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Title: Radical coupling reactions in lignin biosynthesis

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Quantum chemical calculations using density functional theory (DFT) have been performed to study the initial radical coupling reactions involved in lignin biosynthesis. Computed reaction energies and enthalpies for the radical-radical coupling of p-hydroxyphenyl, guaiacyl and syringyl radicals via six major linkage types observed in natural lignin show that 8-O-4 radical coupling is the most favorable among all three monomers, which is in complete agreement with the experimental observation. In the 8-O-4 coupling reaction, coupling of p-hydroxyphenyl at its O4 with C8 of guaiacyl or syringyl radicals is most favorable. Among three monomer units, p-hydroxyphenyl radical coupling via all linkage types is thermodynamically most favorable. This radical species is less stable and more reactive than the other two radicals and is also less sterically hindered because it lacks methoxy groups on its aromatic ring. Steric interactions appear to play a deciding role in the structural arrangement of monomer units during lignin polymerization. Intramolecular hydrogen bonding, a consequence of steric repulsions in guaiacyl and syringyl dimers, increases the bond dissociation energy (BDE) of C-O and C-C bonds to be broken during degradation of lignin. Thus, lignin rich in p-hydroxyphenyl unit should be easily breakable, due to absence of intramolecular hydrogen bond, as compared to guaiacyl and syringyl rich lignin. Our findings, based on thermodynamic control hypothesis, also suggest that the preference for linkage types for all monomer units follows the trend: 8-O-4, 8-8, 8-5, 5-O-4, 5-5 and 8-1.