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## Solvent effects on the electronic state of monolignol radicals as predicted by molecular orbital calculations

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**Abstract** The spin and charge densities in three monolignol radicals were computed using the UB3LYP/6-31G\* method of molecular orbital calculation. As well, the effects of solvents were simulated by using an SCI-PCM model. It was confirmed that an unpaired electron was localized at C<sub>1</sub>, C<sub>3</sub>, C<sub>5</sub>, C<sub>8</sub>, and O<sub>4</sub> for all monolignol radicals. In solvents, the spin density decreased at O<sub>4</sub> with increasing solvent polarity, but increased at C<sub>8</sub>. The atomic charges at all reactive atoms had a negative value and were obviously strengthened at O<sub>4</sub> with increasing solvent polarity. These tendencies support the experimental results for radical coupling reactions of monolignols in various solvents; that is, that 8-O<sub>4</sub>' linkages are produced much more often than 8-8' linkages in nonpolar solvents.

**Key words** Lignin · Radical · Molecular orbital calculation · Spin density · Charge density

### Introduction

Native lignin is an 8-O<sub>4</sub>' ( $\beta$ -O-4) rich polymer. However, demonstrating the formation of this linkage in vitro is difficult because the 8-8' ( $\beta$ - $\beta$ ) linked dimer, for example, syringaresinol from sinapyl alcohol, is the major product in aqueous solution. Tanahashi et al. reported a high yield of 8-O<sub>4</sub>' ether from sinapyl alcohol by a radical coupling reaction in a nonpolar solvent<sup>1</sup> or under hydrophobic conditions produced by hemicellulose matrix gel.<sup>2</sup> It has been suggested that this is due to a change in the electron-withdrawing effect of the methoxyl groups and depends on the polarity of the solvent. Similar behavior was also reported by Terashima and Atalla in diglyme–water solution.<sup>3</sup>

It was previously reported that localization of the unpaired electron in a *p*-coumaryl alcohol radical and the radical coupling reaction toward an 8-O<sub>4</sub>' linkage could be analyzed using a semiempirical molecular orbital calculation, the UHF/PM5 method.<sup>4</sup> It was suggested that the coulombic repulsion between reactive atoms influences the energy barrier in the coupling reaction. The electronic state of the coniferyl alcohol radical was also investigated by Elder and Worley<sup>5</sup> and Russell et al.<sup>6</sup> using a semiempirical molecular orbital method. However, the results they obtained were not very precise because the semiempirical molecular orbital method is of comparatively low accuracy.

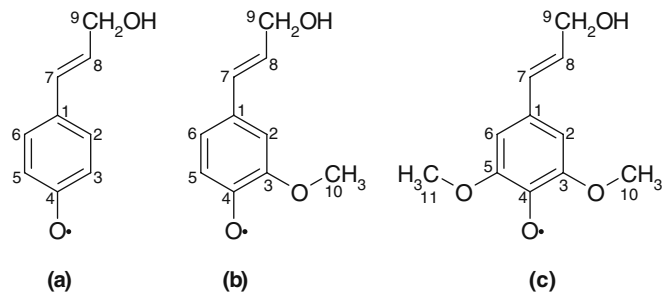
In this report, localization of the unpaired electron in monolignol radicals was computed using a molecular orbital calculation based on density function theory, which is more accurate than semiempirical methods. The examination was also extended to three major monolignols, *p*-coumaryl, and coniferyl and sinapyl alcohols, and the solvent effect is discussed.

