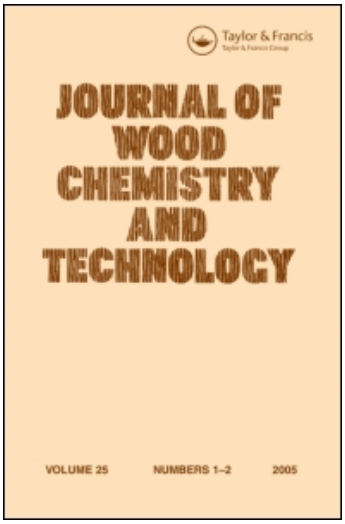

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Characteristics of Dioxane Lignins Isolated at Different Ages of Nalita Wood (*Trema orientalis*)

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Characteristics of Dioxane Lignins Isolated at Different Ages of Nalita Wood (*Trema orientalis*)

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Abstract: Nalita (*Trema orientalis*) is one of the fastest growing trees in the tropical countries. The structural characteristics of lignin isolated at different ages of Nalita wood (*Trema orientalis*) by acidolytic dioxane method were examined by UV, FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy, alkaline nitrobenzene oxidation, molecular weight determination, elemental and methoxyl analysis. The data were compared with aspen lignin. The structural analysis revealed that Nalita wood lignin is syringyl-guaiacyl type. The methoxyl content in Nalita wood lignin was lower than aspen lignin. The C_9 formulas for 30-months-old Nalita was $C_9H_{9.31}O_{3.13}(OCH_3)_{1.27}$, whereas that of aspen was $C_9H_{8.94}O_{3.15}(OCH_3)_{1.47}$. The weight average molecular weight of Nalita wood lignin was decreased from 36,500 to 25,500 with increasing tree age from 12 to 30 months, whereas weight average molecular weight of aspen was 20,000. Both alcoholic and phenolic hydroxyl group in Nalita wood lignin is lower than aspen lignin.

Keywords: Fast growing wood, *Trema orientalis*, syringyl unit, guaiacyl unit, β-*O*-4 structure, *erythro* form

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INTRODUCTION

Nowadays demand for fibrous materials of papermaking is essentially increasing as a result of increase in paper consumption. To maintain a sustainable development in this industry, measure must be taken to keep sustainable supply of papermaking raw materials. On the other hand environmentalists are keeping pressure to the industry for preserving forest. Therefore, forestland for industries is not increased. To keep the growth of paper industry, it is utmost need to increase fiber production using same forestland. Nonwood or fast growing tree may alleviate the shortage of fibrous raw materials for pulping. Literature[1,2] showed that *Trema orientalis* is one of the fast growing trees. Local name of *T. orientalis* is Nalita. Nalita wood requires drastic cooking condition than temperate zone hardwood to get a bleachable grade pulp.[3] To gain knowledge behind the reason of drastic cooking condition, Nalita wood lignin should be characterized.

A great variation is observed in various species in regards to ultimate analysis, methoxyl and hydroxyl content as well as syringyl-guaiacyl ratio. Irrespective of methods employed hardwood lignin is generally show greater variation in chemical structure than softwood lignin.[4]

The characteristics of lignin obtained from wood depend on both the kind of wood (species location, etc.) and depend on the type and intensity of the lignification process. Isolation and characterization of lignin from wood is a fundamental step for investigations of suitable pulping process and conditions. There is still at present no perfect technique that would provide high lignin extraction yield, no chemical modification, and recovery of pure product.[5] Custom methods for lignin isolation can be classified in three types: ball milling/solvent extraction, acidolysis using dioxane/HCl mixture, and enzymatic methods.[5,6] The ball milling/solvent extraction method gave a very low lignin yield from Nalita wood.[7] So, in this study, we isolated lignin by dioxane/HCl mixture. Chemical compositions of Nalita wood were 20–24% lignin, 22–23% pentosan, 48–50% α-cellulose along with extractive and ash.[3]

To learn more about Nalita wood lignin, acidified dioxane lignin (DL) was isolated from 12, 18, 24, and 30 months old Nalita wood and characterized by UV, FTIR, ^{1}H NMR, ^{13}C NMR spectroscopy, alkaline nitrobenzene oxidation, molecular weight determination, and elemental and methoxyl analysis.

EXPERIMENTAL

Raw Materials

The small piece of Nalita wood chips of 12, 18, 24, and 30 months and 10-year-old aspen were ground (40/60 mesh) in a Wiley mill, extracted with alcohol-benzene solvent and dried in vacuum over P_2O_5.

