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Simulation of Reactions with Lignin by Computer (SIMREL). 5. Nondehydrogenative Polymerization in Lignin Formation

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In previous papers of this series,[2] two of us have reported on computer simulation studies of the formation and analysis of softwood lignin.In the last two papers it was demonstrated that the computation of model structures is not possible, which satisfy all experimental results of the elemental analysis, ^1H NMR spectroscopy, and oxidative degradations with nitrobenzene and permanganate, unless the concentration of linkages based on nondehydrogenative polymerization reaches levels of 22–24% of the total number of linkages. The existence of such linkages in lesser concentrations has been known for some time, and has commonly been reported to occur in the form of benzyl aryl ethers (α-O-4) (Type A, Figure 1).[3] However, when all nondehydrogenative linkages in lignin were assumed to be of the α-O-4 type in the simulation, we did not succeed in modeling a lignin structure which could duplicate analytical observations. Experimental and modeled analytical results deviated to a lesser degree if ¾ of all nondehydrogenative linkages were of a benzyl alkyl ether, α-0-γ type (B, Figure 1). In this event, however, modeling consistently required the presence of upwards to 30% double bond containing end groups, an observation which was incidenced by the necessity to limit the abundance of pinoresinol type, β–β linked structures to 2–4%. Such low concentrations of pinoresinol structures in spruce lignin are indicated by the carbon-13 nmr spectra,[4] and have previously been concluded from the absence of pinoresinol among the acidolysis products of spruce lignin.[5] If constraints were introduced in the simulation program to limit the number of end groups to 9%, the value cited by Lai and Sarkanen,[6] dehydrogenative simulated polymerization did not progress. Even lower endgroup concentrations (6%) were quoted in two Swedish publications.[7] This observation led two of us (W.G.G. and H.R.G.) to the conclusion that some kind of vinyl polymerization must occur during the formation of lignin, which leads to nondehydrogenative linkages by involving double bonds.[8] Recent experimental evidence obtained by one of us (H.H.H.N.) provides support for the occurrence of vinyl-type polymerization in lignin through the successful isolation of α–β linked dimers from beech and spruce lignin.[9] We have now jointly explored, by computer simulation, the impact which the presence of several mechanistically conceivable, vinyl-based nondehydrogenative linkages would have on a model lignin structure in terms of expected analytical results. These simulations have resulted in several model structures among 80, which can explain analytical results obtained by elemental analysis (procedure I), ^1H NMR spectroscopy (procedure II), nitrobenzene oxidation (procedure III), permanganate oxidation (procedure IV), and permanganate oxidation following mild alkaline hydrolysis (procedure V). The best of these structures has an empirical formula of $C_9H_{7.11}O_2(H_2O)_{0.41}(OCH_3)_{0.92}$ reflecting a degree of dehydrogenation (DD) of 1.98. Results obtained by Freudenberg and co-workers following extensive structural work of softwood lignin indicate that lignin of spruce wood has the composition of $C_9H_{7.15}O_2(H_2O)_{0.40}(OCH_3)_{0.92}$ and a DD of 1.94.[10] Simulated analytical results of procedures I–V show similar accord with experimental values. Some of them are as follows (experimental values given in parentheses; for reference see papers III and IV of this series[2] and Miksche et al.[11]): Procedure I (in %): C, 65.03 (65.08); H, 5.88 (5.90); O, 29.09 (29.02). Procedure II (acetylated lignin, in H/C_9): aromatic and α-vinylic, 2.7 (2.6); acetoxyl, 4.2 (4.2). Procedure III (yield in %): vanillin, 37.1 (27.5). Procedures IV/V (all as methyl esters, yield in %): veratric acid, 14.8/35.3 (10.6/29.8); isohemipinic acid, 4.4/11.8 (1.9/5.0); metahemipinic acid,[13] 1.5/4.4 (0.8/1.1); 2,2′,3,3′-tetramethoxybiphenyl-5,5′-dicarboxylic acid, 0.0/6.8 (1.1/6.7); 5-(2-methoxy-4-carboxyphenoxy)veratric acid, 2.2/4.4 (1.5/2.1). This lignin model structure is based on a total of 23.4% nondehydrogenative linkages and 8.5 and 4.3% sidechain displacement and phenol dienone rearrangement reactions, respectively (cf. paper I of this series).[2] The concentration of double bond-containing end-groups is 12%, that of phenolic hydroxyl groups 30%, and that of β-β linkages 2.1%.

