

알칼리리그닌의 착색구조(着色構造)에 관한 研究*

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Chromophoric Structures of Alkali Lignin*

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알칼리 펄프화中에 生成되는 리그닌의 着色構造를 究明하기 爲하여 바닐린알코올(α - ^{13}C) 과이아실글리세롤- β -아릴에테르(α - ^{13}C) 혹은 [τ - ^{13}C] 페닐쿠마란(α - ^{13}C) 構造를 各各 165°C에서 1.5 ~ 3時間 알칼리용액을 처리한 後 反應生成物을 單離 또는 反應混合物을 ^{13}C -NMR로 調査한 結果, 바닐린알코올의 알칼리 處理는 Ca-C₁ 및 Ca-C₅의 結合을 갖는 縮合體(II-1~5)로 되며, 이들은 空氣酸化에 依해 퀴노이드 共役型構造(Fig 3-7)로 酸化되며, 과이아실글리세롤- β -아릴에테르의 알칼리 處理는 α -아릴- β -아록시퀴논構造(IV-15, IV-16) 디과이아실-1, 4-펜탄디엔 β , β' -디아록시스티렌메탄(V-4) β -아록시스티렌메탄(V-6)이 生成되며 스티렌메탄 構造는 空氣酸化에 依해 O-퀴논메티드구조(V-8, V-9)로 된다. 페닐쿠마란은 알칼리處理에 依해 多量의 스티벤誘導體를 生成하지만 이 스티벤구조가 퀴논구조로 산화되기 보다는 2量體(VI-11)로 安定化되는 傾向이 있다.

以上과 같은 着色構造는 반응기구의 전지에서 알칼리 펄프화中에 생산되는 중요한 着色構造라고 생각된다.

To investigate the formation of the chromophoric structures taking place during the alkaline pulping vanillyl alcohol [α - ^{13}C] guaiacylglycerol- β -aryl ether [α - ^{13}C or τ - ^{13}C] and phenylcoumarin [α - ^{13}C] units as model lignins were treated with 1N sodium hydroxide at 165°C for 1.5-3 hours. From the chemical structures of the isolated products and ^{13}C -NMR Spectra of the reaction mixtures, the main conclusion is as follows;

- 1) Condensation products of II-1-5 were identified from the reaction mixture of vanillyl alcohol treated with alkali and these compounds afforded the quinonmethide structure(Fig. 3-7)

*Dissertation, Nagoya University, Nagoya, Japan.

Received for Publication on February 1981

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by air oxidation.

2) Treatment of guaiacylglycerol- β -aryl ether unit gave φ -aryl- β -aroxy quinone structures (IV-15, IV-16), diguaiacyl-1, 4-penta-diene β , β -diaroxyl distyrene methane unit, β -aroxy distyrene methane. These distyrene methanes of the compounds are transformed by air oxidation into the corresponding o-quinonemethide units (V-8, V-9).

3) On the treatment of phenylcoumaran, the stilbene derivative was formed in quantitative yield and dimerized (VI-11) in preference to oxidation to the corresponding extended quinone structures.

The chromophoric structures taken place during the alkaline treatment of the model lignins are thought to be some important types in alkaline pulping on the basis of the reaction mechanism in this experiment.

Chapter I General Introduction

Wood is composed mainly of three macromolecular species, cellulose, hemicellulose and lignin, and is important industrial raw materials, particularly as the chief source of pulp. Chemical pulping and bleaching processes provide wood pulp for manufacture of paper and industrial cellulose derivatives, and it is to separate cellulose and hemicellulose from lignin and other wood components. To achieve this so-called delignification, the insoluble cross-linked macromolecule of protolignin must be degraded by breaking bonds, between building stones, and the lignin fragments have to be solubilized to remove from the fiber cell walls.

Lignin is an aromatic polymer composed of phenylpropane units with carbon to carbon and ether linkages, and contains arylglycerol- β -aryl ether, phenylcoumaran, biphenyl ether, diarylpropane and pinosresinol (in softwood lignin) structures as linkage patterns. The β -aryl ether structure of those make up approximately 50%^{1), 2)} of spruce milled wood lignin (MWL). Therefore, in the delignification of wood during pulping, it is important to rupture certain types of these linkages, particularly the β -aryl ether bond and/or to introduce hydrophilic groups into lignin. Alkali and kraft pulpings represent the former and sulfite pulping

the latter. Although color is developed in chemical pulping processes described above, it is usually formed to the greater extent in alkaline operations.

The fragments of lignin formed during alkaline pulping condensed partly to give a mixture like an aldol condensation product. In these condensation, various carbanions of degraded lignin compete with the nucleophiles supplied as the cooking chemicals. These lignin fragments and their condensation products are changed to a chromophoric system by the subsequent oxidation during pulping. MWL is considered to be the least altered lignin among many kinds of lignins isolated from wood. It is cream colored and the color is due to the presence of a quinoid structure³⁾ which is responsible for almost 100% of visible light absorption. The main chromophoric structures of liginosulphonic acid isolated from the waste liquor of sulfite pulping are considered to be of quinoid structure and lignin-metal chelate, and these two types of chromophore are responsible for 80-90%³⁾ of visible light absorption. In kraft lignin, however, the contribution of these two structures to visible light absorption may be only 50%³⁾. On the other hand, the color of soda lignin is almost reduced with sodium borohydride, indicating that the chromophoric element is quinoid structure to a significant degree⁴⁾.

Various types of quinoid system as shown in Fig. 1-1 have been estimated. The structure I-1⁵⁾, I-2⁶⁾, 7) and I-3⁵⁾ arise from the degradation of

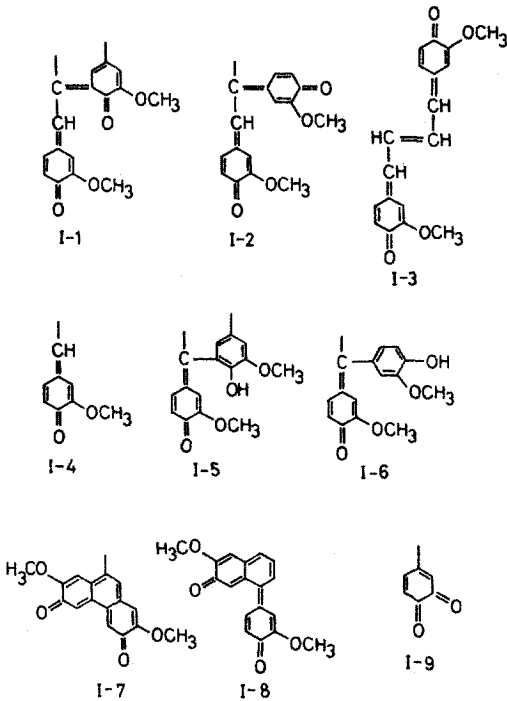


Fig. 1-1

phenylcoumaran, diarylpropane and pinoresinol structures in alkaline media and subsequent oxidation of the degradation products, respectively. The structure I-4 is the most simple quinonemethide unit. The diarylmethane structures formed by condensation reaction between aromatic nuclei and benzylic carbons will yield resonance-stabilised quinonemethide structure⁸⁾ I-5 and I-6. The cyclization products of dihydroxystilbene units and of 1,4-bis-(hydroxyphenyl)-buta-1,3-diene structures undergo subsequent oxidation to the corresponding quinoid structures⁵⁾ I-7 and I-8, respectively. Cleavage of methyl aryl ether bonds by the nucleophilic reagents of the cooking liquor gives rise to catechol groups. They are easily dehydrogenated or undergo autoxidation to yield ortho-quinoid structures I-9⁹⁾ As described above, the benzylic carbons are always involved in the chromophoric systems except the ortho-quinone structure. Therefore, it is expected that many valuable informations on chromophoric structure will be provided by ^{13}C NMR spector-

scopic method from the model experiments in which lignin model compounds are labeled with ^{13}C at benzylic position or at the terminal of the side chain.

This thesis deals with the ^{13}C -NMR spectroscopic studies on formation of chromophoric structures under alkaline pulping condition from representative lignin model compounds labeled with ^{13}C , vanillyl alcohol [α - ^{13}C], arylglycerol- β -aryl ether [α - ^{13}C], arylglycerol- β -aryl ether [γ - ^{13}C] and phenylcoumaran [α - ^{13}C].

Chapter II

Reaction Products from Vanillyl Alcohol with Alkali.

2.1. Introduction

Evidence in support of quinoid units formation in alkali lignin was provided through study on lignin model compounds. On treatment of vanillyl alcohol with alkali-oxygen, Rothenberg and Luner¹⁰⁾ were able to show that a portion of the chromophoric structure in soda lignin may be associated with α -carbonyl, p-quinone and diphenylmethane units. Orthoquinonemethide⁸⁾ from vanillyl alcohol and creosol, and biphenyl structure¹¹⁾ from creosol were responsible for the color or their intermediates in alkaline media. In addition to those functional groups and structures, the catechol units formed by demethylation of guaiacyl nuclei would contribute to the chromophoric structures to a great degree. Recently, Iiyama¹²⁾ reported that a polymeric matter prepared from vanillyl alcohol in alkaline pulping process gave a dark brown color with an absorption spectrum practically identical in character in IR spectrum to that of thiolignin, and exhibited the successive benzylium unit loss in the mass spectrum.

In this part, an attempt is made to reveal the reaction sequence taking place during treatment of

vanillyl alcohol, as a model compound, with alkali to elucidate the intermediate or the precursor of the chromophoric structure formed during the alkaline pulping processes.

2.2. Experimental

2-2-1 Synthesis of vanillyl alcohol.

A solution of 1.58g of acetyl vanillin in 20ml of dry dioxane was reduced with 0.45g of sodium borohydride at room temperature for 3 hours. After the destruction of the excess reducing agent with acetic acid, the reaction mixture was diluted with 100ml of saturated sodium chloride solution and extracted with ethyl acetate. The organic phase was then dried over magnesium sulfate and was evaporated to give an oil, which was employed for the next step without further purification. The resulting oil in 16ml of water was hydrolysed with 20ml of 1N sodium hydroxide at 60° for 15 minutes. The solution was acidified with 4N hydrochloric acid to pH 4 and after saturation with sodium chloride extracted with ethyl acetate. The ethyl acetate phase was dried over sodium sulfate and on removing the solvent a crystalline residue remained.

Recrystallization from a mixed solvent of benzene and ethanol afforded 0.821g of vanillyl alcohol; m.p. 114-115°.

2-2.2 Reaction of vanillyl alcohol with sodium hydroxide¹³⁾.

A solution of 1.232g of vanillyl alcohol in 35ml of water and 3.2g of sodium hydroxide was refluxed for 18 hours under nitrogen. After cooling, the reaction mixture was acidified with 4N hydrochloric acid to pH 4 and extracted with ethyl acetate. The extract was washed with water and dried over sodium sulfate. Removal of the solvent at reduced pressure gave an oil, which was chromatographed on silica gel. Elution with *n*-hexane-ethyl acetate (4:1,

v/v) gave six fractions.

The first fraction was recrystallized from a mixed solvent of *n*-hexane and acetone to afford 146mg (12% from vanillyl alcohol) of II-1 as colorless needles; m.p. 109-110°, NMR δ : 3.80 (8H, s, methoxyl and methylene), 5.45 (2H, s, phenolic hydroxyl), 6.64 (2H, d, J=2Hz, aromatic protons), 6.65 (2H, q, J=9+2Hz, aromatic protons), 6.82 (2H, d, J=9Hz, aromatic protons); MS m/e: 260 (M⁺), 137, 124. The second fraction contained 304mg (25%) of II-2 as a colorless oil: NMR δ : 3.72-3.88 (13H, m, methoxyl and methylene), 5.48 (1H, s, phenolic hydroxyl), 5.50 (1H, s, phenolic hydroxyl), 5.61 (1H, s, phenolic hydroxyl), 6.53-6.87 (8H, m, aromatic protons); MS m/e: 396 (M⁺), 272, 259, 137, 124.

The analytical sample of II-3 (128mg, 10%) was secured after column chromatography of the third fraction on silicagel using *n*-hexane-chloroform (3:7, v/v) as eluent; NMR δ : 3.68-3.90 (18H, m, methoxyl and methylene), 5.45 (1H, s, phenolic hydroxyl), 5.47 (1H, s, phenolic hydroxyl), 5.56 (1H, s, phenolic hydroxyl), 5.58 (1H, s, phenolic hydroxyl), 6.44-6.87 (10H, m, aromatic protons); MS m/e: 532 (M⁺), 408, 272, 137, 124. The fourth fraction was chromatographed again. Elution with chloroform-*n*-hexane (4:1, v/v) gave 66mg (5.4%) of II-4 as a colorless syrup; NMR δ : 3.67-3.95 (23H, m, methoxyl and methylene), 5.45 (1H, s, phenolic hydroxyl), 5.49 (1H, s, phenolic hydroxyl), 5.55 (1H, s, phenolic hydroxyl), 5.57 (1H, s, phenolic hydroxyl), 5.58 (1H, s, phenolic hydroxyl), 6.38-6.84 (12H, m, aromatic protons); MS m/e: 668 (M⁺), 544, 408, 272, 137, 124. The fifth fraction was also chromatographed using chloroform as eluent to afford 36mg (2.9%) of II-5; MS m/e: 290 (M⁺), 166, 124.

2-2-3 Acetylation of the compounds II-1, II-2, II-3, II-4 and II-5.

