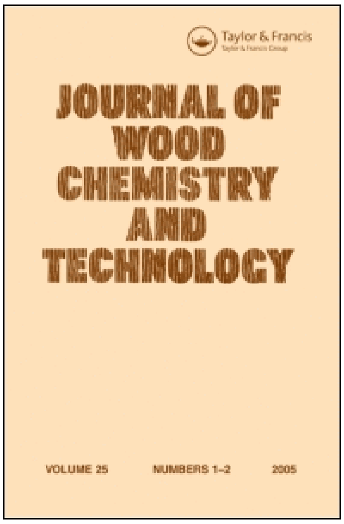

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ANALYSIS OF LIGNINS AS PROPIONATE DERIVATIVES BY NMR SPECTROSCOPY

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ABSTRACT

Lignin propionates were prepared by treating lignin samples with propionic anhydride in pyridine solution and the derivatives obtained were examined by NMR spectroscopic methods. ^1H NMR spectroscopy of lignin propionates offers a possibility to determine the number of hydroxyl groups based on the methyl proton signal ($\delta \approx 1.2$) as well as the methylene proton signal ($\delta \approx 2.5$) of the propionate groups. It was found to be advantageous to use propionate derivatives for the analysis of hydroxyl groups in lignin products exhibiting signals (from >CH– and –CH_2– groups) that interfere with the acetate group signals. Analysis of ester groups by ^{13}C NMR spectroscopy gave practically the same results as those earlier reported for acetate derivatives.

INTRODUCTION

Lignins are frequently analysed as acetates by NMR spectroscopic methods. Among other things NMR examination of such derivatives provides information about the distribution of different types of hydroxyl groups in the lignins. The signals from the methyl protons in the acetate groups constitute the basis for the ^{1}H NMR spectral estimates. Acetylated lignins give signals from acetate groups at $\delta \approx 2.0$ (aliphatic acetate) and $\delta \approx 2.3$ (aromatic acetate).[1] It is difficult to obtain accurate figures for the amounts of aliphatic and phenolic hydroxyl groups on the basis of these two peaks since they are not very well separated. Furthermore, the signals from aromatic acetate in biphenyl structures appear at ca. δ 2.10 and are not included in estimates of phenolic groups on the basis of the δ 2.3 peak.[2] In an attempt to overcome the difficulties faced in NMR analysis of acetate derivatives, we have prepared lignin propionates and examined them by ^{1}H NMR and ^{13}C NMR spectroscopy (for a preliminary report, see Ref. 3).

RESULTS AND DISCUSSION

The ^{1}H NMR spectrum of the propionate of milled wood lignin (MWL) from spruce is shown in Fig. 1. To obtain a basis for the interpretation of the peaks due to propionate groups in the lignin spectrum (appearing in the spectral range δ 0.5-2.8, Fig. 1), the spectra of propionates of a series of lignin model compounds were recorded. Table 1 summarizes the results obtained. From the data in Table 1 it could be concluded that the peaks at $\delta \approx 1.1$ and $\delta \approx 1.3$ in the lignin spectrum (Fig. 1) are due to methyl groups in aliphatic and aromatic propionate groups, respectively. Similarly, the peaks at $\delta \approx 2.3$ and $\delta \approx 2.6$ could be attributed to methylene groups in aliphatic propionate and aromatic propionate, respectively. The quantitative

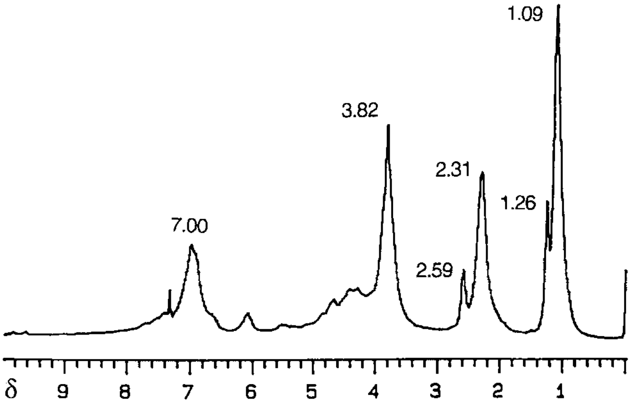


FIGURE 1. ^1H NMR spectrum of the propionate derivative of milled wood lignin from spruce.

estimates based on the peak from CH_2 gave 1.08 aliphatic OH/C_9-unit and 0.23 phenolic OH/C_9-unit. Calculations based on the peak from CH_3 gave 1.10 aliphatic OH/C_9-unit and 0.25 phenolic OH/C_9-unit.

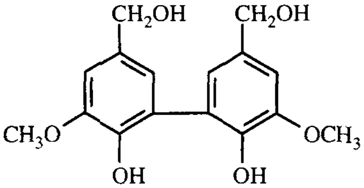
The positions of signals from aromatic propionate in biphenyls deviate (upfield shift) from the corresponding signals of other types of structural elements. This is evident from ^1H NMR spectral data of the propionate of a lignin model compound of the biphenyl type, dehydrodivanillyl alcohol (**1**): the signals from CH_2 and CH_3 in the aromatic propionate groups appear at δ 2.38-2.39 and δ 1.17, respectively (Table 1). Thus the presence of biphenyl structures makes it difficult to determine the distribution of aliphatic and aromatic hydroxyl in the lignin samples. As pointed out in the introductory section of this paper the same type of problem is met in the ^1H NMR spectral analysis of acetate derivatives.

TABLE 1.

