

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597282>

THERMAL INDUCED HOMOLYTIC SCISSIONS OF LIGNIN INTERUNITARY BONDS IN THE HARDWOOD LIGNIN SOLUTION. AN ESR STUDY COMBINED WITH A SPIN TRAPPING METHOD

A. Yoshioka^a; T. Seino^a; M. Takai^a; M. Tabata^b

^a Department of Biotechnology and Department of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo, Japan ^b Department of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo, Japan

Online publication date: 31 May 2001

To cite this Article Yoshioka, A. , Seino, T. , Takai, M. and Tabata, M.(2001) 'THERMAL INDUCED HOMOLYTIC SCISSIONS OF LIGNIN INTERUNITARY BONDS IN THE HARDWOOD LIGNIN SOLUTION. AN ESR STUDY COMBINED WITH A SPIN TRAPPING METHOD', *Journal of Wood Chemistry and Technology*, 21: 2, 127 – 141

To link to this Article: DOI: 10.1081/WCT-100104223

URL: <http://dx.doi.org/10.1081/WCT-100104223>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

**THERMAL INDUCED HOMOLYTIC
SCISSIONS OF LIGNIN INTERUNITARY
BONDS IN THE HARDWOOD LIGNIN
SOLUTION. AN ESR STUDY COMBINED
WITH A SPIN TRAPPING METHOD**

A. Yoshioka,^a T. Seino,^a M. Takai,^{a,*} and M. Tabata^{b,*}

^aDepartment of Biotechnology and

^bDepartment of Molecular Chemistry, Graduate
School of Engineering, Hokkaido University,
Sapporo 060-8628, Japan

ABSTRACT

An electron spin resonance (ESR) method combined with a spin trapping reagent was successfully applied to trap and characterize unstable free radicals which were generated by heat-treatment of the dimethylsulfoxide (DMSO) solution of a hardwood, Japanese beech (*Fagus crenata*) lignin. It was found, consequently, that two unstable secondary carbon radicals, $\sim\text{CH}\cdot$ in the solution were created and the resulting radicals were trapped as the stable nitroxide spin adducts when the DMSO solution was heat-treated in the presence of a spin trapping reagent: 2,4,6-tri-*tert*-butylnitrosobenzene (BNB) at *ca.* 91°C. This means that so-called alkyl phenyl ether bonds, $\sim\text{CH-O-phenyl}$, known as important

* Corresponding author.

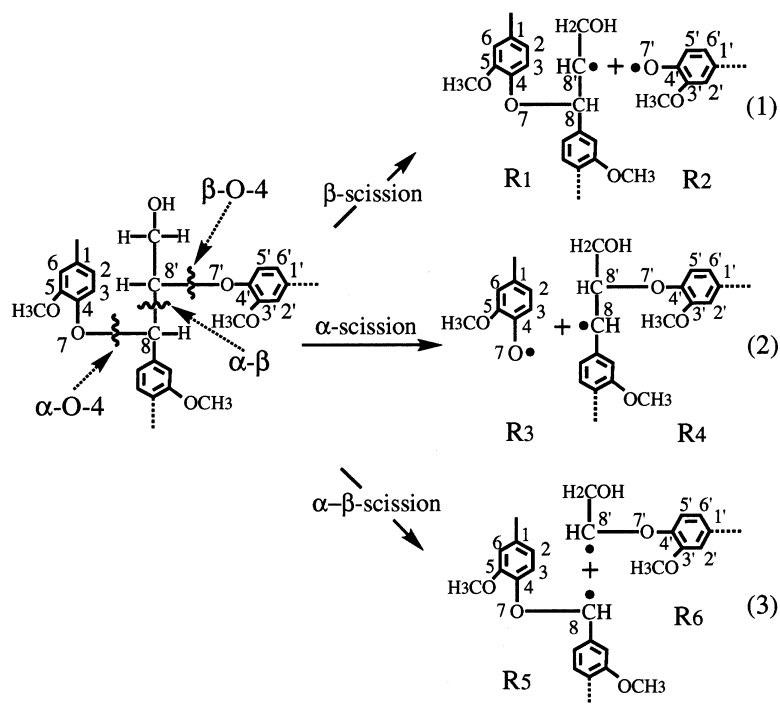
lignin interunitary bonds were homolytically scissioned by the heat-treatment of the lignin solution. Further the detailed analysis of the observed ESR spectrum revealed that two positions of alkyl phenyl ether bonds, i.e., β -O-4 and/or α -O-4 bonds as the interunitary linkages in the lignin are homolytically scissioned, although the phenoxy radical, Ph-O \cdot as the counter radical of the secondary carbon radicals was not trapped by the BNB spin trap. This suggests that fairly large steric hindrances operate between the syringyl with two methoxy moieties at the *ortho* positions and/or guaiacyl moieties with a methoxy moiety at the *ortho* position, and the BNB molecule bearing two bulky *ortho tert*-butyl groups in the phenyl ring.

