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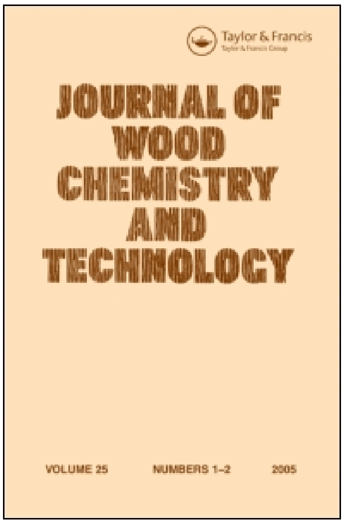

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STEAM-EXPLOSION LIGNINS: FRACTIONATION, COMPOSITION, STRUCTURE AND EXTRACTIVES

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ABSTRACT

The acetone-soluble lignins of steam-exploded *Pinus radiata* and *Eucalyptus regnans* wood were fractionated by sequential extraction with the solvents hexane, diethyl ether, chloroform and acetone. For a given wood and SE process, the fractions showed differences in composition and in the structures of the lignin fragments present. Resin and fatty acid extractives make a significant contribution to the composition of *P. radiata* steam-explosion lignins. They can be partially removed by extraction with hexane, but a fraction may be bound to diethyl ether-soluble lignin fragments. Extractives make an insignificant contribution to the composition of *E. regnans* lignin. The effect of extractives on lignin properties and utilisation of these lignins is briefly discussed.

INTRODUCTION

Steam-explosion pretreatment of lignocellulosics and bioconversion of the carbohydrate fractions to liquid fuels, chemicals or other high value products is an active research area.[1] High value utilisation of the lignin fractions would improve the economic viability of pretreatment and minimise wastage, or low value use, of this substantial component of plant biomass. The composition, structure and properties of lignin fractions are therefore of considerable interest.

The acetone-soluble lignins of steam-exploded *Pinus radiata* wood have a significant wood extractives (resin and fatty acids) content, which may affect their properties and which complicates investigation of their structure by, for example, the technique of ^{13}C NMR spectroscopy.[2] To investigate the role of extractives in composition and structure and to further investigate the structure and properties of these lignins, four steam-explosion (SE) lignins, prepared by three different types of SE process were fractionated by sequential extraction with a number of organic solvents and examined by ^{13}C NMR and IR spectroscopy. One of the lignins was prepared from steam-exploded, extractives-free wood and the remainder from SE whole wood. Structural studies of the unfractionated lignins have been reported previously,[2] except for those prepared by one process, the FRISDP. Two SE processes applied after SO_2 (SD) pretreatment of the wood, the CSIRO, Australia, 'Siropulper' (SSDP) and the Forest Research Institute, New Zealand (FRISDP); and the Siropulper process applied without SO_2 pretreatment (SP), were used to prepare the SE lignins. (See Experimental). SO_2 pretreatment is necessary with softwoods to achieve satisfactory structural breakdown and enzyme access for bioconversion of the cellulosic carbohydrate.[3,4]

A parallel investigation of the acetone-soluble lignin of a hardwood, *Eucalyptus regnans*, SE by one type of process, the SP, was also carried out. A structural study of the unfractionated lignin has been reported previously.[5]

RESULTS AND DISCUSSION

1. Fractionation of *Pinus Radiata* FRISDP Steam-Explosion Lignins

Pinus radiata wood was steam-exploded by the FRISD process before and after removal of extractives with CH_2Cl_2 and the acetone-soluble lignins were prepared. (See Experimental). Both lignins were extracted with hexane (stirred batch) and they gave 6.5% and 0.2% of hexane solubles respectively. (Fig.1).

(a) The Hexane-Insoluble Fractions

These fractions were examined and compared using ^{13}C NMR and IR spectroscopy. Signal assignments have been reported previously,[2,5,6] while revised assignments are discussed below.

All except one of the signals observed in the 0-27 ppm region of the spectra of steam-explosion lignins from whole or (+E) wood are absent in the spectrum of the lignin from extractives-free or (EF) wood and they are therefore attributed to extractives. (See Figs. 1 ,2 and 3).[2]

Signals in the 33-51 ppm region can be assigned primarily to lignin fragments, as eight out of twelve signals are retained in the lignin from (EF) wood. Most of the prominent signals have been assigned, on the basis of their multiplicities and chemical shifts, to side-chain α-methylene groups. A methine group, signal 21' at 47.2 ppm is possibly the β-carbon of a β-β linked (lignan type) of structure. The prominent signal at 50.4 ppm is weak and indefinite in the GASPE (gated spin-echo) spectrum. It may be given by an unusual type of carbon relative to the other types present, or be a composite of

