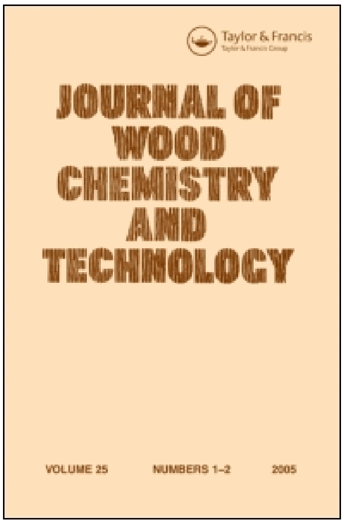

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EXPLODED WOOD LIGNINS FROM PINUS RADIATA WOOD. 2. THE EFFECT OF SO_2 PRETREATMENT ON STRUCTURE

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ABSTRACT

The acetone soluble lignins of *Pinus radiata* wood, which had been steam exploded by the Australian Siropulper process, both with and without SO_2 pretreatment,[1,2] have been examined by ^{13}C NMR spectroscopy. The marked structural effects of SO_2 pretreatment are discussed. A brief comparison of the lignins from wood treated by the Siropulper and Canadian Iotech[3] processes (without SO_2 pretreatment) is also presented.

The soluble lignins from exploded wood treated by either the Siropulper or the Iotech process are very similar in structure and in the relative abundances of structural units. In contrast, SO_2 pretreatment markedly changed relative abundances. β-O-4 linked units were more extensively modified and β-5 linked units, which were stable in the absence of SO_2 pretreatment, were also extensively modified. No sulphur incorporation was detected and some differences between the steam explosion treatment and acidic sulphite pulping are outlined.

INTRODUCTION

Steam explosion treatment of plant biomass usually greatly improves enzymatic digestibility, but softwoods are an exception.[2,3] Pretreatments prior to the explosion treatment (e.g. with acidic gases such as

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SO_2) are currently being investigated and are showing promise of resulting in satisfactory digestibility.[2]

Irrespective of enzymatic digestibility, the structure of softwoods, like that of hardwoods, is broken down substantially and considerable amounts of low molecular weight, soluble and reactive lignins (e.g. ca 10% of dry weight) are formed.[4] Studies of the structure of these lignins should assist in development of possible uses for them.

In a recent publication,[4] a study of the structure of lignin from *Pinus radiata* wood treated by the Canadian Iotech process,[3] was reported. This paper reports a similar study of the lignins from *P. radiata* wood treated by the Australian Siropulper process,[1,2] both with and without SO_2 pretreatment to improve digestibility. A brief comparison of the Iotech and Siropulper processes (without SO_2 pretreatment) is also presented.

^{13}C NMR spectroscopy was the major technique used in the study.

RESULTS AND DISCUSSION

^{13}C NMR Spectra

The lignins were examined at 20 MHz in acetone-d_6/H_2O, (9:1) solvent and the acetone-obscured region was examined in DMSO-d_6. Resolution enhanced and expanded scale spectra were used for detailed comparison (see Experimental). The resolution enhanced spectra of SP.EWL and SP(SO_2)EWL (defined below) are shown in Figs. 1 and 2. The differences in signal intensities discussed below are of sufficient magnitude to be real and not experimental artifacts and their validity is supported by the normal FT spectra.

