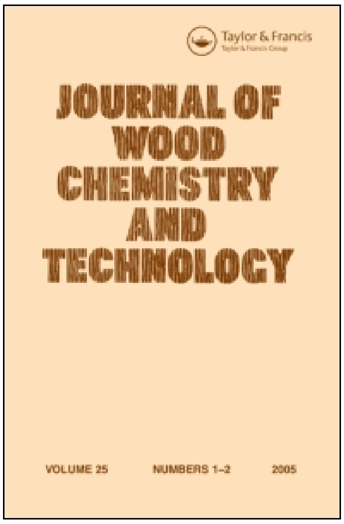

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The Structure of Lignin From Pinus Radiata Exploded Wood

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THE STRUCTURE OF LIGNIN FROM PINUS RADIATA EXPLODED WOOD

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ABSTRACT

The lignin extractable by acetone from *Pinus radiata* wood subjected to the steam explosion process has been examined by ^{13}C NMR spectroscopy and other methods. Comparison with MWL showed structural differences which are discussed and related to possible reactions initiated by the process.

INTRODUCTION

The steam explosion process for treating wood and biomass is currently of considerable interest as a potential source of valuable liquid fuel and chemical feedstocks.[1] Although currently considered unsatisfactory for softwoods in that carbohydrate and lignin components are less accessible to separation than those of hardwoods, the wood structure of *Pinus radiata* is sufficiently broken down for the yield of extractable lignin to be considerable (10% of dry wt.) and its structure to be of interest. This paper therefore reports a study of *Pinus radiata* exploded wood lignin (EWL), using ^{13}C NMR spectroscopy and complemented by PMR, IR, UV, MW and elemental analysis data. Comparison is with *P. radiata* milled wood lignin (MWL)[2] and reported data for softwood lignins.

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RESULTS AND DISCUSSION

^{13}C NMR Spectra

The ^{13}C NMR spectrum examined at 20 MHz in acetone-d_6/H_2O (9:1) is shown in Fig. 1. (See Experimental.) The solvent-obscured region was examined in DMSO-d_6 and is superimposed. The MWL reference spectrum is shown in Fig. 2. Signal assignments based on literature data and some model compounds investigated in this laboratory are shown in Table 1 together with signal multiplicities.[3] Nomenclature is shown in Fig. 1. The effects on the spectrum of chemical treatments of the EWL, (a) mild hydrogenation with PtO_2 as catalyst, (b) reduction with $LiAlH_4$ and (c) acetylation were also examined.

Prominent Features of the EWL Spectrum

1. The 0-50 ppm Region

Signals assigned to non-oxygenated CH_3, CH_2 and CH carbons in the propanoid side-chain are observed between 14 and 50 ppm. In contrast, these signals are mostly absent from the spectrum of MWL and the intensities of the few which do occur are low.

2. The 50-100 ppm Region

The signals characteristic of the propanoid side-chain α, β and γ-carbon atoms in MWL are observed in the EWL spectrum, but have markedly reduced intensities, except for those of C_α and C_β in phenylcoumaran structures, which appear to be unchanged. Signals for β-O-4 linked units appear to have undergone about a threefold reduction in intensity, therefore, if the abundance of β-5 and β-O-4 linked units in MWL is about 15% and 45% respectively,[4] the abundance of β-O-4 in EWL could be of the order of that of β-5.

3. The 100-200 ppm Region

Some aromatic carbon signals show striking differences in intensity when compared with those of MWL.

