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A comparative study of the syringyl, guaiacyl and hydroxyl groups units distribution in some African tropical hardwoods' lignin by Py-GC/MS and spectroscopic techniques

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Abstract

The dioxan acidolysis lignins extracted from the heartwood of *Testulea gabonensis Pellegr. (T. gabonensis), Holoptelea grandis Hutch* (*H. grandis*), *Aucoumea klaineana Pierre* (*A. klaineana*) *and Tieghemella africana Pierre* (*T. africana*), four African tropical hardwoods species collected in Gabon were characterized by pyrolysis-gas chromatography mass spectroscopy (Py-GC/MS) in order to elucidate their syringyl (S) to guaiacyl (S) ratio (S/G) and the relative abundance of the reactive hydroxyl groups of their aromatic moieties was determined by phosphorus nuclear magnetic resonance spectroscopy (^{31}P-NMR). Py-GC/MS has pointed out that *T. gabonensis* had the lowest (S/G)≈0.16, while those from *H. grandis*, *A. klaineana* and *T. Africana* were 0.31, 0.61 and 0.77 respectively. This trend was corroborated by other spectroscopic methods such as solid state ^{13}C NMR, Fourier Transformed Infrared (FTIR) and UV-Visible. The latter has pointed out a shift of wavelength at maximum absorbance (λ_{max}) to short values from *T. gabonensis* to *T. africana*, conforming like this an increase of the symmetric S-type lignin units within the studied dioxan acidolysis lignins as the S/G ratio increased. ^{31}P-NMR revealed that *T. gabonensis* was strongly richer in guaiacyl as well as in phenolic hydroxyl groups than the three other lignins..

1. Introduction

Lignin is an extremely complex three dimensional polymer formed by dehydrogenative polymerization of *p*-hydroxycinnamyl, coniferyl and synapyl alcohols [1]. These three lignin precursors give rise to the so-called H (p-hydroxyphenyl), G (Guaiacyl), and S (Syringyl) phenylpropanoid units which show different abundances in lignins from different group of vascular plants, as well as in different plant tissues and cell walls layers, bonded together by various linkages such as C-C (β-5, β-1, 5-5, β-β and α-β) bonds and α-O-4 and β-O-4 (the most abundant) alkyl-aryl ether bonds [2]. Polymerization of the above *p*-hydroxycinnamyl alcohols is initiated by one electron abstracting enzymes such as plant peroxydases, yielding phenoxy radicals, and proceeds *via* aromatic coupling reactions [3]. Since these phenoxy radicals have the highest π-electron densities at the phenolic oxygen, the formation of aryl ether interunit linkages involving in C_4 position is strongly favoured.

A review of literature revealed that the content of S and G units of temperature zone-softwood and hardwood lignins have been extensively studied by solid state ^{13}C NMR spectroscopy [4, 5], FTIR [6-8], ^{31}P NMR [9] and Py-GC/MS [10, 11] spectroscopy. Tropical hardwoods from South American rain forest were also widely investigated [5, 12] as well. However, the S/G ratio which is an indicator for wood durability and the

distribution of reactive hydroxyl groups of the aromatic moieties and alkyl side chains of African tropical hardwood lignin have received little attention since Faix, Sosanwo and Kleist [13-15].

The aim of this work was to investigate the distribution of the syringyl and guaiacyl unit as well as the reactive hydroxyl groups of the dioxan acidolysis lignins extracted from four African tropical hardwood wastes of commercial interest collected in Gabon, and widely used in building, furnishing or plywood industry for their potential valorisation as biomass candidates in wood based composites, bio-adhesives.

2. Materials and Method

2.1. Chemicals

Toluene, acetone, methanol, dioxan and hydrochloric acid (37%, d=1.2) were purchased from Aldrich and used without further purification.

2.2. Wood samples

Wood samples were collected from a local sawmills and joineries at Libreville (Gabon), ground milled to pass 80 mesh, soxhlet extracted by toluene: acetone: methanol mixture (4:1:1, v/v/v) for 12 h and leached by hot distilled water for 10 h. The samples were air dried and keep in controlled atmosphere at 23°C and 65% RH (Relative Humidity). Wood sawdust was oven dried at 105°C during 16 h before any chemical treatments.

2.3. Extraction of lignin

The lignin was isolated from the pre-extracted wood sawdust (≈5 g) in a nitrogen atmosphere by the dioxan acidolysis method adapted from a previously published procedure [16] as following: Oven dried sawdust was placed in 1L-three necked flask fitted with a reflux condenser, nitrogen bubble, and dropping funnel. The solvent, 125 mL of dioxan/water (9:1, v/v) mixture containing 1.25 g of hydrochloric acid was added slowly from the funnel. The reaction mixture under nitrogen was heated with a heating mantle and refluxed at 90°C for 40 min. Then, the mixture was cooled in nitrogen atmosphere to 50°C. The liquid phase was decanted and the solid residue was extracted with 100 mL of acid dioxan/water solution for 30 min, as described above. Two more extractions were made in the same manner. The last extraction was performed in dioxan/water mixture free from hydrochloric acid. Each portion of extract was concentrated separately, precipitated by cold water and centrifuged with a Jouan BR4 i Centrifuge at 10.000 rpm for 30 min at 10°C. A second step of centrifugation of lignins with 50 mL of diethyl ether was performed. The washed lignins were vacuum dried under phosphorus pentoxide for 48 h and oven dried for 16 h at 30°C.