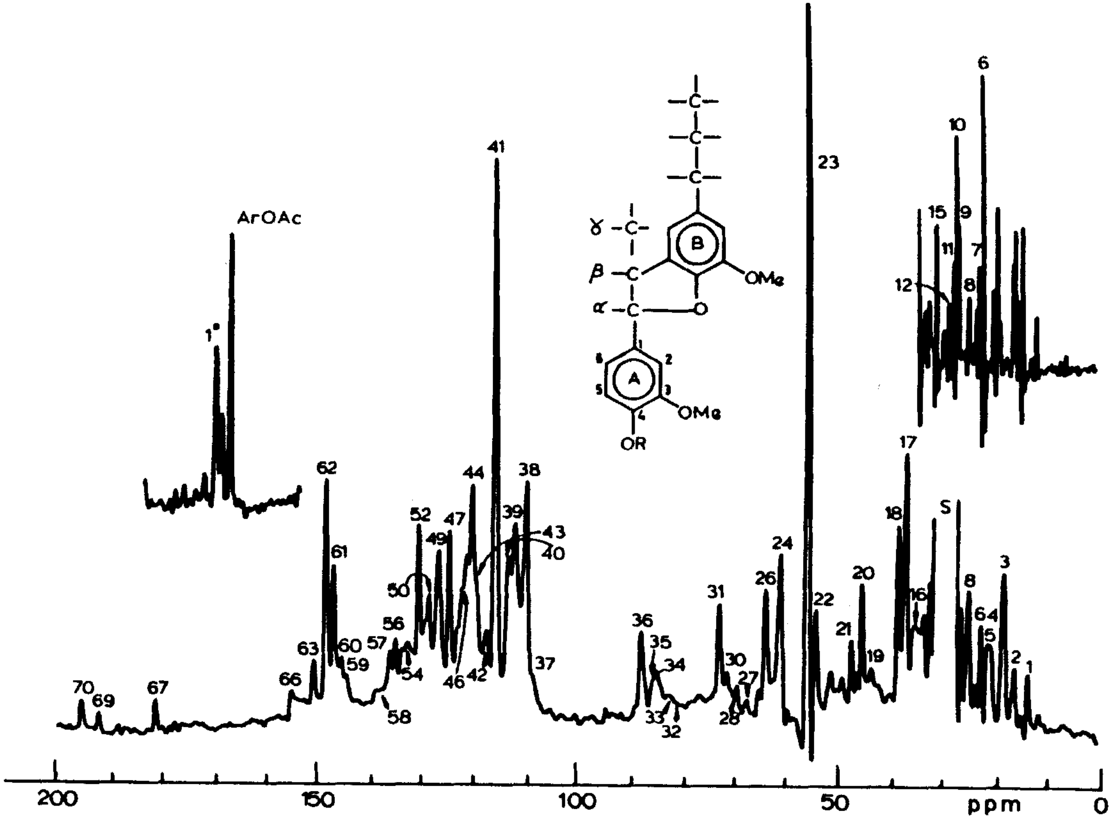

FIGURE 1 Resolution enhanced ^{13}C NMR spectrum of P. radiata SP.EWL in acetone-d_6/H_2O (9:1). Insets: 30 ppm region in DMSO-d_6, 170 ppm region of the acetylated EWL (acetone-d_6).