Isolation of Lignin

The alcohol-benzene extract free wood meals were refluxed with acidic dioxane (9:1) solution. The concentration of HCl in dioxane solution was made 0.2 N. The dioxane to wood meal ratio was 8. The wood meal was refluxed with dioxane solution for about 1 hour in N_2 atm. The N_2 flow was maintained at 50 mm/min. After completing reflux time, wood meal dioxane mixture was filtered in Buckner funnel using filter no. 2. The residue was washed with dioxane solution (9:1). The dioxane solution was then neutralized by adding solid Na_2CO_3 and filtered. The filtrate was concentrated in vacuum evaporator at 40°C. Then conc. dioxane soln. was added drop wise to water to precipitate lignin. The lignin precipitate was washed and dried in vacuum over P_2O_5.

Dried crude lignin was dissolved in dioxane (9:1), and again precipitated in ether with constant stirring by magnetic bar. The precipitated pure lignin was dried in vacuum over P_2O_5 and weighed. The yield of dioxane lignin was calculated based on Klason lignin. The purity of dioxane lignin was determined by measuring Klason lignin. The carbohydrates content of isolated lignin were determined by Tappi test method (T 249 cm 00).

Acetylation

Dioxane lignin 100 mg was added in 1.5 ml of dry pyridine-acetic anhydride (1:1) and kept for 72 h. The solution was added to a 10-fold volume of ice-co ld water whereupon the acetylated sample was recovered as a precipitate, which was purified by successive washing with water and dried under vacuum over P_2O_5.

Elemental Analysis

C, H, O, and N analyses were carried out in analytical center, Kyushu University, Japan. The methoxyl content in dioxane lignin was determined in accordance with Japan International Standard Methods (JIS P8013 1972).

Spectroscopy

Ultraviolet: 7–8 mg dioxane lignin was dissolved in 100 ml dioxane (9:1) followed by two times dilution. Then spectra were recorded using a Hewlett Packard 8452A spectrophotometer.

FTIR: IR spectra were recorded by using a Shimadzu FTIR spectrometer model 8201PC. The dried samples were embedded in KBr pellets in the concentration of about 1 mg/100 mg KBr. The spectra were recorded in the absorption band mode in the range 4000–400 cm^{-1}.

^{1}H NMR: Spectra were recorded for solutions of 100 mg of acetylated lignin contained in 0.5 ml $CDCl_3$, using tetramethylsilane (TMS) as internal standard in a JEOL JNM-EX 400 spectrometer. For quantification of protons, the signal in specified regions of the spectrum were integrated with respect to a spectrum-wide baseline drawn at the level of the background noise, and the results were referred to the signal for methoxyl protons, whose average number per C_9 unit was established as described earlier.

^{13}C NMR: 100 mg of acetylated lignins was dissolved in 0.5 ml $CDCl_3$ and spectra were recorded at 100 MHz in a JEOL JNM-EX 400 spectrometer with TMS as internal standard. A minimum of 10,000 scans was collected for each sample.

Alkaline Nitrobenzene Oxidation

Alkaline nitrobenzene oxidation of Nalita and aspen dioxane lignins was carried out according to Mun's modified method.[8] GC analysis was conducted using a Shimatzu GC 17A gas chromotograph equipped with Neutrabond 1 capillary column (30 m × 0.53 mm). Conditions used were as follows: column temperature was programmed to increase from 150 to 250°C at the rate of 5°C/min; injection and detection temperature were 220 and 250°C, respectively; column flow was rate 6 ml/min and split ratio 30.

Molecular Weight

The weight average (Mw) and number average molecular (Mn) weight of Nalita and aspen acetylated lignins were determined by GPC on a Sodex KF-802.5 column. The samples were dissolved in tetrahydrofuran (THF) and 10 μl was injected. The column was operated at 30°C and eluted with THF at a flow rate of 1 ml/min. The column was calibrated using polystyrene standards.

RESULTS AND DISCUSSION

The yield of dioxane lignin in Nalita wood was 45.0–49.2% depending on tree age (Table 1). But the yield of aspen lignin (37.3%) was lower than Nalita lignin. Although the yield in Nalita milled wood lignin (MWL) was lower than that of aspen MWL.[7] The acidic isolation conditions employed for the lignin extraction process are believed to result in the hydrolysis of lignin-carbohydrate complex (LCC) linkages allowing the release of lignin fragments into the aqueous dioxane solution from Nalita wood.[6] The purity of Nalita wood lignin was 81–83%. The carbohydrates content was about 5%.

