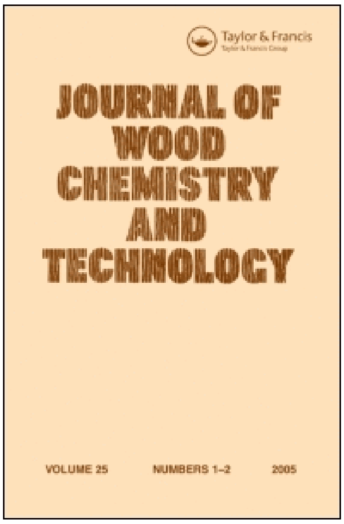

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THE LIGNIN OF THE DIFFUSE POROUS ANGIOSPERM TREE *Triplochyton scleroxylon* K. Schum WITH LOW SYRINGYL CONTENT

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ABSTRACT

"Milled wood lignin" was isolated from *Triplochyton scleroxylon* tree (wawa MWL) and subjected to elemental analysis before and after acid treatment, and to analytical pyrolysis. Both FT-IR and ^{1}H NMR spectra were recorded. For comparison, lignins from spruce and beech isolated by the MWL, dioxane/HCl (DIL), and Cuene (CUL) techniques were also characterized. The residual carbohydrate content of the lignins was estimated. Wawa MWL is a GS lignin with 88 % G and 12 % S content. The utility of analytical pyrolysis and FT-IR for lignin classification is discussed. FT-IR spectroscopy, calibrated with data of 50 MWLs (PLS approach), gives reliable results with a minimum of experimental work. The yields of S phenols obtained by pyrolysis has to be multiplied with a factor around 0.5 for correction if the S content of a lignin is low. The cross-linking indices and OH_{phen}/OH_{aliph} ratios of lignins increase in the order MWL < DIL < CUL. ^{1}H NMR spectroscopy is also helpful to recognize the S/G ratio of a lignin.

INTRODUCTION

The ratio of 4-hydroxyphenylpropane (**H**), guaiacylpropane (**G**), and syringylpropane (**S**) units in a lignin is one of the overriding analytical criteria for lignin classifications, i.e. the designation G, GS, or HGS lignin-types -- judged by the dominance of one or more basic units -- is well established. There is a general agreement, too, that various GS lignins exist with very different S-contents[1].

In this respect, the lignins of extraordinary botanical groups have frequently been studied. Higuchi[2] and Kawakami and Fukuda[3] discussed the enzymatic regulation of G and S biosynthesis, and the lignin composition with regard to G and S units in non-porous hardwoods, respectively. Shio and Higuchi[4] characterized lignins isolated from *Podocarpus, Gnetum, Drimys* and *Pseudowintera.* In general, although exceptions occur, the lignins of plants lacking vessels but containing mainly tracheid cells in their tissues, belong to the G lignin type. It is also evident that there is no rigorous correlation between the lignin type and the evolutionary status of a plant in question. For example, *Tectraclinis articulata* (a coniferous "softwood", Cupressaceae) contains up to 23 % S units[5]. On the other hand, it was reported that *Erythrina christa-galli* (a broad leaf "hardwood", Leguminosae, Fabaceae) contains very low amounts of S units, if any[6,7].

The first approach to differentiate between a G and GS lignin is the Mäule colour reaction[8]. The established chemical degradation techniques using alkaline nitrobenzene (or cupric oxide), potassium permanganate, or ethyl mercaptan with BF_3 (thioacidolysis degradation) as active agents are as well suited for the determination for the S/G ratios as analytical pyrolysis or UV, IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopic techniques[9]. Advantages accrue from the application of the FT-IR spectroscopy and analytical pyrolysis for lignin classification[10,11]. Both techniques require only modest sample preparation, are rapid in performance, and can be applied quantitatively.

In the course of screening experiments with the help of these techniques, we became aware of several angiosperms with low syringyl contents, which did not show otherwise any botanical or anatomical peculiarities. One of these species is the tropical tree *Triplochyton scleroxylon* K. Schum, Sterculiaceae from West Africa. The wood is light (0.35 g/cm^3) and of commercial importance since it is used as indoor construction wood and veneer. It is also known under the trade names "wawa" or "abachi"[12]. To substantiate the preliminary observations on *T. scleroxylon* wood, milled wood lignin (MWL) was isolated and analysed.

