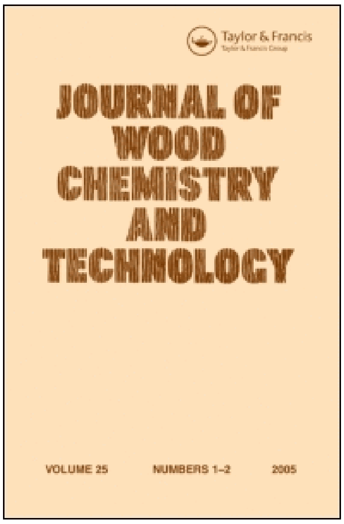

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Structural Aspects of Lignins From Eucalyptus Regnans Wood Steam Exploded By the Iotech and Siropulper Processes

Jacqueline A. Hemmingson[a]
[a] DSIR, Chemistry Division, Petone, New Zealand

To cite this Article Hemmingson, Jacqueline A.(1985) 'Structural Aspects of Lignins From Eucalyptus Regnans Wood Steam Exploded By the Iotech and Siropulper Processes', Journal of Wood Chemistry and Technology, 5: 4, 513 — 534
To link to this Article: DOI: 10.1080/02773818508085209
URL: http://dx.doi.org/10.1080/02773818508085209

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 5(4), 513-534 (1985)

STRUCTURAL ASPECTS OF LIGNINS FROM EUCALYPTUS REGNANS WOOD STEAM EXPLODED BY THE IOTECH AND SIROPULPER PROCESSES

Jacqueline A. Hemmingson
DSIR, Chemistry Division
Private Bag, Petone, New Zealand

ABSTRACT

The lignins extractable by acetone from *Eucalyptus regnans* wood after steam explosion treatment by either the Canadian Iotech Process[1] or the Australian Siropulper Process[2] have been examined by ^{13}C NMR spectroscopy. Comparison with MWL showed structural changes which are discussed, compared for the two processes and compared with those for another hardwood (aspen) and a softwood (*Pinus radiata*). IR, MW and elemental analysis data are also discussed.

The structural changes resulting from the two processes are quite similar and dominated by β-ether cleavage. The modified structures found in *E.regnans* lignin differ from those found in the lignins from *P. radiata* and aspen in the amount and variety of reduced side-chain groups and in the amount of demethylation of aromatic moieties. Structural changes include elimination of hydroxy-groups and formation of carbonyl groups, α,β-unsaturation and carbon-carbon linkages.

INTRODUCTION

Steam explosion processes, which involve the hydrolytic breakdown of wood structure, greatly improve accessibility of the wood carbohydrate components to, for example, bioconversion processes giving liquid and gaseous fuels and protein.[3] They also give low molecular weight, soluble and reactive

0277-3813/85/0504-0513$3.50/0

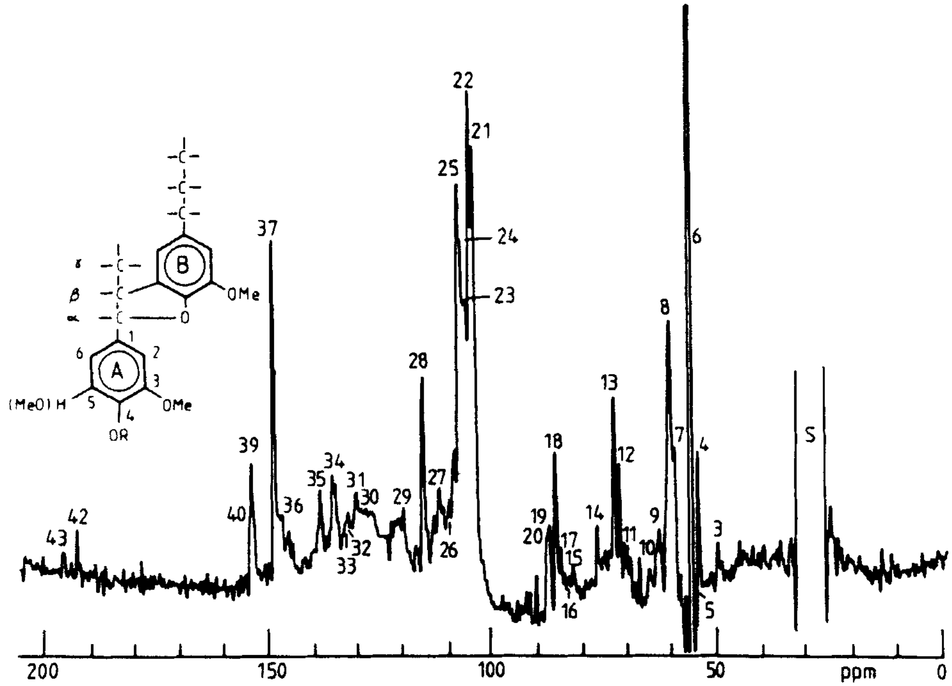

FIGURE 1. Resolution enhanced ^{13}C NMR spectrum of E. regnans IP.EWL in acetone-d_6/H_2O (9:1).

lignins, which have considerable potential for high value utilisation.[3] The structure of these lignins from different species of wood and different explosion processes is therefore of interest and this paper reports a study of the acetone soluble lignins extracted from the hardwood Eucalyptus regnans after treatment by two somewhat different types of steam explosion process.[1,2] The major technique used was ^{13}C NMR, but some IR, MW and elemental analysis data are included. Comparison is with E. regnans MWL and exploded wood lignins from two other wood species, namely Pinus radiata and aspen (Populus tremuloides).