Table 1. Yields of lignin

Sample	Lignin yield, % (based on Klason lignin)
Nalita 12	49.2
Nalita 18	49.8
Nalita 24	46.5
Nalita 30	45
Aspen	37.3

Ultraviolet Spectra

Figure 1 shows that Nalita lignin had well-defined maxima at 280 nm, whereas aspen lignin had 274 nm. This fact contributes to the higher symmetry of the phenylpropane units in aspen lignin caused by the higher syringyl units. It is known that guaiacyl compounds exhibit maxima in the region of 280 nm. However, the substitutions of an extra methoxyl group in the 5-position shift the maxima to lower wavelength. Absorptivities of 30 months old Nalita lignin and aspen lignin were 12.53 and 14.17 L g^{-1} cm^{-1}, respectively, as shown in Table 2. Normally temperate zone hardwood lignins show absorption coefficient as high as 16.[4,9] The shoulder at 310–320 nm in all Nalita lignins revealed that the presence of ester or ether bonds between hydroxycinnamic acids such as *p*-cumaric acid and ferulic acid of lignin. The MWL isolated from grasses gave absorption bands at 315 nm and 280 nm, but the

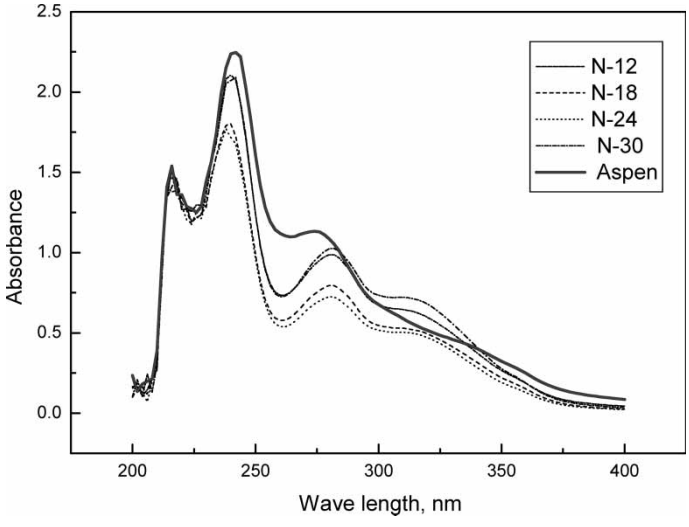

Figure 1. UV spectra of dioxane lignin.

Table 2. UV absorption of dioxane

Lignin	Wave length at max. nm	Absorptivity at max ($Lg^{-1}\,cm^{-1}$)
Nalita-12	280	12.66
Nalita-18	280	11.08
Nalita-24	280	12.5
Nalita-30	280	12.53
Aspen	274	14.17

former absorption disappeared on saponification of the MWL with concomitant release of the *p*-coumaric and ferulic acids.[10]

FTIR SPECTRA

To elucidate the structure of lignin, and to investigate the differences in the structure of the dioxane lignin isolated at different ages of Nalita wood, FT-IR spectra were recorded and are shown in Figure 2 and the assignment[11] given in Table 3. All spectra are showing absorbance near 1330 cm^{-1} (syringyl), which is typical for hardwood lignin and shoulder at 1270 cm^{-1} (guaiacyl). Further evidence of the syringyl content in Nalita and aspen lignin is afforded by its having a band near 835 cm^{-1} but no band at 855 or 815 cm^{-1}, later two guaiacyl bands are typical for softwood lignin not exhibited by hardwoods.[12] The C═O in unconjugated ketone (β-carbonyl) were observed in all spectra at 1710 cm^{-1}, but the intensity of this band

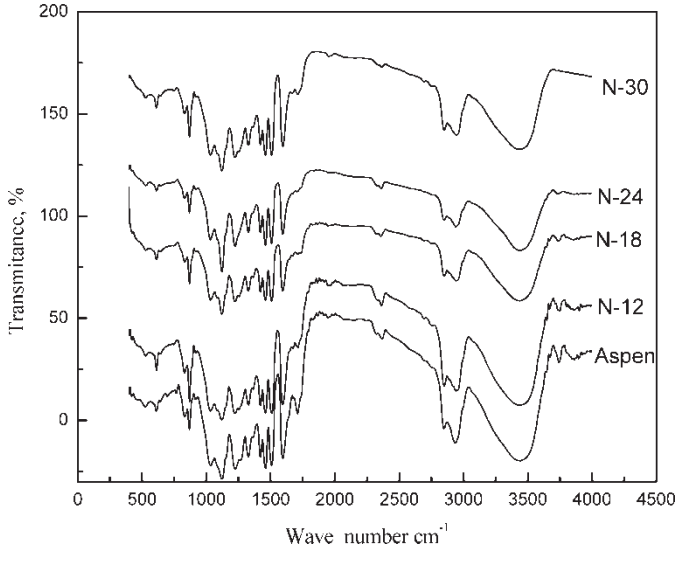

Figure 2. IR spectra of dioxane lignin.

