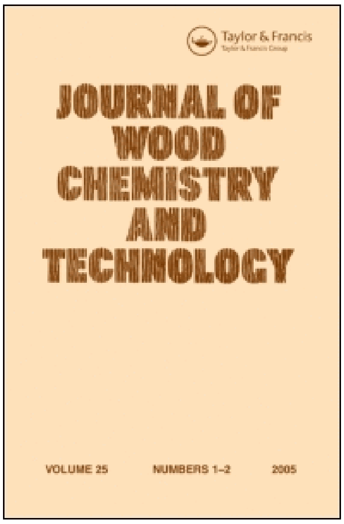

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Condensation Reactions of Some Lignin Related Compounds at Relatively Low Pyrolysis Temperature

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Condensation Reactions of Some Lignin Related Compounds at Relatively Low Pyrolysis Temperature

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Abstract: Condensation reactions of some lignin related compounds were studied under the pyrolysis conditions (air/250°C/2 h). Guaiacol, methylguaiacol and methylveratrole were recovered almost quantitatively with small amount of radical coupling products derived from phenoxy and benzyl radicals. Side-chains ($C_\alpha{=}C_\beta$, C_α-OH) increased the condensation reactivity substantially. From the dimer structures, vinyl condensation and quinone methide mechanisms were indicated as important condensation pathways for these compounds. As for model compounds for the structures formed in lignin primary pyrolysis, coniferyl alcohol (from β-ether structure) was very reactive, while 4,4′-dihydroxy-3,3′-dimethoxystilbene (from β-aryl structure) was stable.

Keywords: Lignin, pyrolysis, condensation, lignin related compound, mechanism

INTRODUCTION

Pyrolysis is the underlying principle of thermochemical conversion processes of plant biomass including gasification, fast pyrolysis (bio-oil production) and carbonization. Understanding the pyrolysis mechanism on molecular basis is very important for understanding the overall pyrolysis behavior and improving the product selectivity.

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Thermogravimetric study[1] indicated that lignin pyrolysis proceeds in a wide temperature range. Our previous study[2] showed that condensation occurs at 200–250°C followed by substantial depolymerization (>300–350°C) and carbonization (polycyclic aromatic hydrocarbon formation) (>350–400°C) in 1 min pyrolysis of Japanese cedar milled wood lignin (MWL) in nitrogen. Furthermore, from the comparison with the model compound reactivity, phenolic α-ether, β-ether and β-aryl types of model compounds became reactive at the temperature where condensation of MWL was observed.[2] Phenolic β-ether and β-aryl types of model compounds formed the $C_\alpha{=}C_\beta$ types of products, coniferyl alcohol and 4,4′-dihydroxy-3,3′-dimethoxystilbene, respectively.[2,3] Thus, these types of structures would also be important in this low temperature condensation.

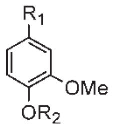
In this paper, condensation reactions of several lignin related compounds at 250°C are discussed, focusing particularly on their susceptibility to polymerization and the structures of the isolated dimers.

EXPERIMENTAL

Thin layer chromatography (TLC, Merck silica gel 60 PF_{254}) was conducted to separate the compounds. ^{1}H-NMR spectrum was measured with a Brucker AC-300 (300 MHz) spectrometer. Chemical shifts and coupling constants are shown as δ and J (Hz) values, respectively. High-performance liquid chromatography (HPLC) was carried out with a Shimadzu LC-10A under the conditions [column: Shimadzu STR ODS-II, flow rate: 0.7 ml/min, eluent: binary gradient 30% (v/v) to 100% (v/v) MeOH/H_2O in 40 min and then isocratically at 100% for another 5 min, detector: $UV_{280\,nm}$, temperature: 40°C]. Gel-permeation chromatography (GPC) was conducted with a Shimadzu LC-10A under the following condition [column: Shodex KF-801, flow rate: 0.6 ml/min, eluent: THF, detector: $UV_{280\,nm}$, temperature: 40°C]. Gas-chromatography/mass-spectroscopy (GC-MS) was conducted with a Hitachi G-7000 gas chromatograph and a Hitachi M-9000 3-dimensional quadrupole mass spectrometer; gas-chromatographic conditions: column: Shimadzu CBP5-M25-O25, injector temperature: 250°C, column temperature: 50°C to 300°C in 25 min and then isocratically at 300°C for another 15 min, carrier gas: He, flow rate: 1.5 ml/min; mass-spectroscopic conditions (electron impact ionization): emission current: 20 μA, ionization time: 2 ms.