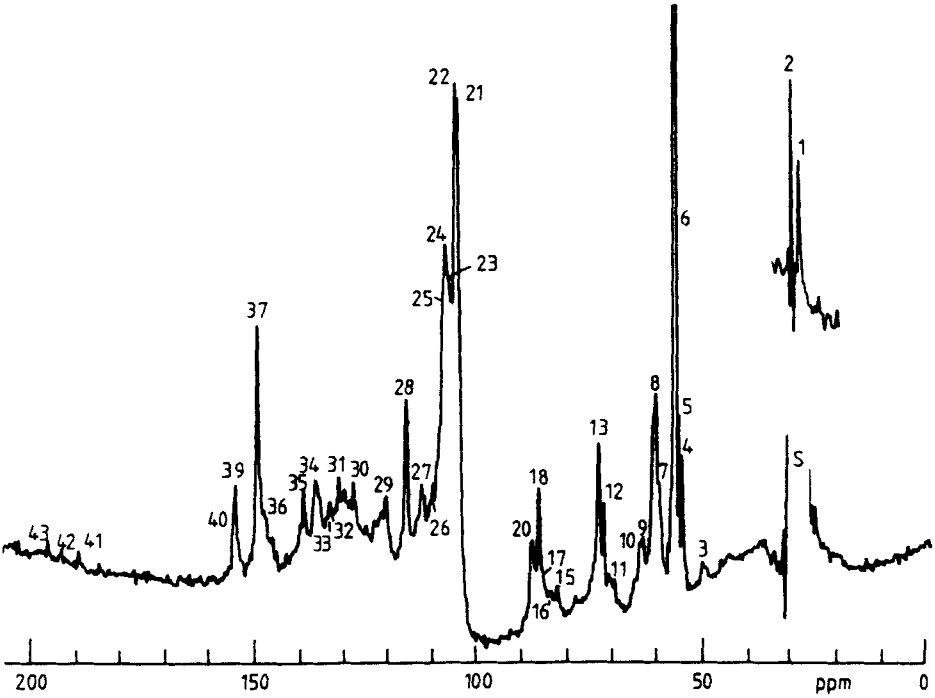

FIGURE 2. Resolution enhanced ^{13}C NMR spectrum of *E. regnans* SP.EWL in acetone-d_6/H_2O (9:1) and DMSO-d_6 (insert).

RESULTS AND DISCUSSION

^{13}C NMR Spectra

The lignins were examined at 20 MHz in acetone-d_6/H_2O (9:1) (see Experimental). Spectra are shown in Figs. 1 and 2 for exploded wood lignins (EWL's) from Iotech processed (IP) and Siropulper processed (SP) *E. regnans* wood and in Fig. 3 for milled wood lignin (MWL). The solvent-obscured region of SP.EWL was examined in DMSO-d_6 and it is shown superimposed in Fig. 2. The spectrum of acetylated

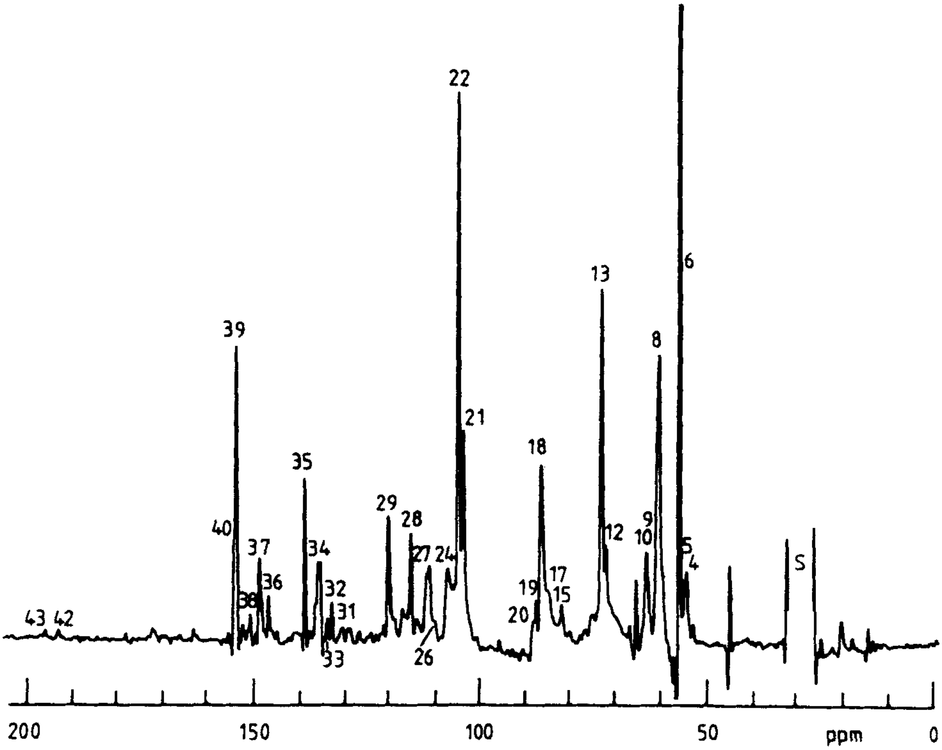

FIGURE 3. Resolution enhanced ^{13}C NMR specrum of *E. regnans* MWL in acetone-d_6/H_2O (9:1).