The principal goal of our work is to gain more information about tropical hardwoods in general, and specifically on those with low S contents. Here, the essential analytical data of wawa MWL shall be described based mainly on the results of FT-IR and ^{1}H-NMR spectroscopy and analytical pyrolysis. The investigation aims at testing these convenient techniques also on a sample with low S content, before starting the routine for quantitative evaluation on a large sample material with heterogenous composition. To render possible a direct comparison, the data of MWL wawa are presented together with those of spruce and beech lignins isolated by the MWL, dioxane/HCl, and Cuene isolation methods.

EXPERIMENTAL

Lignin isolation. Milled wood lignin (**MWL**) isolation and purification was performed according to Björkman[13]. Dioxane lignin (**DIL**) isolation was conducted according to Pepper *et al.*[14] using dioxane/HCl solution (9:1, v/v), with 0.2 M HCl concentration. For Cuene lignin (**CUL**) isolation the method of Renard *et al.*[15] was applied in which cupriethylendiamine is used to remove polysaccharides instead of Schweizer's reagent as described earlier by K. Freudenberg. Briefly, the technique includes several extraction steps: (1) A pretreatment with cold NaOH (2%), (2) Refluxing with H_2SO_4 (1%) for 4 hrs, (3) Extraction with cupriethylendiamine hydroxide for 24 hrs. The experimental steps 1 - 3 were repeated three times.

Elemental analysis and *OMe determination* were obtained using a Heraeus elemental analyzer CHN-O-RAPID (% O by difference) and by a standard Zeisel apparatus, respectively.

Acid hydrolysis of the MWLs: Refluxing with 1 % H_2SO_4 for 1 hr. The carbohydrate content (% CH) can be calculated by the formula:

Equation [1] $\% \text{ CH} = 100(\% \text{ C} - \% \text{ C}_{\text{after hydrol.}})/(45 - \% \text{ C}_{\text{after hydrol.}})$ or,
Equation [2] $\% \text{ CH} = 100 - (100 \%\text{OMe} / \%\text{OMe}_{\text{after hydrol.}})$

For *FT-IR spectroscopy* of the original lignins (before hydrolysis) a Bio-Rad FTS-40 instrument equipped with a DTGS detector was used (KBr technique; 64 scans; 4cm^{-1} resolution). Before normalization to the strongest band a baseline correction between 1800 and 700 cm^{-1} was performed. The numbering of the bands in Figure 1 is the same as in a recent review article[16]. Therefore, the band assignment is not given here. A refinement of the IR band assignments was also presented recently[17]. The cross-linking indices (**CI**) are calculated according to Faix[18] with a slight modification: (1) The sum of 7 minima at 1550, 1484, 1440, 1395, 1300, 1177, and 1070 cm^{-1} was calculated. (2) The sum of 6 maxima at 1505-10(**6**), 1463(**7**), 1423(**8**), 1329(**10**), 1221-27(**12**), and 1140(**14**) or 1125-28(**15**) was calculated. (The numbers in parenthesis refer to the bands in Figure 1). (3) The ratio "sum of minima divided by sum of maxima" was calculated.

The *Proton NMR spectrum* of wawa was recorded at 400 MHz with a Varian VXR-500 instrument (temp.: 300 °K). Solvent: $CDCl_3$ with TMS as internal reference.

Analytical pyrolysis: 60 to 70 µg lignin was pyrolysed with a Pyroprobe 100 instrument at 450 °C (GC column: DB-1701; 30 m; 0.25 mm/0.25µm). Further details regarding GC retention times and MS identification of the pyrolysis products are described in the literature[11].