Materials

Figure 1 summarizes the lignin related compounds used in this study. Guaiacol (2-methoxyphenol, **1**) is a model of the aromatic nuclei of guaiacyl type lignin, and compounds **2–10** have various side-chains [-CH_3 (**2**,**3**), -CH(OH)CH_3 (**4**,**5**), -CH=CH_2 (**6**,**7**), -CH=CH-CH_2OH (**8**,**9**) and -CH=CH-Ar (**10**)]



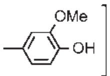
	R_1	R_2
1	-H	-H
2	$-CH_3$	-H
3	$-CH_3$	$-CH_3$
4	$-CH(OH)CH_3$	-H
5	$-CH(OH)CH_3$	$-CH_3$
6	$-CH{=}CH_2$	-H
7	$-CH{=}CH_2$	$-CH_3$
8	$-CH{=}CH{-}CH_2OH$	-H
9	$-CH{=}CH{-}CH_2OH$	$-CH_3$
10	-CH=CH-Ar	-H
	[Ar = ]	

Figure 1. Lignin related compounds.

including phenolic and non-phenolic forms. Coniferyl alcohol [4-(3-hydroxy-1-propenyl)-2-methoxyphenol, **8**] and 4,4′-dihydroxy-3,3′-dimethoxystilbene (**10**) are the primary pyrolysis products from phenolic β-ether and β-aryl types of model compounds, respectively, at 200–400°C.[2,3] Guaiacol (**1**), creosol (2-methoxy-4-methylphenol, **2**) and coniferyl alcohol (**8**) were purchased from Nacalai tesque INC as guarantee grades. Vinylguaiacol (**6**) was prepared by the method described by Griengl et al. [4] Methylveratrole (1,2-dimethoxy-4-methylbenzene, **3**) and vinylveratrole (1,2-dimethoxy-4-vinylbenzene, **7**) were prepared by methylation of the corresponding phenolic derivatives with MeI and K_2CO_3 in DMF at r.t. Compounds **4** and **5** were prepared by reduction of 4-hydroxy-3-methoxyacetophenone and 3,4-dimethoxyacetophenone, respectively, with $NaBH_4$ in THF at r.t. Coniferyl alcohol methyl ether (**9**) was obtained through methylation (MeI/K_2CO_3/DMF/r.t.) and subsequent reduction ($NaBH_4$/THF/r.t.) from coniferyl aldehyde. 4,4′-Dihydroxy-3,3′-dimethoxystilbene (**10**) (*trans* isomer) was prepared by the method reported by Gierer and Nilvebrant.[5]

Pyrolysis and Product Analysis

Pyrolysis was conducted in an ampoule (2.0 ml) made of glass. Lignin related compound was placed at the bottom of the ampoule by evaporating the solution in dioxane *in vacuo* and the ampoule was closed in the air. The ampoule was inserted into a stainless autoclave filled with silicon oil, and the autoclave was heated in a silicon oil bath at 250°C for 2 h. After quenching the reaction by immediate cooling in cold water for 10 min, the ampoule was opened and extracted with ethyl acetate (5.0 ml). The resulting solution was analyzed with HPLC and GPC. Identification of the products was conducted with ^{1}H-NMR spectra of the isolated compounds. Recovery of the starting compound and the product yield were determined from the HPLC chromatogram with *p*-dibromobenzene as an internal standard. Data of the isolated products were shown as follows. Dimers **11–17** were identified with their ^{1}H-NMR as compared with the reported data.[6–12]

3,3′-Dimethoxy-4,2′-biphenyldiol (**11**)[6] and 3,3′-dimethoxy-4,4′-biphenyldiol (**12**)[7]

Guaiacol (**1**) (0.20 ml) gave pale brown oil by evaporating the ethyl acetate solution of the reaction mixture (250°C/2 h). The oil was separated with TLC (ethyl acetate/*n*-hexane = 1/2, v/v, solvent A) to give compounds **11** (1.9 mg) and **12** (0.8 mg).

