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THE INFLUENCE OF SOLVENT AND DERIVATIZATION ON THE ^1H NMR SPECTRAL PROPERTIES OF LIGNIN MODEL COMPOUNDS

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ABSTRACT

^1H NMR spectral data for lignin model compounds are of interest in connection with the interpretation of NMR spectra of lignins recorded by 1D (^1H NMR) and certain 2D spectroscopic techniques. Derivatization influences the peak positions in the ^1H NMR spectra of lignin models to a large extent. Similarly an exchange of solvent often results in dramatic shifts of peak positions. Solvent and derivatization effects can be employed for the interpretation of lignin spectra in structural terms. This is here exemplified by results from analyses of lignin samples with respect to total hydroxyl, phenolic groups, distribution of diastereomers of arylglycerol β -aryl ethers, different types of β - β structures and occurrence of 1-aryl-2-aryloxy-1-propanone structures.

I. INTRODUCTION

^1H NMR spectra of acetate derivatives and propionate derivatives of lignin model compounds dissolved in CDCl_3 , CD_3COCD_3 , CD_3SOCD_3 or pyridine- d_5 have been recorded (Lundquist 1979; Lundquist *et al.* 1983; Hauteville *et al.* 1986; Lundquist and von Unge 1986; Li and Lundquist 1997). Spectra of non-derivatized model compounds in CD_3SOCD_3 or dioxane- d_8 - D_2O (5:1) solution have also been recorded (Lundquist 1981; Li and Lundquist 1994; Li and Lundquist 2001). Spectral data obtained in runs with a series of appropriate lignin models under different conditions are compared and differences in signal positions are registered. Based on the results suitable conditions for runs with lignin samples could be selected for the elucidation of particular structural features. This approach to the description of lignins in structural terms is exemplified.

II. RESULTS AND DISCUSSION

Distribution of diastereomers of arylglycerol β -aryl ethers

The positions of the H_α signals of acetylated *erythro* and *threo* forms of a number of lignin models of arylglycerol β -aryl ether type (Figs. 1 and 2) are listed in Table 1. The signal positions of *erythro* and *threo* forms differ significantly. This provides a basis for the elucidation of the proportions of *erythro* and *threo* forms in lignins. (Hauteville *et al.* 1986).

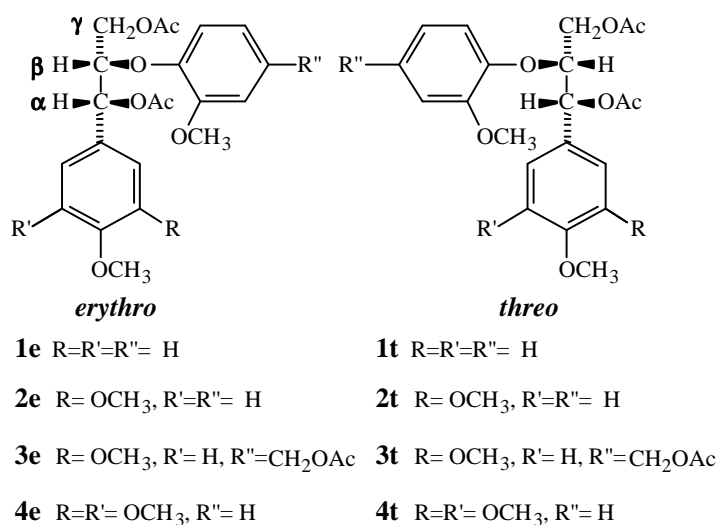


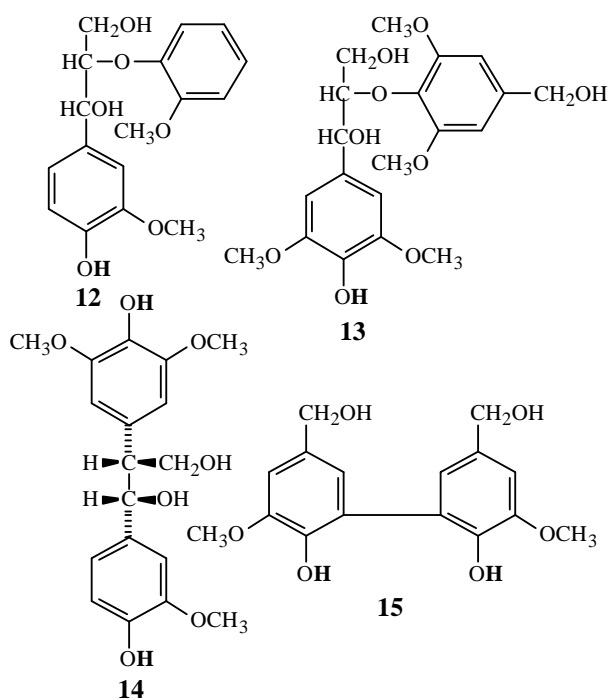
Figure 1. Acetylated lignin models of arylglycerol β -guaiacyl ether type

Table 2. ^1H NMR signal of H_β in **8-10** dissolved in different solvents

Compound	δH_β (ppm)		
	CDCl_3	CD_3COCD_3	$\text{C}_5\text{D}_5\text{N}$
8	3.10	3.10	3.10
9	3.11	3.14	
10	3.10		3.20

Phenolic groups and total hydroxyl

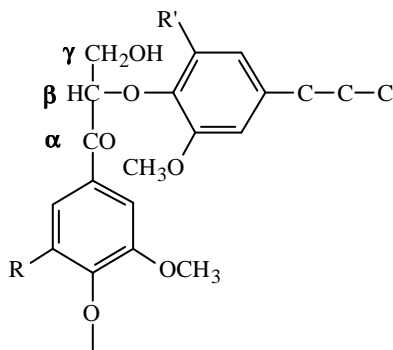
The signals from phenolic groups are separated from other signals in lignin spectra (solvent, CD_3SOCD_3) and quantitative analysis is possible (Li and Lundquist 1994; Li and Lundquist 2001). The location of signals of guaiacyl phenols (excepting biphenyls) and syringyl phenols differ (Table 3). The proportions of these types of phenols can be determined (Li and Lundquist 1994). Total hydroxyl can be determined from spectra of propionate derivatives (CDCl_3) (Li and Lundquist 1997).

**Table 3.** ^1H NMR signal of phenolic OH in **11-15** dissolved in CD_3SOCD_3

Compound	δ Phenolic OH (ppm)
11	8.89
12 (erythro)	8.72
12 (threo)	8.74
13 (erythro)	8.13
13 (threo)	8.11
14	7.93 and 8.63
15	8.21

1-Aryl-2-aryloxy-1-propanones

From ^1H NMR spectra of models and lignins run under different conditions it can be concluded that at most traces of 1-aryl-2-aryloxy-1-propanone structures of type **16** are present in lignins. The presence of small amounts of 1-aryl-2-aryloxy-1-propanone structures of type **17** in hardwood lignins can not be excluded. Enzymic oxidation of benzyl alcohols of syringyl type leads to formation of arylketones (see e.g. Hong *et al.* 2006).



16 R= H or CH_3O , R'= H

17 R= H or CH_3O , R'= CH_3O

III. CONCLUSIONS

Solvents and derivatization of the samples influence the appearance of ^1H NMR spectra to a large extent. Recording of ^1H NMR spectra of lignin samples under different conditions provides structural information that is difficult to obtain by other means.

IV. REFERENCES

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