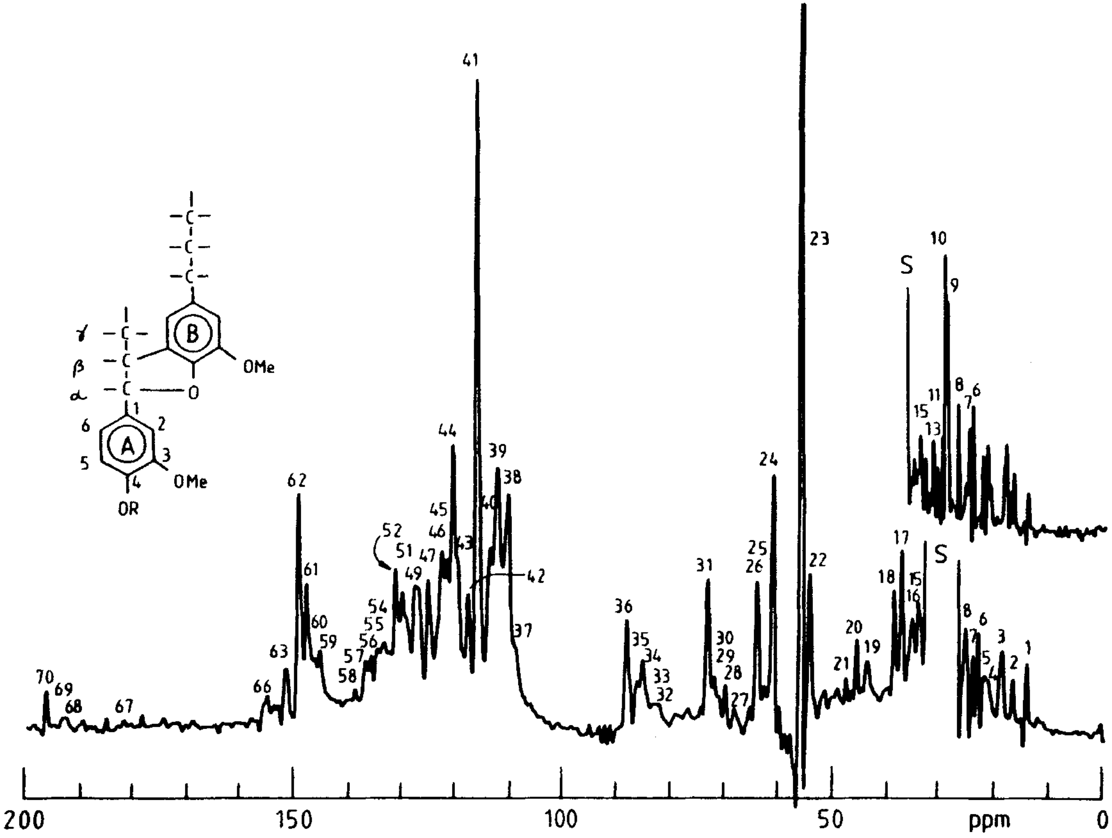

FIGURE 1. Resolution enhanced ^{13}C NMR spectrum of P. radiata EWL in acetone-d_6/H_2O (9:1) and DMSO-d_6 (insert).

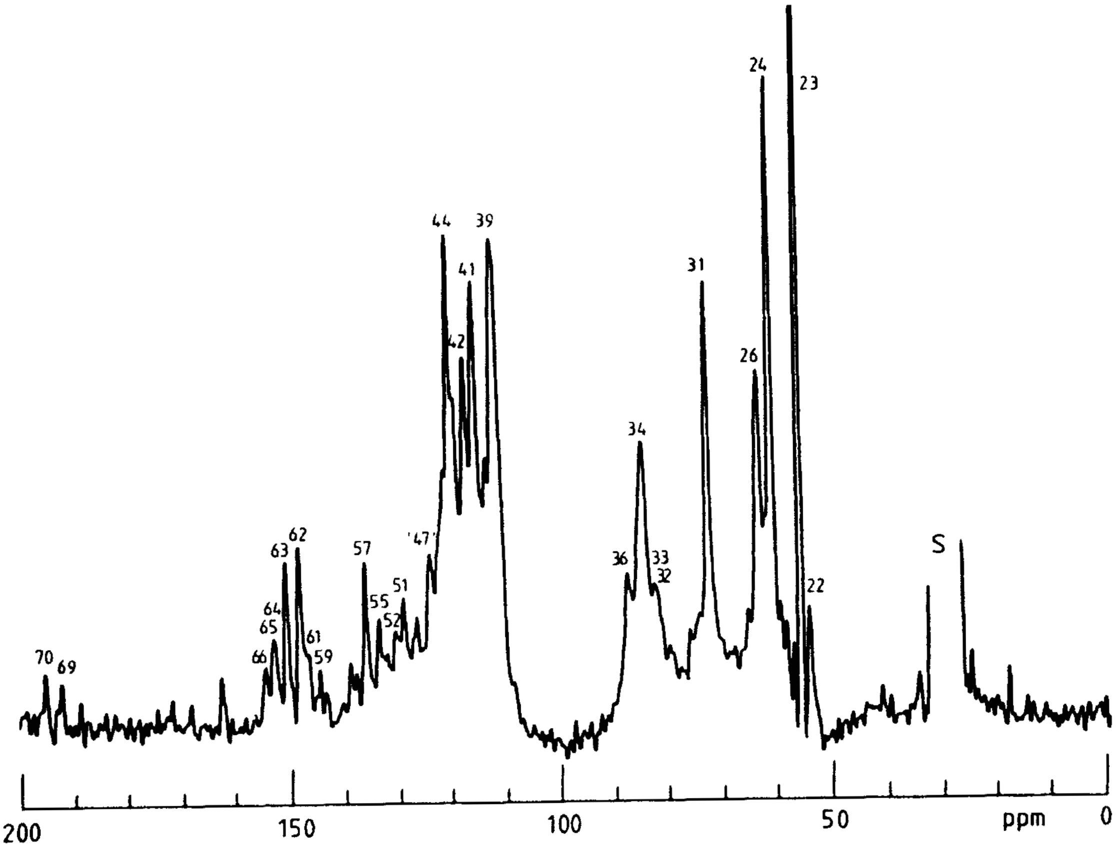

FIGURE 2. Resolution enhanced ^{13}C NMR spectrum of P. radiata MWL in acetone-d_6/H_2O (9:1).