Compound **11**: ^{1}H-NMR ($CDCl_3$) δ: 3.90 (s, 3H, -OCH_3), 3.92 (s, 3H, -OCH_3), 5.61 (s, 1H, -OH), 5.83 (s, 1H, -OH), 6.83 (dd, $J = 2.0$, 7.7, 1H, $C_{4'}$- or $C_{6'}$-H), 6.88 (t, $J = 7.7$, 1H, $C_{5'}$-H), 6.94 (dd, $J = 2.0$, 7.7, 1H, $C_{4'}$- or $C_{6'}$-H), 6.96 (d, $J = 8.3$, 1H, C_5-H), 7.08 (dd, $J = 1.9$, 8.3, 1H, C_6-H), 7.14 (d, $J = 1.9$, 1H, C_2-H).

Compound **12**: ^{1}H-NMR ($CDCl_3$) δ: 3.93 (s, 6H, -OCH_3), 5.57 (s, 2H, -OH), 6.94 (d, $J = 7.9$, 2H, C_5-, $C_{5'}$-H), 7.00 (br. s, 2H, C_2-, $C_{2'}$-H), 7.01 (dd, $J = 1.9$, 7.9, 2H, C_6-, $C_{6'}$-H).

2-Methoxy-6-(2-methoxy-4-methylphenoxy)-4-methylphenol (**13**)[8] and 2,4′-dihydroxy-3,3′-dimethoxy-5-methyldiphenylmethane (**14**)[9]

Heat treatment (250°C/2 h) of creosol (**2**) (0.20 ml) gave pale brown oil after evaporation of the ethyl acetate solution. Compounds **13** (0.7 mg) and **14** (0.9 mg) were isolated from the oil by TLC (solvent A).

Compound **13**: ^{1}H-NMR ($CDCl_3$) δ: 2.18 (s, 3H, arom. -CH_3), 2.31 (s, 3H, arom. -CH_3), 3.83 (s, 3H, -OCH_3), 3.86 (s, 3H, -OCH_3), 5.77 (s, 1H, -OH), 6.31 (d, $J = 2.0$, 1H, C_3-H), 6.44 (d, $J = 2.0$, 1H, C_5-H), 6.68 (dd, $J = 2.0$, 8.0, 1H, $C_{5'}$-H), 6.77 (d, $J = 2.0$, 1H, $C_{3'}$-H), 6.86 (d, $J = 8.0$, 1H, $C_{6'}$-H).

Compound **14**: ^{1}H-NMR ($CDCl_3$) δ: 2.21 (s, 3H, arom. -CH_3), 3.83 (s, 3H, -OCH_3), 3.83 (s, 2H, arom. -CH_2-), 3.84 (s, 3H, -OCH_3), 5.42 (s, 1H, -OH), 5.52 (s, 1H, -OH), 6.48 (d, $J = 2.0$, 1H, C_4-H), 6.53 (d, $J = 2.0$, 1H, C_6-H), 6.7–6.9 (m, 3H, $C_{2'}$-, $C_{5'}$-, $C_{6'}$-H).

3,3′,4,4′-Tetramethoxy-6-methyldiphenylmethane (**15**)[10]

Compound **15** (0.5 mg) was isolated from the heat treatment mixture of methylveratrole (**3**) (92.3 mg) at 250°C for 2 h (TLC, solvent A).

Compound **15**: ^{1}H-NMR ($CDCl_3$) δ: 2.17 (s, 3H, arom. -CH_3), 3.78 (s, 3H, -OCH_3), 3.79 (s, 3H, -OCH_3), 3.83 (s, 3H, -OCH_3), 3.85 (s, 3H, -OCH_3), 3.85 (s, 2H, arom. -CH_2-), 6.58 (dd, $J = 2.0$, 8.0, 1H, $C_{6'}$-H), 6.61 (s, 1H, C_2-H or C_5-H), 6.63 (d, $J = 2.0$, 1H, $C_{2'}$-H), 6.68 (s, 1H, C_2-H or C_5-H), 6.75 (d, $J = 8.0$, 1H, C_5'-H).

1-(4-Hydroxy-3-methoxyphenyl)-3-(4-hydroxy-3-methoxyphenyl)-1-butene (**16**)[11]

Heat treatment (250°C/2 h) of a mixture of vinylguaiacol (**6**) (10 mg) and creosol (**2**) (0.12 ml) gave brown oil. Separation of the oil by TLC (solvent A) gave compound **16** (0.7 mg).