The compounds II-1, II-2, II-3, II-4 and II-5 were

acetylated with pyridine and acetic anhydride in the usual manner to prepare acetylated compounds (II-6, II-7, II-8, II-9 and II-10, respectively). The analytical samples were obtained after column chromatography on silica gel using ethyl acetate-n-hexane (1:4, v/v) as eluent, II-6; IR $\nu_{\max}^{\text{nujol}} \text{cm}^{-1}$: 1760, 1600, 1510, 1370, 1330, 1280, 1270, 1215, 1200, 1190; NMR δ : 2.30 (6H, s, phenolic acetoxy), 3.79 (6H, s, methoxyl), 3.95 (2H, s, methylene), 6.73 (2H, d, J=2Hz, aromatic protons), 6.76 (2H, d, J=2Hz, aromatic protons), 6.95 (2H, d, J=8Hz, aromatic protons). Anal. Calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_6$: C, 66.27; H, 5.85, Found: C, 66.18; H, 5.72. II-7; IR $\nu_{\max}^{\text{direct}} \text{cm}^{-1}$: 1765, 1600, 1510, 1370, 1320, 1280, 1270, 1220, 1200, 1190; NMR δ : 2.23 (3H, s, phenolic acetoxy), 2.28 (6H, s, phenolic acetoxy), 3.75 (6H, s, methoxyl), 3.77 (3H, s, methoxyl), 3.83 (2H, s, methylene), 3.89 (2H, s, methylene), 6.57-7.01 (8H, m, aromatic protons). Anal. Calcd. for $\text{C}_{29}\text{H}_{30}\text{O}_9$: C, 66.65; H, 5.79, Found: C, 66.49; H, 5.73. II-8; IR $\nu_{\max}^{\text{direct}} \text{cm}^{-1}$: 1760, 1600, 1510, 1370, 1280, 1270, 1220, 1200, 1190; NMR δ : 2.19 (3H, s, phenolic acetoxy), 2.21 (3H, s, phenolic acetoxy), 2.27 (6H, s, phenolic acetoxy), 3.74 (12H, s, methoxyl), 3.81 (4H, s, methylene), 3.86 (2H, s, methylene), 6.54-7.00 (10H, m, aromatic protons). Anal. Calcd. for $\text{C}_{39}\text{H}_{40}\text{O}_{12}$: C, 66.85; H, 5.75, Found: C, 66.72; H, 5.84. II-9; IR $\nu_{\max}^{\text{direct}} \text{cm}^{-1}$: 1760, 1600, 1510, 1370, 1330, 1280, 1270, 1220, 1200, 1190; NMR δ : 2.17 (3H, s, phenolic acetoxy), 2.18 (3H, s, phenolic acetoxy), 2.20 (3H, s, phenolic acetoxy), 2.26 (6H, s, phenolic acetoxy), 3.71 (15H, s, methoxyl), 3.79 (6H, s, methylene), 3.83 (2H, s, methylene), 6.51-6.97 (12H, m, aromatic protons). Anal. Calcd. for $\text{C}_{49}\text{H}_{50}\text{O}_{15}$: C, 66.96; H, 5.73, Found: C, 66.71; H, 5.69. II-10; IR $\nu_{\max}^{\text{direct}} \text{cm}^{-1}$: 1770, 1730, 1600, 1500, 1370, 1290-1170; NMR δ : 2.06 (3H, s, alcoholic acetoxy), 2.20 (3H, s, phenolic acetoxy), 2.25 (3H, s, phenolic acetoxy), 3.74 (3H, s, methoxyl), 3.82 (3H, s, methoxyl),

3.83 (2H, s, methylene), 5.01 (2H, s, methylene), 6.63-6.99 (5H, m, aromatic protons). Anal. Calcd. for $\text{C}_{22}\text{H}_{24}\text{O}_8$: C, 63.45; H, 5.81, Found: C, 63.37; H, 5.64.

2-3. Results and discussion

To avoid oxidation with molecular oxygen, vanillyl alcohol was treated in alkaline solution under nitrogen to afford five condensation products which seemed to be concerned with the chromophoric structure of lignin or its intermediates formed during alkaline pulping processes.

The first compound II-1 with the formula $\text{C}_{15}\text{H}_{16}\text{O}_4$ was identified as diguaiacylmethane which has been synthetically prepared¹³⁾.

Though a direct comparison of compound II-1 with the preparation by Pearl¹³⁾ has not been made, the physical and spectral characteristics leave no doubt as to their identity.

The mass spectrum and the elemental analysis of the second isolated compound indicated its formula to be $\text{C}_{23}\text{H}_{24}\text{O}_6$. In the mass spectrum of II-2 an intense peak was found at m/e 272, presumably resulting from the loss of 124 units of guaiacol from the molecular ion at m/e 396. The NMR spectrum showed signals for three methoxyl and two methylene groups at δ 3.72-3.88 and eight aromatic protons at δ 6.53-6.87. In addition, three signals at δ 5.48, 5.50 and 5.61 accounted for all hydroxyl groups in the molecule. On acetylation with acetic anhydride and pyridine, the compound yielded the triacetate II-7, in good yield. On the basis of these data and reaction mechanism, the structure II-2 was proposed for this product, as shown in Fig. 2-1.

It has previously been reported by Nakano and his coworkers^{14), 15)} that the chloroform soluble fraction from the alkali methanol and soda cookings of vanillyl alcohol had contained the compound II-2 as one of the condensation products.

The third product II-3 ($\text{C}_{31}\text{H}_{32}\text{O}_8$) had a similar

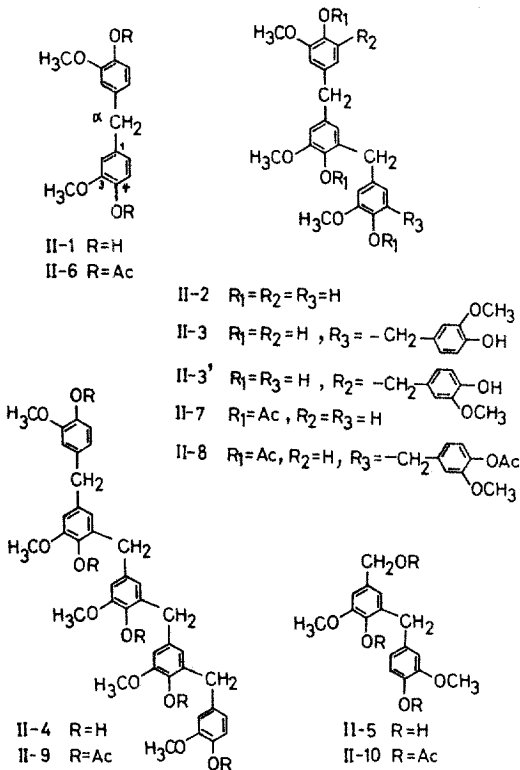


Fig. 2-1

proposed structures was finally made by the NMR spectrum. The low- and high-field absorptions at δ 6.44-6.87 and δ 3.68-3.90, respectively, were assigned to aromatic protons, and methoxyl and methylene protons. In addition, the presence of four non-equivalent phenolic hydroxyl protons was also shown by four singlets at δ 5.45, 5.47, 5.56 and 5.58, indicating that the compound may have the structure of II-3, as shown in Fig. 2-1. As expected, treatment of II-3 with acetic anhydride afforded the tetraacetate II-8, which gave satisfactory spectroscopic data.

The fourth compound II-4 ($C_{39}H_{40}O_{10}$) had also similar absorption patterns to II-2 and II-3 in the IR and NMR spectra. Valuable information for the structural elucidation was obtained from the mass spectrum (Fig. 2-3), which exhibited the molecular ion at m/e 668 and also similar fragmentation patterns (Fig. 2-4) to that of II-3 especially in the field below M^+ -guaiacol. By this interrelation, the structure of the fourth compound was established as II-4 in Fig. 2-1.

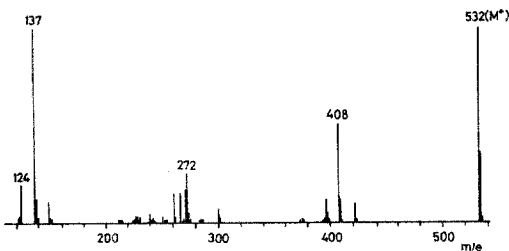


Fig. 2-2 Mass spectrum of II-3.

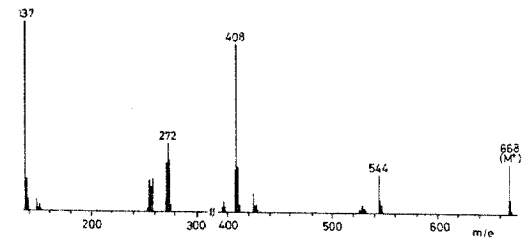


Fig. 2-3 Mass spectrum of II-4.

absorption pattern to that of II-2 in the IR spectra. The mass spectrum, as illustrated in Fig. 2-2, showed the parent peak at m/e 532 and the characteristic ion peak at m/e 408 ($M^+ - 124$), 272 ($M^+ - 260$), 137 and 124, suggesting the probable chemical structure of II-3 or symmetric II-3', which are a condensation product of II-2 with a guaiacymethylene unit at the *o*-position of phenolic hydroxyl group. Decision of the correct one between the

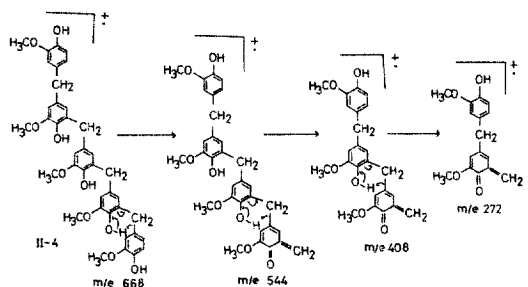


Fig. 2-4 Fragmentation of II-4 in mass spectrum.

The last isolated compound II-5 ($C_{16}H_{18}O_5$) contained phenolic and alcoholic hydroxyl groups, which were readily deduced from the IR absorption of the triacetate II-10 at 1770 and 1730 cm^{-1} , respectively. The mass spectrum of II-5 exhibited a base ion peak at m/e 166 by the loss of a guaiacol unit from the molecular ion at m/e 290. In the NMR spectrum (Fig. 2-5) the triacetate showed three singlets at δ 2.06, 2.20 and 2.25 for an alcoholic and two phenolic acetoxy groups respectively, two singlets at δ 3.74 and 3.82 for two methoxyl groups, two singlets at δ 3.83 and 5.01 for two methylene protons and a broad multiplet at δ 6.63-6.99 for protons on aromatic rings. These results may lead to the conclusion that the compound has the structure II-5, as shown in Fig. 2-1.

Under similar reaction conditions the formation of diguaiacylmethane II-1 has been suggested by Hästbacka^{16,17}) to be initiated by the addition of an anion II-12 to methylene quinone structure II-13 to give an intermediate II-14, followed by the elimination of formaldehyde, as shown in Fig. 2-6. As shown in Fig. 2-7, vanillyl alcohol gave other condensation products^{18,19}) with $C_{\alpha} - C_5$ linkage, which yielded isohemipinic acid on permanganate oxidation. An anion II - 11 attacks the methylene quinone structure II - 13 to produce a reactive intermediate II - 15, which gives the compound II - 5 via the anion II - 16 after neutralization. The carbanion II - 15 competes with the anion II - 16 or its

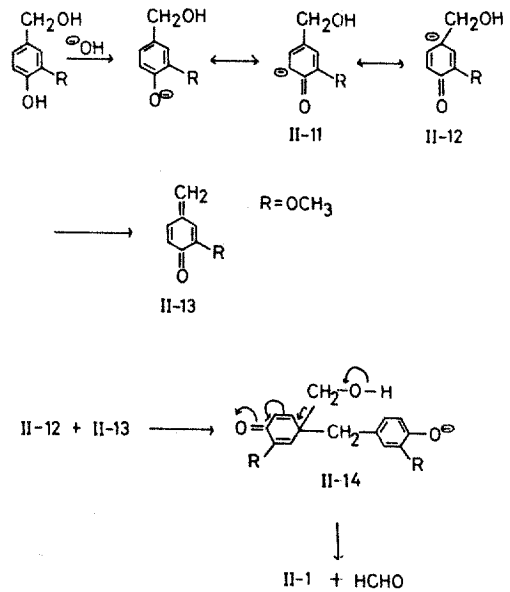


Fig.2-6 Formation of reaction products during alkaline treatment of vanillyl alcohol.

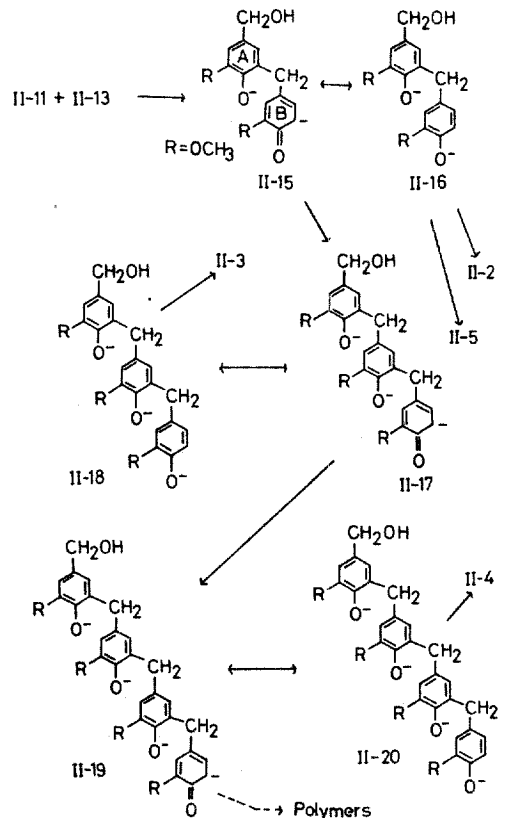


Fig. 2-7 Formation of reaction products during alkaline treatment of vanillyl alcohol.

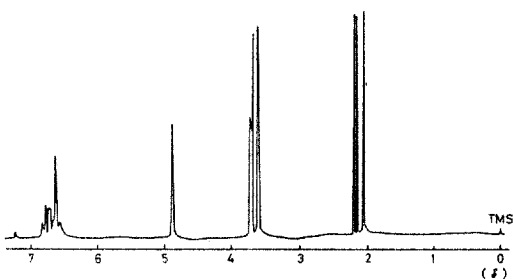


Fig. 2-5 NMR spectrum of II-10.

methylene quinone intermediate at the A ring for reactive site in II - 13 or II - 12 to yield a hydroxy-methyl intermediate II - 17 and the compound II - 2, the latter of which will accompany the liberation of formaldehyde in the formation process as in that of II - 1, respectively. Similarly the anions II - 17 and II - 18 or its methylene quinone intermediate produce the compound II-3 and an intermediate II-19. Experimental support for these reaction mechanisms would be provided by the lack of the symmetrical compound II-3' in the reaction products. If the addition of the carbanion of II-1 to methylene quinone structure II-13 occurs as another formation mechanism, the isomer II-3' are formed. Accordingly, compounds II-2-4 would be synthesized via the reactive intermediates II-16, II-18 and II-20 respectively, with $C_{\alpha}-C_5$ linkages followed by the liberation of formaldehyde after the attack of II-12 to the corresponding methylene quinone units at the A ring of the reactive intermediate without passing through the compound II-1. The pentamer II-4 and other polycondensation products should be formed by a similar addition⁵⁾ of the carbanion II-20 to the quinonemethide II-18.