SP.EWL is shown in Fig. 4. Signal assignments based on literature data for lignins and model compounds are shown in Table 1 together with signal multiplicities determined for the 50-100 ppm region of SP.EWL.[4-6] Signals in acetylated lignin spectra were also assigned from literature data.[7] The assignments are to both established lignin structures and some new structures likely to be present in the EWL's.

1 The 0-50 ppm Region

The spectra of the *E. regnans* EWL's show only two prominent or significant signals, visible when DMSO-d_6

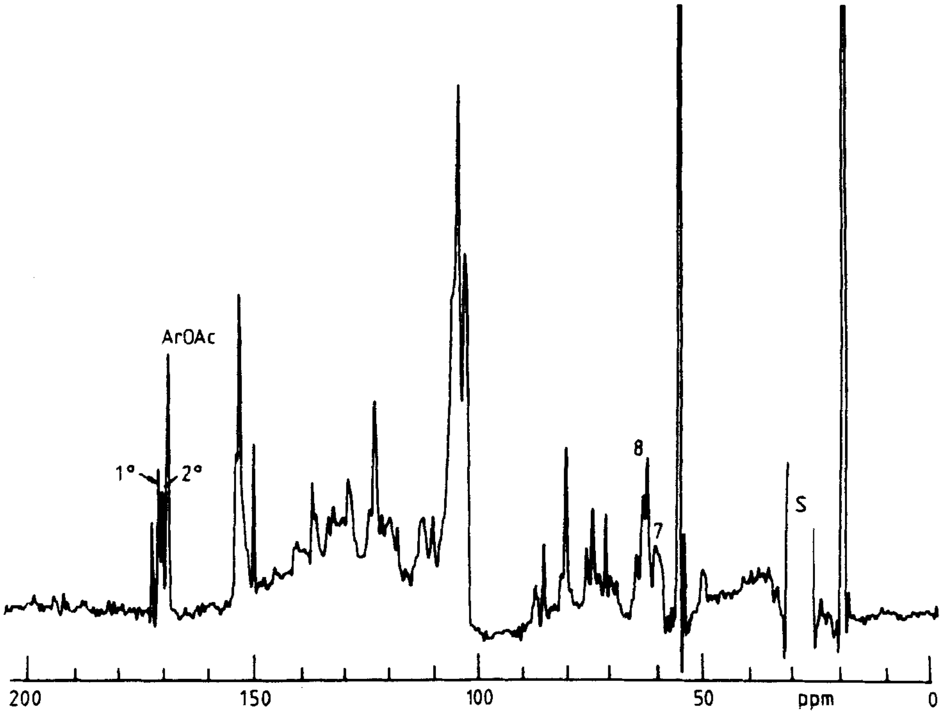

FIGURE 4. Resolution enhanced ^{13}C NMR spectrum of <u>E. regnans</u> acetylated SP.EWL in acetone-d_6.

is the solvent, in this region. This is in contrast to P. radiata EWL. Steam explosion of P. radiata wood resulted in a wide range of prominent or significant signals in this region, assigned to reduced (non-oxygen-bound) side-chain carbon.[5] A number of signals were also observed in the spectrum of the EWL from aspen dissolved in DMSO-d_6.[8] The two signals observed (1 and 2), which occur at 28.9 and 30.6 ppm respectively, have chemical shifts consistent with assignment to bridging methylene carbon (in, for example, a 5-5 linked diguaiacylmethane structure) and to a γ-methyl group adjacent to a β-carbonyl group (Table 1).

TABLE I

^{13}C NMR Assignments

No.	δ	M	Assignments
1*	28.9	-	CH_2 in $ArCH_2Ar$
2*	30.6	-	γ-Me adj. β-CO
3	50.4	CH	
4	55.0	CH	Cβ in β-5
5	55.7	?	Cβ in β-β
6	56.5	CH_3	OMe
7	60.1	CH/CH_3	OMe + ?
8	61.0	CH_2	Cγ in β-O-4
9	63.7	CH_2	Cγ in β-O-4 with α-CO, cinnamyl alcohols,
10	64.4		Cγ in β-5, β-1, Cβ in β-1
11	70.0-71.5	CH_2/CH?	Cγ in alkyl ethers and lignan lactones
12	72.3	CH_2	Cγ in β-β,α-O-γ
13	73.4	CH/CH_2?	Cα in β-O-4, Cγ in alkyl ethers
14	77.4	-	
15	82.8,	CH	Cβ in β-O-4 with α-CO, Cα in alkyl
16	83.9-84.2		ethers
17	85.5-85.7,	CH	Cβ in β-O-4 with α-OH, CO, OR etc.
18	86.7		Cα in β-β,α-O-γ
19	87.9,	CH	Cα in β-5
20	88.4-88.6		

M = multiplicity of carbon, SP.EWL spectrum; * δ in DMSO-d_6;
- not determined; S = syringyl, G = guaiacyl.