RESULTS AND DISCUSSION

Elemental Analysis

The raw data of elemental analysis and OMe determination of MWL wawa are presented in Table 1 together with data of other lignin preparations obtained from spruce and beech by the cupriethylendiamine (CUL) and dioxane/HCl (DIL) isolation techniques. The OMe value of wawa lignin is between that of spruce and beech lignin. The high O/C_{900} values for most of the lignins in Table 1, exceeding the theoretically allowed oxygen limit of 300, are an indication for residual carbohydrates. (High oxygen values of MWLs are also frequently reported in the literature without discussing the theoretical and practical implications of this finding.) From Table 1 it is evident that Cuene lignin isolation leads to very elevated oxygen contents which are far beyond the acceptable range.

In order to reduce the amount of impurities of the MWLs, hydrolysis was performed with 1% sulfuric acid, and the C_{900} formula were once more calculated (Table 2). As expected, C and OMe contents increase after acid hydrolysis as a consequence of polysaccharide elimination.

Judged by the carbon and OMe increment after hydrolysis, the result of this calculation was on an average 5.6 % carbohydrate

TABLE 1. Raw Data of Various Lignin Preparations

	Elemental analysis				C_{900} Formula			
Sample	% C	% H	% O*	% OMe	C	H	O	OMe
DIL Spruce	60.02	5.56	34.42	13.87	900	825	337	88
MWL Spruce	60.74	5.87	33.39	15.04	900	860	315	95
MWL Wawa	60.53	6.01	33.46	16.93	900	866	310	109
CUL Beech	57.02	5.93	37.05	20.14	900	864	366	143
DIL Beech	61.22	6.22	32.56	19.43	900	864	284	126
MWL Beech	59.23	5.95	34.82	19.85	900	835	322	134

* by difference

TABLE 2. Data of MWLs after Acid Hydrolysis

	Elemental analysis and OMe after acid hydrolysis				C_{900} Formula			
Sample	% C	% H	% O*	% OMe	C	H	O	OMe
MWL Spruce	61.60	5.85	32.55	15.5	900	841	298	97
MWL Wawa	61.41	6.26	32.33	17.6	900	893	287	112
MWL Beech	60.17	5.93	33.87	21.1	900	799	299	141

* by difference

elimination when equation [1] (see Experimental) was used. Equation [2] gave 3.2 % carbohydrates. (The discrepancies are due to the limited accuracy of both analytical techniques.) Nevertheless, the recalculated C_{900} formula show "improved" O/C_{900} values, although the corresponding data of MWL spruce (298) and beech (299) are just below the required limit of 300. The corrected OMe value for 100 C_9 units of wawa MWL (112) in Table 2 confirms again the hybrid-character of this species as this datum is between that of spruce (97) and beech MWL (141).

If it is assumed that H units do not participate in the constitution of wawa lignin in considerable amounts, the G and S

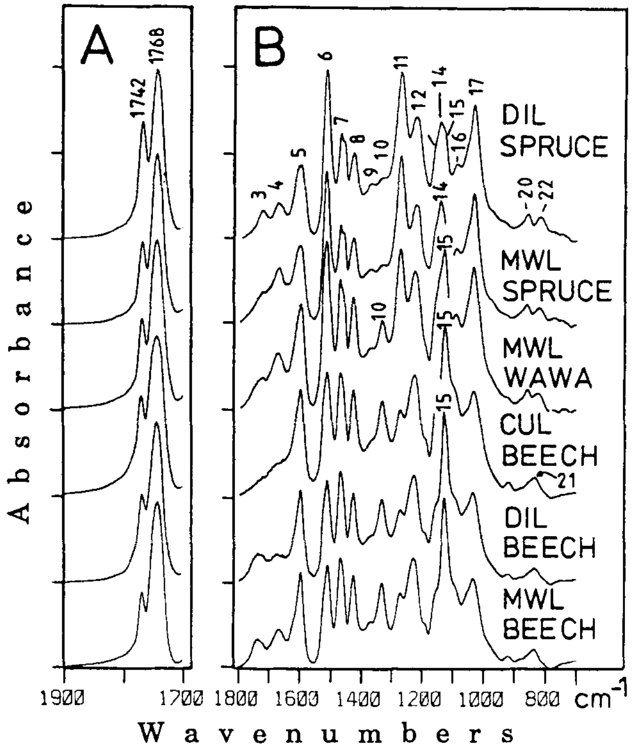

FIGURE 1. FT-IR Spectra of Various Lignin Preparations. (A) The Acetyl Bands of Acetylated Lignins After Deconvolution. (B) The Fingerprint Region of Nonacetylated Lignins.

contents can readily be calculated from the OMe/C_{900} value (112), namely: 88 % G and 12 % S units.