2.4. Solid state ^{13}C-NMR Spectroscopy

Solid state ^{13}C CP/MAS (Cross Polarization-Magic Angle Spinning) NMR spectra of extracted wood samples were performed at room temperature on a Bruker DPX-400 NMR spectrometer (Bruker), using MAS rates of 4 and 8 kHz, at a frequency of 100.61 MHz. Samples previously oven dried at 105°C for 16h and kept in a desiccator containing P_2O_5 were packed in MAS 4 mm °C for diameter zirconia rotors. Chemical shifts were relative to TMS used as external standard. The C-1 anomeric carbon of polysaccharides, calibrated at 105.5 ppm was used as internal reference. All the spectra were run for 15 h (25 000 scans).

2.5. Pyrolysis-gas chromatography/mass spectroscopy

All the analysis were performed using a SGE pyroprobe heated filament pyrolyser interfaced to a Varian Star 3400 CX gas chromatography instrument coupled to a 4D Saturn ion trap mass spectrometer. Approximately 200 µg of finely devised dioxan acidolysis lignin samples were deposited on a ferromagnetic wire, then insert into the glass liner and immediately placed in the pyrolyser. The pyrolysis was performed at 500°C and the Py-GC interface was kept at 200°C. The GC column was a RTX 20 (30 m x 0.2 mm i.d., 0.25µm film thickness) operated from 50 to 280°C at a rate of 6°C/min, holding the initial temperature for 10 min. The injector was set at 200°C. Mass spectra were recorded under electron impact at 70eV with a mass range of *m/z*=35-650 (cycle time 1s), (beam current 100 µA, source temperature 180°C). The lignin pyrolysis products were identified by comparison of their mass spectra and relative retention times with compounds reported in the literature and NIST/EPA/NIH computer libraries. The relative percentages of the pyrolysis products were calculated from the relative areas of the lignin markers.

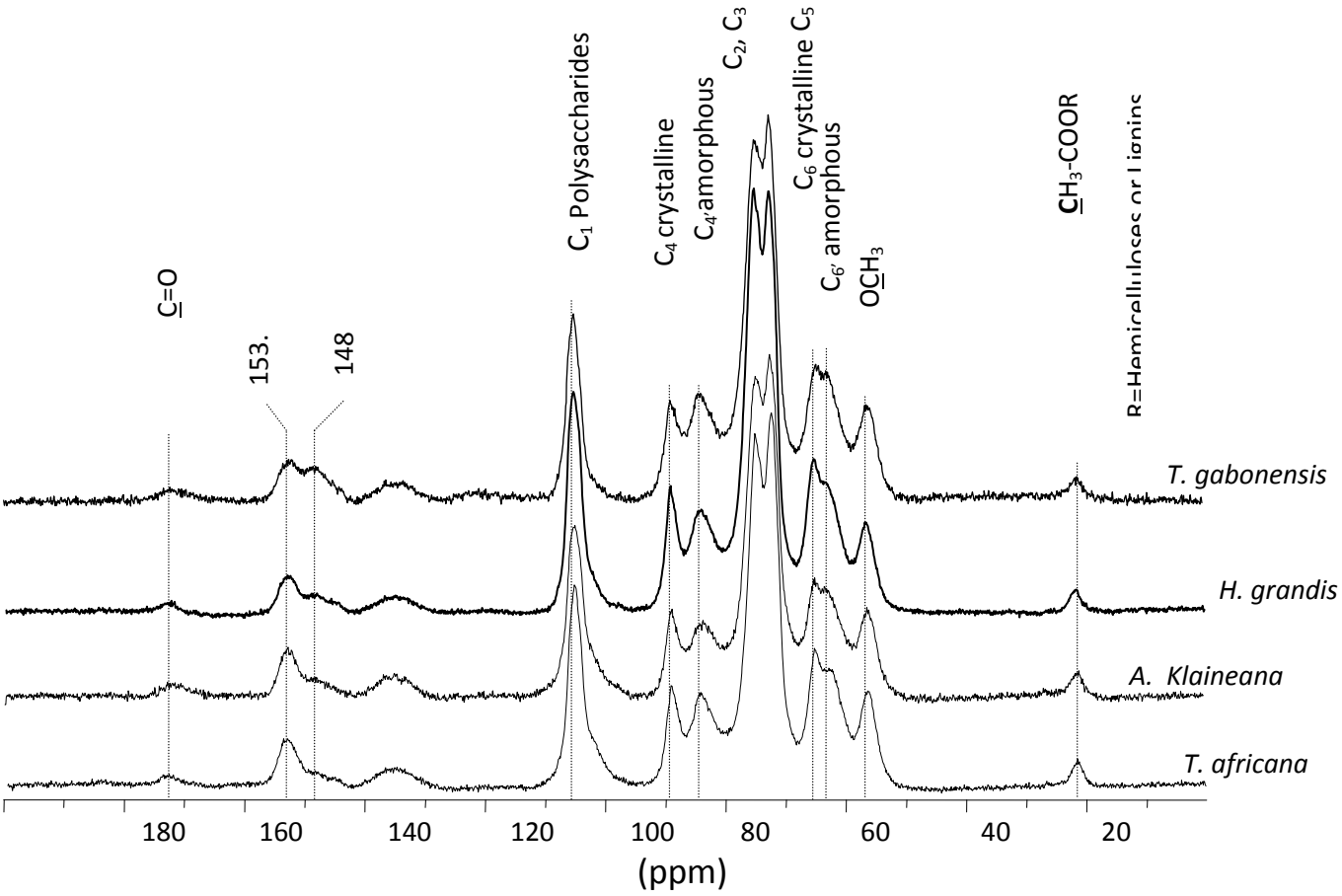

Figure 1: ^{13}C-NMR CP/MAS spectra of extracted African hardwoods' sawdust.

