

NMR Studies of Lignins. 3. ^1H NMR Spectroscopic Data for Lignin Model Compounds

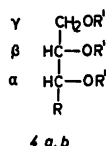
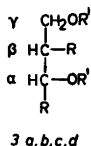
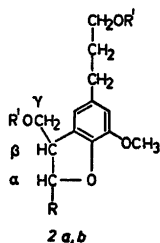
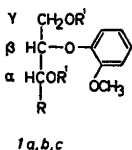
KNUT LUNDQUIST

Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden

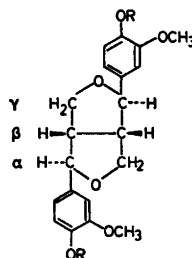
^1H NMR (270 MHz) spectrometric data for a number of appropriate lignin model compounds are reported. The effects of variations in the substitution of aromatic rings on the location of signals from side chain protons are surveyed. The value of accurate and detailed model compound data in interpretations of lignin spectra is exemplified.

Previous papers^{1,2} in this series describe investigations of lignins by ^1H NMR spectroscopy, using a 270 MHz instrument. ^1H NMR spectra of lignin model compounds and published ^1H NMR data for such compounds served as a basis for the interpretation of the lignin spectra in structural terms. Signals in the lignin spectra due to protons in various types

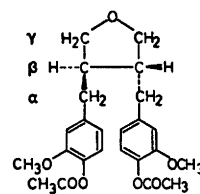
of propyl side chains of lignin units could be largely identified.^{1,2} Continued studies of this type required additional ^1H NMR examinations of lignin model compounds with a 270 MHz instrument. Results from such studies are summarized in the present paper.



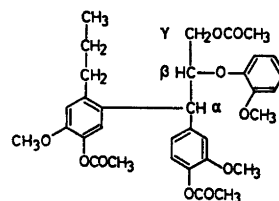
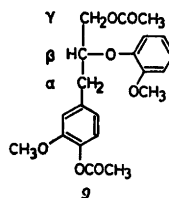
- a. R = 3,4-dimethoxyphenyl, R' = COCH₃
 b. R = 4-acetoxy-3-methoxyphenyl, R' = COCH₃
 c. R = 4-hydroxy-3-methoxyphenyl, R' = H
 d. R = 3,4-dimethoxyphenyl, R' = H



- 5 R = CH₃
 6 R = COCH₃
 7 R = H



8



10

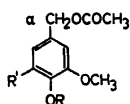
In this series of investigations, lignins have been examined primarily as acetate derivatives in chloroform-*d*, but some spectra of non-derivatized lignin in dioxane-*d*₈-D₂O (5:1) have also been recorded. Lignin model compounds have been examined analogously. Results obtained with acetate derivatives of model compounds are summarized in Tables 1 and 2.

Table 1. NMR data for side-chain protons in compounds 1a–4a, 5, and 8–10 (solvent, CDCl₃).

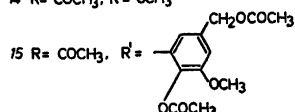
| Compound | δ Value; J values in Hz are given in parentheses | | | | |
|------------------------------------|---|------------------|-----------|-------------------|-----------------|
| | H_α | $H_{\alpha'}$ | H_β | H_γ | $H_{\gamma'}$ |
| 1a (<i>erythro</i>) | 6.02 (5.2) | | 4.70 (m) | 4.23 (4.0, 12) | 4.42 (6.0, 12) |
| 1a (<i>threo</i>) | 6.08 (7.0) | | 4.65 (m) | 4.01 (5.9, 12) | 4.28 (4.0, 12) |
| 2a | 5.46 (7.3) | | 3.76 (m) | 4.31 (7.5, 11) | 4.44 (5.5, 11) |
| 3a (<i>erythro</i>) ^a | 6.05 (7.5) | | 3.35 (m) | 4.11 (6.8, 11) | 4.28 (6.4, 11) |
| 4a (<i>erythro</i>) | 5.94 (6.3) | | 5.41 (m) | 4.24 ^b | |
| 4a (<i>threo</i>) | 5.92 (8) | | 5.44 (m) | 3.81 (5.8, 12) | 4.24 (3.5, 12) |
| 5 | 4.76 (4) | | 3.11 (m) | 3.91 ^c | 4.26 (7, 9) |
| 8 | 2.59 (8.4, 13.5) | 2.69 (5.9, 13.5) | 2.23 (m) | 3.55 (5.9, 8.8) | 3.93 (6.6, 8.8) |
| 9 | 2.98 (6.0, 14) | 3.12 (6.7, 14) | 4.58 (m) | 4.22 (4.8, 12) | 4.28 (5.1, 12) |
| 10 | 4.59 (5.9) | | 5.01 (m) | 4.19 ^d | |