FT-IR Spectroscopy

The FT-IR spectra in Figure 1 confirm this observation. Wawa MWL belongs to the GS 1 spectral type according to the IR classification criteria[16]. This is conspicuous from the following relative band intensities (in parenthesis the band numbers from Figure 1):

TABLE 3. Data Derived from FT-IR Spectra

Sample	Spectral type	Results of PLS calibr.[1] % OMe	% H	% G	% S	cross-link index	Quotient[2] $\frac{1742}{1768}$
DIL Spruce	G	nd	nd	nd	nd	0.395	0.70
MWL Spruce	G	15.7	4	95	1	0.386	0.49
MWL Wawa	GS 1	17.4	0	90	10	0.363	0.54
CUL Beech	GS 3	nd	nd	nd	nd	0.370	0.63
DIL Beech	GS 4	nd	nd	nd	nd	0.340	0.59
MWL Beech	GS 4	21.0	0	55	45	0.310	0.46

[1] PLS, "partial least squares" regression analysis using the Bio-Rad software
[2] From acetylated lignins after deconvolution (see Fig. 1 A)
nd, not determined

1594(**5**) << 1510(**6**) >> 1463(**7**); 1326(**10**) is present but small; 1270(**11**) > 1220(**12**); 1140(**14**)sh, maximum at 1125(**15**). These spectral features suggest that the lignin contains only neglectable amounts of H units, and that the S content is between 5 and 20 %.

To check this, the spectra were submitted to an interactive statistical evaluation, which is part of the Bio-Rad software package, and which uses the *partial least squares* (PLS) approach based on a calibration with the spectral and analytical data of ca. 50 different MWLs as described by Faix *et al.*[19]. The PLS yielded 0 % H, 90 % G and 10 % S units for wawa lignin (Table 3). This result seems reasonable, considering that the same PLS estimation for beech and spruce MWLs resulted in figures within the generally accepted values for these lignins. From the low intensity of the band no. 3 at 1738 cm^{-1}, which is frequently indicative of acetyl groups of polyoses, it can be inferred that the polysaccharide content of the sample is low.

The cross-linking indices (CIs) were calculated from the FT-IR spectra to compare the isolation techniques CUL, DIL, and MWL: lower

CIs mean less secondary changes in the course of isolation, i.e. less formation of new C-C bonds (less "condensation")[18]. In this respect, the cross-linking indices in Table 3 corroborate the earlier results: CI_{DIL} > CI_{MWL}. Moreover, Cuene isolation seems to increase the degree of cross-linkings more than the isolation with dioxane/HCl because CI_{CUL} > CI_{DIL}, a finding which is not surprising in view of the severity of acid and alkaline treatments during a Cuene isolation described in Experimental.

The ratios "Abs. 1742/Abs. 1768" listed in Table 3, which were taken from FT-IR spectra of acetylated MWLs (Figure 1A), are informative. These data are in connection with the phenolic OH group contents: higher quotients indicate more phenolic OH groups. Thus, increasing quotients in the order MWL < DIL < CUL are expected as it is known that ß-O-4 linkages are cleaved under acidolytic conditions[20].

Analytical Pyrolysis

Table 4 is a compilation of the raw data retrieved from the pyrograms of wawa MWL after normalization. (The pyrograms of MWL spruce and beech were described earlier[21]). Approx. 54 major peaks of the pyrograms were taken into consideration for a routine assignment and quantitative evaluation. Most of the peaks can be ascribed to G and S type aromatic structures. Only small amounts of phenols were found without OMe substituents (H units); a result which supports once more the notion about the low H content of this lignin.

