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Cellulose-Lignin Interactions[1]

A Computational Study

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Within a broader program of study of the molecular structure of plant cell walls, molecular dynamics calculations were used to explore the character of the motion of lignin model compounds near a cellulose surface. Model cellulose microfibrils, which have a large number of hydroxyl groups on the surface, appear to have a net attractive interaction with the lignin models examined in this study. The lignin monomer coniferyl alcohol rapidly adsorbed onto the surface from a water layer after it was released 13 Å from the surface. The major long-range force responsible for this adsorption is likely electrostatic. The attractive interaction is sufficient to restrict the motion of coniferyl alcohol when it is within 1 Å of the surface and to orient the phenyl ring parallel to the surface. The *b-O-4*-linked trimer also was observed to adsorb onto the surface with two of its phenyl rings parallel to the surface. These results suggest a mechanism by which the polysaccharide component of the plant cell wall could influence the structure of lignin. Furthermore, they provide a rationalization of the experimental observation that polysaccharides can change the course of dehydrogenation polymerization of cinnamyl alcohols.

A number of recent observations have given indications that the structure of lignin in higher plant cell walls is not amorphous, as is often suggested (Sarkanen and Ludwig, 1971). Raman microprobe studies of secondary walls in *Picea mariana* (black spruce) revealed that phenyl rings of lignin are aligned preferentially in the plane of the cell walls (Atalla and Agarwal, 1985; Agarwal and Atalla, 1986). Furthermore, observation of photoconductivity in woody tissue points to the existence of pathways for electronic charge transport (R.H. Atalla and B. Abosharkh, unpublished results). The level of spatial organization prerequisite for these phenomena implies a coherence of order and connectivity that is not at all consistent with the types of structures usually attributed to lignin. Nor are they the types of structures that one would expect from random free radical coupling reactions. Thus, one is left with fundamental questions about the biological mechanism responsible for the organization of lignin. Answers to these questions will lead to a better understanding of lignin structure and cell wall biogenesis.

Studies of the biogenesis of lignin have usually focused on efforts to generate DHPs of cinnamyl alcohols that approximate, in their patterns of inter-unit linkages, the structures that have been detected in lignins. The desire of Freudenberg (1964) and many researchers who followed him was to synthesize a polymer that had physical, chemical, and spectroscopic properties similar to those of MWLs. But even in these early studies, it was clear that there were significant differences between DHPs and MWLs, and much research has been directed at identifying the factors that may be responsible for the differences.

A factor considered in a number of studies was the effect of the carbohydrate matrix. One of the first studies was concerned with the polymerization of eugenol in plant tissues (Siegel, 1953). This work led to the hypothesis that the polysaccharide component of plant cell walls can modify the course of the polymerization that produces lignin. In an attempt to understand the influence of polysaccharides on the course of the polymerization reaction, subsequent studies focused on the chemical and spectroscopic characteristics of ethanol- and chloroform-insoluble products formed in the presence of various macromolecules (Siegel, 1957). It was found that water-soluble polysaccharides, i.e. methylcellulose, starch, and arabic acid, lead to the formation of material that could be classified as similar to lignin. Although these studies point to the possibility that a polysaccharide matrix can change the course of cinnamyl alcohol polymerization, they give little information about the specific chemical changes that could be attributed to the presence of the matrix.

More detailed information about the chemical nature of the polymer formed in the presence of hemicelluloses and pectic acid was reported by Higuchi et al. (1971). Based on the analysis of the products of oxidation and acidolysis, they concluded that DHPs formed from coniferyl alcohol have linkages similar to MWL, but the mol wts of the DHPs

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Abbreviations: DHP, dehydrogenation polymer; MWL, milled-wood lignin.

were still only approximately half that of MWL. They reported that the addition of polysaccharides tended to increase the mol wt of the DHP slightly. In another study, the presence of mannan was shown to favor the formation of *b*-aryl ether linkages in the DHP formed from sinapyl alcohol (Tanahashi and Higuchi, 1990). Finally, one can conclude from the data reported by Higuchi et al. (1971) that DHPs are not as highly condensed as MWL. Terashima and Seguchi (1988) attempted to look directly at the effect that polysaccharides had on the degree of condensation. In their work, the degree of condensation was assumed to be related to the number of linkages through the 5-position of the phenyl rings. Using an innovative radiotracer technique, they were able to show that the presence of pectin and mannan resulted in the formation of a DHP with more substitution at the 5-position. Since polysaccharides tend to increase the mol wt of DHPs, favor the formation of *b-O*-4 linkages, and enhance condensations via the 5-position, it is reasonable to conclude that DHPs formed in the presence of polysaccharides are more similar to MWL than those formed in free solution. These experiments indirectly indicate that there is an associative interaction between polysaccharides and lignin oligomers. Recently, more direct evidence for such an interaction was reported by Sugino et al. (1994). They showed that coumaryl, coniferyl, and sinapyl alcohols associated with hemicelluloses and pectin.