^a Preparation and stereochemistry. ^b 2 H, approximately doublet ($J=5$ Hz). ^c J values uncertain due to interference of signals from methoxyl protons. ^d 2 H, doublet ($J=5.1$ Hz).

It appears from comparisons of model compound data in Tables 1 and 2 that the position of the signal of H_α is shifted by 0.03–0.06 δ units upfield when an adjacent 4-acetoxy-3-methoxyphenyl group is replaced by a 3,4-dimethoxyphenyl group (representative of 4-alkoxy-3-methoxyphenyl groups in lignins). Etherified and acetylated guaiacyl units in lignins can, therefore, be expected to differ in this respect in a corresponding manner. An exchange of a 4-acetoxy-3-methoxyphenyl group for a 3,4-dimethoxyphenyl group also slightly influences the position of the signals from H_β and H_γ (Table 1, footnotes in Table 2). Compounds 11–14 can be considered as model compounds for etherified and acetylated lignin units of the guaiacyl (11, 12) and syringyl (13, 14) types. The effects of the variation in aromatic substitution on the location of the H_α signal of compounds 11–14 are apparent from Table 2. H_α in compounds 12 and 15 exhibit about the same δ value (Table 2),



- 11 R = CH₃, R' = H
 12 R = COCH₃, R' = H
 13 R = CH₃, R' = OCH₃
 14 R = COCH₃, R' = OCH₃



indicating that the introduction of a biphenyl linkage – representative of those present in lignins – does not change the position of the H_α signal to any great extent.

erythro and *threo* forms of model compounds 1a, 4a, and 3b have been examined. Such stereoisomers differ only moderately in their ¹H NMR properties (Tables 1 and 2). This fact, together with the structural complexity of lignins, makes it difficult to relate signals in the lignin spectra to individual diastereomers of structural elements. However, the large number of β -O-4 structures in lignins^{3,4} (compounds of type 1 are relevant models of such lignin structures)

Table 2. NMR data for H_α in compounds 1b–4b, 6, and 11–15 (solvent, CDCl₃).

| Compound | δ Value | J /Hz |
|------------------------------------|----------------|---------|
| 1b (<i>erythro</i>) ^a | 6.08 | 5.0 |
| 2b ^b | 5.51 | 7.0 |
| 3b (<i>erythro</i>) ^c | 6.10 | 6.5 |
| 3b (<i>threo</i>) ^c | 5.98 | 7.8 |
| 6 ^d | 4.80 | 4.0 |
| 11 | 5.04 | – |
| 12 | 5.07 | – |
| 13 | 5.03 | – |
| 14 | 5.05 | – |
| 15 | 5.08 | – |

^a $\delta(H_\beta)=4.87$, $\delta(H_\gamma)=4.25$ and 4.46 . ^b $\delta(H_\beta)=3.76$, $\delta(H_\gamma)=4.29$ and 4.45 . ^c Preparation and stereochemistry. ^d $\delta(H_\beta)=3.10$, $\delta(H_\gamma)=3.94$ and 4.28 .

