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The Effect of the Intramolecular α-OH$\cdots$O$^{\gamma}$ Hydrogen Bond on the Conformational Composition of β-Aryletheric Lignin Subunits

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The H^1 NMR study of lignin model compounds demonstrates the influence of intramolecualr α-OH$\cdots$O$^{\gamma}$ hydrogen bonds on conformational equilibria of β-aryletheric subunits of lignin polymers. Breaking such bonds by either changing the solvent or methylation of the α-hydroxyl yields the same drastic changes in NMR spectra.

INTRODUCTION

The spatial structure of lignin is a challenging problem in modern wood chemistry. β-aryletheric structures of type I are the most typical »dimeric« subunits of native lignin.[1,2] Therefore, their conformational properties have attracted considerable attention in recent years.[3-6] Nevertheless, the factors that determine their conformational composition have remained unknown. In this study, we used some special effects on the ^1H NMR spectra to clarify the role of the intramolecular hydrogen bond in the conformation stabilization of β-arylethers.

	R^1	R^2	R^3
I	H	OCH_3	H
II	CH_3	OCH_3	H
III	H	H	OCH_3

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RESULTS AND DISCUSSION

Lignin model compounds I–III with the unsubstituted β-methylene group provide a unique opportunity of applying ^{1}H NMR spectroscopy to the conformational analysis of β-arylethers because of the pronounced shift difference of β-methylene protons. The most important problem in the conformational analysis of β-arylethers is how to distinguish between the three rotamers produced by rotation around the C^{α}-C^{β} bond (A,B,C).

The procedure for determining the ratio of these rotamers on the basis of spin-spin coupling constants $J_{\alpha\beta}$ has been described earlier[6], and it was reported that conformer A predominates in nonpolar solutions (compare also[5]). In this study we observed characteristic changes in the ^{1}H NMR spectra (Table I) when changing from a non-polar solvent to a solvent which forms strong intramolecular hydrogen bonds. An intramolecular hydrogen bond was observed in the solution of compound I in deuteriochloroform[6], where, according to the NMR data, the ratio A:B:C is 87:4:9. In deuterioacetone, the ratio is 72:13:15, which indicates the importance of the intramolecular OH· · ·O bond in the relative stabilization of conformer A. It is known that acetone forms strong OH· · ·O=C bonds that compete with intramolecular OH· · ·O bonds. Changing from organic solvents to aqueous alkali (where intramolecular hydrogen bonds are broken) leads to a drastic change in the ^{1}H NMR spectrum, indicating the strong predominance of conformer B, A:B:C = 9:86:5. Methylation of the α-hydroxy group forming II also prevents formation of intramolecular hydrogen bonds and has a similar effect on the ^{1}H NMR spectrum (in deuteriochloroform, A:B:C = = 10:72:18). The data presented show that the main cause of the strong predominance of conformer A is the intramolecular α-OH· · ·O hydrogen bond. Breaking this bond causes B to be the most stable conformer. β-Arylethers are conformationally labile and highly sensitive to solvent effects. It seems that the gauche-effect has no influence on the conformational composition of β-arylethers, the *anti*-ArO-C/C-OH orientation being preferential in the absence of OH· · ·O stabilization.

The conformational preferences of subunits affect conformational equilibria of lignin macromolecules. Therefore, strong influence of a given medium on the spatial

TABLE I

^{1}H NMR data for lignin model β-arylethers I—III δ, ppm (J, Hz)

Compound	I			II	III
Solvent	$CDCl_3$	$(CD_3)_2CO$	1 M $NaOD/D_2O$	$CDCl_3$	$CDCl_3$
α-H	5.04 (9.8,3.4)	4.94 (9.5, 3.7,3.6)		4.59 (8.3,3.3)	5.03 (9.1,3.2)
β-H	4.14 (–10.0, 3.4); 3.98 (–10.0, 9.8)	4.02 (–9.9, 3.7); 3.96 (–9.9, 9.5)	4.04 (–9.9, 9.5); 3.94 (–9.9, 3.2)	4.17 (–10.4, 8.3); 3.98 (–10.4, 3.3)	4.01 (–9.5, 3.2); 3.93 (–9.5, 9.1)
α-OR[1]	–	4.28 (3.6)	–	3.30	–
Ar^A-H	6.80, 7.29 (8.7)	6.78, 7.29 (8.7)	6.61, 7.12 (8.9)	6.82,7.22 (8.7)	6.75,7.32 (8.8)
B-OCH_3	3.89	3.79	3.75	3.83	3.76

structure of lignin is expected. It should be noted that the formation of lignin proceeds in aqueous media, and aqueous alkali is the usual medium in many wood processing procedures. Under these conditions, B should be the most typical orientation, being the most stable one in the case of α-etherified lignin subunits as well. It must be emphasized that this finding does not indicate a preference for the sandwich conformer in the series of lignin model β-arylethers (compare[5]) because the mutual orientation of the two aryl groups does not depend solely on the C_α-C_β torsion. However, in polar media, aryl rings on the β-arylethers subunits of lignin come closer to each other. This media effect resembles the well-known hydrophobic effect in other natural polymers which is of a different nature.

It is important to find out which hydrogen bond has this pronounced effect on conformational composition of β-arylethers. Both α-OH$\cdot\cdot\cdot$O$^\gamma$ and α-OH$\cdot\cdot\cdot$OCH$_3$(B) bonds are possible in molecule I. On the other hand, the distance between the α-hydroxy and methoxy groups in ether III is too long for H- bonding. The ^{1}H NMR spectrum of compound III (Table I.) is very similar to the spectrum of compound I, the ratio A:B:C being equal to 82:9:9. Therefore, the α-OH$\cdot\cdot\cdot$O$^\gamma$ bond is the major factor influencing formation of the spatial structure of lignins.

EXPERIMENTAL

The synthesis of the compounds studied is described elsewhere.[6,7] The ^{1}H NMR spectra of 5% solutions of the compounds were obtained on a Varian Gemini 200 spectrometer. The exact values of the spin-spin coupling constants used in the calculations of the conformational ratios were obtained by computer simulation of the spectra with the standard LAOCOON program.

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SAŽETAK

Efekt intramolekularne α-OH$\cdot\cdot\cdot$O$^\gamma$ vodikove veze na konformacijski sastav β-arileterskih sastavnih dijelova lignina

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^{1}H NMR istraživanje modelnih spojeva lignina pokazuje važnost intramolekularnih α-OH$\cdot\cdot\cdot$O$^\gamma$ vodikovih veza za konformacijske ravnoteže β-arileterskih sastavnih dijelova lignin-skih polimera. Kidanjem takvih veza bilo promjenom otapala ili metiliranjem α- hidroksila vodi do identičnih promjena u NMR spektrima.