Compound **16**: ^{1}H-NMR ($CDCl_3$) δ: 1.41 (d, $J = 7.0$, 3H, C_β-H), 3.48 (m, 1H, C_α-H), 3.87 (s, 3H, -OCH_3), 3.88 (s, 3H, -OCH_3), 5.39 (s, 1H, -OH), 5.58 (s, 1H, -OH), 6.16 (dd, $J = 7.0$, 16.0, 1H, $C_{\beta'}$-H), 6.31 (d, $J = 16.0$, 1H, $C_{\alpha'}$-H), 6.7–6.9 (m, 6H, arom. -H).

2-[1-(4-Hydroxy-3-methoxyphenyl)ethyl]-6-methoxy-4-methylphenol (**17**)[12]

A mixture of hydroxyethylguaiacol (**4**) (10 mg) and creosol (**2**) (0.11 ml) gave brown oil after heat treatment (250°C/2 h). Compound **17** (1.0 mg) was separated from the oil by TLC (solvent A). Compound **17** was converted to the acetyl derivative under the conditions of acetic anhydride (0.2 ml)/pyridine (0.2 ml)/r.t./overnight and purified with TLC (ethyl acetate/*n*-hexane = 1/2, v/v).

Compound **17** (acetate): ^{1}H-NMR ($CDCl_3$) δ: 1.52 (d, $J = 7.3$, 3H, C_β-H), 2.21 (s, 3H, arom. -CH_3), 2.27 (s, 3H, acetyl-CH_3), 2.27 (s, 3H, acetyl-CH_3), 3.74 (s, 3H, -OCH_3), 3.77 (s, 3H, -OCH_3), 4.19 (q, $J = 7.3$, 1H, C_α-H), 6.55 (d, $J = 2.0$, 1H, arom. -H in creosol moiety), 6.61 (d, $J = 2.0$, 1H, arom. -H in creosol moiety), 6.7–7.0 (m, 3H, arom. -H).

1-(4-Hydroxy-3-methoxyphenyl)-3-(2-hydroxy-3-methoxy-5-methylphenyl)-1-propene (**18**) and 4′-hydroxy-3′-methoxy-8-methoxy-6-methylflavan (**19**)

Heat treatment (250°C/2 h) of a mixture of coniferyl alcohol (**9**) (65 mg) and creosol (0.65 ml) gave brown oil. Compounds **18** (13 mg) and **19** (9 mg) were isolated from the oil with TLC (solvent A and subsequently $CHCl_3$).

Compound **18**: ^{1}H-NMR ($CDCl_3$) δ: 2.26 (s, 3H, arom. -CH_3), 3.50 (dd, $J = 1.2$, 2H, 6.8, C_γ-H), 3.87 (s, 3H, -OCH_3), 3.88 (s, 3H, -OCH_3), 5.69 (s, 2H, -OH), 6.21 (dt, $J = 6.8$, 15.7, 1H, C_β-H), 6.38 (dt, $J = 1.2$, 15.7, 1H, C_α-H), 6.58 (br. s, 1H, arom. -H in creosol moiety), 6.60 (br. s, 1H, arom. -H in creosol moiety), 6.82 (d, $J = 8.1$, 1H, arom. -H), 6.86 (dd, $J = 1.6$, 8.1, 1H, arom. -H), 6.89 (d, $J = 1.6$, 1H, arom. -H). ^{13}C-NMR ($CDCl_3$) δ: 21.1, 33.0, 55.9, 56.0, 108.0, 109.6, 114.3, 116.1, 119.8, 122.5, 125.7, 126.4, 128.9, 130.4, 141.1, 144.9, 146.2, 146.5. GC-MS *m/z*: 77 (13%), 91 (12%), 136 (48%), 151 (100%), 152 (33%), 268 (27%), 282 (43%), 300 (83% M^+).