The objective of the present study was to explore, using molecular modeling methods, the modes of association between the monomer or oligomers of coniferyl alcohol and polysaccharide surfaces. The premise underlying the program was that association of lignin precursors with the polysaccharide surfaces may result in some organization of the precursors prior to polymerization, and this in turn could result in influences on the resulting primary structure and the linkage conformations that occur in the polymer. Using molecular dynamics modeling methods, we followed the motion of the monomer or oligomers near a polysaccharide surface and monitored the progress of the association with the polysaccharide substrate. The findings provide some valuable insights concerning the nature of the association and its potential influence on lignin structure.

MATERIALS AND METHODS

Development of the Molecular Model

The major implication of the early work of Siegel (1957) is that ordered arrays of hydroxyl groups seem to be the key to modification of the course of the dehydrogenation polymerization of eugenol. For purposes of this computational study, one must choose a representative molecular system. If one looks to studies of cell wall biogenesis (Terashima et al., 19931, one finds three possible polysaccharides: cellulose, hemicelluloses, and pectic substances. Cellulose can provide ordered arrays of hydroxyl groups, but the solution structures of hemicelluloses and pectic substances are less well defined. Schulz and Burchard (1993) recently suggested that the formation of aggregates in solution by cellulose derivatives is consistent with their light-scattering and hydrodynamic measurements. Thus, it is likely that hemicelluloses do not exist as free chains in solution but as partially ordered arrays. Furthermore, it has been shown that hemicellulose chains can be incorporated into the lattice of cellulose (Atalla et al., 1993; Hackney et al., 1994). This result suggests that hemicelluloses, in the presence of cellulose microfibrils, will likely be adsorbed strongly onto the surface and exhibit chain conformations similar to those of cellulose. Pectin, in the presence of calcium ions, is known to form sheet-like structures in solution (Walkinshaw and Arnott, 1981), but its detailed structure is difficult to characterize. A model of the primary cell wall would include cellulose, hemicelluloses, metal ions, pectic substances, proteins, lignin precursors, lipids, and water, but inclusion of all of these components is not feasible at this time. Thus, for these exploratory studies, we have chosen to limit our scope to the secondary cell wall, in which cellulose, lignin, and water are dominant. Future studies will address the influence of the other components.

The molecular modeling of carbohydrates has been the subject of active research for many years. Examples of many of the computational methods applied to carbohydrates have been published (French and Brady, 1990). More recently studies of carbohydrates in water solution have begun to appear in the literature (Hardy and Sarko, 1993). Although the computational study of carbohydrates is well advanced, the study of lignin models is less well developed. A review of the application of computational methods to lignin structures has been published (Elder, 1989). Although the present work builds on this foundation of previous studies, there appear to be no prior descriptions of computational studies of the interaction of lignin and carbohydrates in water.

Polysaccharide Surface

In the hydrated environment characterizing the nascent cell wall, it is likely that the stable cellulose surfaces are the ones that are compatible with water. This implies that, since cellulose can exhibit both hydrophilic and hydrophobic faces depending on which way the crystal is terminated, the hydrophilic faces will be favored in natural systems (Kuga and Brown, 1991). This prediction has been confirmed by the high-resolution EM studies of Sugiyama et al. (19851, which indicate that the microfibrils of *Valonia macrophysa* exhibit two surfaces. Their conclusion was based on the observation of lattice images that show coherent crystalline domains with crystal plane spacings of 5.4 and 6.0 Å. These correspond to the $(1\bar{1}0)$ and (110) planes, if one defines the axes as shown in Figure 1. Our definition of the axes differs from the one used by Sugiyama et al. in that we have chosen to define the *c* axis parallel to the cellulose chain axis. Molecular modeling of these surfaces confirms that the two surfaces do expose a large number of hydroxyl groups on the surface and thus are largely hydrophilic.