These compounds II-1-5 yielded colored materials in alkaline media by air oxidation.

Chapter III

Chromophoric structures of Condensation Products from Vanillyl Alcohol.

3-1. Introduction

As described in chapter II, treatment of vanillyl alcohol, which serves as a model for uncondensed units in lignin, in alkaline media afforded diguaiacyl-methane and various condensation products with $C_5 - C_{\alpha}$ linkage. This finding leads me to assume these products are the possible source of the chromophoric structure of model alkali lignin¹²⁾. The

present work deals with experiments illustrating the chromophoric structures of the colored materials from vanillyl alcohol mainly by ^{13}C NMR spectroscopy.

3-2. Experimental

3-2-1 Alkaline cooking of vanillyl alcohol.

A solution of 0.504g of vanillyl alcohol in 10ml of 1N sodium hydroxide solution was heated at 165°C in a sealed glass tube for 1.5 hour under nitrogen. After cooling, half volume of the reaction solution was acidified with 4N hydrochloric acid under nitrogen and extracted with ethyl acetate. The organic phase was dried over sodium sulfate and evaporated to give non-colored material. Another half volume of the reaction mixture was then oxidized in air with vigorous stirring for 8 hours at room temperature. The dark solution was acidified with 4N hydrochloric acid and extracted with ethyl acetate. After evaporation of the ethyl acetate solution dried over sodium sulfate, colored material (0.224g) was obtained. At the next step of experiment the colored material was chromatographed on slightly deactivated silica gel. Elution with chloroform, ethyl acetate and methanol gave three fractions (0.133g, 0.059g and 0.008g, respectively).

3-2-2 Treatment of creosol with formaldehyde in alkaline solution.

To a solution of 1.0g of creosol in 10ml of 1N sodium hydroxide was added 0.6g of formalin (HCHO, 37%). The mixture was heated at 160°C for 3 hours and then cooled. After acidification to pH 2, the aqueous solution was extracted with ethyl acetate and the organic phase was dried over sodium sulfate. The solution was concentrated to give an oil, which was purified by chromatography on silica gel using n-hexane and acetone (5:1; v/v) as eluent to afford 42mg of 2,2'-dihydroxy-3,3'-

dimethoxy-5,5'-dimethyldiphenylmethane
III-6^{20,21}); m.p. 132-133°.

3-2-3 Synthesis of vanillyl alcohol- α - ^{13}C (vanillyl alcohol-[carbinol- ^{13}C]) from acetic acid- ^{13}C .

Vanillin- α - ^{13}C (vanilin-[aldehyde- ^{13}C]) was synthesized from guaiacol and acetic acid-1- ^{13}C (^{13}C content; about 90%) by the same method described for preparation of vanillin- α - ^{14}C .²² The ^{13}C content of it was estimated to be about 88% from the IR absorptivity of $^{13}\text{C}=\text{O}$ at 1650cm^{-1} and $^{12}\text{C}=\text{O}$ at 1680cm^{-1} . Reduction of 108mg of vanillin- α - ^{13}C in 28ml of methanol with 85mg of sodium borohydride for 1 hour at room temperature afforded 93mg (85.8%) of vanillyl alcohol- α - ^{13}C .

3-2-4 Alkaline cooking of vanillyl alcohol- α - ^{13}C .

Vanillyl alcohol- α - ^{13}C was treated with alkali in the same manner described above except heating for longer time (3 hours), followed by air oxidation to give the ^{13}C labeled colored material.

3-2-5. Sodium borohydride reduction of the ^{13}C labeled colored material.

A solution of 16mg of the ^{13}C labeled colored material in 4ml of methanol was reduced with 8mg of sodium borohydride at room temperature for 2 days. After destruction of excess sodium borohydride with acetic acid, the solution was diluted with water and extracted with ethyl acetate. The extract, after being dried over sodium sulfate, was concentrated in vacuo to give 13mg of reduction products.

3-2-6 Distribution of molecular weight of non-colored and colored materials.

Gel-filtration was carried out in the same way as described in the previous paper²³.

3-2-7 Measurement of UV and ^{13}C NMR spectra.

UV spectrum was measured in solvents of dioxane and 1N sodium hydroxide using a Shimadzu MPS-50 spectrophotometer. ^{13}C NMR spectrum was recorded on a Jeol JNM-FX 100 pulse Fourier-transform instrument (25.05 MHz). CD_3OD was employed as solvent with TMS as the internal reference.

3-3. Results and discussion

The ^{13}C NMR chemical shifts in CD_3OD for condensation products (Fig. 3-1), which were obtained by treatment of vanillyl alcohol with alkali, are shown in Table 3-1. By comparison of the chemical shifts of III-1 and III-2 with that of III-3 and III-4, it is clear that the chemical shifts of the aromatic carbon atoms depend on the substituents on the aromatic rings, and therefore the aromatic carbon atoms at both ends are easily distinguished from others. The methoxyl carbons possess almost constant chemical shift at 56.1 ppm without influence on substituents. On the other hand, the aliphatic carbons at α -position are affected by the hydroxyl groups at the ortho position and showed an upfield shift of about 5 ppm.

The ^{13}C NMR spectrum of the non-colored material, which was prepared from vanillyl alcohol by treatment with sodium hydroxide at 165° for 1.5 hour, is shown in Fig. 3-2. By comparison with models, the signals (Table 3-1) were assigned at 192.7 (CHO), 148.3 (C-3, -3', -3'' and -3'''), 145.3 (C-4 and -4'''), 142.8 (C-4' and -4''), 134.7-133.2 (C-1, -1', -1'' and -1'''), 129.1-128.9 (C-5' and -5''), 123.7 (C-6' and -6''), 122.2 (C-6 and -6''), 115.8 (C-5 and -5'''), 113.3 (C-2 and -2'''), 110.7 (C-2' and -2'') ppm. In high field region the signals at 56.2, 41.9 and 35.9 ppm correspond to methoxyl carbons, C- α , and C- α' and - α'' , respectively. The signal (30.2ppm) at higher field of the remaining two carbon atoms appears upfield some 5 ppm relative to

corresponding C- α' and C- α'' , suggesting that two hydroxyl groups situate at ortho position of the methylenic carbon. Another peak (128.3-128.0ppm) allowed the assignment of the aromatic carbon attached to the newly formed aliphatic carbon. The formation of the aliphatic carbon is sug-

gested to proceed via the addition of formaldehyde, which was liberated in the formation of diguaiacyl-

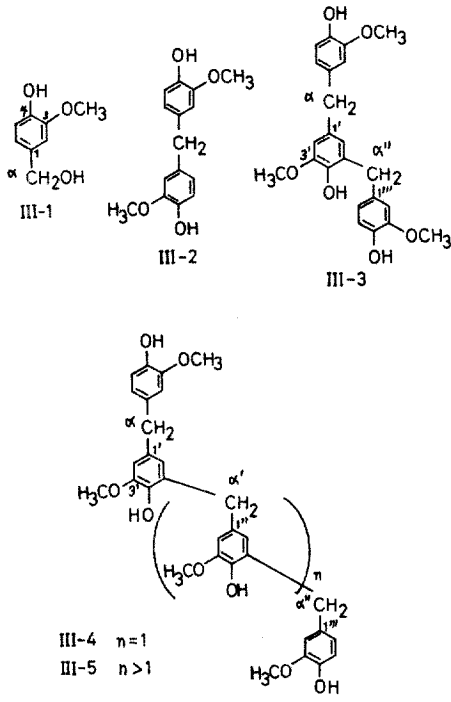


Fig. 3-1

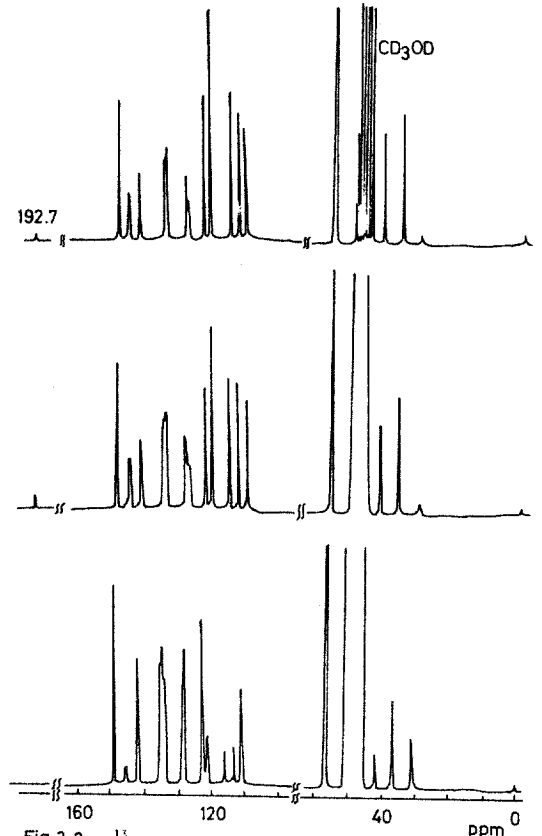


Fig. 3-2 ¹³C NMR spectra of non-colored(top) and colored (middle) materials, and methanol eluted fraction (bottom) of colored material.

Table 3-1 ¹³C NMR Chemical shifts in CD₃OD for model compounds and non-colored material.

Compound	Car.												Cal.		
	1,1''	1,1'	2,2'''	2,2''	3,3'''	3,3'	4,4'''	4,4''	5,5'''	5,5''	6,6'''	6,6''	OCH ₃	α	α',α''
III-1	133.7		111.7		148.5		146.5		115.6		120.7		56.0	65.1	
III-2	134.4		113.1		148.5		145.3		115.8		122.0		56.1	41.8	
III-3	134.0	133.4	113.1	110.5	148.2	148.3	145.1	143.0	115.6	128.9	122.0	123.5	56.1	41.8	35.7
			113.3				145.2				122.1		56.2		
III-4	133.9	133.1	113.9	110.3		148.0	145.8	142.6	115.4	128.3	121.8	123.4	56.0	41.7	35.6
		134.3	133.3	113.1	110.5		148.1	145.0		115.5	128.8	121.9	123.5	56.1	
non-colored material	133.2		113.3	110.7		148.3	145.3	142.8	128.0	128.9	122.2	123.7	56.2	41.9	35.9
		?							?	?					30.2
		134.7							128.3	129.1					
									115.8						

Car. = aromatic carbon, Cal. = aliphatic carbon.

methane units, to the aromatic carbon at C-5 position, followed by dehydration condensation with other aromatic nucleus as illustrated by the well-known phenol-formaldehyde type condensation²⁴). Accordingly this behaviour of the eliminated carbon is analogous to that of the γ -carbons of lignin side chain in alkaline pulping processes^{5),20}).

As might be expected, on treatment with formaldehyde in alkaline media, creosol afforded the compound III-6 and, in fact, the ^{13}C NMR chemical shift of the methylenic carbon of III-6 was in good agreement with that (30.2ppm) of the carbon described above. Therefore, the condensation products from vanillyl alcohol with alkali would have the partial structure III-7, as shown in Fig. 3-3, in addition to the diguaiacylmethane unit and the elemental structure with $\text{C}_5\text{-C}_\alpha$ linkage. After alkaline cooking followed by air oxidation in alkaline media, vanillyl alcohol afforded the colored material. The ^{13}C NMR spectrum (Fig. 3-2) of the material did not show any specific absorption which was concerned with a chromophoric structure, indicating that the proportion of the chromophoric structure is very low on the whole. To concentrate

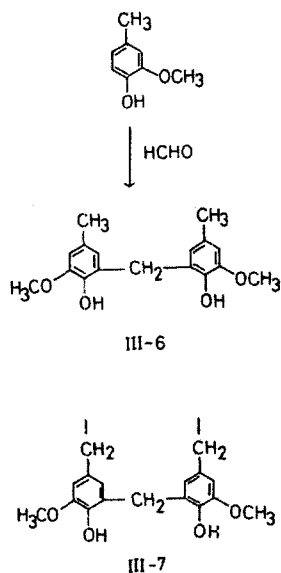


Fig. 3-3

on the structural units, the colored material was subjected to column chromatography on slightly deactivated silica gel. Elution with chloroform, ethyl acetate and methanol gave three fractions. In these fractions ethyl acetate eluted part of the colored material was dark brown, and methanol eluted fraction almost dark. Unfortunately, no specific absorption of the chromophoric structure was detectable even in the ^{13}C NMR spectrum (Fig. 3-2) of the methanol eluted material. However, the intensity ratio of peaks at 113.3, 115.8, 122.2 and 145.3 ppm for C-2 and -2'', C-5 and -5'', C-6 and -6'', and C-4 and -4'', respectively, in the aromatic ring situated at both ends diminished to a great extent, suggesting that the material would contain more high-molecular-weight molecules.

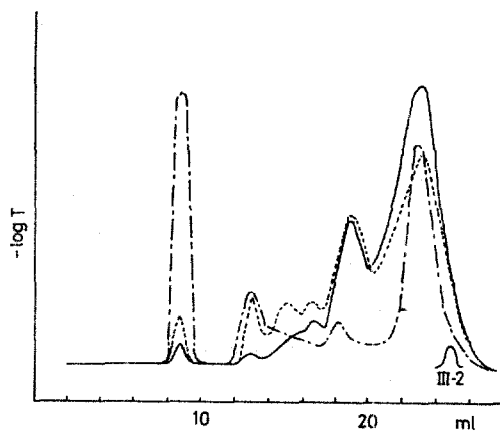


Fig. 3-4 Gel-filtration curves of non-colored(—) and colored(---) materials, and methanol eluted fraction(- · - ·) of colored material.