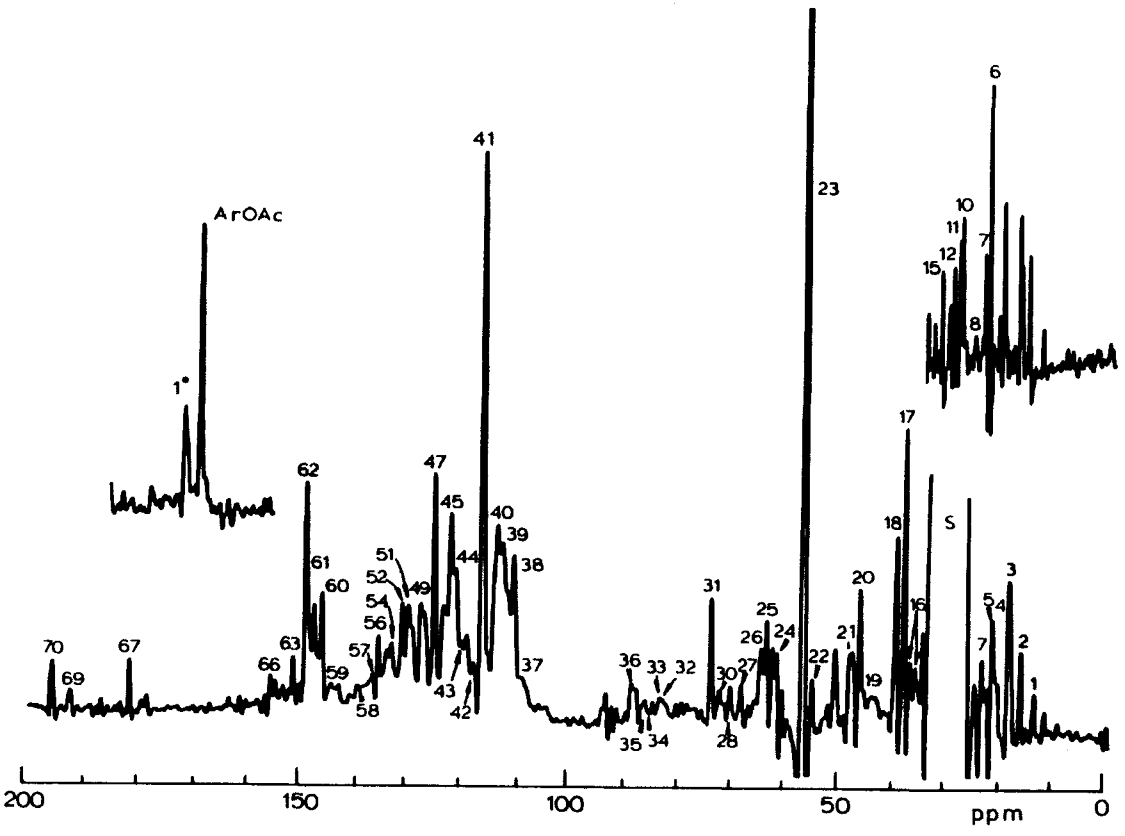

FIGURE 2 Resolution enhanced ^{13}C NMR spectrum of *P. radiata* $SP(SO_2)EWL$ in acetone-d_6/H_2O (9:1). *Insets:* 30 ppm region in DMSO-d_6, 170 ppm region of the acetylated EWL (acetone-d_6).

Signal assignments are in general the same as reported previously,[4] with some additions based on recent literature data.[5,6] However, it has recently been found that these EWL's may have an extractives content (resin and fatty acids) contributing significantly to signal intensities in the 0-50 ppm region.[7] The relative contributions of signals from lignin side-chains and extractives is currently being evaluated. Signal overlap in other regions is not a problem with the signals discussed in this paper.

Comparison of Processes (SP.EWL and IP.EWL).

The spectra of the lignins from wood treated by the Siropulper steam explosion process (SP.EWL) (Fig. 1) and the Iotech process (IP.EWL) (published in reference 4) were found to be very similar. It appears, therefore, that the two types of steam explosion treatment bring about very similar changes in the structure of this softwood lignin.

Cleavage of about two-thirds of the major β-0-4 interunit linkages with formation of free phenolic hydroxy-groups, but retention of the β-5 linkage with no hydrofuran ring opening are effects of treatment relevant to this paper.

Effects of SO_2 Pretreatment (SP(SO_2)EWL).

The spectra of SP(SO_2)EWL (Fig. 2) and SP.EWL (Fig. 1) show a quite similar range of chemical shifts and hence assignments, but they differ markedly in the intensities of some signals, particularly in the 50-100 ppm region. Two major interunit linkages are involved, namely the β-0-4 and β-5. A discussion of each spectral region follows.

1. The 0-50 ppm Region

This region of the spectrum of SP(SO_2)EWL is similar to that of SP.EWL and IP.EWL. (See comment above on signal assignments.) No changes suggesting the introduction of sulphur-containing moieties were detected.

2. The 50-100 ppm Region

Signals 24 and 34-35 corresponding to C-γ and C-β respectively in β-0-4 units and signals 22, 26 and 36 corresponding to (or containing) C-β, C-γ and C-α respectively in β-5 units are all markedly reduced in intensity in the spectrum of SP(SO_2)EWL. This clearly shows that SO_2 pretreatment prior to steam explosion results in a greatly reduced abundance of residual unmodified β-0-4 and β-5 linked units in the EWL. Possible reasons for the low abundance of β-0-4 linked units include more extensive cleavage of the β-0-4 linkage or, alternatively, retention with side-chain modification, e.g. enol ether formation with elimination of C-γ as formaldehyde.[8] In the case of β-5 units, hydrofuran ring opening with stilbene formation and recyclization with methyl-substituted phenylcoumarone formation are possibilities,[9] as the cyclic ether bond is apparently cleaved by the more acidic conditions. The possibilities are examined further below and some interesting differences between the steam explosion treatment and acidic sulphite pulping are discussed.