TABLE 1. ^{13}C NMR Assignments

No.	δ	M	Assignments	No.	δ	M	Assignments
1	14.2	Me	γ-Me in n-propyl side ch.	13	31.5	CH_2	β-CH_2 in ω-hydroxypropyl side ch.
2	16.7	Me	γ-Me adj. β-OAr	14	32.2	Me	γ-Me adj. β-CO
3	18.7[b]	CH_2		15	34.2[b]	CH_2/Me	α-CH_2 in lignans, etc.
4	21.2[ab]	CH_2/Me	γ-Me adj. β-OH	16	35.4[b]	CH_2	α-CH_2 in ω-hydroxypropyl side ch.
5	22.0[ab]	CH_2	β-CH_2	17	37.4	CH_2	
6	23.1	Me	γ-Me adj. β-OH	18	38.8	CH_2	α-CH_2 in n-propyl side ch.
7	24.0	CH_2	β-CH_2	19	43.9[ab]	CH	β-CH in lignans
8	25.3	CH_2	β-CH_2 in n-propyl side ch.	20	45.8	CH	
9*	28.7	CH_2	CH_2 in n-alkyl or branched alkyl side ch.	21	47.5	CH_2	α-CH_2 adj. β-OH
10	29.2	CH_2		22	54.6	CH	C_β in β-5, β-β
11	29.7	CH_2		23	56.2	Me	OMe
12	30.8	Me	γ-Me adj. β-CO	24	61.4	CH_2	C_γ (C_ω) in β-O-4, ω-hydroxypropyl side ch.

M = multiplicity of carbon. * δ in DMSO-d_6 for signals 9-14.

[a] Signals between 14 and 48 ppm affected by hydrogenation,

[b] affected by reduction.

(continued)

TABLE 1 CONT'D

No.	δ	M	Assignments	No.	δ	M	Assignments
25	63.1	CH_2	Cγ in β-O-4 with α-CO, coniferyl alcohol side ch. etc.	37	109.2	CH	C_2 in 5-5, 5-O-4, α-6′
26	64.4	CH_2	C_γ in β-5, $C_{\beta,\gamma}$ in β-1	38	110.2	CH	C_2 in β-5 (A ring), C_2 with α,β-unsat. side ch.
27	68.4	CH_2	C_γ in lignan lactones	39	112.2	CH	C_2 in β-O-4 with α-OH and in general
28	69.9	CH_2		40	113.5	CH	C_2 with α-CH_2, α-CO, in β-5 (B ring with sat. side ch.)
29	71.1	CH_2	C_γ in cyclic and non-cyclic alkyl ethers	41	115.9	CH	C_5, $C_{3/5}$ in p-hydroxyphenyl
30	72.0	CH_2		42	117.5	CH	C_6 in β-5 (B ring with sat. side chain)
31	73.3	CH/CH_2	C_α in β-O-4, C_γ in alkyl ethers	43	119.4	CH	C_6 in β-5 (A ring)
32	82.1	CH	C_β in β-O-4 with α-CO, C_α in alkyl ethers	44	120.3	CH	C_6 in general
33	83.3	CH		45	121.3^c	CH	C_6 with α-CH_2, CH_3 and in α-6′, C_1 in 5-5, 5-O-4
34	85.0	CH	C_β in β-O-4 with α-OH, CO, OR etc.	46	122.2^c	CH	
35	86.0	CH		47	124.8^c	CH	C_5, C_6 and C_1 (with unsat. side ch.) in 5-5
36	88.2	CH	C_α in β-5	48	126.5^c	C/CH	C_6 with α-CO, C_1 in β-β, α-6′ (B ring)

[c] Signals between 121 and 136 ppm enhanced cf. MWL.

(continued)

TABLE 1 CONT'D

No.	δ	M	Assignments	No.	δ	M	Assignments
49	127.2^{c}	CH	As for No. 48	60	145.3	C	C_4 with α-CH_2, $C_{3/4}$ in catechol
50	128.6^{c}	CH	C_β in coniferyl alcohol	61	147.0	C	C_4 in non-etherified units
51	129.4	CH	$C_{2/6}$ in p-hydroxyphenyl	62	148.5	C	C_3 in general, C_4 in β-5 (B ring with unsat. side ch.)
52	130.7^{c}	C/CH	C_1, C_5 in β-5 (B ring), C_1 with α,β-unsat. side ch., α-CH_2 (in lignans, etc.)	63	150.9	C	C_4 in etherified units, C_3 with α-CO
53	131.7	CH	C_α in coniferyl alcohol, C_1 with α-CO	64	152.2	C	C_4 with α-CO, CHO
54	133.0^{c}	C/CH	C_1 with α-CH_2 (in lignans), C_β in coniferaldehyde	65	153.0	C	
55	134.1	C	C_1 in non-etherified units	66	154.3	CH	C_α in coniferaldehyde
56	135.2^{c}	C	C_1 in α-6′ and with α-CH_2	67	181.0	C	lactone >C=O
57	136.2	C	C_1 in etherified units	68	191.4	?	>C=O
58	138.0	C?	C_6′ in α-6′	69	192.0	CH	α-CHO
59	144.5	C	C_4 in β-5 (B ring with sat. side ch.)	70	195.2	CH	α,β-unsat. γ-CHO, α-CO

a) The C_2 signals at 110-113 ppm are changed in relative intensity and cover a wider field, which indicates that structural changes have occurred in propanoid side-chains.

b) The intensity of the C_5 signal at 115.9 ppm is considerably enhanced so that it now dominates this region. Possible causes including demethylation and demethoxylation are discussed below.

c) The signal at 130.7 ppm (C_1',C_5' in β-5 units etc.) now dominates the 130-140 ppm region, due in part, to about a threefold reduction in the intensity of the signal at 136.2 ppm for C_1 in etherified guaiacyl units.

d) The signal for C_4 in etherified guaiacyl units at 150.9 ppm is reduced in intensity at least threefold, while that for C_4 in non-etherified units at 147.0 ppm is correspondingly sharpened and enhanced in intensity. The drastic reduction in the intensity of C_4 at 150.9 ppm results in the signal for C_3 at 148.5 ppm dominating the 140-155 ppm region.

