

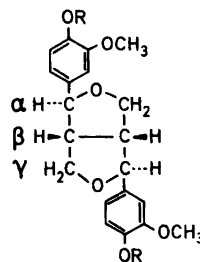
## NMR Studies of Lignins. 6. Interpretation of the $^1\text{H}$ NMR Spectrum of Acetylated Spruce Lignin in a Deuterioacetone Solution

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$^1\text{H}$  NMR investigations of spruce and birch lignins have been reported in this series.<sup>1</sup> Attempts to detect  $\beta$ - $\beta$  structures of the pinosresinol type (1) in spruce lignin have failed,<sup>1d,e</sup> while clear evidence for the occurrence of this type of structure could be obtained in studies of birch lignin.<sup>1b,c</sup> It has now been found that signals from pinosresinol structures appear in spectra of acetylated spruce lignin in an acetone solution. Such spectra also exhibited signals which could be attributed to the presence of trace amounts of coniferyl alcohol end groups. Furthermore, the spectra provided a basis for a discussion of the occurrence of  $\alpha$ -aryloxypropionophenone structures in spruce lignin. The exchange of chloroform for acetone as a solvent results in distinct alterations of the spectrum of



- 1 R = H or adjacent lignin unit
- 2 R =  $\text{CH}_3\text{CO}$
- 3 R =  $\text{CH}_3$

acetylated spruce lignin (see Ref. 1d and Fig. 1). Since the spectral changes are those expected from model compound studies, the solvent dependence provides support for the interpretations presented in Table 2 and in Ref. 1d.

Model compound data are summarized in Table 1. The results from both the present examination of model compounds and previous studies of chloroform solutions of model compounds<sup>1c</sup> provided a basis for the interpretation of the spectrum for spruce lignin (Fig. 1) given in Table 2.

A small but clearly discernible peak at  $\delta$  3.12 in the lignin spectrum (Fig. 1) is attributed to  $\text{H}_\beta$  in  $\beta$ - $\beta$  structures of the pinosresinol type (the peak at  $\delta$  3.12 was found in spectra of Björkman lignins as well as in those of lignins purified by liquid-liquid extraction, cf. Ref. 1d). A compari-

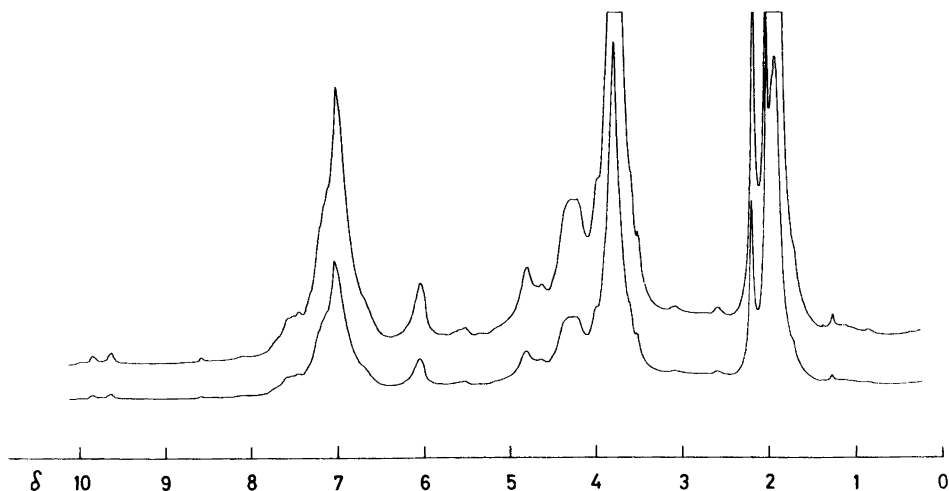
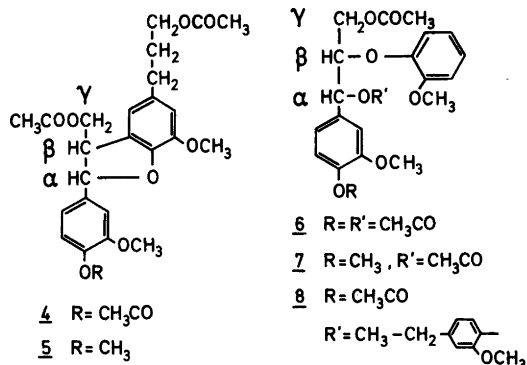


Fig. 1.