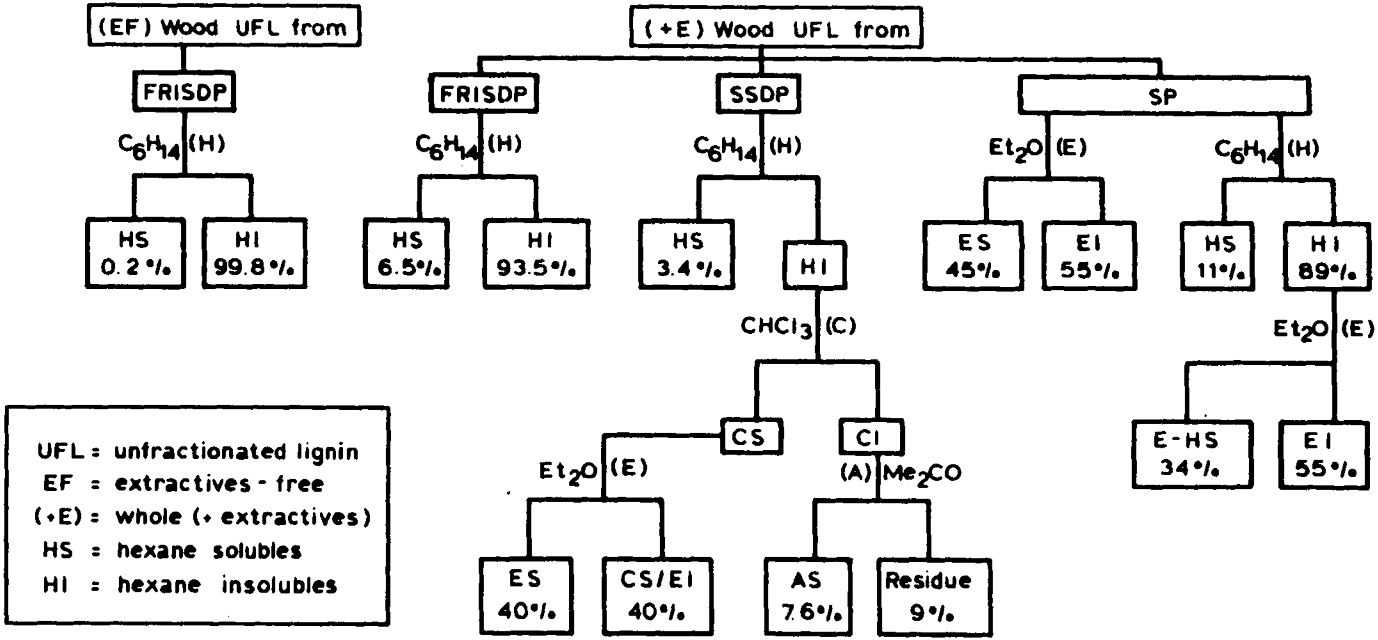

FIGURE 1 Fractionation of acetone-soluble, steam-explosion lignins of *P. radiata* wood.

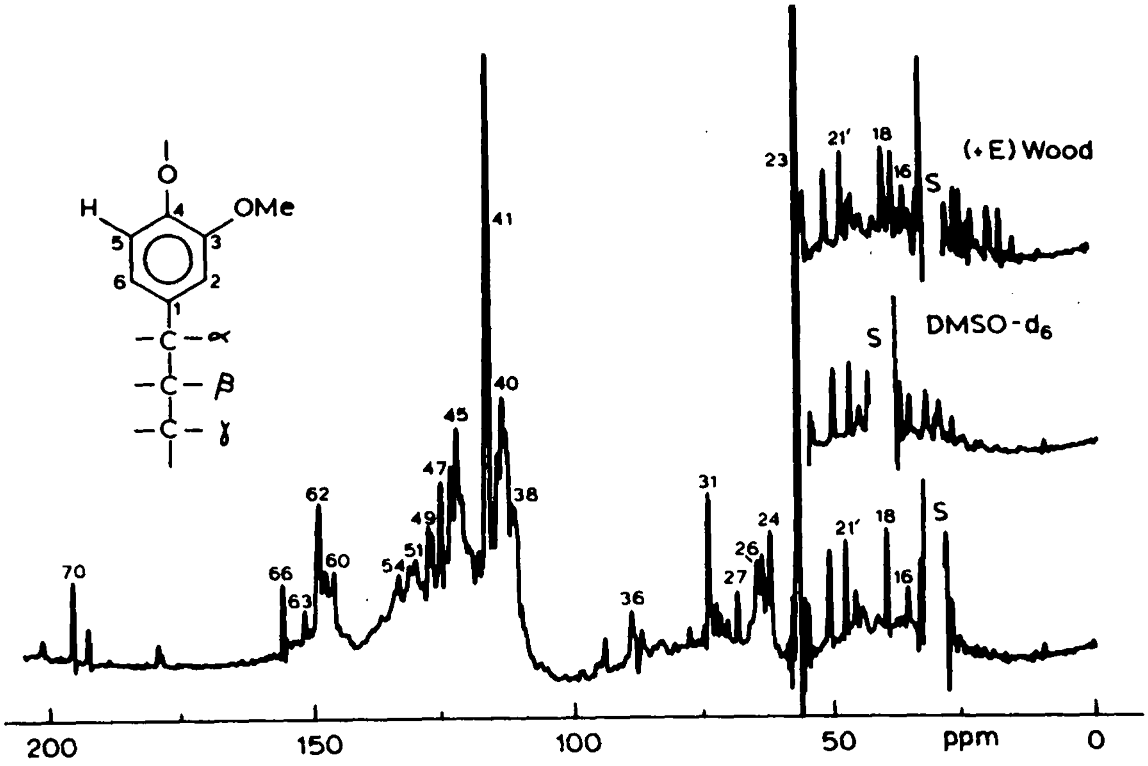

FIGURE 2 Resolution enhanced, ^{13}C NMR spectrum of *P. radiata* FRISDP (EF) wood lignin in acetone-d_6/H_2O (9:1). Insets: 0-50 ppm region in DMSO-d_6, 0-50 ppm region of (+E) wood lignin.

