarin yellow GG, O,O'-di(trimethylsilyl) in afrormosia extract was detected. In heat-treated Duka wood ethanol extract several sugars like arabinofuranose, D-(+)-talofuranose, β-D-xylopyranose, 1,2,3,4,5,6-hexa-O-trimethelsilyl-myo-inositol and Lactulose were noticed.

Most of the water extract compounds could not be volatized and remained in the vial as an insoluble residue. This is probably due to the high mass of these compounds that would require a different analysis. The main identified compounds in afrormosia water extract were several sugars, especially disaccharides that could not be completely identified but most of them recognized as Sucrose, carboxylic and hydroxy acids like, malic acid, 2-pentanedioc acid, 4-pentenoic acid, 2-butenedioc acid, 2-methyl-2,4-dihydroxy-pentanedioic acid and citric acid and deoxy acids like 3-deoxy-pentonic acid. Similar compounds were found in the water extract of duka wood with some extra compounds like tartaric acid or 3-deoxy-arabino-hexaric acid and 2-furanacetaldehyde and protocatechoic acid.

CONCLUSIONS

With the developed work it is possible to conclude that the most affected structural wood compounds by the thermal modification were the hemicelluloses, followed by cellulose and lignin. Although lignin percentage increased, the extractives analysis showed several compounds normally associated to lignin thermal degradation. There was not much difference between afrormosia and duka woods structural compounds behaviour along thermal modification. Extractives increased essentially for mild treatments. This increase was mostly due to water and ethanol extractives. While the extractives increased along the treatment for afrormosia, in duka wood there was an initial increase followed by a decrease with the increase of heating time, which was probably due to the high amount of initial ethanol extractives in duka wood that are degraded along the treatment. The new formed compounds that increased along the thermal modification found in dichloromethane extract are vanillin, syringaldehyde, vanilic acid and syringic acid. For the most severe treatment (2 h), coniferaldehyde, sinapaldehyde and acetovanillone were also detected. All these compounds have been associated to lignin heat degradation showing that although the percentage increases, there is still some lignin thermal degradation. The compounds identified as resulting from lignin degradation in dichloromethane extracts still represent a significant amount in ethanol extracts of both heat-treated woods. Additionally, several other compounds like hydroxy acids, deoxy-pentonic acids, deoxy-hexonic acids γ-lactone and levoglucosan were found in ethanol extract. On heat-treated duka some carbohydrates were also found. All these compounds have been associated to C5 and C6 carbohydrate thermal decomposition. The results have contributed to the understanding of the chemical degradation path of modified wood by monitoring extractive content transformations and have shown the importance of optimizing the treatment for each wood species in order to make the best utilization of this material.

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