Signal Positions (δ Values) for Protons in the Propionate Groups in Propionate Derivatives of Lignin Model Compounds.

Model compounds[a]	Aliphatic propionate CH_2	Aliphatic propionate CH_3	Aromatic propionate CH_2	Aromatic propionate CH_3
1-(4-Hydroxy-3-methoxyphenyl)-1-ethanol	2.35	1.14	2.60	1.26
threo-1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol	2.27 2.33	1.08 1.11	2.60	1.26
erythro-1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol	2.30 2.37	1.10 1.13	2.60	1.26
threo-1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol	2.28 2.30	1.09	--	--
erythro-1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol	2.30 2.35	1.10 1.11	--	--
erythro-2-(4-Benzyloxy-3-methoxyphenyl)-1-(4-hydroxy-3-methoxyphenyl)-1,3-propanediol	2.22 2.30	1.00 1.05	2.59	1.26
erythro-1,2-Bis(3,4-dimethoxyphenyl)-1,3-propanediol	2.21 2.23	1.00 1.06	--	--
Dehydrodivanillyl alcohol (**1**)	2.38-9	1.07	2.38-9	1.17

[a]Chemical names in this column refer to the non-derivatized models.



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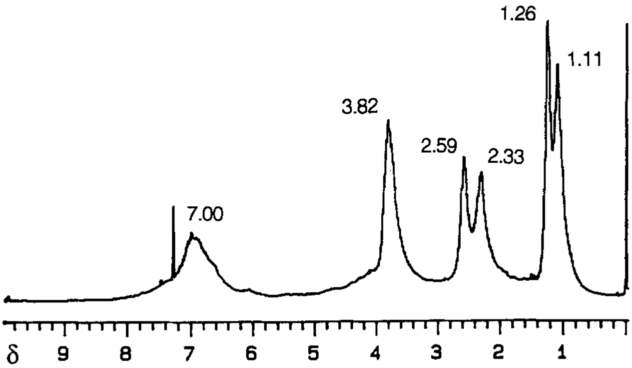

FIGURE 2. ^1H NMR spectrum of the propionate derivative of kraft lignin from pine.

The ^1H NMR spectrum of the propionate of a kraft lignin sample (Fig. 2) was analysed. Calculations based on the peaks due to CH_2 gave 0.88 aliphatic OH/aromatic ring and 0.73 phenolic OH/aromatic ring (total hydroxyl, 1.61). Estimates based on the CH_3 peaks gave 0.74 aliphatic OH/aromatic ring and 0.55 phenolic OH/aromatic ring (total hydroxyl, 1.29). The difference in total hydroxyl can be explained by the occurrence of signals from other structures than propionate groups at $\delta \approx 2.5$. The signal due to CH_3 in propionate ($\delta \approx 1.2$) is only slighly influenced by signals from groups present in the non-derivatized lignin and the estimate of total hydroxyl based on the $\delta \approx 1.2$ peak is therefore expected to be the most accurate one.

^1H NMR spectroscopy of propionates of lignins offers a possibility to check the reliability of results from determinations of hydroxyl groups, since the estimates can be made based on the methyl proton signal ($\delta \approx 1.2$) as well as the methylene proton signal ($\delta \approx 2.5$) of the propionate groups. It is advantageous to use propionate derivatives for the analysis of modified lignins (e.g., kraft lignin) since they in many cases exhibit signals (from >CH– and $-CH_2-$ groups) that interfere with the acetate group signals. Thus we consider that examination of lignin propionates is of value in connection with ^1H NMR spectral analyses of lignins, although the spectra are comparatively complex as noted by Glasser and Jain.[4]

On the basis of the carbonyl group signals, ^{13}C NMR spectroscopy of lignin acetates has been used for the quantitative determination of primary, secondary and phenolic hydroxyl in lignins.[5] Analysis of carbonyl groups in lignin propionates gave results similar to those obtained with acetate derivatives. Signals appeared at δ 172.3 (phenolic), δ 173.1 (secondary) and δ 174.1 (primary). It seems that the signals from primary and secondary ester groups are somewhat better separated than the corresponding signals [5] in spectra of acetate derivatives.

EXPERIMENTAL

For the preparation of propionate derivatives of lignin samples and lignin model compounds a previously described[1] procedure for the acetylation of lignins was adapted [Propionic anhydride-pyridine (1:1). Repeated addition and removal (film evaporation) of ethanol results in the removal of propionic acid and pyridine from the samples. Alternatively propionic acid could be removed by azeotropic distillation with *p*-xylene or octane.]. ^1H NMR spectra of the propionates of lignins and model compounds were recorded at

400 MHz with a Varian XL-400 (VXR-5000) instrument. $CDCl_3$ was used as solvent (temperature, 300 K). TMS was used as internal reference. In quantitative runs the sample concentration was ≈200 mg/0.6 ml and the pulse interval was ≈9 s [Examinations of the lignin propionates showed that T_1 was ≈1.2 s for CH_2 (in CH_3CH_2CO) and ≈1.6 s for CH_3 (in CH_3CH_2CO)]. The number of scans was ≈1000. Quantitative estimates of hydroxyl groups in lignins were based on the assumption that the peak due to aromatic protons at $\delta \approx 7$ corresponds to 2.7 H/C_9-unit in the case of MWL from spruce and 2.5 H/aromatic ring in the case of kraft lignin (cf. Ref. 1). ^{13}C NMR spectra were recorded at 100.6 MHz with a Varian XL-400 (VXR-5000) instrument (solvent, $CDCl_3$).

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