INTRODUCTION

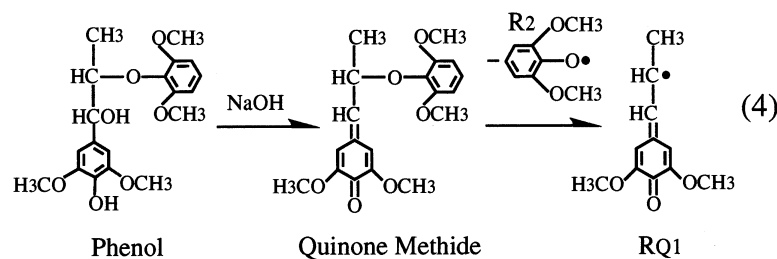
The reactivity of alkyl phenyl ether bonds, i.e., β -O-4 and α -O-4 bonds as the interunitary linkages in wood lignin has focused the interest of many chemists concerned with pulping processes, although the types of frequencies of the interunitary linkages and the lignin contents are different to some extent in each wood.^{1,2} Because efficient fabrication of high quality pulps is necessary for delignification in not only woods but also unbleached pulps, many basically studies with regard to the delignification have been proposed, including chemical oxidations using chlorine dioxide,³ oxygen,⁴ and KMnO₄.⁵ It is also considered that the efficient ruptures of the ether bond, e.g., β -O-4 and/or α -O-4 bonds in wood lignins are necessary not only to produce the high quality pulp but also to decrease the chlorinated compounds which are generated by the products in the chlorine dioxide bleaching pulping process. Therefore, it is very important to determine whether the key ether bonds are scissioned and what kinds of unstable chemical species are produced by ruptures of the β -O-4 and/or α -O-4 bonds as the major and/or minor linkages, respectively, connecting with the three dimensional interunitary linkages of wood lignins shown partly in Scheme 1.

Miksche has reported that homolytic scission of the β -O-4 interunitary bond *via* quinone methides using a small model compound of wood lignins under alkaline conditions where so-called β -O-4 scissions take place to produce RQ1 and R2 radicals as secondary carbon radicals and phenoxy radical (see Scheme 2)⁶ Tsutsumi et al. showed that the β -aryl ether cleavages of lignin model compound was enhanced by the presence of syringyl units.⁷ Reitberger et al. has reported that the radicals, initially formed in bleaching processes, are generated by the action of radical bleaching reagents such as ozone, rather than by homolytic cleavage of the substrate.⁸





Scheme 1. Homolytic scissions of phenyl ether bonds and α - β bond in lignin.



Scheme 2. Homolytic scission of phenolic β -O-4 via quinone methides.

Recently, we reported that the alkyl phenyl ether bonds of hardwood, *Fagus crenata* lignin are homolytically scissioned by ultrasonic irradiation and that the resulting secondary carbon radical, $\sim\text{CH}\cdot$ as the counter radical of phenoxy radical, $\sim\text{Ph-O}\cdot$ is successfully trapped to produce the



stable nitroxide radicals, e.g., $\sim\text{CH-N}(\text{-O}\cdot)\sim$ known as nitroxide spin adducts.⁹ This clearly shows that unstable chemical species, i.e., radicals produced during the lignin and the model compound which were proposed by Miksche⁶ can be trapped and identified if the spin trapping technique combined with ESR method was applied to their solutions. Therefore, we studied whether the ESR method combined with the spin trapping reagent could be successfully applied to trap and identify unstable lignin radicals which were generated by the heat-treatment of the dimethylsulfoxide solution containing Japanese beech lignin and the spin trapping reagent, i.e., 2,4,6-tri-*tert*-butylnitrosobenzene, BNB, at *ca.* 24~91°C. In this report we also show that two kinds of radical species, $\sim\text{C}_\beta\text{H}\cdot$ and $\sim\text{C}_\alpha\text{H}\cdot$, respectively, can be observed as the stable nitroxide spin adducts when the lignin solution was *heat-treated* in the presence of the BNB spin trapping reagent at 91°C, just as when ultrasonic irradiation induced the bond cleavage of the ether bonds.^{9,10}

RESULTS AND DISCUSSION

¹³C NMR

The ¹³C NMR spectrum of the acetylated Japanese beech lignin is shown in Figure 1, where the spectral range regarding the aromatic ring is limited between 100 and 160 ppm and the range is enlarged. It is clear that the larger peaks at 154 ppm are ascribed to those of *o*-methoxy phenyl moieties, i.e., C3 and C5, in the syringyl group as a feature of the hardwood lignin together with the peak at 105 ppm and 107 ppm due to C2 and C6 in the syringyl group.¹¹ These peaks clearly evidenced that the obtained lignin is assigned to that of the hardwood lignin.

