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Author's Review

Theoretical Approaches to Lignin Chemistry*

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A critical review is presented of the applications of theoretical methods to the studies of the structure and chemical reactivity of lignin, including simulation of macromolecular properties, conformational calculations, quantum chemical analyses of electronic structure, spectra and chemical reactivity. Modern concepts of spatial organization and chemical reactivity of lignins are discussed.

INTRODUCTION

Lignin is an amorphous cementing material that binds cellulose fibres, grants strength to wood and protects carbohydrates from oxidative destruction.[1] Lignin is a natural polymer that constitutes about one fourth of the plant biomass; its depolymerization is the main process in numerous pulping technologies. Therefore, the structure and chemical reactivity of this polymer is of paramount interest for science and industry.

The complex chemical and macromolecular structure of lignin makes its studying a difficult task. Lignin chemistry seems to be a rather backward field of science when compared with the chemistry of other natural products. The chemical structure of lignin is not quite clear yet. Nevertheless, the main types of structural units of lignin are known (Scheme 1)[2] and this constitutes the basis of today's is theory of its chemical reactivity. Methodology of model studies in wood chemistry is essentially close to the composite molecule approach, which is popular in general theoretical chemistry.[3] It includes thorough studies of the properties of small molecules that simulate structural units of the polymer, followed by the analysis of perturbations resulting from the binding of the units. Theoretical approaches are especially important in lignin chemistry because of the limited applicability of convenient experimental methods in structural studies of this natural polymer. Thus, being amorphous and irreggular, lignin is inaccessible to the X-ray analysis.

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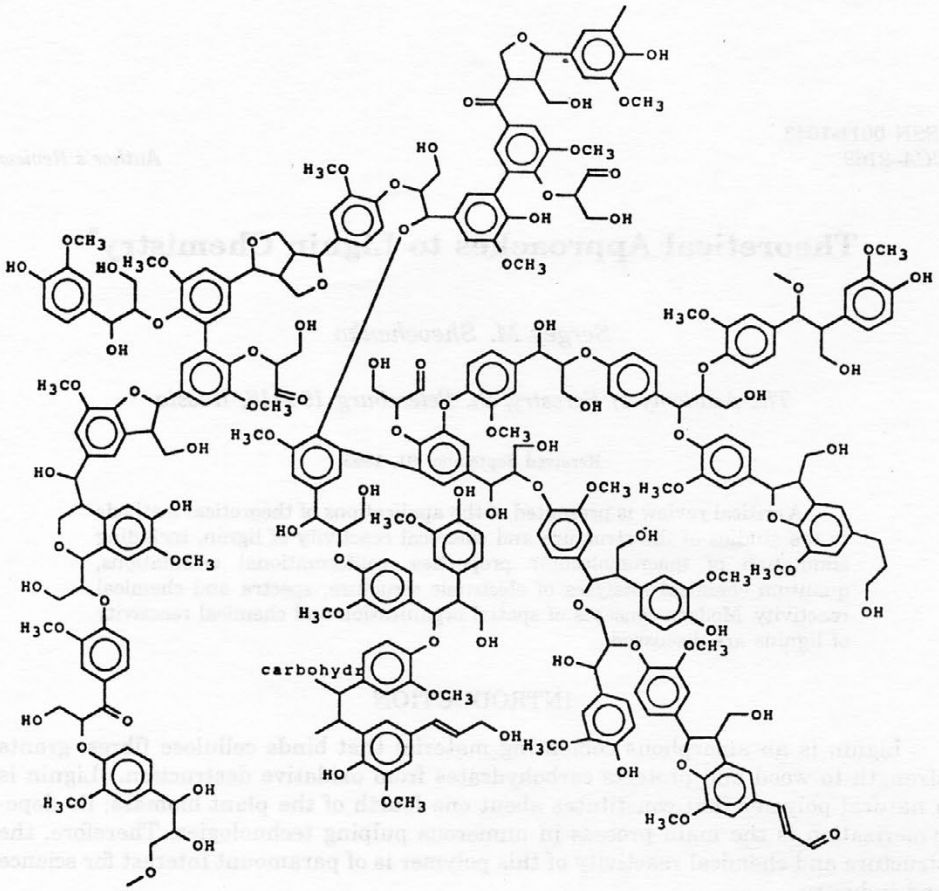
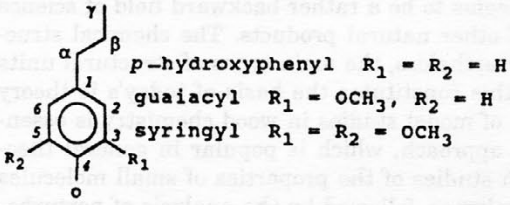


Arylpropane structural units:



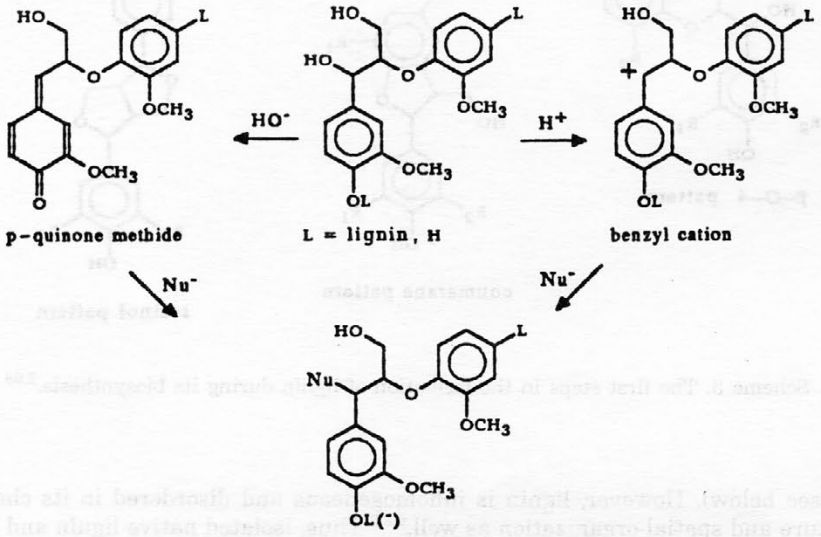
Scheme 1. A tentative lignin formula.[2]

Application of theoretical methods to lignin chemistry has developed along the following major lines: conformational calculations of lignin units, theoretical analysis of chemical reactivity, quantum chemical calculations of the electronic structure of basic lignin chromophores, studies of the intra- and intermolecular hydrogen

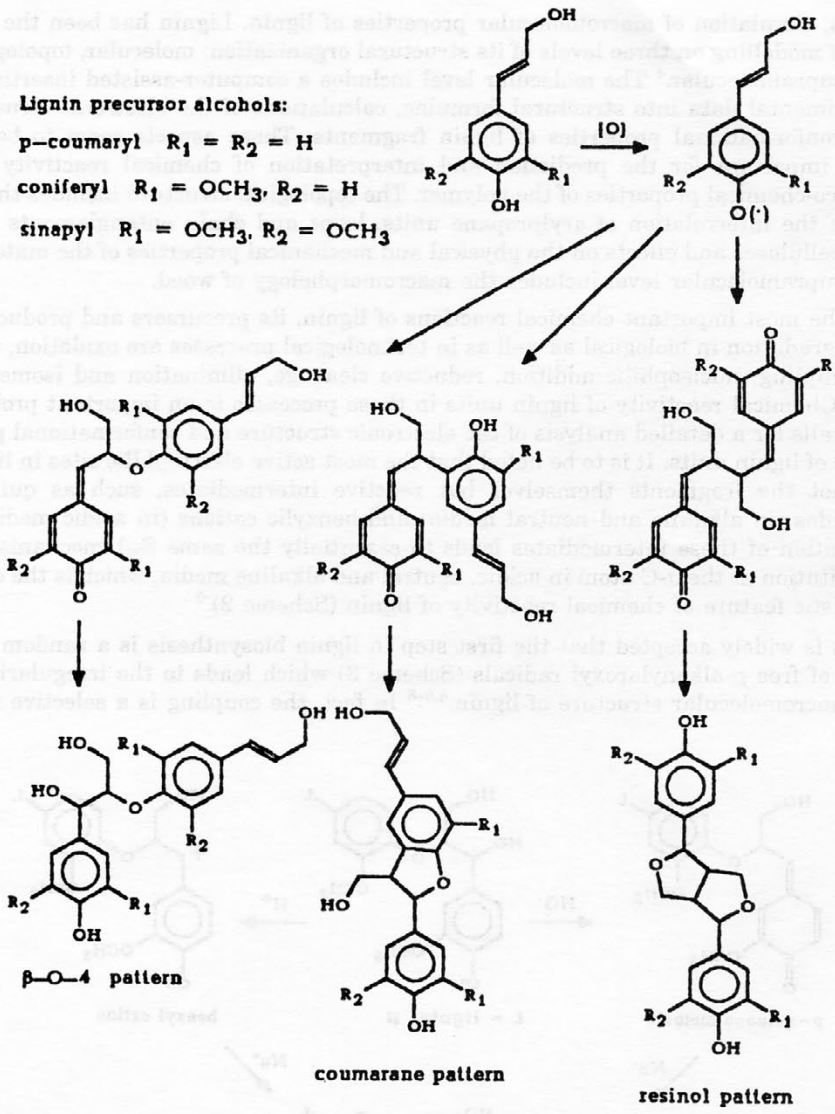
bonds, simulation of macromolecular properties of lignin. Lignin has been the subject of modelling on three levels of its structural organization: molecular, topological, and supramolecular.[4] The molecular level includes a computer-assisted insertion of experimental data into structural formulae, calculations of the electronic structure and conformational properties of lignin fragments. These aspects seem to be the most important for the prediction and interpretation of chemical reactivity and physico-chemical properties of the polymer. The topological structure includes the order of the interrelation of arylpropane units, loops and chain entanglements with hemicelluloses and effects on the physical and mechanical properties of the material. The supramolecular level includes the macromorphology of wood.

