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^{1}H NMR SPECTRA OF LIGNIN MODEL COMPOUNDS

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ABSTRACT

^{1}H NMR spectral data for lignin model compounds are of interest in connection with the interpretation of NMR spectra of lignins recorded by 1D (^{1}H NMR) and certain 2D spectroscopic techniques. A database comprising such spectral data is being created. Derivatization influences the peak positions in the ^{1}H 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. Stereochemistry strongly influences the position of signals in ^{1}H NMR spectra. This offers a possibility to elucidate the stereochemistry of the structural elements in lignins based on ^{1}H NMR spectral data of model compounds.

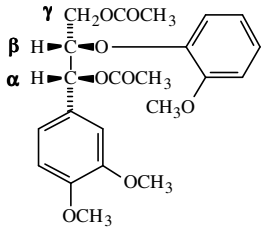
BACKGROUND

A database comprising ^{1}H NMR spectral data of derivatized and non-derivatized lignin model compounds in different solvents is being created. Structural elucidation of lignin model compounds by X-ray crystallography [Ref. 1 and preceding work] provides a firm basis for the assignment of stereoisomers of the model compounds. ^{1}H 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 [2,3]. Spectra of non-derivatized model compounds in CD_3SOCD_3 [4] or dioxane-d_8-D_2O (5:1) [2] solution have also been collected. The elucidation of structural features in lignins based on ^{1}H NMR spectral data of lignin model compounds is exemplified. Excerpts from the database are given below. It is commented on potential applications in lignin analysis.

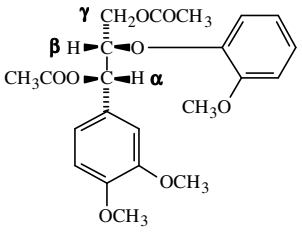
RESULTS AND DISCUSSION

Erythro and *threo* forms of arylglycerol β-aryl ethers (acetate, $CDCl_3$)

The location of the H_α signal differ in *erythro* and *threo* forms (Figure 1).



400 MHz, $CDCl_3$, 300K, $(CH_3)_4Si$	
δ (ppm)	
2.03	3H, s; CH_3CO
2.07	3H, s; CH_3CO
3.79	3H, s; CH_3O
3.86	3H, s; CH_3O
3.87	3H, s; CH_3O
4.23	1H, dd, *J*=4.0 and 11.9 Hz; H_γ
4.42	1H, dd, *J*=5.8 and 11.9 Hz; H_γ
4.70	1H, m; H_β
6.02	1H, d, *J*=5.2 Hz; H_α
≈7	7H, m; H-Ar



400 MHz, $CDCl_3$, 300K, $(CH_3)_4Si$	
δ (ppm)	
2.02	3H, s; CH_3CO
2.03	3H, s; CH_3CO
3.83	3H, s; CH_3O
3.87	6H, s; CH_3O
4.01	1H, dd, *J*=5.9 and 11.9 Hz; H_γ
4.28	1H, dd, *J*=4.0 and 11.9 Hz; H_γ
4.63	1H, m; H_β
6.08	1H, d, *J*=6.8 Hz; H_α
≈7	7H, m; H-Ar

Figure 1: Database sheets showing signal positions of acetylated *erythro* (top) and *threo* (bottom) forms of an arylglycerol β-aryl ether in $CDCl_3$.

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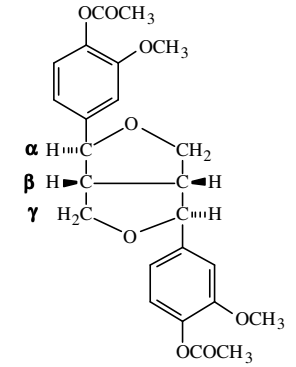
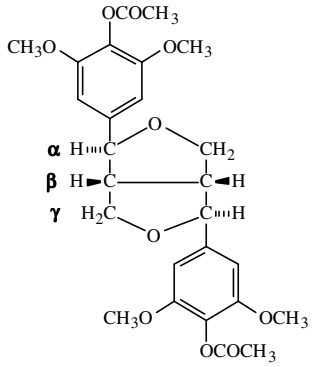
Pinoresinol and syringaresinol (acetate, pyridine)

The locations of the H_β signal of acetylated pinoresinol and syringaresinol differ (Figure 2).