Molecular Weight of the MWL

Molecular weight and molecular weight dispersity of the Japanese beech lignin obtained after the acetylation were estimated as $\bar{M}_n = 3000$ and $\bar{M}_w/\bar{M}_n = 2.0$, respectively, using a gel permeation chromatography, GPC, tetrahydrofuran as eluent and polystyrenes as standards.

Spin Trapping

The 2,4,6-tri-*tert*-butylnitrosobenzene, BNB used as the spin trap reagent is known to function as follows; a small radical such as a primary



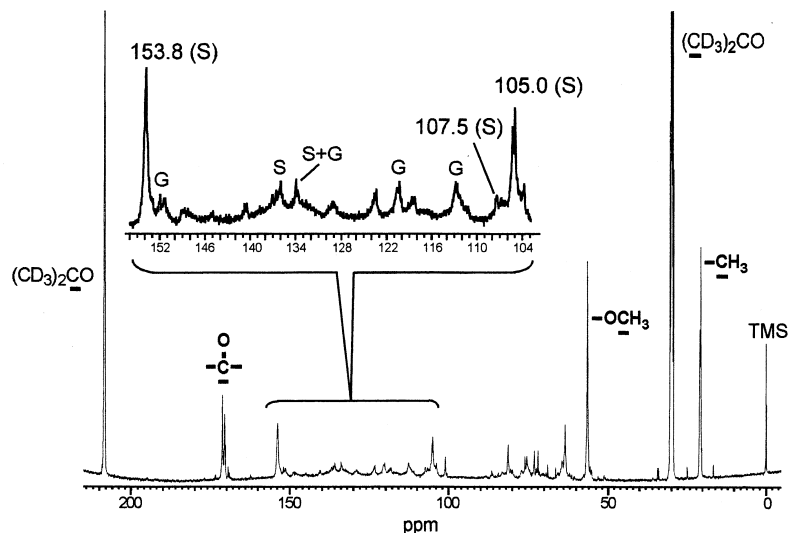


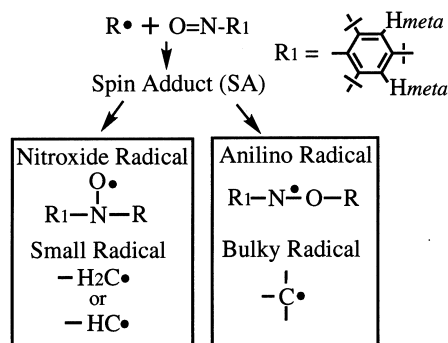
Figure 1. ^{13}C NMR spectrum on the acetylated lignin of Japanese beech (*Fagus crenate*). S; Syringyl group, G; Guaiacyl group.

carbon radical, $\sim\text{CH}_2\cdot$ or a secondary carbon radical, $\sim\text{CH}\cdot$ is trapped to generate a spin adduct (SA) in the form of a nitroxide, $\text{R}(\text{N}-\text{O}\cdot)\text{-CH}_n\sim$ ($\text{R} = \textit{tert}$ -butylbenzene and $n = 1$ or 2) whose ESR parameters show g value, $g = \textit{ca.}$ 2.0065 and nitrogen (nuclear spin number $I = 1$) coupling constant, $a^{\text{N}} = \textit{ca.}$ 13 Gauss, and $a^{\text{Hmeta}} = \textit{ca.}$ 0.8 Gauss as a *meta* hydrogen coupling constant in the tri-*tert*-butylbenzene ring. On the other hand, a relatively large radical such as a *tert* butyl radical, $\equiv\text{C}\cdot$ is trapped to generate an anilino type spin adduct, $\text{R}-\text{N}^{\cdot}\text{O}-\text{C}\equiv$ giving ESR parameters, $g = \textit{ca.}$ 2.004~5, a smaller nitrogen coupling constant, $a^{\text{N}} = \textit{ca.}$ 10G, and $a^{\text{Hmeta}} = \textit{ca.}$ 2G as a *meta* hydrogen coupling constant. Therefore, the radicals produced by the scission of the alkyl phenyl ether bonds may be in principle classified clearly and the chemical structures of the resulting spin adducts are depicted as shown in Scheme 3.