2.6 Fourier Transformed Infrared spectroscopy: Infrared absorption spectra of the dioxan acidolysis lignins were collected with a Perkin Elmer Paragon 100 PC spectrometer using the (Bromide Potassium) KBr technique. Oven dried lignin (3 mg) was dissolved and finely ground in KBr (300 mg). The background was made with a KBr pellet disk between 4000-500 cm^{-1} with 50 scans. The integrated peak intensities were measured using the baseline method [17]. The lignin aromatic rings symmetric stretching out of the plan, ν_{soop} at 1508-1511 cm^{-1} was used as internal reference. The S and G units content were estimated as the ratios between the integrated peak heights, respectively at 1328-1330 cm^{-1} and at 1266-1268 cm^{-1} vs. that of lignin at 1508-1510 cm^{-1} as previously published [18].

2.7 UV-Visible spectroscopy

UV-Visible spectra of lignins were recorder on a Perkin Elmer Lambda 18 spectrometer. The lignins samples were dissolved in a dioxan: Water (9:1, v:v) mixture and the lignin concentration was 4×10^{-3} mg/mL.

2.8 Quantitative phosphorus NMR

^{31}P NMR spectra of the phosphitylated dioxan acidolysis lignins were recorded on a Bruker DPX-200 spectrometer operating at 81 MHz on lignin samples after phosphitylation. An inverse gated decoupling sequence was used with a pulse width of 90° and a relaxation delay between pulses of 5 s. About 1000 transients were acquired to ensure high signal/noise ratio.

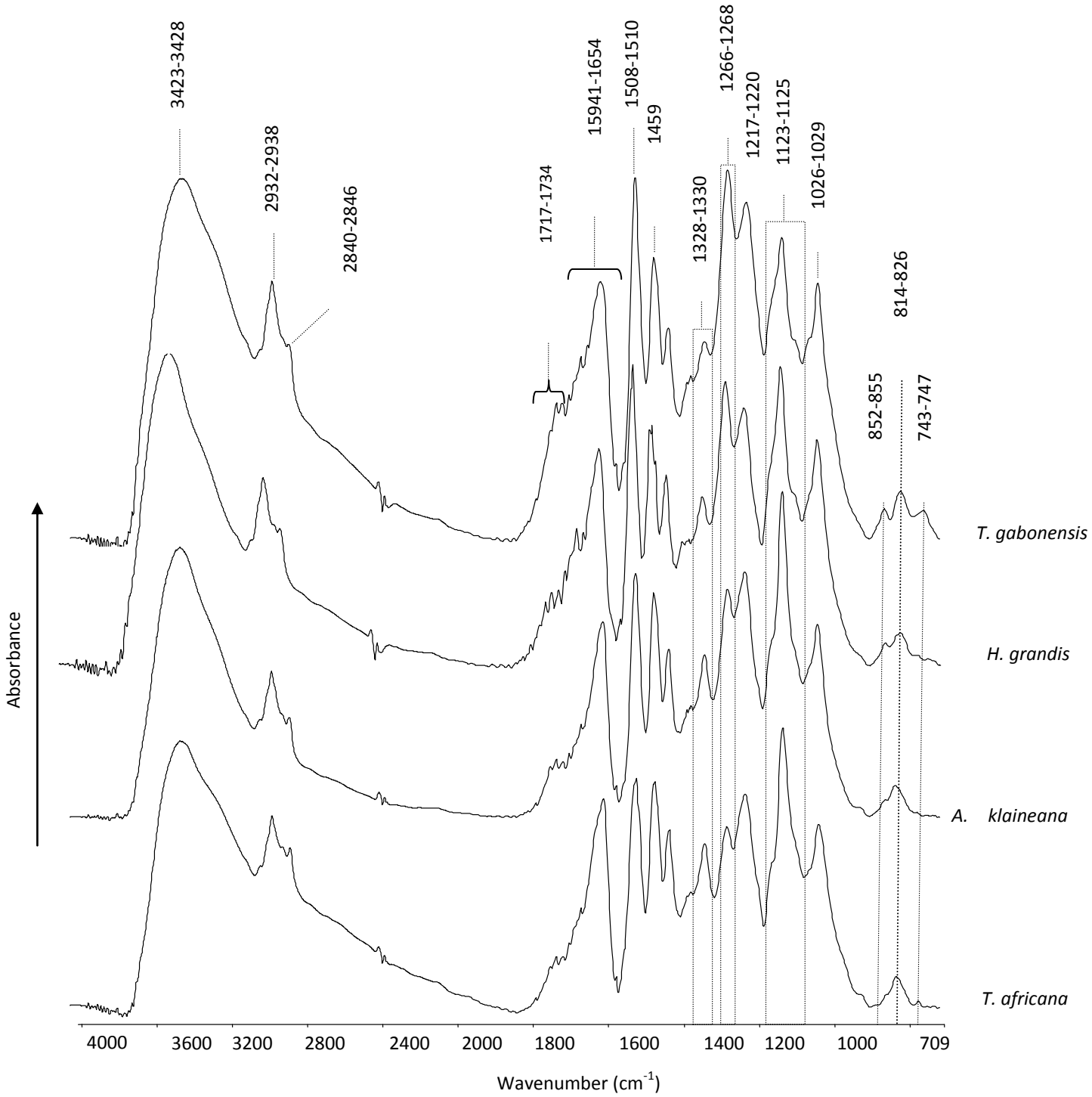

Figure 2: FTIR spectra of African tropical hardwoods dioxan acidolysis lignins.