The model cellulose surface was extracted from the cellulose I lattice as refined by Gardner and Blackwell (1974). The five cellulose chains for the model surface are high-

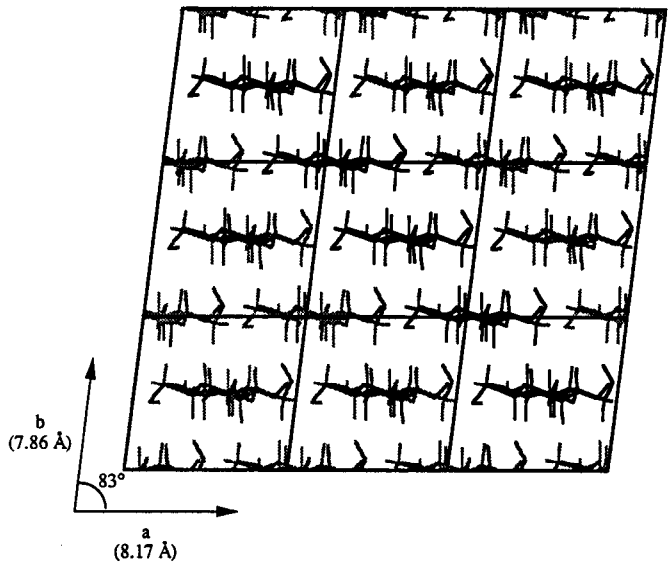

Figure 1. View of the cellulose I lattice as described by Gardner and Blackwell (1974). This view is along the *c* axis, which is also the chain axis. The highlighted chains were used to construct the model cellulose (110) surface.

lighted in Figure 1. Although some questions remain concerning the accuracy of this model (Atalla, 1987), it represents a sufficiently close approximation for the computer model. Each of the five chains had seven anhydroglucose units. The computational box conformed to the shape of the surface generated by truncation at the glycosidic linkages between Glc units. This results in a nonrectangular computational box, since adjacent chains are offset by 2.5 Å relative to each other. This point is illustrated in Figure 2. The model surface of 35 anhydroglucose units was placed at the bottom of a computational box, as is shown in Figure 3. The box conformed to the size and shape of the surface such that periodic boundary conditions could be used to approximate an extended system (Allen and Tildesley, 1987). The application of periodic boundary conditions to this system means that copies of the computational box are placed on all sides of the central box, and when a molecule

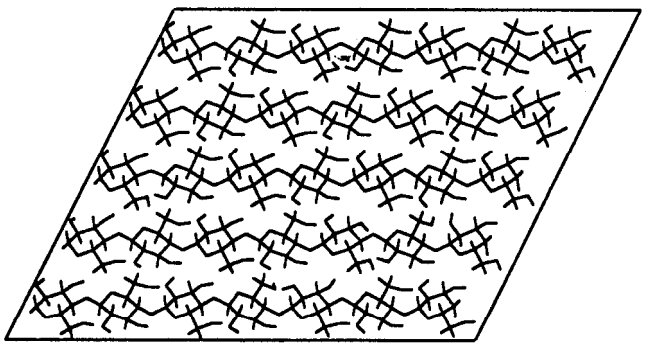

Figure 2. A top view of the model cellulose surface. An acute angle of 64.5° was required because of the 2.5 Å offset of adjacent chains. This surface is composed of five chains with seven Glc units per chain.

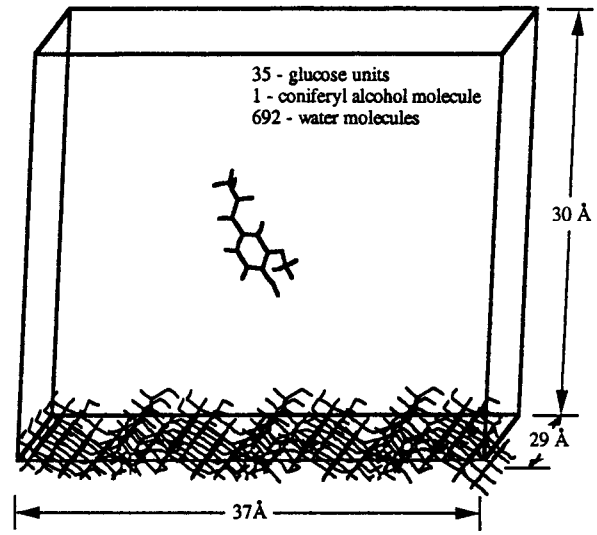

Figure 3. Illustration of the computational box used for the molecular dynamics calculations. The carbon and oxygen atoms of the cellulose surface have been fixed at the bottom of the box.

moves out of one side of the box it is returned to the other side. The carbon and oxygen atoms of the cellulose surface were held in fixed positions at the bottom of the box, but the hydrogen atoms were allowed to move. This constraint allows the cellulose surface to approximate the surface of a cellulose microfibril and, at the same time, allows the hydroxyl groups to rotate to accommodate the adsorption of water or lignin. This model likely results in the surface being too rigid. The addition of one or two more layers of cellulose to the model would be required to relax this constraint, but the resulting system would be beyond current computational power.