ESR Spectra and Analysis

Figure 2b shows the ESR spectrum, observed at 91°C of the dimethylsulfoxide, DMSO solution, 0.5 ml involving the Japanese beech lignin, 250 mg, and BNB, spin trap reagent, 5.01 mmol/l. The ESR spectra were in





Scheme 3. Possible structures of the BNB spin adducts.

detail analysed by the aid of computer simulations by which major spectral components were determined clearly as shown in Figure 2c, d and e. The observed spectrum, 2b consists of three spectral components as represented by stick diagrams, i.e., Spin Adduct (SA) I, Spin Adduct (SA) II, and III as shown in Figure 2c, d and e. Computer simulations of the observed spectral components, SAI were carried out assuming ESR parameters, i.e., g value, $g = 2.0072$ and isotropic hyperfine (hf) coupling of 11.8 Gauss (G) for one nitrogen(1N) with $I = 1$, 13.2G for one β -proton, i.e., H_β which corresponds to a proton bonded to the β -carbon separated by one chemical bond from a nitrogen having the unpaired electron (see Scheme 4), and a Gaussian line width (maximum slope length, ΔH_{msl}) of $\Delta H_{msl} = 0.55G$.

The ESR parameters used for the best fit simulations of SA I are summarized in Table 1. Since the coupling due to one proton was observed in addition to the nitrogen coupling, SA I was assigned to a spin adduct formed by trapping a secondary carbon radical, $\sim CH\cdot$. Each peak of the double triplet of SA I is split into a small triplet with a small separation of 0.8G and relative intensity, 1:2:1, as shown in the stick diagram and the simulated spectrum (see Figure 2c). The relative intensities indicate an equal coupling with two protons, which are ascribed to the *meta* protons in the tri-*tert*-butylbenzene ring because of their known coupling constant, *ca.* 1.7G.¹² However, the spectrum line shape between not only the center of the spectrum but also the third line and fourth line shown in Figure 2b is not in agreement with that of the simulated spectrum c. Therefore the simulation was also performed to determine the unknown spectral components, assuming an isotropic hyperfine coupling of 12.6G (due to one nitrogen, N), and 12.1G for one β proton, H_β and 0.8G for *meta* hydrogen. H_{meta} and a Gaussian line width of $\Delta H_{msl} = 0.3G$ together with the singlet having



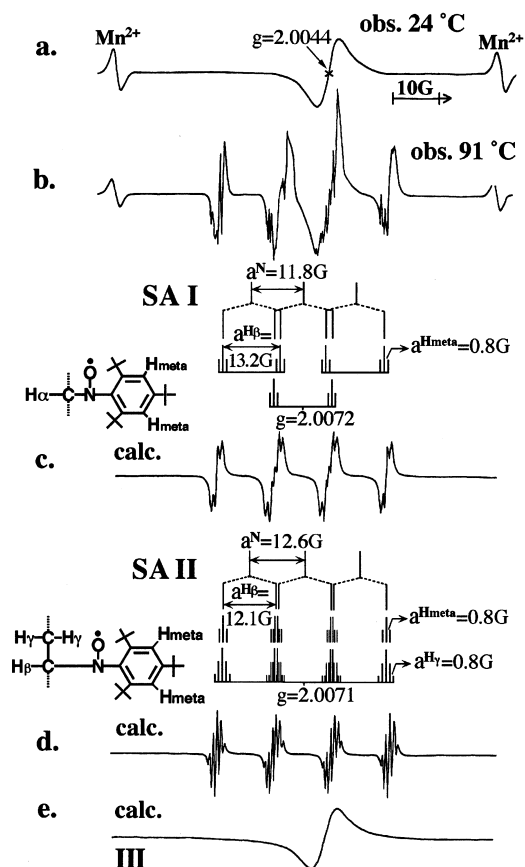
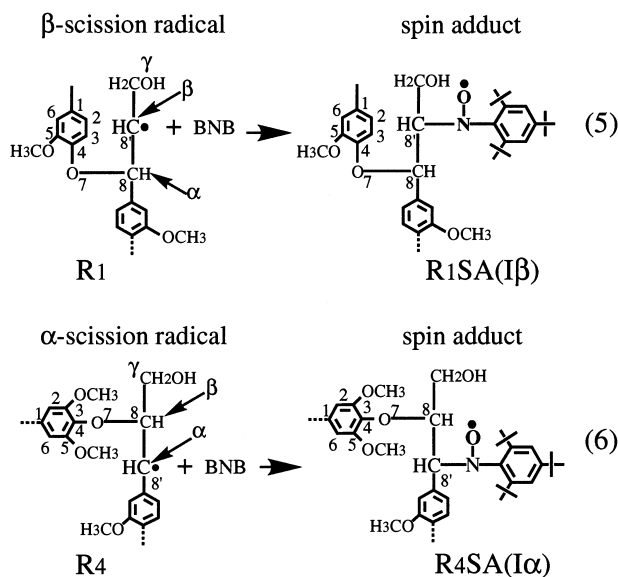


