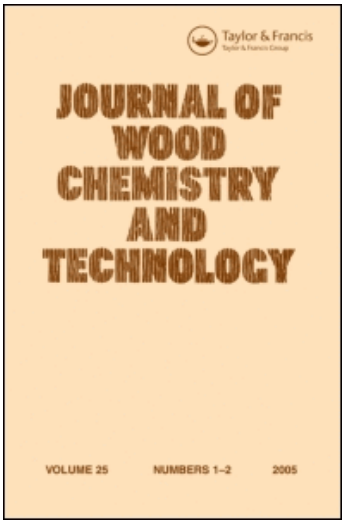

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Structure and Reactivity of Spruce Mechanical Pulp Lignins. IV: ^{13}C-NMR Spectral Studies of Isolated Lignins

Xiaoqi Pan[a]; Dominique Lachenal[a]; Vincent Neirinck[b]; Danielle Robert[b]
[a] Ecole Française de Papeterie, Institut National Polytechnique de Grenoble, France [b] CEA/DRFMC/SESAM/Lab. Macromol. Vegetales, France

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STRUCTURE AND REACTIVITY OF SPRUCE MECHANICAL PULP LIGNINS IV: ^{13}C-NMR SPECTRAL STUDIES OF ISOLATED LIGNINS

Xiaoqi Pan and Dominique Lachenal
Ecole Française de Papeterie, Institut National Polytechnique de Grenoble, BP 65, 38402 Saint Martin d'Hères Cedex, France

Vincent Neirinck and Danielle Robert*
CEA/DRFMC/SESAM/Lab. Macromol. Vegetales,
CENG 85X- 38041 Grenoble Cedex, France

ABSTRACT

^{13}C-NMR spectroscopy has been used to characterize the lignins extracted by an organosolv flow-through process from spruce TMP, bleached TMP (BTMP) and yellowed BTMP (YBTMP). In general, the ^{13}C-NMR spectra of these lignins are similar to that of spruce MWL, indicating that the lignins underwent limited structural changes. Thus they may be an acceptable substrate for lignin structural study. However, these lignins appear to have a significant amount of condensed aromatic carbons assigned mainly to β-5, 5-5 and diarylmethane structures. These were likely formed during the organosolv cook, or initially present in TMP and extracted with this organosolv process. On the other hand, the hydrogen peroxide bleaching causes little change in the lignin overall structure. As a favorable effect, elimination of the coniferaldehyde structures can clearly be seen. The photoyellowing appears to result in the creation of aromatic carbonyl and carboxyl groups. This suggests that oxidative cleavage of Cα, Cβ bonds is one of the important photodegradation reactions of lignin.

* Affiliated with the Universite Joseph Fourier, Grenoble, France

INTRODUCTION

Our previous works[1-3] have been directed towards developing a new procedure for isolation of lignin and elucidating the structural changes in lignin during hydrogen peroxide bleaching and brightness reversion (photoyellowing) of thermomechanical pulp (TMP). Lignin fractions were extracted from spruce wood chips and various TMP pulps with a flow-through reactor using ethanol-water as solvent and acetic acid as catalyst and were used for structural study with regard to the effects of the bleaching and photoyellowing. It has been demonstrated that the lignins thus obtained suffered a limited modification. In addition, no substantial changes in lignin took place upon the H_2O_2 bleaching under the pertinent technical conditions. However, the photoyellowing under the condition simulating solar irradiation caused pronounced changes in the lignins. All information about the structure of lignins was provided by an original chemical degradation technique, i.e., thioacidolysis followed by Raney nickel desulfuration. It has successfully been applied on both fiber materials (wood or pulp) and lignin preparations isolated from these fibers.

As a spectrometric alternative and non-degradative technique ^{13}C-NMR spectroscopy was chosen for further and complementary studies of the lignins. This paper reports on both qualitative and quantitative ^{13}C-NMR analyses of the aforementioned lignins. Investigations were also conducted into the effects of delignification conditions, hydrogen peroxide bleaching and photoyellowing on the structure of the organosolv lignins.

RESULTS AND DISCUSSION

1. Organosolv Fractionation of Lignin in the Flow-Through Reactor

Lignin extraction was conducted in a flow-through reactor[2] designed to minimize secondary reactions of the lignins released from the lignocellulosic matrix.[4,5] Delignifying solvent, ethanol-water 1:1