270 MHz, C_5D_5N, ≈300K, $(CH_3)_4Si$	
δ (ppm)	
2.28	6H, s; CH_3CO
3.10	2H, m; H_β
3.76	6H, s; CH_3O
4.01	2H, dd, *J*=3.6 and 9.1 Hz; H_γ
4.29	2H, dd, *J*=6.9 and 9.1 Hz; H_γ
4.95	2H, d, *J*=4.0 Hz; H_α

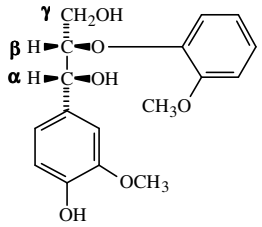


270 MHz, C_5D_5N, ≈300K, $(CH_3)_4Si$	
δ (ppm)	
2.32	6H, s; CH_3CO
3.20	2H, m; H_β
3.76	12H, s; CH_3O
4.08	2H, dd, *J*=3.7 and 9.1 Hz; H_γ
4.37	2H, dd, *J*=6.9 and 9.1 Hz; H_γ
5.00	2H, d, *J*=4.0 Hz; H_α

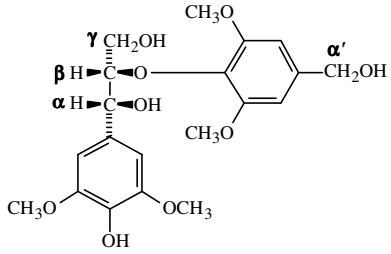
Figure 2: Database sheets showing signal positions of acetates of pinoresinol (top) and syringaresinol (bottom) in pyridine-d_5.

Phenolic groups of the guaiacyl and syringyl types (non-derivatized, CD_3SOCD_3)

The signal from the phenolic group in guaiacyl units and syringyl units are located at different positions (Figure 3). ^{13}C NMR data for β-ether model compounds in CD_3SOCD_3 were recently published [5].



400 MHz, CD_3SOCD_3, 28°C, $(CH_3)_4Si$	
δ (ppm)	
3.59	2H, m; H_γ
3.70	3H, s; CH_3O
3.72	3H, s; CH_3O
4.29	1H, m; H_β
4.57	1H, ≈t, *J*=5.6 Hz; C_γ-OH
4.71	1H, ≈t, *J*=4.8 Hz; H_α
5.28	1H, d, *J*=4.8 Hz; C_α-OH
6.6-7.1	7H, m; H-Ar
8.72	1H, s; Ar-OH

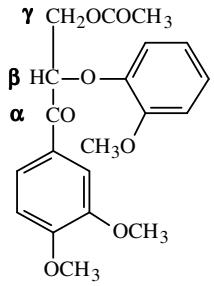


400 MHz, CD_3SOCD_3, 28°C, $(CH_3)_4Si$	
δ (ppm)	
3.39	1H, m; H_γ
3.71	1H, m; H_γ
3.74	6H, s; CH_3O
3.76	6H, s; CH_3O
3.97	1H, ≈t, *J*=6.0 Hz; C_γ-OH
4.09	1H, m; H_β
4.43	2H, d, *J*=5.6 Hz; $H_{\alpha'}$
4.82	1H, ≈t, *J*=5.0 Hz; H_α
5.10	1H, d, *J*=4.8 Hz; C_α-OH
5.15	1H, t, *J*=5.6 Hz; $C_{\alpha'}$-OH
6.61	2H, s; H-Ar
6.64	2H, s; H-Ar
8.13	1H, s; Ar-OH

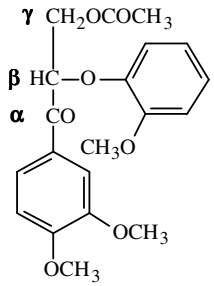
Figure 3: Database sheets showing signal positions of phenolic groups of the guaiacyl and syringyl types.

1-Aryl-2-aryloxy-1-propanones (acetate in CD_3COCD_3 and $CDCl_3$)

The signal from H_β in 1-aryl-2-aryloxy-1-propanones are located at different positions in CD_3COCD_3 and $CDCl_3$. Data for 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)-1-propanone are shown (Figure 4).



270 MHz, CD_3COCD_3, 308K, $(CH_3)_4Si$	
δ (ppm)	
1.96	3H, s; CH_3CO
3.78	3H, s; CH_3O
3.85	3H, s; CH_3O
3.90	3H, s; CH_3O
4.48	1H, dd, *J*=6.4 and 11.8 Hz; H_γ
4.60	1H, dd, *J*=4.0 and 11.8 Hz; H_γ
5.75	1H, dd, *J*=4.0 and 6.4 Hz; H_β



400 MHz, $CDCl_3$, 311K, $(CH_3)_4Si$	
δ (ppm)	
2.03	3H, s; CH_3CO
3.77	3H, s; CH_3O
3.92	3H, s; CH_3O
3.94	3H, s; CH_3O
4.53	1H, dd, *J*=6.8 and 12 Hz; H_γ
4.66	1H, dd, *J*=3.8 and 12 Hz; H_γ
5.59	1H, m; H_β
≈6.9	5H, m; H-Ar
7.68	1H, d, *J*=1.7 Hz; H-Ar
7.84	1H, dd, *J*=1.7 and 8.5 Hz; H-Ar

Figure 4: Database sheets showing signal positions of 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)-1-propanone in CD_3COCD_3 (top) and $CDCl_3$ (bottom).

CONCLUSIONS

Examinations of lignin model compounds show that the interpretation of ^1H NMR spectra of lignins in structural terms is facilitated by recording spectra of non-derivatized and derivatized lignin samples in different solvents.

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