Chemical shifts were calibrated using the ^{31}P signal at 144.9 ppm arising from the reaction product between the 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxophospholane and cyclohexanol. Phosphitylation was performed as described by [19] with minor changes. A solvent mixture composed of pyridine and $CDCl_3$ (1:1.6, v:v), dried with molecular sieves, was used as stock solution. In addition, a solution of chromium (III) acetylacetonate in pyridine/$CDCl_3$ (5mg/mL) was used as relaxation reagent stock solution. The lignins were phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxophospholane. Cholesterol (43 mg/mL) was used as internal standard. Thirty milligrams of lignin sample was dissolved in 0.5 mL of DMF in a 2 mL vial sealed with a Teflon-faces septum. Then 0.3 mL of pyridine/$CDCl_3$ stock solution was added, followed by addition of 0.1 mL of the internal standard and relaxation reagent solutions. To this mixture, the phosphitylation reagent (0.1 mL) was added, and the flask, tightly closed, was shaken to ensure thorough mixing. After derivatization, the mixture was transferred to a 5-mm tube for ^{31}P-NMR measurements.

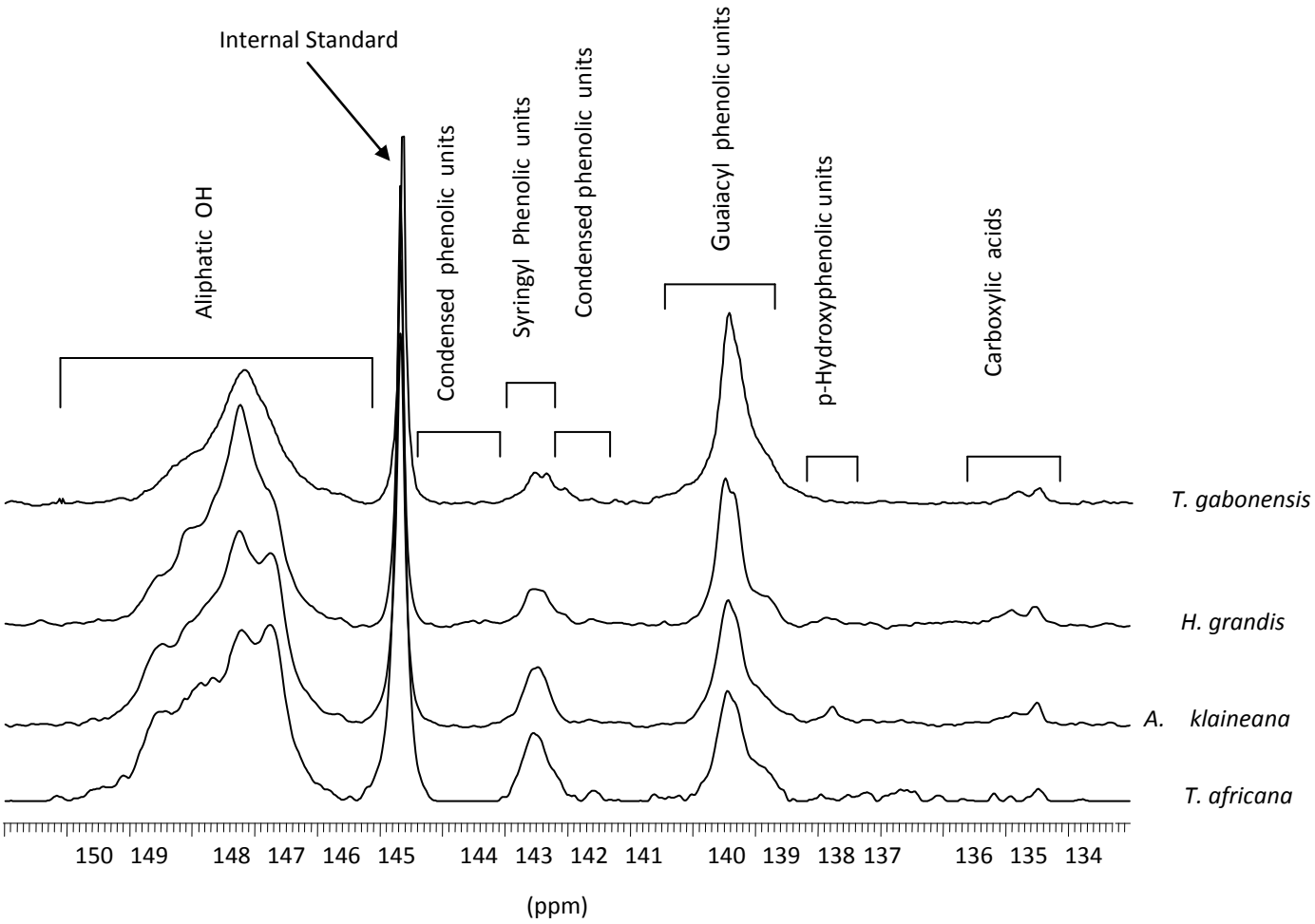

Figure 3: Quantitative ^{31}P-NMR spectra and signal assignment of African tropical hardwoods dioxan acidolysis lignins.

3 Results and discussion

As expected, pyrograms of the dioxan acidolysis lignins (Figure 4) did not exhibit typical sugar peaks above 25 min (retention time). The FTIR spectra (Figure 2) exhibit typical peak at 3423-3428 cm^{-1} assigned to the O-H stretching (ν_{O-H}) of lignin hydrogen bonds derived from O-H groups [20]. The peaks at 2932-2938 cm^{-1} and 2840-2846 cm^{-1} were assigned to the C-H stretching (ν_{c-H}) of alkanes [20]. It is noteworthy that the lignins did not point out peaks at 807-808 cm^{-1} assigned to glucomannanes [20], neither those at 760-774 cm^{-1} of xylan α-type glycosidic link [21] previously described in hardwood hollocellulose fibers [22]. The lignins obtained displayed high level of purity and were suitable for physicochemical analysis. Nevertheless, some α-alkyl, α-aryl and β-aryl ether bonds cleavage during the acidolysis isolation cannot be completely ruled out [23, 24].