### Experimental

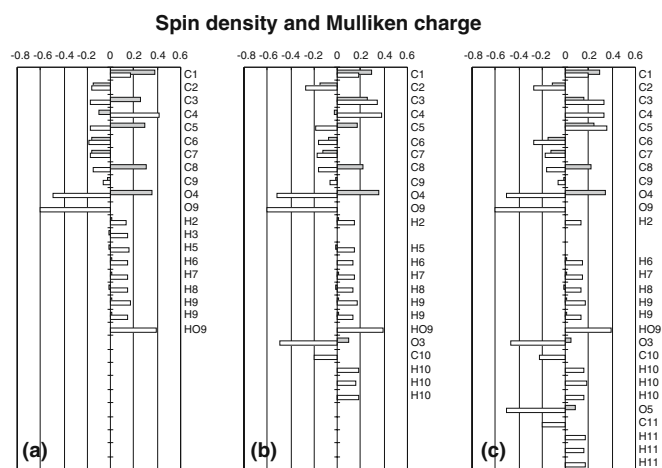
The optimum geometries of monolignol radicals were determined by the conformer search protocol built in the Spartan '04 Win (Wavefunction) using the UHF/3-21G basis set. The conformer candidates obtained were further optimized with the UB3LYP/6-31G\* level of a density function theory, and the lowest energy conformer was then determined. 6-31G\* of the basis set was adopted because of its good accuracy and computing time, as confirmed for the coniferyl alcohol radical.<sup>7</sup> The carbon numbers were defined as shown in Fig. 1.

The electronic states of the monolignol radicals in solvents were determined by UB3LYP/6-31G\* optimization with an SCI-PCM model built in Gaussian03 (Gaussian). In solution, the electrostatic effect of solvents existing between unbound atoms cannot be disregarded. In the SCI-PCM model, the solvent effect is assigned by the dielectric constant. In this report, the dielectric constants adopted were

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**Fig. 1a–c.** Structures of monolignol radicals. **a** *p*-Coumaryl alcohol radical, **b** coniferyl alcohol radical, and **c** sinapyl alcohol radical. Numerals show the carbon numbers defined in this report



**Fig. 2a–c.** Spin density and Mulliken charge at each atom of monolignol radicals in the absence of solvent calculated by UB3LYP/6-31G\* molecular orbital calculations. **a** *p*-Coumaryl alcohol radical, **b** coniferyl alcohol radical, and **c** sinapyl alcohol radical. Gray bars, spin density; white bars, Mulliken charge

2.274 for benzene, 4.8 for chloroform, 20.7 for acetone, and 78.4 for water.<sup>8</sup>

## Results and discussion

### Spin and charge densities at reactive atoms in monolignol radicals

The distribution of an unpaired electron could be expressed as the spin density at each atom. Figure 2 shows the spin densities and Mulliken charges in three monolignol radicals. From these diagrams, it can be seen that the unpaired electron was localized at C<sub>1</sub>, C<sub>3</sub>, C<sub>5</sub>, C<sub>8</sub>, and O<sub>4</sub> for all monolignol radicals. This result qualitatively agrees with our previous results obtained using UHF/PM5 semiempirical molecular orbital calculations.<sup>4</sup> However, a quantitative disagreement was observed between the results of the previous work and the results of the present study. For example, the spin density ratio of O<sub>4</sub> on C<sub>1</sub> in the *p*-coumaryl alcohol radical was 0.410 for UHF/PM5, but 0.946 for UB3LYP/6-31G\*. This disagreement is the result of the different approximation protocols used in the calculations. Because density

function theory is more accurate than the semiempirical method, our confidence regarding the present data is higher than that for the previous data. It was concluded that the unpaired electron is localized at reactive atoms and the charge density is the highest at O<sub>4</sub> for the reactive atoms (i.e., C<sub>3</sub>, C<sub>5</sub>, C<sub>8</sub>, and O<sub>4</sub>).

As described in a previous report,<sup>4</sup> charge density at the reactive atoms in a monolignol radical is important for the coupling reaction. The Mulliken charges at all reactive atoms, that is, C<sub>5</sub> (including C<sub>3</sub> for the *p*-coumaryl alcohol radical), C<sub>8</sub>, and O<sub>4</sub> were negative and were lowest at O<sub>4</sub>. During the approach of two radicals, their negative charges cause coulombic repulsion and hinder the approach regarded as the primary step of the coupling reaction. Because the charge at O<sub>4</sub> is the most negative, a high repulsion would be produced between O<sub>4</sub> and the other reactive atom. Therefore, it is suggested that the 8-O<sub>4</sub>' coupling (producing β-ether bond) is more difficult than the other couplings, for example, 5-8' (coumaran structure) and 8-8' (resinol structure).