(continued)

TABLE I cont'd

No.	δ	Assignments
21	104.2-104.4,)	$S^{e,f}_{2,6}$ in syringaresinol, syringic acid etc.
22	105.0)	$S^{e,f}_{2,6}$ in β-O-4, β-1(A ring)
23	106.3)	$S^{e,f}_{2,6}$ with α,β unsaturation, α-CO, α-CHO, in α-6' and in β-1(B ring)
24	107.1)	
25	107.7)	
26	110.1	G_2 in β-5(A ring), G_2 with α,β-unsat. side-ch.
27	112.3	G_2 in β-O-4 with α-OH and in general
28	115.7	G_5, $PHP_{3,5}$, $C_{2,5}$ in catechol
29	120.1	G_6 in general
30	127.4	G_6 with α-CO, Cα,β unsaturation (e.g. Cα or Cα,β in stilbenes)
31	130.7	G_1,G_5 in β-5(B ring), G_1 with α,β-unsat. side-ch., Cα in cinnamyl alc.
32	132.6)	Cβ in cinnamaldehyde, S_1G_1 in β-1(B Ring) etc., G_1 and Cα,β in β-1 with α,β unsaturation(A ring)
33	133.6)	
34	134.8-135.8	G^e_1, S^f_4
35	138.5	$S^e_{1,4}$
36	147.0	G^f_4
37	148.6	$S^f_{3,5}$, G_3
38	150.2	G^e_4
39	153.5)	$S^e_{3,5}$
40	154.0)	Cα in cinnamaldehyde
41	188.4	>C=O
42	192.3	α-CHO
43	195.0	α-CO, α,β-unsat. γ-CHO

2 The 50-100 ppm Region

Signals for β-O-4, β-β (pino/syringaresinol) and β-5 side-chain structures are observed in the spectra of both EWL's, but, whereas the signals for β-β and β-5 linked units appear to have similar intensities to those of MWL, signals 13 and 17-18 for (or containing) Cα and Cβ in β-O-4 linked units appear to be at least halved in intensity. (Only estimates are of course possible with these spectra.) Signal 8 for Cγ in β-O-4 units, is reduced in height and broadened and a weak shoulder (7) at 60.1 ppm becomes prominent and resolved, particularly in IP.EWL. A shoulder, visible in the expanded scale spectra, also appears at 61.5-61.7 ppm. Using higher field spectrometers, signals 4 and 5 at 55.0 and 55.7 ppm have been assigned to Cβ in β-5 and β-β linked units respectively.[9] In acetylated SP.EWL (Fig.4), Cβ in β-β is at 55.2 ppm and Cβ in β-5, β-1 gives a broad signal at 51.2 ppm, which probably has a contribution from the weak 50.4 ppm signal of the underivatized lignin.

There is little evidence for the presence of β-1 linked structures with an α-hydroxy-group in either EWL, or in MWL, as signals in the 75.0 ppm region appear to be insignificant.[9] The Cβ,γ in β-1, Cγ in β-5 signals (9 and 10) at 63.7-64.4 ppm are weak in both EWL's and the multiplicity determination gave no indication of a CH component. In contrast, the sharp signal in MWL appears to be stronger (relative to, for example, the signals for Cβ in β-β and β-5 linked units) and it is not resolved. Therefore, β-1 linked units, which are thought to comprise 7-15% of bond types in birch and beech lignins,[10] can only be assumed to be present in the lignins from E. regnans. Their presence could be obscured by having other substituents at Cα, e.g. in the case of MWL, substituents giving ether linkages,[11] and, in the case of the EWL's, α-6' linkages. Unfortunately, relevant chemical shift data are not available or the signals would be overlapped by those of other structures. It may be noteworthy that a signal at 66.1 ppm in MWL has not been assigned and that no signal has been assigned to Cα in the spectra of the lignins from aspen.[8]

The broadened Cγ in β-O-4 signal at 61.0 ppm in the EWL's has an upfield methine or methyl carbon component, or components, which could be 50% of the signal and includes the 60.1 ppm shoulder (7). Acetylation does not affect the upfield components of this signal, as a broad signal at 60.2-61.6 ppm with an intensity about half that of the signals for Cγ in β-O-4 units (at 63.5-64.4 ppm) is observed (Fig. 4). The more hindered methoxy-group of syringyl moieties substituted at C_2 or C_6 as a result of condensation reactions could make a substantial contribution to the signal 7 region, as chemical shifts occurring in this region have been reported for similarly hindered methoxy-groups.[12] One can only speculate about a contribution arising from β-1 linked units in the absence of data for model compounds and definite evidence for their presence in MWL.

Spectrum Detail

(a) A weak signal (3) at 50.4 ppm in the EWL's could indicate the presence of Cα in α-1,β-ether linked structures.[6] These could be formed, for example, by nucleophilic addition of an aryl unit to the α-carbon atom of a protonated C_6C_2-enol ether formed during hydrolysis of β-O-4 linked structures.[13] Cβ would be obscured by signal 13.

(b) A quite prominent signal at 77.4 ppm given by IP.EWL (signal 14) is absent from both SP.EWL and MWL.

Cα,β in β-O-4 units with a γ-methyl substituent would occur at 77.5 and 88.8 ppm.[14] No signal for γ-Me at 16.3 ppm is detectable, but there may be a weak signal 2 ppm upfield.

(c) Signal 15 at 82.3 ppm in MWL, which has been assigned to Cβ in β-O-4 with α-CO, or Cα in non-cyclic and lignan monocyclic alkyl ethers,[5] appears to be weaker in both of the EWL's. It is not affected by acetylation, which supports assignment to Cα in ethers.

(d) Weak signals at 70.0-71.5 ppm in the spectrum of SP.EWL, which were assigned in the case of P. radiata EWL to Cγ in alkyl ethers and lignan lactones are not shifted by acetylation and they appear to be due primarily to methylene carbon.

