

## NMR Studies of Lignins. 1. Signals Due to Protons in Formyl Groups

KNUT LUNDQUIST and TOMAS OLSSON

Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, S-402 20 Göteborg 5, Sweden

The occurrence of structural elements with formyl groups in spruce lignin (units of the coniferaldehyde, vanillin,  $\alpha$ -aryloxyacrolein, and glyceraldehyde-2-aryl ether type) has been studied by  $^1\text{H}$  NMR spectroscopy. Signals from formyl protons were found to be essentially due to coniferaldehyde and vanillin units. By integration the amount of coniferaldehyde units was determined as 4 %.

Proton NMR spectra of lignins have been published by several authors.<sup>1-3</sup> In most cases acetate derivatives of the lignins have been examined. A comprehensive  $^1\text{H}$  NMR study of

lignins and lignin model compounds was published as early as 1964.<sup>4</sup> In the present work a 270 MHz instrument has been used. The lignin spectra recorded with this instrument permit a more detailed interpretation than is possible with spectra taken with the lower frequency instruments used in earlier work. The present paper deals with a study of protons in formyl groups. Signals due to such protons have not been previously detected in NMR spectra of lignins.

A  $^1\text{H}$  NMR spectrum of acetylated milled wood lignin (MWL) from spruce (Fig. 1) ex-

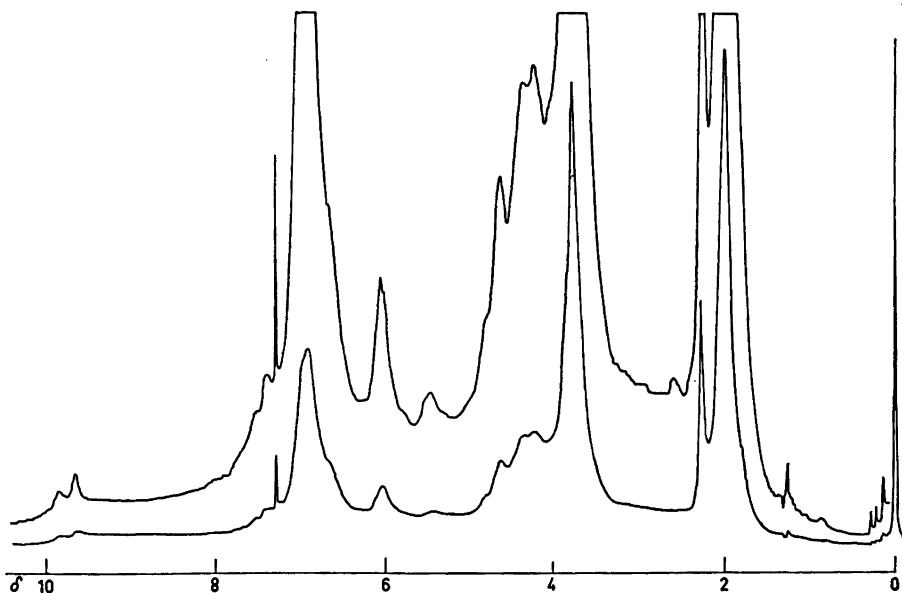


Fig. 1.  $^1\text{H}$  NMR spectrum of acetylated MWL from spruce (solvent,  $\text{CDCl}_3$ ).