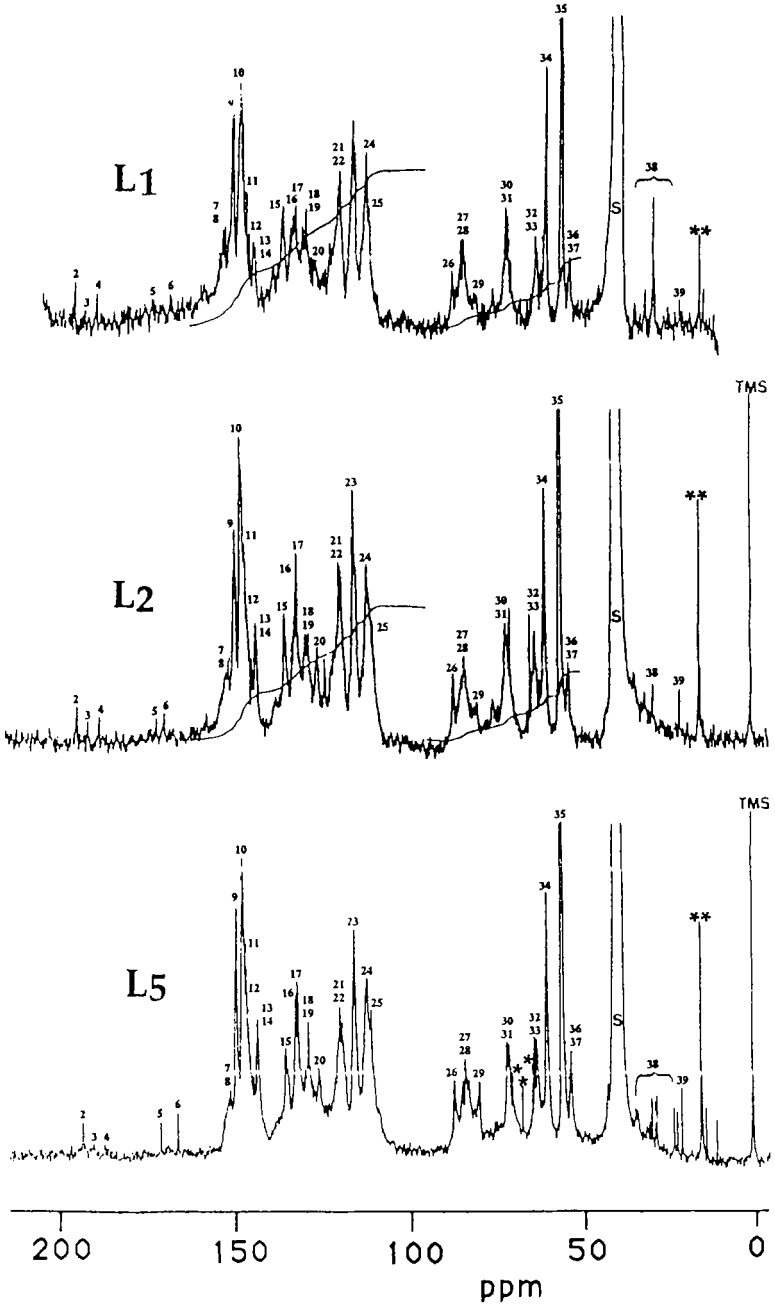

FIGURE 1. ^{13}C-NMR spectra of L_1, L_2 and L_5 organosolv lignin fractions extracted from Spruce TMP by means of ethanol/water flow-through process; S = Solvent (DMSO-d_6). *CH_2, **CH_3 signals in ethoxyl groups.

v/v containing 0.1 M acetic acid, was introduced into the reactor under nitrogen atmosphere after pre-heating up to the cooking temperature. The liquor was circulated in an ascendant way in the reactor and was penetrated through the interior of fibers to remove lignins from the lignocellulosic matrix. At the exit of the reactor, the effluents were cooled down rapidly and recovered in numerous successive fractions. The organosolv lignin preparations studied here, L_1, L_2 and L_5 were collected from three different cooking time periods, namely, 0 - 30, 30 - 60 and 120 - 300 min., respectively.

1-1. Qualitative Analysis

The ^{13}C-NMR spectra of L_1, L_2 and L_5 are shown in Figure 1. The signals assignment summarized in Table 1 was made according to the method and tables of values found in the literature.[6 - 10]

TABLE 1. Chemical Shifts (δ) and Signals Assignments in ^{13}C-NMR Spectra of Organosolv Lignins Fractions L_1, L_2, L_5 and Spruce MWL in DMSO-d_6 Solution.

Signal No	δ (ppm/TMS)	Assignments
1	210 - 200	Non conjugated ketonic C=O
2	194	γ-CHO in cinnamaldehyde
3	191.6	α- CHO in benzaldehyde
4	188	Unknown (quinones ?)
5	173 - 171	C=O in aliphatic acides or esters
6	167 - 165	C=O in aromatic acides or esters
7	152.9	C-3/C-3' of etherified 5-5 units
8	152.6	C-4 in G e with α-C=O, C-3/C-5 in 4-O-5, C-α in cinnamaldehyde
9	149.1	C-3 in G e units
10	147.4	C-4 in G e units
11	146.9	C-3 in G ne units

TABLE 1. (Continued)

Signal No	δ (ppm/TMS)	Assignments
12	145.3	C-4 in G β-O-4 ne units
13	144	C-4 in β-5 units
14	143.4	C-4/C-4' in e 5-5 units
15	135.3	C-1 in G β-O-4 e units
16	133	C-1 in G β-O-4 ne units
17	132.4	C-5/C-5' in 5-5 e units
18	128 - 130	C-α and C-β of cinnamic alcohols
19	i.d.	i.d.
20	126.3	C-β of cinnamaldehydes and C-5/C-5' in 5-5 ne units
21	120.3	C-6 in G e and ne units
22	119.5	i.d.
23	115.2	C-5 in G e and ne units
24	111.4	C-2 in G units
25	110.9	C-2 in G-G stilbene units
26	87.2	C-α in β-5 units
27	85.3	C-α in β-β units
28	84.5	C-β in G β-O-4 units
29	82 - 80	C-β and C-α in β-O-4 / α-O-4 units
30	71.4 - 72.5	C-α in G β-O-4
31	71.2	C-γ in β-β units
32	63	C-γ in β-5/β-O-4 units with α-C=O
33	61.7	C-γ in cinnamic alcohol
34	60.0	C-γ in G β-O-4
35	55.9 - 55.7	Aromatic methoxyl groups
36	53.7	C-β in β-β units
37	53.1	C-β in β-5 units
38	15 - 40	CH_3 and CH_2 in saturated aliphatic chain
38a	29.7	CH_2 in diarylmethane structure
39	20	CH_3 in acetyl groups

G = guaiacyl; S = syringyl; H = p-hydroxyphenyl; e = etherified; ne = non etherified.

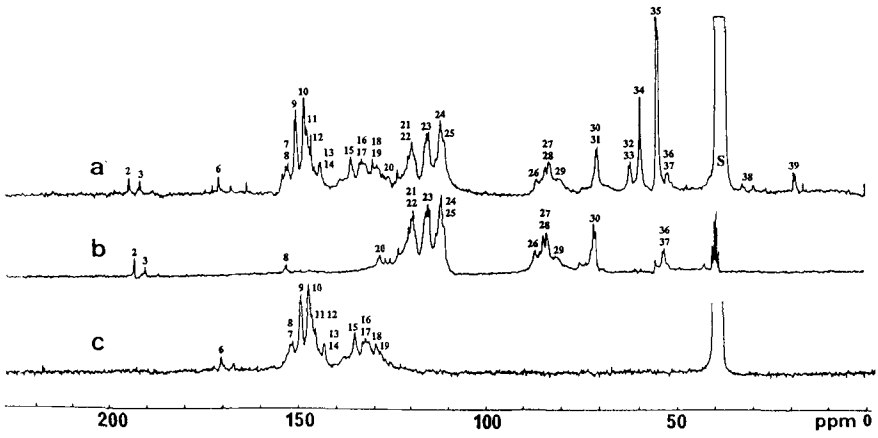

FIGURE 2. ^{13}C-NMR spectra of spruce MWL, a) total spectrum, b) DEPT edited spectra for CH signals, c) spectrum edited for quaternary carbons only; S = Solvent (DMSO-d_6).

From the NMR spectra the three lignin fractions appear to be very similar, which suggests that the residential time in the flow-through reactor does not appreciably affect the lignin structure. This is what is expected from such a fractionation which minimizes degradation and modification during the delignification stage.[5] A minor difference is the presence of O-acetyl groups in L_2 and L_5 fractions but not in L_1, as shown by signals 5/39 at 171-173/20 ppm. The O-acetyl groups may be originally present as part of xylan in the TMP. Alternatively, lignin in TMP may undergo acid catalyzed acetylation of hydroxyl groups during the cook because the cooking liquor contains acetic acid. Some relative variations of intensity are seen among the three spectra, because they are very small they will only be interpreted qualitatively.