These changes in C_4, C_1 and C_2 show cleavage of β-0-4 linkages to be the major structure-breaking reaction induced by the explosion process.

Spectrum Detail and the Effect of (a) Hydrogenation and (b) $LiAlH_4$ Reduction

1. The 0-50 ppm Region

Twenty-one signals with intensities 20-200% of that of C_α in β-5 linked units occur in this region (Table 1). These include signals assigned to γ-methyl groups in n-propyl side-chains and adjacent to β-carbon-oxygen linkages, α- and β-methylene groups in n-propyl and ω-hydroxypropyl side-chains and β-methine groups in β-β linked lignan units. Signals suggesting higher alkyl or branched alkyl side-chains are also present.

Hydrogenation of the EWL caused minor changes in three of the fifteen signals observable in acetone-water, while $LiAlH_4$ reduction introduced a few weak signals and enhanced or resolved some original signals. Those affected are indicated in Table 1.

It appears therefore, that the explosion process extensively modifies a substantial proportion of side-chains by, for example, complete or partial hydrogenation, carbon-carbon coupling and β-ketone formation.

2. The 50-100 ppm Region

This region of the spectrum is still dominated by the signals of C_α, C_β and C_γ in β-0-4 and β-5 linked units, but extensive cleavage of the former type of linkage results in signals much more similar in intensity to those of the β-5 units. This contrast with MWL is also shown well by the spectra of the acetylated lignins. The reduction in the intensity of the signals for γ- and α-carbon linked to a hydroxy group appears to be somewhat less than that in the signal for the β-ether linkage. This suggests that the γ-OH linkage is more resistant to cleavage and may suggest the formation of linkages giving signals in the α-carbon region, e.g. a β-OH linkage.

While the signals observed upfield of 65 ppm are similar to those shown by MWL, those observed downfield show some significant differences. These involve Cβ in β-0-4 linked units, C_α in β-5 linked units and signals from minor units of about 3-5% abundance in EWL.

a) C_β in β-0-4 Units

This signal is broad and asymmetric for both EWL and MWL but, whereas for EWL it has a maximum at 85.0 ppm, a weaker maximum at 86.0 ppm and a shoulder at

84.5 ppm, for MWL it has a maximum at 85.4 ppm and a shoulder only at 86.0 ppm. This suggests that the range of environments for C_β in units surviving the explosion process is different from that in MWL, due most likely to changes at C_α, but possibly also due to changes at C_γ and in the side-chain of the β-linked substituent. The composition of this signal is of considerable interest to the field of lignin structure. Lüdemann and Nimz have assigned contributions _ca_. 1ppm upfield and 0.5 ppm downfield of the major component (reported at 86.1-86.5 ppm), to units having an α-CO group and to C_α in pinoresinol units respectively.[5] However, as noted below, there appears to be little of the latter in EWL, while Lüdemann and Nimz have also assigned signals at 81-83.3 ppm to units having an α-CO group.

Both hydrogenation and reduction of EWL change the signal. The former reduces the resolution of the maxima and also the intensity at 85.0 ppm, while the shoulder becomes more pronounced. The latter increases the resolution of the maxima, reduces the intensity of and broadens the signal at 85.0 ppm, and resolves the shoulder into a small signal of lower intensity. This suggests that the units contributing to the maximum at 86.0 ppm have less labile or reactive side-chain substituents or groups than those contributing to the maximum at 85.0 ppm. Leary has found that C_β in a non-cyclic, α-alkyl ether model compound gives signals at 85-85.6 ppm.[6] A C_α alkyl ether linkage would be more stable than the C_α-OH linkage, so its presence in EWL would be possible. Therefore, β-0-4 units with this type of α-linkage may contribute to the downfield maximum, while units having α-OH or α-CO groups contribute to the upfield maximum.

A broad signal with maxima at 82.1 and 83.3 ppm, corresponding to perhaps 5% of structural units in EWL and 15% in MWL is affected to some extent by both chemical reactions. Signals in this region have been assigned to β-0-4 units having an α-CO group (see above), to C_α in the lignan cyclic alkyl ether, lariciresinol and recently, by Leary, to C_α in the non-cyclic alkyl ether discussed above.[6,7]

b) C_α in β-5 Units

This signal, observed at 88.2 ppm has a shoulder at 87.7 ppm, which is reduced in intensity by hydrogenation of EWL and which becomes a small resolved signal after reduction. A similar signal is observed as a distinct minor maximum in MWL. These observations suggest changes in and different contributions from, units with more labile or reactive substituents or groups in the B ring side-chain.

c) Signals from Minor Units

A signal at 69.9 ppm, and weaker signals at 68.4, 71.1 and 72.0 ppm, which appear to be absent or insignificant in the spectrum of MWL, are significant in that of EWL. These signals, except for a possible reduction in the intensity of those at 68.4 and 69.9 ppm brought about by $LiAlH_4$ reduction, appear unaffected by the chemical reactions. Their multiplicity and δ values correlate with C_γ in lignan lactones such as hydroxymatairesinol and lignan mono- and bicyclic alkyl ethers, while C_γ in non-cyclic alkyl ethers may also appear in this region.[6,7,8] A methylene carbon signal observed under the C_α methine carbon signal in DMSO-d_6 may have the latter origin. Literature values for side-chain signals in pinoresinol units do not correlate well with possible signals in EWL or MWL, so the presence of these units in significant amounts appears unlikely.