Figure 2. ESR spectra of spin adducts obtained by heating of DMSO solution of *Fagus crenata* lignin in the presence of 2,4,6-tri-*tert*-butylnitrosobenzene, BNB. ESR spectrum observed at 24°C, a, ESR spectrum observed at 91°C, b, simulated spectrum of spin adduct, SA I, c, simulated spectrum of spin adduct, SA II, d, and simulated spectrum of phenoxy radical, III, e.

$g=2.0071$. The ESR parameters used for the best fit simulations are also summarized in Table 1. Interestingly, the simulated spectrum d can also be ascribed to that of a spin adduct of secondary carbon radicals, $\sim\text{CH}\cdot$ since this spin adduct shows the coupling constant, 0.8G due to the two *meta* protons. Since this spectrum d is considered to have an isotropic hyperfine coupling of 0.8G for two protons due to γ position of phenyl propane chain in the lignin structure, the secondary carbon radical, $\text{R}_1\text{SA}(\text{I}_\beta) = \sim\text{C}_\beta\text{H}\cdot$ called





Scheme 4. Possible structure of the secondary carbon radicals trapped by BNB.

Table 1. ESR Parameters Observed in Spin Adducts and Phenoxy Radicals Generated by the Heat-Treatment of the Dimethylsulfoxide Solution of *Fagus crenata* Lignin at 91°C in the Presence of the BNB Spin Trap

Nitroxide ^a	a^{N} (G) ^b	$a^{\text{H}\beta 1}$ (G) ^b	a^{Hmeta} (G) ^b	$a^{\text{H}\gamma}$ (G) ^b	g value ^c	ΔH_{msl} (G) ^b	$\theta(^{\circ})^{\text{d}}$
SAI	11.8	13.2	0.8	—	2.0072	0.6	45.4
SAII	12.6	12.1	0.8	0.8	2.0071	0.3	47.8
III	—	—	—	—	2.0043	4.3	—

^aR = 2,4,6-tri-*tert*-butylbenzene.

^bcalculated coupling constants and line width.

^cg values observed.

^dthe dihedral angle θ_1 between the pz orbital of the unpaired electron and H $_{\beta}$ or H $_{\alpha}$ bond calculated using the McConnell's equation.

a β -scission radical may be produced by the ruptures of the β -O-4 bonds of the mother lignin molecules. On the other hand, the spectrum c was also ascribed to that of the secondary carbon radical, R $_4$ SA(I $_{\alpha}$) = \sim C $_{\alpha}$ H $^{\bullet}$ known as the α -scission radical which may be produced by the ruptures

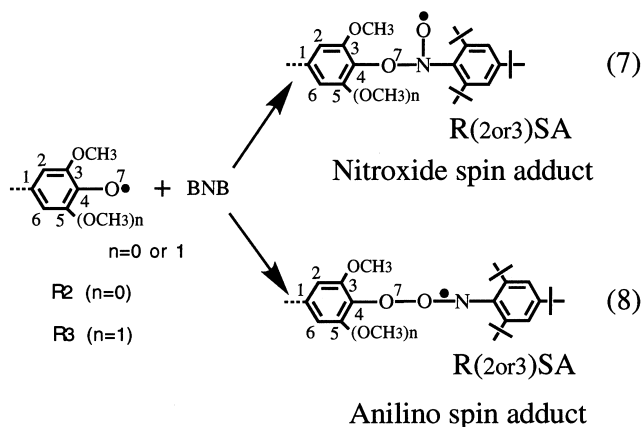


of the α -O-4 bonds. Thus two kinds of radicals, i.e., the secondary carbon radical, $R_1SA(I_\beta)$ known as the β -scission radical and $R_4SA(I_\alpha)$ known as the α -scission radical, respectively, may be produced by the ruptures of the β -O-4 and/or α -O-4 bonds of the mother lignin molecules which were subjected to heat-treatment in the DMSO solution as shown in Scheme 1 and 4.