Importantly enough is the general qualitative ressemblance of these spectra to that of a spruce MWL (Figure 2a), taken as a reference for a non-degraded lignin, with the exception of differences in the relative intensities of some particular signals which will be discussed later. Usually, the ^{13}C-NMR spectra of technical lignins reveal more

structural differences with MWL spectra , for example wider signals, implying a larger chemical heterogeneity, altered propane side chain and the presence of saturated CH_2 groups, as in the case of kraft lignins,[11,12] lignins from exploded wood[13] and alkali lignins.[14,15]

Nevertheless, there are some differences between the spectra of the organosolv lignins and that of spruce MWL. Among them is the presence in the organosolv lignins of ethoxyl groups which give a CH_3 signal at 15.1 ppm and CH_2 signals at 64.6, 67.5 and 70.4 ppm, shown by Figure 1 and confirmed by DEPT spectra (Figure 3a-b). Recently, Aoyama and co-workers[16] proved that etherified (non-phenolic) β-O-4 type model compounds with α hydroxyl groups produced α-ethoxyl derivatives in addition to the cleavage of β-O-4 bond via benzyl carbonium ion intermediate on treatment with ethanol-water in the presence of a Lewis acid, but not phenolic β-O-4 substructures. Thus it is likely that acid-catalyzed O-ethylation occurred at C_α of an etherified substructure with α-hydroxyl group under the reaction conditions. This is also in good agreement with previously reported results[17-19] which showed that acid-catalyzed O-alkylation occurred at the C_α during alkyl alcohol delignification processes. It is not possible, without using proper model compounds, to determine the precise side chain position to which ethoxyl groups are introduced. From Figure 1, one notices that ethoxyl groups are present in smaller amount in the L_1 fraction, thus confirming that the degree of O-ethylation increases with increasing residential time as it was already shown in the results obtained for the same organosolv lignin fractions by chemical method.[2] Another difference with MWL is the presence, although modest, of saturated CH_2 and CH_3 groups in the 15 to 35 ppm region, as shown by Figure 3a-b; CH_2 signal at 29.7 ppm can be assigned to methylene group in diaryl methane structures which are known to be formed by condensation of formaldehyde and phenyl groups,[9] the other saturated groups can possibly come from unextracted resins and extractives.

Other structural differences betwen MWL and organosolv lignins as well as among organosolv lignin fractions themselves are revealed by the differences in the relative intensities of some particular

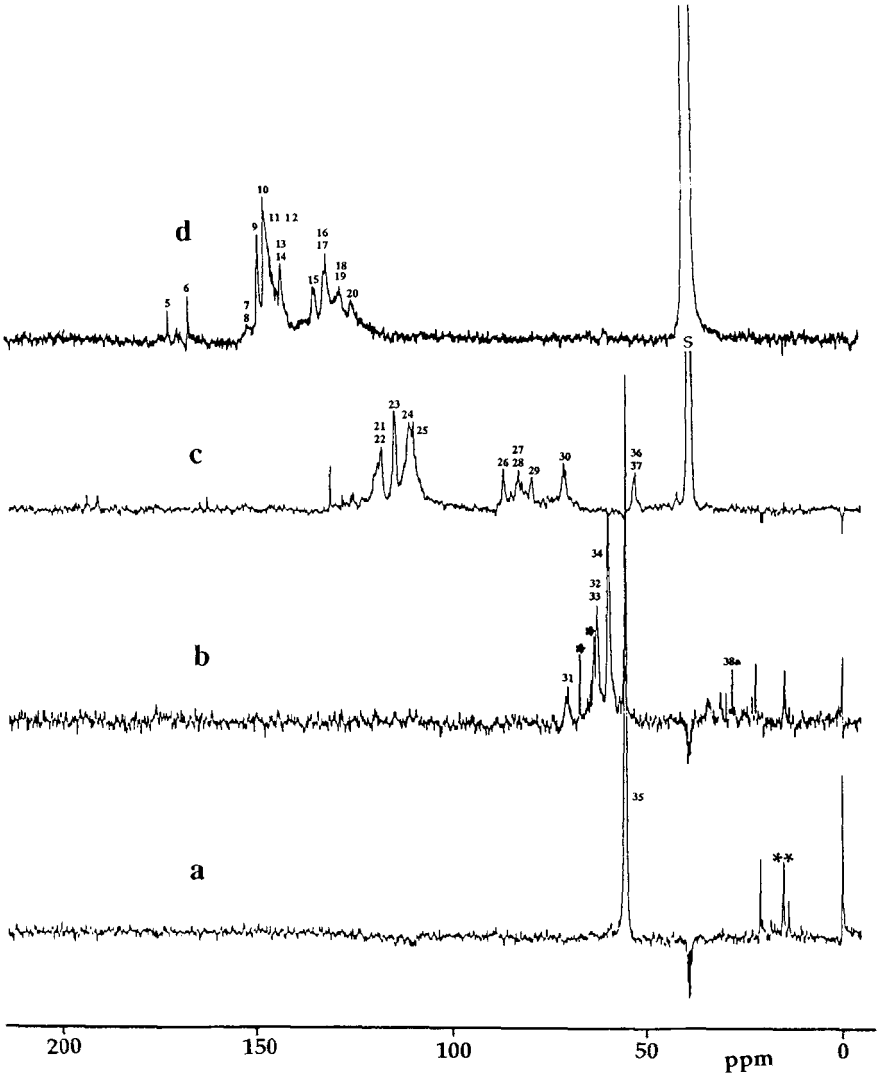

FIGURE 3. DEPT edited ^{13}C-NMR spectra for L_5 fraction: a) CH_3 signals, b) CH_2 signals, c) CH signals; d) edited spectrum for quaternary carbons only; S = Solvent (DMSO-d_6); *CH_2 and **CH_3 : signals in ethoxyl groups.

signals. Quantitative information can be obtained from the comparison of spectra without going through a real quantitative analysis, provided some precautions are taken:

1) From spectra recorded with routine conditions one can compare signals integral, as long as they correspond to carbons having the same T_1, and measure the ratio of monomeric types present, cluster of signals being taken as structural internal reference; actually this will not be the real ratio but a valid comparative measure among a set of lignins.[20]

2) One can also compare structural contents without considering the integral but just the signals intensity, assuming that a scaling to the methoxyl signal intensity taken as internal reference is valid from one spectrum to another.[15]