It appears, therefore, that a proportion of the major structural units which survive the explosion process is modified at C_α or C_γ, or in the side-chain of the B ring. In general, minor structural units appear to be reduced in abundance, but some are maintained and perhaps increased, while some new ones giving signals in this region may be formed. The latter may include alkyl ethers, lactones and units having a C_β-hydroxy substituent.

3. The 100-200 ppm Region

This region shows very clearly that extensive structural changes are brought about by the explosion process. A discussion of aromatic carbon and of carbonyl signals follows.

a) C_2 Signals (109-114 ppm)

The C_2 signals of EWL and MWL differ considerably in both their range of δ values and intensity distribution. In EWL, signals assigned to C_2 in the A ring of β-5 linked units and in units with α,β-unsaturation contribute to an intense upfield shifted band at 110.2 ppm which is not observed in the spectrum of MWL, while the signals of C_2 in β-O-4 linked units and C_2 in general give a much narrower, less dominant band. The signals assigned to units with α-CH_2 and α-CO groups, and to C_2 in the B ring of β-5 units (with a saturated side-chain) contribute to a fairly intense unresolved band in EWL, but are observed as a discrete signal of much lower intensity in MWL. The signals are apparently unaffected by hydrogenation of EWL, but $LiAlH_4$ reduction splits the upfield band and possibly reduces the intensity of the band at 112.2 ppm, while a weak signal is introduced further upfield at 108.5 ppm.

b) The C_5 Signal (115.9 ppm)

The high intensity of this signal results in it dominating the aromatic region of the spectrum. It behaves like a normal C_5 (in guaiacyl) or $C_{3/5}$(in p-hydroxyphenyl) signal, in that acetylation of EWL shifts it to 123.5 ppm. Closer examination of the signal showed it to be asymmetric with shoulders at 115.4 and 116.2 ppm, while the coupled spectrum showed that all three components have the same J_{CH}, i.e. 160.3 Hz. Possible reasons for the high intensity of this signal include demethoxylation and demethylation of the guaiacyl moiety to p-hydroxyphenyl and catechol moieties (the latter is supported by the shoulders observed), cleavage of 5-0-4 linkages and sharpening of the signal due to cleavage of C_4 ether linkages. Demethoxylation and demethylation of autohydrolysis lignin and EWL from aspen wood have been reported.[9,10]

c) The C_6,C_1 Region (117-136 ppm)

This region of the spectrum of EWL, when compared with that of MWL showed some signals to be enhanced two-threefold in intensity (those at 121.3, 122.2, 126.5, 127.2, 128.6, 130.7 and 133.0 ppm), one to be both shifted and enhanced (124.2 → 124.8 ppm), and one essentially new signal at 135.2 ppm. In contrast, the signal at 136.2 ppm corresponding to C_1 in etherified guaiacyl units is reduced more than twofold in intensity. The enhanced signals are indicated in Table 1 and some possible assignments are given. These involve units having an α-CH_2 group or an α-6' interunit linkage in a range of environments, 5-5 and 5-0-4 linked units and units with an α-CO group. The multiplicity assignment of the signal in most cases supports the possibilities, but in some signals the presence of a quaternary carbon component may be masked by other components.

The signals at 121.3, 122.2, 130.7 and 135.2 ppm appeared unaffected by both hydrogenation and reduction of the EWL. Hydrogenation resulted in minor changes in some of the other signals which would correlate with changes in α,β-unsaturation, while reduction had a much greater effect and the other enhanced signals were modified and showed more, or greater resolution of, components. These changes most likely reflect reduction of α-CO groups, coniferaldehyde side-chains and some α,β-unsaturation. Some changes, including the introduction of five weak new signals, together with changes in other regions would correlate with reduction of a lignan α-CO to α-CHOH, or reduction of α-CO, or α-CHOH, to α-CH_2.

d) The C_3,C_4 Region (144-154 ppm)

This region of the spectrum of EWL differs markedly from that of MWL because of the virtual reversal of the relative intensities of the signals for C_4 in free and etherified guaiacyl units and the consequent dominance of the C_3 signal. The intensity of the signal at 145.3 ppm is enhanced in EWL, possibly as a result of contributions from C_4 in units with an α-CH_2 group. The C_4 signals of units having an α-carbonyl group are weaker and more dispersed in EWL. This may in part correlate with a lower abundance of α-CHO groups, as the intensity of the carbonyl signal at 192.0 ppm is also lower.