Nondehydrogenative linkages contained in this model structure are of five different types, and these are shown in Figure 1. The relative frequencies of these linkages amount to: types A (α-O-4) and B (α-O-γ) 25% each, types C (α-β, 6-α; indan) and D (α-β) 15% each, and type E (α-β, γ-O-α; pyran) 20%.

The formation of type C–E structures can be explained through cationic vinyl polymerization involving benzylium ions. A related effect of the natural acidity of cell saps on coniferyl alcohol has earlier been suspected by Freudenberg, Maercker, and Nimz,[12] who thought that the H^+ concentration at the cell boundaries may influence tree lignification. In this study, coniferyl alcohol was polymerized at pH 2.5–3, and dimeric and trimeric structures similar to the ones proposed here were isolated. However, the suspected presence of such structures in native lignin has later been abandoned.

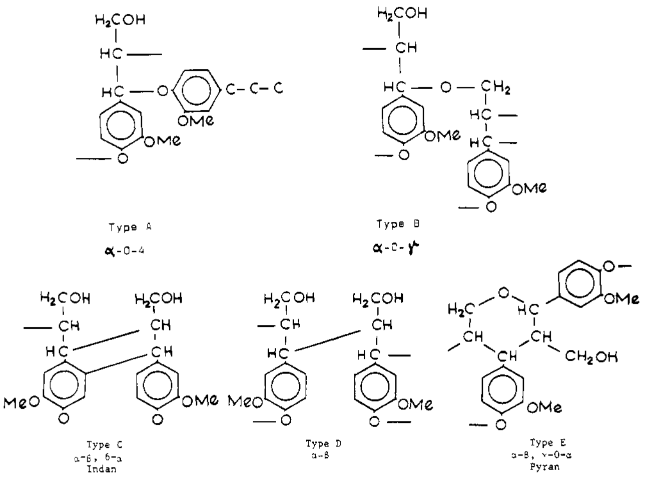

Figure 1. Proposed nondehydrogenative linkages in lignin.

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In simulation studies, we now find that the presence of such structures in relatively small concentrations in softwood lignin is required if this lignin structure is to explain all experimental observations. These concern in particular the balance and distribution of hydroxyl groups (phenolic and primary and secondary aliphatic), the concentration of β–β, 5–5, and ether linkages, and the frequency of double bonds and external water additions to quinonemethide intermediates. Computer simulation techniques have again been found to provide a valuable aid to correlating structural details with a variety of analytical observations in lignin chemistry.

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(13) The higher yields from simulated oxidative degradations must be explained with the great instability of particularly benzene–dicarboxylic acids in the reaction medium.

A Method for Calculating Dihedral Angles in Helical Polymers with Given Values of Unit Height and Unit Rotation[1]

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Many homopolymers, sequential copolymers, and sometimes even random copolymers take helical conformations in solution and/or in crystal. In such fields as the x-ray crystrallography and the conformational energy analysis, oftentimes it becomes necessary to find a set of backbone dihedral angles $\omega_1, \omega_2, \ldots, \omega_m$ in a unit structure that generates a helical conformation with given values of unit height h and unit rotation ϕ. This paper describes a mathematical method to find such a set of dihedral angles. The case in which the value of the unit height h is not specified and only the value of the unit rotation ϕ is specified has been recently studied and solved by Yokouchi, Tadokoro, and Chatani.[3] The method in the present note is similar to the one developed previously[4] for finding a set of dihedral angles that generates conformations of cyclic chain molecules with C_n, I, or S_{2n} symmetry. Therefore we use some of the quantities and equations given in ref 4 without redefining them in the present paper.

The unit height h and the unit rotation ϕ are functions of the dihedral angles $\omega_1, \omega_2, \ldots, \omega_m$ in a unit structure, i.e.,

$$h = h(\omega_1, \omega_2, \ldots, \omega_m) \tag{1}$$

$$\phi = \phi(\omega_1, \omega_2, \ldots, \omega_m) \tag{2}$$

Our problem is to find sets of values of $\omega_1, \omega_2, \ldots, \omega_m$ for which the functions h and ϕ assume given values. In order to solve this problem we assume that the values of $\omega_1, \omega_2, \ldots, \omega_{m-2}$ are preassigned and regard eq 1 and 2 as algebraic equations for a pair of unknowns ω_{m-1} and ω_m. As before[4] we designate ω_{m-1} and ω_m by ξ and η in order to emphasize that they are unknowns.

