

Compositions of Monomeric Sugars in Some Nigerian Hardwoods

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Abstract

Compositional analysis of monomeric sugars in carbohydrate fractions of 10 African angiosperms has been carried out using acid hydrolysis and high performance anion exchange chromatography with borate post column derivatization (HPAEC-Borate). The monomeric sugars in the wood stems were dominated by glucose, primarily from the cellulosic fraction of the biomasses. Xylose and small fractions of mannose constituted the main sugars from the hemicellulose fractions. The concentration of glucose peaked at 510 mg/g (dry sample) in *Sterculiar rhinopetala*, the lignocellulose with the least concentration of mannose among the samples. The ratio of the xylose to 4-O-methylglucuronic acid in *Terminalia ivorensis* suggested that this sample has more acidic xylan than *Trilepsium madagascariensis*, the sample with the richest xylan content (15 wt. %). The concentration of arabinose, rhamnose and galactose were mostly below 10 mg/g (dry sample) in all samples. The analysis of the non holocellulosic fractions of the samples revealed high lignin contents, which ranged 19.4 wt. % - 33.8 wt. % and high extractive contents, ranged between 1.8 wt. % and 11.0 wt. % (on dry basis).

Keywords: Biomass, Extractives, Hardwoods, Lignin, Monomeric sugar, Polysaccharide

1. Introduction

The potential role of renewable resources in ameliorating detrimental effects of petroleum on the environment has given impetus to the revival of researches in biomass-derived chemical products in the recent time. The concept of sustainable development is promoting research and development in the production of fuels and chemicals from biomasses, whose utilizations will result in zero-net carbon on the environment (Clark, 2007). Leap frogging from pollution-inducing scientists, demands efforts towards generating energy and chemical needs to support life from renewable sources like biomass (Kamm et al., 2006). To avoid creating more problems than solving (food shortage), the use of lignocelluloses, not involved in food chain, as raw materials for the production of fuels and platform chemicals becomes imperative. Potential candidates in this regard include forestry, agriculture, trade and industry (sawn and wood industry) residues (Kamm et al., 2006; Foyle et al., 2007).

Lignocellulose matter mainly consists of polysaccharides and lignins. Other minor constituents are extractives and inorganic fractions. These minor components constitute less than 8 wt. % of the biomass, except in some extractive- and inorganic rich species (Azeez et al., 2010). The polysaccharides make up about 70 wt. % in many woods. This fraction is made up of cellulose and hemicellulose. The combination of cellulose and hemicellulose is qualified as holocellulose. Cellulose is formed from β -D-glucopyranose units, linked through (1-4)-glycosidic bonds to form the dominant semi-crystalline biomass homopolymer (Fengel and Wegener, 1984; Sjöström 1993). On the other hand, heteroglycans, the hemicelluloses in biomass, consist of varying combinations of C₆ and C₅ sugars. The dominant hemicellulose in angiosperm is *O*-acetyl-4-*O*-methylglucurono- β -D-xylan (glucuronoxylan). Glucuronoxylan. It accounts for 80-90 relative percentage of hemicellulose in hardwood (Fengel and Wegener, 1984). Glucomannans dominates the hemicellulose fraction of gymnosperms. Other main hemicelluloses in woods include arabinomethylglucuronoxylan, galactoglucomannan, arabinogalactan, other forms of galactans and pectins (Spiridon and Popa, 2008). The monomeric sugars in hemicelluloses are D-xylose, L-arabinose, D-glucose, D-mannose, D-galactose, D-glucuronic acid, 4-*O*-methyl-D-glucuronic acid, D-galacturonic acid, small amounts of L-rhamnose and many *O*-methylated neutral sugars (Sjöström, 1993; Sun et al., 2005; Maki-Arvela et al., 2011).