Hydrogenation appears to broaden and enhance the signal at 145.3 ppm, while the signal at 154.3 ppm, which includes that for C_α in coniferaldehyde side-chains is modified. Reduction brings about more drastic changes, which involve loss of the signals at 152-155 ppm, modification of the signal at 150.9 ppm and changes in the 145-146.5 ppm region. The latter may correlate with partial reduction of α-CO to α-CH_2 and some reduction of α-CHOH to α-CH_2. Two of three weak new signals are also shown by MWL.

e) The Carbonyl Region (160-220 ppm)

The signal for units with an α-CHO group is broad in EWL and its intensity is much lower than that of the sharper signal in MWL, while the γ-CHO signals at 195.2 ppm have more similar intensities. A search for other carbonyl signals from EWL in both acetone-water and DMSO showed one at 181.0 ppm, which could be assigned to lignan lactones,[7,8] a weak signal at 191.4 causing broadening of the α-CHO signal and inconclusive signals at 188.2, 207.9 and 210.0 ppm. The signal at 181.0 ppm was resistant to $LiAlH_4$ reduction, while multiplicity determination of the signal at 195.2 ppm showed a large aldehyde component.

The 100-200 ppm region of the spectrum clearly shows the extent of cleavage of β-0-4 linkages and the retention of β-5 linkages. It also shows more dominant signals from other structures with carbon-carbon inter-unit linkages, from units with side-chains stabilized by an α-methylene group and possibly from 5-0-4 linked units.

The wider range and changed abundances of structural units in EWL compared with MWL is shown particularly well by the field coverage and intensities of the signals for C_2, C_5, C_1 and C_6.

The formation of free phenolic hydroxy-groups is perhaps best demonstrated by the spectrum of acetylated EWL in which the carbonyl signal for aromatic acetate has twice the intensity of that for primary aliphatic acetate, while in the spectrum of MWL it has about one third the intensity. Formation of the catechol moiety would also enhance this signal.

Complementary Spectral, MW and Elemental Analysis Data

1. The PMR Spectrum

The spectra of (i) acetylated and (ii) non-derivatized EWL are shown in Fig. 3. Noteworthy are (a), the high content of free phenolic hydroxy-groups/ phenylpropane unit, *ca.*0.9, cf. Lundquist's ratio of

II

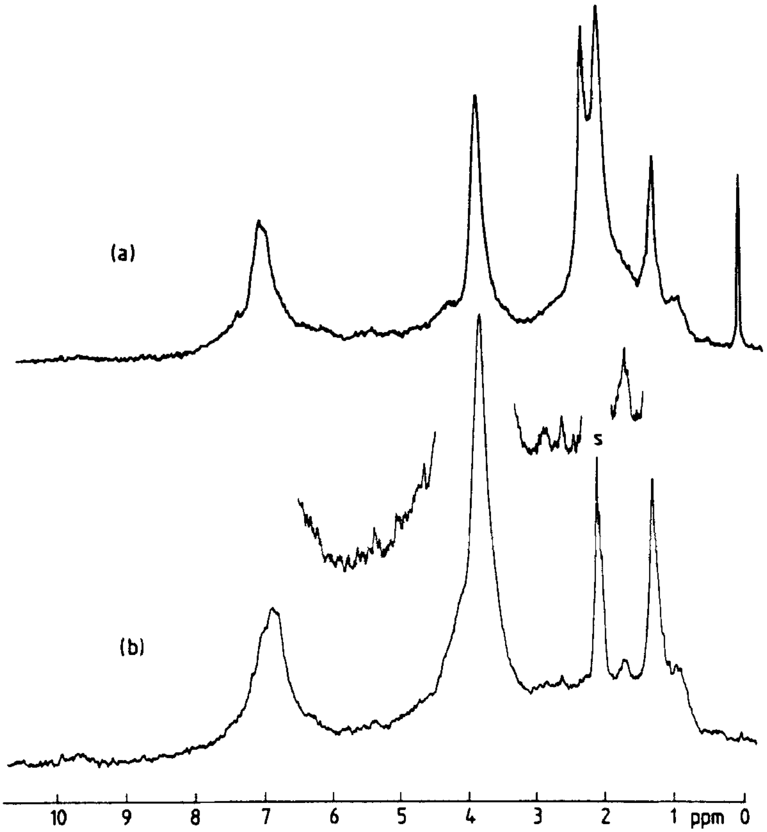

FIGURE 3. PMR spectra of (a) acetylated and (b) non-derivatized EWL in $CDCl_3$ and acetone-d_6 respectively.

0.26 for spruce MWL, (b) the signals for methyl and methylene protons at 0.93 and 1.28 ppm, which are also observed in the spectrum of aspen EWL,[10] (c) the signals at 1.71 and 2.61 ppm assigned by Lundquist to the β- and α-protons in lignan units with α-CH_2 and γ-CH_2OH groups and in units with ω-hydroxypropyl side-chains, (d) the failure to detect signals assigned to H_β and H_α in β-O-4 units (at 4.65 and 6.06 ppm and 4.30 and 4.86 ppm in (i) and (ii) respectively) and