The major lignin pyrolytic breakdown compounds discussed in this current study are listed in Table 1. The lignin-derived phenols released belong to the *p*-hydroxyphenylpropanoid (H), guaiacylpropanoid (G) and syringylpropanoid (S) units. Majors lignins derived from H units were phenol (1), 2-methylphenol (2), 4-methylphenol (3), 2,6-dimethylphenol (5), and 3-ethylphenol (6). Those from G units were guaiacol (4), 3-methylguaiacol (7), 4-methylguaiacol (8), 4-ethylguaicol (10), 4-vinylguaiacol (13), eugenol (14), *cis*-isoeugenol (16), vanillin (17), *trans*-isoeugenol (18), 4-propylguaiacol (20), acetoguaiacone (21), vanillic acid methylester (22), guaiacylacetone (23), vanillic acid (24), guaiacyl vinyl ketone (25). The S units' markers were syringol (15), 4-methylsyringol (19), 4-allyl syringol (26), *cis*-4-propenylsyringol (27), *trans*-4-propenylsyringol (28), acetosyringone (29), syingylacetone (30), propiosyringone (31). Note is worthy that the four lignins released high content of phenols arising from G units. The dominant peaks were 2-methoxyphenol (4) and 4-methylguaiacol (8) should result from the cleavage of C_{ar}-C_{α} or C_{β}-O bond of lignin alkyl chain [23, 25, 26].

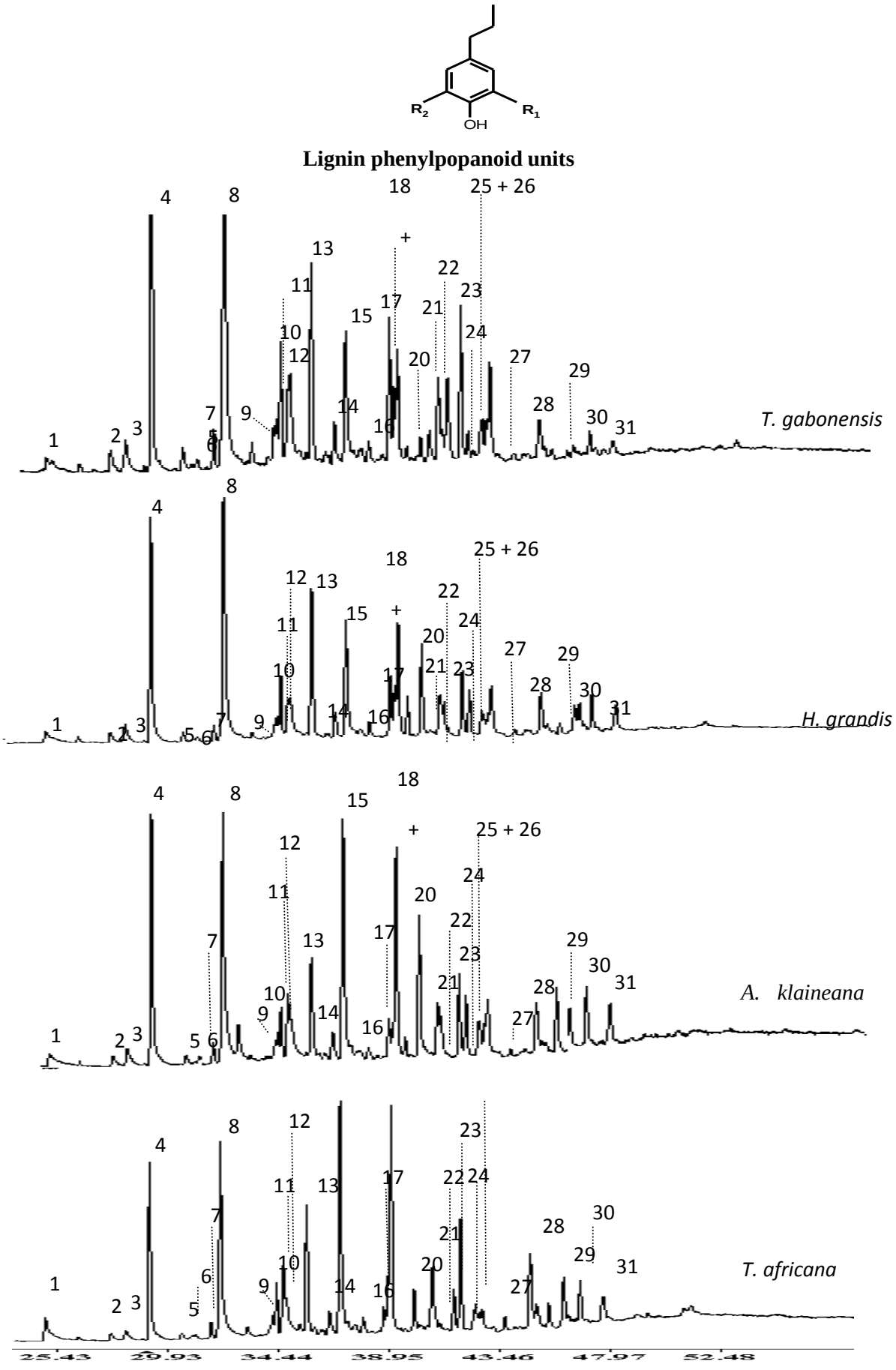

Figure 4: Pyrograms of the African tropical hardwoods dioxan acidolysis lignins. Peaks numbers correspond to those listed in Table 1.