Table 3. Assignment of FTIR spectra of lignin

Peak location range cm^{-1}	Assignment	Nalita lignin of different ages				Aspen lignin
		12	18	24	30	
3412–3460	O-H stretching	3442.7	3440.8	3442.7	3436.9	3442.7
3000–2842	C-H stretch in methyl and methylene group	2941.2	2941.2	2941.2	2943.2	2937.4
1738–1709	C═O stretch in unconjugated ketone, carbonyl, and ester groups	1714.6	1714.1	1720.2	1710.7	1710.7
1675–1655	C═O stretching in comjugated p-subst. Aryl ketones	1675.1	1676.1	s	1673.5	1670.2
1593–1605	Aromatic skeleton vibrations plus C═O stretching; S > G: $G_{condensed}$ > $G_{etherified}$	1595.0	1595.0	1595.0	1596.9	1595.0
1505–1515	Aromatic skeleton vibrations (G > S)	1510.2	1510.2	1508.2	1510.2	1508.2
1460–1470	C-H deformations (asym in -CH_3 and -CH_2–)	1460.0	1460.0	1460.0	1460.0	1460.0
1422–1430	Aromatic skeleton vibrations combined with C-H in plane deformations	1421.4	1421.4	1421.4	1421.4	1421.4
1365–1370	Aliphitic C-H stretching in CH_3 and phen. OH	s	s	s	1365.0	1365.0
1325–l1330	Condensed S and G ring (G ring bound via position 5)	1328.9	1328.9	1328.9	1328.9	1328.9
1266–1270	G ring plus C + O stretching	—	—	—	—	s
1221–1230	C-C + C-O + C═O stretching ($G_{condensed}$> $G_{etherified}$)	1224.7	1224.7	1224.7	1224.7	1226.6
1166	Typical for HGS lignins; C═O in ester groups (conj.)	—	—	—	—	—

(*continued*)

Table 3. Continued

Peak location range cm^{-1}	Assignment	Nalita lignin of different ages				Aspen lignin
		12	18	24	30	
1140	Aromatic C-H in-plane deformation (typical of G unit; $G_{condensed} > G_{etherified}$)	—	—	—	—	—
1125–1128	Typical of S unit; also secondary alcohol & C=O strt.	1122.5	1122.5	1122.5	1122.5	1122.5
1086	C-O deformation in sec. alcohol & aliphatic ether	1083.9	1083.9	1083.9	1082.0	s
1030–1035	Aromatic C-H in-plane deformation (G > S) plus C-O deform. in primary alcohols plus C-H stretching (unconjugated)	1033.8	1035.7	s	1033.8	1033.8
966–990	-HC=CH- out of plane deformation. (trans)	920.0	920.0	920.0	921.9	918.1
915–925	C-H out of plane (aromatic ring)					
853–858	C-H out of plane in positions 2, 5 and 6 (G units)					
834–835	C-H out of plane in positions 2 and 6 of S units	833.2	833.2	833.2	833.2	833.2
817–832	C-H out of plane in positions 2, 5 and 6 of G units					

was lower in Nalita lignin than aspen lignin. Aromatic vibration in the lignin fraction are assigned at 1595, 1510, 1421 cm^{-1}. The band at 1460 cm^{-1} indicates the C-H deformation and aromatic ring vibrations. The strong intensities of the band at 1329 and 1122 cm^{-1} are associated with syringyl structure in the lignin molecule. The bands at 1225, 1034, and shoulder at 1156 cm^{-1} are associated with guaiacyl units in lignin molecules, which indicated the presence of both guaciyl and syringyl unit in the lignin molecule.

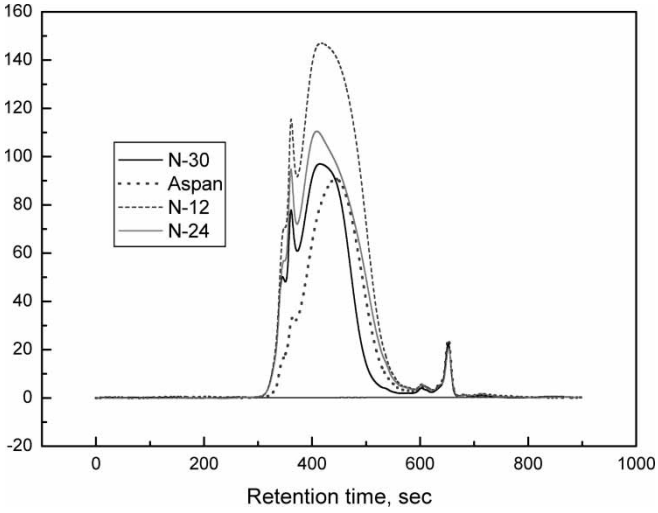

Figure 3. GPC chromatogram of dioxane lignin.