Apart from the low content of unmodified β-0-4 and β-5 structures, this region of the spectrum of SP(SO_2)EWL shows a prominent new, or greatly enhanced signal at 50.2 ppm, enhanced prominence of signal 25 (C-γ in β-0-4 with α-CO, coniferyl alcohol side-chain, etc.), a discrete signal between signals 24 and 25, either absent or masked by signal 24 previously, and apparently retained prominence of signal 31 (C-α in β-0-4). Signal 31 at 73.3 ppm could be at least partly due to C-β in addition products of the enol ether GCH=CHOAr, which is an intermediate in the hydrolysis of β-0-4 linked units, formed by elimination of C-γ as formaldehyde.[8] Significant hydrolysis via this type of enol ether has recently been proposed for aspen EWL.[10] Addition products, e.g. GG'CH·CH_2OAr and GCHOR·CH_2OAr, could be formed by protonation of the enol ether at C-β and subsequent reaction of the resulting carbocation with an aromatic ring dipole or aliphatic hydroxy-group. C-α would occur in the region of 50 ppm and 81 ppm respectively,[5,6] so the signal observed at 50.2 ppm could be evidence for formation of the α-diguaiacyl structure. This could account for the retained prominence of signal 31 despite the low content of unmodified β-0-4 structures and it is supported by the multiplicity of signal 31, which now appears to be comprised entirely of methylene carbon.

The signal at 93.4 ppm could correspond to C-α in β-5 units modified by reduction of the C-γ hydroxymethyl group to a methyl group.[5] C-β would contribute to signal 20. Reduction of the double bond of the phenylcoumarone discussed above would give this structure and could involve hydrogen radicals.[4]

3. The 100-200 ppm Region

The 117-136 ppm region of the spectrum of SP(SO_2)EWL shows some significant differences. Signal 44 (C-6 in β-0-4 etc.) appears to be markedly reduced in intensity. This would be consistent with the low content of unmodified β-0-4 linkages discussed above. Signal 52, which contains the β-5 signals C-1,5(B ring) also appears to be considerably reduced in intensity and signal 57 (C-3 in β-5 etc.) appears to be rather weak, relative to, for example, signals 56 and 63. This region of the spectrum therefore supports SP(SO_2)EWL having a similar range of side-chain structures to SP.EWL and IP.EWL, but differences in the abundances of unmodified β-0-4 and β-5 linked units.

Overlap of signals and the complexity of this region would inhibit detection of stilbene or phenylcoumarone formation from β-5 linked units. For example, C-α,β signals of the former would most probably overlap signals 46 and 51.[5]

The 144-154 ppm region of the spectrum differs significantly from that of the lignins from wood not SO_2 pretreated, in the intensity of signal 60, which is assigned to C-4 with α-CH_2, C-3,4 in catechol and C-β in the C_6C_2-enol ether defined below and discussed above. The enhanced intensity of this signal may correlate with the low content of unmodified β-0-4 linked structures. Recent work on the hydrolysis of β-0-4 linked structures via the C_6C_2-enol ether, which is formed by elimination of C-γ as formaldehyde, has shown that the enol ether itself can be a significant product,[8] as it is much less easily hydrolyzed than the C_6C_3 ether, which is formed with retention of C-γ. A new signal at 118.7 ppm between signals 42 and 43 could possibly be assigned to the C-6 carbon atom. The product of β-ether cleavage is $GCH_2{\cdot}CHO$,[8] while addition products have been discussed above.

The relative intensities of signals 61 and 63 (C-4 in non-etherified units, and C-4 in etherified units, C-3 with α-CO, respectively) are similar to those of IP.EWL and perhaps lower than those of SP.EWL, so there is no evidence from these signals for a higher free phenolic hydroxy-group content in SP(SO_2)EWL as a result of more extensive β-ether cleavage. Formation of the enol ether and addition products discussed above, which retain this linkage would therefore help account for this observation.

Signal 59 (C-4 in β-5) appears to be weakened in the spectrum of SP(SO_2)EWL, which would be consistent with opening and modification of the hydrofuran ring.

The carbonyl region (160-220 ppm) appears to be very similar for all the lignins. A carbonyl search in DMSO-d_6 above 200 ppm showed possible signals at 200.5 - 200.9 ppm and 206.4 ppm in the spectrum of SP(SO_2)EWL.

