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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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. Special attention was paid to the geometry of the β-O-syringyl linkage, since the reactivity of this linkage is of particular interest in connection with pulping reactions. The crystal structures of the model compounds suggest that two types of conformations are predominating; in both of them the aromatic rings are separated by ca. 4.5 Å (maximal distance 4.9-5 Å). 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.

Keywords: Arylglycerol β-syringyl ethers; Conformation; Crystallography; Lignin

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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 comparable bond angles and bond distances in the model compounds are almost identical. Therefore it is reasonable to assume that the bond angles and bond distances in the model compounds agree very closely 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 derived from crystal structures of model compounds. 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).

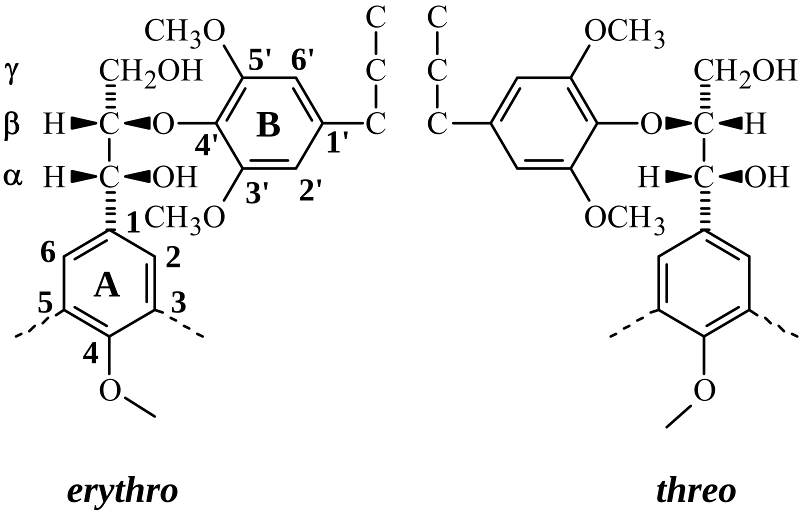
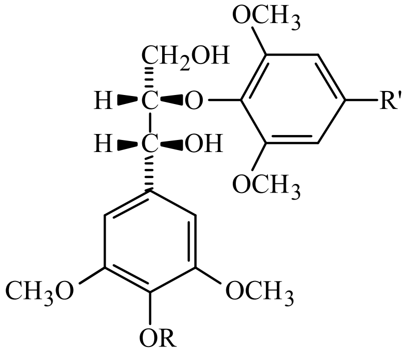


Fig. 1. The *erythro* ($\alpha R^*,\beta S^*$) and *threo* ($\alpha R^*,\beta R^*$) forms of arylglycerol β-syringyl ethers

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). The probability of the occurrence of such sequences is supported by studies of beech lignin (Yamasaki *et al*. 1978), birch lignin (Hori and Meshitsuka 2000; Westbye *et al*. 2008), and eucalyptus lignin (Evtuguin and Amado 2003). Our study is based on examinations of crystalline dimeric arylglycerol β-syringyl ethers.

MATERIALS AND METHODS

Crystal structures of **1e** (Langer *et al*. 2002a), **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*. 2002b) have been reported. Crystal structure data in the references and data calculated based on these data of relevance for a discussion of the conformation of the compounds are given in Table 1. The data presented in Table 2 are calculated using the result of crystal structure analyses. Based on the molecules in the crystal structures of **5t**, **2e**, **1e**, and **4e**, an oligomer consisting of structural elements of arylglycerol β-syringyl ether type was constructed digitally. This was accomplished by replacing ring B (Fig. 1) in **5t** with ring A (*p*-methoxy group removed) in **2e** and subsequently ring B in **2e** was replaced by ring A (phenolic group removed) in **1e**. Finally ring B in **1e** was replaced by ring A (phenolic group removed) in **4e**. In general terms: ring B in one compound is superimposed with ring A (without substituent in position 4) in another compound and the substituents of ring B at positions 1'-3', 5' and 6' are deleted. In each case there are two options for the replacement of the aromatic ring because of the symmetry of the syringyl group. The computer work required was carried out using the program MERCURY (Macrae *et al.* 2006). MERCURY is a program for visualization and analysis of crystal structures. In its full version, provided to users of the Cambridge Structural Database system, display and overlay of multiple structures as well as editing of molecules is possible. The geometries of the two rings (A and B) are almost identical, implying that all the geometrical details of the constructed oligomers are identical or practically identical with those found in the crystal structures. The constructed oligomer is shown in Results and Discussion.