The most important chemical reactions of lignin, its precursors and products of its degradation in biological as well as in technological processes are oxidation, radical coupling, nucleophilic addition, reductive cleavage, elimination and isomerization. Chemical reactivity of lignin units in these processes is an important problem that calls for a detailed analysis of the electronic structure and conformational properties of lignin units. It is to be noted that the most active electrophilic sites in lignin are not the fragments themselves but reactive intermediates, such as quinone methides (in alkaline and neutral media) and benzylic cations (in acidic medium). Formation of these intermediates leads to essentially the same S_N1 mechanism of substitution at the α-C atom in acidic, neutral and alkaline media, which is the characteristic feature of chemical reactivity of lignin (Scheme 2).[5]

It is widely accepted that the first step in lignin biosynthesis is a random coupling of free *p*-alkenylaroxyl radicals (Scheme 3) which leads to the irregularity of the macromolecular structure of lignin.[4,6–8] In fact, the coupling is a selective reac-



Scheme 2. Formation of electrophilic reactive intermediates from lignin units in the way of a nucleophilic reaction.[5]



Scheme 3. The first steps in the formation of lignin during its biosynthesis.[2,68]

tion (see below). However, lignin is inhomogeneous and disordered in its chemical structure and spatial organization as well.[6,8,9] Thus, isolated native lignin and lignin model polymers are amorphous according to X-ray data.[10]

Lignin is a three-dimensional polymer of an inhomogeneously cross-linked structure.[11–14] Wood itself is the polymeric composite that mainly consists of cellulose,

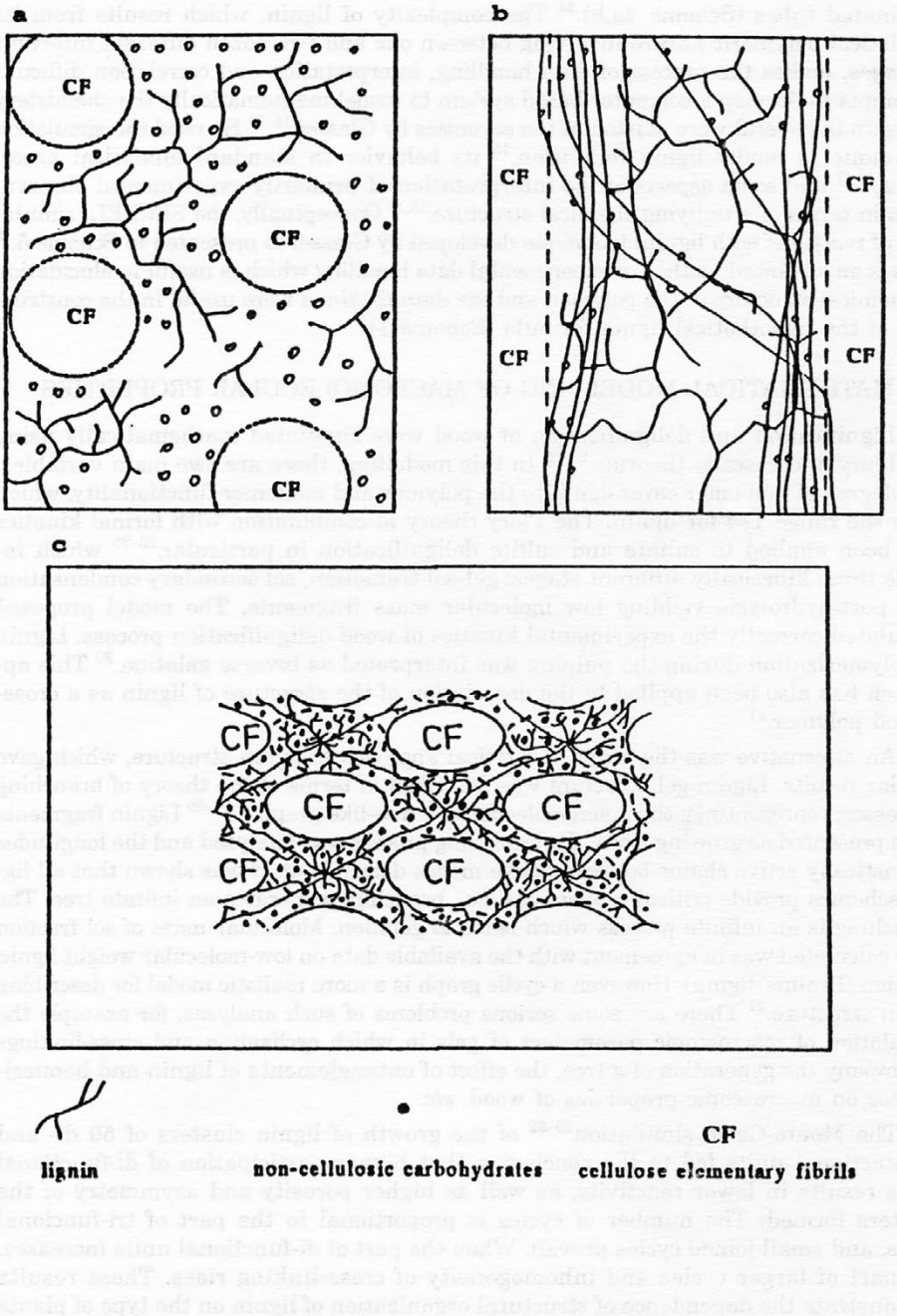
hemicelluloses and lignin. It may be described as a construction made of armored laminated tubes (Scheme 4a,b).[14] The complexity of lignin, which results from its statistical polymeric nature involving between one and two dozen different interunit linkages, makes the process of data handling, interpretation and correlation difficult. Attempts to develop a computer-based system to model mathematically the chemistery of lignin in general were started in the seventies by Glasser.[15–19] He used the simulation technique to model lignin formation,[15] its behavior in standard analytical procedures,[16,17] and some aspects of the interpretation of primarily experimental observations in terms of a unifying chemical structure.[18,19] Conceptually, the SIMREL (simulation of reactions with lignin) technique developed by Glasser is presented in Scheme 5.[19] This is an advanced method of experimental data handling which is useful in elucidation of chemical structure of the polymer, and the data obtained were useful in the construction of the hypothetical lignin formula (Scheme 1).

MATHEMATICAL MODELLING OF MACROMOLECULAR PROPERTIES

Lignification and delignification of wood were simulated mathematically using the Flory and cascade theories.[20–26] In this modelling, there are two main variables: the degree of monomer coversion into the polymer and monomer functionality, which is in the range 1–4 for lignin. The Flory theory in combination with formal kinetics has been applied to sulfate and sulfite delignification in particular,[23–25] which include three kinetically different stages: gel-sol transition, sol secondary condensation and post-hydrolysis yielding low molecular mass fragments. The model proposed simulated correctly the experimental kinetics of wood delignification process. Lignin depolymerization during the pulping was interpreted as inverse gelation.[20] This approach has also been applied to the description of the structure of lignin as a cross-linked polymer.[21]

An alternative was the graph theoretical approach to lignin structure, which gave similar results. Lignin gel structure was described in terms of the theory of branching processes, representingg the macromolecule as a tree-like graph.[22,27–29] Lignin fragments were presented as growing trees, the branching process was analyzed and the longitudes of elastically active chains between active modes determined. It was shown that all lignin schemes provide critical conversions, *i.e.*, branching generates an infinite tree. The branching is an infinite process which leads to gelation. Molecular mass of sol fraction thus calculated was in agreement with the available data on low-molecular weight lignin fraction (Brauns' lignin). However, a cyclic graph is a more realistic model for describing lignin structure.[27] There are some serious problems of such analyses, for example the calculation of macroscopic parameters of gels in which cyclization and cross-linkings accompany the generation of a tree, the effect of entanglements of lignin and hemicelluloses on macroscopic properties of wood, *etc.*

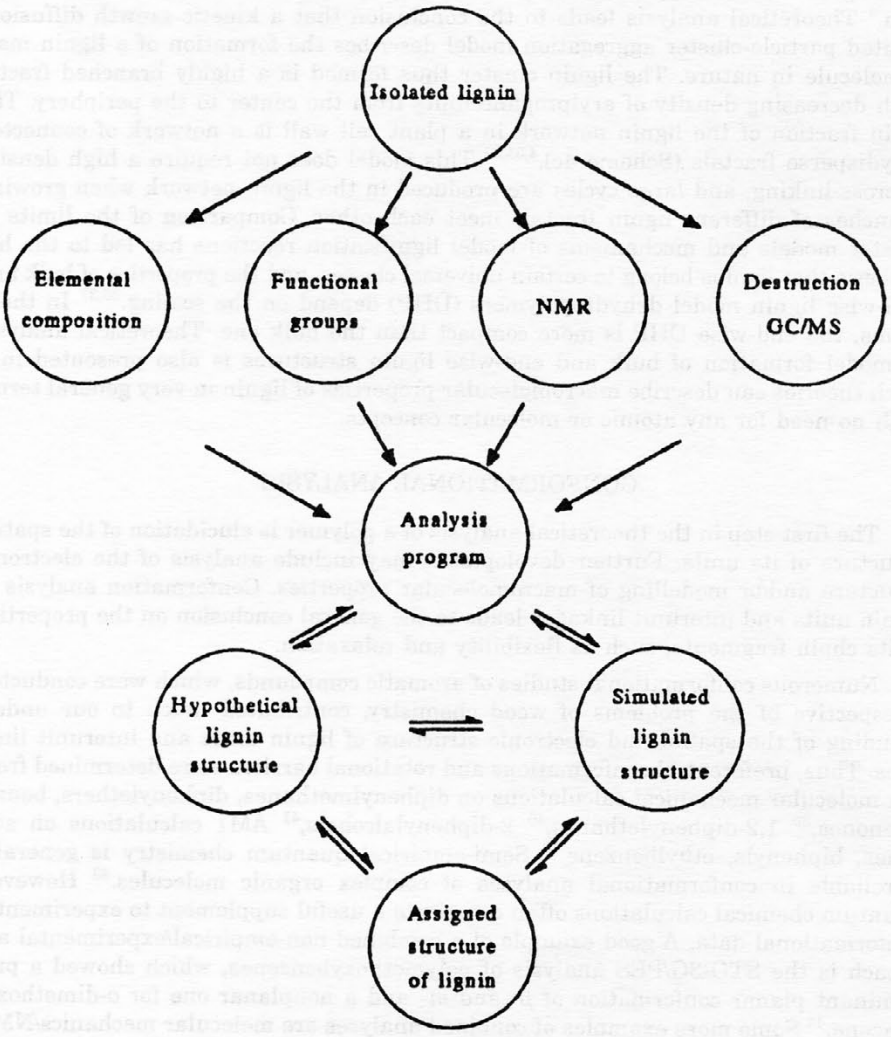
The Monte-Carlo simulation[30–32] of the growth of lignin clusters of 50 di- and tri-functional units led to the conclusion that higher participation of di-functional units results in lower reactivity, as well as higher porosity and asymmetry of the clusters formed. The number of cycles is proportional to the part of tri-funcional units, and small joined cycles prevail. When the part of di-functional units increases, the part of larger cycles and inhomogeneity of cross-linking rises. These results demonstrate the dependence of structural organization of lignin on the type of plants which are characterized by different ratios of basic units (Scheme 1). The shape of a 50-unit fragment formed by random coupling is predicted to be ellipsoid rather



