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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).

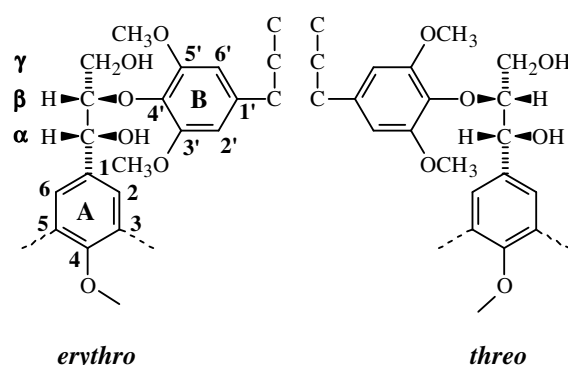


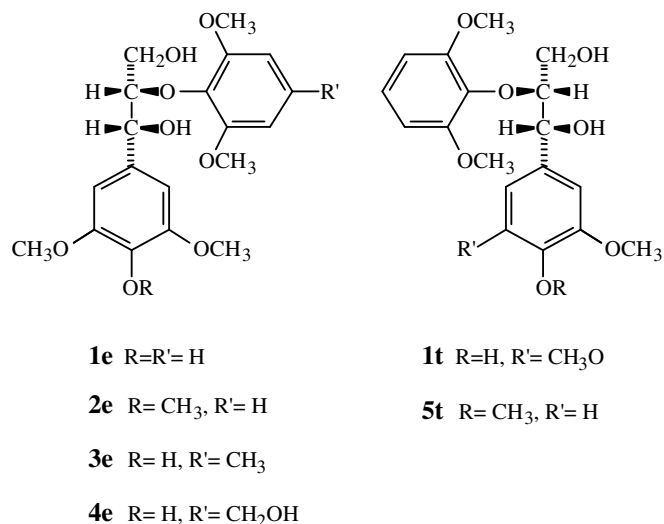
Figure 1. The erythro (αR^* , βS^*) and threo (αR^* , βR^*) forms of arylglycerol β -syringyl ethers

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.

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 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.

III. 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. 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 $C_{\text{aryl}}-C_{\alpha}-C_{\beta}-O$ and $C_{\text{aryl}}-O-C_{\beta}-C_{\alpha}$ (Fig. 2).

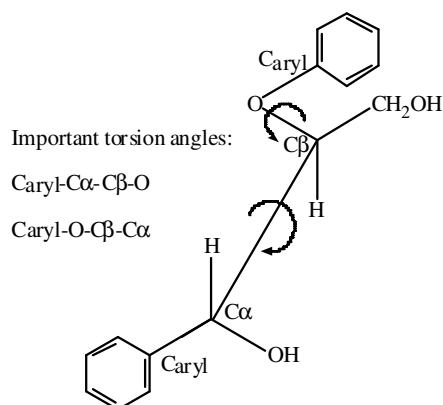


Figure 2. Torsion angles of importance for the conformation of arylglycerol β -aryl ethers: $C_{\text{aryl}}-C_{\alpha}-C_{\beta}-O$ and $C_{\text{aryl}}-O-C_{\beta}-C_{\alpha}$

Relevant conformational data for models **1e-4e**, **5t** and **1t** are collected in Table 1. The $C_{\text{aryl}}-C_{\alpha}-C_{\beta}-O$ angle is either about -70° (**3e**, **4e**, **5t**) or about 180° (**1e**, **1t**, **2e**). When this angle is about -70° the angle $C_{\text{aryl}}-O-C_{\beta}-C_{\alpha}$ is about -150° (**3e**, **4e**, **5t**). When the $C_{\text{aryl}}-C_{\alpha}-C_{\beta}-O$ angle is about 180° the angle $C_{\text{aryl}}-O-C_{\beta}-C_{\alpha}$ is about -80° (**1e**, **2e**) or about 150° (**1t**). The aromatic rings are well separated in all the compounds 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 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).