Acetylation of the lignins resulted in spectra differing markedly in the relative intensities of the acetate carbonyl signals, with the signal for secondary acetate being much weaker in the spectrum of SP(SO_2)EWL, (cf. insets Figs. 1 and 2). This is further support for the low content of unmodified β-0-4 units. In addition, signal 31 is not shifted, which supports assignment to an ether linked carbon atom as discussed above, but does not support assignment to C-α in β-0-4 linked structures. The ratio of aromatic acetate to primary aliphatic acetate may be a little higher in acetylated SP(SO_2)EWL. Both opening of the hydrofuran ring of β-5 structures and loss of, or reduction at, C-γ would have this effect. A higher ratio was also supported by the p.m.r. spectra.

Elemental Analysis Data

No sulphur was found in SP(SO_2)EWL, indicating that, if sulphur-containing moieties are introduced by

SO_2 pretreatment prior to steam explosion by the Siropulper process, they are not retained.

A Comparison with Acidic Sulphite Pulping

It is interesting to compare the effects on lignin structure of SO_2 pretreatment followed by steam explosion treatment, with those of acidic sulphite pulping.[11,12]

In acidic sulphite pulping, sulphonation at the α-carbon atom of β-aryl ethers competes effectively with enol ether formation, for the carbocation formed initially.[11,12] In contrast, with the steam explosion process, sulphonation is not observed and formation of enol ethers, which undergo further reactions appears to prevail.[8]

Also in contrast to steam explosion treatment, the phenylcoumaran ring of β-5 linked structures is not opened or modified by acidic sulphite pulping and sulphonation at C-γ takes place instead. It appears, therefore, that the nucleophilicity of SO_2 is insufficient under the conditions of this steam explosion process for sulphonation to take place, so that catalysed reactions prevail. In acidic sulphite pulping, sulphonation is the dominant reaction.

Conclusions

1. The major effect of SO_2 pretreatment on the structure of the soluble lignin appears to be a decrease in the abundance of unmodified β-0-4 and β-5 linked units. The NMR data appear to be consistent with substantial retention of these interunit linkages and modification by, for example, formation of the C_6C_2-enol ether GCH=CHOAr and addition products of it, in the case of β-0-4 linked units. In the case of β-5 linked units, modification could include formation of stilbene and methyl-substituted phenylcoumarone and

phenylcoumaran structures. It appears, therefore, that the SO_2 pretreatment of the cook affects the relative importance of hydrolysis pathways and changes the distribution of hydrolysis products, presumably as a result of the higher acidity.

2. A knowledge of side-chain reactivity is important for development of uses for exploded wood lignins. The side-chain reactivity of SP.EWL and IP.EWL has a substantial contribution from hydroxy groups, as well as from carbonyl groups and α,β unsaturation, but, in the case of $SP(SO_2)EWL$, the latter may make the greatest contribution, while hydroxy-groups are likely to be less important.

3. SO_2 appears to act only as a catalyst.

EXPERIMENTAL

Steam explosion treatment of New Zealand *Pinus radiata* wood by the Siropulper Process[1,2] was carried out by the Division of Chemical and Wood Technology, CSIRO, Australia. This process differs from the Iotech,[3,13] in cooking temperature and time, addition of gas to the digester and discharge nozzle design.[2,14] SO_2 pretreated wood was steam exploded using the same processing conditions as for the untreated wood (205°C, 13.8 MPa, 15 min. cook). SO_2 pretreatment involved exposing the chips to SO_2 gas at ambient temperature and atmospheric pressure, prior to the steam explosion treatment.[2]

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 7-10% of dry wood weight.

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

<u>^{13}C NMR Spectra</u> were run at 30°C on a Varian FT-80A spectrometer operating at 20 MHz as described previously.[4] The solvent was acetone-d_6/H_2O (9:1 by volume). The acetone-obscured region was examined in DMSO-d_6. Resolution was improved by Lorentzian to Gaussian transformation using the same function for each spectrum and signal multiplicities were determined by a gated spin-echo sequence.[4]

<u>Elemental Analyses</u> were carried out by the University of Otago Chemistry Department, Dunedin.

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