

NMR Studies of Lignins. 2. Interpretation of the ^1H NMR Spectrum of Acetylated Birch Lignin

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The structure of milled wood lignin from birch (*Betula verrucosa*) has been investigated by ^1H NMR spectroscopy, using a 270 MHz instrument.

The advantage of using a 270 MHz instrument in ^1H NMR spectroscopy of lignins has been exemplified in a previous paper.¹ The present paper describes a ^1H NMR spectrometric study of milled wood lignin (MWL) from birch (*Betula verrucosa*) with such an instrument. The MWL preparation examined had a relatively low xylan content² (2 %); xylan is the predominant carbohydrate constituent in MWL of birch.

The 270 MHz spectrum of MWL from birch (acetate derivative) is shown in Fig. 1. Its comparatively good resolution facilitates an interpretation in structural terms. Such an interpretation is presented below together with a discussion of the results in the light of earlier structural studies of birch lignin and the closely related beech lignin. The high resolution of the 270 MHz spectra of lignins (Fig. 1 and Ref. 1) indicates that ^1H NMR spectroscopy with a 270 MHz instrument can be used to good advantage in comparisons of lignins of different origin and for studies of chemical changes of lignins caused by various treatments.

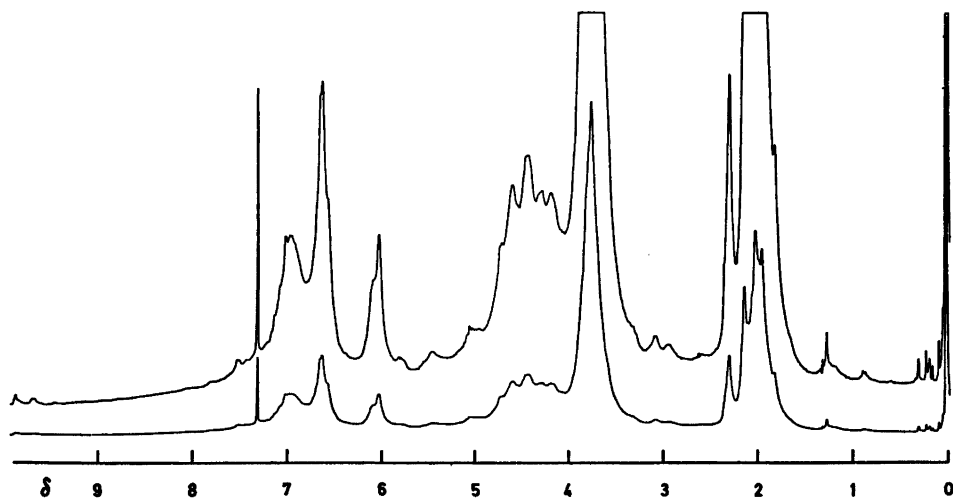
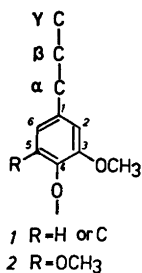


Fig. 1. ^1H NMR spectrum of acetylated milled wood lignin from birch. For peak positions and assignments of peaks, see Table 1.

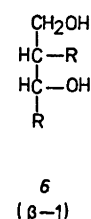
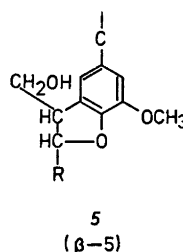
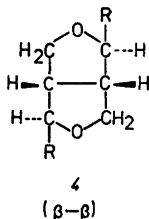
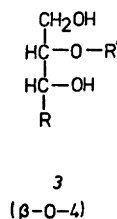


¹H NMR spectra of lignin model compounds and published ¹H NMR data for such compounds (for a review, see Ref. 3) served as a basis for the interpretation of the birch lignin spectrum in Fig. 1. Decoupling experiments were also used for the assignments of the peaks. Due to the polymeric nature of the sample, decoupling was observed as small changes at the expected δ values. The assignments of the peaks are given in Table 1. Data from Table 1 are used in the following without reference. Results from integrations given below are based on the assumption that the peaks in the range δ 6.3–8.0 (aromatic protons and, to some extent, vinyl protons) correspond to 2.3 H/phenylpropane unit. [Assuming equal amounts of units of types 1 and 2 (see below) the number of aromatic protons per unit will vary between 2.0 and 2.5, depending on the proportion of units of type 1 carrying a hydrogen atom at the C-5 position].