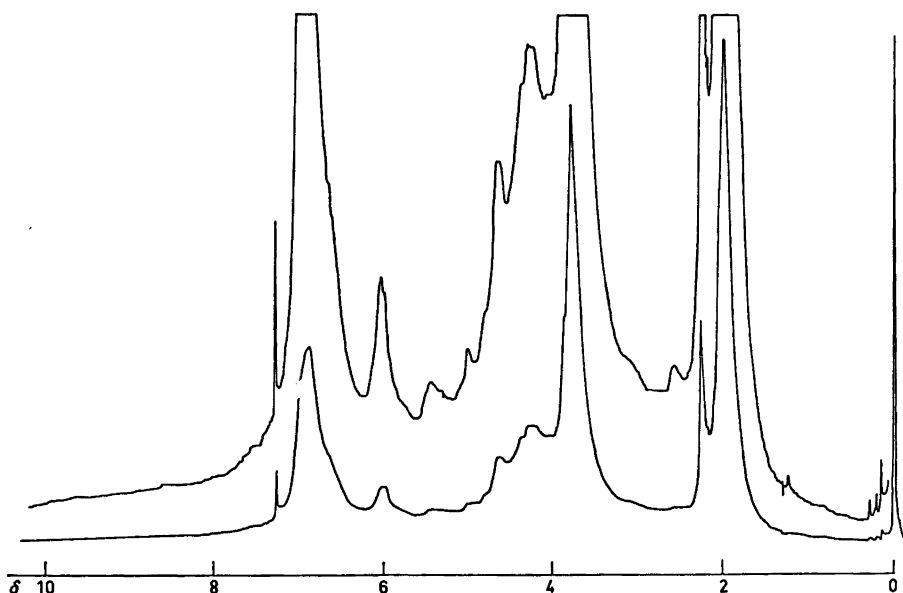
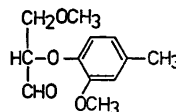
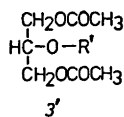
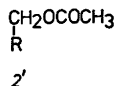
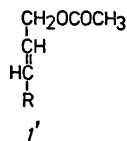
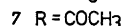
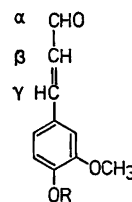
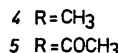
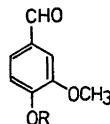
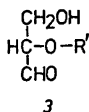
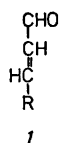


Fig. 2. <sup>1</sup>H NMR spectrum of borohydride reduced and acetylated MWL from spruce (solvent, CDCl<sub>3</sub>).

hibits signals in the range  $\delta=9-10$  with  $\delta$  values 9.64, 9.84, and 9.94 (shoulder) which can be attributed to protons in formyl groups. Spectra of borohydride reduced and, subsequently, acetylated MWL show no signals in this region (Fig. 2). Spectral studies of model compounds (Table 1) suggest that the peak at  $\delta=9.64$  is due to formyl groups in cinnamaldehyde units (1). The signals around  $\delta=9.9$  can be attributed to formyl groups in benzaldehyde

units (2) or glyceraldehyde-2-aryl ether units (3) (Table 1). Spectra of nonderivatized MWL in dioxane-*d*<sub>8</sub>-D<sub>2</sub>O (5:1) showed peaks at  $\delta=9.56$  and  $\delta=9.74$ . It appears from Table 1 that these data support the interpretation of the results obtained with acetylated MWL. Spectra of a model compound for units of type 3, compound 8, in dioxane-water medium



R= aromatic nucleus of the guaiacyl type  
R'= guaiacylpropane unit

Table 1. NMR data for formyl protons in model compounds 4–8 (for further model compound data, see Refs. 1, 5, 6, and 7).

Compound	$\delta$ Value		$J/\text{Hz}$
	$\text{CDCl}_3$	Dioxane- $d_6$ – $\text{D}_2\text{O}$	
4 <sup>a</sup>	9.86	9.77	—
5	9.94	—	—
6 <sup>b</sup>	9.67	9.58	7.8
7	9.70	—	7.5
8	9.88	9.70	1.5

<sup>a</sup>  $\delta$  Values for aromatic protons *ortho* to the formyl group were 7.42 ( $J=2$  Hz) and 7.47 ( $J=2$  and 8 Hz).

<sup>b</sup>  $\delta_{\text{H}\gamma}=7.42$  ( $J=16$  Hz),  $\delta_{\text{H}\beta}=6.62$  ( $J=16$  and 7.8 Hz).

showed a comparatively weak formyl proton peak due to partial hydration of the carbonyl group. Acetylation of compound 8 and examination of the product by NMR (solvent, deuteriochloroform) showed that the formyl group had to a large extent disappeared. The experiments with compound 8 and data presented below suggest that the peak in Fig. 1 at  $\delta=9.84$  (as well as the peak at  $\delta=9.74$  in the spectrum of nonderivatized lignin) is essentially due to benzaldehyde units of type 2 linked to the lignin by ether bonds; the shoulder at  $\delta=9.94$  may

reflect the presence of minor amounts of benzaldehyde units with a *p*-acetoxy group (Table 1). The spectrum of acetylated compound 8 showed a small peak at  $\delta=9.43$  which can be explained by partial conversion into  $\alpha$ -aryloxyacrolein.<sup>5</sup> A very small peak at the same position was found in spectra of acetylated MWL. This may be due to formation of  $\alpha$ -aryloxyacrolein structures from units of type 3 in the original MWL. However, since structural elements with  $\alpha$ -aryloxyacrolein groups have been suggested as being present in untreated lignin,<sup>6</sup> there is an alternative explanation for the occurrence of this peak.