Recently, we have also reported that the alkyl phenyl ether bonds of hardwood, *Fagus crenata* lignin are homolytically scissioned by ultrasonic irradiation and the resulting secondary carbon radical, $\sim CH\cdot$ as the counter radical of phenoxy radical, $\sim Ph-O\cdot$ is successfully trapped to produce the stable nitroxide radicals, e.g., $\sim CH-N(-O\cdot)\sim$ known as nitroxide spin adducts.⁹ However the observed ESR spectra do not give enough information to determine which ether bond is selectively ruptured by the irradiation owing to fairly wider line widths observed in the spin adduct. Further it is reasonable to conclude that the major ether linkage, i.e., β -O-4 bonds compared to that of the minor α -O-4 bonds,² can be more often homolytically ruptured by the ultrasonic irradiation if so-called ultrasonic cavitation is generated at random in the DMSO solution to rupture the ether bonds according to statistic probability, although the α -O-4 ether as the minor interunitary linkages is also ruptured by irradiation to some extent.

The computer simulation was also carried out to determine the ESR parameters of the spectral component, III assuming the following parameters, $g = ca. 2.0043$ and $\Delta H_{msl} = ca. 4.3G$. These obtained parameters suggest that the broad signal component, III can be ascribed to that of the phenoxy radical, $Ph-O\cdot$, because such a broad signal is already observed even before heat-treatment of the DMSO solution involving BNB spin trap as shown in Figure 2a, although the spectral intensity observed at $91^\circ C$ is larger than that of the spectrum of Figure 2a observed at $24^\circ C$. This indicates that the bond scissions of the relevant β and/or α ether bonds in the lignin molecules were induced by the heating of the DMSO solution and the broad singlet component III is a fairly stable radical at not only $24^\circ C$ but also $91^\circ C$ in the solution. Therefore it is concluded that the observed broad component III is reasonably ascribable to a radical bearing a relatively wide π -conjugated system to stabilize the unpaired electron. It should be noted that such a broad singlet bearing the same g value has been already observed not only in solid lignin but also wood powders.¹³ It is concluded, thus, that the so-called syringoxy and/or guaiacoxo radicals, $Ph-O\cdot$ as the aromatic radicals which are generated by the scissions of the alkyl phenyl ether bonds can also exist not only in the solid lignin but also in the DMSO solution at $91^\circ C$ as observed in Figure 2b. In other words, the phenoxy radical, $Ph-O\cdot$ [see eq. (7) and (8) in Scheme 5] can not be trapped in order to form the nitroxide spin adduct, $R_{(2 \text{ or } 3)}SA$ or the anilino spin adduct, $R_{(2 \text{ or } 3)}SA$, because the nitroxide and/or the so called





Scheme 5. Possible phenoxy radicals trapped by BNB.

peroxide are too unstable chemical species (see Scheme 5). In the case of model lignin compound other homolytic scission called α - β cleavage may operate to produce the R5 and R6 radicals as different secondary carbon radicals (see Scheme 1).¹⁴ However, the resulting secondary carbon radicals, R5 and R6 radicals have an oxygen in the vicinity of the radical centers. Therefore ESR parameters of these radicals should be fairly different from those of the parameters of present secondary carbon radicals, e.g., R1 and R4 generated when the lignin solution was heat-treated as can be deduced from the work by Tabata et al.¹⁵ Thus the possibility for formation of such secondary carbon radicals containing an adjacent oxygen is excluded clearly. Miksche has reported that homolytic scission of the β -O-4 interunitary *via* quinone methides is induced in the small model compound of wood lignins under the condition of an aqueous alkaline solution where so-called β -O-4 bonds are scissioned to produce RQ1 and R2 radicals as secondary carbon radicals and phenoxy radical (see Scheme 2).⁶ However, our experiment was carried out at fairly lower temperature at *ca.* 50°C using neutral DMSO solution so that such thermal induced cleavage *via* the quinone methides in the aqueous alkaline solution should not take place. Further the spin adduct of the secondary carbon radicals which were produced by the cleavage reaction shown in Scheme 4 is not an ordinary carbon radical but so-called allyl radicals. Therefore, the two radicals can be also distinguished by the ESR method due to different ESR parameters as reported by Tabata et al.,¹⁵ although the phenoxy radical is the same as the counter radical. Thus it is clearly concluded



that the secondary carbon radicals which were generated by the thermal treatment of the hardwood lignin solution are assigned to not to the allyl radical as RQ1 shown in Scheme 2 but the secondary carbon radicals, R1 and R4 shown in Scheme 1.

It is also noteworthy that the major unstable chemical species, i.e., radical which can be trapped by the BNB spin trap should be those produced by not the secondary step scission but the primary scission of the linkage in the lignin according to statistic probability, though the allyl radical may convert to the enolether radical as the secondary reaction (see Scheme 2).