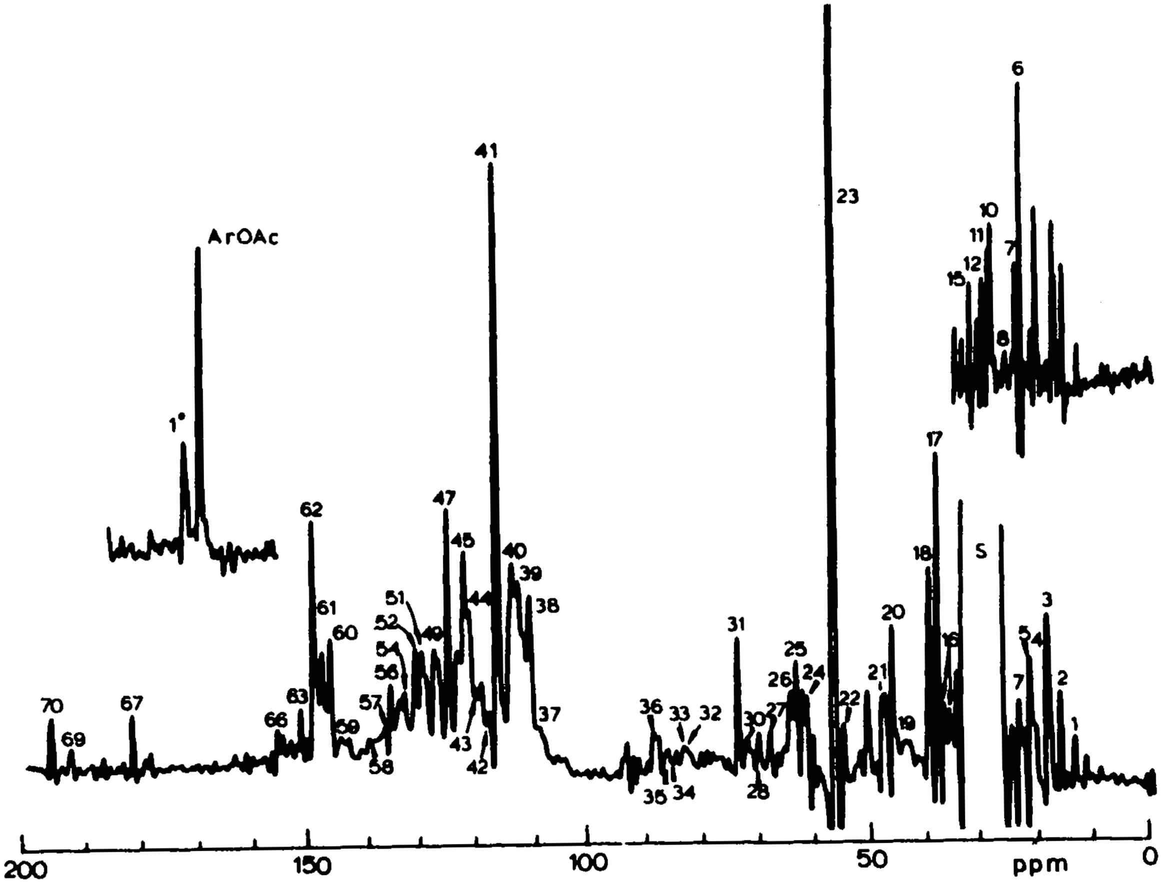

FIGURE 3 ^{13}C NMR spectrum of *P. radiata* SSDP unfractionated lignin in acetone-d_6/H_2O (9:1). Inset: 30 ppm region in DMSO-d_6.[2]

methine and methylene carbon. This signal was assigned previously to diaryl substituted α-carbon, e.g., as in $GG'CH.CH_2OAr$.[2] A contribution from the structure $GCH_2.CHO$ is also possible and may be supported by the presence of a weak carbonyl signal at 201.1 ppm.

The solvent-obscured region (27-33 ppm) was examined in DMSO-d_6 solvent (Fig. 2 inset). Three signals were observed for the lignin from (EF) wood compared with six for lignins from (+E) wood. Therefore lignin fragments, as well as extractives, contribute to the signals observed in this region. The lignin signals are due to methylene carbon and their chemical shifts (28.9, 29.5 and 31.3 ppm) would be consistent with bridging methylene groups in, for example, 5-5 linked $ARCH_2Ar$ and with the β-methylene group of an ω-hydroxypropyl side-chain.

Repetitive (3X) extraction of the acetone-soluble lignin from (+E) wood with hexane did not completely remove the signals assigned to extractives, which may be evidence for some incorporation of them into the SE lignin (Fig. 2 inset and Fig. 3). Only one very weak signal attributable to extractives is detectable downfield of 50 ppm, at 180.9 ppm, in the hexane-extracted lignin. This signal occurs at 185.1 ppm in $CDCl_3$, while levopimaric acid and a mixture of resin acids give a signal for carboxyl group carbon at 180.7 ppm in acetone-d_6/H_2O (9:1). The weak signal is therefore assigned to the carbonyl carbon of the carboxyl group of resin acids. When hexane extraction is not carried out, a further signal at 135.0 ppm may be contributed by extractives and the signal at 180.9 ppm is quite prominent, but there do not appear to be significant differences in any other signals, arising from, for example, the presence of unsaturated carbon atoms of resin acids. This may be due to a combination of factors, such as the complexity and overlapping of signals in this region, the content and composition of the extractives and structural changes resulting from bonding to lignin fragments. (Also see section 3c).

The spectra of the FRISDP and SSDP lignins (see Fig. 3 and below) are almost identical, which indicates that the structural effects of the two processes are very similar. IR spectroscopy also supported this view, however, elemental analysis showed the presence of 0.44% sulphur in the hexane-extracted FRISDP lignin from (EF) wood, while none was detected in the SSDP lignin. Assuming sulphonation of lignin units, 2.5% of units would be involved.

The IR spectrum of the hexane-extracted lignin from (EF) wood (Fig. 4) shows a weak band at 972cm^{-1} (trans double bond), a strong band at 1664cm^{-1} (conjugated carbonyl) and a somewhat weaker band at 1714cm^{-1} (unconjugated, carboxyl and lactone carbonyl). The IR spectrum of the corresponding lignin from (+E) wood is almost identical to that of the (EF) lignin, the band at 1664cm^{-1} appearing to be slightly weaker in the former. The 1714cm^{-1} band is not detectably stronger. In contrast, the spectrum of a sample of (+E) wood unfractionated lignin (i.e. lignin which had <u>not</u> been extracted with hexane) showed somewhat stronger 1714cm^{-1} and 2940cm^{-1} bands (Fig. 4). However, the extractives appear to make only a fairly minor contribution to the strength of the 1714cm^{-1} carbonyl band, which therefore appears