The conversions of lignocellulose via chemical, thermochemical and biochemical processes to fuel and chemical products are chief means of harnessing the economic values of these matters to mitigate our environmental problems. Depending on the chemical composition of the lignocellulose, the major fractions of the matter are convertible to chemical products through the second generation biofuel routes (Cherubini, 2010). Better still, they can serve as chemical platforms for the production of fuels and higher molecular chemical products, similar to products obtainable from petroleum (Kamm et al., 2006; Lan et al., 2011). Based on their percentage abundance in lignocellulose, holocellulose holds the key role as renewable carbon source, especially via thermochemical and biochemical conversion routes (Cherubini, 2010). They can effectively be hydrolysed to hexose and pentose (C₆ and C₅) monomeric sugars. These monomers can be employed in the production of bio-derived transportation fuels (Alonso et al., 2010). In addition, formic acids, sorbitol, levulinic acid and hydroxymethyl furfural are derivable from D-glucose, while xylitol and furfural can be obtained from xylose, the main hemicellulose fraction in hardwood (Werpy and Petersen, 2004; Chheda et al., 2007). Many of these

chemicals are known as bio-derived platform chemicals, from which other valuable chemical products can be obtained. For an effective utilization of polysaccharides in the production of renewable chemical products, the determination of their monomeric composition is desirable, for reliable technical and economic evaluations of the feedstock and the conversion process (Sevcik et al., 2011). Monomeric sugars such as glucose, xylose, arabinose, galactose, mannose and fructose are essential raw materials of interest (Agblevor et al., 2004).

There are many methods of quantifying monosaccharides in biomass. Accurate compositional quantification of polysaccharides in lignocellulose can be carried out using the hydrolysate of sample. This is obtained following the depolymerisation of the cellulose and hemicellulose into their constituent sugars either by acidic or enzymatic hydrolysis of extract-free sample. It has been noted that enzymatic hydrolysis work better only on delignified lignocellulose (Willför et al., 2009). Another depolymerisation method that can be used to liberate the monosaccharide sugars is the acid methanolysis (De Ruiter et al., 1992). The liberated sugars can be quantified through chromatographic analytical techniques such as gas chromatography (GC) or high performance liquid chromatography (HPLC), fitted with appropriate detectors (Agblevor et al., 2004; Rovio et al., 2008). These detectors include mass spectrometry (Kilic et al., 2010; Bogolitsyna et al., 2011) (MS), refractive index (RI) detection (Foyle et al., 2007), pulsed amperometric detection (PAD) (Sullivan and Douek, 1994) and evaporative light scattering detection (ELSD) (Liu et al., 2012). The use of HPLC in the analysis of sugars is more widely acceptable (Sluiter et al., 2010), because acid hydrolysed sugar sample for GC analysis requires reduction and derivatization. Both involve long procedures, capable of reducing the overall efficiency of the analysis (Davis, 1998). The use of high performance anion-exchange chromatography (HPAEC) has considerable advantage over other methods in terms of its sensitivity as well as separation efficiency (De Ruiter et al., 1992; Willför et al., 2009).

According to the estimation of Dionco-Adetayo (2001), log production in Nigeria in 2012 stood at 417 227 200 m³ with approximately 80% of the timber wasted during wood harvesting and logging operations. Over 90% of these residues are incinerated. In fact, wood residue is considered to be of no economic benefit in Nigeria (Dionco-Adetayo, 2001; Adeyi, 2010). With a huge annual waste tonnage, effective utilization of these residues can generate wealth from waste and also attenuate the release of carbon oxides into the atmosphere. But, the knowledge of average sugar composition of major woody lignocelluloses (majority of which are hardwoods) in Nigeria is scarce, because little or no work has previously been carried out to analyse them. Existence of this knowledge can create awareness on derivable products from the resource. And with the development of biomass fractionation processes, such as clean fractionation, steam explosion, ionic liquid, microwave irradiation, ultra sonication etc., to obtain major components of lignocellulose, different chemical fractions of wood wastes can be earned in the production of fuel and chemical products (Bozell et al., 2011; Lan et al., 2011; Peng et al., 2012). The aim of this study is therefore to investigate the amount of the monomeric sugars present in some Nigerian hardwoods. This will assist in evaluating their potential utilizations in fuel and chemicals production.