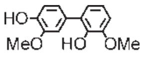
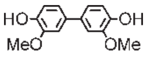
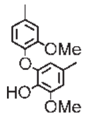
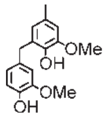
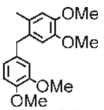
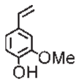
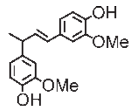
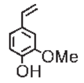
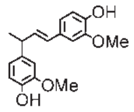
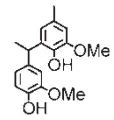
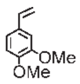
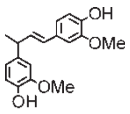
Compound **19**: ^{1}H-NMR ($CDCl_3$) δ: 2.03–2.22 (m, 2H, C_β-H), 2.27 (s, 3H, arom. -CH_3), 2.73 (dt, $J = 4.7$, 16.5, 1H, C_γ-H), 2.92 (ddd, $J = 6.0$, 10.5, 16.5, 1H, C_β-H), 3.82 (s, 3H, -OCH_3), 3.87 (s, 3H, -OCH_3), 5.03 (dd, $J = 2.7$, 9.4, 1H, C_α-H), 5.58 (s, 1H, -OH), 6.51 (br. s, 1H, arom. -H in creosol moiety), 6.56 (br. s, 1H, arom. -H in creosol moiety), 6.88–6.90 (m, 2H, arom. -H) 6.96 (br. s, 1H, arom. -H). ^{13}C-NMR ($CDCl_3$) δ: 21.0, 24.8, 29.8, 55.9, 55.9, 77.7, 108.8, 110.5, 114.1, 119.2, 121.5, 122.3, 129.1, 133.8, 142.3, 145.2, 146.5, 148.2. GC-MS *m/z*: 77 (18%), 107 (15%), 121 (10%), 135 (28%), 151 (100%), 152 (31%), 165 (10%), 268 (12%), 283 (15%), 300 (61% M^+).

RESULTS AND DISCUSSION

Table 1 summarizes the recovery of starting compound and yields of some products after heat treatment of compounds **1–7** at 250°C for 2 h. The product yield in Table 1 is shown as based on the monomer used in the experiment. For compounds **4** and **6**, heat treatment in creosol (**2**) (20 molar equivalent for compound **4** or **6**) were also conducted to enhance the formation of dimer fraction. Reactivity as indicated from the recovery varies significantly depending on the structure. Compounds **1–3** with no side-chain or only a methyl substituent group were very stable (recovery: ~100%), while compounds **4–7** with C_α-OH or $C_\alpha{=}C_\beta$ type of side-chain were comparatively reactive as suggested from their relatively low recoveries (0–49.8%).

From compounds **1–3**, several dimeric products were isolated although their yields are very low. ^{1}H-NMR analysis revealed the aryl-aryl (**11**, **12**), aryl-*O*-aryl (**13**) and diphenyl methane (**14**, **15**) structures. Coupling sites in these products were assigned with the coupling constants observed for the aromatic protons in their ^{1}H-NMR spectra. Formation of these dimers strongly suggest the existence of various radical species derived from phenoxy and benzyl radicals as summarized in the formation mechanisms (Figs. 2 and 3). Consequently, some of the phenolic O-H and benzylic C-H bonds in compounds **1–3** are suggested to be dissociated at 250°C before

Table 1. Recovery and yields of some isolated products in heat treatment of compounds **1**–**7** (air/250°C/2 h)

Model compound	Recovery (%)	Isolated products (yield, mol%)[a]
1	~100	 **11** (1.0%)  **12**(0.4%)
2	~100	 **13** (0.3%)  **14** (0.4%)
3	~100	 **15** (0.3%)
4	0.3	 **6** (4.3%)  **16** (6.0%)
4 +creosol (20 mol eq.)	39.2	 **6** (41.9%)  **16** (9.0%)  **17** (9.0%)
5	49.8	 **7** (8.0%)
6	0.0	 **16** (9.0%)
6 +creosol (20 mol eq.)	37.8	
7	13.0	

[a] Based on monomer.

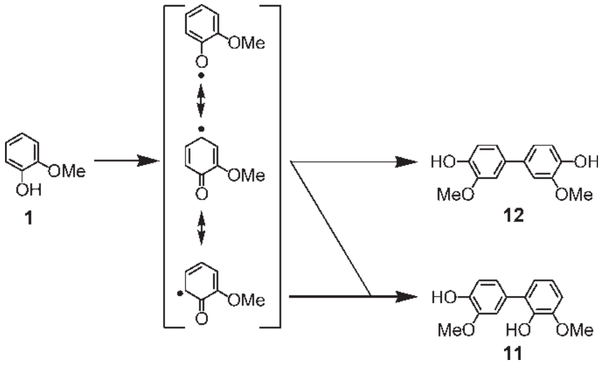


Figure 2. Dimerization mechanisms of guaiacol (**1**).

radical coupling reactions occur, although their reactivities are not so high compared to the reactivity of compounds **4–7** with C_α-OH or $C_\alpha{=}C_\beta$ type of side-chain.