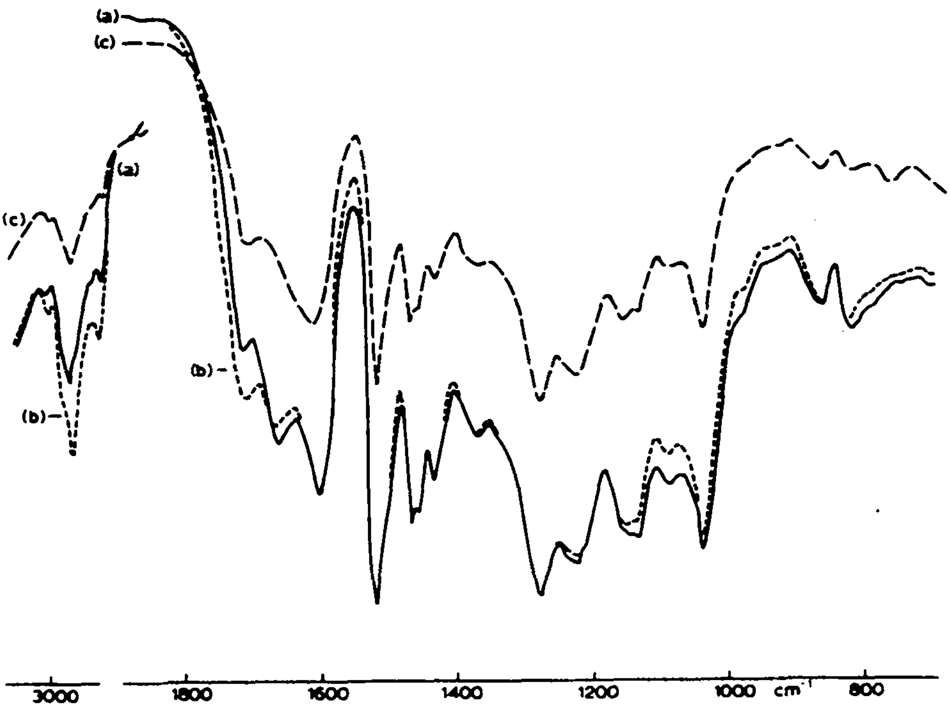

FIGURE 4 IR spectra of *P. radiata* lignins: (a) FRISDP (EF) wood lignin, (b) FRISDP (+E) wood UFL and (c) the SSDP acetone-soluble fraction.

to be primarily due to carbonyl groups in lignin fragments.

(b) The Hexane-Soluble Fractions

The IR spectrum of the hexane-soluble fraction obtained from the (+E) wood unfractionated lignin showed strong bands characteristic of resin acids, but only weak bands characteristic of lignin phenolics, while the spectrum of the fraction obtained from the (EF) wood lignin was characteristic of lignin. These fractions are compared with that from SSDP lignin and discussed further in section 2d.

The (+E) wood HS fraction was also examined by TLC and GLC. It was found to be comprised primarily of resin and fatty acids in the ratio of about 2:1. Abietic acid was the predominant resin acid and oleic the predominant fatty acid, with palmitic and linoleic the next most abundant.

2. Fractionation of *Pinus Radiata* SSDP Steam-Explosion Lignin

The acetone-soluble lignin of *Pinus radiata* wood steam-exploded by the SSD process was fractionated by sequential extraction with (1) hexane, (2) chloroform and (3) acetone in a soxhlet apparatus. The chloroform soluble fraction was further extracted with diethyl ether, repetitively (4x), by the stirred batch method. The fractionation gave 3.4% hexane solubles, 40% diethyl ether solubles, 40% chloroform solubles/ether insolubles, 7.6% acetone solubles and 9% residue. (Fig. 1). The two major fractions were examined by ^{13}C NMR spectroscopy. The size of these fractions should be noted, as ether and chloroform, while accepted as being good solvents for extractives are not normally regarded as solvents for lignins.

(a) The Chloroform-Soluble/Ether-Insoluble Fraction

The spectrum downfield of 50ppm is very similar to that of the unfractionated lignin (UFL). (Fig.3).[2] A few signals are apparently absent (a) or weaker (w), these being at 180.9 (a), 135.0 (a), 130.8 (w), 127.2 (a), 124.6 (w) and 62.2 (a) ppm, while signals corresponding to C-2 and C-γ of β-O-4 linked units (at 112.4 and 61.7 ppm) may be stronger. (The first two absent signals were assigned above to extractives and the others have been assigned to carbon in less abundant or more structurally modified units of the original lignin).[2,6]

The 33-51 ppm region of the spectrum is almost identical to that of the FRISDP lignin from (EF) wood discussed above, i.e. units with structurally modified side-chains containing non-oxygen-bound carbon appear to be retained in this fraction. In the 0-27 ppm region, there are only a few weak and very weak signals, showing this fraction to be essentially free of extractives.

(b) The Diethyl Ether-Soluble Fraction

In contrast to the chloroform-soluble /ether-insoluble fraction, the spectrum of this fraction is rich in the signals assigned to extractives, in the 0-50 ppm region, and signals 56 and 67 at 135.0 and 181.0 ppm are prominent. (Fig. 5a). The other signals apparently absent or weaker in the spectrum of the chloroform-soluble /EI fraction are also prominent. The presence of a stilbene in this fraction is suggested by TLC, which gave an orange spot.[7] Stilbenes and C-5 linkages give signals in the 120-130 ppm region.[8] The lignin fragments appear to be depleted in β-O-4 and β-5 linked units (e.g. signals 24 (C-γ), 35 (C-β), 39 (C-2), and 22 (C-β), 36 (C-α), 59 (C-4)), and in units etherified at the C-4 carbon atom (signal 63), and to be enriched in less abundant or more structurally modified units of the original lignin. The apparently high extractives content of this