facilitates the detection of the two possible diastereomers of this type of structure in lignins. Spectra of acetylated birch lignin exhibit a peak with a maximum at $\delta=6.01$ and an inflexion at $\delta=6.07$ which essentially can be attributed to H_α in β -O-4 structures.³ Comparisons with model compound data (Table 1, see also Ref. 4) suggest that the *erythro* forms of such structural elements dominate in birch lignin. This is supported by the occurrence of a pronounced signal at $\delta=4.43$ in the birch lignin spectra³ (H_γ in *erythro* forms of β -O-4 structures; Tables 1 and 2, see also Ref. 4). Birch lignin consists of about equal proportions of guaiacyl and syringyl units and aromatic groups with 4-alkoxy substituents strongly predominate.³ The effects of the variation in aromatic substitution on the position of the signals from side chain protons (Tables 1 and 2) should not jeopardize the conclusion above. Results from ^1H NMR studies of spruce lignin suggest about equal amounts of *erythro* and *threo* forms of β -O-4 structures in this type of lignin.⁵

Results from examinations of nonderivatized model compounds in dioxane- d_6 - D_2O (5:1) are summarized in Table 3. Signals from H_α and H_β are located fairly close to each other (Table 3) and, unfortunately, signals from H_γ , methoxyl protons, and solvents are found in the same region. The possibilities of identifying signals from side chain protons are, therefore, rather limited. However, the signals from H_β in model compounds *3c* and *3d* (representative of 1,2-diaryl-1,3-propanediol structures) appear in a region where lignin spectra exhibit only slight absorption. This may offer a possibility of detection of 1,2-diaryl-1,3-propanediol structures in lignins by the NMR spectral technique; this has hitherto failed.

Table 3. NMR data for H_α and H_β protons in model compounds *1d*, *3c*, *3d*, *5*, and *7* [solvent, dioxane- d_6 - D_2O (5:1)].

| Compound | δ Value | |
|------------------------------|----------------------|-----------|
| | H_α | H_β |
| <i>1d</i> (<i>erythro</i>) | 4.85 (d, $J=5.5$ Hz) | 4.31 (m) |
| <i>3c</i> (<i>erythro</i>) | 4.90 (d, $J=5.5$ Hz) | 2.88 (m) |
| <i>3d</i> (<i>erythro</i>) | 4.97 (d, $J=5.5$ Hz) | 2.91 (m) |
| <i>5</i> | 4.70 (d, $J=4$ Hz) | 3.06 (m) |
| <i>7</i> | 4.67 (d, $J=4$ Hz) | 3.05 (m) |

EXPERIMENTAL

^1H NMR spectra were recorded on a 270 MHz instrument working in the pulse Fourier mode (Bruker WH 270). Solvents were chloroform- d (internal reference TMS) and dioxane- d_6 - D_2O (5:1) (internal reference was the sodium salt of 3-(trimethylsilyl)propanesulfonic acid). Temperatures were around 300 K. The concentration of the samples were 5–50 mg in 0.5 ml solvent; changes in signal positions larger than 0.01 δ units were not observed when the concentration was varied within the given range.

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REFERENCES

- Lundquist, K. and Olsson, T. *Acta Chem. Scand. B* 31 (1977) 788.
- Lundquist, K. *Acta Chem. Scand. B* 33 (1979) 27.
- Sarkanen, K. V. and Ludwig, C. H. *Lignins*, Wiley-Interscience, New York 1971.
- Johansson, B. and Miksche, G. E. *Acta Chem. Scand.* 26 (1972) 289; Erickson, M. and Miksche, G. E. *Acta Chem. Scand.* 26 (1972) 3085.
- Lundquist, K. *In preparation*.
- Lundquist, K. and Miksche, G. E. *Tetrahedron Lett.* 1965 (2131) and unpublished data; Nakatsubo, F. and Higuchi, T. *Holzforschung* 29 (1975) 193.

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