Only 4 to 6 % carbohydrate type pyrolysis product are detectable (Table 5). This result is similar to that obtained by acid hydrolysis. Catechols and unidentified substances represent about 2.6 % of the normalized peak areas in the pyrograms. Table 5 also contains the normalized peak areas of the identified phenols without catechols and unidentified substances, so that the sum of phenols is 100. As pointed

TABLE 4. Peak Assignment, Retention Times (RT), and Relative Retention Times (RRT) Based on Vanillin of a Wawa MWL Pyrogram from Pyrolysis (a). For Summarized Results of Runs (a) and (b) see Table 5.

Peak No.	Substance	RT min	RRT	Area %	CH %	H %	G %	S %	Cate-chols- %	? %
1	Acetic acid	5.907	0.154							
2	Hydroxypropanone	7.065	0.184	0.61	0.61					
3	Pyran-(2H)-2-one, 4-hydroxy-5,6-dihydro-	20.999	0.547	0.19	0.19					
4	Phenol	23.381	0.609	0.17		0.17				
5	Guaiacol	23.892	0.622	6.54			6.54			
6	Cresol-(o-)	25.256	0.658	0.20		0.20				
7	Guaiacol, 3-methyl-	26.654	0.694	0.59			0.59			
8	Guaiacol,4-methyl-	27.892	0.727	8.17			8.17			
9	Phenol, 2,4-and 2,5-dimethyl-ˆ	28.383	0.739	0.32		0.32				
10	Guaiacol, 3-ethyl-	30.281	0.789	0.41			0.41			
11	Guaiacol, 4-ethyl-	31.005	0.808	1.05			1.05			
12	Catechole, 3-methoxy-; Guaiacol,4-vinyl-; Phenol,4-vinyl-	33.069	0.861	6.50		1.30	4.55		0.65	
13	Eugenol	33.922	0.884	1.35			1.35			
14	Guaiacol, 4-propyl-	34.029	0.886	0.22			0.22			
15	Syringol	34.936	0.910	2.64				2.64		
16	Isoeugenol (cis)	35.847	0.934	0.73			0.73			
17	Catechol, 3-methyl-	36.173	0.942	0.29					0.29	
18	unknown Phenol: m/z 107,109,138	36.318	0.946	0.45						0.45
19	Isoeugenol (trans)	37.597	0.979	4.39			4.39			
20	Syringol, 4-methyl-	38.048	0.991	2.71				2.71		
21	Vanillin	38.390	1.000	7.45			7.45			
22	unknown phenolic compound: m/z 163,194	38.581	1.005	0.29						0.29
23	G-C=C=C	38.770	1.010	1.11			1.11			
24	G-C=C=C	39.107	1.019	0.86			0.86			
25	Homovanillin	40.274	1.049	2.41			2.41			
26	Syringol, 4-ethyl-	40.443	1.053	0.57				0.57		
27	unknown: m/z 59,172	40.761	1.062	0.37	0.37					
28	Acetoguaiacone	41.015	1.068	2.96			2.96			
29	Syringol, 4-vinyl-	42.282	1.101	2.13				2.13		
30	Guaiacylaceton	42.595	1.110	1.29			1.29			
31	Syringol, 4-allyl- and Syringol, 4-propyl-	42.849	1.116	0.87				0.87		
32	unknown compound: m/z 149...178	43.091	1.122	0.92						0.92
33	Propioguaiacone	43.602	1.136	0.62			0.62			
34	G-CO-CH=CH2	44.030	1.147	3.63			3.63			
35	G-CO-CO-CH3	44.295	1.154	0.47			0.47			
36	Syringol, 4-propenyl- (cis)	44.455	1.158	0.66				0.66		
37	S-C=C=C	45.775	1.192	0.51				0.51		
38	Levoglucosan = ß-D-Glucopyranose,1,6-anhydro-	45.535	1.186	2.11	2.11					
39	Syringol, 4-propenyl- (trans)	46.207	1.204	2.44				2.44		
40	Dihydroconiferyl alcohol (?)	46.385	1.208	0.36			0.36			
41	Syringaaldehyde	47.165	1.229	5.22				5.22		
42	Homosyringaaldehyde	48.401	1.261	0.95				0.95		
43	Anhydrosugar: unknown m/z 45,...	48.929	1.275	0.21	0.21					
44	Acetosyringone	49.110	1.279	1.32				1.32		
45	Coniferyl alcohol (trans)	49.618	1.292	6.91			6.91			
46	Coniferylaldehyde	50.218	1.308	7.44			7.44			
47	Syringylaceton	50.419	1.313	0.32				0.32		
48	Propiosyringone	51.203	1.334	0.34				0.34		
49	S-CO-CO-CH3	51.386	1.339	0.27				0.27		
50	S-CO-CH=CH2	51.633	1.345	1.05				1.05		
51	Isomer of Sinapyl alcohol	51.781	1.349	0.54				0.54		
52	Sinapyl alcohol (cis)	54.090	1.409	0.84				0.84		
53	Sinapyl alcohol (trans)	55.709	1.451	0.61				0.61		
54	Sinapinaldehyde	55.944	1.457	4.41				4.41		
				100.00	3.50	1.99	63.50	28.41	0.94	1.66