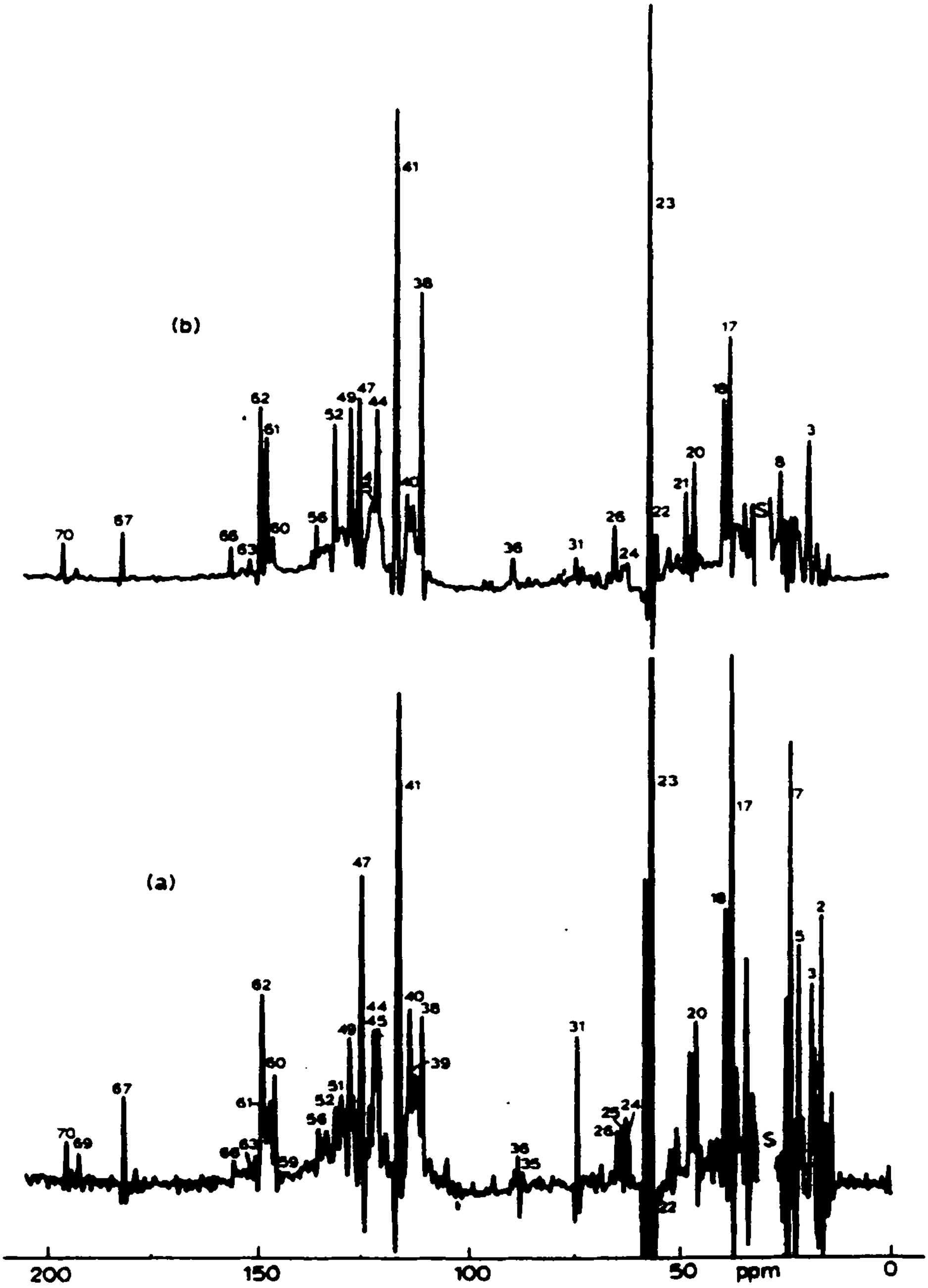

FIGURE 5 ^{13}C NMR spectra of *P. radiata* lignin fractions: (a) ES from the SSD process, (b) E-HS from the S process.

fraction, despite the hexane extraction step, may be evidence for some incorporation of them into lignin fragments, as suggested above for the FRISDP lignin and in section 3 below. However, less efficient removal by soxhlet, as opposed to stirred batch, extraction may contribute to the high content in this case. It is estimated that about half the extractives content of the UFL has been retained in this fraction.

(c) IR Spectroscopy of Extractives-Free Fractions

A comparison of the IR spectra of the chloroform-soluble/ether-insoluble fraction, the acetone-soluble fraction and the acetone-insoluble residue found them to be identical except for a weak band at 755cm^{-1} (an aromatic C-H deformation band). This band was very weak in the spectrum of the chloroform-soluble/EI fraction and most prominent in the spectrum of the acetone-soluble fraction and it may reflect differences in the mix of aromatic ring substitution patterns. The IR spectra of these three fractions have a weak trans double bond band at 972cm^{-1} and a moderately strong carbonyl band at 1714cm^{-1}. (Fig. 4). Any band at 1664cm^{-1} is not resolved from the strong 1605cm^{-1} aromatic skeletal band and the moderately strong 1714cm^{-1} carbonyl band. In the spectrum of the unfractionated lignin, although the 1714cm^{-1} band would be enhanced by extractives, the 1664cm^{-1} band is resolved and the 972cm^{-1} band appears to be stronger, which indicates some depletion of lignin side-chain unsaturation and conjugated carbonyl groups in the above three fractions.

(d) Comparison of the Hexane-Soluble Fractions of the SSDP and FRISDP Steam-Explosion Lignins

The IR spectra of the HS fractions of SSDP and FRISDP (+E) wood, steam-explosion lignins show only weak, or very weak bands characteristic of lignin phenolics, but strong bands at 1707-1700cm^{-1} and 1469-1465cm^{-1} characteristic of resin acids. (Fig. 6). In contrast, the IR spectrum of the HS fraction of the FRISDP (EF) wood lignin is characteristic of lignin and it has strong bands at 1668cm^{-1} for aryl conjugated carbonyl groups, at 1748cm^{-1} as discussed below, and at 1034cm^{-1} for primary alcohol groups (Fig. 6). However, the yield of these lignin fragments given by the steam-explosion process appears to be very low, in comparison to the yield of HS material (primarily extractives) obtained from the (+E) wood lignin, being 0.2%, cf. 6.5%, of the UFL. (Fig. 1).

All the HS fractions, including that of the FRISDP (EF) wood lignin, show a band at 1748-1732cm^{-1}. It appears, therefore, that this band is given by lignin fragments and it could be due to the carbonyl of a lactone or ester group.

3. Fractionation of *Pinus Radiata* SP Steam-Explosion Lignin

The acetone-soluble lignin of *Pinus radiata* wood steam-exploded by the S process was fractionated as follows: (1) by stirred batch extraction with diethyl ether, giving 45% ether solubles (ES) and 55% ether insolubles (EI); (2a) by stirred batch extraction with hexane, giving 11% hexane solubles (HS) and 89% hexane insolubles (HI); (2b) by stirred