Table 1: Phenolic markers released by Py-GC/MS fragmentation of *T. gabonensis, H. grandis, A. klaineana* and *T. Africana* dioxan acidolysis lignins.

Label	Assignment	Origin	Lignins phenolic markers			
			***T. gabonensis* (%)**	***H. grandis* (%)**	***A. klaineana* (%)**	***T. africana* (%)**
1	phenol	L-H	0.47	1.51	1.02	2.30
2	2-methylphenol	L-H	1.25	0.93	0.90	0.64
3	4-methylphenol	L-H	1.99	1.89	1.65	0.94
4	gaïacol	L-G	19.3	16.7	14.7	12.2
5	2,6-dimethylphenol	L-H	0.98	0.65	0.50	0.46
6	3-ethylphenol	L-H	1.37	0.24	0.56	0.16
7	3-methylguaiacol	L-G	0.37	0.90	0.96	0.88
8	4-methylguaiacol	L-G	25.7	21.4	16.5	13.9
9	4-methylcathecol	L-Ca	0.58	0.18	0.13	0.06
10	4-ethylguaicol	L-G	3.22	2.71	1.69	2.20
11	3-methoxycathecol	L-Ca	0.49	0.55	2.17	2.76
12	3-methylcathecol	L-Ca	1.01	0.49	0.27	0.26
13	4-vinylguaiacol	L-G	8.11	9.95	5.36	8.14
14	eugenol	L-G	1.80	1.89	1.98	2.05
15	syringol	L-S	5.99	8.63	14.1	16.1
16	cis isoeugenol	L-G	0.63	1.04	0.75	1.04
17	vanillin	L-G	4.98	2.93	1.41	0.86
18	trans isoeugenol	L-G	1.03	0.89	0.12	0.73
19	4-methylsyringol	L-S	2.59	4.69	8.90	10.2
20	4-propylguaiacol	L-G	0.77	5.81	7.88	2.43
21	acetoguaiacone	L-G	2.89	2.05	1.77	5.20
22	vanillic acid methylester	L-G	3.61	0.18	0.12	0.06
23	guaiacylacetone	L-G	6.14	4.20	4.10	2.30
24	vanillic acid	L-G	0.28	0.09	0.03	0.02
25	guaiacyl vinyl ketone	L-G	0.36	0.69	0.46	0.32
26	4-allyl syringol	L-S	0.02	0.05	0.09	0.11
27	4-propenylsyringol (*cis*)	L-S	0.25	0.49	0.35	0.81
28	4-propenylsyringol (*trans*)	L-S	1.91	2.99	3.10	5.24
29	acetosyringone	L-S	0.40	1.24	2.68	2.96
30	syringylacetone	L-S	0.81	2.09	2.95	2.40
31	propiosyringone	L-S	0.74	2.05	2.88	2.35

The highest amount of G units was exhibited by *T. gabonensis* (Table 2). This trend was corroborated by solid state ^{13}C NMR (Figure 1) for which *T. gabonensis* exhibited the most pronounced broad centred at 148 ppm corresponding to C-3 and C-4 in G units not O-alkylated at C-4 position [27]. In addition, the peak height of guaiacyl ν(C-O) at 1268-1270 cm^{-1}, and those at 852-854 and 743-747 cm^{-1} assigned to the C-H bending out of plan of G units [28] are strongest for *T. gabonensis* (Figure 2). That corroborates the abundance of G units within *T. gabonensis* than the three other wood lignins.

Furthermore, UV-Visible has pointed out that the lignin derived from *T. gabonensis* displayed (Table 3) the highest wavelength at maximum absorbance (λ_{max}=281 nm) ascribable to the ^1L_b singlet excited state of G units [29, 30].

The shifting of λ_{max} to short wavelength is in close agreement with the decrease of G units within the four lignins as observed in Py-GC/MS, FTIR and ^{13}C-NMR spectroscopy. The phenolic hydroxyls groups revealed by quantitative ^{31}P-NMR (Table 4) has pointed out that all the studied dioxan acidolysis lignins are rich in G-type hydroxyl groups (G-OH), and *T. gabonensis* was found to be the most abundant in G-OH units.

Table 2: Percentages of H (*p*-hydroxypehnyl), G (Guaiacyl) and S (Syringyl) lignins markers derived from pyrolysis products.

Dioxan acidolysis lignin type	**H (%)**	**S (%)**	**G (%)**
T. gabonensis	6.06	12.71	79.15
H. grandis	5.22	22.24	71.33
A. klaineana	4.63	35.00	57.82
T. africana	4.49	40.12	52.30

Table 3: Maximum absorbance (A_{max}) and wavelength at maximum at absorbance (λ_{max}) of African tropical hardwood dioxan acidolysis lignin derived from UV-Visible spectroscopy.

Dioxan acidolysis lignin type	**A_{max}**	**λ_{max} (nm)**
T. gabonensis	0.68	281
H. grandis	0.62	280
A. klaineana	0.46	279
T. africana	0.34	278

Table 4: Hydroxyl group distribution (mmol/g) as derived by quantitative ^{31}P-NMR analysis of the samples for witch spectra are displayed in Figure 3.

Dioxan acidolysis lignin type	**Aliph-OH**	**Cond-OH**	**S-OH**	**G-OH**	**p-H-OH**	**O=C-OH**
T. gabonensis	1.32	0.20	0.12	0.79	-	0.13
H. grandis	1.52	0.16	0.10	0.43	0.04	0.07
A. klaineana	1.32	0.13	0.15	0.36	0.04	0.07
T. africana	1.30	0.17	0.14	0.47	0.06	0.08

Aliph-OH (Aliphatic hydroxyl groups), Cond-OH (hydroxyl groups of condensed units), S-OH (Syringyl hydroxyl groups), G-OH (Guaiacyl hydroxyl groups), p-H-OH (p-hydroxyphenyl hydroxyl groups), O=C-OH (Hydroxyl groups of carboxylic acids).