TABLE 5. Data Generated from Analytical Pyrolysis

		Basic units normalized			Corrected basic units with factors 0.5 and 0.8 for S units		
Sample	%CH	% H	% G	% S	% H	% G	% S
MWL Spruce	6.1	2.3	92.3	5.4	ca. 2.3	94.9-93.4	2.7- 4.3
MWL Wawa a	3.5	2.2	67.6	30.2			
MWL Wawa b	3.6	1.3	68.8	29.9			
average	3.6	1.6	68.2	30.1	ca. 2.0	74.1-82.9	15.0-24.1
MWL Beech	4.0	0.8	37.8	61.4	1.2-1.0	67.9-49.8	30.7-49.1

CH, carbohydrate content
a and b, data retrieved from two pyrolysis experiments

out by Sarkanen and Hergert[1], all chemical degradation techniques overestimate the S units. The same holds true for analytical pyrolysis[11]. The reason for this resides in the diminished accessibility of S units for electrophilic condensation reactions both during lignin biosynthesis and chemical degradation. It has been earlier demonstrated that S values from pyrolysis should be multiplied with factors between 0.5 to 0.8 to obtain a result corresponding to a realistic S value in a lignin[21,22]. This finding were corroborated and refined based on a large plant and lignin material just recently[23] using OMe determination, nitrobenzene oxidation, FT-IR spectroscopy for calibration of the pyrolysis results. The lower the apparent S content found by pyrolysis the more correction (i.e. lower correction factors) will be needed. Thus in the case of wawa lignin, a correction factor around 0.5 seems to be appropriate. Data corrected in this way and normalized anew are presented in Table 5. Accordingly, S contents around 15 % (G ca. 85 %) can be expected after re-evaluation of the pyrolysis results. This estimation is a little higher than the S values discussed above (12