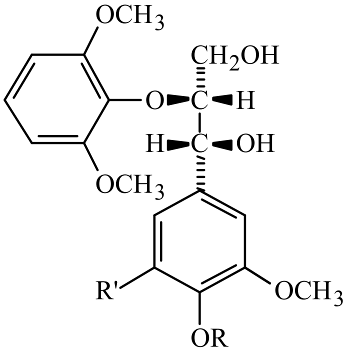


1e R=R'= H

2e R= CH_3, R'= H

3e R= H, R'= CH_3

4e R= H, R'= CH_2OH



1t R=H, R'= CH_3O

5t R= CH_3, R'= H

RESULTS AND DISCUSSION

We have studied the conformational options of structural elements of β-syringyl ether type based on X-ray crystallography of lignin model compounds. An X-ray crystallographic study of the conformation of arylglycerol β-guaiacyl ethers was presented in a previous paper (Langer *et al.* 2007). Computational studies constitute an alternative approach to study the conformation of this type of structural elements (Besombes *et al.* 2003). In the following discussion of torsion angles we have considered the isomer with *R*-configuration at C_{α}. Important torsion angles are C_{aryl}-C_{α}-C_{β}-O and C_{aryl}-O-C_{β}-C_{α} (Fig. 2). Relevant conformational data for models **1e**-**4e**, **1t** and **5t** are collected in Table 1. The C_{aryl}-C_{α}-C_{β}-O angle is either about -70° (**3e**, **4e**, **5t**) or about 180° (**1e**, **1t**, **2e**). When this angle is about -70° the angle C_{aryl}-O-C_{β}-C_{α} is about -150° (**3e**, **4e**, **5t**). When the C_{aryl}-C_{α}-C_{β}-O angle is about 180° the angle C_{aryl}-O-C_{β}-C_{α} is about -80° (**1e**, **2e**) or about 150° (**1t**). The aromatic rings are well separated in all the compounds (Table 1) but it is only in **1t** the distance (4.88 Å) is close to the maximum for C1-C4' (4.9-5 Å). It follows from what is said above and Table 1 that there is a tendency to regularities regarding conformation in the model compounds examined. However, such tendencies are more pronounced in arylglycerol β-guaiacyl ethers (Langer *et al.* 2007).

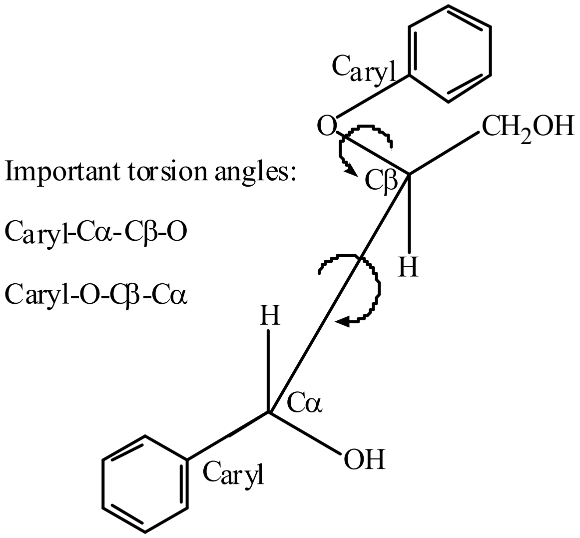


Fig. 2. Torsion angles of importance for the conformation of arylglycerol β-aryl ethers: C_{aryl}-C_{α}-C_{β}-O and C_{aryl}-O-C_{β}-C_{α}

Table 1. Data of Relevance for the Conformation of **1e**-**4e**, **1t** and **5t** (for denotations see Figs. 1 and 2).

	Torsion angles (°)		**Distance C1-C4´ (Å)**	**Ring plane angle (°)**
Substance	C_{aryl}-O-C_{β}-C_{α}	C_{aryl}-C_{α}-C_{β}-O		
1e	-75.3	-177.3	4.45	57.3
2e	-89.2	178.6	4.50	76.0
3e	-152.7	-70.8	4.43	64.1
4e	-150.6	-71.0	4.42	116.9
1t	149.1	173.8	4.88	117.3
5t	-148.2	-70.5	4.32	104.2

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). Since lignins are racemic (Ralph *et al.* 1999, Akiyama *et al.* 2000), an even distribution of enantiomers has been pursued. 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 arylglycerol β-syringyl ethers in 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 the vast majority of 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). Interestingly, sequences of the type shown in Fig. 3 have recently been synthesized and examined by NMR spectroscopy (Kishimoto *et al*. 2008).