Gel-filtration on sephadex G-15, as shown in Fig. 3-4, exhibited that the air oxidation of the alkaline cooking products from vanillyl alcohol in alkaline solution brought about polymerization to a small extent, and the methanol eluted fraction contained more polymers in agreement with the results of the ^{13}C NMR spectrum.

As illustrated in Fig. 3-5, the UV spectra measured in dioxane (0.074% concentration) would suggest the presence of quinonemethide structure⁸)

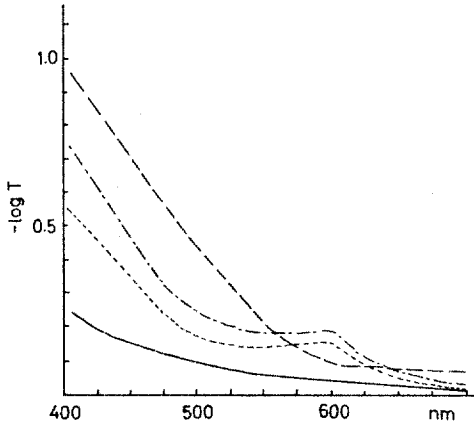


Fig. 3-5 Visible region absorption spectra(0.074%) of colored material at pH 7(—) and pH 12 (---), ΔEt curve(-·-·-), and methanol eluted fraction(- - -) of colored material.

in the colored material.

It was difficult to obtain the information on the chromophoric structures of the colored material by a simple method of concentration of chromophoric structural units followed by ^{13}C NMR measurement. In consideration of the estimation^{5),8),10),25)} that quinonemethide structures have held a very important position on the chromophoric structures of alkali lignin vanillyl alcohol specifically labeled with ^{13}C at benzylic position was used as an experimental material.

On treatment with alkali for a somewhat longer time (3 hours) followed by air oxidation in the similar way as that of non-labeled vanillyl alcohol, vanillyl alcohol- α - ^{13}C gave the colored material. In the ^{13}C NMR spectrum, as shown in Fig. 3-6, of the material, the three big peaks at 41.8, 35.9 and 30.1 ppm were assigned to C- α , C- α' and - α'' , and the methylenic carbon of III-7, respectively. In the low field region, the chemical shifts of carbonyl carbons of aldehyde and keto, such as a benzophenone, appear at 193.1-192.8 and 196.2ppm, respectively. In the aromatic and olefinic field regions two peaks at 101.7 and 104.6 ppm, both of which were not detected in the ^{13}C NMR spectra of the non-labeled colored materials, were observed, and

would be assigned to quinonemethide structures in terms of the chemical shifts. On the basis of the chemical structures of the condensation products (in chapter II) obtained by treatment of vanillyl alcohol with alkali, the structural units, as shown in Fig. 3-7, could be estimated in interpreting the observed absorptions of the chromophoric carbon. As expected, in the ^{13}C NMR spectrum (Fig. 3-6) of the reduction products of the ^{13}C labeled colored material with sodium borohydride²⁶⁾ in methanol solution, these two peaks disappeared, although some of the carbonyl carbon remained without reduction, and shifted to higher field.

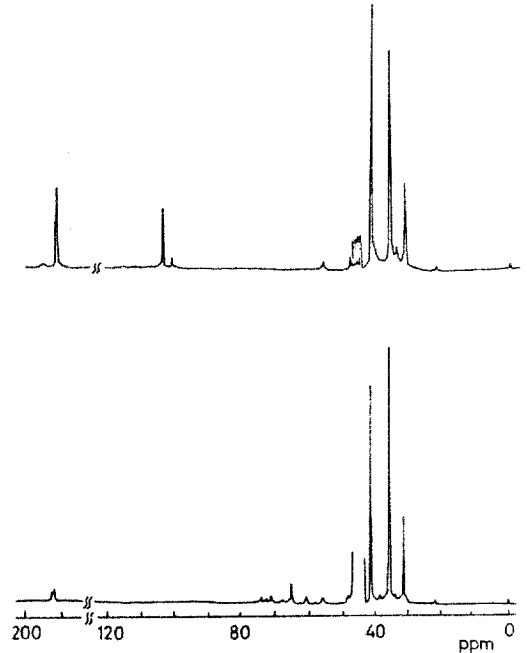


Fig. 3-6 ^{13}C NMR spectra of ^{13}C labeled(top) and its $NaBH_4$ -reduced(bottom) materials.

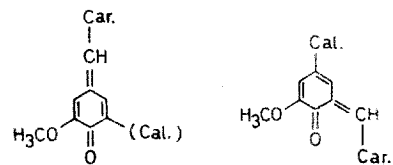


Fig. 3-7 The estimated chromophoric structures of colored material. Car.=aromatic carbon, Cal.=aliphatic carbon.

Therefore, these results will indicate the presence of the quinonemethide structures, as shown in Fig. 3-7, as possible chromophoric units formed by alkaline cooking of vanillyl alcohol followed by air oxidation.

It has been known^{25),27),28),29)} the presence of ortho quinone structure as a chromophoric structure of alkali lignin and, in particular, vanillyl alcohol, was easily demethylated³⁰⁾ by alkaline cooking, suggesting that the ortho quinone unit would play an important role of the chromophoric structure derived from vanillyl alcohol. In fact, comparison between the UV spectra, as shown in

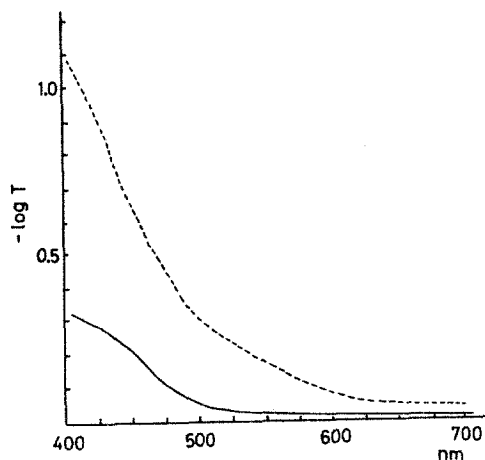


Fig. 3-8 Visible region absorption spectra of colored materials in 50 ml of 1N NaOH solution from vanillyl(50 mg) and p-hydroxybenzyl(50 mg) alcohols(----- and ———, respectively).

Fig. 3-8, of the colored materials from vanillyl alcohol and p-hydroxy benzyl alcohol indicated that the catechol unit was responsible for 60-70% of the chromophoric structure from vanillyl alcohol. In these alkaline solutions free radicals³¹⁾ in addition to anions of condensation products would give rise to chromophoric systems to a great extent.

Chapter IV

Chromophoric Structures of Condensation Products from Guaiacylglycerol- β -Aryl Ether [α - ^{13}C].

4.1. Introduction

It was proposed in chapter III that treatment of a simple lignin model compound, vanillyl alcohol, under alkali pulping conditions followed by air oxidation afforded the oxidation products of diphenylmethane derivatives, and that the products held an important position of the chromophoric structures in which benzylic carbon was included. Such diphenylmethane units, although condensation reactions³²⁾ would easily occur in acidic media, are formed by the nucleophilic attack of aromatic nuclei on quinonemethide intermediates and alkali pulping of wood could not avoid the formation of these condensation products as results of side reactions.

In continuation of the work on the chromophoric structures of alkali lignin, the behavior of guaiacylglycerol- β -aryl ether [α - ^{13}C] IV-1a which is the main structural element of lignin has now been studied.

4-2. Experimental

4-2-1 Synthesis of the guaiacylglycerol- β -aryl ether [α - ^{13}C] IV-1a.

Dehydration reaction, as described in chapter III, of guaiacol and acetic acid-1- ^{13}C (^{13}C content; about 90%) with PPA yielded acetoguaiacone, which was then transformed into IV-1a by the same method reported³³⁾ earlier.

4-2-2 Alkaline cooking of the non-labeled and labeled IV-1a.

Both compounds of the non-labeled and labeled IV-1a were treated with alkali in the same method of preparing non-colored and colored products of vanillyl alcohol to yield condensation products IV-4 and IV-7, and subsequent oxidation mixtures IV-5 and IV-8, respectively.

4-2-3 Sodium borohydride reduction of the ^{13}C

labeled oxidation products IV-8.

Reduction of IV-8 was carried out in the same way as described in chapter III.

4-2-4 Sodium hydrosulfite reduction of the sodium borohydride reduction products IV-9.

A solution of 30mg of IV-9 in 2ml of 4N NaOH was reduced with 3ml of 10% $\text{Na}_2\text{S}_2\text{O}_4$ under an atmosphere of nitrogen at room temperature for 24 hours. After acidification with 4N HCl, the solution was extracted with ethyl acetate. The extract was then washed with water, dried over Na_2SO_4 and evaporated in vacuo to give reduction products.

4-2-5 Alkaline cooking of a β -aryl ether IV-14a.

By the method described above, the β -aryl ether IV-14a, which was synthesized by use of the same procedure as Adler³⁴, was treated with alkali to yield a dark oil. The reaction products were separated by means of the column chromatography on silica gel with a mixed solvent of n-hexane and acetone (8:2 v/v) to isolate creosol, isoeugenol, vinyl ether IV-3b and an colorless syrup (1.5% yield). The last compound was crystallized from a mixed solvent of n-hexane and acetone as crystals; m.p. 179-181°, IR ν $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$ cm^{-1} : 3400, 1595, 1505, 1260, 1220, 1135, 1030; NMR δ : 1.12 (3H, d, J=6Hz), 2.15 (3H, s), 3.65 (9H, s), 3.75-4.18 (1H, m), 4.86-5.10 (1H, m), 6.36-7.21 (9H, m); MS m/e: 424 (M^+), 287, 259, 165. Anal. Calcd. for $\text{C}_{25}\text{H}_{28}\text{O}_6$: C, 70.74; H, 6.65, Found: C, 70.64; H, 6.68.

4-2-6 Distribution of molecular weight and measurement of UV and NMR spectra.

All of the methods are described in chapter III except employing hexadeuteroacetone-heavy water (9:1 v/v) as NMR solvent.

4-3. Results and discussion

As shown in Fig. 4-1-A, the ^{13}C NMR spectrum

of the alkali condensation mixture IV-4 of non-labeled IV-1a had many absorption signals at 150.5 (1), 150.1 (2), 148.3 (3), 147.8 (4), 145.9 (5), 144.9 (6), 144.5 (7), 144.3 (8), 144.2 (9), 141.1 (10), 134.5 (11), 134.0 (12), 129.3 (13), 127.8 (14), 122.5 (15), 121.7 (16), 119.2 (17), 118.7 (18), 116.5 (19), 115.8 (20), 115.4 (21), 114.4 (22), 113.3 (23), 113.0 (24), 112.2 (25), 109.6 (26), 56.0 (27), 21.0 (28) ppm. On the consideration of chemical shift and relative intensity of each peak, the products IV-4 composed mainly of creosol IV-2 and the β -aroxystyrene derivative IV-3a. The explanation of these data is reasonable, since alkaline treatment of IV-1b under more mild condition has afforded guaiacol and IV-3c in 15 and 70% yield, respectively, as reported by Miksche³⁵) In the spectrum (Fig. 4-1-B) of the oxidation products IV-5, which were prepared by air oxidation of IV-4 in the alkaline solution for 8 hours, the absorption intensities due to that of IV-2 and vanillin IV-6

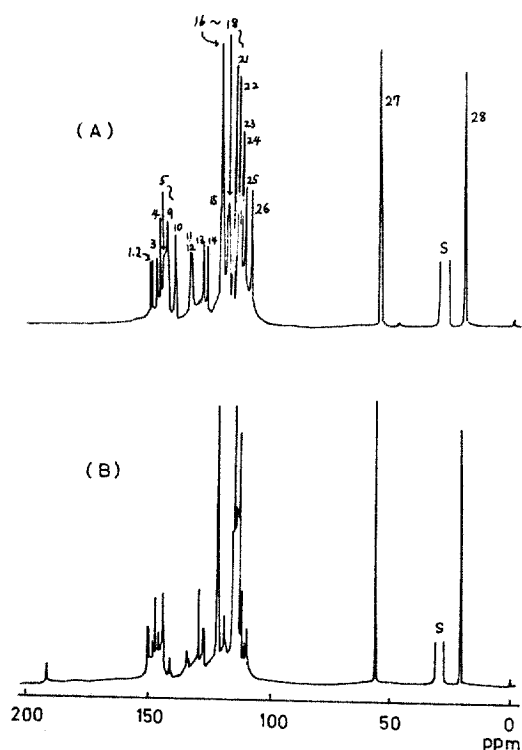


Fig. 4-1 ^{13}C NMR spectra of non-labeled IV-4(A) and IV-5(B).

increased indicating that oxidation reaction degraded IV-3a to IV-2 and IV-6. The formation³⁶⁾ of these compounds is suggested to proceed via the α,β -epidioxy intermediate, an addition product of oxygen to α,β -double bond of IV-3a, which undergoes the alkaline rearrangement with fragmentation and subsequent degradation.