In our case we notice some differences in relative signals intensity interesting to interpret but difficult to estimate precisely by integral measurements, despite the fact that spectra (Figures 1, 2a) were recorded under conditions suitable for quantitative analysis, because the differences are quite small and the signals more or less overlapping. Therefore, we compare the relative intensity of signals which belong to carbons of the same nature within the same cluster of signals, the cluster being used as an internal structural reference. For exemple in the range of the quaternary aromatic carbons we observe that within the cluster 7-14, where are found all the C_{-3}/C_{-4} aromatic carbons of spruce lignin, the relative signal intensity of signals 13/14 at 143.4 - 144 ppm increases when going from MWL to lignin fractions L_2 and L_5; so does the relative intensity of signals 17 and 20 in the cluster 15-20 which represent the C_{-1} carbons in spruce lignin structure. These observations are confirmed unambigously by the comparison of the subspectra giving the NMR signals only for the quaternary carbons, Figures 2c and 3d. Moreover signal 20 which is hardly seen in MWL spectrum shows up clearly in L_2 and L_5 spectra. In the aliphatic range of etherified carbons, within the cluster 26-29 corresponding to C_β in β-O-4 and C_α in β-5 units, the relative intensity of signal 26 at 87.2 ppm increases from MWL to L_2 and L_5 fractions; it is even more obvious if

one compares the DEPT edited spectra for CH signals in L_5, Figure 3c, and in MWL, Figure 2b.

As the spectra are recorded for quantitative analysis we can compare signal intensities of carbons of different nature from signals 36/37, C_β in β-β and β-5, to signals 27/31, C_α and C_γ in β–β, and notice that the relative intensity of 36/37 increases from MWL to L_1, L_2 and L_5. The set of signals 13 at 144.0 ppm, 26 at 87.2 ppm, 32 at 63.0 ppm and 37 at 53.1 ppm, is assigned, respectively, to C_4, C_α, C_γ and C_β carbons in β-5 structure;[21] moreover these signals increase from L_1 to L_5. The formation of β-5 structures upon organosolv cook has been explained by a mechanism proposed by Sarkanen.[17] As illustrated in Figure 4, it is established that α-hydroxyl or α-aroxyl groups are eliminated from β-O-4 structures in lignin to form water and the corresponding phenols during the organosolv cook. The resulting quinonemethide intermediates then undergo homolytic cleavage of β-O-4 bonds producing quinonemethide C_β radicals and phenoxyl radicals. Phenylcoumaran (β-5) structures are produced by recombination of a C_β radical and a C_5 radical derived from the phenoxyl radical by mesomerism, followed by intramolecular nucleophilic addition of phenolic hydroxyl groups on C_α of the resulting quinonemethide moiety. To our knowledge, this is the only type of lignin in which β-5 units have such an important contribution in the overall structure. This NMR evidence is in agreement with the results obtained by thioacidolysis;[2] the lignins investigated are thus rich in β-5 structure with a number increasing from L_1 to L_5.

The other group of enhanced signals, 14 at 143.4 ppm, 17 at 132.4 ppm and 20 at 126.3 ppm can be assigned, respectively, to $C_4/C_{4'}$ and $C_5/C_{5'}$ in etherified 5-5 units and to $C_5/C_{5'}$ in 5-5 non-etherified units.[9] In addition, signal 23 at 115.2 ppm, corresponding to tertiary aromatic C_5H in guaiacyl units, become more narrow, compared to signals 21/22 and 24/25, in L_1, L_2 and L_5 spectra than in MWL spectrum, indicating a decrease in tertiary C_5H carbons. There is no clear mechanisms known supporting the formation of aryl-aryl bonds during the delignification process, however Sarkanen[17] has suggested that condensations might occur on the C_6 position. As an alternative

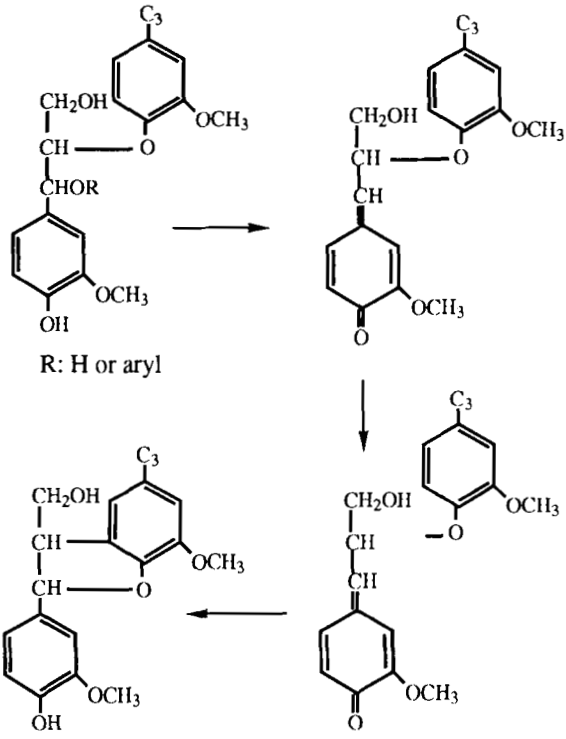

FIGURE 4. Rearrangement reactions caused by homolytic cleavage of β-aryl ether bonds in phenolic lignin structures.

and complementary explanation, we can assume that with the delignification degree increasing the lignin fractions collected are richer in more condensed units because they are formed in a larger amount as the cook proceeds and/or because the process is able to extract these units which in this case belong to the original lignin structure. It is not the case of spruce MWL that represents only about 20 % of the total lignin in the spruce wood. And, most of spruce MWL originates from the secondary cell wall that contains the least condensed lignin. Last but not least the presence among the saturated CH_2 groups (Figures 1 and 3b) of signal 38a at 29.7 ppm is attributed to the methylene carbon

of diarylmethane structures; these structures are formed[17] by a reverse Prins reaction involving elimination of formaldehyde at the γ carbon with formation of a vinylphenol structure, followed by condensation of phenols with formaldehyde through a Lederer-Manasse type reaction.

To better characterize the organosolv lignins extracted from TMP and to determine the effect of TMP process, we investigated an organosolv lignin fraction extracted from spruce wood chips under the same conditions. As shown in Figure 5, the spectra of these two types of lignin have a total analogy, only a few signals differ slightly in intensity. It is the delignification process, more than the state of the starting material (wood chip or defibrated), that determines the structure of the extracted lignins.