GPC chromatograms of the reaction mixtures obtained from compounds **4–7** are shown in Fig. 4. The $C_\alpha{=}C_\beta$ types **6** and **7** gave substantial amount of products in high molecular weight (MW) regions regardless of their aromatic structures (phenolic vs. non-phenolic). Contrary to this, products from the

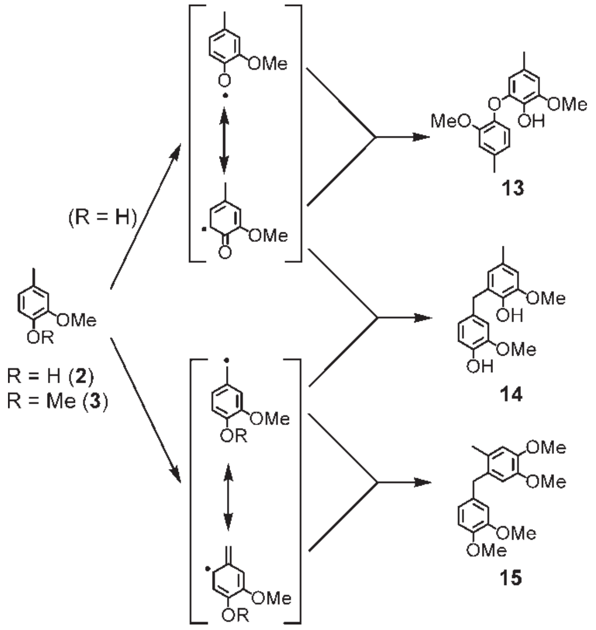


Figure 3. Dimerization mechanisms of creosol (**2**) and methyl veratrole (**3**).

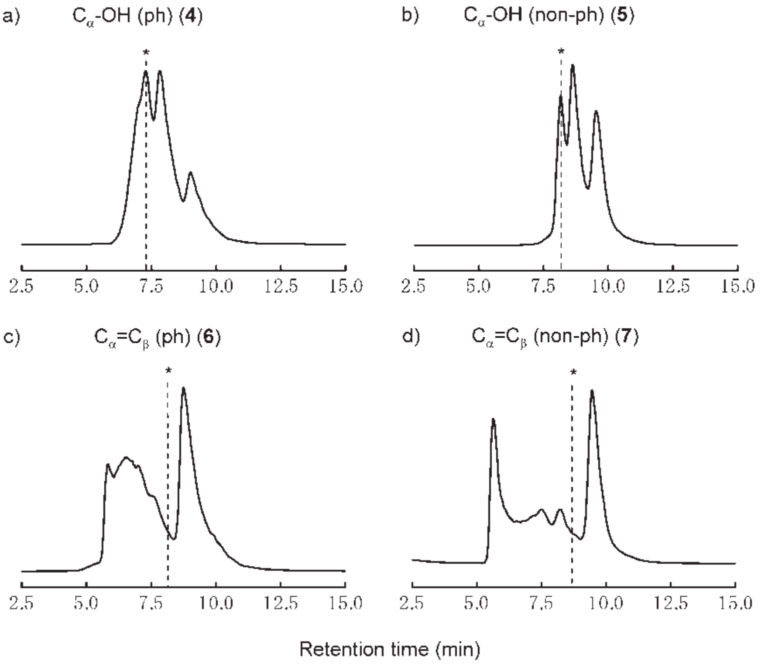


Figure 4. GPC chromatograms of the reaction mixtures obtained from the heat treatment of compounds **4**–**7** (air/250°C/2 h). *Retention time of compound **4**, **5**, **6** or **7**.

C_α-OH types **4** and **5** are not observed in such high MW regions even in the phenolic form. These results suggest that C_α=C_β is an important structure rather than the phenolic structure in thermal condensation of compounds **4**–**7**.