At present, about 90% of sawn and wood residues annually generated in Nigeria are often incinerated (Dionco-Adetayo, 2001). In fact, wood residue is considered to be of no economic benefit (Adeyi, 2010). With a huge annual waste tonnage, effective utilization of these residues can generate wealth from waste and also attenuate the release of carbon oxides into the atmosphere. But, the knowledge of average sugar composition of major woody lignocelluloses (majority of which are hardwoods) in Nigeria is scarce, because little or no work has previously been carried out to analyse them. Existence of this knowledge is crucial to designing most appropriate conversion processes to earn fuel and chemical products from them. The aim of this study is therefore to investigate the amount of the monomeric sugars present in some Nigerian hardwoods in order to evaluate their potential utilizations in fuel and chemicals production.

2. Materials and Methods

2.1 Materials

Fifteen identified wood logs, designated for the production of timbers, were collected at Omolayo sawmill, Ado Ekiti, Nigeria. The logs were originally obtained from 20-25 years old mature trees in a natural reserve at Igbemo Ekiti, Nigeria. Cross-sections of wood stems were obtained from different portion between the heights of 1.2-1.8m above ground. The portions were debarked, reduced to about 7 x 6 x 10 cm sizes and sun-dried. Thereafter, samples were milled using Retch cutting mill (SM2000) and sieved to obtain 200 μ m - 500 μ m sizes. The milled fractions of samples were collected and stored in polypropylene bags. Investigated wood samples and their local names are shown in Table 1.

2.2 Methods

Two-step acid hydrolysis was used according to TAPPI T 249 cm-85 method. In a typical procedure, about 200mg of milled wood sample (40-mesh) was pre-hydrolysed with 2ml 72% H₂SO₄ in reaction glass tube placed, in thermostatic water bath (30 °C) for 1 h. The pre-hydrolysis phase was terminated with 40ml ultra-pure water and the sample transferred into Systec VX-75 autoclave (Systec GmbH, Germany) for the hydrolysis at 120 °C

for 50min. The hydrolysed sample was made up to mark in 100 mL standard flask and allowed to cool. The sample was then filtrated using 0.45 μm fritted-glass filter. The residue was dried at 105 °C and gravimetrically determined for condensed lignin. And an aliquot of filtrate was taken for the analysis of various sugars. The qualitative analysis of various sugars in samples was carried out as described by Willfor et. al (2009).

A High-Performance Borate-Complex Anion-Exchange Chromatography (Ultimate 3000, Dionex Corp.), fitted with a 6.6mm bore column of 115mm length (Omnifit) was used. The column is packed with strong anion exchange resin (MCI Gel CA08F (Mitsubishi) at 60 °C). The mobile phase was made of (A) 0.3M potassium borate buffer pH 9.2 and (B) 0.9M potassium borate buffer pH 9.2. A gradient elution of 0.7 mlmin⁻¹ was employed for the separation. Separation began with 90% A and 10% B, and ended at 10% A and 90% B through a linear gradient elution within 35mins. The data acquisition lasted 47 min. Wood sugars were quantified by after-column derivatization with Cu-bichinconinate as described by previous authors (Willför et al., 2009). All analyses were carried out in duplicate and their average values reported. The total lignin contents in samples were determined as sum of acid insoluble (AIL) and acid soluble lignin (ASL). The AIL was obtained according to TAPPI T 222 om-88. The ASL was obtained by measuring the absorbance of the supernatant on UVIKON 943 UV/Vis Spectrometer at 205 nm according to TAPPI Useful Method UM 250.