1-2. Quantitative Analysis

Functional groups and interunit linkages which give signals not overlapping too much, assigned without ambiguity and observed with a good signal to noise ratio can be estimated by ^{13}C NMR analysis in a reliable way.[22, 23] Results from this type of analysis for L_1, L_2 and L_5 fractions and for MWL are given in Table 2, they are reported as number of carbons per aromatic unit.[8]

The number of quaternary aromatic carbons is particularly interesting to know because it reflects the degree of condensation of the aromatic ring. It is difficult, if not impossible, to get this precise data by chemical analysis; however it can be achieved by ^{13}C-NMR when the DEPT sequence is used in combination with a sequence for quantitative analysis.[8,13] From the CH spectra edited with the DEPT sequence, Figures 2b and 3c, and from the spectra giving the quaternary carbons only, Figures 2c and 3d, the respective range of quaternary (124.5-162 ppm) and tertiary (102-124.5 ppm) aromatic carbons can be delimited quite precisely. As a matter of fact, between 124.5 and 132 ppm are the vinylic signals and the C_{-2}/C_{-6} carbons of H units, which are in very low amount and totally overlapped mianly by the quaternary carbons and partly by the tertiary carbons, so we split this very small

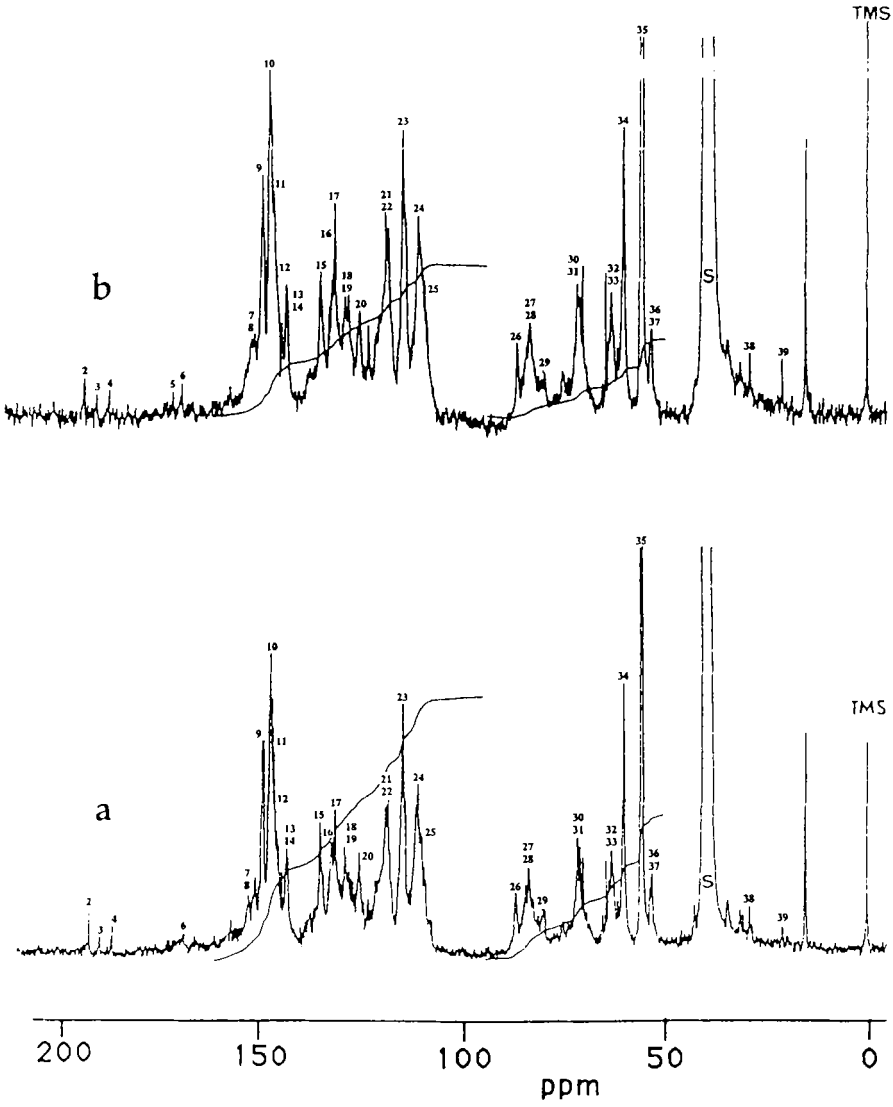

FIGURE 5. ^{13}C-NMR spectra of L_2 fraction extracted from a) spruce chips and b) TMP; S = Solvent (DMSO-d_6).

TABLE 2. Number of Carbons per Aromatic Unit of Different Functional Groups and Interunit Linkages in Spruce TMP Organosolv Lignin Fractions and in Spruce MWL.

	Aromatic carbons		Aliphatic carbons
	Quat. C	Tert. C	linked to oxygen
L_1	3.75	2.25	2.25
L_2	3.90	2.10	2.20
L_5	3.85	2.15	2.20
MWL	3.35	2.65	2.25

* precision +/- 5%

contribution between tertiary and quaternary aromatic carbons. No correction has been made to take into account the contribution of vinylic carbons and C_{-2}/C_{-6} in H units in the aromatic region as well as that of ethoxyl groups $-CH_2-$ carbons in the 50 - 90 ppm region. These contributions are minor and very difficult to estimate with precision.

The variation of the number of substituted sites on the aromatic ring and of the aliphatic etherified carbons within the three fractions L_1, L_2 and L_5 is not significant, as reported in Table 2, which confirms the similarity observed in the qualitative analysis and emphasizes this organosolv process as a non-disruptive procedure towards the lignin structure. For the methoxyl content we take the average of the three figures found for these groups in the three fractions, i.e., 0.90 $-OCH_3$ per aromatic moiety, because the differences fall within the measurement precision, +/-5 %, and cannot be reasonably interpreted.