From integrations of the aldehyde peaks in spectra of acetylated MWL the proportion of units carrying formyl groups was determined to be 7%. The number of cinnamaldehyde units could be estimated as 4%, which is in good agreement with results obtained by other methods.<sup>9</sup> Similar results were obtained from integrations of spectra of nonderivatized MWL.

To verify the assignments of the formyl proton signals in Fig. 1, a difference spectrum (Fig. 3) was made by subtracting the spectrum of acetylated MWL in Fig. 1 from the spectrum of borohydride reduced and acetylated MWL in Fig. 2. This was made by the computer connected to the NMR spectrometer. In the difference spectrum negative peaks appear at  $\delta=9.84$  and 9.64 corresponding to signals due to formyl protons. The negative peak at  $\delta=7.40$

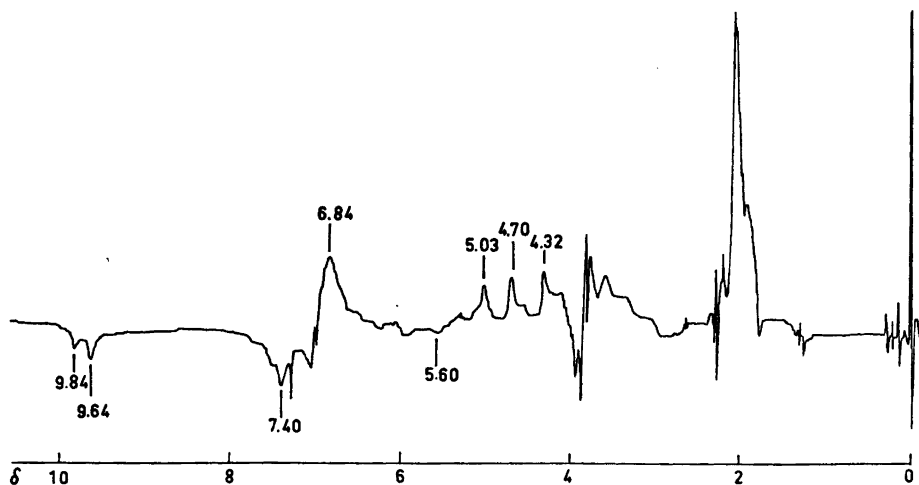
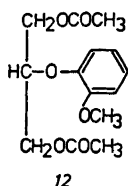
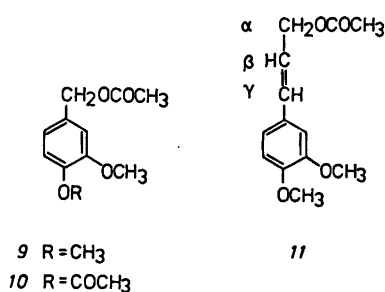


Fig. 3. Difference spectrum obtained by subtraction of the spectrum in Fig. 1 from the spectrum in Fig. 2.



and the positive peak at  $\delta = 6.84$  are expected from shifts in signal positions caused by exchange of units of types 1 and 2 for units of types 1' and 2'. Some of the protons in units of types 1 and 2 give rise to signals around  $\delta = 7.40$  (footnotes in Table 1). The signals from the corresponding protons in units of types 1' and 2' appear at other positions (footnote in Table 2; according to experiments with model compounds signals due to aromatic protons in units of types 1' and 2' are located close to  $\delta = 6.84$ ). The positive peaks at  $\delta = 4.70$  and  $\delta = 5.03$  agree well with signals of methylene protons in units of types 1' and 2' (Table 2). The difference spectrum also exhibits a positive peak at  $\delta = 4.32$ . This peak can be attributed to presence of units of type 3' in borohydride reduced and acetylated MWL (Table 2). Since on borohydride reduction-acetylation units of

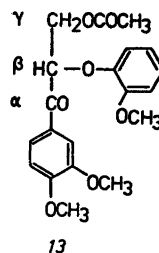
Table 2. NMR data for methylene protons in model compounds 9–12 (solvent, CDCl<sub>3</sub>).

