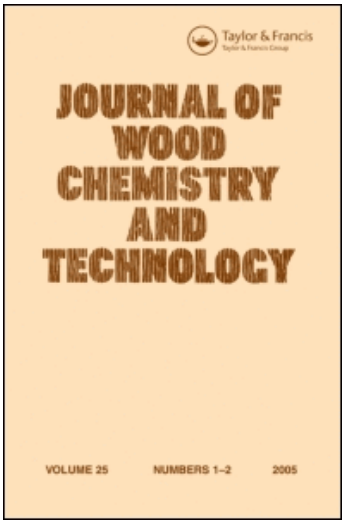

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ON THE OCCURRENCE OF β-1 STRUCTURES IN LIGNINS

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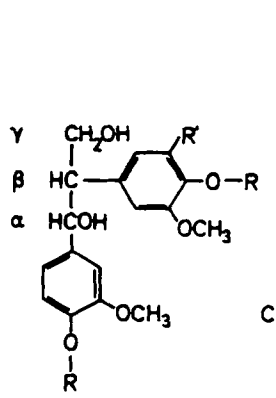
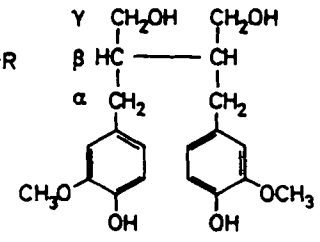
ABSTRACT

^{1}H NMR spectral evidence for the occurrence of β-1 structures in lignins is presented. The number of β-1 side chains may be 1-2% in spruce lignin and perhaps as much as 5% in birch lignin.

INTRODUCTION

Degradation products which could be derived from lignin structures of the β-1 type (i.e. compounds like 1 and 4 attached to the lignin macromolecule) are produced from lignin and wood upon several types of treatments (see, e.g., Refs.1-3). Although experiments with lignin model compounds suggest that in some cases these products may originate from β-O-4 structures (kraft cooking[4], hydrolysis at 180 C° [5]) rather than





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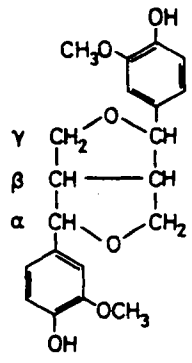

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1 R=R'=H
2 R=CH_3, R'=H
3 R=$PhCH_2$, R'=H
4 R=H, R'=OCH_3

β-1 structures, the existence of the latter type of structures in lignins is very strongly supported by degradation studies. ^{13}C NMR spectroscopy has provided indications for the presence of β-1 structures in lignins[6], but clearcut spectroscopic evidence for this has not been presented as yet. On the basis of examinations of non-derivatized lignins in dioxane--water solutions, it could be concluded from ^{1}H NMR studies that the number of β-1 structures must be small in lignins.[7] Under these conditions the signal from Hβ in β-1 structures is located in a region of the spectrum where very few other lignin signals are found. However, large solvent signals appear fairly close to the position of the signal from Hβ in β-1 structures.[7] One can eliminate this drawback by the use of DMSO-$\underline{d}_6$--deuterioacetic acid (9:1) as solvent, and this solvent system has been used in the present ^{1}H NMR spectral study of the occurrence of β-1 structures in lignins.

RESULTS AND DISCUSSION

^{1}H NMR spectral data for lignin model compounds of the β-1 type are summarized in Table 1 (Table 1 includes data for β-1 compounds (1-4) as well as model compounds (5-6) for structures which exhibit signals in the neighbourhood of the signal for Hβ in β-1 structures).

It is clear from Table 1 that signals from Hβ in β-1 structures can be expected to be found in the range δ2.76-2.93. The spectrum of spruce lignin (Figure 1) exhibits only low intensity signals in this region (a weak signal at δ2.76 is discernible) and suggests that at most 1-2% β-1 side chains are present in the lignin. Birch lignin shows a signal at δ2.77 which can be attributed to β-1 side chains (Figure 2). There may be

TABLE 1

^{1}H NMR Data for Side Chain Protons in Lignin Model Compounds. Solvent, DMSO-d_6--CD_3COOD (9:1).