Lignin Precursors

The selection of coniferyl alcohol and its oligomers for this initial modeling venture was based on a desire to focus on a system that is relatively simple and at the same time an approximation of the secondary wall of gymnosperms. The dominant lignin functionalities in these systems are the guaiacyl types, and they usually occur without much incorporation of any paracoumaryl alcohol. From a modeling perspective, we considered the major features of lignin to be aromatic rings, hydroxyl groups, and methoxy groups; coniferyl alcohol exhibits all three of these features.

Two different molecules were used to represent lignin in these computations. The structures and nomenclature of the lignin models are shown in Figure 4. The monomer in this case is coniferyl alcohol. A trimer was formed by linking three coniferyl alcohol monomers via two *b-O*-4 linkages. The structure of a *b-O*-4 linkage is illustrated by a dimer in Figure 4. The trimer has four chiral centers, the α and *b* carbons of the two side chains involved in the linkages. Both of the α carbons were *R* and both of the *b* carbons were *S*. This structure is one of the low energy forms of the trimer that has recently been reported (Faulon and Hatcher, 1994). The initial structure of the lignin trimer

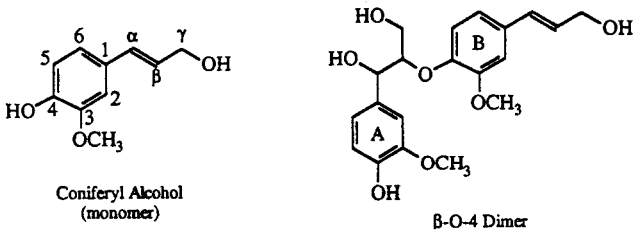

Figure 4. The structures and nomenclature of the lignin models.

was the *erythro* isomer which is a potential energy minimum for the *b*-O-4 linkage, as has been previously reported (Elder, 1989). Although there are many other possible linkage types and structure, this single model was chosen as representative of lignin oligomers. Exploration of the behavior of oligomers with other possible linkages will be the subject of future communications.

Water

Water is a critical component of the model system. During lignification, the cell wall is a hydrated polysaccharide gel, and thus, if lignin precursors are to associate with the cellulose surface, they must do so in the presence of water. Before one can be confident of the results of lignin adsorption, the model system of polysaccharide and water must be tested. We have recently used similar methods to study the behavior of disaccharides in water solution (C.J. Houtman and RH. Atalla, unpublished results). This study showed that the inclusion of water molecules in the computations was required to obtain accurate predictions of optical rotation and NMR data for cellobiose and xylobiose. Thus, the force field appears to represent correctly the interaction between water and polysaccharides. Furthermore, these results suggest that water has two effects on the system. It can shield charges from each other, and it can modify conformation by providing hydrogen-bonding bridges.

Computational Methods

All molecular dynamics calculations were done using INSIGHTII, version 2.3, and DISCOVER, version 2.95, distributed by Biosym Technologies, Inc. (San Diego, CA). The general purpose force field CVFF was used for all of the calculations. Partial charges for the atoms were the default values, which are consistent with the force field parameterization. This force field does not include an explicit term for hydrogen bonds but approximates them as a combination of electrostatic attraction and van der Waal's repulsion. The calculations were done using the minimum image convention for the periodic boundary conditions. The computational box was monoclinic with dimensions of a = 37 Å, b = 29 Å, c = 30 Å, an γ = 64.5°. For the calculation with coniferyl alcohol, 692 water molecules were included, which corresponds to a density of 1.1 g/cm^3. For the trimer of coniferyl alcohol, the number of water molecules included was reduced to maintain a constant density. Since electrostatic charges are treated using group contributions, a cutoff of 13 Å was used to reduce the amount of calculation without a significant loss in accuracy. The dielectric constant was set to 1.0. All calculations were done in the canonical ensemble: constant number of molecules, volume, and temperature. The temperature for all of the calculations was 300 K. The calculations were performed on either a Silicon Graphic, Inc. (Mountain View, CA) Indigo XS24 R4000 or the National Energy Research Supercompter Center (Livermore, CA) Cray C90. Calculation of a typical 0.3-ns trajectory required 360 central processing unit hours on the Silicon Graphic Iris or 37 central processing unit hours on the Cray C90.