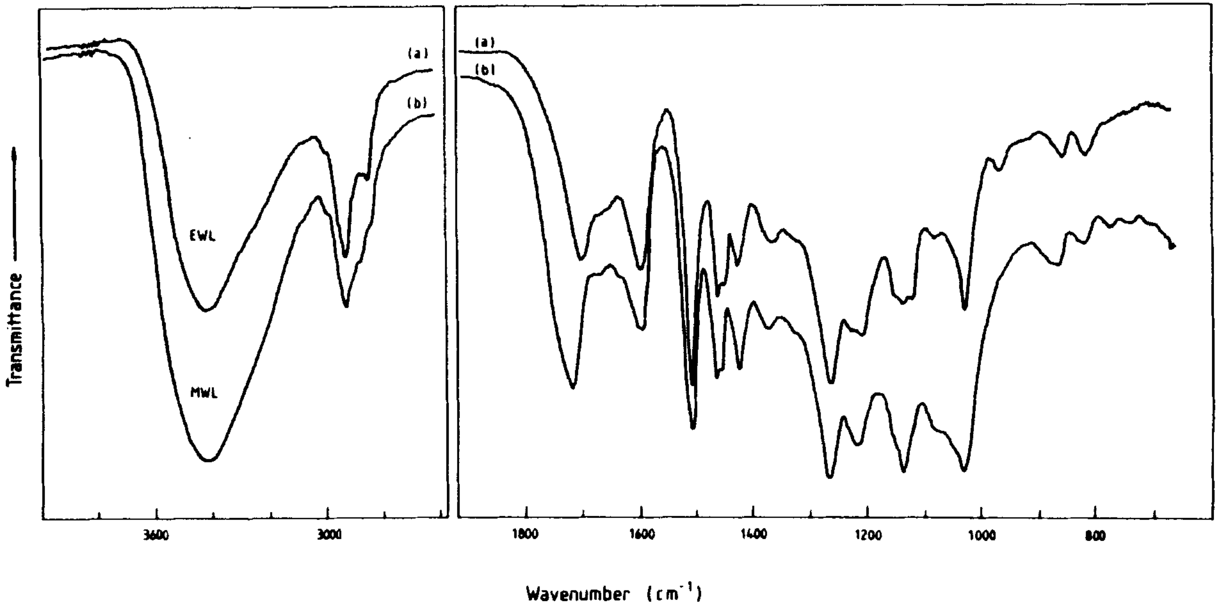

FIGURE 4. IR spectra of (a) EWL and (b) MWL.

(e) the detection of signals at 5.40 and 6.30 ppm in (ii), corresponding to H_α in β-5 units and H_β in coniferyl alcohol side-chains. Other weak signals attributed by Lundquist to protons in units with carbonyl groups and with a C_5 linkage, and to H_γ in various units are also detectable.

An interesting feature of the NMR spectra of both P. radiata and aspen EWL is the intensity of the PMR signal at 1.28 ppm and the ^{13}C NMR signals at 28-30 ppm.[10] These signals, which appear to be from CH_2 groups in higher normal or branched alkyl groups are also given by biodegraded sprucewood lignin.[12] Assuming these alkyl groups are side-chains of lignin units, they may be formed in reactions with fragments which may, or may not be derived from lignin.

The structural features shown by the PMR spectra clearly support those shown by the ^{13}C NMR spectra, i.e. cleavage of the β-0-4 linkage, a high phenolic hydroxy-group content, the survival of β-5 and other carbon-carbon linkages such as 5-5, the presence of lignan linkages (but not pinoresinol) and the presence of reduced side-chains.

2. The IR Spectrum

The IR spectra of EWL and MWL are shown in Fig.4. The most interesting difference between these spectra is shown by the carbonyl region. The absorption band at 1704 cm^{-1} in EWL may indicate the presence of unconjugated carbonyl groups, i.e. of β-CO groups in the side-chains of some units.Guaiacylacetone and the keto form of β-hydroxyconiferyl alcohol have bands at 1705 and 1709 cm^{-1} respectively.[13] The more intense band in MWL occurs at 1725 cm^{-1}, i.e. is shifted more into the region of unconjugated acids and esters and may in part be due to residual carbohydrate.

Also noteworthy is the weak band at 970 cm^{-1}, observed in EWL but not in MWL, which shows the presence of α,β-unsaturation and α-CO groups.[13] Hydrogenation and subsequent $NaBH_4$ reduction of EWL reduced the intensity of the band at 1704 cm^{-1} and removed the band at 970 cm^{-1}.

The well defined shoulder for CH_2 and CH_3 groups at 2860 cm^{-1} in the aliphatic C-H stretch band at 2938 cm^{-1} is also worth noting.

3. The UV Spectrum

The spectrum in neutral or acid and basic solution and the Δε ionisation curve are similar to those reported for other softwood lignins such as spruce MWL.

$277\ (\lambda_{max}^{EtOH}),\ 325\ (sh.)\ \xrightleftharpoons[H^+]{EtO^-}\ 292\ (\lambda max),\ 352\ (sh.),$

415 (sh.)

Δεi 250, 300, 367 (λmax), 415 (sh.)

Hydrogenation of EWL removed the shoulder at 415 nm, due to the α,β-unsaturated aldehyde chromophore, while subsequent $NaBH_4$ reduction removed the maximum at 367 nm, which is therefore due to conjugated α-CO chromophores.

4. The Molecular Weight of EWL

The molecular weight was determined by gel permeation chromatography and compared with that of MWL. EWL gave values of 823, 2473 and 3.0 for Mn, Mw and Mn/Mw respectively, while MWL had values of 5470, 13300 and 2.4. The extensive cleavage of interunit linkages in this type of lignin is thus clearly shown by the low molecular weight. The polydispersity, although somewhat greater than that of MWL is moderate and this, together with the low Mw would account for the high solubility of EWL in organic and aqueous-organic solvents.