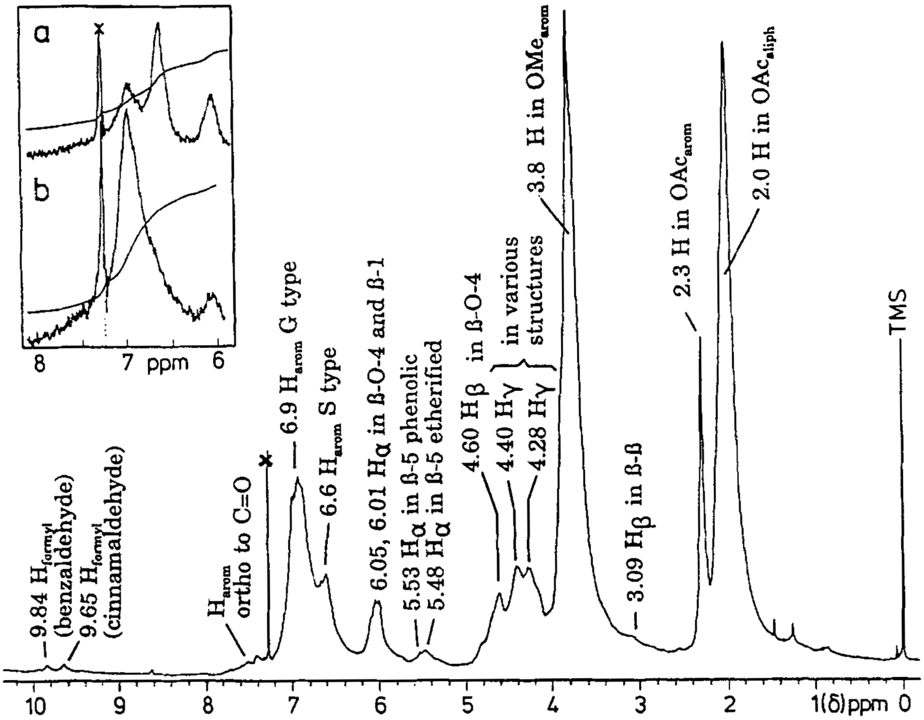

FIGURE 2. Proton NMR Spectrum (400 MHz) of Acetylated Wawa MWL. (a) and (b): ^1H NMR Spectra at 80 MHz between 6 and 8 ppm of Beech and Spruce MWL, respectively.

% from Table 2; 10 % from PLS estimation in Table 3). However, due to the error limits of these calculations (as a rule ± 3 % basic units), all three estimations are in principal harmony with each other. (Probably, factors even lower than 0.5 should be used for the S correction in case of very low S contents.)

Proton NMR Spectroscopy

Proton NMR spectroscopy also belongs to the standard methods of lignin characterization[24,25]. Especially, modern 270 to 500 MHz instruments can be used to good advantage[26]. The ^1H NMR spectrum in Figure 2 furnishes a further evidence for the low syringylpropane content of wawa lignin. This can easily be perceived on the aromatic part of the spectrum between 6.3 and 7.8 ppm, since the signal around 6.6 ppm is typical for S type and that around 7 ppm for G type aromatic protons[24,27]. The intensity of the former is very low in comparison to the latter. This is especially obvious by a visual comparison with the aromatic signals of MWL beech (Figure 2 a) and MWL spruce (Figure 2 b), both recorded with a 80 MHz spectrometer. The peak indicating syringyl units at 6.6 ppm is only slightly higher for wawa MWL than that of spruce. The assignments in Figure 2 are according to Lundquist[25,28].

For estimating the phenolic and aliphatic OH group content of the wawa MWL, the integral of the OMe signal was used as a quasi internal standard, since it is known that 112 OCH_3 groups per 100 C_9 units, (see Table 2) caused this measure. The aromatic and aliphatic -CO-CH_3 groups per 100 C_9 units thus were calculated from their corresponding integrals at 2.3 and 2.0 ppm assuming direct proportionality to the OCH_3 signal. The reshaped summative formula of wawa MWL from Table 2 is then:

$$\mathbf{C_{900}\,H_{773}\,O_{167}\,(OH\mathit{phen})_{20}\,(OH\mathit{aliph})_{100}\,OMe_{112}}$$

The NMR spectrum does not give evidence for a considerable amount of carbohydrate impurities, which would be visible e.g. at 5.03 ppm[29].

CONCLUSIONS

All methods applied suggest that *Triplochyton scleroxylon* contains a GS lignin with a S content around 12 %, which is calculated as an average from 12 % (based on C_{900} formula), 10 % (based on FT-IR-

PLS approach) and 15 % (based on pyrolysis, S value corrected with factor 0.5). Thus *T. scleroxylon* is another example for an angiosperm with low S content but one which does not belong to a transition state botanical group and which does not have any extraordinarily deviating anatomical peculiarities.

FT-IR spectroscopy proved to be the simplest way for rapid lignin classification. The FT-IR-PLS calibration set based on MWLs afforded a good quantitative approximation even for low S contents. For qualitative recognition of small amounts of S units, the band at 1330 cm^{-1} (no. 10 in Figure 1) is as useful as the change of the maximum at 1140 cm^{-1} (typical for G lignin) to 1228-25 cm^{-1} (typical for GS lignin) in the presence of a few % S units.

As revealed by FT-IR spectra, lignin isolation by dioxane/HCl or cupriethylenediamine leads to cleavage of ß-O-4 bonds as indicated by increased phenolic OH group contents. Moreover, these techniques cause condensation reactions which are manifest as an increase of the cross-linking indices as determined by FT-IR spectroscopy.

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