Acetyl groups. Peaks at δ 1.95, 2.02, 2.13 and 2.29 are due to acetyl groups. Integrations suggested a total of 1.5 acetyl groups/phenylpropane unit; this figure should correspond to the number of hydroxyl groups in the original lignin preparation. The peak at δ 2.29 (aromatic acetate) corresponds to 0.18 phenolic

Table 1. Assignments of signals in the ¹H NMR spectrum of acetylated birch lignin (Fig. 1). Several peaks are broad and have irregular shapes; δ values given refer consistently to the highest point of the peak.

δ Value/ppm	Assignment
1.26	Hydrocarbon contaminant
1.95	Aliphatic acetate
2.02	Aliphatic acetate (including acetyl groups in xylan ²)
2.13	Aliphatic acetate (including some aromatic acetate, cf. Ref. 3)
2.29	Aromatic acetate
2.94	Unknown; the peak is absent in the spectrum of NaBH ₄ reduced lignin (acetate)
3.08	H _{β} in β - β structures
3.76	Protons in methoxyl groups
4.18	H _{γ} in several structures
4.28	H _{γ} in several structures
4.43	H _{γ} in several structures
4.60	H _{β} in β -O-4 structures
4.70	H _{α} in β - β structures, methylene protons in cinnamyl alcohol units, ¹ xylan. ²
5.04	Xylan. ²
5.44	H _{α} in β -5 structures and non-cyclic benzyl aryl ethers
5.76	Xylose endgroups? (cf. Ref. 2)
6.01	H _{α} in β -O-4 and β -1 structures, certain vinyl protons. ¹
6.60	Aromatic protons in syringyl units (2)
6.94	Aromatic protons in guaiacyl units (1) (a sharp peak at δ 6.99 (Fig. 1) has about the same intensity as the broad 6.94 peak)
7.29	Chloroform (solvent)
7.50	Aromatic protons located <i>ortho</i> to carbonyl groups ¹
9.67	Formyl protons in cinnamaldehyde units ¹
9.86	Formyl protons in benzaldehyde units ¹



R = C-1 in 1 or 2
R' = C-4 in 1 or 2

groups/phenylpropane unit (certain phenolic groups in biphenyl structures are not included in this figure³). This result is in close agreement with earlier estimates of the number of phenolic groups in MWL of birch (Ref. 4, *cf.* also Ref. 5).

β - β Structures (4). (Spectral data for model compounds representative of β - β structures are given in Experimental). The peak at δ 3.08 can be attributed to H_β in β - β structures. This could be confirmed by decoupling experiments. Thus, irradiation at δ 3.08 (but not at δ 3.00 or 3.15) resulted in the appearance of a small peak at δ 4.73; this δ value fairly closely corresponds to the position of the signal from H_α in β - β units. Furthermore, irradiation at δ 4.73 resulted in a sharpening of the 3.08 peak. Integrations suggested that around 6% of the units are involved in β - β structures. This figure is rather uncertain since the 3.08 peak is small and it is difficult to find an adequate baseline (Fig. 1), but in any case the frequency of β - β structures must be rather low. Other studies of hardwood lignins (birch⁷ and beech⁸ lignin) support this view.

β -5 Structures (5). The peak at δ 5.44 can be attributed to H_α in β -5 structures. From model compound data⁶ it can be concluded that signals from H_α in noncyclic benzyl aryl ethers also should contribute to this peak. Integrations suggest some 10% units with H_α in β -5 structures or noncyclic benzyl aryl ethers. This is fairly well in agreement with other studies of birch lignin.⁴

β -1 Structures (6). Separate peaks which can be attributed to β -1 structures do not occur in the birch lignin spectrum and, consequently, no information about such structures can be derived.

β -O-4 Structures (3). The peaks at δ 4.60 (H_β) and 6.01 (H_α) can essentially be attributed to β -O-4 structures. This was supported by decoupling experiments. Irradiation at δ 4.60 caused changes of the 6.01 peak. An additional maximum at δ 6.07 and a shallow minimum at δ 6.04 appeared. The 6.01 peak is fairly well separated from other peaks and is therefore suitable for quantitative estimations. Integration of the 6.01 peak suggested that 40–50% of the units are attached to an adjacent unit by a β -O-4 linkage. Vinyl protons in cinnamyl alcohol units and H_α in β -1 structures contribute to the 6.01 peak, while signals from H_α in