Table 1.  $^1\text{H}$  NMR data for lignin model compounds (solvent,  $\text{CD}_3\text{COCD}_3$ ).  $\delta$  Values;  $J$  values in Hz are given in parentheses.

Compound	$\text{H}_\alpha$	$\text{H}_\beta$	$\text{H}_\gamma$	$\text{H}'_\gamma$	$\text{CH}_3\text{O}$	$\text{CH}_3\text{CO}$
2	4.79(4.2)	3.14(m)	3.92(3.7,9.1)	4.29(7.0,9.1)	3.82 <sup>a</sup>	2.22 <sup>a</sup>
3	4.71(4.3)	3.10(m)	4.22(m) <sup>b</sup>	4.44(5.5,11.1)	3.80 <sup>a</sup> , 3.81 <sup>a</sup>	—
4	5.57(6.6)	3.76(m)	4.32(7.7,11.1)	4.41(5.6,11.0)	3.82, 3.86	1.98, 2.01, 2.22
5	5.49(7.0)	—	4.31(7.5,11.0)	4.38(5.9,11.8)	3.79, 3.80, 3.85	1.98, 2.01
6 (erythro)	6.07(5.1)	4.83(m)	4.22(4.2,11.8)	4.35(6.1,11.9)	3.81, 3.83	1.93, 2.07, 2.22
7 (erythro)	6.01(5.0)	4.82(m)	4.19(4.0,11.9)	4.23(3.8,11.9)	3.79, 3.80, 3.81	1.93, 2.03
7 (threo)	6.06(7.0)	4.78(m)	3.97(5.7,11.9)	4.55(5.8,11.8)	3.79, 3.80, 3.82	1.96, 1.97
8 (erythro)	5.54(5.4)	4.84(m)	4.46(3.9,11.8)	4.41(4.1,11.6)	3.77, 3.79, 3.85	1.89, 2.19
8 (threo)	5.58(4.8)	4.84(m)	4.13(6.5,11.6)	4.60(4.0,11.8)	3.78, 3.79, 3.81	1.92, 2.21
9	—	5.75(4.0,6.4)	4.48(6.4,11.8)	—	3.78, 3.85, 3.90	1.96
10	6.62(1.4,16)	6.22(6.4,16)	4.66(1.4,6.4) <sup>b</sup>	—	3.80, 3.83	2.02
Diaryl-propanediol <sup>c</sup>	6.08(7.4)	3.41(m)	4.11(6.9,11.1)	4.26(6.3,11.1)	3.72, 3.76, 3.78 <sup>a</sup>	1.91 <sup>a</sup>

<sup>a</sup> 6H. <sup>b</sup> 2H. <sup>c</sup> The diacetate of erythro-1,2-bis(3,4-dimethoxyphenyl)-1,3-propanediol.



son with the peak due to formyl protons in cinnamaldehyde units ( $\delta$  9.62) suggests that 2–3 % of the units are involved in pinosresinol structures. The number of cinnamaldehyde units has previously been determined as 4 %, <sup>1a</sup> a result which is in agreement with those obtained by an independent method. <sup>2</sup> The baseline for the 3.12 peak is difficult to define due to the vicinity of the large methoxyl ( $\delta$  3.81) and acetate ( $\delta$  2.21 and 1.95) peaks; this makes the estimation uncertain. Assuming that the peak at  $\beta$  3.12 is actually due to  $\text{H}_\beta$  in  $\beta$ - $\beta$  structures, their number cannot be much less than 2–3 %. A substantially higher frequency (about 5 %) cannot be excluded, however, but seems unlikely judging from earlier experiments with non-derivatized spruce lignin. <sup>1e</sup>