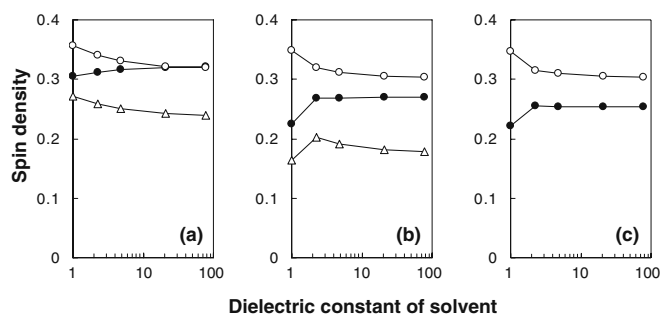
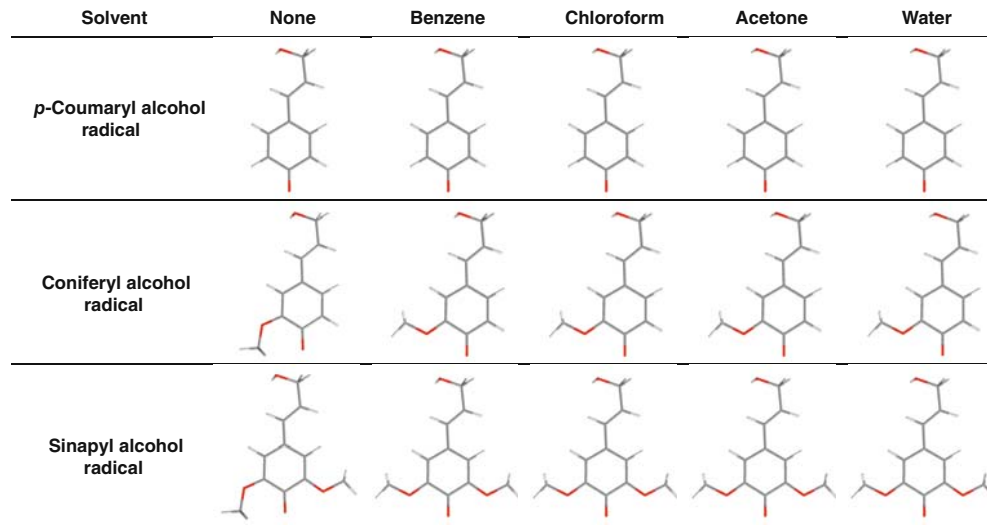
### Optimum conformations of monolignol radicals in various solvents

Figure 3 shows the optimum conformations of three monolignol radicals in various solvents as determined by UB3LYP/6-31G\* optimization. These conformations were obtained during molecular orbital calculations to derive the localization of the unpaired electron. For the *p*-coumaryl alcohol radical, geometries in all solvents were almost identical. For the coniferyl and sinapyl alcohol radicals, geometries in the solvents were different from those in the absence of solvent. The major difference was the direction of the methoxyl group; that is, C<sub>10</sub> (or C<sub>11</sub> for the sinapyl alcohol radical) turned toward O<sub>4</sub> in the absence of solvent, but stayed away when solvent was present. This behavior may be caused by the solvent effect on the electrostatic interaction between C<sub>10</sub> (or C<sub>11</sub>) and O<sub>4</sub>. In solvent, a high dielectric constant cushions the electrostatic repulsion between O<sub>3</sub> (or O<sub>5</sub>) and O<sub>4</sub>, allowing the approach of lone pairs of O<sub>3</sub> toward O<sub>4</sub>. There is a similar solvent effect on the optimum conformation of methoxyl groups in methoxyphenols.<sup>9,10</sup>