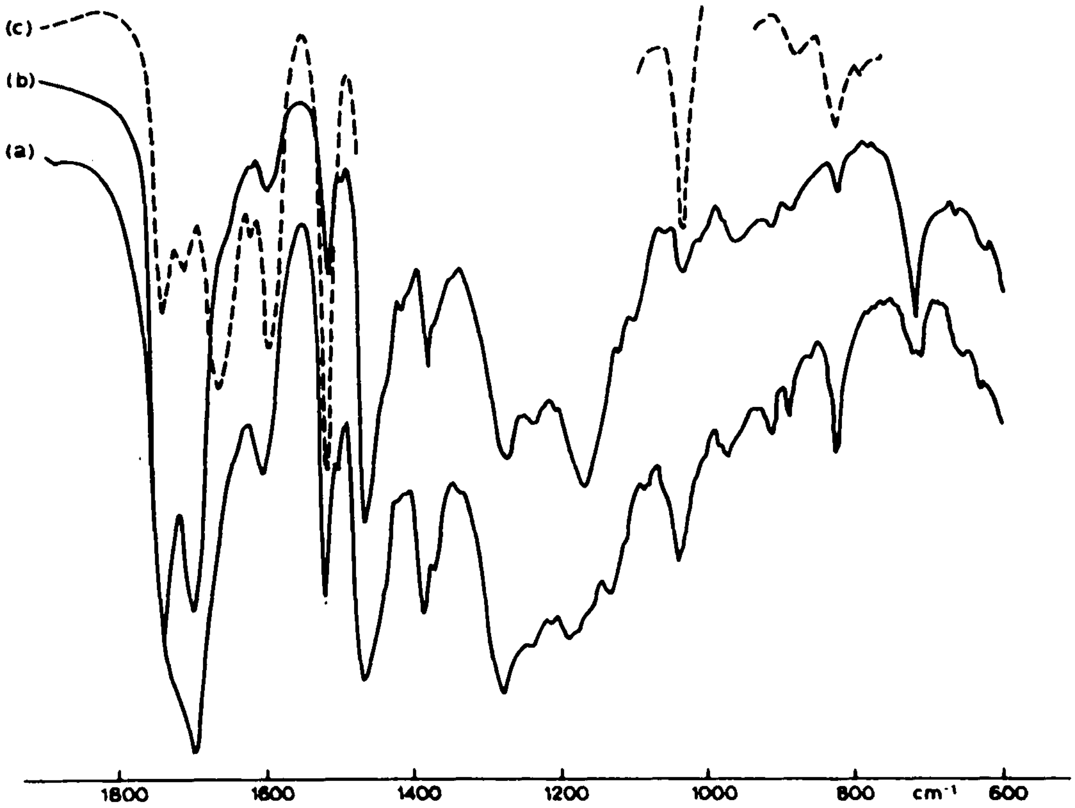

FIGURE 6 IR spectra of *P. radiata*, hexane-soluble fractions from: (a) the SSD process, (b) the FRISD process and (+E) wood, (c) the FRISD process and (EF) wood.

batch extraction of the HI with diethyl ether, giving an ether-soluble fraction free of hexane solubles (E-HS), corresponding to 34% of the UFL. (Fig. 1).

(a) The Ether-Insoluble and Hexane-Insoluble Fractions

The spectra of both fractions are quite similar, but they do show the following differences: (i) In the 0-50 ppm region, the EI fraction (in acetone-d_6/H_2O) shows only a few weak signals with chemical shifts corresponding to signals 3, 8, 16, 17 and 19 reported previously.[2,6] In contrast, the HI fraction shows a range of stronger signals, identical to that in the unfractionated lignin,[2] reflecting incomplete removal of extractives. (ii) In the 50-200 ppm region, the only significant differences are apparently weaker signals 38, 47, 49 and 52 (at 110.0, 124.8, 126.9 and 130.7 ppm) in the EI fraction (see (b) below) and a much weaker signal at 181.0 ppm. Therefore, the spectrum of the HI fraction more closely resembles that of the UFL, from which it differs only in having considerably lower signal intensities in the 0-50 ppm region (about 1:2.5), possibly slightly lower intensities of signals 47 and 52, and an apparently weaker signal at 181.0 ppm.

The amount of β-ether cleavage and the ratio of β-O-4 to β-5 linked units appear to be similar in the HI, the EI and the UFL. However, the actual amounts of these two units present appear to be higher in the EI fraction and the amount of β-ether cleavage is possibly somewhat lower.

The IR spectra of the UFL and of the HI and EI fractions differ only in the strength of the carbonyl band at 1704cm^{-1}, which is slightly weaker in the HI spectrum and considerably weaker in the EI spectrum, due to the removal of extractives and ES lignin fragments.

(b) The Ether-Soluble and E-HS Fractions

Both of these fractions show a range of prominent signals in the 0-50 ppm region like that given by the UFL, but signal intensities are about 2.5 times higher in the ES fraction. (Fig. 5b). The rest of the spectra are very similar, apparently differing only in the intensities of signal 50 at 128.8 ppm (assigned in part to unsaturated carbon), and an unassigned signal at 123.6 ppm, which are very weak in the E-HS spectrum and therefore concentrated in the HS fraction.

In the aromatic region, both fractions are enriched in the signals depleted in the EI fraction, namely 38, 47, 49 and 52. These signals have been assigned in part to carbon in C-5 linked structures and in units having α,β-unsaturation, α-carbonyl and α-methylene groups.[2,6] In comparison with the insoluble fractions, or the UFL, both fractions are severely depleted in β-O-4 and β-5 linked units and they contain considerably more lignin units with a free phenolic hydroxy-group. The E-HS fraction therefore appears to be richer in structurally modified units and in the less abundant units of the original lignin, with depletion of β-O-4 linked units being greater than that of β-5. The prominence of the signals in the 0-27 ppm region of the ES fraction and the failure of hexane extraction to more effectively remove them may again reflect some bonding of non-phenolic extractives of the original wood to lignin fragments. The E-HS fraction therefore appears to be rich in lower MW lignin fragments containing, for example, side-chain unsaturation, carbonyl groups, 5-5 and β-5 linkages, and also to contain extractives, which may be bound to the fragments. The presence of stilbenes is supported by TLC of the E-HS fraction, which showed an orange spot, as reported above for the ES fraction of the SSDP lignin.

In comparison, the EI fraction appears to be rich in less structurally modified and higher MW material. By analogy with the lignins from the steam-explosion processes with SO_2 pretreatment, the signals in the 0-50 ppm region of the SP lignin are most likely due to non-oxygen-bound carbon of modified lignin fragments and to extractives, both phenolic and non-phenolic (resin and fatty acids), of the untreated wood.

(c) <u>The Hexane-Soluble Fraction</u>

The ^{13}C NMR spectrum of this fraction in <u>$CDCl_3$</u> shows signals concentrated in the 0-50 ppm region. It appears to be comprised largely of non-phenolic (i.e. resin and fatty acid) extractives, as for example, signals attributable to abietic acid and signals at 29.1 and 29.6 ppm are prominent, and there is a strong carbonyl signal at 185.1 ppm and a weaker one at 180.0 ppm.[9,10] Signals attributable to lignin phenolics are weak. The IR spectrum also shows only weak bands attributable to lignin phenolics, at 1518 and 1610cm^{-1}, while bands characteristic of resin and fatty acids are prominent, e.g. at 2938, 2860, 1700, 1465, 1280 and 720-710cm^{-1}.