It has been considered that in the course of the so-called bleaching processes radicals are produced by the action of bleaching reagents, e.g., ClO_2 ,¹⁶ O_2 ¹⁷ or O_3 ,⁸ although the resulting unstable radicals are not trapped and identified clearly up to date. It is suggested, however, that the oxygen as the bleaching reagent acts as the trapping reagent of the lignin radical such as secondary carbon radical and/or phenoxy radical which were generated during the thermal treatment. Because the oxygen molecule is so-called triplet state even at the ground state so that the oxygen may scavenge the unstable chemical species such as the secondary carbon radical and/or phenoxy radical in order to produce peroxy radicals of the corresponding radicals. This may mean that the unstable radicals produced during the bleaching processes are not recombined with each other to make a crosslinking but trapped with the oxygen to produce the corresponding peroxyde, associating with decrease of the original molecular weight of the lignin in the solution. Therefore, the role of the oxygen molecules is similar to that of the spin trapping reagent, BNB, although the hyper fine structure of the peroxyde is not possible to observe due to non nuclear spin of the oxygen. It is not clear, unfortunately, that in the case of ClO_2 the role of the chemical species is too complicate to be understood at present so that no explanation on the degradation of the original lignin can not be proposed.

Local Structure of Lignin

Watanabe et al.¹⁸ have shown that the local structure in the solution of synthetic polymers, i.e., a polystyrene can be deduced by analysis of the ESR spectra of the spin adduct (see Figure 3) by the aid of the McConnell's equation.^{19,20} Therefore, we also estimated the local conformation of the Japanese beech (*Fagus crenata*), lignin molecules. It is noteworthy that there is a possibility that the local structure of the observed spin adduct might be used as finger prints and/or to classify various wood lignins. The spatial



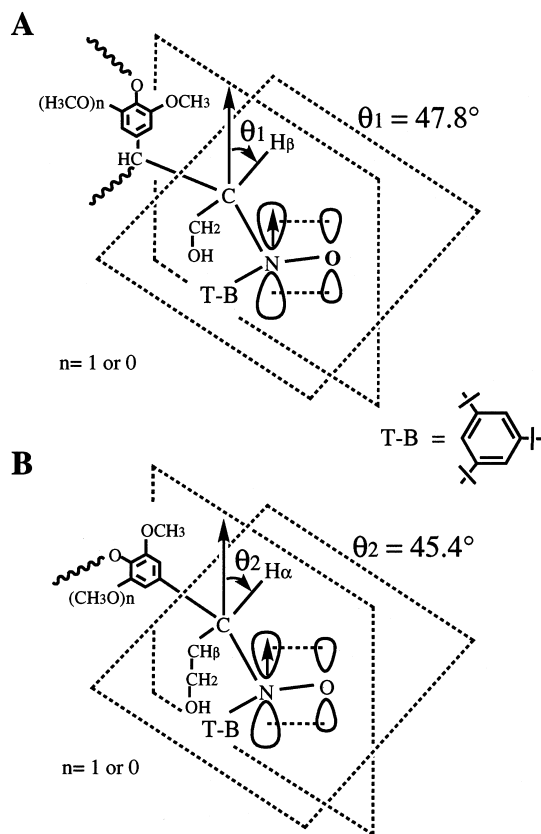


Figure 3. Perspective views for the spin adducts of secondary carbon radical produced by ruptures of the β -O-4 (A) and α -O-4 (B) bonds in the lignin.

conformation of the spin adducts R1SA(I_β) and R4SA(I_α) as the secondary carbon radical are depicted in Figure 3 where McConnell's equation (9) is applied. The dihedral angle θ between the p_z orbital of unpaired electron and H_β or H_α bonds is estimated using the McConnell equation as $\theta_1 = 47.8^\circ$ and $\theta_2 = 45.4^\circ$, respectively, where B_0 is zero and B is assumed as 26.8 Gauss.¹⁸

$$a^{H_\beta \text{ or } H_\alpha} = B_0 + B \cos^2 \theta \quad (9)$$

($B_0 = 0, \quad B = 26.8 \text{ Gauss}$)



EXPERIMENTAL

Preparation and Acetylation of MWL

The crude lignin known as MWL of the hardwood, Japanese beech (*Fagus crenata*), was prepared according to the method described in the literature²¹ and the obtained lignin was purified using a modified Lundquist method.²² The purified lignin was dried at room temperature for 48 h under vacuum at *ca.* 10^{-2} Torr.

The acetylation of MWL was performed according to the method by Chen and Robert²³ using anhydrous acetic acid and pyridine.

Spin Trap Reagent

The spin trap reagent, 2,4,6-tri-*tert*-butylnitrosobenzene (BNB) was synthesized according to the method described in the literature²⁴ and used after purification.

Preparation of Solution

The lignin sample (250 mg) was dissolved in dimethylsulfoxide (DMSO) (Junsei Chem. Japan), 0.5 mL at room temperature, to prepare the homogeneous solution including 0.6 mg of the BNB, and the solution was poured in the flat ESR cell.