The ¹³C NMR spectra of the ¹³C labeled alkaline condensation products IV-7, the air oxidation mixture (IV-8) of IV-7 and the sodium borohydride reduction products (IV-9) of IV-8 were shown in Fig. 4-2-A, B and C, respectively: The ¹³C content at the benzylic position of these reaction products IV-7, IV-8 and IV-9 was about 90%, as described in chapter III, and, therefore, all of resonances except those at 121.8, 56.1 and 20.9 ppm were assigned to the α -carbons of the various compounds as described later on comparison with the non-labeled spectra in Fig. 4-1. The lowest field signal at 195.9ppm (1) assigned to that of α -keto compound IV-10, which would be formed by the alkaline air

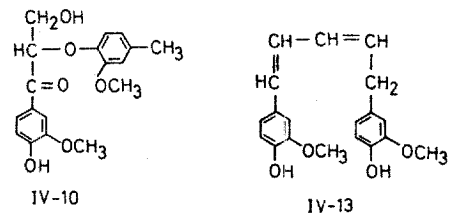
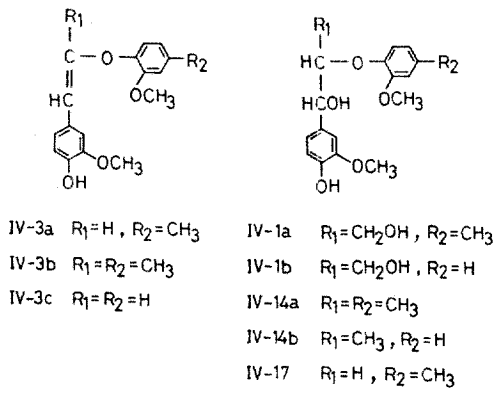


Fig. 4-3-1

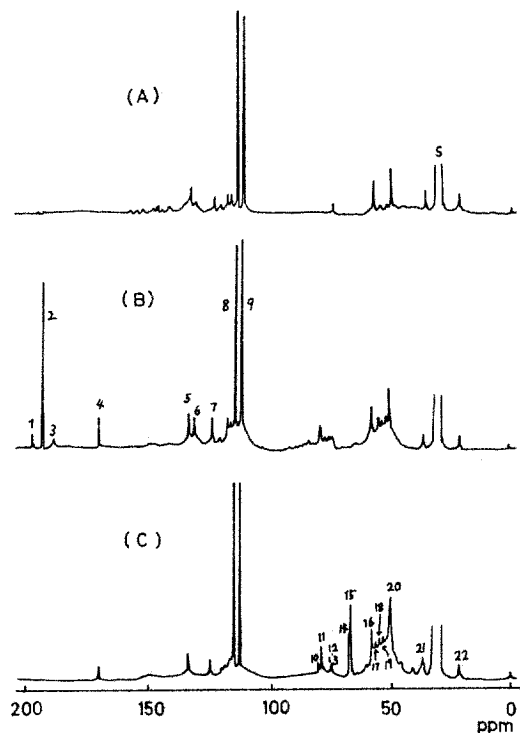


Fig. 4-2 ¹³C NMR spectra of labeled IV-7(A), IV-8(B) and IV-9(C).

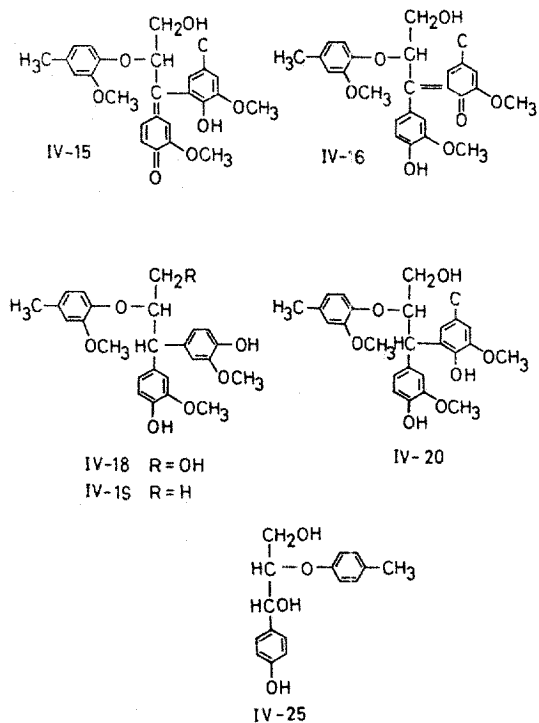


Fig. 4-3-2

Table 4-1 Chemical shifts of compounds IV-3a and IV-10.

Compound	Car.*1												OCH ₃	Cal.*1			
	1	1'	2	2'	3	3'	4	4'	5	5'	6	6'		α	α'	β	γ
IV-3a*2	134.2	127.9	109.6	113.1	148.0	145.1	146.0	150.2	114.4	116.0	118.8	121.8	56.1	109.8	21.1	141.2	
	134.7	128.1			148.5	144.6	146.1	150.7	115.5	116.7	119.4	122.6		112.4		144.3	
IV-10	128.0	132.2	112.3	114.1	148.4	145.5	152.9	149.8	116.0	115.5	124.6	121.5	56.1	195.6		83.2	63.8

*1 Car. = aromatic carbon, Cal = aliphatic carbon.

*2 This compound is the mixture of trans and cis isomer.

oxidation of the starting material IV-1a. The next higher field signal at 191.7 ppm (2)³⁷⁾ was assigned to the carbonyl carbon of vanillin IV-6 and was shifted upfield with transformation into the corresponding vanillyl alcohol (64.4ppm (15)) by reduction. The chemical structure for the α -carbonyl signal at 187.5ppm (3) is under investigation. The signal at 168.3ppm (4)³⁷⁾ must be due to that of vanillic acid IV-11, the oxidation product of IV-6 and, in fact, the alkaline air oxidation of IV-6 yielded IV-11.

In an aromatic region, several weak peaks from 121.8 to 113.4 ppm would be due to non-labeled aromatic carbons of IV-2 and IV-3a. Very strong signals at 112.3 (8) and 109.8 (9) ppm were assigned to the α -carbons of the trans and cis isomers of IV-3a, respectively, and such an assignment was supported by the pattern of signals obtained for the α -carbon of non-labeled IV-3a (Table 4-1). The two characteristic olefinic carbon signals appear at 131.5 (5) and 129.3 (6) ppm. There is no difficulty in assigning the former due to the α -carbons of coniferyl alcohol IV-12, its alkaline condensation product IV-13³⁸⁾ and/or the derivative of IV-13 such as a dimer from IV-12 and IV-3a, having a conjugated double bond in the side chain. Experimental support for the assignment was provided by the findings that (1) the alkaline treatment of IV-14a with γ -methyl group instead of IV-1a with easily eliminable hydroxymethyl group at the same position under the cooking conditions described in experimental part (4-2-2) gave isoeugenol, by the homo-

Table 4-2 Chemical shifts and assignment of signals in the spectra of Fig. 4-2.

No.	A	B	C	Assignment	
1	195.9	-	w*	IV-10	
2	191.7	VW	VS	Vanillin	
3	187.5	-	W	CO	
4	168.3	-	W	Vanillic acid	
5	131.5	W	W	IV-12, IV-13 and/or	
6	129.3	-	W	IV-15 and/or IV-16 a derivative of IV-13	
7	121.8	W	W		
8	112.3	VS	VS	} Trans and cis IV-3a	
9	109.8	VS	VS		
10	77.5	-	VW	} Ph-CHOH-C	
11	76.6	-	m		
12	73.1	-	VW	IV-1a	
13	72.3	W	W	IV-17	
14	64.6	-	-	W	
15	64.4	-	-	m	Vanillyl alcohol
16	56.1	m	m	m	OCH ₃
17	53.6	VW	VW	VW	IV-18
18	51.5	VW	VW	VW	
19	50.6	VW	VW	VW	
20	49.0	m	m	m	IV-20
21	34.7	W	W	W	Ph-CH ₂
22	20.9	W	W	W	Ph-CH ₃

* Intensity: VW = very weak, W = weak,
m = medium, S = strong,
VS = very strong.

lytic cleavage of β -aryl ether and hydroxyl groups, in high yield; (2) this signal was split into doublet in the off-resonance spectrum; and (3) the signal did not disappear by both of sodium borohydride and

sodium hydrosulfite reductions. On the other hand, and latter would be reasonably assigned to the absorption of the α -carbons of the chemical structure IV-15 and/or IV-16 on the basis of the fact that (1) the corresponding oxidation product of the diphenylmethane derivative, as described in chapter III, from vanillyl alcohol had the chemical shift of 105 or 102 ppm; (2) the structure was easily reduced with sodium borohydride; and (3) in the ^{13}C NMR spectrum of the reduction products (Fig. 4-2-c), the relative absorption intensity due to IV-20, which was assumed to be the corresponding reduction product of IV-15 and/or IV-16 as described later, increased by an amount corresponding to that of IV-15 and/or IV-16 in Fig. 4-2-B. However, it is difficult to differentiate between the two because the *s*-cis and *s*-trans conformation³⁹⁾ of α,β -unsaturated ketones could not be distinguished.

In the aliphatic region, the resonances at 77.5 (10) and 76.6 (11) ppm would be due to that of benzyl alcohol derivatives, although the structural assignment could not be made without hesitation. The weak signal at 73.1 ppm (12) belonged to that of the starting material IV-1a. The signal at 72.3 ppm (13)³⁷⁾ was assigned to the α -carbon of the compound IV-17, which would be produced by the hydration reaction⁴⁰⁾ of IV-3a. No assignable peak appeared at 64.6 ppm (14) and all non-labeled methoxyl groups resonated at 56.1 ppm (16). In order to deduce the chemical structure for the characteristic signal at 53.6 ppm (17), the compound IV-14a was treated with alkali to isolate the diphenylmethane derivative IV-19 in low yield. The chemical shift of the α -carbon of IV-19 was 57.9 ppm. In general, the signal of the α -carbon of lignin model compounds with γ -methyl group appears upfield some 4 ppm in comparison with that of the corresponding compounds with γ -hydroxymethyl group. Therefore, the 53.6 ppm peak should correspond to the condensation product IV-18 with γ -hydroxymethyl group. Two peaks at 51.5 (18)

and 50.6 (19) ppm could not be assigned to suitable structures. Since the methylene carbon of diphenylmethane derivative in chapter III is expected to be shifted about 5 ppm upfield due to one ortho hydroxyl group, the medium signal at 49.0 ppm (20) could be ascribed to the benzylic carbon of the structure IV-20. The signal at 34.7 ppm (21) showed a triplet in the off-resonance spectrum, suggesting that the compound had the methylene group on a guaiacyl ring and the signal at 20.9 ppm (22) was assigned to the methyl group on an aromatic ring.

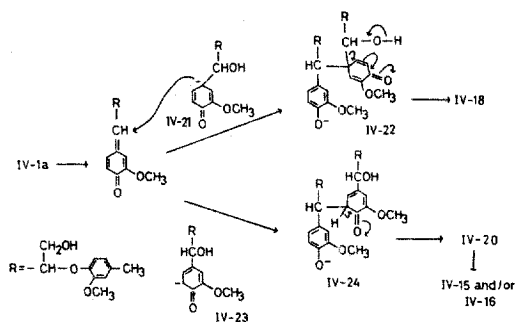


Fig. 4-4 Formation mechanism of IV-18 and IV-20.

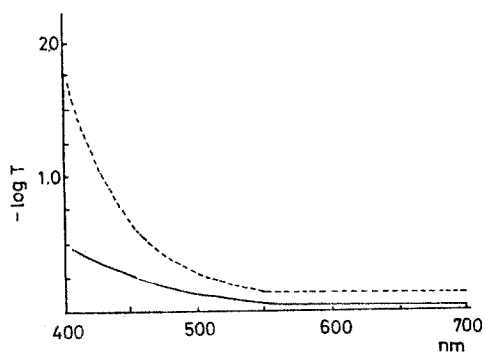


Fig. 4-5 Visible region absorption spectra of alkaline condensation products in 50 ml of 1N NaOH from IV-1a (50 mg, ----) and IV-25 (50 mg, —).

The formation mechanisms of the condensation products IV-18 and IV-20 are shown in Fig. 4-4. An intermediate IV-22 was formed by nucleophilic

attack of the carbanion IV-21 from IV-1a on the quinonemethide from IV-1a and by subsequent facile elimination of a side chain into IV-18. On the other hand, the same nucleophilic attack of another carbanion IV-23 on the quinonemethide yielded an anion IV-24, which was then aromatized to IV-20.

In this experiment, only one chromophoric structure IV-15 and/or IV-16 was detected in the oxidation products IV-8 and would be formed by air oxidation of IV-20 as in the same behavior of the diphenylmethane derivatives from vanillyl alcohol, indicating that the structural element IV-15 and/or IV-16 would be the important type of chromophore in which benzylic carbon of the guaiacylglycerol- β -aryl ether IV-1a was included. Although no chromophoric structure from IV-18 could be found in the oxidation mixture, such a structure must be contained as a trace because of the facile oxidation⁸⁾.

By comparison between the UV spectra of the air oxidation mixtures from IV-1a and p-hydroxyphenylglycerol- β -aryl ether IV-25, as shown in Fig. 4-5, suggested that the catechol unit was responsible for 60-70% of the chromophoric structure.

Chapter V

Chromophoric Structures of Condensation Products from Guaiacylglycerol- α -aryl ether [γ - ^{13}C]

5-1. Introduction

As described in chapter III and IV, treatment of vanillyl alcohol [α - ^{13}C] and guaiacylglycerol- β -aryl ether [α - ^{13}C] in alkaline solution afforded the diphenylmethane derivatives with $\text{C}_{\alpha}\text{-C}_1$ and $\text{C}_{\alpha}\text{-C}_5$ linkages. Subsequent air oxidation converted these condensation products to extended chromophoric systems.

On the other hand, it has been known for a long

time that the other type of diphenylmethane derivatives are formed in phenol-formaldehyde reaction. The γ -hydroxymethyl group in guaiacylglycerol- γ -aryl ether^{41),42),43)} is eliminated as formaldehyde in a reversed aldol reaction of quinonemethide intermediate, followed by recondensation to the aromatic nucleus with free phenolic hydroxyl group. The other elimination reaction of formaldehyde with alkali is given by phenylcoumaran,^{44),45),46)} dilignol with $\text{C}_{\beta}\text{-C}_1$ ^{47),48),49),50)} and pinoresinol⁵⁾. The liberated formaldehyde reacts with the activated free 5-positions of phenolic nuclei to afford hydroxymethyl derivatives in lignin-related model compounds^{11),24),51)} and in lignin,^{52),53)} and in part the formation of the diphenylmethane bridges occurs mainly between them.^{11),24),51)} Therefore, there is the possibility of forming chromophoric structures from the diphenylmethane derivatives derived from the γ -carbons of side chains by air oxidation. The present work is concerned with the contribution of the γ -carbon of guaiacylglycerol- β -aryl ether as a lignin model compound to chromophoric systems.