Compound	$\delta$ Value	$J$ /Hz
9	5.04	—
10	5.07	—
11 <sup>a</sup>	4.71	6.5
12	4.33	5.0

<sup>a</sup>  $\delta_{\text{H}_\gamma} = 6.60$  ( $J = 16$  Hz),  $\delta_{\text{H}_\beta} = 6.16$  ( $J = 16$  and 6.5 Hz).

type 3 are converted into units of type 3' this provides support for the occurrence of units of type 3 in the original MWL. The size of the 4.32 peak in the difference spectrum seems to be of the order expected from studies<sup>5</sup> of the number of glyceraldehyde-2-aryl ether units in spruce lignin.

Data obtained in the present studies, supplemented with results from estimates<sup>5</sup> of the number of glyceraldehyde-2-aryl ether units in lignin, suggest that the number of formyl protons in MWL from spruce is about 0.09/OCH<sub>3</sub>. The total amount of carbonyl groups in MWL from spruce has been determined as 0.20/OCH<sub>3</sub>.<sup>8</sup> Thus the number of ketone groups would be about 0.11/OCH<sub>3</sub>. It is plausible that ketone units of the  $\alpha$ -aryloxypropiofenone type are present in lignin. A model compound for



such structures, compound 13, has been examined. The  $\delta$  value for H $_\beta$  was 5.62 ( $J = 7.1$  and 3.7 Hz) and signals from aromatic protons *ortho* to the carbonyl group were observed at  $\delta = 7.68$  and  $\delta = 7.85$ . However, no pronounced negative peaks appeared at these  $\delta$  values in the difference spectrum (Fig. 3). Consequently, the present studies suggest that the number of  $\alpha$ -aryloxypropiofenone structures in lignin is small. To explain the rest of the carbonyl groups, we think that units of quinone and quinonoid types should be considered.<sup>9</sup>

## EXPERIMENTAL

<sup>1</sup>H NMR spectra were taken with a 270 MHz instrument working in the pulse Fourier mode (Bruker WH 270). Solvents were chloroform-*d* (internal reference TMS) and dioxane-*d*<sub>6</sub>–D<sub>2</sub>O (5:1) (internal reference was the sodium salt of 3-(trimethylsilyl)propanesulfonic acid). Temperatures were in the range 300–308 K (lignin spectra were all run at 308 K). In the case of lignin preparations the concentration was about 0.1 g in 0.5 ml solvent.

*Acetylations* were performed by treatment with acetic anhydride – pyridine (1:1) for 24 h. Lignin acetates were precipitated by dropping the reaction mixture into ether. The products were purified by precipitation in ether from a chloroform solution.

## REFERENCES

1. Ludwig, C. H. In Sarkanen, K. V. and Ludwig, C. H. *Lignins*, Wiley-Interscience, New York 1971, p. 229.
2. Becker, H. and Nimz, H. *Z. Pflanzenphysiol.* 72 (1974) 52.
3. Kirk, T. K. and Chang, Hou-min *Holz-forschung* 29 (1975) 56.
4. Ludwig, C. H., Nist, B. J. and McCarthy, J. L. *J. Am. Chem. Soc.* 86 (1964) 1186, 1196.
5. Berndtson, L., Hedlund, K., Hemr , L. and Lundquist, K. *Acta Chem. Scand. B* 28 (1974) 333.
6. Connors, W. J., Chen, C.-L. and Pew, J. C. *J. Org. Chem.* 35 (1970) 1920.
7. Lundquist, K. and Hedlund, K. *Acta Chem. Scand.* 25 (1971) 2199.
8. Adler, E. and Marton, J. *Acta Chem. Scand.* 13 (1959) 75.
9. Lundquist, K. and Ericsson, L. *Acta Chem. Scand.* 25 (1971) 756; Hemr , L. and Lundquist, K. *Ibid.* 27 (1973) 365.

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