Scheme 4. *A priori* model of association of cell wall components (a – transverse section, b – longitudinal section)[14] and lignin in a cell wall according to computer simulation (c).[4]

than spherical.[27,33] The analysis reveals that the different topology of lignins similar in chemical structure and numbers of edges and vertexes may possess different physical properties.[27,28] The methods described and similar, but more sophisticated, simulation approaches[34] provide good agreement with the available analytical data and conventional concepts of lignin structure.

A more general physical approach, based on the classes of universality, critical phase transitions, scaling and fractals, has been developed by Gravitis *et al.*.[4,35] They maintain that lignin, as an irregular polymer, is scale-invariant (dilation symmetry)



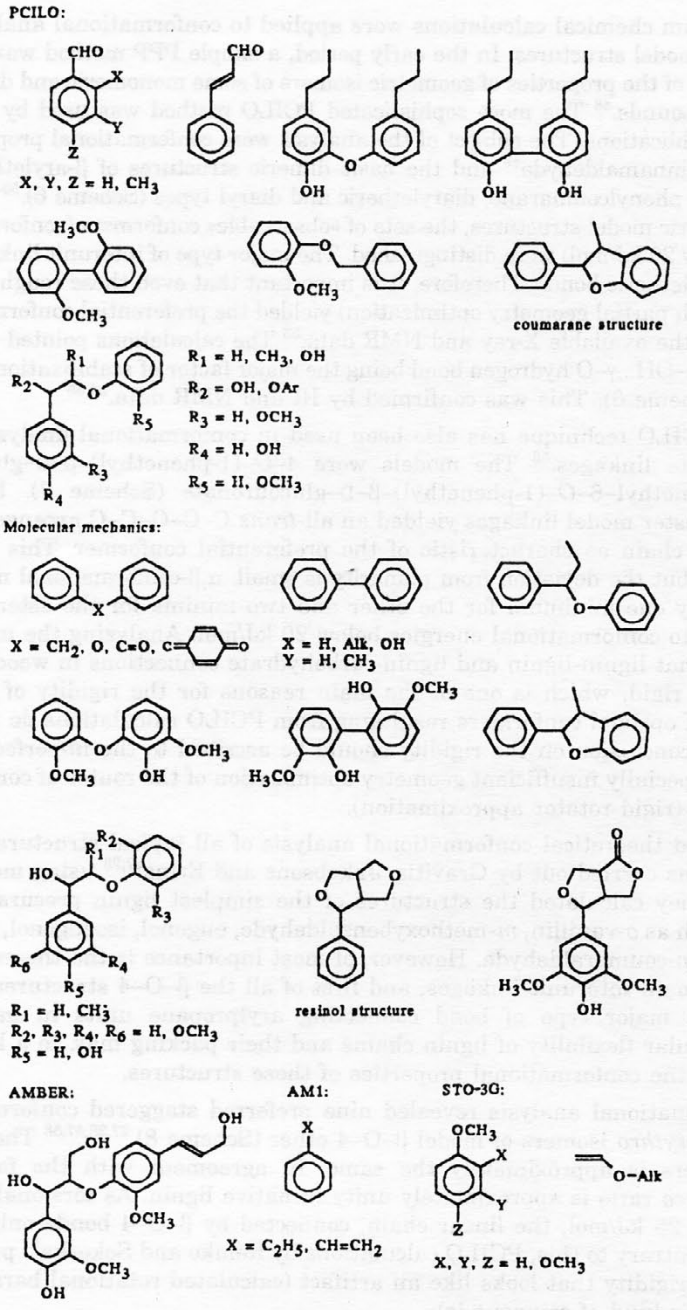
Scheme 5. The SIMREL approach.[19]

and belongs to the class of random fractals. This is based on the assumption that lignin biosynthesis proceeds *via* random recombination of *p*-alkenylaroxyl radicals. This provides a statistical scale invariance or self-similarity of the structure. On the other hand, wood delignification may lead to self-similarity in the dissolved fragments of lignin. Gravitis has calculated the fractal dimension of dioxane lignin to be about 2.5 from the known molecular mass, contraction factor, viscosity and diffusion parameters. This value is characteristic of the kinetic growth model (non-equilibrium polymerization and aggregation limited diffusion). Therefore, the lignin network has been described as a network of connected polydisperse fractals, and a non-equilibrium character has been ascribed to the structure of lignin. Experimental data agree with the hypothesis that wood cell polymers form a non-equilibrium system.[4] Theoretical analysis leads to the conclusion that a kinetic growth diffusion-limited particle-cluster aggregation model describes the formation of a lignin macromolecule in nature. The lignin cluster thus formed is a highly branched fractal with decreasing density of arylpropane units from the center to the periphery. The main fraction of the lignin network in a plant cell wall is a network of connected polydisperse fractals (Scheme 4c).[4,35,36] This model does not require a high density of cross-linking, and large cycles are produced in the lignin network when growing branches of different lignin fractals meet each other. Comparison of the limits of cluster models and mechanisms of model lignification reactions has led to the hypothesis that lignins belong to certain universal classes, and the properties of bulk and end-wise lignin model dehydropolymers (DHP) depend on the scaling.[35,37] In these terms, the end-wise DHP is more compact than the bulk one. Theoretical analysis of model formation of bulk and end-wise lignin structures is also presented in.[38] Such theories can describe macromolecular properties of lignin in very general terms with no need for any atomic or molecular concepts.

CONFORMATIONAL ANALYSIS

The first step in the theoretical analysis of a polymer is elucidation of the spatial structure of its units. Further development may include analysis of the electronic structure and/or modelling of macromolecular properties. Conformation analysis of lignin units and interunit linkages leads to the general conclusion on the properties of its chain fragments, such as flexibility and relaxation.

Numerous conformational studies of aromatic compounds, which were conducted irrespective of the problems of wood chemistry, contributed much to our understanding of the spatial and electronic structure of lignin units and interunit linkages. Thus, preferential conformations and rotational barriers were determined from the molecular mechanical calculations on diphenylmethanes, diphenylethers, benzophenones,[39] 1,2-diphenylethanes,[40] 2-diphenylalcohols,[41] AM1 calculations on styrenes, biphenyls, ethylbenzene.[42] Semi-empirical quantum chemistry is generally unreliable in conformational analyses of complex organic molecules.[43] However, quantum chemical calculations often constitute a useful supplement to experimental conformational data. A good example of a combined non-empirical/experimental approach is the STO-3G/PES analysis of polymethoxybenzenes, which showed a predominant planar conformation of *p*- and *m*- and a nonplanar one for *o*-dimethoxybenzene.[44] Some more examples of conbined analyses are molecular mechanics/NMR on 1,2-diaryl- and alkylarylethanes,[45] STO-3G/NMR on methyl group rotatiòn in enol ethers,[46] PCILO/NMR on methoxybenzaldehydes.[47]



Scheme 6. Basic lignin model structures studied by the means of PCILO, molecular mechanics, AMBER, AM1, and *ab initio* STO-3G calculations.