RESULTS

Coniferyl Alcohol Monomer

Unlike chemical reactions, physical associations between molecules are often difficult to quantify. When studying covalent bonds, it is a simple matter to determine whether a bond exists or not, since covalent bonds have rather fixed geometries. With physical associations, such as adsorption, the task is complicated by ever-changing geometries. One must turn to other criteria to determine whether a molecule is adsorbed or not. In the specific case of coniferyl alcohol adsorption on a cellulose surface, several possibilities exist: (a) distance of the center of mass from the surface, (b) minimum distance between any atom and the surface, (c) angle between the normal of the plane defined by the phenyl ring and the normal of the surface, and (d) rate of tumbling of the molecule. In fact, no single analysis method is likely to fully describe the dynamics of this complicated interaction. Fortunately, after a molecular dynamics calculation, we have the positions and velocities of all the atoms of the system at each time step and can use all of these methods to study the same system.

Because of the periodic boundary conditions, the computational system is composed of layers of cellulose separated by 25 Å. The interlayer space is filled with water. To minimize the effect of the starting configuration, the coniferyl alcohol molecule was placed so that its center of mass was at the center of the water layer. This corresponds to a distance of 13 Å from the surface. Figure 5 shows the position of the center of mass of the phenyl ring during a 400-ps trajectory. Each segment represents 500 fs. As can be seen in Figure 5, the molecule began at 13 Å, the point marked A, and followed a convoluted path to the surface. The path ended with the molecule located near the surface at the point marked B. Note that for the last 100 ps of the trajectory the molecular motion appears restricted, since there is a higher density of segments near point B. In this case the center of mass of the phenyl ring was restricted to a hemisphere that is 4 A in diameter. Thus, although one would likely define the coniferyl alcohol as adsorbed, it still had some freedom of motion and did not appear to be fixed over a particular adsorption site on the surface. Figure 6 shows a plot of the distance between the van der Waal's surfaces of the coniferyl alcohol and the cellulose. Although there is a general trend toward the surface, there were times during the trajectory that the molecule was moving away from the surface. Even when the molecule

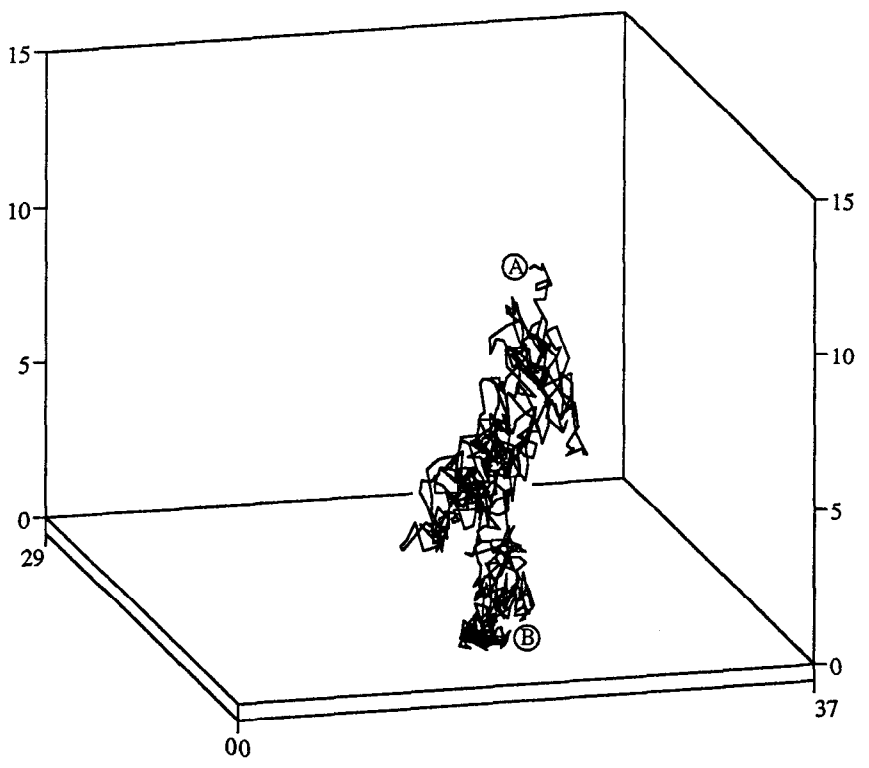

Figure 5. A plot showing the motion of the center of mass of the phenyl ring of the monomer relative to the cellulose surface. Distances are shown in Å. The letter A indicates the starting point of the trajectory, and the letter 6 indicates the ending point.

was adsorbed, after 325 ps, it still had a range of motion perpendicular to the surface of approximately 1 Å.

As the molecule moved toward the surface, there appeared to be a restriction of the rotational freedom of the phenyl ring. Figure 7 shows a plot of the angle between the normal of the surface and the normal of the plane defined by the phenyl ring of the lignin monomer. From this plot there appear to be three stages during the trajectory, each characterized by a different average angle. From Figure 6 one can conclude that the stage with an average angle of 16° corresponded to the coniferyl alcohol being adsorbed on the cellulose surface. The rotational freedom during this stage also was more limited than the others, since the fluctuations in angle appear to be less. There also appears to be a preadsorption stage at which the lignin model is beginning to be influenced by the surface. Although there is a statistically significant difference between the means of all of the stages shown in Figure 7, this behavior may just be coincidence, since we only show the analysis of a single trajectory.