5-2. Experimental

5-2-1 Synthesis of guaiacylglycerol- β -aryl ether [γ - ^{13}C] V-1_b

To a solution of 0.15g of ω -(2-methoxy-4-methyl-phenoxy)-acetoguaiacone³³⁾ in 3ml of ethanol was added 2g of formalin ^{13}C (HCHO, 20% and ^{13}C content, about 90%) and 0.1g of sodium carbonate. The mixture was heated at 50°C for 4 hours. After acidification to pH 3, the aqueous solution was extracted with ethyl acetate and the organic phase was dried over sodium sulfate. The solution was evaporated to give crude α -(2-methoxy-4-methyl-phenoxy)- β -hydroxypropioguaiacone [β - ^{13}C], which was then transformed into V-1_b by the same method³³⁾ reported earlier.

5-2-2 Alkaline cooking of V-1_b and subsequent air oxidation of the ¹³C labeled condensation products from V-1_b.

Reactions were carried out in same way as described in chapter III.

5-2-3 Sodium borohydride reduction of the ¹³C labeled oxidation products.

A solution of 50mg of the ¹³C labeled oxidation products in 10ml of ethanol and 5ml of 3% sodium hydroxide was reduced with 30mg of sodium borohydride under an atmosphere of nitrogen at room temperature for 2 days. After acidification to pH3 under an atmosphere of nitrogen, the solution was extracted with ethyl acetate. The extract was dried over sodium sulfate and then concentrated to give 45mg of reduction products.

5-2-4 Hydrogenation of the sodium borohydride reduction products over palladium.

A solution of 45mg of the reduction products in 5ml of acetic acid-dioxane (1:1 v/v) containing 20mg of 5% Pd-C was stirred vigorously under hydrogen at room temperature. After 40 hours, palladium charcoal was filtered off, and washed with ethyl acetate and dioxane-water (9:1 v/v) successively. The combined filtrate was diluted with saturated sodium chloride solution and was extracted with ethyl acetate. The ethyl acetate layer dried over sodium sulfate was evaporated to give a light yellow oil.

5-2-5 Treatment of creosol and isoeugenol with formaldehyde.

A solution of 3g of creosol in 30ml of 2N NaOH and 3.5g of formalin (HCHO, 37%) was heated at 165°C for 3 hours. The column chromatation mixture gave 0.53g (16.9%) of V-3. According to the above procedure, treatment of 3g of isoeugenol afforded 0.26g (8.4%) of V-5 as a colorless syrup; MS m/e: 340 (M⁺); NMR (10% in CDCl₃) δ: 1.84

(3H, d, J=6Hz, methyl), 3.81 (1H, s, methylene), 3.84 (3H, s, methoxyl), 5.66 (1H, s, phenolic hydroxyl), 5.92-6.40 (2H, m, olefinic protons), 6.58 - 6.78 (2H, m, aromatic protons). Anal. Calcd. for C₂₁H₂₄O₄: C, 74.09; H, 7.11, Found: C, 74.25; H, 7.24.

5-3. Results and discussion

¹³C NMR spectrum (Fig. 5-2a) of ¹³C labeled condensation products of V-1_b showed intense signals due to the non-labeled aromatic carbons in comparison with that due to ¹³C labeled carbons. This differed markedly from the fact that only the absorptions due to labeled carbons was detectable in the spectrum of the condensation products having about 90% ¹³C content at the benzylic position. A possible explanation is that a part of formaldehyde liberated from side chain polymerized⁵⁴⁾ and a part of it unchanged⁵⁵⁾ without reaction in the reaction solution under the conditions employed here, and therefore these polymerized and unchanged formaldehydes were removed in the course of extraction.

In comparison with the ¹³C NMR spectrum of non-labeled condensation products of V-1a, the ¹³C labeled alkaline condensation products of V-1_b revealed the presence of new signals at 15.6 (1), 16.5 (2), 29.5 (3), 30.7 (4), 32.2 (5), 35.3 (6), 36.2 (7), 38.4 (8), 101.5 (9), 103.6 (10), 105.1 (11) ppm. The highest field absorptions at 15.6 and 16.5 ppm could not be assigned to suitable structures. The next lower field signal at 29.5 ppm was assigned to the methylene carbon of the diphenylmethane derivative V-3 formed from creosol and formaldehyde. As might be expected, the chemical shift (29.4 ppm) of that of the synthetic diphenylmethane derivative V-3 was in good agreement with that (29.5 ppm) of the corresponding carbon described above. On the other had, alkaline degradation of V-1a under conditions used here has given the

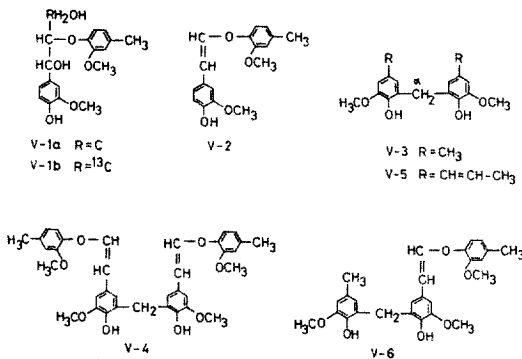
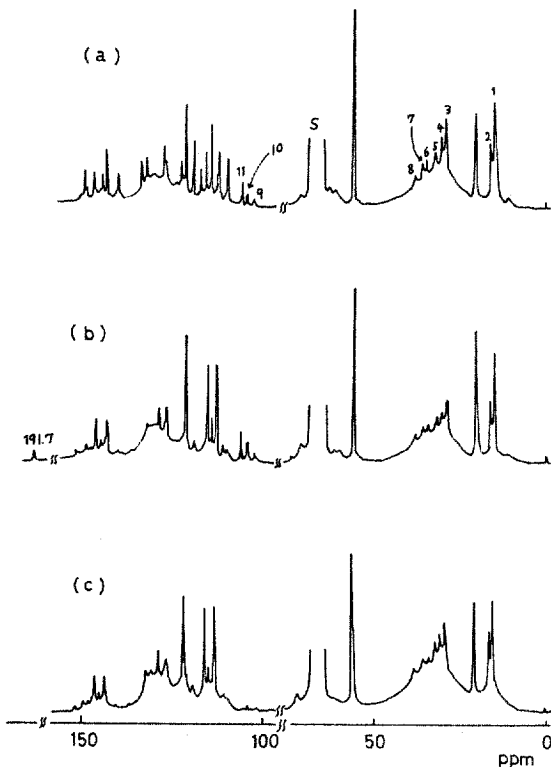


Fig. 5-1

Fig. 5-2 ¹³C NMR spectra of condensation products (a) of V-1b, air oxidation products (b), and hydrogenation products (c).

β -aroxystyrene derivative V-2 (Fig. 5-1) in addition to creosol and, therefore, the signal assigned to the methylene carbon of V-4 with conjugated double bonds in side chain is expected to be in the aliphatic region of the spectrum. Isoeugenol was treated with formaldehyde under alkaline conditions to synthe-

size the compound V-5, which would serve as a model for the assignment of the chemical shift of V-4. In V-5 the signal due to the methylene carbon was located at 33.1 ppm in deuteriochloroform. The absorption at 32.2 ppm was assigned to the corresponding methylene carbon of V-4. The difference in chemical shifts of those of diguaiacylmethan between them can be attributed to the effect of the aryl ether group instead of the methyl group, at the side chain. The synthetic yield of V-3 was about twice higher than that of V-5. The difference between them can be explained by the functional groups at the side chains. By comparison with V-3 and V-4, the signal at 30.7 ppm must be due to the methylene carbon of V-6 derived from creosol and β -aroxystyrene units. No assignable peaks appeared at 35.3, 36.2 and 38.4 ppm.

In the aromatic region, there were three characteristic signals at 101.5, 103.6 and 105.1 ppm. In the extended quinonemethide structures (chapter III) of the diphenylmethane derivatives from vanillyl alcohol the α -carbons resonated at 101.7 and 104.6 ppm. Therefore, these signals must be assigned to the α -carbons of the extended quinonemethide structures V-7, V-8 and V-9, as shown in Fig. 5-3, derived from V-3, V-4 and V-6, respectively, but it was difficult to differentiate among the three. The significant chromophoric structures V-7, V-8 and V-9 would be formed by oxidation of V-3, V-4 and V-6 with remaining oxygen in the reaction solution and/or dehydrogenation⁸⁾ by the effect of the heat.

In the ¹³C NMR spectrum (Fig. 5-2_b) of the air oxidation products of the alkaline condensation material, the signals at 101.5-105.1 ppm increased slightly in intensity.

The air oxidation products were treated with sodium borohydride to support the assignment that the three absorptions in the aromatic region belong to the α -carbons of V-7, V-8 and V-9 as described above. However, these signals in the aromatic

region did not disappear in the spectrum of the sodium borohydride reduction products. The chromophoric units in the air oxidation products was also stable for lithium aluminum hydride and sodium hydrosulfite, indicating that those chromophoric systems V-7, V-8 and V-9 are somewhat more stable than the chromophoric units derived from vanillyl alcohol and guaiacylglycerol- β -aryl ether [α - ^{13}C]. At the next stage of the degradation reaction of these chromophoric systems, the sodium borohydride reduction products were hydrogenated over 5% Pd-C in acetic acid-dioxane (1:1 v/v). The ^{13}C NMR spectrum, as shown in Fig. 5-2C, of the hydrogenation products did not show any absorption at 101.5 to 105.1 ppm as expected, and these signals would shift upfield and would appear at 29.5 to 32.2 ppm in the form of the diphenylmethane structures. The disappearance of the chromophoric systems on charcoal, because on treatment of the sodium borohydride reduction products with charcoal in the same solvent the starting material were recovered.

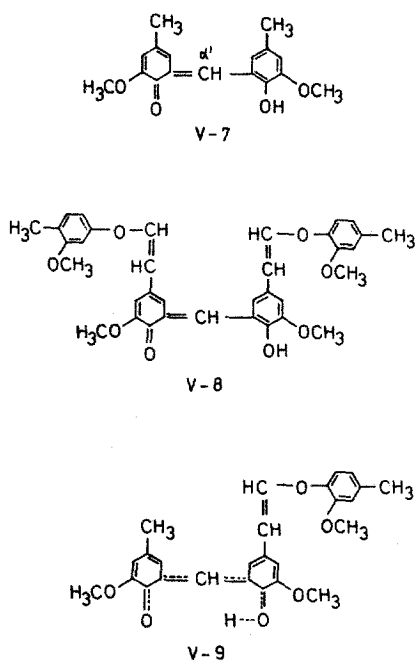


Fig. 5-3

The chromophoric systems with the extended paraquinonemethide units such as galvinoxyl and the products from guaiacylglycerol- β -aryl ether [α - ^{13}C], and/or with the para and ortho quinonemethide units in the equilibrium such as those from vanillyl alcohol was readily reduced with sodium borohydride. Taking this observation into consideration, the extended ortho quinonemethide structures or the chromophoric systems derived from the diphenylmethane derivatives with two phenolic hydroxyl groups at the ortho position would be stable under the milder reduction conditions. In a separate experiment, the color of the sodium borohydride reduced products of the chromophoric material from the synthetic diphenylmethane V-3 was qualitatively brown, but changed to light yellow after catalytic hydrogenation over Pd-C. Nakano et al.^{5),56)} observed by sodium borohydride reduction and methylation that in alkali lignin (Kraft lignin) the contribution of the quinoid structure and lignin-metal chelate to visible light absorption might be 50%. Therefore, the chromophoric systems such as V-7, V-8 and V-9 would contribute to the remaining color of alkali lignin after sodium borohydride reduction, to some extent.

The chromophoric systems such as V-7, V-8 and V-9 would be derived not only from the guaiacylglycerol- β -aryl ether unit as described above, but also from phenylcoumaran, dilignol with $\text{C}_\beta\text{-C}_1$ and pinoresinol structures, which contained free phenolic hydroxyl groups, in alkaline pulping processes.

Chapter VI

Degradation and Subsequent Oxidation Reactions of Phenylcoumaran Structure

6-1. Introduction

It has been known that treatment of a phenylcou-

maran structure, one of the major structural elements in lignin, with sodium hydroxide or white liquor under pulping conditions gave a stilbene derivative after the elimination of the γ -carbon as formaldehyde. If the oxidation of the stilbene derivative in alkaline solution by the action of oxygen or air is carried out as in the case of oxidation, as described in above chapters, of diphenylmethane units to extended quinonemethides, the corresponding quinoid structure should be formed as a chromophoric structure. In fact, a stilbenequinone Q in Fig. 6-1 has been estimated by Gierer⁵⁾ as one of chromophoric systems.

This chapter concerns with the behavior of the alkalipromoted degradation products of the phenylcoumaran toward the action of oxygen or air in alkaline solution in view of chromophoric structures of alkali lignin.

6-2. Experimental

6-2-1 Synthesis of the phenylcoumaran VI-1

The model compound VI-1 was synthesized by the similar procedure of Nakatsubo and Higuchi⁵⁷⁾.

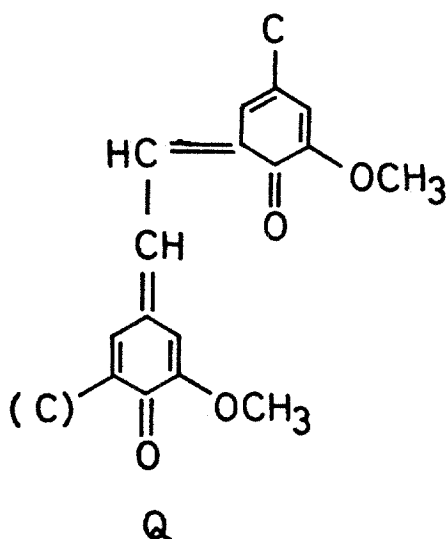


Fig. 6-1

6-2-1-1 Reaction of creosol with allyl bromide.