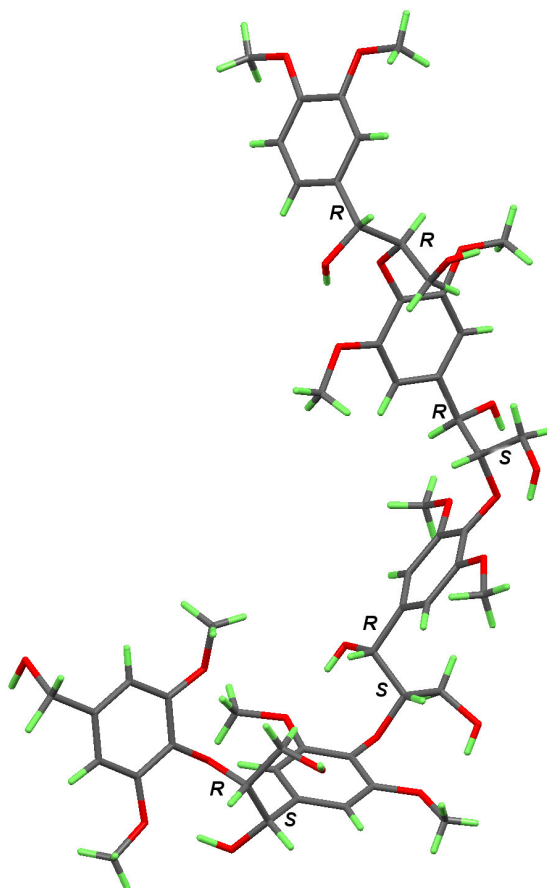


Figure 3. Stereoisomer of a lignin model consisting of a sequence of 5 units attached to each other by β -syringyl ether linkages

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.

V. REFERENCES

- E. Adler, Lignin chemistry-past, present and future, *J. Wood Chem. Technol.* **1977**, *11*, 169-218.
- M. Bardet, D. Robert, K. Lundquist and S. von Unge, Distribution of *erythro* and *threo* forms of different types of β -O-4 structures in aspen lignin by using the ^{13}C NMR 2D INADEQUATE experiment, *Magn. Reson. Chem.* **1998**, *36*, 597-600.
- S. Besombes., D. Robert, J.-P. Utille, F.R. Taravel and K. Mazeau, Molecular modelling of syringyl and *p*-hydroxyphenyl β -O-4 dimers: Comparative study of the computed and experimental conformational properties of lignin β -O-4 model compounds, *J. Agric. Food Chem.* **2003**, *51*, 34–42.
- D.V. Evtuguin and F.M.L. Amado, Application of electrospray ionization mass spectrometry to the elucidation of the primary structure of lignin, *Macromol. Biosci.* **2003**, *3*, 339-343.
- K. Hori and G. Meshitsuka, Structural heterogeneity of hardwood lignin: characterization of end-wise lignin fraction, In: *Lignins: historical, biological, and materials perspectives*, **2000**, Eds. Glasser W.G., Northey, R.A. and Schultz, T.P., ACS Symp. Ser. 742. pp. 172-185.
- C.A. Hunter, and J.K.M. Sanders, The nature of π - π interactions, *J. Amer.Chem. Soc.* **1990**, *112*, 5525-5534.
- V. Langer, S. Li and K. Lundquist, *erythro*-2-(2,6-Dimethoxyphenoxy)-1-(4-hydroxy-3,5-dimethoxyphenyl)-1,3-propanediol, *Acta Cryst. E* **2002**, *58*, o42-o44.
- V. Langer and K. Lundquist, *erythro*-2-(2,6-Dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)-1,3-propanediol, *Acta Cryst. E* **2001**, *57*, o1219-o1221.
- V. Langer, K. Lundquist, R. Stomberg and S. von Unge, *threo*-2-(2,6-Dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1,3-propanediol, *Acta Cryst. E* **2002**, *58*, o90-o92.
- V. Langer, K. Lundquist and G. Miksche, *erythro*-2-(2,6-Dimethoxy-4-methylphenoxy)-1-(4-hydroxy-3,5-dimethoxyphenyl)propane-1,3-diol, *Acta Cryst. E* **2005**, *61*, o1001–o1003.
- V. Langer, K. Lundquist and J. Parkås, The stereochemistry and conformation of lignin as judged by X-ray crystallographic investigations of lignin model compounds: Arylglycerol β -aryl ethers, *BioResources* **2007**, *2*, 590-597.
- K. Lundquist, V. Langer, S. Li and R. Stomberg, Lignin stereochemistry and its biosynthetic implications, *Proc. of the 12th International Symposium on Wood and Pulping Chemistry*, Madison, Wisconsin, USA, June 9-12, **2003**, pp. 239–244.
- K. Lundquist, S. Li and V. Langer, *threo*-2-(2,6-Dimethoxyphenoxy)-1-(4-hydroxy-3,5-dimethoxyphenyl)propane-1,3-diol: a conformational study, *Acta Cryst. C* **2005**, *61*, o256-o258.
- C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler and J. van de Streek, Mercury: visualization and analysis of crystal structures, *J. Appl. Cryst.* **2006**, *39*, 453-457.
- R. Stomberg and K. Lundquist, On the stereochemistry of lignin model compounds of the arylglycerol- β -aryl ether type: Crystal structure of *erythro*-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(4-hydroxymethyl-2,6-dimethoxyphenoxy)-1,3-propanediol, $\text{C}_{20}\text{H}_{26}\text{O}_9$, *J. Crystallogr. Spectrosc. Res.* **1989**, *19*, 331–339.
- P. Westbye, T. Köhnke and P. Gatenholm, Fractionation and characterization of xylan rich extracts from birch, *Holzforschung* **2008**, *62*, 31-37.