It is reasonable to hypothesize that, if there is a net attractive force between the lignol and the surface, the

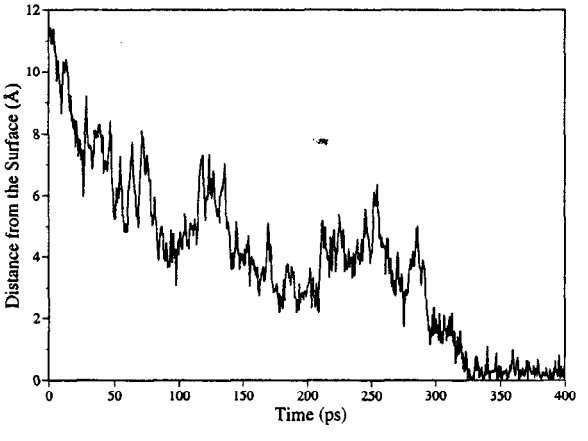

Figure 6. A plot of the center of mass of the phenyl ring of coniferyl alcohol as a function of time. Distance from the surface has been defined as the distance between the van der Waal's surfaces of the coniferyl alcohol and the cellulose surface.

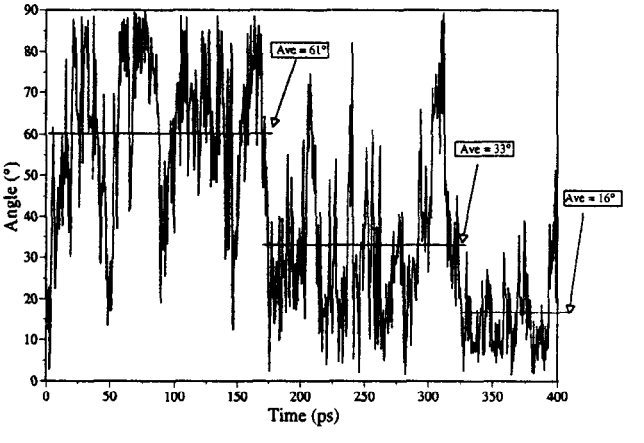

Figure 7. A plot of the angle between the normals of the phenyl ring of coniferyl alcohol and the cellulose surface. An angle of zero means that the phenyl ring is parallel to the surface. Ave, Average.

phenyl ring of the lignol will orient itself parallel to the surface to maximize its enthalpy of adsorption. If this hypothesis is true, then one would expect there to be a correlation between distance from the surface and the orientation of the phenyl ring. Figure 8 shows a plot of orientation of the normal of the phenyl ring and the distance from the surface. In this case, the distance from the surface is defined as distance between the van der Waal's surfaces of the atoms of the surface and the atoms of the lignol. In Figure 8 a smooth curve has been added that shows the average angle at each distance. From this figure, it is clear that there is a strong correlation between angle and distance when the lignol is within 1 Å of the surface; furthermore, there appears to be a decrease in the range of rotations available to the phenyl ring, since the points are less scattered in this region. In contrast, beyond 1 Å there does not appear to be any correlation between angle and distance; nor does there appear to be significant restriction of the rotation. This figure suggests that, if there is a preadsorption state, as suggested above, its effect on orientation angle is not very significant. Another method to quantify the restriction of motion is to calculate the P_2 (cos*q*) autocorrelation function (Allen and Tildesly, 1987). This statistic normally follows an exponential decay with a time constant related to the correlation time of the direction of a vector. This method is often used to estimate the tumbling rates of molecules for the calculation of NMR relaxation rates. In the case of coniferyl alcohol, there are two vectors that can be defined for the phenyl ring: one connecting C_1 and C_4 and the other connecting C_3 and C_5. The numbering of the phenyl rings is shown in Figure 4. The C_1 to C_4 vector is expected to reorient more slowly because of the influence of the propene side chain. The correlation times for the two vectors for different portions of the molecular dynamics trajectory are given in Table I. During the initial portion of the trajectory, the molecule is likely moving with little influence from the surface, but as it moves closer to the surface its movements are being restricted. The point at which the influence begins to become important appears to be approximately 0.5 A. This is indicated by the 6-fold increase in correlation time of the C_1 to C_4 vector over the value for the early part of the trajectory.