Conclusions Regarding Side-Chain Modification

(i) Changes in signal intensities (see above) indicate that cleavage of at least 50% of the major β-O-4 linkages is the major effect of steam explosion treatment on abundant units of this hardwood lignin. Cyclic ether bonds are not cleaved, while the presence and modification of β-1 linked structures is uncertain. If the abundance of β-O-4 linkages was originally about 60%,[4,9] the abundance in the EWL's is likely to be <30%. In addition, if the original distribution of interunit linkages was similar to that of beech or birch lignin,[10] carbon-carbon interunit linkages in the EWL's, without including those formed in condensation reactions during hydrolysis, should be of similar abundance to β-O-4.

(ii) Only minor process differences are observed. Differences in the abundances of modified structures would arise from differences in process temperature, cooking time and possibly technique of pressure release, affecting the relative rates and products of delignification and modification reactions.

(iii) Species-related differences are observed, e.g. in the content and variety of reduced side-chain groups giving signals in the 0-50 ppm region.

(iv) The broad signal for methine or methyl carbon, which contributes to the Cγ in β-0-4 signal is reasonable evidence for the presence of hindered aromatic methoxy-groups arising from condensation reactions. The methylene carbon of hydroxymethylated aromatic rings can also occur in this region,[6] (see (v) below), and a minor contribution would not affect the multiplicity determination. A contribution arising from β-1 units is only a possibility.

(v) A significant amount of condensation of aromatic carbon with formaldehyde to give diarylmethane structures appears to have taken place (signal 1). Formaldehyde is a product of hydrolysis reactions, formed by elimination of Cγ.[10,13]

(vi) Hydrolysis products of β-0-4 linked units are the most probable source of the β-CO with γ-Me side-chains, which appear to make a substantial contribution to side-chain structure (Signal 2).[10] They can also be formed from β-1 linked units with accompanying migration of the aryl group to the α-carbon atom.[10]

3 The 100-160 ppm Region

Both EWL's give $S_{2,6}$ ($C_{2,6}$ of syringyl units) signals of similar composition, but there appear to be differences in component abundances. For example, in SP.EWL, the peak observed at 107.7 ppm in IP.EWL (25) is only a shoulder on the 107.1 ppm peak (24), while the latter is only a shoulder in IP.EWL. In the spectra of both EWL's, the intensity of the upfield signal band at 104-105 ppm (21-22), corresponding to $S_{2,6}$ in major units (β-0-4, β-β, β-1 (A ring)), is no more than twice that of the downfield signal band at 106-108 ppm

(23-25), which corresponds to signals in units with α,β-unsaturated, α-CO, α-6', etc. groups and linkages and in β-1 units (B ring). In contrast, in MWL, the upfield band is several times more intense than the downfield. This difference is consistent with changes involving the major β-0-4 linkage, as side-chain modification tends to shift the signals downfield (see above). The 104.2 ppm signal appears to be less affected by the explosion process than the 105.0 ppm signal, which may indicate a substantial contribution from syringaresinol structures, or structures with stable Cα linkages, to this signal.

The extensive cleavage of aryl ether interunit linkages and formation of free phenolic hydroxy-groups is clearly shown by the relative intensities of (a) signals 34 at 135-136 ppm and 35 at 138.5 ppm, which contain S_4 in free (S^f_4) and etherified (S^e_4) syringyl units respectively and (b) signals 37 at 148.6 ppm and 39 at 153.5 ppm, which contain $S^f_{3,5}$ and $S^e_{3,5}$ respectively. In the case of MWL, the $S^e_{1,4}$ signal (35) is twice as high as the $S^f_4G^e_1$ signal (34) and the $S^e_{3,5}$ signal (39) is about three times as intense as the $S^f_{3,5}$, G_3 signal (37), while in the EWL's, the S_4 signals are of similar height and the $S^e_{3,5}$ signal has only one third to one half the intensity of the $S^f_{3,5}$, G_3 signal. Signal 38 for G^e_4 at 150.2 ppm in MWL is not observed in the EWL's, while signal 36 for G^f_4 is observed at 147.0 ppm in the EWL's, slightly downfield of the signal assigned to G^f_4 in MWL, which occurs at 146.2 ppm. It is interesting that non-etherified guaiacyl units appear to predominate over etherified in MWL. The extent of aryl ether cleavage is similar for both steam explosion treatments, with about 60% cleavage appearing to be a reasonable estimate of the extent.

The high content of free phenolic hydroxy-groups is well shown in the spectra of the acetylated lignins. In the spectra of the acetylated EWL's, the phenolic acetate carbonyl signal has about twice the intensity of the primary aliphatic acetate signal, which in turn is more intense than the secondary acetate signal, while in the spectrum of MWL the phenolic acetate signal is weak relative to both of these signals. Comparison with other signals such as $S_{3,5}$ and G_5 gives similar results.

Spectrum Detail

Structural changes in the guaiacyl units of the EWL's are clearly shown by the dispersion and greatly reduced prominence of the G_2 and G_6 signals at 110-112 and 120.1 ppm respectively (26-27 and 29) and the prominence of the G_5 signal at 115.7 ppm (28).[5] As observed with the guaiacyl lignin of P. radiata, the $G_{1,6}$ region of the EWL's at 117-138 ppm becomes more complex. Minor differences between the explosion processes are detectable in the $G_{1,2,6}$ signals, the most obvious being the intensity of signal 30 at 127.4 ppm in SP.EWL, which could indicate a higher content of units with α-CO groups and α,β-unsaturation. The significant enhancement of the G_5 signal observed with P. radiata EWL appears to be absent in the case of these hardwood lignins, indicating that less demethylation to catechol structures has occurred.