Although isolation of dimer from the reaction mixture obtained from the phenolic C_α=C_β type **6** was unsuccessful, dimer **16** (*trans* isomer) (8.0%) was isolated from the reaction mixture after heating in 20 molar equivalent of creosol. Dimer **16**, which is a coupling product between C_α and C_β, was identified with the ^{1}H-NMR spectrum compared with the reported data.[11] Stereochemistry (*trans* isomer) in dimer **16** was confirmed from the large coupling constant (16.0 Hz) observed for the two vicinal protons attached to the double bond. Dimer **16** was reported in thermal decarboxylation of ferulic acid[11,13] and cationic polymerization of vinylguaiacol with strong acidic catalyst.[14,15] Although polymerization mechanism (radical or cationic) is not known at the moment, formation of dimer **16** and high condensation reactivity of the non-phenolic type **7** indicate the vinyl condensation mechanism for the C_α=C_β types **6** and **7** (Fig. 5). Thermal polymerization of styrene has been reported in similar temperature ranges,[16,17] and the condensation mechanism including self-initiation mechanism has been studied.[18,19] Reduced polymerization reactivity of compound **6** in creosol (recovery of **6**: 37.8%) would be due to the dilution effect of creosol.

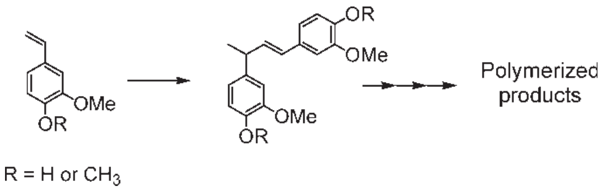


Figure 5. Condensation mechanism of the $C_\alpha{=}C_\beta$ types (**6** and **7**).

The Cα-OH types **4** and **5** gave the dehydration products **6** and **7** with $C_\alpha{=}C_\beta$ structure, respectively, and dimer **16** (6.0%) was also isolated from the phenolic form **4**. These results indicate that vinyl condensation mechanism is also provable for the C_α-OH types via dehydration into $C_\alpha{=}C_\beta$ structures, although these polymerization reactivities are quite low compared to the $C_\alpha{=}C_\beta$ structures (GPC, Fig. 4).

From the reaction mixture of the C_α-OH type **4** in creosol, dimer **17** (9.0%), which is a coupling product between C_α and the creosol-C_6, was isolated. The coupling site was determined by the characteristic small *meta* coupling constant (2.0 Hz) for the two aromatic protons of the creosol moiety in the ^{1}H-NMR spectrum of dimer **17** (acetate). Formation of dimer **17** suggests the quinone methide intermediate which is subject to the nucleophilic addition of creosol. This condensation pathway competes with the $C_\alpha{=}C_\beta$ formation and the following vinyl coupling (Fig. 6). However, relatively high yields of vinylguaiacol (**6**) (41.9%) and its dimer **16** (9.0%) even in the presence of 20 molar equivalent of creosol suggest that the nucleophilic addition of aromatic nuclei to quinone methide is not so effective in compound **4**. Dimer **17** was not detected in heat treatment of the phenolic $C_\alpha{=}C_\beta$ type **6** in creosol.

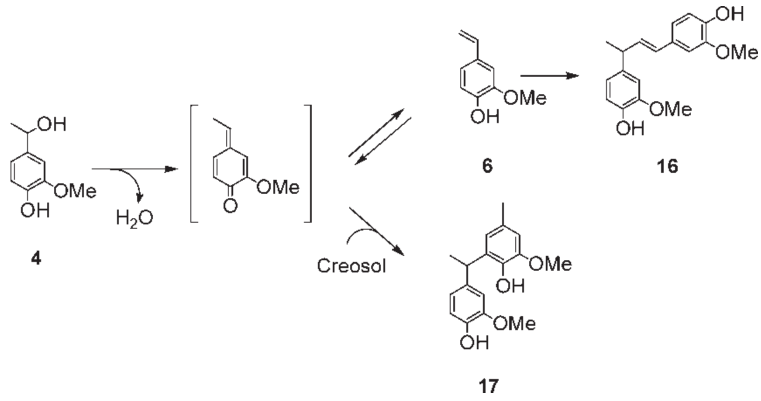
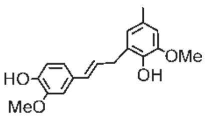
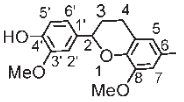


Figure 6. Condensation mechanism of the phenolic C_α-OH type (**4**).