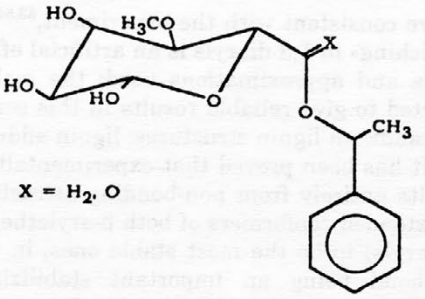
Quantum chemical calculations were applied to conformational analysis of typical lignin model structures. In the early period, a simple PPP method was used in the comparison of the properties of geometric isomers of some monomeric and dimeric lignin model compounds.[48] The more sophisticated PCILO method was used by Remko in a series of publications. The subject of the analysis were conformational properties of *cis*- and *trans*-cinnamaldehyde[49] and the basic dimeric structures of β-arylетheric, benzyl arylетheric, phenylcoumarane, diarylетheric and diaryl types (Scheme 6).[50–52] In the series of dimeric model structures, the sets of »observable« conformers (conformational energies below 20 kJ/mol) were distinguished. The major type of interunit linkage in lignin is the β-arylетheric bond.[2] Therefore, it is important that even these rough calculations (PCILO with partial geometry optimization) yielded the preferential conformer in agreement with the available X-ray and NMR data.[53] The calculations pointed to the intramolecular α–OH...γ–O hydrogen bond being the major factor of stabilization of this conformer (Scheme 6). This was confirmed by IR and NMR data.[54,55]

The PCILO technique has also been used in conformational analysis of lignin-carbohydrate linkages.[56] The models were 4–*O*–(1-phenethyl)–β–D–glucopyranose and 4–*O*–methyl–6–*O*–(1-phenethyl)–β–D–glucouronate (Scheme 7). Both benzyl ether and ester model linkages yielded an all-*trans* C–C–O–C–C arrangement of the connecting chain as characteristic of the preferential conformer. This fragment is nonplanar, but the deviation from planarity is small. α,β-conformational maps demonstrated only one minimum for the ether and two minima for the ester, which corresponded to conformational energies below 20 kJ/mol. Analyzing the maps, Remko supposed that lignin-lignin and lignin-carbohydrate connections in wood are conformationally rigid, which is one of the main reasons for the rigidity of wood itself. However, if optimal conformers resultigng from PCILO calculations do not look unlikely, the conclusion on the rigidity should be ascribed to the imperfections of the method, especially insufficient geometry optimization of the routes of conformational transitions (rigid rotator approximation).

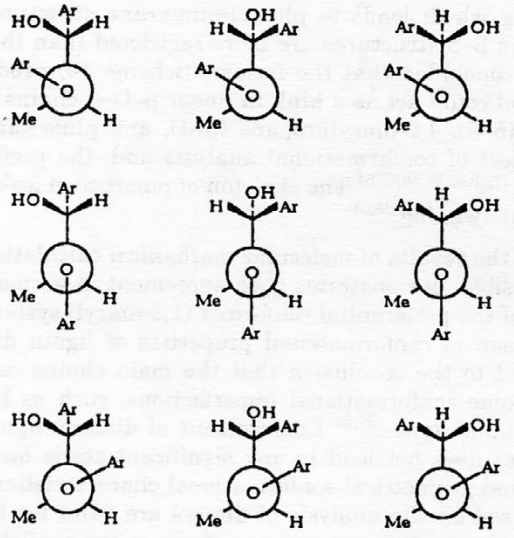
Detailed theoretical conformational analysis of all typical structural fragments of lignin was carried out by Gravitis, Jakobsons and Erins[27,28] using molecular mechanics. They calculated the structures of the simplest lignin precursor and unit models such as *o*-vanillin, *m*-methoxybenzaldehyde, eugenol, isoeugenol, coniferyl alcohol, and *p*-coumaraldehyde. However, of most inportance is the theoretical analysis of the main interunit linkages, and first of all the β–O–4 structures which constitute the major type of bond connecting arylpropane units in native lignin. Intramolecular flexibility of lignin chains and their packing may, to a large extent, depend on the conformational properties of these structures.

Conformational analysis revealed nine preferred staggered conformers of both *threo* and *erythro* isomers of model β–O–4 ether (Scheme 8).[27,28,57,58] The stability of both isomers is approximately the same, in agreement with the fact that the *erythro*/*threo* ratio is approximately unity in native lignin. As torsional barriers do not exceed 25 kJ/mol, the linear chain, connected by β–O–4 bonds only, should be flexible. Contrary to this, PCILO calculations by Remko and Sekerka[51] predicted certain space rigidity that looks like an artifact (calculated rotational barriers are too high for this kind of compounds).

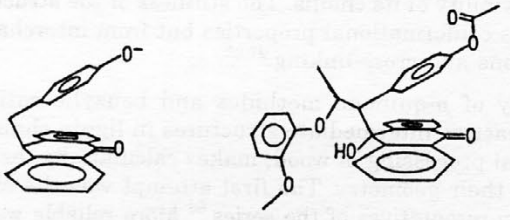
The most stable conformer of β–O–4 structures was the subject of contradictory reports: molecular mechanical[57,58] and AMBER[59] calculations gave a sandwich conformer but PCILO calculations[50,60] gave the extended one as the most stable. In this



Scheme 7. Lignin-carbohydrate model structures studied by the PCILO method.[56]



Scheme 8. Conformers of *erythro*-isomer of dilignol β–O–4 according to molecular calculations.[27,28]



Scheme 9. Sandwich-like lignin adducts with anthracene derivatives (model structures).[62,63]

case, PCILO results are consistent with the experiment,[53,54] and it was shown that computational »sandwiching« in 1,3-diaryls is an artificial effect resulting from some features of force fields and approximations used; the molecular mechanics force fields should be coreected to give reliable results in this series.[61] However, there is a special class of real sandwich lignin structures: lignin adducts with anthracene derivatives (Scheme 9). It has been proved that experimentally observed sandwiching in these systems results entirely from non-bonding attraction.[61–63] PCILO calculations[60] predicted the extended conformers of both β-arylethers (1,3-diaryls) and benzyl aryl ethers (1,2-diaryls) to be the most stable ones, in the first case the intramolecular hydrogen bond being an important stabilizing factor (see below). According to the calculations, non-specific solvation does not affect the relative stability of the preferential conformer. However, it is not the non-specific but specific solvation that affects intramolecular hydrogen bonds, thus changing the preferential conformer to the more folded one.[55]

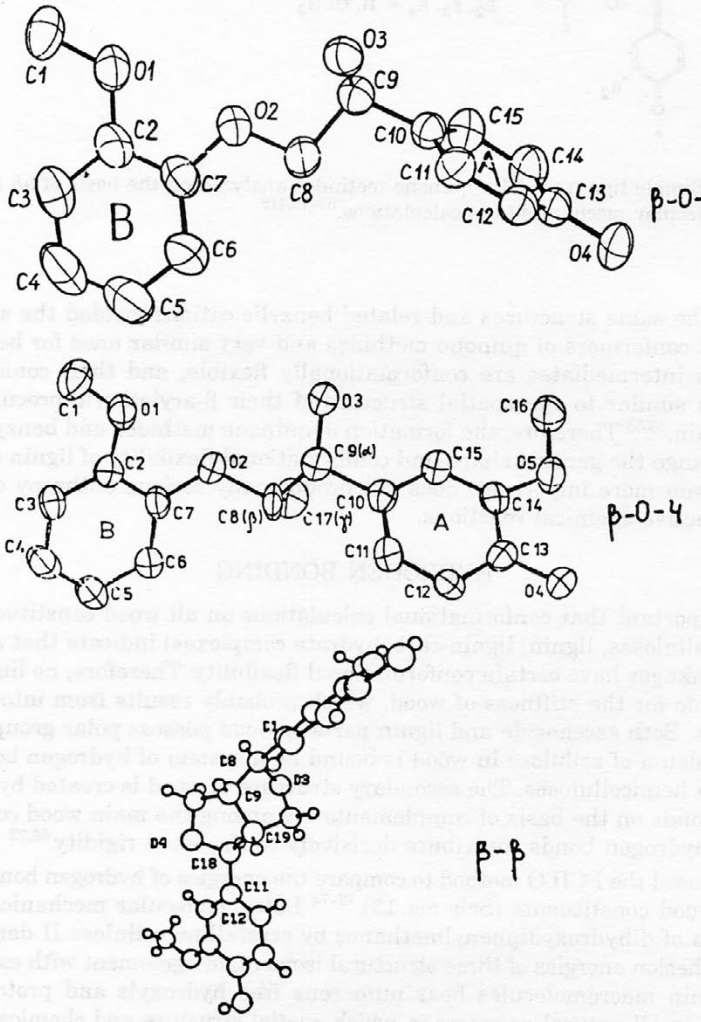
Another pattern that plays an important role in the formation of lignin structures is the β–5 coupling which leads to phenylcoumarane structures.[27,28,50] Conformational transitions in β–5 structures are more restricted than these in β–O–4 structures, and it was concluded that the former (Scheme 10) produces some bending in lignin chains and could act as a kink in linear β–O–4 chains.[27,28] Diphenyl ether (4–O–5) biphenyl (5–5), 1,2-diarylpropane (β–1), and pinoresinol (β–β) structures were also the subject of conformational analysis and, the preferential conformers found (Scheme 10).[27,28,49,50,58,63,64] The skeleton of pinoresinol looks rigid, but actually it allows significant twisting.[63,64]

Comparison of the results of molecular mechanical calculations with experimental data, when possible, demonstrates good agreement in geometry parameters and the correct choice of the preferential conformer (1,3-diaryl) systems present a special case).[63,64] Comparison of conformational properties of lignin dimers modelling interunit linkages led to the conclusion that the main chains constituted by β–O–4 linkages contain some conformational imperfections, such as bends of »jog« (β–5), »fold« (β–β), and »kink« types.[27,28] Enlargement of dimeric lignin model fragments to the trimeric ones does not lead to any significant steric hindrance resulting in similar energetic and geometrical conformational characteristics.[65] This proves that the conclusions based on the analysis of dimers are valid for larger lignin chains. The general conclusion is that numerous conformers are available for lignin chains, which are, therefore, thermodynamically flexible. Most barriers to conformational transitions do not exceed 25 kJ/mol, which is also consistent with the kinetic flexibility of lignin chains. Higher ratio of syringyl units probably brings some kinetic rigidity, which cannot be high. There are no »frozen« conformers in lignin, which explains the high flexibility of its chains. The stiffness of the structures of this polymer results not from its conformational properties but from interchain (mostly hydrogen bonding) interactions and cross-linking.[27,28]