The organosolv lignins have rather higher content of aromatic quaternary carbons than the MWL (Table 2). A repartition of these carbons between different structures can be made. From the data we know already from quantitative NMR analysis, in the case of spruce MWL,[16] among the 3.35 estimated aromatic quaternary carbons, 2 of them belong to the C_{-1} and C_{-4} positions, 0.95 to C_{-3} substituted by

-OCH_3 groups, 0.25 and 0.05, respectively, to C_{-5} in 5-5 and β-5 structures, the remaining 0.10 quaternary carbons could include 4-O-5 structures in very low amounts, C_{-6} substituted moieties or some other condensed units not yet identified. In the case of L_1, L_2 and L_5 fractions, considering a 0.90 average methoxyl content per aromatic and 3.80 average quaternary carbons, it means 0.90 carbons for other condensed sites other than C_{-1}, C_{-4} and C_{-3}; if we assume, like in the case of MWL,[19] that initially 0.40 carbons belong to β-5, 5-5, 4-O-5 moieties it leaves 0.50 additional condensed carbons which might be created during the delignification or be already present in the original lignin and extracted more thoroughly during the organosolv delignification process. To identify these condensed units we refer to some of the conclusions of the qualitative analysis and propose that part of them are β-5 and 5-5 units. Because of overlapping signals it is difficult to evaluate precisely how much the β-5 structures contribute to the increase of quaternary carbons in the organosolv lignins; nevertheless a rough estimation from the integral of signal 26 and 37 in Figures 3c and 2b would give no more than 0.15 β-5 additional structures per phenyl unit, it leaves another 0.35 quaternary carbons to be assigned. We assume that the major part of these condensed aromatic carbons belong to 5-5 structures. But they are not the only possible contribution to the extra 0.35 condensed carbons; diarylmethane structure can contribute (see signal 38a assigned to CH_2 group in this structure), which can be formed by condensation of formaldehyde and phenyl groups.[17] Condensation on the C_{-6} aromatic position also can occur; indeed it was established that C_{-6} condensed structures increased appreciably on treatment of spruce lignin with acid.[24]

Quantitatively there is no meaningful difference between MWL and L_1, L_2 and L_5 lignin fractions concerning the oxygenated carbons in side chains. This again shows that the organosolv process is non-degradative towards the structure of lignins.

^{13}C-NMR allows an easy quantitative determination of the hydroxyl groups.[25] After acetylation the acetoxyl signals corresponding to primary, secondary and phenolic hydroxyl functions appear distinctly in the 162 - 175 ppm region where there is basically no serious

TABLE 3. Number of Hydroxyl Groups per Aromatic Unit Calculated by Integration of the Acetoxyl Signals (δ in ppm/TMS) in the Acetylated Lignin Samples of Spruce TMP L_2 fraction and of MWL.

	Total OH	Prim. OH (δ)	Sec. OH (δ)	Phenolic OH (δ)
TMP L_2	1.32	0.67 (170.1)	0.27 (169.2)	0.38 (168.4)
MWL[25]	1.38	0.78 (170.8)	0.31 (170.0)	0.20 (168.9)

*Precision: +/- 5 %

risk of overlapping with other signals. The content of hydroxyl groups obtained for L_2 and MWL expressed on the basis of the aromatic unit is given in Table 3.

From Table 3, it can be seen that differences exist between TMP L_2 and spruce MWL. Although the total hydroxyl contents are similar, L_2 has less primary hydroxyl groups but more phenolic groups than MWL does. The lower content of primary hydroxyl groups in L_2 reflects the possible loss of γ carbons, i.e., elimination of $-CH_2OH$ [17, 26] and the possible ethoxylation at γ position of the side chain during the organosolv delignification. The higher content of phenolic hydroxyl groups indicates a splitting of the α-O-4 and β-O-4 linkages during the organosolv delignification.

Larger numbers than those determined by ^{19}F-NMR [2] are found for both alcoholic and phenolic hydroxyl groups, the relative values are nevertheless comparable for these two methods. The discrepancy observed could be due to the removal of low molecular weight lignin fractions rich in hydroxyl groups during the preparation of 2-fluorobenzoic ester derivatives needed for ^{19}F-NMR hydroxyl analysis.

2. Bleaching and Photoyellowing

In this section, emphasis is put on the 165 - 210 ppm region where conjugated carbonyl and carboxyl resonances occur. Changes of

these functions reflect the effects of bleaching and photoyellowing.[1, 3] Figure 6 shows the ^{13}C-NMR spectra of the L_2 lignin fractions extracted from TMP, bleached TMP (BTMP) and yellowed BTMP (YBTMP-1), respectively.

The signal intensity for C=O carbons is in general weak because they correspond to carbons with longer relaxation times compared to other types of carbons.[8, 23] In addition, they belong to minor structures, which makes it difficult to gain a reliable integration. Therefore, only qualitative analysis has been done (Tables 1 and 4); in Table 4 are given the assignments of the signals and are mentioned the presence or absence of these signals.

It is of interest to identify signal 4 at 188 ppm because the signal could originate from quinone structures. Indeed the carbonyl signals in differently substituted para-benzoquinones are found at 186 - 188 ppm.[27] Confirmation of this hypothesis, by the study of appropriate benzoquinonic lignin model compounds, would indicate that photo-induced yellowing of mechanical pulps could at least partially be due to formation of quinones.

Importantly, a clear-cut modification displayed in Table 4 shows that the bleaching leads to a complete disappearance of the γ-CHO in coniferaldehyde structure, signal 2 at 194 ppm. This result confirms those obtained by thioacidolysis for both *in situ* and isolated lignins.[1, 3] The elimination of coniferaldehyde structures is also in good agreement with earlier works on degradation of coniferaldehyde structures in lignin by alkaline peroxide oxidation.[28, 29] Moreover, the photoyellowing appears to increase the intensity of signal at 167 - 171.8 ppm, implying the creation of carboxyl acids or their esters during this process. This result agrees with the increase of IR absorptivity at 1720 cm^{-1} and the increased yield of vanillic acid related products in the thioacidolysis reaction mixture.[3] The rest of the structure seems to be unchanged by both the bleaching and photoyellowing conducted in this work.

Effect of the photoyellowing has further been examined by ^{13}C-NMR analysis on a lignin sample (**I-1** SP) recovered upon direct irradiation of the lignin absorbed in filter paper sheets.[3] Figure 7 shows