3. Result and Discussion

3.1 Monomeric sugars in samples

The absolute amount of monomeric sugars in all samples, as shown in Table 2, ranges between 65.5 % and 52 %. *Celtis zenkeri* and *Triplochiton scleroxylon* contain the highest and lowest amounts respectively. The difference stems majorly from their glucose and xylose contents. While some of the values reported in Table 2 appear slightly low for woody biomass, they are not unusual for African hardwoods with high extractive, ash and lignin contents. Many African hardwoods have lower cellulose contents compared to hardwoods from other regions of the world (Fengel and Wegener, 1984). Most of these samples have not been previously analysed for their individual sugars. However, monosaccharide contents of the samples significantly agree with values reported for similar angiosperms; *Populus tremula* and *Eucalyptus obliqua* (Willför et al., 2009; Chirat et al., 2012). These samples were analysed using analogous analytical methods employed in this investigation. The depolymerisation of cellulose during acid hydrolysis yields its monomeric forms. Consequentially, the main concentration of glucose in the hydrolysate of lignocellulose is derived from the cellulosic fraction. Almost 80-90% of the glucose is derived from the cellulosic fraction of the lignocellulose. A minor fraction from heteropolymer hemicellulose is also included in the amounts of glucose reported in Table 2, since both the cellulose and hemicellulose have been depolymerised in the hydrolysate. The result of individual monomeric sugars in all the analysed samples indicated that *Sterculia rhinopetala* contains the highest amount of glucose with an absolute concentration of 50.8 % and *Triplochiton scleroxylon* contained the least (37.7 %).

The relative amount of glucose in the hydrolysates of all samples ranged between 68% and 81% (Figure 1). Hydrolysates of samples such as *Terminalia ivorensis*, *Sterculia rhinopetala*, and *Ficus mucoso* were found to contain more than 75 relative percentage of glucose. Glucose rich hydrolysate is an appropriate raw material in the production of second generation biofuels. With adequate and proper engineering design, such glucose-rich sample can be converted into ethanol via microbial fermentation process (Alonso et al., 2010). A triple dehydration of glucose produces hydroxymethylfurfural (HMF). This yellow low-melting solid is a building block molecule capable of yielding various bio-based chemicals. Amongst the list of top 12 bio-based platform chemicals are levulinic acid and 2,5-furandicarboxylic acid (FDA) (Werpy and Petersen, 2004). And both chemical products can be obtained from HMF through oxidation reaction. FDA has found applications in the production of fire foams (polymer) and in the removal of kidney stones (Boisen et al., 2009). Sorbitol is another important valuable chemical that is nowadays exclusively produced by catalytic hydrogenation of D-glucose using Raney Nickel or supported ruthenium catalyst. And this polyol has found extensive applications in food industry (Cabiacc et al., 2011).

Xylose forms the dominant hemicellulose-derived monomeric sugar in all samples as shown in Table 2 and Figure 1. This sugar constitutes the main fraction of O-acetyl-4-O-methylglucuronoxylan, otherwise known as xylan, the most dominant hemicellulose in hardwood. Xylose forms an homopolymer, interlinked by $\beta(1\rightarrow4)$ glycosidic bonds. Groups of 4-O-methylglucuronic acid are irregularly bonded to chains of xylanic homopolymers mostly by ratio of 10:1 (Xyl:Me-GluU), forming the hemicellulose in hardwood (Fengel and Wegener, 1984). The highest concentration of xylose (151 mg/g), representing 24.3 relative weight percentage of the biomass sugar, was found in *Trilepsium madagascariensis*. *Terminalia ivorensis* contains the least (77 mg/g). The xylans of *Sterculia rhinopetala* and *Terminalia ivorensis* exhibit lowest Xyl:Me-GluU as shown in Table 2. This compositional variation in various constituents is generally recognised in lignocellulose even among the same wood sample (Sun et al., 2005). Xylose is a pentose sugar like arabinose that is industrially used for the production of furfural. This conversion proceeds via acid catalysed cyclo-dehydration reaction (Campos Molina et al., 2012). Xylitol is an important chemical product obtainable from the xylose. It is commercially produced

from the C₅ sugar via hydrogenation reaction. It has large potential for the production of ethylene glycol and 1,2-propanediol via hydrogenation (Cherubini and Strømman, 2011). Xylitol and ethanol can easily be produced from hydrolysate mixture containing glucose, xylose and other monomeric sugars (Delgenes et al., 1998; Martínez et al., 2012).