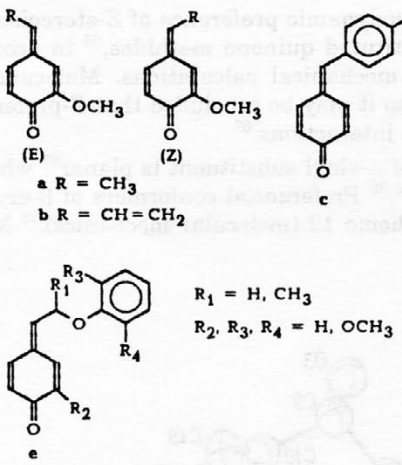
The instability of *p*-quinone methides and benzylic cations, which are the most important reactive intermediate structures in lignin chains during its biosynthesis and chemical processing of wood, makes calculations the only instrument for obtaining data on their geometry. The first attempt was the MINDO/3 calculation of the simplest representatives of the series.[66] More reliable were *ab initio* and molecular mechanical calculations, which are in good agreement for simple lignin model quinone methides (Scheme 11).[67] Bond alteration in these structures is typi-

cal of quinonoid compounds. Thermodynamic preference of *Z*-stereoisomer is characteristic of all monomethoxy-substituted quinone methides,[68] in accordance with STO-3G, but not with molecular mechanical calculations. Molecular mechanics treats steric interactions correctly, so it may be concluded that *Z*-preference is a result of electronic rather than steric interactions.[67]

The preferential conformation of α-vinyl substituent is planar[67] whereas that of α-phenyl group is twisted to *ca.* 60°.[69] Preferential conformers of β-aryletheric quinone methides are presented in Scheme 12 (molecular mechanics).[70] MNDO calcu-



Scheme 10. β–O–4 Lignin chains and β–β imperfections.[53,63–65]



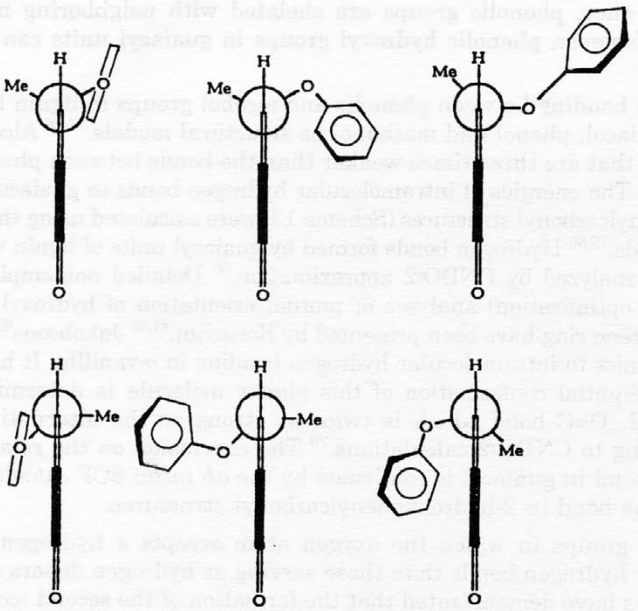
Scheme 11.. Simple lignin model *p*-quinone methides analyzed on the basis of *ab initio* 3-21G (a,b) and molecular mechanics (a-e) calculations.[67–70,116]

lations on the same structures and related benzylic cations yielded the same set of preferential conformers of quinone methides and very similar ones for benzylic cations.[71] Both intermediates are conformationally flexible, and their conformational structure is similar to the spatial structure of their β-arylетheric precursor structures of lignin.[53,55] Therefore, the formation of quinone methides and benzylic cations does not change the general shape and conformational flexibility of lignin chains and (which is even more important) does not produce any serious enthropy constraints of the respective chemical reactions.

HYDROGEN BONDING

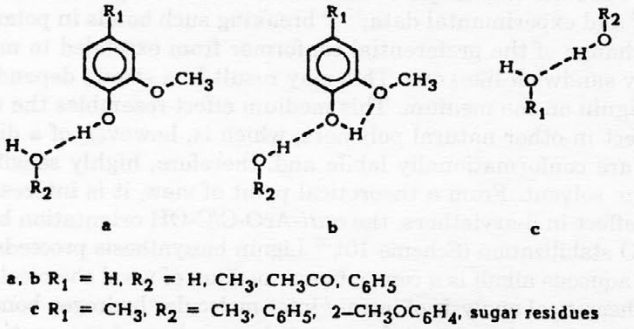
It is important that conformational calculations on all wood constituents (cellulose, hemicelluloses, lignin, lignin-carbohydrate complexes) indicate that all types of interunit linkages have certain conformational flexibility. Therefore, no linkage itself is responsible for the stiffness of wood, which probably results from intermolecular interactions. Both saccharide and lignin parts of wood possess polar groups, and the fibrillar skeleton of cellulose in wood is bound by a system of hydrogen bonds to lignin through hemicelluloses. The secondary structure of wood is created by numerous hydrogen bonds on the basis of complementarity among the main wood components, and these hydrogen bonds contribute decisively to the wood rigidity.[55,72]

Remko used the PCILO method to compare the energies of hydrogen bonds between the main wood constituents (Scheme 13).[72–74] Later, molecular mechanical study of the sorption of dihydroxydiphenylmethanes by crystalline cellulose II demonstrated different adhesion energies of three structural isomers, in agreement with experimental data.[75] Lignin macromolecules bear numerous free hydroxyls and proton-acceptor groups, like in all natural polymers in which spatial structure and chemical reactivity is under a strong influence of intra- and intermolecular hydrogen bonds. It is to be noted that proton-acceptor solvents which participate in the strongest hydrogen



Scheme 12. Calculated conformers of lignin model *p*-quinone methides of the β–O–4 type.[70]

bonds are the best solvents for lignins.[76] The spatial structure of cellulose chains and fibrils is governed by intra- and intermolecular hydrogen bonds, which was the subject of numerous investigations. Much less is known about the role of hydrogen bonds in the spatial organization of lignin. Most of the free hydroxyl groups in lignin



Scheme 13. Model hydrogen bonded structures studied by the PCILO method.[72–74] R_1 = H, lignin; R_2 = lignin, hemicelluloses, cellulose (*a*, *b* R_1 = H, R_2 = H, CH_3, CH_3CO, C_6H_5; *c* R_1 = CH_3, R_2 = CH_3, C_6H_5, 2-$CH_3OC_6H_4$, sugar residues).

are alcoholic ones; phenolic groups are chelated with neighboring methoxyls (see Scheme 1). However, phenolic hydroxyl groups in guaiacyl units can act as proton acceptors.

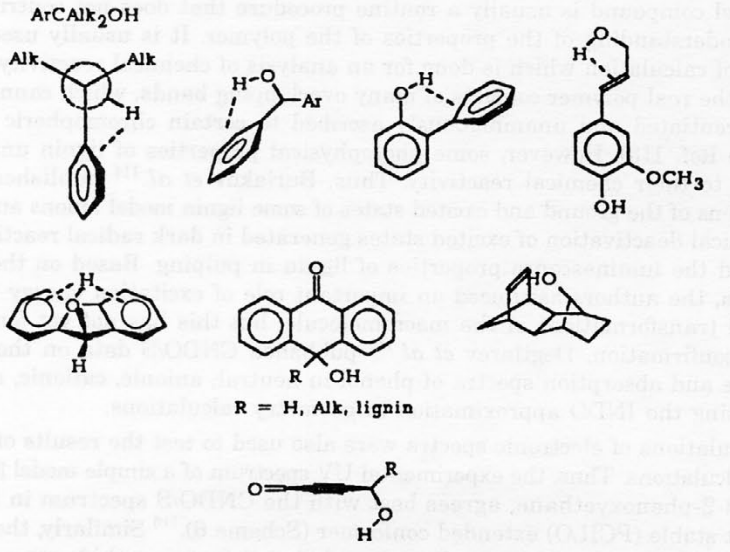
Hydrogen bonding between phenolic and alcohol groups in lignin has been studied using guaiacol, phenol and methanol as structural models.[77,78] Alcohols form hydrogen bonds that are three times weaker than the bonds between phenol and guaiacol molecules. The energies of intramolecular hydrogen bonds in guaiacol, syringol and 2-hydroxyphenylcarbonyl structures (Scheme 13) were calculated using the CNDO/2 and PCILO methods.[79,80] Hydrogen bonds formed by guaiacyl units of lignin with proton acceptors were analyzed by CNDO/2 approximation.[80] Detailed non-empirical (STO-3G, full geometry optimization) analyses of mutual orientation of hydroxyl and methoxyl groups at benzene ring have been presented by Konschin.[81,82] Jakobsons[63,83] applied molecular mechanics to intramolecular hydrogen bonding in *o*-vanillin. It has been shown that the preferential conformation of this planar molecule is determined by intramolecular OH...O=C bond which is twice as strong as the alternative OH...OCH_3 bond, according to CNDO/2 calculations.[79] The conclusion on the relative weakness of hydrogen bond in guaiacol is confirmed by the *ab initio* SCF calculations.[81] Much stronger is the bond in 2-hydroxyphenylcarbonyl structures.