In order to obtain the explicit forms of eq 1 and 2, a local coordinate system is defined corresponding to each of the variable backbone dihedral angles. Then, the mth coordinate system is related to the 0th one by the symmetry operation of helix. If we designate the matrix of rotation to bring the mth coordinate system into the same orientation as that of the 0th one by $\mathbf{U}$ and the position vector of the origin of the mth coordinate system with respect to the 0th one by $\mathbf{p}$, the explicit forms of eq 1 and 2 are given by

$$\mathrm{Tr}\,\mathbf{U} = 2\cos\phi + 1 \tag{3}$$

$$\mathbf{u}\cdot\mathbf{p} = h \tag{4}$$

Here Tr means trace. The explicit forms of matrix $\mathbf{U}$ and vector $\mathbf{p}$ are given by eq I-7 and I-8 in terms of the backbone dihedral angles $\omega_1, \omega_2, \ldots, \omega_m$. The unit vector $\mathbf{u}$, about which the rotation of the matrix $\mathbf{U}$ takes place, is given by eq I-34 in terms of elements of $\mathbf{U}$ and the angle of rotation ϕ. In some cases it is prefereable to use the following equation instead of eq 4.

$$\mathbf{p}\cdot\mathbf{Up} = h^2(1 - \cos\phi) + p^2\cos\phi \tag{5}$$

This equation can be derived from eq I-12 and 4. The matrix $\mathbf{U}$ and the vector $\mathbf{p}$ depend on the unknown backbone dihedral angles ξ and η in such a way that they can be expressed as $\mathbf{AXBY}$ and $\mathbf{a} + \mathbf{AXb}$, respectively, where $\mathbf{A}$ and $\mathbf{B}$ on one hand and $\mathbf{a}$ and $\mathbf{b}$ on the other hand are matrices and vectors, respectively, depending only on the known dihedral angles (i.e., $\omega_1, \omega_2, \ldots, \omega_{m-2}$), and $\mathbf{X}$ and $\mathbf{Y}$ are the matrices of rotation about the x axis by ξ and η, respectively. Explicit forms of these matrices and vectors are given in ref 4. If an additional matrix $\mathbf{C}$ is defined by $\mathbf{AXB}$ (eq I-36), eq 3 and 4 can now be written respectively as

$$\alpha\cos\eta + \beta\sin\eta + \gamma = 0 \tag{6}$$

and

$$\alpha'\cos\eta + \beta'\sin\eta + \gamma' = 0 \tag{7}$$

with

$$\begin{aligned} \alpha &= c_{22} + c_{33} \\ \beta &= c_{23} - c_{32} \\ \gamma &= c_{11} - 1 - 2\cos\phi \end{aligned} \tag{8}$$

and

$$\begin{aligned} \alpha' &= p_1(c_{23} - c_{32}) - p_2c_{13} + p_3c_{12} \\ \beta' &= -p_1(c_{22} + c_{33}) + p_2c_{12} + p_3c_{13} \\ \gamma' &= p_2c_{31} - p_3c_{21} + 2h\sin\phi \end{aligned} \tag{9}$$

where c_{ij} is the i,j element of matrix $\mathbf{C}$, and p_i is the i component of vector $\mathbf{p}$. In case eq 5 is used instead of eq 4, eq 5 can also be written as eq 7, but now with

$$\begin{aligned} \alpha' &= p_2(p_1c_{12} + p_2c_{22} + p_3c_{32}) + p_3(p_1c_{13} + p_2c_{23} + p_3c_{33}) \\ \beta' &= p_2(p_1c_{13} + p_2c_{23} + p_3c_{33}) - p_3(p_1c_{12} + p_2c_{22} + p_3c_{32}) \\ \gamma' &= p_1(p_1c_{11} + p_2c_{21} + p_3c_{31}) \\ &\qquad - \cos\phi(p_1^2 + p_2^2 + p_3^2) - (1 - \cos\phi)h^2 \end{aligned} \tag{10}$$