Majors S-type units obtained by Py-GC/MS were syringol (15) and 4-methylsyringol (19), they are probably released by the cleavage of the C_{ar}-C_{α} or the C_{β}-O bond of lignin alkyl side chains [31].
The percentage of lignin markers collected in Table 2 has pointed out that the S-units increased from *T. gabonensis* to *T. africana* as corroborated by FTIR (Figure 2) which has shown an increase of the peaks height at 1123-1125 cm^{-1} assigned to the C-H deformation in the plane, δ_{ip}(C-H) of syringyl units is in the same order as Py-GC/MS.

In addition, the relative peaks height at 1328-1330 cm^{-1} of ν(C-O) of syringyl supported that *T. africana* was the richest in S-units. That is in close agreement with the λ_{max} values displayed in Table 3 which pointed out an increase of the high symmetric S units from *T. gabonensis* to *T. africana*. Therefore, the dioxan acidolysis lignin of the latter should be assumed to be richer in S units than the three others wood species. Nevertheless, the S-OH content displayed by ^{31}P-NMR (Table 4) did not increase as the S-units content increased.
However, the H content (Table 2) released by the lignin pyrolysis was surprisingly higher than those reported for other hardwood species [12], and it did not agree with the low condensed OH groups we found in ^{31}P-NMR (Table 4), not ever with the lack of n-π^* transition of carbonyl groups and π-π^* transition of conjugated double bonds of p-coumaric and ferulic acids in the range of 310 and 320 nm as observed in UV-Visible spectroscopy. That overestimation of H units should be the fact of more extensive depolymerisation of condensed lignin moieties formed by the C-C bonded G and H units during pyrolysis [12, 32]. However, some lignin demethoxylation [31, 32] and demethylation [33] cannot be ruled out.

Table 5: Syringyl to guaiacyl ratio (S/G) of tropical hardwoods dioxan acidolysis lignin derived from quantitative ^{31}P-NMR analysis, Pyrolysis GC-MS and FTIR spectroscopies.

	^{31}P-NMR	Py-GC/MS	FTIR
Dioxan acidolysis lignin type	**$(S/G)_{P\text{-}NMR}$**	**$(S/G)_{Py\text{-}GC/MS}$**	**$(S/G)_{FTIR}$**
T. gabonensis	0.15	0.16	0.12
H. grandis	0.23	0.31	0.24
A. klaineana	0.42	0.61	0.44
T. africana	0.47	0.77	0.68

The corresponding S/G obtained by Py-GC/MS increased in the same trend as those derived from FTIR and ^{31}P-NMR spectroscopy (Table 5). It is noticeable that the dioxan acidolysis lignin extracted from *T. gabonensis* exhibited the lowest S/G ratio whereas that from *T. africana* displayed the highest S/G value whatever the spectroscopic analysis indeed. On the other hand, the $(S/G)_{FTIR}$ and the $(S/G)_{P\text{-}NMR}$ are strongly correlated with the $(S/G)_{Py\text{-}GC/MS}$ (Figure 5).

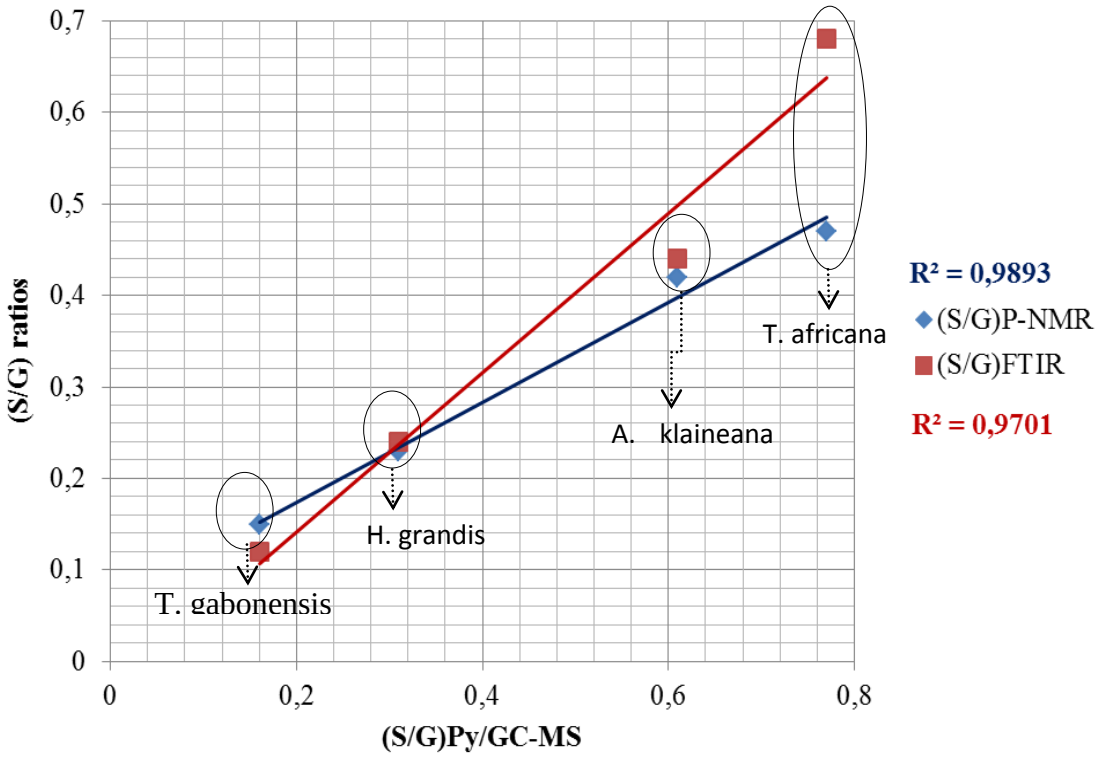

Figure 5: Correlation between the S/G ratios derived from Py/GC-MS, FTIR and ^{31}P NMR, respectively labelled $(S/G)_{Py/GC\text{-}MS}$, $(S/G)_{FTIR}$ and $(S/G)_{P\text{-}NMR}$ of the studied African tropical hardwood lignins.