Hydroxyl groups in which the oxygen atom accepts a hydrogen bond usually form stronger hydrogen bonds than those serving as hydrogen donors only. However, PCILO studies have demonstrated that the formation of the second »cooperative« hydrogen bond, in which guaiacol hydroxyl group accepts a hydrogen bond (systems *cis*-guaiacol – proton donor), results in a lower barrier to hydroxyl group rotation and a lower energy of an intramolecular hydrogen bond (in guaiacol itself, 3.9 kJ/mol).[73] On the other hand, an increasing effect has been determined for the second »cooperative« hydrogen bond on the energy of the intermolecular bond formed by two aliphatic hydroxyl groups.[74] The strongest intermolecular hydrogen bond for proton donors is formed by carbonyl groups.[73,74] Experimentally, in polar media where surrounding small molecules compete effectively with intramolecular hydrogen bonding counterparts, intramolecular hydrogen bonds do not affect the spatial structure or lignin fragments.[53,55]

The intramolecular α–OH...γ–O bond determines the most stable conformer of β–O–4 lignin subunits (the major substructure of native lignin), according to PCILO calculations[52] and experimantal data;[53,55] breaking such bonds in polar media results in a drastic change of the preferential conformer from extended to more folded (but no necessarily sandwich-like) one. This may result in a strong dependence of spatial structure of lignin on the medium. This medium effect resembles the well-known hydrophobic effect in other natural polymers, which is, however, of a different nature. β-Arylethers are conformationally labile and, therefore, highly sensitive (conformationally) to the solvent. From a theoretical point of view, it is interesting that there is no *gauche*-effect in β-arylethers, the *anti*-ArO-C/C-OH orientation being preferred, lacking OH...O stabilization (Scheme 10).[55] Lignin biosynthesis proceeds in an aqueous medium, and aqueous alkali is a conventional medium of wood chemical processing.[11,12] Therefore, a theoretical analysis of intra- / inter-molecular hydrogen bonds in lignin and lignin-in-medium is so important for our understanding of the spatial organization of the polymer.

A special type of hydrogen bonding is the OH...π interaction, typical of many unsaturated alcohols. Generally, this interaction is weaker than the typical OH...O

bonds,[84] but sometimes strong enough to determine the preferential conformer in benzyl alcohols,[85] 2-phenylethanol,[86] 2-phenylphenol[87] 7-norbornadienol,[88] *etc.* (Scheme 14). Thus, the major conformer of 2-phenylethanol with hydroxyl proton pointing towards phenyl ring is stabilized to the extent of 5 kJ/mol over the other ones because of the OH...π bonding. Comparison of the results of STO-3G, 4-31G, MNDO and molecular mechanical calculations showed that the latter (charge interactions included) is the best method for modelling the conformational composition.[86] STO-3G calculations suggest OH...π bonding in 2-arylalcohols, which makes it necessary to add an extra energy term in molecular mechanical models of such molecules.[89] So far, no theoretical study on lignin or lignin model compounds has treated OH...π bonding explicitly. The effect of such hydrogen bonds on the spatial organization and electronic structure of lignin is an interesting open problem. Intramolecular bonding was proved to have almost no effect on the choice of the most stable conformer in allyl alcohols (STO-3G),[90] some 1,2--diarylethanols and benzyl alcohols (^{1}H NMR)[91] but, in special cases such as 9-fluorenols and anthracenols, OH...π interactions are strong and result in such molecules existing only as *endo*-conformers (Scheme 14).[92] Surprinsingly, it has been demonstrated experimentally[92] and theoretically[93] that no actual intramolecular hydrogen bond exists in these systems. The interaction should be ascribed to the repulsion between the lone pair electrons of the hydroxyl oxygen and the π-electrons of the aromatic ring. Therefore, it is correct to say »OH...π interaction« but not »hydrogen bond.« This OH...π electrostatic interaction affects the electron donor properties of a π-system by increasing the first π-ionization potential; a typical example is coniferyl alcohol[94] which is one of the most important model structures in lignin chemistry. On the other hand, O...π through-space interactions decrease this potential noticeably.[95]



Scheme 14. Some examples of molecules whose conformational composition is under the effect of OH...π interaction.

Another type of intramolecular interaction, which should be considered in lignin, is the CH...π attraction ascribed to the contribution of dispersive forces.[45,89,96] Both experimental data and molecular mechanical (MM2) calculations give the phenyl/alkyl *gauche* conformer as the preferred one in 1-phenylethyl compounds. A detailed examination of energy terms revealed a contribution of the attractive non-bonded interaction between vicinal alkyl and phenyl groups in the stabilization of the *gauche* conformer. Analyses of contributions to the molecular mechanical conformational energy usually give information on a particular force field but not on the physical nature of the phenomenon under consideration. However, this CH...π effect gives an example of a real interaction, which is usually not taken into account in theoretical analyses of lignin structure.

SPECTRAL PROPERTIES

The color of wood and wood pulp is to be ascribed mostly to their lignin components because unsaturated lignin systems contain chromophores that absorb light in the visible region.[97] Moreover, lignin also contains numerous leukochromophoric structures that can be transformed into colored products during the chemical processing of wood.[98] Light absorption by lignin is an important technical and economic problem connected with pulp yellowing and lignin photodegradatiion.[99]

The chromophoric properties of lignin arylpropane, cinnamaldehyde,[100,101] diphenyl,[102] quinonoid,[103] and quinone methide[104] units were analyzed by CNDO/S and CNDO/CI techniques. Some model structures, including flavonoids, stilbenes and coumarans, were also studied by the PPP method.[102,105] PPP *106* and CNDO/S[103,107–112] calculations on *p*-quinone methide intermediates reproduced experimental electron absorption spectra of model compounds of this class and demonstrated characteristic substituent effects on the spectra. The calculation of the electronic spectrum of a lignin model compound is usually a routine procedure that does not contribute much to the understanding of the properties of the polymer. It is usually used to test a method of calculation which is done for an analysis of chemical reactivity. The spectrum of the real polymer consists of many overlapping bands, which cannot be readily differentiated and unambiguously ascribed to certain chromophoric structures (compare Ref. 113). However, some photophysical properties of lignin units may be relevant to their chemical reactivity. Thus, Burlakov *et al.*[114] published CNDO/S calculations of the ground and excited states of some lignin model anions and analyzed the physical deactivation of excited states generated in dark radical reactions, which explained the luminescence properties of lignin in pulping. Based on the energetic diagrams, the authors assumesd an important role of excitation energy transfer in chemical transformations of the macromolecule, but this has not yet found experimental confirmation. Degtiarev *et al.*[115] published CNDO/S data on the electronic structure and absorption spectra of phenol in neutral, anionic, cationic, and radical forms using the INDO approximation in geometry calculations.

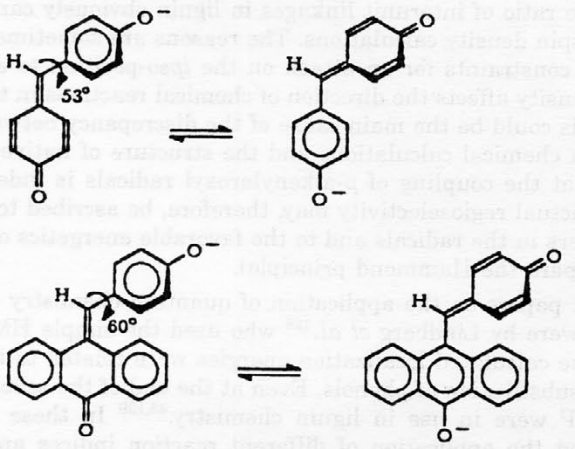
Calculations of electronic spectra were also used to test the results of conformational calculations. Thus, the experimental UV spectrum of a simple model β-arylether, 1-phenyl-2-phenoxyethane, agrees best with the CNDO/S spectrum in the case of the most stable (PCILO) extended conformer (Scheme 6).[116] Similarly, the spectra of optimized conformers of intermediate β-arylether quinone methide were calculated, and also gave the best agreement with the most stable conformer (Scheme 11).[112] It is important that both in β-arylethers and the corresponding quinone methides, the

first observable low energy band corresponds to the π–π^* transition in the same phenolic (or quinone methidic) fragment but not to a charge transfer. On the other hand, in β-aryletheric α-cations, LUMO is localized on benzylic cationic and HOMO on β-aroxyl fragments, that suggests the possibility of light-induced charge transfer in such structures.[71]

As to the absorption spectrum of lignin itself, the maximum at *ca.* 280 and a shoulder at 300–350 nm are characteristic.[117] The maxima calculated for a typical β-aryletheric structure[116] and also for the less common cinnamaldehyde[100] and diphenyl[102] units fit very well with the main maximum in the lignin spectrum. The shoulder may be ascribed to minor quinonoid and cinnamaldehyde structures.[100,103]

p-Quinone methides have attracted special attention as lignin chromophores.[97] Regular quinone methides are short-life intermediates in lignin chains but α-aryl substituents stabilize such systems.[68] Many typical colored compounds, *e.g.* the alkaline form of phenolphtalein, belong to this class. Numerous experimental and quantum chemical data show that simple quinone methides are slightly colored.[68,103] The color is markedly increased by their combination with hydroxyaromatic units, especially in their ionized forms. Remko and Polcin have analyzed this effect using some typical tautomeric structures.[103,104] However, they assumed planar structures for these compounds, which is obviously wrong.[69] α-Arylquinone methides are characterized by a twist of the substituent, and the deep color of the anions of such compounds has been ascribed to the charge transfer band from the donor α-hydroxyl to the acceptor quinonoid part of the anion (Scheme 15).[118]

A special problem is the simulation of the medium effect on the electronic spectra. Field simulation gives good results in the prediction of the spectra of neutral molecules and anions;[104,119] the simulation of specific hydration by modelling of hydration shells around anionic centers also yields remarkable improvement of the spectra of phenolic anion by the CNDO/S technique.[120]



Scheme 15. Spatial structure and tautomerism in the anions of α-(*p*-hydroxyaryl) quinone methides.[69,118]

Besides electronic spectra, IR and NMR spectra have also been the subject of theoretical simulation. Molecular mechanics proved to be a poor instrument in the prediction of vibrational spectra of aromatic molecules related to lignin.[121] In an attempt to relate the calculated result to experimental finding for lignin model compounds, theoretically determined electron densities and ^{13}C NMR chemical shifts were compared in a series of »monomeric« models.[122] Regression analysis resulted in a poor fit of the data. This is not surprising since the chemical shift depends on numerous factors of which electron density is only one.[123] Sorting the data for each carbon gives reasonable linear relationships fo carbons 4 and 6 of the aromatic ring, and for the α- and β-carbons of the side chain.