Molecular Weight

The weight average (Mw) and number-average (Mn) molecular weight, and polydispersity of different ages of Nalita lignin and aspen dioxane lignin were computed from their chromatograms (Figure 3) and show in Table 4. The data show that the Nalita lignin had Mw between 25,500–35,500, which was higher than that of aspen lignin. Mw was decreased with tree age of Nalita. Mw of Nalita MWL was a little bit higher than the present dioxane lignin.[7] The highest Mw reported for analytical lignins are 77,000 for an enzymatically isolated MWL of Eastern hemlock (*Tsuga Canadensis*), and 85,000 for a dioxane spruce lignin fraction.[13] The molecular weight of MWL also depends on milling conditions. The molecular weight of spruce MWL decreased with increasing milling time.[14] The polydispersity was decreased with tree age (Table 4).

Table 4. Molecular weight of lignin

Sample	Mw	Mn	Mw/Mn
Nalita-12	35,543	4,465	8.0
Nalita-18	32,654	4,543	7.1
Nalita-24	30,087	4324	7.0
Nalita-30	25,491	3,708	6.9
Aspen	20,587	3,651	5.6

Table 5. Yield of alkaline nitrobenzene oxidation products of lignin

	Aldehyde, %			
Age of tree, month	P	V	S	S/V (molar ratio)
N-12	0.7	13.6	21.6	1.6
N-18	0.7	14.6	22.3	1.6
N-24	2.2	12.2	21.9	1.8
N-30	2.8	11.8	20.7	1.7
Aspen	0.2	10.1	30.9	3.1

P = *p*-hydroxy benzaldehyde, V = vanillin, S = syringyldehyde.

Alkaline Nitrobenzene Oxidation

Table 5 shows the yield of alkaline nitrobenzene oxidation products from the different ages of Nalita wood lignin and compared with aspen lignin. From the Table 5 it is seen that the predominant product was identified to be syringaldehyde (S), which comprised 21–23% of lignin. Aspen wood lignin contained 31% syringadehyde. It resulted from the degradation of noncondensed syringyl unit. Vanillin (V) appeared as the second major degradation products resulted from the noncondensed guaiacyl unit. Total aldehyde yield of Nalita wood lignin was 35–38%, whereas it was 41% for aspen lignin. Therefore, aspen wood lignin contains less condensed structure than Nalita wood lignin. The relative ratio of S to V was 1.6–1.8 for Nalita wood lignin and 3.1 for aspen wood. A minor amount of *p*-hydroxyphenyl unit was also present in Nalita wood lignin (0.7–2.2%). The S/V ratio of temperate hardwood is higher than that of tropical hardwood as reported elsewhere.[15] The results appeared to be in general agreement with the range of S to V ratios obtained from hardwood lignin.[10,16]

Elemental and Methoxyl Analysis

Table 6 summarizes the results from C, H, N, O and methoxyl analyses of different ages of Nalita lignin and aspen lignin. The elemental results were corrected on the basis of the presence of 5% xylan content. The number of methoxyl group per C_9 unit in different ages of Nalita lignin was varied from 1.27–1.32 depending on tree age, which was lower than aspen lignin. Aspen lignin contents 1.47 OCH_3/C_9. It seems that the methoxyl group in Nalita lignin isolated at different ages was moderately constant. Slight variation may be due to isolation of lignin from a different layer of wood cell. It is known that the secondary wall of hardwood lignin is enriched in syringyl units.[15] Therefore, variation in OCH_3 per C_9 in different ages of Nalita may also be associated with secondary wall lignin. Lee et al.[18] showed that the OCH_3 per C_9 increased with milling time.