The concentration of mannose ranked next to glucose and xylose among the sugars in most analysed wood samples. The maximum concentration of this sugar was found in *Khaya senegalensis* (30mg/g). *Sterculia rhinopetala* barely contain this monomer (2 mg/g). This sugar exists in hardwood in association with glucose units, forming the heteropolymer backbone called glucomannans. The ratio of these monomers in most hardwoods hemicelluloses earlier investigated is 1-2:1 (Sjöström, 1993; Fengel and Wegener, 1984; Peng et al., 2012). Glucomannans have a 60-70 degree of polymerisation in hardwood and are considered of minor importance compared to xylan (Fengel and Wegener, 1984). Neglecting some of the minor contributions from other extraneous glucans, the amount of glucose from cellulosic fraction of a sample can be approximately obtained by subtracting the contribution from glucomannan from the total glucose in the hydrolysate. Mannose is a C₆ sugar like glucose.

Arabinose, galactose and rhamnose were all detected as the least monomeric sugars in all samples. These sugars are present in concentrations less than 10 mg/g across all samples. Unlike in softwood, where arabinose and galactose slightly constitute major parts of the xylan and glucomannan backbone respectively, hardwood scarcely contains these sugars. Even though they are present, they exist in much low amounts compared to their concentrations in softwoods. It has been reported that minor amount of rhamnose and galacturonic acids can be found in the xylan backbone structure of some hardwoods (Fengel and Wegener, 1984). In terms of application, the quantity of minor hemicellulose sugars notwithstanding, it has been noted that all sugars in hydrolysate of lignocellulose can be converted to 2,3-Butanediol glycol (2,3-BD) (Menon and Rao, 2012). 2,3-BD is an important feedstock chemical with wide applications in the production of solvent and liquid fuel. It serves as precursor for the production of many synthetic polymers and resins.

3.2 Extractive and lignin fractions

The result of successive extraction shown in Table 3 as total extractives reveals the presence of large extractives in most samples. The amount of extractives in samples ranged between 1.8 wt. % and 11.0 wt. % (moisture free basis). The highest extractive was obtained from *Entandrophragma cylindricum*, while *Gmelina arborea* and *Fiscus mucus* contain the least. The concentration of total extracts in *Ceiba pentandra*, *Terminalia ivorensis*, *Entandrophragma angolensis* and *Entandrophragma cylindricum* were also higher than 7.5%, the average extractives in tropical woods (Brémaud et al., 2011). The extractives were mostly soluble in acetone fraction, except in the case of *Ceiba pentandra* and *Fiscus mucoso*, whose extracts exhibited higher polarity than others. Lignin constitutes the largest non-carbohydrate fraction of lignocellulose. As shown in Table 3, lignin contents of *Sterculia rhinopetala* (19.4 wt. %) and *Antiaris toxicaria* (33.8 wt. %) constitute the two extreme values in the investigated samples. The acid soluble fraction of lignin in *Gmelina arborea* and *Sterculia rhinopetala* are the most outstanding. This fraction constitutes 21% and 25% of the total lignin content both samples. Only 3.5% of the lignin content of *Antiaris toxicaria* was detected as acid soluble lignin. A fair linearity as illustrated by Figure 2 was observed between acid hydrolysis residues and lignin contents among samples. The result suggests a good solubility of the inorganic fraction during hydrolysis. The ease of removing indigenous alkali and alkaline earth in lignocellulose has been discussed by previous authors (Kleen and Gellerstedt, 1995; Scott et al., 2001). They noted that most of these metals can be removed by washing using hot water or dilute acids. The presence of large amount of silicates in sample could however affect such correlation. Lignin can serve as cheap raw material in the production of aromatic compounds such as vanillin and various phenolic compounds.