To a solution of 28.5g of sodium creosolate in 200ml of *N,N*-dimethylformamide (DMF) was added 26.4g of allyl bromide. The mixture was heated at 50°C for 1 hour. The reaction solution was diluted with water and extracted with ethyl acetate. The extract was washed with water, dried over sodium sulfate and evaporated to give 28.4g (94.4% from creosol) of a crude ether VI-2.

6-2-1-2 Rearrangement of the ether VI-2 with *N,N*-dimethylaniline.

A solution of 20.0g of the ether VI-2 in 60ml of *N,N*-dimethylaniline was heated at 190°C for 7 hours. After cooling, the solution was acidified with 1N hydrochloric acid and extracted with benzene. The benzene layer was washed with water, dried over sodium sulfate and evaporated to afford an oil. Chromatography of the oil on silica gel column with acetone-*n*-hexane (1:9 v/v) as eluent gave 17.4g (87.0%) of a phenol VI-3; ¹H NMR (CDCl₃) δ : 2.21 (3H, s), 3.33 (2H, d, *J*=6Hz), 3.78 (3H, s), 4.91 - 5.42 (2H, m), 5.48 (1H, s), 5.72 - 6.16 (1H, m), 6.47 (2H, s). Anal. Calcd. for C₁₁H₁₄O₂: C, 74.13; H, 7.92, Found: C, 74.11; H, 7.93.

6-2-1-3 Benzylation of the phenol VI-3 with benzyl chloride.

A mixture of 16.0g of the phenol VI-3 and 16.0g of benzyl chloride in 50ml of 20% aqueous sodium hydroxide and 320ml of ethanol was refluxed. After 11 hours, the solution was concentrated at reduced pressure up to 60ml of volume and extracted with benzene. A reaction product was purified by means of the column chromatography on silica gel with *n*-hexane to give 21.5g (89.2%) of a benzyl ether VI-4; ¹H NMR (CDCl₃) δ : 2.27 (3H, s), 3.30 (2H, d, *J*=7Hz), 3.80 (3H, s), 4.90 (2H, m), 4.80 - 5.14 (2H, m), 5.64 - 6.06 (1H, m), 6.48 - 6.61 (2H, m), 7.12 - 7.41 (5H, m). Anal.

Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51, Found: C, 80.47; H, 7.50.

6-2-1-4 Oxidation of the benzyl ether VI-4 with osmium tetroxide and sodium metaperiodate.

A solution of 20.4g of the benzyl ether IV-4 and 1.5g of osmium tetroxide in 400ml of dioxane was stirred at 0°C for 15 min. After 120ml of water has been added to the solution, 50g of sodium metaperiodate in 214ml of water was added at 0°C over a period of 30min, and the stirring was continued at room temperature. After 24 hours, precipitates were filtered out, and the filtrate was extracted with ethyl acetate. The extract dried over sodium sulfate was evaporated at reduced pressure to give a crude aldehyde VI-5, which was used in subsequent experiment without purification.

6-2-1-5 Oxidation of the aldehyde VI-5 with the Jones reagent.

To a solution of the aldehyde VI-5 in 250ml of acetone was added 32ml of the Jones reagent (the solution of 1g of chromium trioxide and 5ml of concentrated sulfuric acid in 24ml of water) at 0°C, and the stirring was continued at the same temperature. After 30min, the reaction solution was immediately diluted with saturated sodium chloride solution and extracted with ethyl acetate. The extract was washed with water, dried over sodium sulfate and evaporated to give a yellow oil. Crystallization of the oil from n-hexane-ethyl acetate secured 8.21g (37.7% from IV-4) of a carboxylic acid VI-6; m.p. 101-103°C, IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1700; $^1\text{H NMR}$ (CDCl_3) δ : 2.27 (3H, s), 3.51 (2H, s), 3.82 (3H, s), 4.95 (2H, s), 6.56 (1H, d, J=1Hz), 6.62 (1H, d, J=1Hz), 7.14 - 7.44 (5H, m). Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34, Found: C, 71.26; H, 6.33.

6-2-1-6 Methylation of the carboxylic acid VI-6 with diazomethane.

A solution of 8.01g of the carboxylic acid VI-6 in 50ml of ethyl ether was methylated with excess diazomethane in an usual manner. The resulting product was purified on silica gel column with acetone-n-hexane (1:9 v/v) as eluent to give 8.12g (96.7%) of an ester IV-7; IR $\nu_{\text{max}}^{\text{direct}}$ cm^{-1} : 1635. Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71, Found: 71.96; H, 6.58.

6-2-1-7 Condensation of the ester VI-7 and benzyl vanillin.

To a stirred solution of 2.40ml of diisopropylamine (dried over potassium) in 60ml of dry THF was added 13.2ml of n-butyl lithium in n-hexane (15% solution) at 0°C over a period of 30min under nitrogen. The solution was stirred for 1 hour at the same temperature. After cooling to -73°C, 3.60g of the ester VI-7 in 30ml of dry THF was added over a period of 1 hour, and 2.90g of benzyl vanillin in 30ml of dry THF was added over a period of 2 hours. After 4 hours at the same temperature, the reaction mixture was diluted with saturated sodium chloride, neutralized with 1N hydrochloric acid and then extracted with ethyl acetate. The extract was washed with water, dried over sodium sulfate and evaporated at reduced pressure to give a yellow oil. The pure sample was secured after column chromatography on silica gel using n-hexane-acetone (7:3 v/v) as eluent to give 5.62g (86.5% from bezyl vanillin) of VI-8; $^1\text{H NMR}$ (CDCl_3) δ : 2.27 (3H, s), 3.57 (3H, s), 3.64 (3H, s), 3.74 (3H, s), 4.29 (1H, d, J=11Hz), 4.44 (1H, d, J=8Hz), 4.81 (1H, d, J=11Hz), 5.03 (2H, s), 5.01 - 5.24 (1H, m), 6.47 - 6.78 (5H, m), 7.24 - 7.51 (10H, m). Anal. Calcd. for $C_{33}H_{34}O_7$: C, 73.04; H, 6.32, Found: C, 72.91; H, 6.27.

6-2-1-8 Reduction of VI-8 with lithium aluminum hydride.

To as stirred suspension of 1.44g of lithium aluminum hydride in 180ml of dry THF was added

dropwise 4.80g of the compound VI-8 in 90ml of dry THF at room temperature. After 30min, the excess of lithium aluminum hydride was destroyed with aqueous acetone. The solution was neutralized with 4N hydrochloric acid and extracted with ethyl acetate. The extract dried over sodium sulfate was evaporated to give an colorless oil VI-9, which was used in subsequent experiment without purification.

6-2-1-9 Transformation of the diol VI-9 to VI-1

A suspension of the diol VI-9 and 2.81g of 5% Pd-C in 120ml of methanol was stirred under hydrogen for 2 hours at room temperature. The catalyst was filtered out and the filtrate was evaporated to give a reaction mixture.

A solution of the reaction mixture in 160ml of methylene chloride and 16 drops of boron trifluoride etherate was stirred for 1 hour at room temperature under nitrogen. The solution was then diluted with 5% aqueous sodium carbonate and extracted with ethyl acetate. The extract was washed with water, dried over sodium sulfate and evaporated at reduced pressure. The resulting oil was purified by column chromatography on silica gel with n-hexane-acetone (7:3 v/v) as eluent to afford 1.85g (66.1% from VI-8) of the model compound VI-1; $^1\text{H NMR}$ (CDCl_3) δ : 2.32 (3H, s), 3.44 - 3.98 (3H, m), 3.84 (3H, s), 3.86 (3H, s), 5.51 (1H, d, $J=7\text{Hz}$), 5.68 (1H, s), 6.60 - 6.94 (5H, m); $^{13}\text{C NMR}$ hexadeuteroacetone-heavy water ($\text{An-d}_6\text{-D}_2\text{O}$; 9:1 v/v) δ : 21.1, 54.7, 56.1, 64.4, 87.9, 110.3, 114.0, 115.5, 118.0, 119.1, 129.5, 131.0, 134.3, 144.4, 146.7, Found: C, 68.24; H, 6.31.

6-2-2 Synthesis of the phenylcoumaran [$\alpha\text{-}^{13}\text{C}$] VI-1

A sample of 0.481mg of benzyl vanillin [$\alpha\text{-}^{13}\text{C}$] was transformed into 0.368g (58.6% from benzyl vanillin [$\alpha\text{-}^{13}\text{C}$]) of the phenylcoumaran [$\alpha\text{-}^{13}\text{C}$] VI-1 in the same manner described above.

6-2-3 Alkaline cooking of the non-labeled and labeled VI-1, and subsequent air oxidation of the products.

Reactions were carried out in the same way as described in chapter V.

6-2-4 Isolation of the stilbene VI-10 from the alkali degradation mixture of the non-labeled VI-1

A solution of 0.451g of the non-labeled VI-1 in 15ml of 1N sodium hydroxide was heated as described in chapter V to give a yellow oil, which was subjected to column chromatography on silica gel with n-hexane-acetone (8:2 v/v) to afford 0.360g (90.0%) of VI-10; m.p. 126-128°C; $^1\text{H NMR}$ ($\text{An-d}_6\text{-D}_2\text{O}$ (9:1)) δ : 2.24 (3H, s), 3.79 (3H, s), 3.86 (3H, s), 6.58 - 7.42 (7H, m); $^{13}\text{C NMR}$ ($\text{An-d}_6\text{-D}_2\text{O}$ (9:1)) δ : 21.2, 56.2, 110.1, 111.6, 116.0, 118.8, 120.7, 121.6, 128.9, 129.2, 130.9, 142.4, 147.1, 148.2, 148.6. Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_4$: C, 71.32, H, 6.34, Found: C, 71.26; H, 6.31.

6-2-5 Isolation of the dimer VI-11 from the air oxidation products of VI-10.

A solution of 0.280g of VI-10 in 5ml of 1N sodium hydroxide was vigorously stirred for 8 hours at room temperature under air. The solution was neutralized with 4N hydrochloric acid and extracted with ethyl acetate. The extract was washed with water, dried over sodium sulfate and evaporated to give a red-brown oil. The oil was chromatographed by the procedure described above with n-hexane-acetone (3:1 v/v) to give 0.237g (84.9%) of the dimer VI-11; m.p. 223-224.5°C; $^1\text{H NMR}$ (dioxane- b_8) δ : 2.54 (6H, s), 3.16 - 3.30 (2H, m), 3.58 (6H, s), 3.78 (6H, s), 5.34 (2H, d, $J=4\text{Hz}$), 6.12-6.60 (12H, m); $^{13}\text{C NMR}$ (dioxane- d_8) δ : 21.0, 55.5, 56.1, 86.2, 108.8, 114.8, 115.3, 118.2, 118.4, 128.9, 130.8, 134.7, 144.8, 146.2, 147.4, 147.8; MS m/e: 570 (M^+), 285. Anal. Calcd. for $\text{C}_{34}\text{H}_{34}\text{O}_8$: C, 71.56; H, 6.01, Found: C, 71.55;

H, 6.58.

6-2-6 Alkaline cooking of the phenylcoumaran VI-12 and subsequent air oxidation of the product VI-13.

The phenylcoumaran VI-12 (1.50g) was treated with 1N sodium hydroxide in the same way described above (section 6-2-3) to give cis-and trans-isomers of the stilbene VI-13⁵⁸⁾ (0.961g) in 64.0% yield.

A sample of 0.521g of VI-13 was oxidized with air as in the case of VI-11. The oxidation products were then chromatographed on silica gel with ethyl acetate-n-hexane (1:19 and 1:4 v/v, successively) to afford 0.361g (69.7%) of VI-14 and 0.037g (6.8%) of VI-15. VI-14; ¹H NMR (An-d₆-D₂O (9:1)) δ⁵⁸⁾: 0.95 (3H, 6, J=7Hz), 1.50 - 1.92 (2H, m), 2.38 (3H, s), 2.67 (2H, t, J=7Hz), 3.89 (3H, s), 3.95 (3H, s), 6.66 - 7.39 (5H, m); ¹³C NMR (An-d₆-D₂O (9:1)) δ: 9.6, 14.0, 25.7, 38.9, 56.2, 108.3, 110.1, 110.9, 111.3, 116.1, 120.7, 123.8, 133.6, 138.5, 141.7, 145.3, 147.5, 148.5, 151.8; MS m/e⁵⁸⁾: 326 (M⁺); IR ν_{direct max} cm⁻¹: 3450, 1600, 1510, 1270, 1220, 1145, 1090, 1060. VI-15; ¹H NMR (An-d₆-D₂O (9:1)) δ: 0.94 (3H, t, J=7Hz), 1.50 - 1.84 (2H, m), 1.61 (3H, s), 2.55 (2H, t, J=7Hz), 3.81 (6H, s), 5.12 (1H, s), 6.68 - 7.35 (5H, m); ¹³C NMR (An-d₆-D₂O (9:1)) δ: 14.0, 24.7, 25.6, 38.4, 56.2, 56.4, 94.3, 95.3, 112.6, 114.3, 115.0, 116.1, 121.4, 127.6, 135.0, 136.7, 145.1, 146.1, 146.8, 147.9, MS m/e: 344 (M⁺), 301. Anal. Calcd. for C₂₀H₂₄O₅: C, 69.75, H, 7.02, Found: C, 69.51; H, 7.04.

6-2-7 Dehydration of VI-15 with p-toluenesulfonic acid.

A solution of 2mg of VI-15 in 1ml of dry benzene and 1mg of p-toluenesulfonic acid was stirred at room temperature. After 30min, the solution was washed with water, dried over sodium sulfate and then evaporated to give 1.5mg of VI-14.

6-3. Results and discussion

The phenylcoumaran [α -¹³C] was synthesized from benzyl vanillin [α -¹³C] and the ester VI-7 in 59% yield, by the similar procedure of Nakatsubo and Higuchi⁵⁷⁾.

¹³C NMR spectrum (Fig. 6-2-a) of the reaction mixture, which was prepared by treatment of the non-labeled VI-1 in 1N sodium hydroxide at 165°C for 3 hours, indicated that the mixture composed exclusively of the stilbene VI-10, as shown in Fig. 6-4. In fact, the stilbene VI-10 was isolated in 90% yield from the mixture. During soda and kraft cooks, a phenolic phenylcoumaran model is generally transformed with an accompanying elimination of the γ -methylol group as formaldehyde into a stilbene derivative^{44),45),46)}.