PREDICTION OF CHEMICAL REACTIVITY

Martesson and Karlsson[124] were likely the first to analyze theoretically the π--electron spin densities of the coupling aroxyl radicals that form lignin polymer. The PPP spin density was found highest at the phenolic oxygen in each of the radical structures considered. This was interpreted as theoretical evidence in agreement with experimental data, indicating that the β–O–4 linkage is the predominnt mode of combination in softwood lignin. Methoxyl, aroxyl, and aryl substituents *ortho* to the phenolic group (Scheme 1) affect the spin density distribution noticeably. In particular, the spin density in the position *para* to phenolic oxygen is reduced at the expense of the carbon to which the substituent is attached. However, the high spin density in this position does not represent a site of elevated reactivity.[125,126]

Later, Elder and Worley[127] used the MNDO technique to examine the structure of coniferyl alcohol and its corresponding phenolate anion and radical. It was found that the calculated spin densities and charge values for the reactive sites did not correlate with bond frequencies in lignin, but the polymerization occurred through the positions with partial negative charge and positive spin densities. Radical coupling during the biosynthesis of lignin is a regioselectivity reaction in which the β–O–4 bonding predominates (Scheme 3).[126] The regioselectivity of aroxyl radical coupling and the ratio of interunit linkages in lignin obviously cannot be explained on the basis of spin density calculations. The reasons are sometimes trivial, such as thermodynamic constraints for an attack on the *ipso*-position to alkyl substituent. Anyhow, spin density affects the direction of chemical reactions in the case of kinetic control only. This could be the main cause of the discrepancy between the results of simple quantum chemical calculations and the structure of native lignin. However, it was found that the coupling of *p*-alkenylaroxyl radicals is indeed under kinetic control.[126] The actual regioselectivity may, therefore, be ascribed to nucleophilicities of reaction centers in the radicals and to the favorable energetics of the β–O–4 path (Scheme 3, compare the Hammond principle).

The earliest papers on the application of quantum chemistry to chemical reactivity of lignin were by Lindberg *et al.*[128] who used the simple HMO method. They reported that the calculated localization energies were related to the reaction rates of electrophilic substitution of phenols. Even at the end of the seventies such simple methods as PPP were in use in lignin chemistry.[48,129] In these publications, the authors analyzed the application of different reaction indices and theoretical approaches to lignin reactivity but without any definite conclusion. Zarubin *et al.* used Pearson's hard-soft acid-base theory to interpret the reactions of lignin.[130] They published numerous HMO data on lignin model structures, which constituted a basis

for the softness scales of lignin model electrophiles and nucleophiles. The HMO method seems to be too rough for reliable estimation; HOMO(LUMO) energy cannot be treated as the only measure of softness. However, the general approach developed by these authors proved to be productive in lignin chemistry.

In a theoretical study on the chlorination of lignin model compounds, Elder and Worley[131] compared electronic parameters to the energy difference between the ground state molecules and chlorinated intermediates. The results indicated that, in case of coniferyl alcohol, the position exhibiting the greatest negative charge is the methoxyl oxygen, while the position with the highest electron density of HOMO is *para* to the phenolic hydroxyl. Atomic contributions to HOMO are expected to control regioselectivity, since the mechanism of chlorination is the electrophilic attack of chloronium ion on the nucleophilic coniferyl alcohol substrate. Favorable reaction indices notwithstanding, these positions have the two highest energy barriers to chlorination. Similarly, an attack on the β-carbon in the aliphatic side chain leads to the lowest energy barrier, but this atom does not have a correspondingly high negative charge or HOMO electron density. It can be seen that steric considerations may strongly influence the reactivity od these sites, favoring the largely unhindered carbon, while the others with greater reaction barriers are stongly hindered. If these three positions are neglected, leaving aromatic positions and the α-carbon of the side chain, it is found that the size of the negative charge does not reflect the order of the energy differences. In contrast, the HOMO electron density at the various positions increases in the same sequence as the energy barrier toward chlorination. It may be concluded, therefore, that the chlorination reaction is more sensitive to orbital control and steric factors than simple Coulombic attraction.

The MNDO study of the formation of methylol derivatives of phenols (one of the possible routes of lignin condensation during alkaline pulping) showed that the regioselectivity of the initial reactions of phenol and formaldehyde is not charge but HOMO mediated.[132] However, the following analysis of reaction routes based on MNDO energies in this study and other methodologically similar analyses of the mechanism of anthraquinone-alkaline pulping[133] are doubtful because solvation obviously changes the energy balance of the reaction of ionized substances, in comparison with the data of »gas phase« calculations of isolated species. More productive is the approach based on the analysis of orbital characteristics of molecules and units of the polymer which participate in the chemical reactions under consideration (see below).

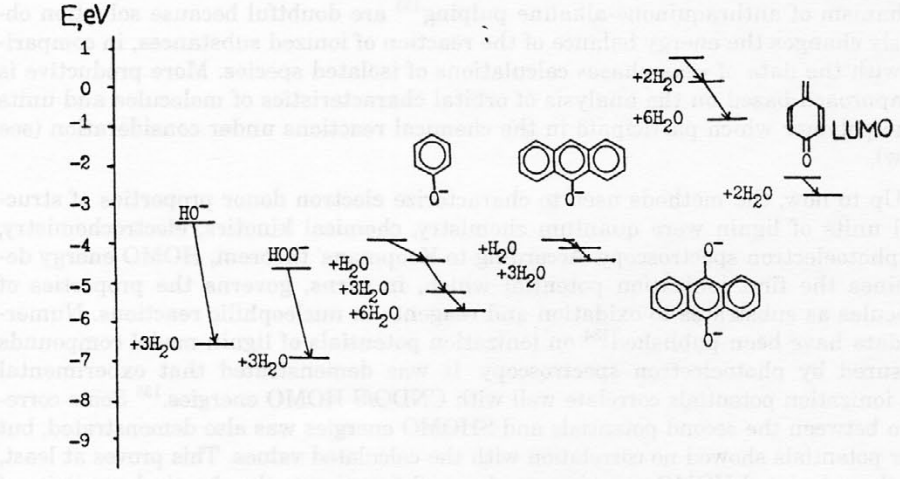
Up to now, the methods used to characterize electron donor properties of structural units of lignin were quantum chemistry, chemical kinetics, electrochemistry, and photoelectron spectroscopy. According to Koopmans' theorem, HOMO energy determines the first ionization potential which, in turns, governs the properties of molecules as substrates to oxidation and reagents in nucleophilic reactions. Numerous data have been published[134] on ionization potentials of lignin model compounds measured by photoelectron spectroscopy. It was demonstrated that experimental first ionization potentials correlate well with CNDO/S HOMO energies.[135] Some correlation between the second potentials and SHOMO energies was also demonstrated, but lower potentials showed no correlation with the calculated values. This proves at least, that the calculated HOMO energies may be used to estimate the chemical reactivity of the structural units of lignin. The quantum chemical interpretation of photoelectron spectra of some model compounds was also pubished.[136] In the earlier theoretical stud-

ies, some effects of the typical lignin substituents on the aromatic π-HOMO energy were demonstrated. It has been shown that the difference in reactivity between lignin structural units decreases upon ionization of the phenolic hydroxy group.[48,137]

In all lignin structural units, the first ionization potentials correspond to electron abstraction from the π-HOMO.[135,138] Different types of lignin subunits do not differ too much by their ionization energies, and the difference becomes less pronounced on binding the units into a polymer chain.[135] It is interesting to note that transformation of typical *p*-hydroxybenzyl alcohol structures to parent *p*-quinone methides does not increase the first ionization potential much, but affects regioselectivity (HOMO is localized on the α-atom of quinone methide but not in its precursor).[67,112,139]

In alkaline pulping, active species are nucleophilic anions whose chemical reactivity may be ranged by their nucleophilicities. On the other hand, nucleophilicity is related to electron-donor properties and ionization energies.[140] There is a large energy gap between HOMO and SHOMO in ionized phenols and, hence, the affinities of nucleophilic anions to lignin electrophilic substrates in soft-soft interactions correlate with HOMO energies, regioselectivity being determined by AO contributions to HOMO.[141,142] This is the explanation of the 10-C-regioselectivity of the reaction of anthracenols with lignin in anthraquinone-alkaline pulping and the much higher activity of the reduced forms of the catalyst in comparison with lignin phenols and hydroxide anions (Scheme 16).[142]

Solvent effects present a special problem in quantum chemical estimation of chemical reactivity. As to lignin, its biosynthesis proceeds in the presence of water and, in wood chemical processing, it also needs aqueous or some other polar media. Actually, there are two problems to be solved: non-specific solvent effects and specific solvation. Non-specific solvation can be simulated in quantum chemical calculations through an imposed field and dielectric parameters. In geometry calculations, average medium effect may be allowed for by applying a given dielectric constant.[143]



Scheme 16. HOMO energies of hydrated anions and the LUMO energy of the simplest *p*-quinone methide, eV (CNDO/S).[7,120]

Similarly, in the electronic structure calculations, one may apply an artificial external field, which leads to a good correlation between the predicted and experimental data in neutral molecules.[110] Analyses have been published of the interaction of nucleophiles with carbonyl compounds[144] and of non-specific solvent effects on the electronic structure and chemical reactivity of lignin nucleophiles (dielectric continuum simulation)[119,145] and *p*-quinone methides (field simulation).[110] Ionization potentials and reactivity of nucleophiles decrease when going from isolated species to the solution[119,145] but the electrophilicity of quinone methides is increased because of polarization.[110] In both cases, frontier orbital energies were regarded as a measure of chemical reactivity *i.e.* soft-soft (frontier orbital controlled) reactions were under consideration. Specific hydration reduces both the LUMO energy of *p*-quinone methide and HOMO energy of nucleophilic anions which may attack lignin during pulping, the harder anions being more influenced than the softer. This means that water strongly differentiates between hard and soft nucleophilic anions by their chemical reactivities, which makes the preference of softer anions in soft-soft interactions more pronounced (Scheme 16).[120]