4. Conclusion

The compositional analysis of monomeric sugars has revealed the dominance of glucose and xylose in the analysed hardwood samples. In overall, *Celtis zenkeri*, *Sterculia rhinopetala* and *Khaya senegalensis* contain the highest sugars fractions. The glucose found in *Sterculia rhinopetala* constitutes more than 50 wt. % of the lignocellulose. The amount of xylose found in the 4-*O*-methylglucuronic acid of *Trilepisium madagascariensis*, *Entandrophragma cylindricum*, and *Khaya senegalensis* almost double the concentration in *Terminalia ivorensis*. The correlation between hydrolysis residue and lignin content established the reliability of using the former as a rough estimate for the amount of lignin in lignocellulose. The sum of reported values for analysed monosaccharide does not represent the exact amount of polysaccharides in individual sample since the amount of acetyl, methyl and other functional groups in the polysaccharides of samples were not evaluated. But the sum of these functional groups in wood samples is usually very small. The high lignin contents in the samples can also serve as raw materials in the production of phenolic chemical products. This can be achieved by the thermochemical conversion of the lignin fraction, following the removal of the polysaccharides in the sample. Expectantly, the data presented in this work will provide a sound basis for consideration to produce high valued

products from waste from the wood samples rather than incineration.

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Table 1: Investigated wood species and their local (Yoruba) names

Local Name (Yoruba)	English	Botanical Name	Family
Araba	Kapok	<i>Ceiba pentandra</i> (L) Gaertn	Malvaceae
Idigbo	Black Afara	<i>Terminalia ivorensis</i> A. Chev	Combretaceae
Ita	African celtis	<i>Celtis zenkeri</i> Engl.	Ulmaceae
Kokogbo	African Star Chestnut	<i>Sterculia rhinopetala</i> K. Schum	Malvaceae
Mahogany	Africa Mahogany	<i>Khaya senegalensis</i> (Desr) A.Juss	Meliaceae
Melaina	Gmelina	<i>Gmelina arborea</i> Roxb	Lamiaceae
Obeche	African maple wood	<i>Triplochiton scleroxylon</i> K. Schum	Malvaceae
Oriro	Antiaris/false iroko	<i>Antiaris toxicaria</i> Lesch.var <i>africana</i>	Moraceae
Orunpa		<i>Trilepisium madagascariensis</i> DC	Moraceae
Sapeli Mahogany	Sapele	<i>Entandrophragma cylindricum</i> (Sprague)	Meliaceae

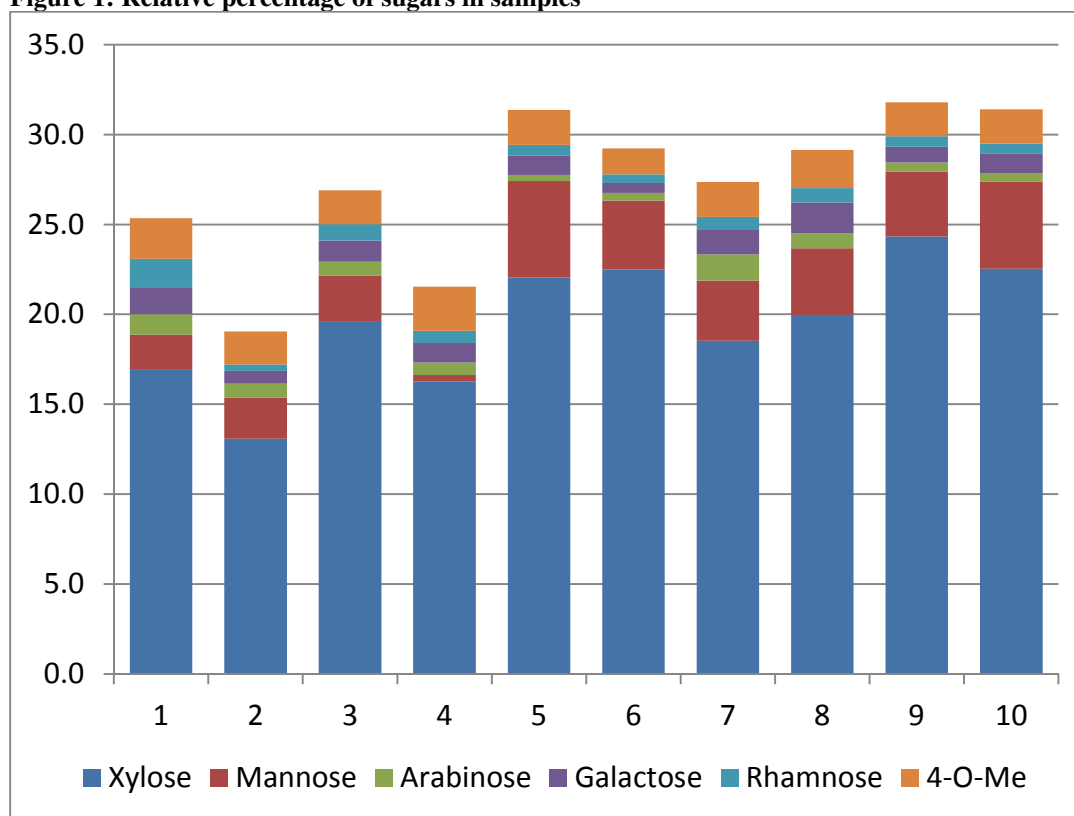
Table 2: Absolute concentrations of monomeric sugars in wood samples