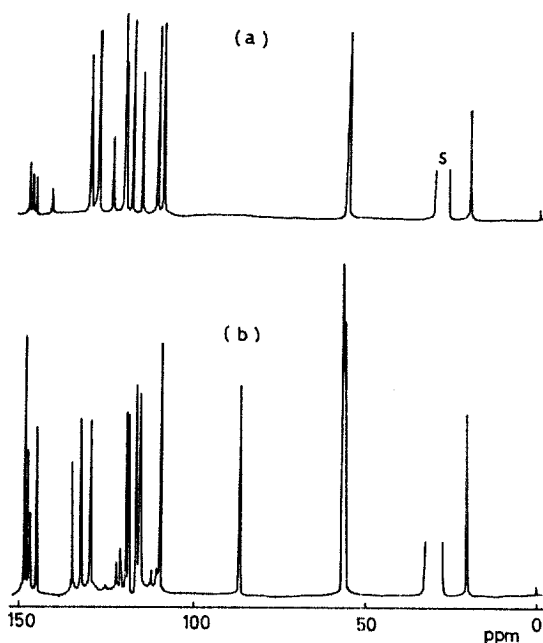


Fig. 6-2 ¹³C NMR spectra of degradation (a) and subsequent oxidation (b) products of non-labeled VI-1.

The alkali-catalyzed degradation products were then oxidized in alkaline solution under air. ¹³C NMR spectrum, as shown in Fig. 6-2-b, of the oxidation mixture was very simple and suggested

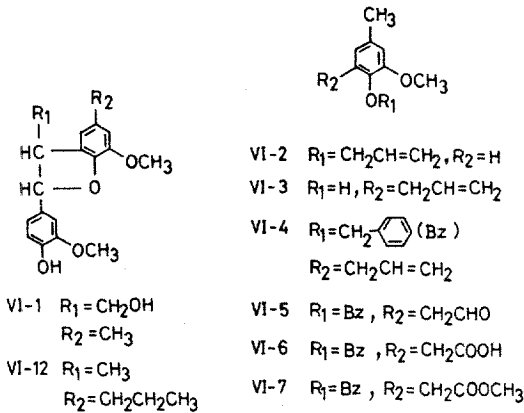


Fig. 6-3

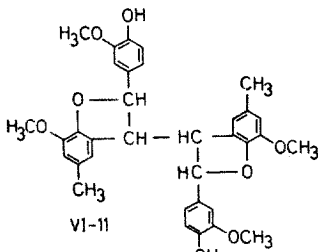
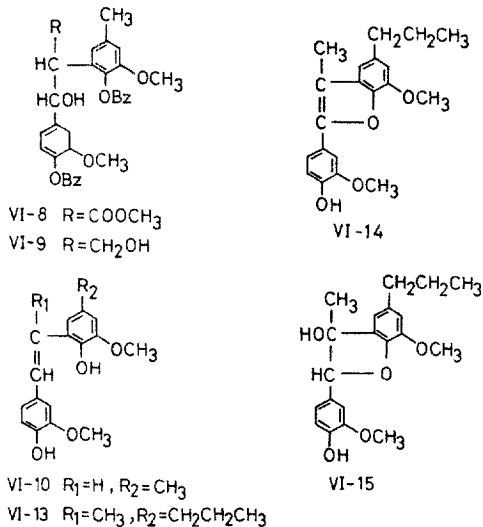


Fig. 6-4

the reproduction of a phenylcoumaran structure. The mass spectrum of the compound VI-11, which was isolated from the mixture in 85% yield, exhibited characteristic peaks at m/e 570 (M^+) and 285, indicating that VI-11 may be a dimer of VI-10.

In ^{13}C NMR spectrum of VI-11, two aliphatic field signals except two resonances at 21.0 and 56.1 ppm due to methyl and methoxyl carbons appeared at 55.5 and 86.2 ppm which were assigned to β - and α -carbons of the side chain, respectively. ^1H NMR spectrum showed a multiplet at δ 3.16 - 3.30 (β -H) and a doublet with coupling constant 4Hz at δ 5.34 (α -H). Therefore, above spectroscopic behaviors suggest that the compound has the structure formed by oxidative dimerization of the stilbene VI-11, as shown in Fig. 6-4.

^{13}C NMR spectrum (Fig. 6-5-a) of the ^{13}C labeled degradation product of VI-1 showed only one intense signal at 129.1 ppm due to the olefinic α -carbon of VI-10. In ^{13}C NMR spectrum of Fig. 6-5-b, the oxidation mixture of the ^{13}C labeled degradation product exhibited intense resonance at 86.1 ppm due to the α -carbon of VI-11 and very weak signal at 87.7 ppm may be due to the α -carbon of the isomer of VI-11. In aromatic region, the low field signal at 129.1 ppm was assigned to the α -carbon of VI-10 which remained unchanged, but any absorption due to the carbon of chromophoric structure, e.g. the quinoid structure Q, was not shown. The signal at 191.6 ppm in the lowest field must be due to the carbonyl carbon of vanillin, which was formed by the oxidative cleavage of the double bond at the side chain.

The outline of reaction mechanisms is summarized in Fig. 6-6. One possible pathway involves the formation of a phenoxide radical 2 from the dianion 1 by the action of molecular oxygen as a one-electron oxidizing agent and further attack of the radical 2 on the double bond at the side chain, leaving a phenylcoumaran- β -radical 3 as an inter-intermediate. Another possibility for the radical formation lies in the reaction of the nucleophilic attack of phenoxide ion 4 (B ring) on the quinonemethide (A ring). Finally, the radical 3 is dimerized, without oxidation to the quinoid structure Q, to form the dimer VI-11.

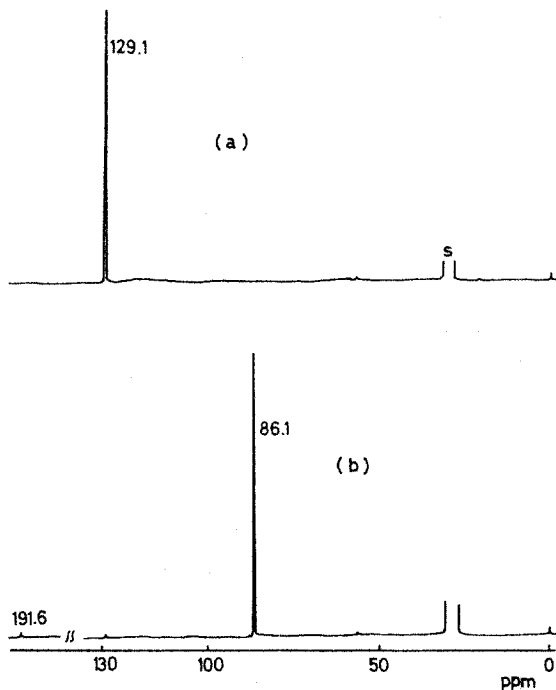


Fig. 6-5 ^{13}C NMR spectra of degradation (a) and subsequent oxidation (b) products of ^{13}C labeled VI-1.

Formation of the small amount of vanillin is interpreted in terms of oxidation and subsequent degradation of 1 following a route analogous to those of an aroxystyrene⁵⁹⁾.

On the other hand, in the case of the stilbene VI-13 formed after the alkali-promoted degradation of the phenylcoumaran VI-12 with a methyl group at the γ -position of the side chain, the air oxidation of VI-13 afforded the phenylcoumarone VI-14⁵⁸⁾ as a main product and the diol VI-15. The chemical structure of VI-15 was determined as shown in Fig. 6-4, in comparison with spectroscopic data of VI-12. This was further supported from the fact that dehydration of the diol VI-15 with *p*-toluenesulfonic acid had given the phenylcoumarone VI-14 in good yield. The formation of the compound VI-15 may be explained by assuming that oxidation of VI-13 to an epoxide occurs which is followed by opening of the epoxide and subsequent cyclization, as shown in Fig. 6-7.

Accordingly, the stilbene structure which was

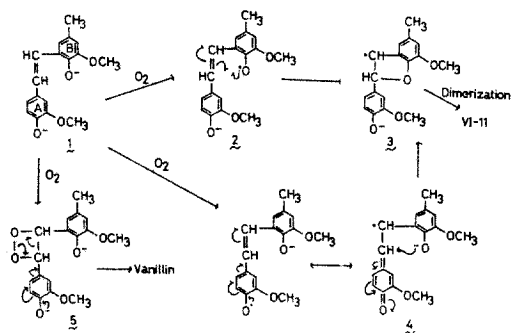


Fig. 6-6 Formation mechanism of reaction products.

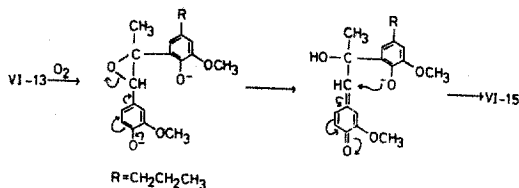


Fig. 6-7 Formation mechanism of VI-15.

produced from the phenylcoumaran unit during alkali pulping processes may be stabilized with accompanying reproduction of the phenylcoumaran from the phenylcoumaran- β -radical. However, a *p,p'*-dihydroxystilbene structure has readily been oxidized with Fetizon reagent, composed of celite and silver carbonate, to a corresponding quinoid compound⁶⁰⁾, indicating a little possibility of transformation of the stilbene derivative into the quinoid structure in the presence of heavy metals. Red-brown color of the oxidation mixture appeared in this experiment may be attributed to catechol units which were introduced by the hydroxylation of aromatic nuclei and by the degradation of methoxy groups, radicals and/or the diphenylmethane structure, as described in chapter V, which were formed by the condensation of formaldehyde and aromatic nuclei.

Chapter VII

Conclusion

To investigate lignin reaction sequences and the formation of the chromophoric structures taking place during the alkaline pulping, vanillyl alcohol, vanillyl alcohol [α - ^{13}C], guaiacyl-glycerol- β aryl ether [γ - ^{13}C] guaiacylglycerol- β -aryl ether [γ - ^{13}C] and phenylcoumaran, as lignin model compounds, were treated with 1N sodium hydroxide at 165°C for 1.5 - 3 hrs in a sealed tube under nitrogen. The products in alkaline media were then oxidized in air with vigorous stirring for 8 hrs at room temperature. From the chemical structures of the isolated products and ^{13}C NMR spectra of the reaction mixtures, the following conclusion was obtained;

1) Alkali-catalyzed condensation of vanillyl alcohol gave five compounds of II-1, II-2, II-3, II-4 and II-5 thought to be the intermediates of the chromophoric structures.

2) On treatment with alkali followed by air oxidation, vanillyl alcohol afforded the colored material. ^{13}C NMR spectrum of the mixture did not show any absorptions assigned to the carbons of chromophoric structures, but gave the valuable information on the chemical structures of the condensation products. The colored material specifically labeled by ^{13}C at the benzylic position was prepared by alkali treatment of vanillyl alcohol [α - ^{13}C] followed by air oxidation, and ^{13}C NMR spectra of the mixture exhibited absorptions at 101.7 and 104.6 ppm due to the carbons of quinonemethide structures, indicating that the quinonemethide unit would be one of the important types of chromophore in which the benzylic carbon of vanillyl alcohol was included.

3) Treatment of guaiacylglycerol- γ -aryl ether with alkali gave the mixture composed mainly of the β -aroxystyrene derivative IV-3a, which was

formed by liberation of the hydroxymethyl group at γ -position, and on air oxidation in the alkaline media the mixture IV-7 yielded the dark oil having vanillin and creosol as main products. ^{13}C NMR spectra of the non-oxidized and oxidized mixtures, which were labeled with ^{13}C at the benzylic position, revealed the presence of the diphenylmethane derivatives in addition to various degradation and condensation products and of the chromophoric structures IV-15 and/or IV-16 in the oxidation products.

4) On alkaline treatment of guaiacylglycerol- β -aryl ether [γ - ^{13}C] V-1b, creosol, the β -aroxystilbene derivative V-2 and other phenolic degradation products attached on formaldehyde formed by cleavage between β and γ carbons of the side chain, followed by condensation to afford various condensation products. The products contained at least three diphenylmethane derivatives V-3, V-4 and V-6.

From ^{13}C NMR spectra, these diphenylmethane derivatives were found to be transformed by air oxidation into the corresponding ortho-quinonemethide derivatives V-7, V-8 and V-9, indicating that the latter derivatives were important chromophoric structures in which the terminal carbon of the side chain of V-1b was included. The chromophoric systems were stable for sodium borohydride reduction, but readily hydrogenated over palladium catalyst.

5) On treatment of the phenylcoumaran [α - ^{13}C] in alkaline solution, the stilbene derivative was formed in quantitative yield after the elimination of the γ -carbon as formaldehyde. The degradation product, i.e. the stilbene derivative gave the dimer VI-11 in almost quantitative yield by air oxidation. In the ^{13}C NMR spectrum of the air oxidized reaction mixture, the weak peak due to the olefinic carbon of the stilbene derivative and the intense signal due to α -carbon of the dimer appeared at 129.1 and 86.1 ppm, respectively, but any

absorptions assigned to the carbon of chromophoric structures were not shown in aromatic region. This means that by air oxidation the stilbene derivative is dimerized in preference to oxidation to the corresponding extended quinone structure.

In alkaline pulping, complicated sequence of reactions leading to chromophoric structures essentially same as those revealed by these model experiments is considered to take place.

Acknowledgement

I tender my sincere and respectful thanks to Professor N. Terashima and Associate professor S. Yasuda of the Department of Forest Products, University of Nagoya, for their kind supervision and valuable advice.

I am deeply grateful to Dr. H. Kawakami and Dr. T. Fukuda for their helpful advice and constructive criticism.

Finally, I am also thankful to Emeritus Professor T. Kanda of Nagoya University, Mr. S. Kitamura, Miss. M. Ohnuki and all members of the Laboratory of Chemistry of Forest Products, Faculty of Agriculture, University of Nagoya, for their help and cooperation.

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