β -O-4 structures with an aryl ether group in the α position (noncyclic benzyl aryl ethers) are located elsewhere.⁶ It is assumed that these errors approximately compensate each other. Earlier ¹H NMR spectroscopic studies of MWL from birch⁹ can also be interpreted to indicate a similar frequency of β -O-4 structures. According to the ¹H NMR spectroscopic measurements β -O-4 structures are the predominant type of structural element in birch lignin. This is in agreement with the fact that acidolytic degradation⁷ of MWL of birch results in the formation of considerable amounts of arylpropanonols and arylpropanones derived from β -O-4 structures.¹⁰ Similarly, results from oxidative (birch⁴) and reductive (beech⁸) degradations as well as ¹³C NMR spectroscopic studies (beech⁸) stress the importance of this type of structure in hardwood lignins.

Aromatic groups. The birch lignin spectrum exhibits two strong peaks in the aromatic region which roughly correspond to guaiacyl units (1) (δ 6.94) and syringyl units (2) (δ 6.60), respectively. Integrations suggest similar amounts of syringyl and guaiacyl units which is in accord with earlier estimates.^{11,12,4}

Formyl groups. The signals at δ 9.67 and 9.86 can be attributed to protons in formyl groups (*cf.* Ref. 1). Integrations indicated that the numbers of such groups were 1–2% each of the benzaldehyde and the cinnamaldehyde types. The number of cinnamaldehyde units in MWL of birch has previously been determined as 1–2% by a UV spectroscopic method.¹² It has earlier been suggested that benzaldehyde units are present in MWL of birch.⁷ It should also be pointed out that the occurrence of benzaldehyde units in beech lignin has been demonstrated by ¹³C NMR spectroscopy.⁸

Comments. The estimates made in the present study account for 60–70% of the side chains in birch lignin. (Side chains in β -1 structures and cinnamyl alcohol groups are included in this figure, although separate estimates of their numbers have not been made.) Residual side chains can be attributed to a variety of structural elements (“detached side chains”,¹³ aryl ketone structures,¹² units with an ester or a carboxylic group,¹² quinonoid structures¹⁴ or their conversion products, dibenzyltetrahydrofuran structures (*cf.* Ref. 8), α - β structures (*cf.* Ref. 8), α - α structures,¹⁵ and certain struc-

tures involving side chains linked to aromatic rings, primarily in the 2 or 6 position⁴). It should be pointed out that even moderate errors in the ¹H NMR measurements markedly influence the number of "residual side chains". The most likely alternative for a lower number of "residual side chains" is a higher frequency of β -O-4 linkages.

The occurrence of α - α structures in lignin has very recently been suggested on the basis of the formation of products with such linkages on oxidation of isoeugenol by a quinonmethide (2,6-di-*tert*-butyl-4-methylenecyclohexa-2,5-dienone).¹⁵ The formation of α - α linkages under these conditions should involve benzyl radicals. It seems possible that benzyl radical intermediates also are involved in the formation of other types of structures in lignin (e.g. α - β , β -2 and β -6 structures).

EXPERIMENTAL

¹H NMR spectra were recorded with a 270 MHz instrument working in the pulse Fourier mode (Bruker WH 270). Chloroform-*d* was used as a solvent. Temperatures were in the range 300–302 K.

¹H NMR spectrum of the diacetate of (\pm)-*syringaresinol* (4, R = 4-acetoxy-3,5-dimethoxyphenyl) (δ units): 2.33 (6 H, s; CH₃CO), 3.10 (2 H, m; H _{β}), 3.84 (12 H, s; OCH₃), 3.96 (2 H, dd, J = 3.5 and 9 Hz; H _{γ}), 4.31 (2 H, dd, J = 7 and 9 Hz; H _{γ}), 4.77 (2 H, d, J = 4 Hz; H _{α}), 6.60 (4 H, s; aromatic protons).

¹H NMR spectrum of the diacetate of (+)-*pinioresinol* (4, R = 4-acetoxy-3-methoxyphenyl) (δ units): 2.31 (6 H, s; CH₃CO), 3.10 (2 H, m; H _{β}), 3.85 (6 H, s; OCH₃), 3.94 (2 H, dd, J = 4 and 9 Hz; H _{γ}), 4.28 (2 H, dd, J = 7 and 9 Hz; H _{γ}), 4.80 (2 H, d, J = 4 Hz; H _{α}), \approx 6.9 (6 H, m; aromatic protons).

Acetylations were performed as described in Ref. 1.

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