4 The 160-200 ppm Region

In the spectrum of MWL, weak signals are observed at 192.4 and 195.2 ppm (42 and 43) and also in the region for carboxylic acids and esters (160-180 ppm), e.g. at 171.8 ppm. Nimz has attributed a signal at 171.8 ppm to the carbonyl group in glycerate ester linkages, which would hydrolyse on steam explosion.[4]

In the spectra of the EWL's, the signals for α-CHO at 192.3 ppm and α-CO, α,β-unsat. γ-CHO at 195.0 ppm may be more prominent than in MWL, particularly those of IP.EWL, while SP.EWL shows an additional signal at 188.4 ppm (41). Other possible carbonyl signals in the EWL's are indistinguishable from background noise.

Conclusions Derived from the 100-200 ppm Region

(i) Changes in signals in this region indicate cleavage of about 60% of the aryl ether linkages. The extent of cleavage appears to be similar for both explosion processes and similar to that found in P. radiata and aspen EWL's.

(ii) Structural modification of both syringyl and guaiacyl units is clearly evident, but not of the stable β-5 and β-β linked structures. The complexity and broadening of the EWL signals observed in this region, cf. those of MWL, indicates a diversity of structural modification.

(iii) Demethylation of guaiacyl units appears to be less than was observed with the softwood lignin (see also Table 2 below).

Supplementary Data

1 Elemental Analysis

The composition of a number of lignins is shown in Table 2.

In contrast to P. radiata EWL and aspen EWL which show a rise in hydrogen content cf. that of MWL,[5,8] the E. regnans EWL's show a substantial fall in both H and O content in about a 1:1 ratio, which is further support for the differences in the content and variety of reduced side-chain groups discussed above.

Also in contrast to P. radiata and aspen EWL's, the methoxyl content is only slightly lower than that of MWL, which is further support for demethylation

TABLE 2

Composition of Various EWL's and MWL's

E. regnans	MWL[a]	$C_9 H_{7.72} O_{2.75} (OMe)_{1.54}$
	IP.EWL[b]	$C_9 H_{7.16} O_{2.23} (OMe)_{1.51}$
	SP.EWL[b]	$C_9 H_{6.98} O_{2.06} (OMe)_{1.44}$
P. radiata	IP.EWL[c]	$C_9 H_{8.78} O_{2.34} (OMe)_{0.56}$
aspen	MWL[d]	$C_9 H_{8.70} O_{3.05} (OMe)_{1.47}$
	EWL[d]	$C_9 H_{9.2} O_{2.7} (OMe)_{1.1}$

(a) ref. 15, (b) this work, (c) ref. 5 and (d) ref. 8.

being relatively minor with this wood species. Process conditions appear to affect the magnitude of H,O loss and demethylation, which is slightly greater for the lower temperature, but longer cooking time Siropulper process.

2 Infra-red Spectral Data

The IR spectra of *E. regnans* IP.EWL, SP.EWL and MWL are shown in Fig. 5.

Marked differences between the EWL's and MWL are shown by the carbonyl region. The aromatic skeletal C-O stretch band at 1598 cm^{-1} in MWL is broadened and shifted to 1612 cm^{-1}. The shoulder at 1620 cm^{-1} and the maximum at 1653 cm^{-1} for α,β-unsaturated aldehyde and α-CO groups are no longer observed, while new maxima are observed at 1703 cm^{-1} for SP.EWL and 1715 cm^{-1} for IP.EWL. The band in MWL with a maximum at 1732 cm^{-1} is absent from both EWL spectra. The 1715-1703 cm^{-1} band appears to be more intense in the SP.EWL spectrum. As observed previously with *P. radiata* MWL and EWL, the band at 1732 cm^{-1} is likely to be due to unconjugated acid and ester groups and the