Table 6. Elemental analyses, methoxyl contents, and per-C_9-unit formula of Nalita and Aspen lignin

	Elemental analysis, %					
Lignin sample	C	H	N	O	OCH_3	C_9 formula[a]
Nalita-12	59.26	6.22	0.06	34.52	19.56	$C_9H_{9.00}O_{3.18}(OCH_3)_{1.31}$
Nalita-18	58.12	6.28	0.12	35.25	18.91	$C_9H_{9.46}O_{3.38}(OCH_3)_{1.29}$
Nalita-24	58.78	6.19	0.09	34.78	19.67	$C_9H_{9.06}O_{3.24}(OCH_3)_{1.32}$
Nalita-30	59.04	6.29	0.06	34.61	19.01	$C_9H_{9.31}O_{3.13}(OCH_3)_{1.27}$
Aspen	58.93	6.01	0.05	34.78	20.74	$C_9H_{8.94}O_{3.15}(OCH_3)_{1.47}$

[a]Empirical analyses formula $C_xH_yO_z(OCH_3)_n$, were calculated as follows: $n = (\%OCH_3)/31.04$; $x = (\%C)/12 - n$; $y = (\%H) - 3n$; $z = (\%O)/16 - n$.

^{1}H NMR

The integrated NMR spectrum obtained for acetylated Nalita and aspen dioxane lignin samples are shown in Figure 4, and Table 7 lists the position of signal assigned by Lundquist.[19]

Hydroxyl group: The number of free aliphatic and phenolic hydroxyl groups per C_9 unit were determined from the corresponding acetate signals. The

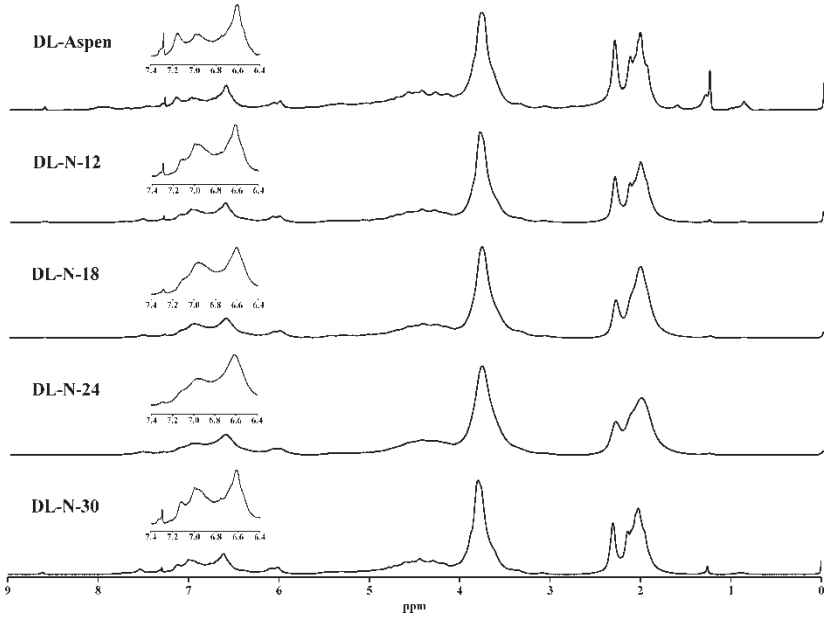

Figure 4. ^{1}H NMR spectra of dioxane lignin from Nalita.

Table 7. Assignments of signals and protons per C_9 structural unit in the ^1H NMR spectra of acetylated lignin

		Proton per C_9 unit				
Range ppm	Main assignments	N-12	N-18	N-24	N-30	Aspen
7.25–6.80	Aromatic proton in guaiacyl units	0.84	0.67	0.68	0.84	0.44
6.80–6.25	Aromatic proton in syringyl units	0.96	1	1.03	0.91	1.02
6.25–5.75	Hα of β-*O*-4 and β-1 structures	0.26	0.31	0.28	0.24	0.27
5.75–5.24	Hα of β-5 structure	0.14	0.09	0.08	0.17	0.25
5.20–4.90	H of xylan residue	0.19	0.13	0.13	0.2	0.28
4.90–4.30	Hα & Hβ of β-*O*-4 structures	1.00	1.00	1.12	1.26	1.47
4.30–4.00	Hα of β-β structures H of xylan residue	0.67	0.60	0.67	0.68	0.81
4.00–3.48	H of methoxyl groups	3.93	3.87	3.96	3.81	4.41
2.50–2.22	H of aromatic acetates	1.08	0.84	0.86	1.04	1.40
2.22–1.60	H of aliphatic acetates	2.84	3.2	2.95	2.85	3.34
Total proton per C_9 structural unit		11.94	11.71	11.76	12.53	13.69

proton of phenolic hydroxyl group of Nalita lignin was varied from 0.28 to $0.36/C_9$ with tree age, whereas it was $0.47/C_9$ for aspen. This result may explain the lower reactivity of Nalita lignin as compared to aspen lignin in an alkaline pulping. The proton of aliphatic hydroxyl group was $0.95–1.07/C_9$ for Nalita and $1.11/C_9$ for aspen.