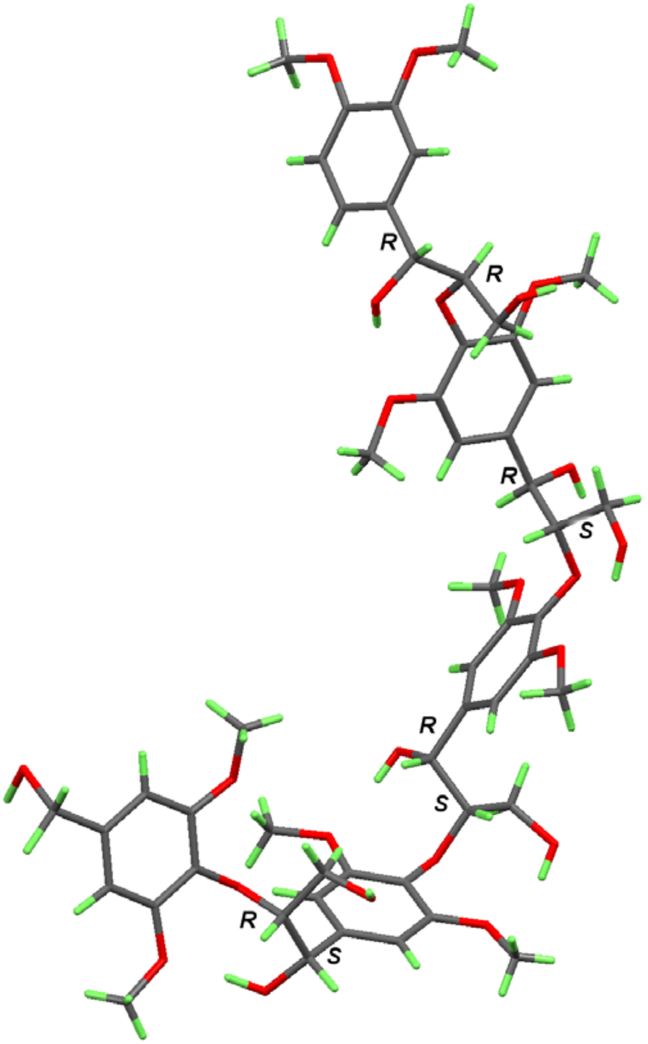
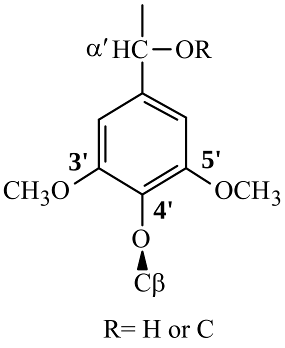


Fig. 3. Stereoisomer of a lignin model consisting of a sequence of 5 units attached to each other by β-syringyl ether linkages

As judged from experiments with model compounds (C_β replaced by CH_3) structural elements in lignin of type **6** can be expected to react comparatively slowly in acid-catalysed reactions involving the benzylic group ($C_{\alpha'}$) such as hydrolysis of benzyl ethers (Meshgini and Sarkanen 1989) or isomerization (Brunow *et al*. 1993).



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The incomplete acid-catalysed methylation of the benzyl alcohols in birch lignin (Adler *et al*. 1987) may be related to the fact that there are many groups of type **6** in birch lignin. Meshgini and Sarkanen (1989) discussed the possibility that a lack of coplanarity of etherified syringyl groups (e.g. **6**) influenced the reactivity. Lack of coplanarity may lower the stability of the benzylic carbocations supposed to be intermediates in acid-catalysed reactions of structural elements in lignins of type **6**. The B-rings (Fig. 1) in model compounds **1e**-**4e**, **1t** and **5t** are representative of the rings in lignin structures of type **6**. It appears in Table 2 that the alkoxy groups of the B-rings in the model compounds are bent out of the ring plane. This is in accordance with the opinion that lack of coplanarity contributes to the low reactivity of lignin structures of type **6** in acid-catalysed reactions.

Table 2. Bond Angles and Deviation of O Atoms from the Ring Plane in the B-Ring of **1e**-**4e**, **1t** and **5t** (see formula **6**). C_β is considered to be located above the ring plane (on an average +1.15 Å).*

	Deviations from the B-ring plane (Å)			**Bond angles (°)**	
Substance	**O3´**	**O4´**	**O5´**	**C4´-C3´-O**	**C4´-C5´-O**
1e	-0.02	-0.05	-0.06	115.6	115.6
2e	-0.02	-0.07	-0.01	115.4	115.0
3e	0.00	-0.09	+0.05	115.9	115.1
4e	+0.02	-0.09	-0.01	114.8	115.0
1t	-0.03	-0.06	-0.04	114.4	115.2
5t	+0.01	-0.11	0.00	114.9	114.7

* Corresponding data for the A-ring in **2e** are: -0.03, -0.11, +0.05, 115.5 and 115.1.

CONCLUSIONS

1. Stereochemistry strongly influences the structure and conformation of lignins.
2. The lack of coplanarity of syringyl alcohols with etherfied phenolic group counteracts the reactivity of such groups in acid-catalysed reactions.
3. 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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