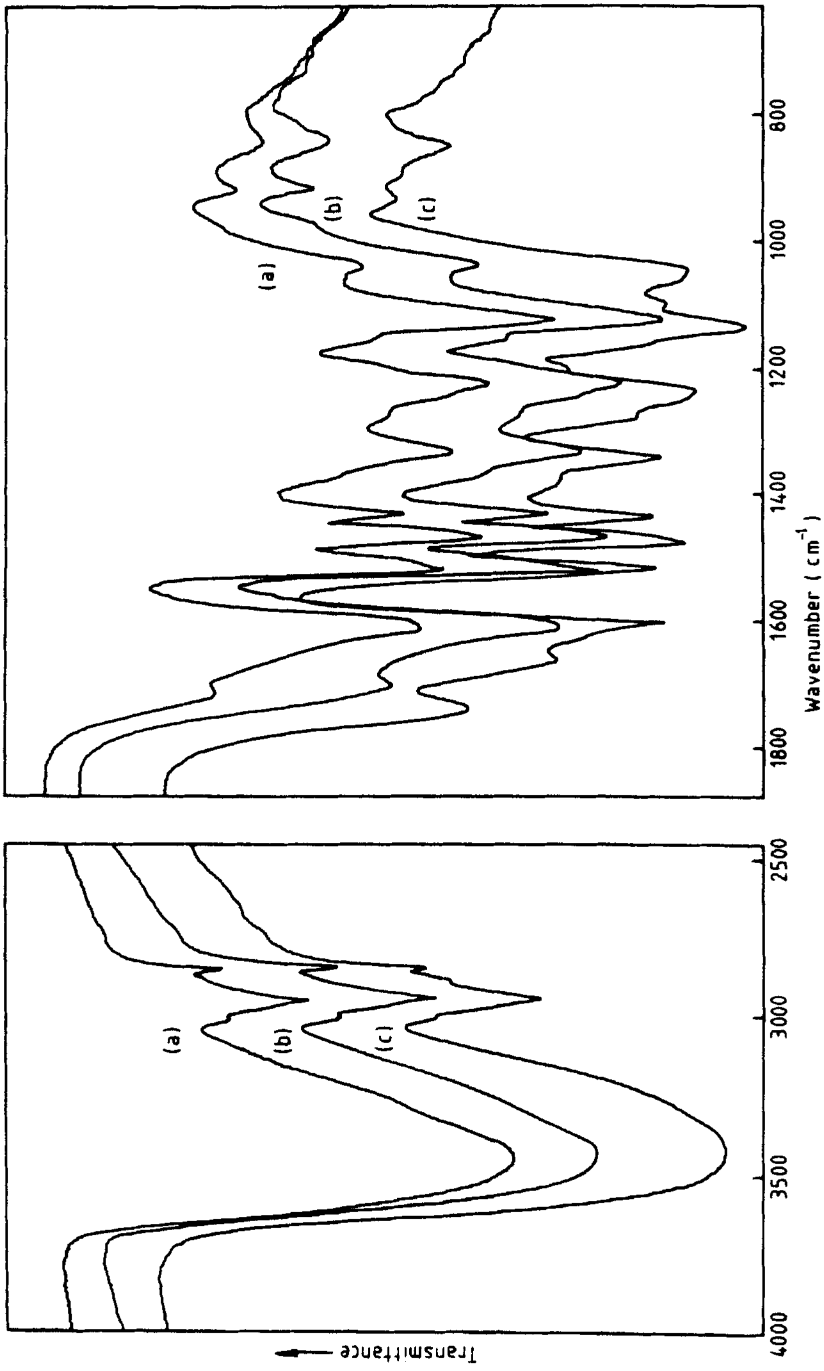

FIGURE 5. IR spectra of (a) IP.EWL, (b) SP.EWL and (c) MWL.

band at 1715-1703 cm^{-1} to formation of unconjugated carbonyl, e.g. β-CO groups, in the side-chains of some units.[5] The broadening of the 1598 cm^{-1} band could be due in part to formation of unsaturation in the side-chain, as hydrogenation of SP.EWL ($PtO_2/H_2/EtOH$) sharpened the 1612 cm^{-1} band.

The band for primary alcohol groups at 1030 cm^{-1} is much weaker in the EWL spectra, while the secondary alcohol band at 1089 cm^{-1} is not observed. This reflects the reduction in γ- and α-hydroxy-group content.

A shoulder is observed at 973 cm^{-1} in the spectra of both EWL's, but it is weaker for IP.EWL. It is removed by hydrogenation, which indicates the presence of trans ethylenic double bonds (as in cinnamyl compounds and stilbene structures).

A weak band at 920 cm^{-1} in the spectrum of MWL is enhanced about three-fold and shifted to 918-915 cm^{-1} in the EWL spectra. This band, which in MWL is characteristic of syringyl units,[16] is unaffected by hydrogenation. The enhancement observed in this region may therefore be indicative of changes in the substitution pattern of EWL aromatic rings and evidence for the occurrence of electrophilic substitution or self-condensation reactions involving aromatic carbon and side-chain aliphatic carbon or formaldehyde. Smaller changes take place in the major band characteristic of the syringyl moiety, which occurs at 839 cm^{-1}.[16]

The IR spectra therefore support structural modification involving formation of unconjugated carbonyl groups, α,β-unsaturated moieties, a reduction in OH content and changes in ring substitution patterns.

The Molecular Weight of IP.EWL

The molecular weight was determined as described previously for *P. radiata* EWL.[5] Values of 896, 2317 and 2.6 were obtained for M_n, M_w and M_w/M_n respectively. The values of M_n and M_w are similar to those for *P. radiata*, of 823 and 2473 respectively, but the polydispersity is lower, 2.6 c.f. 3.0. Values of 1700-1900 for M_w and 2.4-2.7 for M_w/M_n have been reported for aspen EWL.[8] Therefore the molecular weight and polydispersity of exploded wood lignins appear to be of the order of 2000 and 2.5-3.0 respectively and to be not greatly dependent on wood species. It should be noted however, that the yield of extracted lignin was higher from the hardwood. (13-16%, c.f. 10%, of dry wood weight).

General Conclusions

(i) Structural modification of the hardwood lignin involves extensive cleavage of the major β-0-4 interunit linkage, elimination of α- and γ-hydroxy-groups, formation of carbonyl groups, particularly unconjugated β-carbonyl groups, an increase in α,β-unsaturation and condensation reactions forming aliphatic carbon to aromatic carbon bonds, such as α-6' and methylene-bridged aromatic carbon. The hydrolysis pathway via C_6C_2-enol ether formation from β-0-4 linked units, (and possibly stilbene formation from β-1 units), which releases formaldehyde by side-chain shortening $C_{\beta,\gamma}$ cleavage could be the source of formaldehyde for condensation reactions, as well as some unconjugated carbonyl groups.[10,13]

(ii) A major difference between this hardwood (*E. regnans*) and the softwood studied previously (*P. radiata*) is that with the softwood, depolymerization results in a wide range of reduced side-chain groups and a gain in hydrogen content, whereas with the hardwood, depolymerization results in elimination of both hydrogen and oxygen from the side-chain. A further difference is the extent of demethylation which appears to be much less with the hardwood. In contrast, de-etherification appears to be similar in extent and the molecular weights of the EWL's similar in magnitude. It is possible, therefore, that the hardwood lignin would have a higher content of reactive side-chains.