Aromatic protons: Nalita dioxane lignins spectrum show two peaks in the aromatic proton region, which correspond to guaiacyl units (δ 6.9) and syringyl units (δ 6.6). Aspen dioxane lignin shows stronger peak in syringyl units region (δ 6.6) than guaiacyl units region (δ 6.9). All Nalita lignins had higher syringyl proton than guaiacyl proton. NMR integration suggests that 30-month-old Nalita lignin had $0.84 + 0.91 = 1.75$ aromatic protons per C_9 units. The corresponding aromatic protons in the aspen lignin were $0.44 + 1.02 = 1.46$. From analytical composition, considering 100 C_9 units and their methoxyl contents, the proportion of the syringyl and guaiacyl units was calculated to be 27–32% and 68–73% for Nalita lignin and 47% and 53% for aspen lignin, respectively.

β-O-4 structure: The aryl glycerol β-O-4 aryl ether linkage constitutes the main intermonomeric connection in lignin.[20] NMR spectra of Nalita and aspen dioxane lignin show that the structural element may contain both *erythro* and *threo* configurations due to the presence of proton at

the C-α position of the side chain. The *erythro* protons (Hα) give stronger peak at 6.01 ppm than the corresponding peak for *thero* form at δ 6.09 in both Nalita and aspen lignins. The proton of the C-β and C-γ gave a peak at 4.6, according to Lundquist and van Unge[21] and corresponded to $1.00-1.26/C_9$ protons for Nalita lignin and $1.47/C_9$ for aspen lignin.

β-5 and β-β structures: The proportion of phenylcumarane configurations in Nalita lignin was estimated to be $0.08-0.17$ per C_9 unit.

^{13}C NMR

The ^{13}C NMR spectra of acetylated Nalita and aspen lignins are shown in Figure 5 and their main signals are listed in Table 8. Because the ^{13}C NMR spectra were recorded under conditions that did not allow quantification, they provide only limited information. The Nalita and aspen lignin had sharp signals in both the aromatic and aliphatic regions. For hardwood lignin the most intense signals in this region are C3/C5 and C2/C6 at 152.8 and 104.2 ppm, respectively, of syringyl units and their appearance in both Nalita and aspen dioxane lignins confirmed GS type.[22] Similar results were reported in eucalyptus lignin.[23] The moderately strong signal at 111.4 and 104.2 ppm in Nalita lignin as compared to aspen lignin

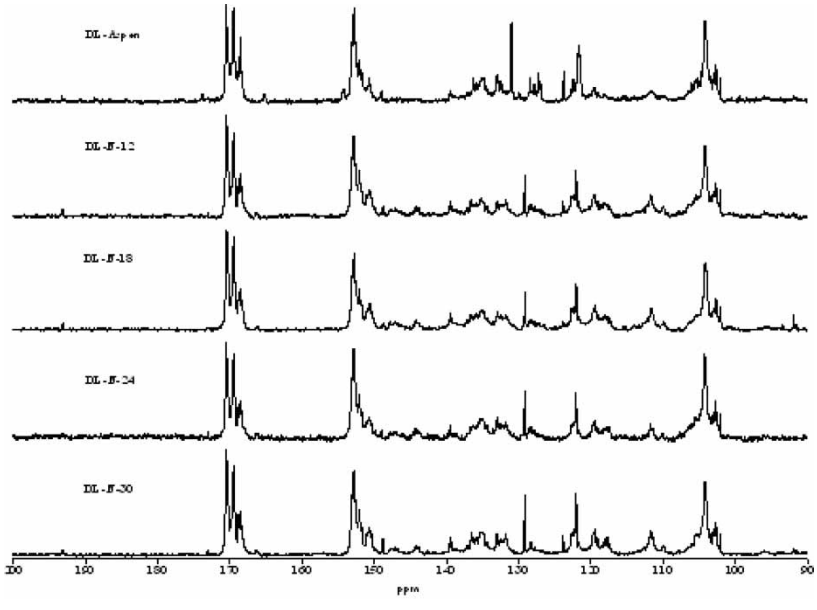

Figure 5. ^{13}C NMR spectra of dioxane lignin from Nalita.