¹³C NMR

The lignin sample (250 mg) obtained after acetylation, was dissolved in 3 mL of mixed solvent, deuterium oxide : deuterium 1,4-dioxane (1:9), and the solution was poured in 10 mm sample tubes. ¹³C NMR spectrum was recorded on a Bruker MSL-400 spectrometer and observed at ambient temperature.

GPC

Molecular weights of the lignin obtained after acetylation, were measured using a JASCO gel permeation chromatography (GPC) with Shodex KF-804L columns and tetrahydrofuran as an eluent, and polystyrenes as standards.



ESR

Electron spin resonance (ESR) spectra were recorded on a Jeol FE1XG (100 kHz field modulation) and observed in the temperature range of 24~91°C. Spectral simulations were performed using a Macintosh computer to estimate the parameters of the ESR spectra observed at 91°C.

ACKNOWLEDGMENTS

We wish to thank Professor Y. Sano at the graduate school of Agriculture, Hokkaido University, for his very kind advice and help.

REFERENCES

1. M. Erickson, S. Larsson, and G.E. Miksche, *Acta. Chem. Scand.*, **27**, 903 (1973).
2. H. Nimz, *Angew. Chem.*, **86**, 336 (1974).
3. P.S. Rajan, C.-L. Chen, J.S. Gratzl, and R.G. Hise, *Holzforschung*, **48** (suppl.), 117 (1994).
4. K. Kratzl, J. Gratzl, and P. Claus, *Adv. Chem. Ser.*, **59**, 157 (1966).
5. K. Freudenberg, A. Janson, E. Knopf, and A. Haag, *Zur Kenntnis des Lignins*, Jahrg **69**, 1415 (1936).
6. G. Miksche, *Acta Chem. Scand.*, **27**(4), 1355 (1973).
7. Y. Tsuutsumi, R. Kondo, and H. Imamura, *J. Wood Chem. Technol.*, **13**(1), 25 (1993).
8. T. Reitberger, T. Eriksson, M. Ragnar, and P. Brandt, *Pro. 10th ISWPC*, Vol. 1, p. 302-307, Japan, 1999.
9. T. Seino, A. Yoshioka, M. Fujiwara, K.-L. Chen, T. Erata, M. Tabata, and M. Takai, *Wood Sci. and Technol.*, **35**(1/2), 107 (2001).
10. A. Yoshioka, T. Seino, M. Tabata, and M. Takai, *Holzforschung*, **54**(4), 357 (2000).
11. H.-D. Lüdemann and H. Nimz, *Makromol. Chem.*, **175**, 2409 (1974).
12. M. Tabata, T. Miyazawa, O. Kobayashi, and J. Sohma, *Chem. Phys. Lett.*, **73**, 178 (1980).
13. D.N.-S. Hon, and W.G. Glasser, *Tappi*, **62**(10), 107 (1979).
14. H. Ohi and M. Kishino, *Holzforschung*, **51**(4), 343 (1997).
15. Y. Tabata, Y. Ito, and S. Tagawa, *CRC Handbook of Radiation Chemistry*, 556 (1991).



HOMOLYTIC SCISSIONS

141

16. K.V. Sarkanen, K. Kakehi, R.A. Murphy, and H. White, *Tappi*, *45*(1), 24 (1962).
17. K. Kratzl, P. Claus, W. Lonsky and J.S. Gratzl, *Wood Sci. and Technol.*, *8*, 35 (1974).
18. O. Watanabe, M. Tabata, and J. Sohma, *Macromolecules*, *17*, 1139 (1984).
19. C. Heller and H.M. McConnell, *J. Chem. Phys.*, *32*, 1535 (1960).
20. J.J. Windle, J.A. Kuhnle, and B.H. Beck, *J. Chem. Phys.*, *50*, 2630 (1969).
21. A. Björkman, *Svensk Papperstidn*, *59*, 477 (1956).
22. K. Lundquist, B. Ohlsson, and R. Simonson, *Svensk Papperstidn*, *80*, 143 (1977).
23. C.-L. Chen and D. Robert, In *Methods in Enzymology: Biomass*, p. 137–174, Academic Press, San Diego, California, 1988.
24. R. Okazaki, T. Hosogai, M. Hashimoto, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, *42*, 3559 (1969).



Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the [U.S. Copyright Office](#) for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on [Fair Use in the Classroom](#).

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our [Website User Agreement](#) for more details.

[Order now!](#)

Reprints of this article can also be ordered at

<http://www.dekker.com/servlet/product/DOI/101081WCT100104223>