A correlation of the presence of syringyl units with the difference in side-chain modification is an interesting possibility. Hydrolysis of β-0-4 linkages of syringyl units is reported to be faster than that of guaiacyl units,[9] so that competition between reaction pathways, including reductive side-chain modification pathways possibly involving radicals could change with syringyl content. The effect of the more acidic conditions of hardwood hydrolysis, due to the higher content of acetyl groups, would also be to facilitate hydrolysis, as well as condensation, reactions.

(iii) Hardwood lignins may show diversity in the effects of steam explosion because of the greater structural and composition variability available to them through the S/G unit ratio and unique properties. Aspen lignin is almost unique in that it contains up to about 10% by weight of p-hydroxybenzoate groups.[17]

(iv) Different steam explosion processes have some effect on the relative abundances of the products of depolymerisation reactions.

EXPERIMENTAL

Steam explosion of New Zealand *Eucalyptus regnans* wood was carried out by Iotech Corporation Ltd, Canada and the Division of Chemical and Wood Technology, CSIRO, Australia.[1,2] The exact conditions used by Iotech Corporation for treating our sample were not divulged, but were presumably in the range normally used, i.e. a steam pressure of about 5.5 MPa and cooking at about 230°C for about 60 sec.[1,18] In contrast, the Siropulper process used steam at 1.7 MPa to heat the chips to 205°C and then the pressure was raised to 6.9 MPa with a 60/40 volume mixture of CO_2/N_2. After 15 min., the pressure was released and the digester contents were discharged through a specially designed nozzle.[19]

The wet exploded wood was extracted with acetone. Addition of the concentrated extract to water precipitated the lignin which was washed, air dried and then dried under vacuum. Yields were 13-16% of dry wood weight.

E. regnans MWL was prepared in this laboratory.

Acetylation was carried out in acetic anhydride-pyridine 1:1.

^{13}C NMR Spectra were run at 30°C on a Varian FT-80A spectrometer operating at 20 MHz, as described previously.[5] The solvent was acetone-d_6/H_2O (9:1 by volume) except where noted. Resolution was again improved by Lorentzian-to-Gaussian transformation,[20] and expanded scale spectra were used to assist detailed comparison.

IR Spectra were run on KBr disks.

Molecular Weight was determined by HPLC separation of the acetylated lignin as described previously.[5]

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

ACKNOWLEDGEMENTS

The author is grateful to Dr R.H. Newman and Dr H. Wong of Chemistry Division, DSIR, for ^{13}C NMR spectra, to

Mr D.A. Sawtell, for preparation of MWL and to Mr E.A. DeLong of Iotech Corporation Ltd, Canada and Dr H. Mamers of the Division of Chemical and Wood Technology, CSIRO, Australia, for treatment of wood samples by the Iotech and Siropulper processes respectively.

REFERENCES

1. E.A. DeLong, Canad. Patent 1,096,374 (1981). Iotech Corporation Ltd, Ontario, Canada.

2. H. Mamers and J.E. Rowney, U.S. Patent 4,163,687 (1979).

3. International Bio-Energy Directory and Handbook, P.F. Bente, Jr. (ed.), The Bio-Energy Council, Washington, D.C., 1984.

4. H. Nimz, Angew. Chem., (Internat. Edn.), 13, 313 (1974).

5. J.A. Hemmingson, J. Wood Chem. Technol., 3, 289 (1983).

6. K.P. Kringstad and R. Mörck, Holzforschung, 37, 237 (1983).

7. H.H. Nimz, M. Nemr, P. Schmidt, C. Margot, B. Schaub and M. Schlosser, J. Wood Chem. Technol., 2, 371 (1982).

8. R.H. Marchessault, S. Coulombe, H. Morikawa and D. Robert, Can. J. Chem., 60, 2372 (1982).

9. H.H. Nimz, U. Tschirner, M. Stähle, R. Lehmann and M. Schlosser, J. Wood Chem. Technol., 4, 265 1984.

10. E. Adler, Wood Sci. Technol., 11, 169 (1977).

11. W.G. Glasser, in Pulp and Paper - Chemistry and Chemical Technology, 3rd Edn., Vol. I, Chap. 2, p.50, J.P. Casey (ed.), Wiley, New York, 1980.

12. K.R. Markham and V.M. Chari, in The Flavonoids: Advances in Research, Chap.2, spectra 40,41, J.B. Harborne and T.J. Mabry (eds), Chapman and Hall, London, 1982.

13. L.H. Hoo and K.V. Sarkanen, J. Wood. Chem. Technol., 3, 223 (1983).

14. H-D. Lüdemann and H. Nimz, Makromol. Chem., 175, 2393 (1974).

15. D.E. Bland and M. Menshun, Appita, 23, 427 (1970).

16. H.L. Hergert, in Lignins, p.280, K.V. Sarkanen and C.H. Ludwig (eds), Wiley-Interscience, New York, 1971.

17. M.G.S. Chua and M. Wayman, Can. J. Chem., 57, 1141 (1979).

18. L. Jurasek, Dev. Ind. Microbiol., 20, 177 (1978).

19. V.P. Puri and H. Mamers, Biotechnol. Bioeng., 25, 3149 (1983).

20. A.G. Ferrige and J.C. Lindon, J Magn. Reson., 31, 337 (1978).