Compound	δ/p.p.m. vs. TMS (J/Hz)			
	Hα	Hβ	H(γ_1)	H(γ_2)
1[1]	4.82(5.3)	2.76(m)	3.48(7.0,10.3)	3.7(m)
1[2]	4.68(8.0)	2.85(m)	3.72(6.7,10.6)	3.86(6.0,10.6)
2[1]	4.89(5.3)	2.82(m)	3.6[3]	
3[2]	4.75(7.9)	2.93(m)	3.76(6.8,10.6)	3.87(5.7,10.6)
4[1]	4.81(5.5)	2.76(m)	3.49(6.7,10.5)	3.7(m)
5	2.5[3]	1.84(m)	3.40(4.4)[3]	
6	4.62(4.0)	3.04(m)	3.75(m)	4.13(6.7,8.7)

[1] Erythro form. [2] Threo form. [3] 2 H.

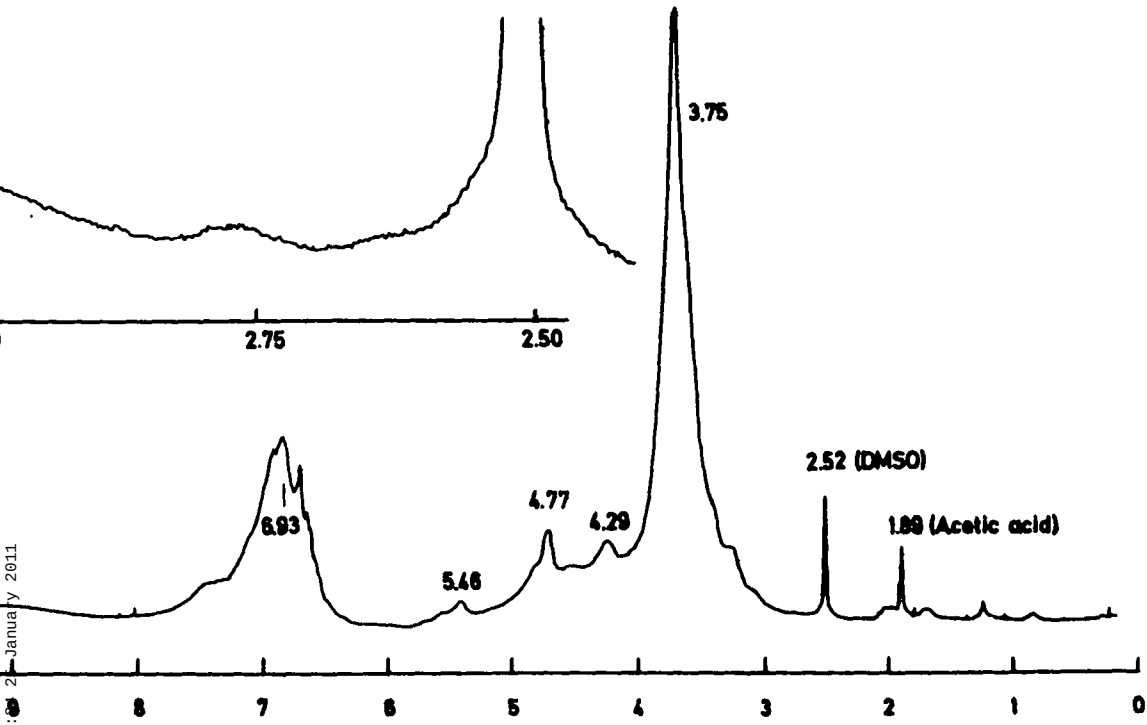

FIGURE 1. ^{1}H NMR spectrum of spruce lignin in DMSO-d_6--CD_3COOD (8:1).