Convincing evidence for the occurrence of pinosresinol structures in spruce lignin has previously been obtained in <sup>13</sup>C NMR investigations of acetylated spruce lignin. <sup>3</sup> Ogiyama and Kondo <sup>4</sup> concluded from the yield of "dilactone" in nitric acid oxidation that spruce lignin contained 5–10 % units in pinosresinol structures. Our results point to a figure which, at the most, is in the neighborhood of the lower limit of this interval.

In previous <sup>1</sup>H NMR spectral studies of spruce lignin it was concluded that the frequency of  $\alpha$ -aryloxypropiophenone structures was low <sup>1a</sup> (presumably less than 2 % of the units). This was

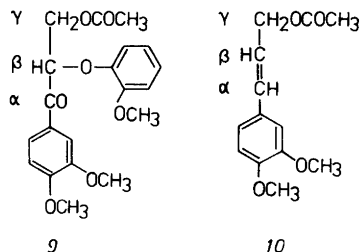


Table 2. Assignment of signals in the  $^1\text{H}$  NMR spectrum of acetylated spruce lignin (Fig. 1). Solvent,  $\text{CD}_3\text{COCD}_3$ . Several peaks are broad and have irregular shapes;  $\delta$  values given always refer to the highest point of the peak.

$\delta$ Value/ppm	Assignment
1.29	Hydrocarbon contaminant
1.95	Aliphatic acetate
2.04	Acetone (solvent)
2.21	Aromatic acetate
2.62	$\text{Ar}-\text{CH}_2-$ (cf. Refs. 1d and 1e)
3.12	$\text{H}_\beta$ in pinoresinol structures
3.81	$\text{CH}_3-\text{O}-$
4.24, 4.32	$\text{H}_\gamma$ in several types of structures
4.65	Methylene protons in cinnamyl alcohol groups
4.81	$\text{H}_\beta$ in $\beta\text{-O-4}$ structures
5.54	$\text{H}_\alpha$ in benzyl aryl ethers (cyclic as well as non-cyclic)
6.05	$\text{H}_\alpha$ in $\beta\text{-O-4}$ structures
7.03, 7.45	Aromatic protons
9.62, 9.84, 9.99	Formyl protons (cf. Ref. 1a)

derived from attempts to reveal the signal from  $\text{H}_\beta$  in such structures ( $\delta$  5.58 in  $\text{CDCl}_3$ ). In acetone solution the signal from  $\text{H}_\beta$  in such units ( $\delta$  5.75) is distinctly separated from signals of other types of structures (Table 1). The absence of a peak at  $\delta$  5.75 in the lignin spectrum (Fig. 1) supports the conclusion drawn in previous  $^1\text{H}$  NMR studies.

*Experimental.*  $^1\text{H}$  NMR spectra were recorded with a 270 MHz instrument, working in the pulse Fourier mode (Bruker WH 270). Acetone- $d_6$  was used as a solvent (internal reference TMS). Temperature: 308 K. Number of scans (lignin spectra): 1000–1200.

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1. a. Lundquist, K. and Olsson, T. *Acta Chem. Scand. B* 31 (1977) 788; b. Lundquist, K. *Acta Chem. Scand. B* 33 (1979) 27; c. Lundquist, K. *Acta Chem. Scand. B* 33 (1979) 418; d. Lundquist, K. *Acta Chem. Scand. B* 34 (1980) 21; e. Lundquist, K. *Acta Chem. Scand. B* 35 (1981) 497.
2. Adler, E. and Marton, J. *Acta Chem. Scand.* 13 (1959) 75.
3. Nimz, H. H. and Lüdemann, H.-D. *Holzfor-schung* 30 (1976) 33.
4. Ogiyama, K. and Kondo, T. *Mokuzai Gak-kaishi* 14 (1968) 416.

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