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THE STRUCTURE AND CONFORMATION OF LIGNIN AS JUDGED BY X-RAY CRYSTALLOGRAPHIC INVESTIGATIONS OF LIGNIN MODEL COMPOUNDS: ARYLGLYCEROL β -SYRINGYL ETHERS

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ABSTRACT

Structural elements of the arylglycerol β -syringyl ether type are very frequent in hardwood lignins. A variety of crystalline dimeric lignin models representing different diastereomeric forms of structural elements in lignin of this type have been studied using X-ray crystallography. Bond distances and bond angles in the model compounds are in all probability nearly identical with those of the corresponding structural elements in lignins. Based on X-ray crystallographic data from four compounds a sequence of units (5 aromatic rings, 8 chiral C-atoms) attached to each other by β -syringyl ether linkages was constructed. The appearance of the resulting oligomer illustrates that stereoisomerism can be expected to influence the shape of the lignin molecules to a great extent. The constructed oligomer constitutes one of 256 possible stereoisomers (128 racemates).

I. INTRODUCTION

Aiming at an elucidation of the stereochemistry and conformation of the lignin molecules, the conformation of a variety of lignin models, representative of different types of lignin structures, was examined by X-ray crystallography (Lundquist *et al.* 2003). It was found that the bulky aromatic groups in many cases tend to be far apart from each other in the conformations adopted. This suggests that π - π electron repulsion (Hunter and Sanders 1990) between aromatic groups plays a role. However, it is evident that other factors (e.g. hydrogen bonding) also influence the conformations of the model compounds examined. It is notable that the bond angles and bond distances in the model compounds in all probability are almost identical with comparable features of the lignin molecules. This implies among other things that approximate descriptions of the geometry of the reactive sites in lignins can be obtained from crystal structures of model compound. We have paid special attention to model compounds representative of arylglycerol β -aryl ethers, since such structures represent a major type of structural elements in lignins. Here we have focused on sequences of arylglycerol β -syringyl ethers (Fig. 1).

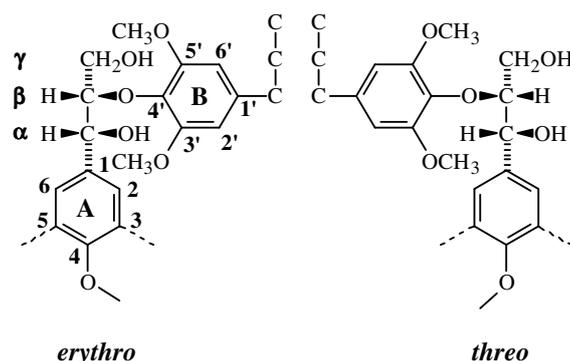


Figure 1. The erythro (αR^* , βS^*) and threo (αR^* , βR^*) forms of arylglycerol β -syringyl ethers

Sequences of such structural elements can be expected to occur rather frequently in hardwood lignins since the number of β -syringyl ethers is large in such lignins (Adler 1977). That this is the case is supported by the fact that such sequences have been detected in birch lignin (Hori and Meshitsuka 2000, Westbye *et al.* 2008) and eucalyptus lignin (Evtuguin and Amado 2003).

II. EXPERIMENTAL

Crystal structures of **1e** (Langer *et al.* 2002), **2e** (Langer and Lundquist 2001), **3e** (Langer *et al.* 2005), **4e** (Stomberg and Lundquist 1989), **1t** (Lundquist *et al.* 2005) and **5t** (Langer *et al.* 2002) have been reported.

is a tendency to regularities regarding conformation in the model compounds examined. However, such tendencies are much more pronounced in arylglycerol β -guaiacyl ethers (Langer *et al.* 2007).

Table 1. Torsion angles of importance for the conformation of arylglycerol β -aryl ethers (Fig. 2): $C_{\text{aryl}}-C_{\alpha}-C_{\beta}-O$ and $C_{\text{aryl}}-O-C_{\beta}-C_{\alpha}$

Substance	Torsion angles ($^{\circ}$)	
	$C_{\text{aryl}}-O-C_{\beta}-C_{\alpha}$	$C_{\text{aryl}}-C_{\alpha}-C_{\beta}-O$
1e	-75.26	-177.27
2e	-89.25	178.58
3e	-152.71	-70.76
4e	-150.55	-70.96
1t	149.08	173.76
5t	-148.25	-70.54

We have constructed an oligomer consisting of a sequence of arylglycerol β -syringyl ethers based on different enantiomeric forms of the crystal structures of **5t**, **2e**, **1e** and **4e** (Fig. 3). The configuration (*R,S*) of the chiral carbon atoms in the oligomer is shown. The *erythro/threo* ratio in the constructed sequence is 3:1. The corresponding *erythro/threo* ratio in a lignin sample has been determined as 55:15 (Bardet *et al.* 1998). The constructed oligomer illustrates the influence of stereochemistry on the shape of the lignin molecules. The "lignin model" constructed (Fig. 3) is representative of segments of lignin molecules, and it should not be viewed as a model for individual lignin molecules. Comparable bond distances and bond angles in the crystal structures are in all probability almost identical with those in corresponding structural elements in lignins. This also holds true for the constructed oligomer since all the geometrical details of the constructed oligomer are identical or practically identical with those found in the crystal structures. The conformation of the model compounds is retained in the constructed oligomer. Therefore it seems reasonable to assume that the conformation of the constructed oligomer represents a plausible alternative. The constructed oligomer represents one of the 256 possible stereoisomers (128 racemates).

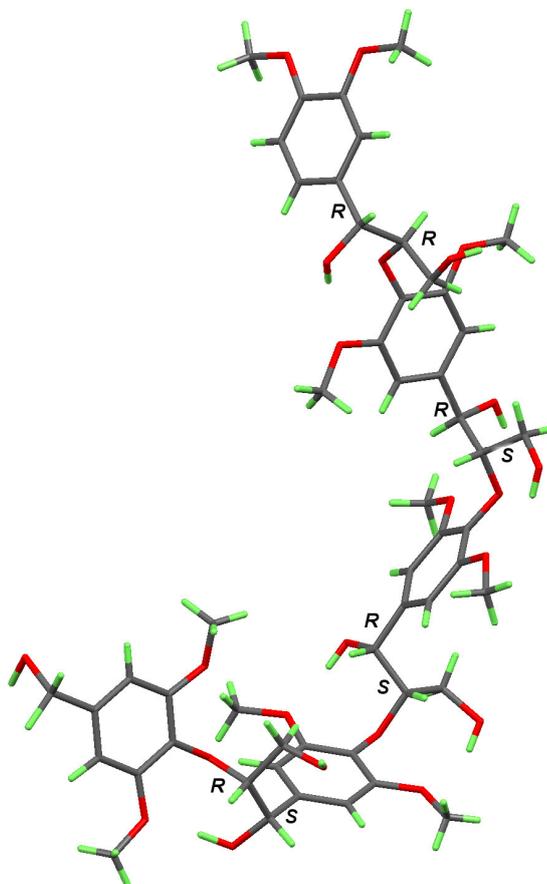


Figure 3. Stereoisomer of a lignin model consisting of a sequence of 5 units attached to each other by β -syringyl ether linkages

IV. CONCLUSIONS

Stereochemistry and conformation have a decisive influence on the shape of the lignin molecules. The sequence of arylglycerol β -syringyl ethers studied exists in a very large number of stereoisomeric forms. This provides an idea about the considerable contribution of stereochemistry alone to the complexity of the lignin structure.

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