5. Elemental Analysis Data

The composition of EWL determined from C, H and MeO data and O by difference is $C_9H_{8.78}\,O_{2.34}(OMe)_{0.56}$.

Compared with other softwood lignins such as Norway spruce MWL, for which a composition of $C_9\,H_{7.92}\,O_{2.40}(OMe)_{0.92}$ is reported,[14] the methoxyl content of EWL is low and thus in accordance with considerable demethylation or demethoxylation having occurred during the explosion process. However, the methoxyl content of a sample of *P. radiata* MWL was found to be 12.9%, cf. 10.1% for EWL, so the decrease in methoxyl content is probably somewhat less than the above comparison suggests.[15]

The oxygen content does not appear to be significantly reduced, which may indicate demethylation rather than demethoxylation and which would also correlate with the high free phenolic hydroxy-group content. The higher hydrogen content most probably reflects the sidechain hydrogenation resulting from the process.

SUMMARY

The above results indicate that the explosion process cleaves about two-thirds of the β-aryl ether linkages, generates a high content of free phenolic hydroxy-groups and extensively modifies propanoid side-chains. Similar results have recently been reported for aspen EWL.[10] As the β-5 and cyclic aryl ether linkages of phenylcoumaran units are not cleaved, they apparently become of similar abundance to β-O-4 as an interunit linkage. As they are also most probably the second most abundant interunit linkage in *P.radiata* lignin, they now share with β-O-4 the role of a major interunit linkage in EWL. Other less abundant carbon-carbon linkages and possibly 5-O-4 diaryl ether linkages are also retained and some may be augmented, e.g.

α-6' and β-β, so that basic interunit linkages survive the process, but with changed relative abundances. Some novel interunit linkages may also be introduced.

Most types of carbon-oxygen bonds are subject to extensive cleavage and while a substantial amount of the resulting side-chain modification is reductive, in that it removes oxygen-containing substituents particularly from the α-carbon atom, a variety of side-chain structures with various combinations of reduced and oxygen-linked carbon atoms is apparently formed. There is also some evidence for modification of the basic phenylpropane units involving demethylation and the incorporation of non-lignin fragments.

The steam explosion process is likely to involve a combination of mild acid hydrolysis and radical reactions, the former initiated by deacetylation of polysaccharide acetates during the steaming step and the latter by homolytic cleavage of some carbon-oxygen and oxygen-hydrogen bonds during the explosion step. The former would give cleavage of C-O bonds and interunit linkages with partial side-chain deoxygenation and form a variety of acidolysis products. Additional formation or reformation of some interunit linkages, such as α-6' and alkyl ether is also likely to be included among the carbocation reactions which take place. The latter could include more drastic hydrogenation of side-chains and formation of novel or augmented carbon-carbon linkages.

EWL from Pinus radiata is therefore a low molecular weight, fairly extensively modified lignin in which carbon-carbon linkages between phenylpropane units almost certainly predominate. Its high free phenolic hydroxy-group content and low molecular weight make it a very reactive and soluble lignin and while reduction, particularly at the α-carbon atom has stabilized some side-chains, the content of labile groups including α-hydroxy is still considerable.

EXPERIMENTAL

Steam explosion of New Zealand *Pinus radiata* wood was performed by Iotech Corporation Ltd, Canada.[1] *P. radiata* MWL was prepared in this laboratory and at Forest Research Institute, Rotorua.[2]

The wet exploded wood was extracted with acetone. Addition of the concentrated extract to water precipitated the lignin which was washed, air dried at 25-30°C and then dried under vacuum.

Hydrogenation of the EWL was carried out in ethanol at atmospheric pressure in the presence of PtO_2 for 2 hr.

Reduction was carried out in THF with $LiAlH_4$ at 35°C for 50 hr. The reaction mixture was worked up with NH_4Cl(sat.) to give a 75% yield of the reduced lignin.

Acetylation was carried out in acetic anhydride-pyridine 1:1 at 15°C for 14 days.

NMR Spectra

^{13}C NMR Spectra were run at 30°C on a Varian FT-80A spectrometer operating at 20 MHz. The solvent was acetone-d_6/H_2O (9:1 by volume) except where noted. Chemical shifts were measured relative to TMS in a coaxial tube, with a magnetic susceptibility correction of 0.06 ppm. Resolution was improved by Lorentzian-to-Gaussian transformation.[16] Signal multiplicities were determined by a gated spin-echo sequence.[17]

PMR Spectra were run in acetone-d_6(non-derivatized EWL) and deuterochloroform (acetylated EWL) on a Varian EM-360 spectrometer at 60 MHz, with internal TMS.

IR Spectra were run as KBr disks on a Perkin-Elmer 580 spectrometer.

Molecular Weight determinations involved HPLC separation of the acetylated lignins in THF on μ-Styragel columns. A Waters Associates ALCGPC 244 instrument with UV detection and calibrated with polystyrene standards was used.

Elemental Analyses were carried out by the University of Otago Chemistry Department, Dunedin.

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