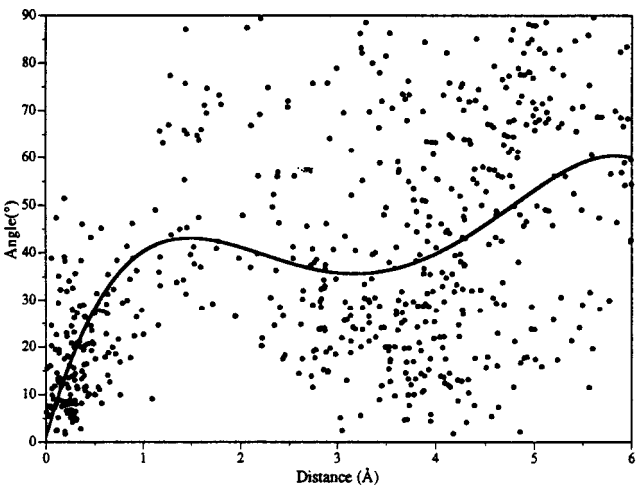

Figure 8. A plot showing the correlation between the distance from the surface and the angle between the normals of the phenyl ring and the surface.

Table I. *Correlation times for two directions defined by the plane of the phenyl ring of coniferyl alcohol*

Time Span	Average Distance from the Surface	Vector C_1-C_4	Vector C_3-C_5
ps	*Å*	*ps*	*ps*
0-100	7.0	5.5	5.6
200-300	3.8	10.6	8.5
300-400	0.5	36.7	23.6

In summary, coniferyl alcohol appears to adsorb rapidly onto a cellulose surface. Although this adsorption does not result in the lignin model being fixed over a single position of cellulose surface, it does significantly restrict the motions of the molecule. The molecule is held within 1 Å of the surface, and the orientation of the phenyl ring of the coniferyl alcohol tends to be parallel to the surface.

Coniferyl Alcohol Trimer

Since coniferyl alcohol adsorbs rather rapidly on the cellulose surface, one might expect the oligomers to adsorb also. Using the methods applied above, we also studied the motions of a trimer. As expected, the *b-O*-4-linked trimer adsorbed onto the surface of the cellulose. In fact, this molecule adsorbed more rapidly than the monomer. One of the phenyl rings became adsorbed on the surface within 100 ps of the start of the simulation. After one ring was adsorbed, another was rapidly pulled down to the surface. A typical structure of the timer adsorbed onto the surface of cellulose is shown in Figure 9. This figure shows that two of the phenyl rings are closely associated with the

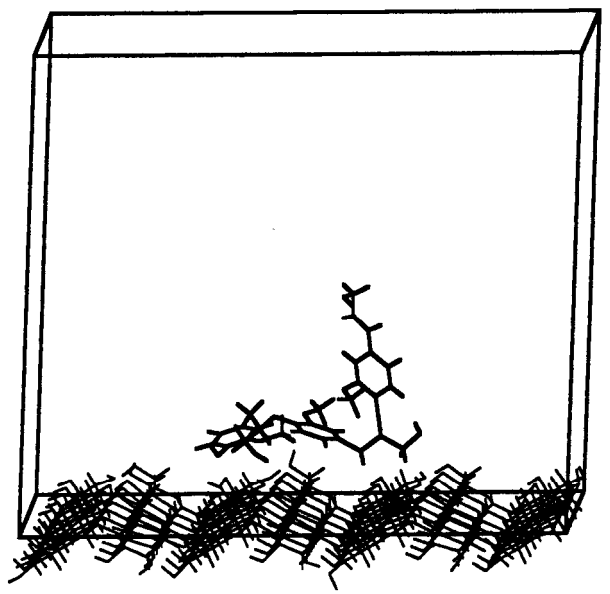

Figure 9. A representation of a typical association between the cellulose surface and a *b-O*-4 trimer lignin model.

surface, but the third continues to remain free from strong associations with the surface. The adsorption of this third phenyl ring appears to be inhibited by the constraints of the *b-O*-4 linkage. Analysis of the cellulose surface shows that the lignin model is adsorbed over a region of high concentration of hydroxyl groups. This suggests that the dominant force holding the lignin model on the surface is electrostatic dipole-dipole interactions.

DISCUSSION

The results of this modeling study are consistent with the experimental observations of the lignin/polysaccharide system. If the phenyl rings of the lignin are adsorbed on the surface of cellulose microfibrils, one would expect them to be aligned preferentially in the plane of the cell walls, as has been observed in Raman microprobe studies (Atalla and Agarwal, 1985; Agarwal and Atalla, 1986). Furthermore, the experimental observation that polysaccharides tend to result in more condensed DHPs (Terashima and Seguchi, 1988) is consistent with the adsorption of coniferyl alcohol onto polysaccharide chains.