Table 8. ^{13}C NMR spectra of acetylated lignin

δ (ppm)					Assignment
N-12	N-18	N-24	N-30	Aspen	
170.5	170.5	170.5	170.5	170.5	CO in acetates of primary alcohols
169.6	169.6	169.6	169.6	169.6	CO in acetates of secondary alcohols
168.6	168.6	168.6	168.6	168.5	CO in acetates of phenols
152.8	152.8	152.8	152.8	152.8	Sa3/5 (α-OR), S 3/5 (α-OAc), C-α in cinamaldegyde
		151.7		151.7	
150.6	150.6	150.6	150.6	150.6	Ga3 (α-OAc), G4 (α-OR and -OAc)
148.3	148.1			148.3	Ge-3 (α-OR and α -OAc)
137.0					S4 (α-OAc), Sa 1(α-OAc), S1(α-OR)
135.0					
		134.7	135.1	134.8	G1 ((α-OR), S1((α-OAc)
		133.0	131.8	133.0	G1 (α-OAc) and C-β in cinnamaldehyde
129.2	129.2	129.2	129.1	131	S4 (α-OAc), Sa 4(α-OAc), S4(α-OR)
119.4	119.4	119.4	119.6	121.5	G6 (α-OR and α -OAc)
111.4	111.5	111.5	111.5		G2 and Ga2 (α-OR and α -OAc)
104.1	104.2	104.2	104.2	104.1	S2/6 (α-OR and α -OAc)
80.6	80.6	80.6	80.6	80.6	C-β in β-O-4 and β-O-4S
74.4	74.5	74.4	74.4	74.5	C-α in β-O-4
71.7	71.7	71.7	71.7	71.7	C-3 in xylan
62.7	62.4	62.7	62.7	62.7	C-γ in β-O-4
56.0	56.0	56.0	56.0	56.0	OCH_3
20.7	20.7	20.7	20.7	20.7	CH_3 in acetyl

confirmed that Nalita lignin contain more guaiacyl lignin than aspen lignin. This result was also confirmed by ^{1}H-NMR and alkaline nitrobenzene oxidation. The signal at 170.5, 169.6, and 168.5 ppm generated by acetyl carbonyl carbon atom in primary aliphatic secondary aliphatic, and aromatic acetates, respectively, and their relative intensities reflected approximately the concentrations of primary hydroxyl, secondary hydroxyl, and phenolic hydroxyl in the dioxane lignin. The relative intensity at 168.5 ppm was much smaller in Nalita dioxane lignin than aspen dioxane lignin, which suggested a lower free phenolic hydroxyl group in Nalita lignins. Red beech had smaller relative intensity than softwood lignin at 168.5 ppm as found by Nimz and Ludemann.[24] The signal at 121.3–122.0 ppm indicates the presence of *p*-hydroxyphenyl group in Nalita and aspen dioxane lignin. Nimz et al.[25] identified *p*-hydroxyphenyl group in the compression wood at δ 128.5 and 121.7 ppm. The signal at δ 80.6, 74.5, and 62.7 can be assigned to carbon atom β, α, and γ in β-*O*-4 structure, respectively.[24,25] Nalita lignin showed stronger intensity for C γ in β-*O*-4 than aspen dioxane lignin.

CONCLUSIONS

The OCH_3/C_9 for Nalita was 1.27 to 1.32 depending on tree age, whereas that of aspen was 1.47. The molar ratio of syringyldehyde to vanillin was 1.6 to 1.8 for Nalita lignin and 3.1 for aspen. Presence of *p*-hydroxyphenyl unit in Nalita lignin was observed. The UV spectra showed absorption maxima at 280 nm for Nalita lignin and 274 nm for aspen lignin, which indicated higher guaiacyl unit in Nalita than aspen lignin. Nalita lignin showed a shoulder at 315 nm. From the ^{1}H NMR spectra, the number of proton of phenolic and aliphatic hydroxyl group was estimated to be 0.28–0.36 and 0.95–1.07 for Nalita lignin and 0.47 and 1.11 for aspen lignin per C_9 unit, respectively. ^{1}H NMR study of Nalita lignin showed that the β-*O*-4 structural unit was increased with tree age. Total number of proton per C_9 unit in 30-month-old Nalita lignin was higher than that of other ages of Nalita lignin, which indicated less condensed structure in 30-month-old Nalita lignin. Nalita and aspen lignin contained both *erythro* and *threo* configuration, but *erythro* proportion was higher. The molecular weight of 30-month-old Nalita was the lowest among all ages of Nalita lignin that was consistent with ^{1}H NMR data. In general, the results of this investigation indicate that the Nalita lignin is of guaiacyl–syringyl type. Nalita wood of 30-months old had less condensed lignin. So this age is better for Nalita pulping.

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