Comparison of the NMR spectrum with the spectra of the ether-soluble fractions indicates that, in the aromatic region, signals 45, 47, 49, 50-51, 52, 56, and the one at ca. 123.6 ppm (between 46 and 47), could be enhanced by contributions from the unsaturated carbon of non-phenolic extractives and other unidentified hexane-soluble material.

Steam-explosion of extractives-free wood, as described above for the FRISD process, would be necessary to further clarify the role of extractives in this process, but such a study is now unwarranted, as the much more effective processes with SO_2 pretreatment have superceded those without.[3,4]

Summary

The lignins extracted by acetone from steam-exploded *Pinus radiata* wood contain extractives, which consist primarily of resin and fatty acids. These extractives are incompletely (e.g. about 60%) removed by repetitive extraction with hexane, which may indicate some reaction with and incorporation into the SE lignin. The nature of the bonding involved is unclear and merits further investigation. Ester linkages and covalent bonding involving their unsaturated carbon are possibilities. The unfractionated lignins are therefore a source of non-phenolic extractives, which can be partially removed, together with a small amount of phenolic material, by extraction with hexane. Depending on their content in the UFL's, the presence of these extractives could affect the properties and utilisation of these lignins, e.g. their thermal softening, or glass transition, temperatures and the

properties of phenolic adhesive, or polymer, formulations.

For steam-explosion processes both with and without SO_2 pretreatment, a large fraction of the hexane-extracted UFL, corresponding to 34-40% of the total UFL, is soluble in diethyl ether. It contains both lignin fragments and the residual, possibly lignin bound, extractives. The remaining fraction, ca. 55% of the UFL, is essentially free of non-phenolic extractives. A surprisingly large amount of this fraction may be soluble in chloroform, as shown by the 71% solubility for the SSDP lignin. Simple sequential extraction with a number of solvents can therefore effect a separation into fractions, which differ widely in composition and properties.

The lignin fragments in the ether-soluble fractions of the SP lignin appear to be enriched in lower MW, more structurally modified fragments and less abundant units of the original lignin, but depleted in the major units, i.e. those with β-O-4 and β-5 linkages. The situation is a little different for the SSD and FRISD processes, in that fewer unmodified β-O-4 and β-5 linked units survive.[2] Potential uses for this type of fraction would most likely require further separation and identification of its components. Despite possible depletion of some reactive groups, substantial amounts of unsaturation, carbonyl groups, side-chain and free phenolic hydroxy-groups, and structurally modified side-chains appear to be retained in the EI fractions. They may therefore have potential for modification and use in polymer formulations.

4. Fractionation of *Eucalyptus Regnans* SP Steam-Explosion Lignin

The acetone-soluble lignin of *Eucalyptus regnans* wood steam-exploded by the S process was fractionated by sequential extraction with hexane, chloroform and 95% acetone-water in a soxhlet apparatus, as described for *Pinus radiata* SSDP lignin in section 2 above. The chloroform-soluble fraction was further extracted with diethyl ether (4x by the stirred batch method). Fractionation gave 0.1% hexane solubles, 11% diethyl ether solubles, 58% chloroform solubles/ether insolubles, 12% acetone solubles and 19% residue. The diethyl ether-soluble and chloroform-soluble/ether-insoluble fractions were examined by ^{13}C NMR spectroscopy.

(a) The Chloroform-Soluble/Ether-Insoluble Fraction

The spectrum of this fraction is almost identical to that of the unfractionated lignin published previously,[5] but the extent of β-ether cleavage could be slightly higher and signal 30 at 127.4 ppm (reflecting α,β-unsaturation or an α-CO group) appears to be weaker. The IR spectrum of this fraction is also identical to that of the UFL published previously.[5]

(b) The Ether-Soluble Fraction

This fraction is essentially free of syringyl units etherified at C-4, as signals at 153.5 and 138.5 ppm are very weak (Fig. 7). Signals 22, 8, 13 and 17 for C-2,6, C-γ, C-α and C-β in β-O-4 linked units also appear to be weak or absent, indicating that there are very few residual units containing the major interunit linkage, in this fraction. In