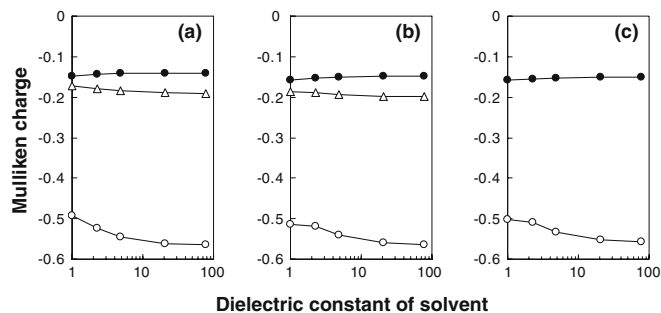
### Solvent effect on spin and charge densities

Figure 4 shows the effect of solvents on spin density. For all radicals, the spin density decreased at O<sub>4</sub> but increased at C<sub>8</sub> with an increasing solvent dielectric constant. The solvent effect on the spin density at C<sub>5</sub> (or the average of C<sub>3</sub> and C<sub>5</sub> for the *p*-coumaryl alcohol radical) was complex, but seemed to decrease with an increasing solvent dielectric constant. There was a marked change in the spin density for coniferyl and sinapyl alcohol radicals when the dielectric constant changed from 1 to 2.274. This may have been a result of the change in the geometry of the methoxyl group between these dielectric constants, or the other reasons. Figure 5 shows the effects of solvent on the Mulliken charge. For all

**Fig. 3.** Optimum conformations of monolignol radicals in various solvents calculated by UB3LYP/6-31G\* with the SCI-PCM solvation method



**Fig. 4a–c.** Effect of the dielectric constant of solvents on the spin densities of monolignol radicals calculated by UB3LYP/6-31G\* with the SCI-PCM solvation method. **a** *p*-Coumaryl alcohol radical, **b** coniferyl alcohol radical, and **c** sinapyl alcohol radical. *Triangles*, at  $C_5$  (or average of  $C_3$  and  $C_5$  for *p*-coumaryl alcohol radical); *closed circles*, at  $C_8$ ; *open circles*, at  $O_4$



**Fig. 5a–c.** Effect of the dielectric constant of solvents on the Mulliken charges of monolignol radicals calculated by UB3LYP/6-31G\* with the SCI-PCM solvation method. *Symbols* are the same as for Fig. 4

radicals, the charge at  $O_4$  clearly decreased, but did not change at  $C_5$  and  $C_8$ .

From these results, quantum chemistry predicts that the 8- $O_4'$  coupling reaction is unfavorable in a polar solvent because of the decrease in spin density at  $O_4$  and the high coulombic repulsion between  $C_8$  and  $O_4'$ . For the opposite reason, the 8-8' coupling reaction is favored in polar sol-

vents. Consequently, it is suggested that the 8- $O_4'$  coupling is more difficult to produce in polar solvents than in nonpolar solvents. This suggestion is in agreement with the experimental results as noted in the Introduction; that the amount of 8- $O_4'$  coupling product increases in nonpolar solvents and decreases in polar solvents.<sup>1–3</sup>

The change in the electronic state under different solvent conditions may be caused by the dependence of the most favorable conformation and the solvation energy on the solvent. The tendencies of the spin and charge with the polarity of the solvent were similar in all monolignol radicals. Furthermore, the changes of electronic state at  $O_4$  and  $C_5$  were large, but small at  $C_8$ . This suggests that the solvent effect may be ascribed to the solvation effect of a polar solvent around  $O_4$  rather than to the change in electron withdrawal by methoxyl groups.

## Conclusions

To clarify the reactivity of monolignol radicals in different solvents, the spin densities and charges were determined by molecular orbital calculations. The spin density decreased at  $O_4$  with increasing solvent polarity, but increased at  $C_8$ . The negative charge at  $O_4$  was strengthened with increasing solvent polarity. These changes suggest that 8- $O_4'$  linkages are produced much more often than 8-8' linkages in nonpolar solvents, but not in polar solvents.

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