Sample	Weight, mg/100mg of dry sample						
	Glucos e	Xylos e	Mannos e	Arabinos e	Galactos e	Rhamnos e	4-O-Me- GluA
<i>Ceiba pentandra</i>	42.9	9.7	1.1	0.7	0.8	0.9	1.3
<i>Terminalia ivorensis</i>	47.7	7.7	1.3	0.5	0.4	0.2	1.1
<i>Celtis zenkeri</i>	47.7	12.8	1.7	0.5	0.8	0.6	1.2
<i>Sterculia rhinopetala</i>	50.8	10.5	0.2	0.5	0.7	0.4	1.6
<i>Khaya senegalensis</i>	43.9	14.1	3.4	0.2	0.7	0.4	1.2
<i>Gmelina arborea</i>	41.8	13.3	2.3	0.3	0.3	0.3	0.9
<i>Triplochiton scleroxylon</i>	37.7	9.6	1.7	0.8	0.7	0.4	1.0
<i>Antiaris toxicaria</i>	40.2	11.3	2.1	0.5	1.0	0.4	1.2
<i>Trilepisium madagascariensis</i>	42.3	15.1	2.2	0.3	0.5	0.4	1.2
<i>Entandrophragma cylindricum</i>	42.3	13.9	3.0	0.3	0.7	0.4	1.2

Table 3: Extractive, lignin and ash contents of samples

Sample Name	weight percent (moisture free basis)		
	Total Extractive	Ash content	Klason lignin
<i>Ceiba pentandra</i>	8.9	4.9	28.0
<i>Terminalia ivorensis</i>	8.4	0.3	33.2
<i>Celtis zenkeri</i>	4.9	1.7	20.8
<i>Sterculia rhinopetala</i>	3.7	1.5	19.4
<i>Khaya senegalensis</i>	5.3	1.0	24.8
<i>Gmelina arborea</i>	1.8	1.2	26.6
<i>Triplochiton scleroxylon</i>	4.5	2.4	29.9
<i>Antiaris toxicaria</i>	2.3	2.3	33.8
<i>Trilepisium madagascariensis</i>	3.0	1.3	25.8
<i>Entandrophragma cylindricum</i>	10.1	0.7	28.3

Figure 1: Relative percentage of sugars in samples



1- *Ceiba pentandra*; 2- *Terminalia ivorensis*; 3- *Celtis zenkeri*; 4- *Sterculia rhinopetala*;
 5- *Khaya senegalensis*; 6- *Gmelina arborea*; 7- *Triplochiton scleroxylon*; 8- *Antiaris toxicaria*; 9- *Trilepisium madagascariensis*; 10- *Entandrophragma cylindricum*

Figure 2: Relationship between Klason lignin and the acid-hydrolysis residue