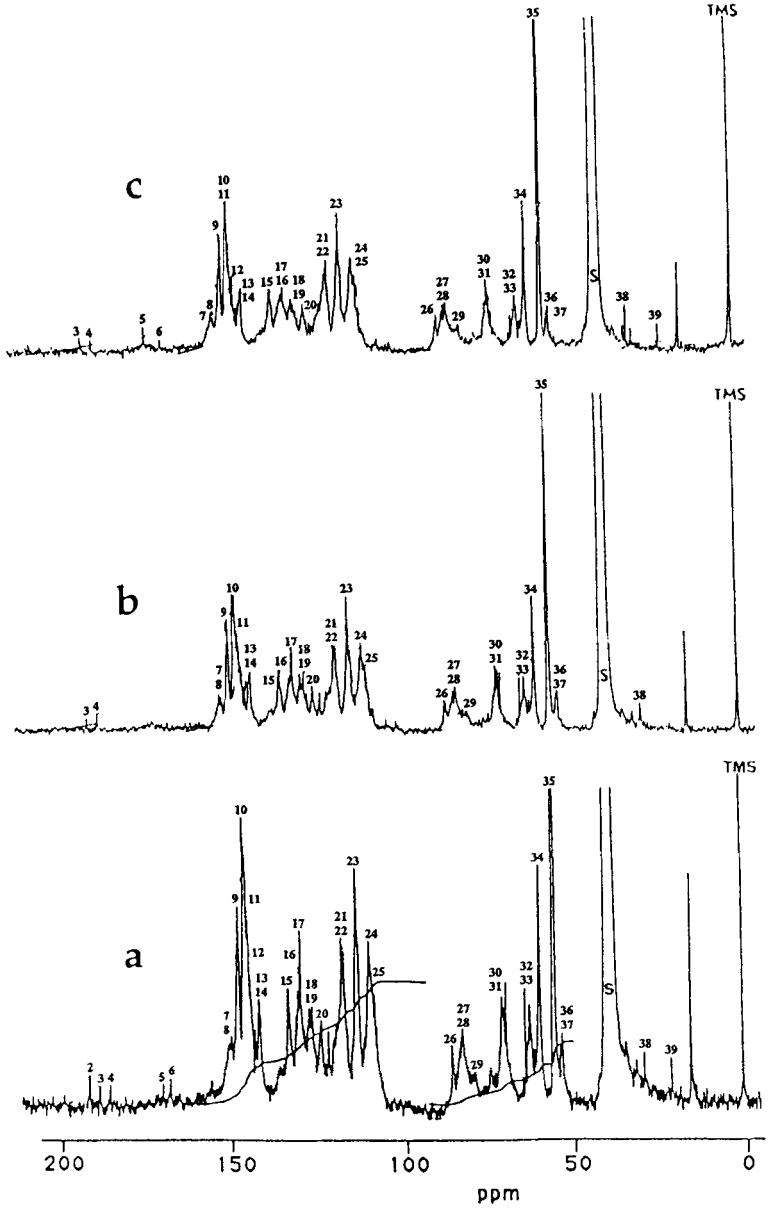

FIGURE 6. ^{13}C-NMR spectra of organosolv lignin L_2 fractions extracted from a) TMP, b) BTMP and c) YBTMP-1; S = Solvent (DMSO-d_6).

TABLE 4. ^{13}C-NMR Detection of C=O Signals in Spectra of Organosolv Lignin L_2 Fractions Isolated from Spruce TMP, BTMP) and YBTMP-1.

Origin in Lignin		Coniferaldehyde	Vanillin	?	Esters and Acids
Type of carbon		γ-CHO	α-CHO	>C=O	-COOR(H)
δ ppm /TMS		194	191	188	165 - 175
	TMP	+	+	+	+
L_2	BTMP	0	+	+	-
	YBTMP-1	0	+	+	+

+: presence; -: decrease compared to +; 0: disappearance.

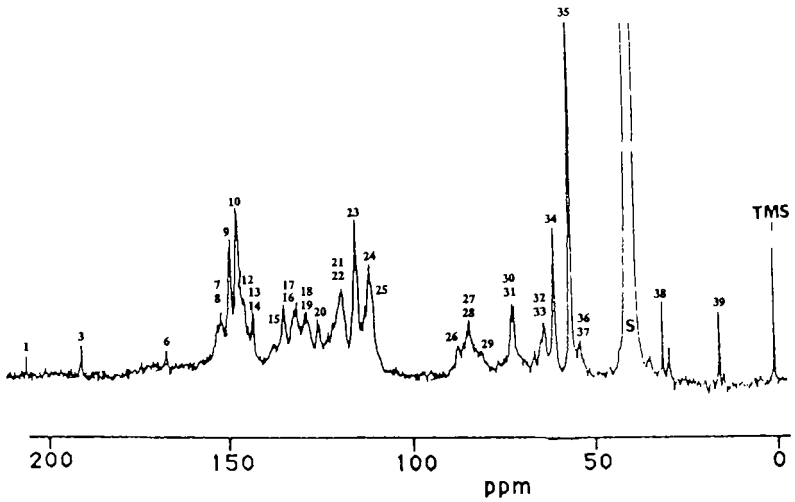

FIGURE 7. ^{13}C-NMR spectrum of a lignin sample **I-1** SP: acetone-soluble part of the BTMP L_2 irradiated on filter paper sheet in the presence of UV filter for 24 hrs.[3]

TABLE 5. Number of Hydroxyl Groups per Aromatic Unit of the Organosolv Lignin L_2 Fractions Extracted from TMP, BTMP and YBTMP-1.

	Total OH	Primary OH	Secondary OH	Phenolic OH
TMP L_2	1.32	0.67	0.27	0.38
BTMP L_2	1.33	0.61	0.29	0.42
YBTMP-1 L_2	1.31	0.56	0.30	0.45

the spectrum of the resulting lignin sample. Compared to the spectrum of the starting material (BTMP L_2) in Figure 6, this treatment causes a significant increase of the signals of carbonyl groups in vanillin unit (signal 3 at 191 ppm) and of aromatic carboxyl groups (signal 6 at 165 - 167 ppm). The latter is likely of vanillic acid type structures. This further supports the result obtained by thioacidolysis of the same lignin sample.[3] The result reported here once again suggests that oxidative cleavage of C_α, C_β bonds is one of the important light-induced degradation reactions of lignin.[30, 31]

In addition, it can be observed that the irradiation causes an appearance of ketonic carbonyl groups (signal 1 at 207 ppm). Recently, photodegradation of β-O-4 type lignin model compounds was investigated by several authors.[32 - 34] The benzylic carbon of β-O-4 type structures undergoes hydrogen abstraction to produce a corresponding ketyl radical that decomposes into corresponding acetoguaiacone type structure and aroxyl radicals. The latter would further initiate radical chain reactions leading to further degradation of lignin. The formation of acetophenone type compounds may be an important reaction in the photoyellowing of mechanical pulp. Compounds of this type are photosensitizers and would initiate lignin photodegradation producing chromophoric structures that are responsible for the photoyellowing.

Effects of the bleaching and photoyellowing on the hydroxyl contents of L_2 lignin fractions extracted from TMP, BTMP and YBTMP-

1 are studied. Table 5 summarizes the results. Neither the bleaching nor the photoyellowing changes meaningfully the total hydroxyl content. However, there is a slight decrease in the amount of primary hydroxyl groups and an increase in the phenolic hydroxyl groups in particular on photoyellowing. Although it may not be warranted to interpret such a small change, it could reflect possible elimination of γ-CH_2OH groups and cleavage of aryl ether bonds during bleaching and photoyellowing.