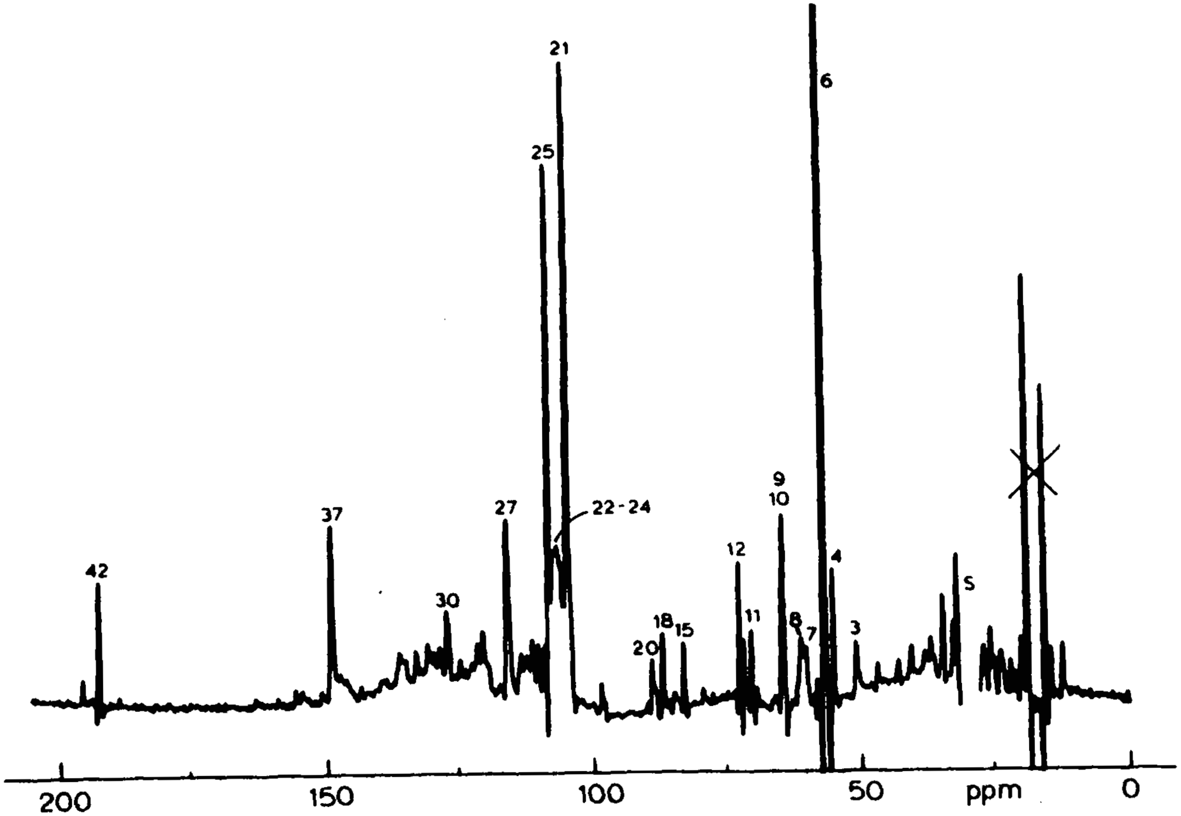

FIGURE 7 ^{13}C NMR spectrum of the ether-soluble fraction of *E. regnans* lignin.

contrast, signals for syringaresinol, syringaldehyde, β-5 linked units, α-CHO groups (signals 21, 25, 4, 9-10, 12, 18, 20 and 42), and units with minor or modified side-chains, e.g. signals 11, 15 and 30, (at 70.0-71.5, 82.8 and 127.4 ppm) are prominent.[5] The fraction appears to be enriched in guaiacyl units and the very high free phenolic hydroxy-group content is support for it containing primarily low MW fragments comprised of the less abundant units of the original lignin and units with modified side-chains. The origin and identity of weak signals in the 0-50 ppm region, which were insignificant in the spectrum of the UFL, are not clear. Some may be given by lignin fragments and others by non-lignin material or contaminants.

(c) The Hexane-Soluble Fraction

This insignificant fraction of the UFL (0.1%), was examined by IR spectroscopy. The spectrum showed bands characteristic of lignin fragments and a strong carbonyl band with maxima at 1738-1718cm^{-1} and 1682cm^{-1}. An enhanced band at 1468cm^{-1} and bands at 1200-1175 and 732-722cm^{-1} suggested the presence of fatty acid extractives.

Summary

The unfractionated lignin of this hardwood contains a negligible amount of extractives and it gives only a small diethyl ether-soluble fraction, comprised of low MW fragments with a high content of free phenolic hydroxy and α-CHO groups. Syringaldehyde, syringaresinol, β-5 linked units and possibly alkyl ethers appear to be the predominant structures present. A large fraction is chloroform soluble and structurally very similar to the UFL, i.e. it has a substantial content of fragments with β-O-4 linkages in an unmodified environment, as well as of fragments with β-β, α-O-γ; and β-5 linkages. It has a high content of free phenolic hydroxy-groups and alone, or in combination with the less soluble fractions, appears to have potential for modification and use in polymer formulations. Utilisation of the ether-soluble fraction may depend on further separation and identification of the components. Alternatively, as the extractives content is negligible and the ether-soluble fraction small, the UFL may have similar potential for use, to that of the less soluble fractions discussed above.

In comparison to the steam-explosion lignins of the softwood, the very low extractives content and higher yield of the hardwood lignin appear to be advantages. (Yields are given in the Experimental Section). On the other hand, extractives, particularly resin and fatty acids, are valuable products. A comparison of the chloroform-soluble (major) fractions of the *P. radiata* SSDP and *E. regnans* SP lignins shows that both contain substantial amounts of reactive groups, i.e. free phenolic and side-chain aliphatic hydroxy, carbonyl and unsaturated groups. There are also indications of condensation reactions of aromatic ring carbon with formaldehyde or other electrophilic centres and there is the potential for further reactions. These should be favoured by the guaiacyl lignin with its lower ring substitution and they would introduce additional reactive groups and carbon-carbon linkages between fragments. Prospects for utilising both types of lignin in the production of valuable products therefore appear to be quite promising.

EXPERIMENTAL

Steam-explosion treatment of *Pinus radiata* and *Eucalyptus regnans* wood chips by the CSIRO, Siropulper (S) and Siropulper with SO_2 pretreatment (SSD) processes has been described previously.[2,5] Treatment by the Forest Research Institute with SO_2 pretreatment (FRISD) process was carried out at the FRI, New Zealand. It involved heating the SO_2 pretreated *P. radiata* with steam at 215°C for 3 minutes before pressure release. One sample of the sawdust used was pre-extracted with methylene chloride, to remove extractives, prior to steam explosion. This process differs from the SSDP in cooking temperature and time (215°, 3 min. cf. 205°, 15 min.), discharge nozzle design, method of heating and pressurising the digester and amount of SO_2 absorbed during pretreatment (2.5% cf. 6%).

The acetone-soluble lignins were prepared as described previously.[2,5] They were obtained in yields corresponding to 8.9, 8.5 and 7.2% of the total (water solubles + insolubles), dry, SE wood sample, when *P. radiata* was treated by the FRISD, SSD and S processes respectively. Yields were 8.5% for extractives-free *P. radiata* treated by the FRISD process and 17% for *E. regnans* treated by the S process. The lignins were fractionated by extracting them with hexane, diethyl ether, chloroform and acetone, using either a repetitive stirred batch or soxhlet extraction method, as outlined in the text and Fig. 1.

^{13}C NMR and IR spectra were run on Varian FT-80A and Perkin-Elmer 580 instruments. The former operated at 20MHz. Lorentzian to Gaussian transformation functions were applied to improve resolution and signal multiplicities were determined by a gated spin-echo sequence, as described previously.[6] The solvent was acetone-d_6/H_2O (9:1, v/v) and DMSO-d_6 was used to examine the acetone-obscured region. IR samples were run either as KBr disks or films. Differences in NMR signal intensities discussed in the text were of sufficient magnitude to be real and not artifacts and their validity is based on examination of both resolution enhanced and normal FT spectra. Normal FT spectra were also used to check that the line sharpening parameters used for the resolution enhanced spectra were not producing artifact peaks.

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

TLC of ether-soluble fractions was carried out using 75% ether-hexane and chloroform-methanol-water (8:2:0.1). For TLC of resin and fatty acids and their methyl esters, hexane-ether-acetic acid (90:10:1) was used.

GLC of the extractives was carried out on a BP-1 capillary column at 150→300°C.

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