Beyond the explanation of experimental observations, this work has implications for our understanding of the structure and biogenesis of plant cell walls. Perhaps the most significant conclusion is the negation of the traditional view that lignin and its monomers and oligomers, because they are hydrophobic, cannot adsorb on polysaccharide surfaces. This view is based on extrapolation of macroscopic behavior to the molecular level and ignores the details of molecular structure in the lignin-polysaccharide system. Coniferyl alcohol, for example, has aromatic and aliphatic entities, and it also has hydroxyl and methoxyl groups, which can be expected to interact strongly with the polar functionalities in cellulose and other polysaccharides. One of the major advantages of molecular dynamics simulations is that the structural details of individual species can be included explicitly, and it is not necessary to conduct analyses of molecular behavior on the basis of categories of average behavior such as hydrophobic or hydrophilic.

Recognition of the associative interactions possible between lignin oligomers and polysaccharides also raises questions concerning the validity of two-phase models of plant cell walls. Most models of plant cell walls incorporate the assumption that two phases are present. Crystalline cellulose microfibrils are thought to be embedded in a matrix made up of lignin and the hemicelluloses. This is not unlike models of man-made fiber-based composites, but there is a significant difference in the scale of the substructures. Cellulose microfibrils in plants are 3.5 to 6 nm in diameters, whereas the finest man-made fibers are usually larger than 1 μm in diameter. The properties and structure of a fiber that is 1 μm in diameter is dominated by the bulk properties of the material, since only a small fraction of the molecules are at the surface. With a cellulose microfibril, however, a significant fraction of the molecules is at the surface and thus is strongly affected by other molecules near them. Furthermore, since lignin oligomers seem to adsorb onto cellulose surfaces, it is likely that lignin interacts sufficiently strongly with cellulose so that lignin can influence the properties of cellulose and cellulose can influence both the structure and properties of lignin. Neither component will, in the native state, exhibit its bulk behavior. These observations suggest that thermodynamic arguments based on two-phase models are not applicable to plant cell walls, and it is not clear that the usual remedies based on notions of surface tension can be used to correct the model.

The calculations also contribute to a possible resolution of a troublesome question concerning lignin biogenesis. The accepted view of lignin synthesis is based on a free radical-coupling polymerization reaction (Freudenberg, 1964). The difficulty with this view is that it implies that the primary structure of lignin is determined by the balance between rates of a number of competing reactions. Since biological systems exert precise control over the structures of constitutive macromolecules, it seems inconsistent that lignin would be assembled by processes much more susceptible to perturbation by environmental variables, such as temperature. On the other hand, if monolignols and oligolignols are efficiently adsorbed by the polysaccharide substructures, it is possible to envision the polysaccharides, both cellulose and the hemicelluloses together, as providing a template for the assembly of lignin. The variability in the structures of the hemicelluloses can be envisioned as providing the avenue for intracellular control of the patterns of assembly of lignin. The plausibility of this view is further enhanced by the observation that most secondary wall tissues contain an amount of hemicelluloses that is approximately the same as the amount of lignin. In the compression wood of gymnosperms the variability of lignin content is correlated with variability of the hemicellulose content (Timell, 1986). This view is also consistent with the sequence of formation of cell wall constituents, because the polysaccharide matrix is always deposited prior to lignification. In the middle lamella and the primary wall, a major component of the template may be the pectic substances, which in the presence of calcium ions can form aggregates (Walkinshaw and Arnott, 1981). In the subsequent formation of the secondary wall, the cellulose and the hemicelluloses would dominate control of the lignin structure.

CONCLUSIONS

The molecular dynamics simulations described in this report suggest that lignin precursors and lignin oligomers can adsorb on the surface of cellulose microfibrils. The adsorption represents a constraint on the movement of these molecules and a likely influence on their freedom to participate in random polymerization reactions. This effect is quite likely a key factor in the influence of polysaccharide matrices on the structures of DHPs prepared in the presence of the polysaccharides. The adsorption process also has broader implications for the processes involved in the assembly of the cell wall. Although the computations presented here do not point to such an effect, the results of

Shigematsu et al. (1994) suggest that the different saccharides differ in their interaction with lignin precursors in subtle ways. Thus, different saccharides are likely to bind the different lignin precursors in different ways or to different degrees. Such interactions then provide the basis for selective binding of the different lignin precursors in a manner that can impart spatial organization to the lignin and hence an avenue for expression of intracellular regulation of the structure of lignin through regulation of the architecture of the hemicelluloses that are deposited within the cell wall matrix.

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