EXPERIMENTAL

1. Material

A spruce wood (*picea abies*) was used for preparing various pulp samples, as in detail described in Part I of our work.[1] Defibration led to a TMP (50 % ISO). Bleached TMP (BTMP) was made by treatment of TMP with H_2O_2 (5 % on O.D. pulp) and its brightness was 76 % ISO. A yellowed pulp, YBTMP-1 (59 % ISO), was prepared by irradiating BTMP in a solar simulator (Original Hanau suntest).

Extraction of lignins from the above-mentioned wood chips and pulps was conducted in a flow-through reactor using ethanol-water 1:1 v/v containing 0.1 M acetic acid at 175 °C for 5 hrs. The extracted lignins were recovered in five successive fractions L_1 - L_5 according to delignification time, i.e., 0 - 30, 30 - 60, 60 - 90, 90 - 120 and 120 - 300 min. The detailed procedures were previously reported.[2]

Spruce MWL was prepared and purified according to the Bjorkman's procedure.[35]

2. ^{13}C-NMR analysis

The ^{13}C NMR spectra have been recorded at 303 K on a Bruker WM 250 spectrometer (ν ^{13}C = 62.82 MHz) for samples in DMSO-d_6 solution (250 to 400 mg in 1.8 ml). For quantitative analysis the inverse gate decoupling sequence was used with the following parameters: 225 ppm sweep range, 16 K memory, 90° pulse angle, 10s and 11-12s pulse delay for unacetylated and acetylated samples, respectively, an average of 7,500 to 10,000 scans depending upon the concentration.

The DEPT experiment was generated from the computer software using a (1/2J) delay with a 150 Hz average value for the scalar couplings ^{1}J C-H, the recovery delay was 3s; 3,500 transients were accumulated for the pulse angle $\pi/4$ and $3\pi/4$ and 7,000 transients for the $\pi/2$ pulse angle on protons. In the sequence giving only the quaternary carbons [36] protons were decoupled during 5 s periods and $1/2J = 0.033$ s refocusing periods were used between the $\pi/2$ and π pulses on carbons; a $\pi/2$ pulse was send on protons simultaneously with the π pulse on carbons.

The portions of integral considered in the quantitative analysis correspond to the chemical shift ranges given in the literature.[8]

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REFERENCES

1. X. Pan, D. Lachenal, C. Lapierre and B. Monties, J. Wood Chem. Technol., 12 (2), 135 (1992).

2. X. Pan, F. Pla, D. Lachenal, C. Lapierre and B. Monties, J. Wood Chem. Technol., 12 (3), 279 (1992).

3. X. Pan, D. Lachenal, C. Lapierre and B. Monties, J. Wood Chem. Technol., 13 (2), 145 (1993).

4. M. Dolk, F. Pla, J. F. Yan and J.L. McCarthy, Macromol, 19, 1464 (1986).

5. A. Labidi and F. Pla, Holzforschung, 46 (1), 53 (1992).

6. H. D. Lüdemann and H. H. Nimz, Biochem. Biophys. Res. Commun., 52, 1162 (1973).

7. R. Mörck and K. Kringstad, Holzforschung, 39, 109 (1985).

8. D. Robert, p 250-273 in Methods in Lignin Chemistry (S.Y. Lin and C.W. Dence eds.), Springer Verlag, Berlin, Heidelberg, 1992.

9. M. Drumond, M. Aoyama, C. L. Chen and D. Robert, J. Wood Chem. Technol. 9 (4), 421 (1989).

10. M. G. Drumond, D. PiloVeloso, S. D. Santos, S. A. Lemos de Morais, E. A. do Nascimento and C. L. Chen, Holzforschung, 46, 127 (1992).

11. G. Gellerstedt and D. Robert, Acta Chem. Scand., B 41, 541 (1987).

12. A. Labidi, D. Robert and F. Pla, Holzforschung, 47, 213 (1993).

13. M. Bardet, PhD Thesis, Grenoble University, France (1987).

14. A. Labidi, D. Robert and F. Pla, Holzforschung, 47, 133 (1993).

15 L. L. Landucci, J. Wood Chem. Technol., 4(2), 171 (1984).

16. M. Aoyama, C. L. Chen and D. Robert, J. Chinese Chem. Soc., 38, 77 (1991).

17. K. V. Sarkanen, Tappi, 73 (10), 215 (1990).

18. J. Nakano, H. Daima, S. Hosoya and A. Ishizu, The Ekman Days Int. Sym. Wood Pulp. Chem., Stockholm, Proceedings 2, 72 (1981).

19. G. Brunow and K. Lundquist, Holzforschung, 45 (1), 37 (1991).

20. J. R. Obst and J. Ralph, Holzforschung, 37, 297 (1983).

21. H. Y. Hassi, M. Aoyama, D. Tai, C. L. Chen and J. S. Gratzl, J. Wood Chem. Technol., 7, 555 (1987).

22. D. Robert and D. Gagnaire, The Ekman Days Int. Symp.Wood Pulp Chem., Stockholm, Proceedings 1, 86 (1981).

23. L. Landucci, Holzforschung, 39, 355 (1985).

24. H. Richtzenhain, Acta Chem. Scand.,4, 589 (1950).

25. D. Robert and G. Brunow, Holzforschung, 38 (2), 85 (1984).

26. G. C. Goyal and J. H. Lora, 6th Int. Sym. Wood Pulp. Chem., Melbourne, Proceedings 1, 205 (1991).

27. S. Berger and A. Rieker, Tetrahedron, 28, 3123 (1972).

28. R. H. Reeves and I. A. Pearl, Tappi, 48(2): 121(1965).

29. G. Gellerstedt and R. Agnemo, Acta Chem. Scand., B24, 275(1980).

30. J. A. Hemmingson and H. Wong, Holzforschung, 43 (2), 141 (1989).

31. G. Gellerstedt and E.L. Pettersson, Acta Chem Scand, B29, 1005 (1975).

32. J. C. Scaiano, J. C. Netto-Ferreira and V. Wintgens, J. Photochem. Photobiol., 59, 265 (1991).

33. R. C. Francis, C. W. Dence, T. C. Alexander, R. Agnemo and S. Omori, Tappi J., 74 (12), 127 (1991).

34. J. A. Schmidt and C. Heitner, J. Wood Chem. Technol., 13(3), 309 (1993).

35. A. Bjorkman, Svensk Papperstidn., 59, 477 (1956).

36. M. R. Bendall and D. T. Pegg, J. Magn. Res., 53, 272 (1983).