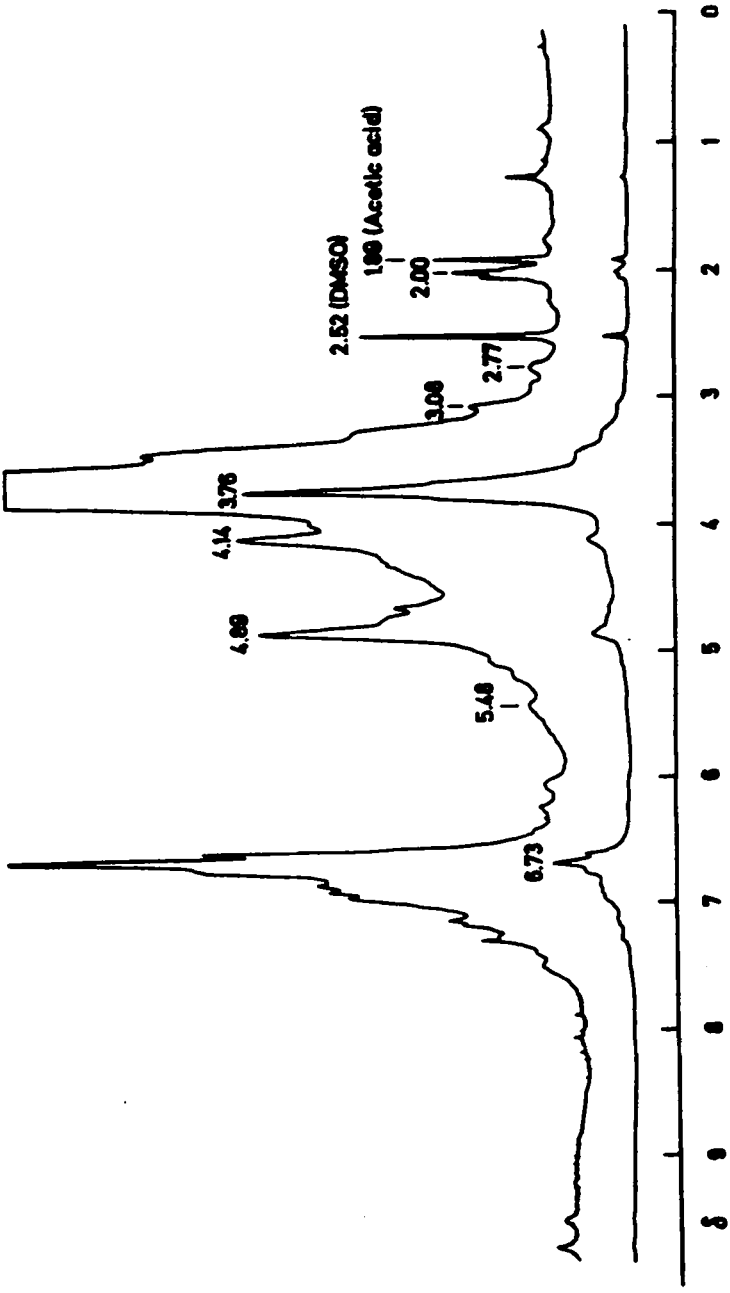

FIGURE 2. ^{1}H NMR spectrum of birch lignin in DMSO-d_6--CD_3COOD (8:1).

as much as 5% β-1 side chains in birch lignin. (Assignments of signals in Figures 1 and 2 could be made on the basis of the data in Table 1 and Ref.7; the peak at δ2.00 in the birch lignin spectrum is due to acetate in xylan.)

The position of the signal from Hβ in β-1 structures varies with stereochemistry (Table 1). This complicates any attempt to quantitatively evaluate the lignin spectra with respect to the occurrence of such structures. The distribution of erythro and threo forms of β-1 structures in lignins is not known. Lignin degradations seem to provide the erythro forms of β-1 compounds , but the presence of the erythro as well as the threo form of compound 1 in wood extractives has been reported.[8]

The failure to detect the signal from Hβ in β-1 structures in earlier ^{1}H NMR studies of lignins in dioxane--water solution[7] may have been due to overlap with large solvent peaks. Another obvious reason would be the absence of significant amounts of β-1 structures in the lignin samples. If this is the case one must provide an explanation for the presence of signals which could be attributed to β-1 structures in the present ^{1}H NMR studies of lignins in DMSO--acetic acid solution. Such an explanation might be the acid-catalysed formation of β-1 structures in the NMR-solvent from "precursors" of dienone type.[9,10] Such "precursors" can be expected give rise to lignin degradation products attributed to β-1 structures. This may explain why lignin degradation studies[2,3] indicate larger amounts of β-1 structures in lignins than NMR-studies do.[7,8]

EXPERIMENTAL

^{1}H NMR spectra were recorded on a 270 MHz instrument working in the pulse Fourier mode (Bruker WH270). DMSO-d_6--deuterioacetic acid (9:1) was used as solvent (internal reference, TMS). The number of β-1 side chains in the lignin samples was estimated by comparing the peak area at δ≈2.8 (Hβ) with that due to the aromatic protons (δ≈7) (Figures 1 and 2).

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