Table 2. Recovery and yields of some isolated products in heat treatment of compounds **8**–**10** (air/250°C/2 h)

Model compound	Recovery (%)	Isolated products (yield, mol%)[a]	
8	0.9		
8 + creosol (20 mol eq.)	3.5	 **18** (12.0%)	 **19** (8.3%)
9	6.8		
10	~100		

[a] Based on monomer.

As for model compounds formed from the β-ether and β-aryl types of structures, recoveries of coniferyl alcohol (**8**), coniferyl alcohol methyl ether (**9**) and 4,4′-dihydroxy-3,3′-dimthoxystilbene (**10**) in heat treatment at 250°C for 2 h are summarized in Table 2 with some isolated products. Although stilbene **10** was very stable (recovery: ~100%), coniferyl alcohol (**8**) (recovery: 0.9%) and its methyl derivative **9** (recovery: 6.8%) were comparatively reactive and gave condensation products as indicated from the GPC chromatograms (Fig. 7). Especially, phenolic type **8** was quite reactive to give high MW products even after 1 min heating.

Although dimer fraction could not be isolated from the reaction mixture of compound **8** or **9**, dimers **18** (12.0%) and **19** (8.3%) were isolated from the reaction mixture of coniferyl alcohol **8** in creosol. These dimers are the coupling products of coniferyl alcohol and creosol. Large coupling constant (15.7 Hz) observed between the double bond protons indicates the *trans*

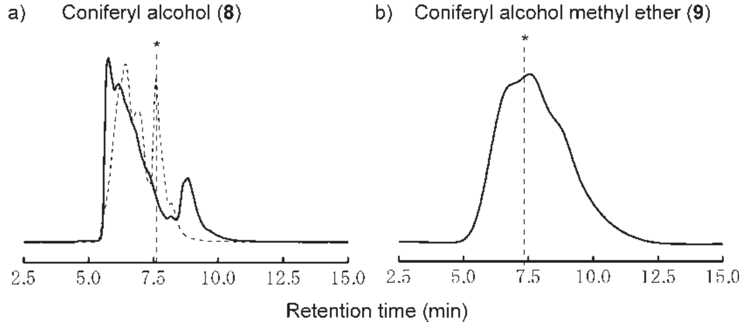


Figure 7. GPC chromatograms of the reaction mixtures obtained from the heat treatment of compounds **8** and **9** [(air/250°C/2 h or lmn(broken line))]. *Retention time of compound **8** or **9**.

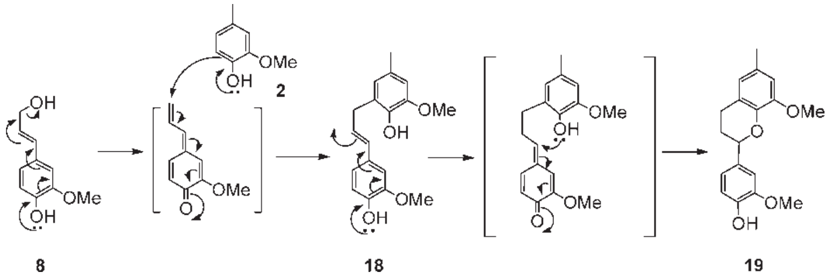


Figure 8. Formation mechanism of dimers **18** and **19** from coniferyl alcohol with creosol.

isomer of compound **18**. Dimers **18** and **19** are expected to be formed via nucleophilic attack of creosol-C_6 and hydroxyl group in creosol moiety to quinone methide intermediates, respectively, as illustrated in Fig. 8.

Vinyl condensation is also possible in the coniferyl alcohol types **8** and **9**. However, much higher polymerization reactivity of the phenolic form **8** than the non-phenolic form **9** (GPC, Fig. 7) indicates that quinone methide formation, which is especially effective in phenolic form, is more important than the vinyl condensation. Lower polymerization reactivity of coniferyl alcohol methyl ether (**9**) than vinylveratrole (**7**) (Figs. 4 and 7) would be due to higher steric hindrance around double bond in compound **9**.

CONCLUSIONS

Vinyl condensation, quinone methide and radical coupling mechanisms have been indicated as condensation pathways of some lignin related compounds at 250°C. Although further study is necessary to understand the condensation reactions in lignin macromolecule, these results provide a valuable insight into the low temperature pyrolysis of lignin.

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