It was observed also that the four dioxan lignins displayed small content of catechol compounds such as 4-methylcatechol (9). Its low amount compared with the corresponding 4-methylguaiacol (8) suggests that it should has been generated by thermal demethylation of guaiacyl units in minor secondary reaction as described elsewhere [34]. Note is worthy that the relative amount of 4-methylcatechol (9) decreased together with the S units increase (Table 1) as previously found for Australian wood species [35]. On the other hand, 3-methoxycatechol (11) and 3-methylcatechol (12) were identified in small amount relative to syringol (15) (Figure 1 and Table 1); which indicates that demethylation and demethoxylation of syringol (15) subsequent to β-O-4 bond cleavage occurred during lignin pyrolysis [25, 36]. The content of 3-methoxycatechol (11) increased from *T. gabonensis* to *T. africana* dioxan lignins as the S units increased (Table 1).
Investigating de hydroxyl groups of the alkyl side chains has shown that vanillin (17) was released in various extents by the four dioxan lignins, its abundance decreased from *T. gabonensis* to *T. africana* as the G units decreased (Table 1). That aromatic compound bearing a carbonyl group (C=O) should result from the C_α-OH

bond cleavage of G-type units alkyl side chain of the studied hardwood lignins as previously found for other wood species [32, 37, 38]. In addition, both *cis*-eugenol (16) and *trans*-eugenol (18) were yielded in low content (Table 1). These compounds which are usually produced by the pyrolytic breakdown of β-O-4 linkages of G-type units with OH groups in C_α position have been previously observed in black spruce's lignin [24]. However, the studied dioxan lignins released high content of *trans*-4-propenylsyringol (28), which indicates that the S-type units of the studied lignins should be rich in β-O-4 linkages with a C_α-OH groups less cleaved than those from G-type units. Furthermore, 4-propenylsyringol (28) content increased from *T. gabonensis* to *T. africana* as the S-units content increased within the dioxan acidolysis lignins.

In addition, guaiacylacetone (23) arising from G units as well as its S-unit counterpart, namely syringylacetone (30) were released. The presence of C_β=O bonds within both guaiacylacetone and syringylacetone indicates that some oxidation occurred at the C_β-OH position either in G and S phenolic moieties as previously reported for other lignins [38].

Nevertheless, the amount of C_β-OH within the selected lignins need further investigations assuming that those hydroxyl groups could have been released in same extent by the β-O-4 alkyl-aryl bonds cleavage during the lignin extraction as found in black spruce lignin [24].

A small amount of vanillic acid (23) was observed in the studied pyrograms; that is in agreement with FTIR spectroscopy which has pointed out weak peak heights at 1717-1734 cm^{-1} assigned to the ν(C=O) stretching of carbonyl groups of lignins (Figure 2). However, the highest content of vanillic acid (23) exhibited by *T. gabonensis* (Table 1) is consistent with ^{31}P-NMR (Table 4) which has pointed out that *T. gabonensis* was the richest in (HO) groups from carboxylic acids (HO-C=O). Nevertheless, the decarboxylation of these polar moieties in analytical pyrolysis which was observed in Eucalyptus lignin [37] would explain the lowest vanillic acid content in those dioxan lignins.

Finally, ^{31}P NMR has pointed out that *T. gabonensis* was slightly richer in C_5 condensed OH groups than the three other hardwood lignins (Table 5). That is consistent with the abundance of G-type units not substituted at the C_5 position of the aromatic ring of *T. gabonensis* dioxan acidolysis lignin. The following hydroxyl group content order was released (Table 5) by the four hardwood lignins: aliphatic > guaiacyl phenolic > condensed phenolic~syringyl phenolic > carboxylic hydroxyls > *p*-hydroxyphenyl hydroxyls. That order is different with that found for other hardwood lignins [39].

Conclusion

The S/G ratios of the dioxan acidolysis lignin extracted from *T. gabonensis, H. grandis, A. klaineana and T. africana* wood wastes has shown significant variability among the hardwood species. The S/G ratio obtained from Py-GC/MS was well correlated with those displayed by FTIR and ^{31}P NMR, and all the studied lignins exhibited an S/G<1. The lignin from *T. gabonensis* was found to be the richest in G-type units whereas *T. africana* was the most abundant in S-type units. *A. klaineana* displayed an intermediate S/G ratio. ^{31}P NMR has pointed out that hydroxyl groups were the highest in aliphatic side chains while the guaiacyl units were rich in phenolic hydroxyls. The pyrolysis breakdown process of the lignins has shown variability in the distribution of β-O-4 linkages with a C_α-OH groups as well as C_β-OH in the studied lignins. According to the strong reactivity of lignin hydroxyl groups towards carboxylic acids, anhydride molecules and resins as well as the S/G ratio incidence in the natural durability of wood based materials; the results obtained in this study should lead to a selective valorisation of African hardwoods wastes from timber industry in various fields like wood composite materials or lignin based products.

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