Electrophilicity, softness and electron affinity of *p*-quinone methides and related benzyl cations (Scheme 2) are much higher than those of any other structural units of lignin, including carbonyl groups which are the strongest electron acceptor units in lignin.[5,146] This is why quinone methides and benzyl cations are key intermadiates in the reactions of lignin with nucleophiles both in biosynthesis and chemical pulping (Schemes 2,3).[5,68] *p*-Quinone methides belong to quinone derivatives, in some aspects intermediates between *p*-benzoquinones and *p*-quinodimethanes; a classification of their atomic orbitals was presented in a review.[147] The electronic structure of quinone methides and benzylic cations attracts attention because of the acute problems of lignin reactivity and chromophoric properties. Early HMO and PPP calculations revealed the major features of the electronic structure of quinone methides and benzyl cations;[106,130,148] numerous semiempirical (CNDO/2, CNDO/S, CNDO/S3, MNDO)[59,106,109–112,114,130,141,142,145,149–151] and *ab initio*[67] calculations were performed later. According to the CNDO/S3 data,[109] the energies of singlet-triplet excitation in quinone methides are too high for these compounds to be treated as diradicals in the ground state; triplet states cannot be generated in thermal processes and may play a significant role in photochemical reactions only (compare Ref. 149). The zwitter-ionic structure[130] does not correspond to a minimum of potential energy surface in the ground state.[109,150] Therefore, it may be concluded that the classical quinonoid structure is characteristic of quinone methides, and their chemical reactivity is not connected with diradical or zwitter-ionic states.[68]

It has been shown that both quinone methides and benzyl cations are very soft electrophiles, whose reactions are under orbital control.[5,68,146] This is the key to the explanation of chemio- and regioselectivity of nucleophilic addition to these electrophiles. The relative chemical reactivity of these substrates is governed by LUMO energies; CNDO/S3 energies correlate with experimental electrochemical reduction potentials (here an electron may be treated as the simplest soft nucleophile).[152] Regioselectivity is determined by relative AO contributions to the frontier orbital. In both quinone methides and benzylic cations, the contribution of α-C AO to LUMO predominates.[68,109,146] Only in vinyloguous quinone methides (Scheme 11) a lower but comparable contribution of γ-C atom appears. The α-C atom of quinone methides bears a small negative charge. Therefore, preferential addition of a negatively charged nucleophile to this atom cannot be explained by charge control. Even in benzylic cations,

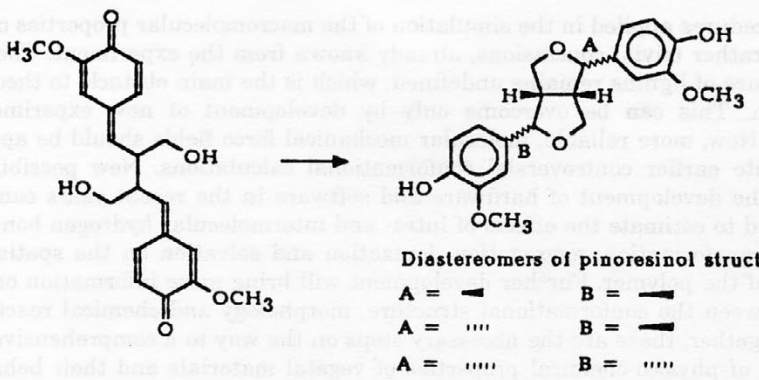
the positive charge on α-C atom does not exceed 0.3 a.u. (CNDO/2) and is strongyly delocalized. On the other hand, nucleophiles can be classified by their affinities to quinone methides and benzylic cations accordigng to their HOMO energies.[120,140] This is the way to explain the chemioselectivity of nucleophilic reactions of lignin in which these intermediates are formed. Neither solvation[120] nor mutaul approach of reactants[153] change the qualitative conclusions based on the analyses of frontier orbitals of isolated molecules. The calculations of the systems of approaching phenolic nucleophiles and the *p*-quinone methide substrate pointed to the conclusion that thermal electron transfer is possible for ionized anthracenols but not with phenols, *i.e.* in catalytic cleavage but not condensation of lignin during alkaline pulping.[153]

Quantum chemical calculations elucidated the major structural effects on the frontier orbitals of the main participants of typical reactions of lignin and constituted the basis of the modern theory of chemical reactivity of lignin which explains the major characteristic features of the behavior of this polymer in natural and technological conditions. The problem of transferability of the results of calculations of isolated small fragments onto the polymer in a medium and also onto a reacting system was considered as well. The conclusion was that the correspondence does exist and qualitative results are transferable.[5,68] Some still unresolved problems remain in the stereochemistry of lignin reactions. This field is still almost untouched but promises much in the studies of fine details of chemical tranformations and biosynthesis of lignin. Thus, pure steric consideration may give an explanation (although the context is outside Curtin-Hammer's principle[154]) of the formation of pinoresinol stereosiomers (Scheme 17) in lignin biosynthesis.[64] MMX calculations have demonstrated that all three stereoisomers are of equal energy but conformers of their precursor quinone methide differ in energy, and the lowest energy conformer is that yielding the preferential isomer of pinoresinol.

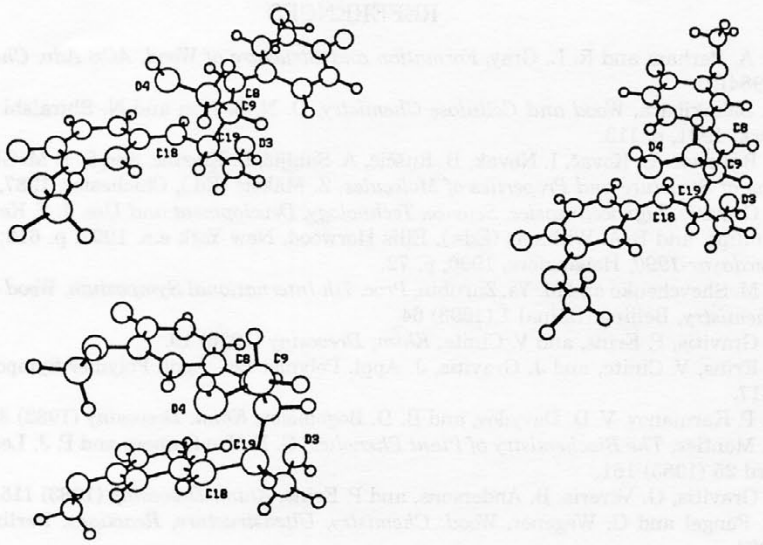
Nucleophilic addition to β–O–4 quinone methides is a stereodifferentiating reaction[68,155] which cannot be explained in terms of steric hindrance only (compare Ref. 70 and Ref. 155). This may be a result of the conformationally dependent electrostatic non- equivalence of the two sides of the skeleton plane of the substrate.[71] Frontier orbital energies and their AO contributions are almost insensitive to the conformational isomerism of β-aryletheric quinone methides and benzylic cations.[59,68,71,112] The partial charge distribution is also insensitive to conformation. However, the spatial distribution of electrostatic potential, which affects charged nucleophiles over long distances, is quite different in different conformers of quinone methides and on different sides of the stereodifferentiating plane of the same conformer.[71] This situation may strongly influence the direction of a nucleophilic attack and lead to the preference of a particular stereoisomer of the product. There is much less stereodifferentiation in benzylic cations, where both sides of the plane are electrostatically indistinguishable because of the positive charge.

CONCLUSION

Theoretical lignin chemistry was developing fast in the last decade. It brought a better understanding of structural and spatial organization as well as electronic properties and chemical reactivity of lignins. Lignin biosynthesis and depolymerization were successfully simulated, providing information on the primary structure and morphology of lignins and kinetics of their chemical reactions. Molecular me-



Conformers of the intermediate quinone methide:



Scheme 17. Formation of three stereoisomers of pinoresinol and the respective conformers of the precursor *p*-quinone methide.[64]

chanical calculations clarified the conformational properties of basic structrues in the polymer. Quantum chemical calculations explained chemio- and regioselectivity of lignin reactions, which are of most importance for the chemistry of wood processing. On numerous examples, it was demonstrated that qualitative conclusions on spatial structure and chemical reactivity of model lignin units can be transferred to the polymer. Theoretical research explained the key role of a few important intermediates in chemical transformations of lignins.

However, much else should be done to achieve the level of development which is characteristic of the chemistry of more regular biopolymers. Sophisticated mathe-

matical procedures applied in the simulation of the macromolecular properties of lignins led to rather trivial conclusions, already known from the experiment. The primary structure of lignins remains undefined, which is the main obstacle to theoretical reserach. This can be overcome only by development of new experimental techniques. New, more reliable, molecular mechanical force fields should be applied to re-evaluate earlier controversial conformational calculations. New possibilities opened by the development of hardware and software in the recent years can and must be used to estimate the effects of intra- and intermolecular hydrogen bonding, reversible transformation, aggregation, ionization and solvation on the spatial organization of the polymer. Further development will bring more information on the relation between the conformational structure, morphology and chemical reactivity of lignin. Together, these are the necessary steps on the way to a comprehensive understanding of physico-chemical properties of vegetal materials and their behavior in both biological and technological pprocesses.

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SAŽETAK

Teorijski pristupi kemiji lignina

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Kritički su prikazane primjene teorijskih postupaka u proučavanju strukture i kemijske reaktivnosti lignina, uključujući simulaciju makromolekulskih svojstava, račun konformacije, kvantno-kemijsku analizu elektronske strukture, spektara i kemijske reaktivnosti, kao i suvremeni koncepti prostorne organizacije i kemijske reaktivnosti lignina.