

바닐릴 알콜 縮合生成물의 同定*¹尹 炳 虎*²Identification of Condensation Products from Vanillyl Alcohol*¹Byung Ho Yoon*²

알카리 리그닌의 着色構造를 確實히 하기 爲하여 리그닌 모델 化合物인 바닐릴알콜을 室素下에 알카리로 處理하였다. 그림-1과 같이 α -1結合인 化合物 I., α -1와 α -5의 結合 構造인 化合物 II, III, IV와 α -5結合 構造인 化合物 V를 單離·同定하였다. 이들 化合物은 空氣酸化 및 알카리 處理에 依해 着色되었다.

INTRODUCTION

The exact nature of the color causing structures of alkaline lignin is uncertain, but CH=CH double bonds conjugated with the aromatic ring and quinone methides and quinone which also may serve as the oxidative species creating further chromophores structures are likely to contribute the color of alkaline lignin.

The well known darkbrown color of alkaline lignin was the subjected investigations.

Rothenberg and Luner¹⁾ reported that quinone methide, the oxidated products of diguaiacylmethane and P-benzoquinone isolated from vanillyl alcohol treated with alkaline solution caused to color. The other hand, 伊藤 K. Iiyama²⁾ has studied the condensation structure given from vanillyl alcohol and the nature of its polymer causing to color in air. In general it has been known that products of treated with alkaline solution in nitrogen turned to dark brown color on contact of air. This means that it gives the active structure of intermediate and quinone type structure changing to coloring structure. But little is known about the chemical nature of the coloring causing structure of the alkaline lignin itself.

This paper is discussed the products given by alkaline treatment of vanillyl alcohol in nitrogen to clear coloring structure of alkaline lignin.

EXPERIMENTAL

one point two three gr. of vanillyl alcohol was dissolved in 35ml solution involved 3.5g sodiumhydroxide. It was refluxed for 18 hrs. and acidified at pH5 by 2N-HCl in nitrogen.

Reaction solution was extracted by ethylacetate and evaporated. This reaction mixture was eluted by n-Hexane-Ethylacetate on silica gel chromatography. Fragments isolated were compound I(146mg), II(304 mg), III(128mg), IV(66mg) and V(36mg).

RESULT AND DISCUSSION

COMPOUND I.

All of these fragments were acetylated with anhydrous acetic acid and pyridine. IR spectra of those acetates are shown a very strong band near 1760cm^{-1} originated from carbonyl adsorption. Therefore, all of the compounds indicated to contain phenolic hydroxyl groups.

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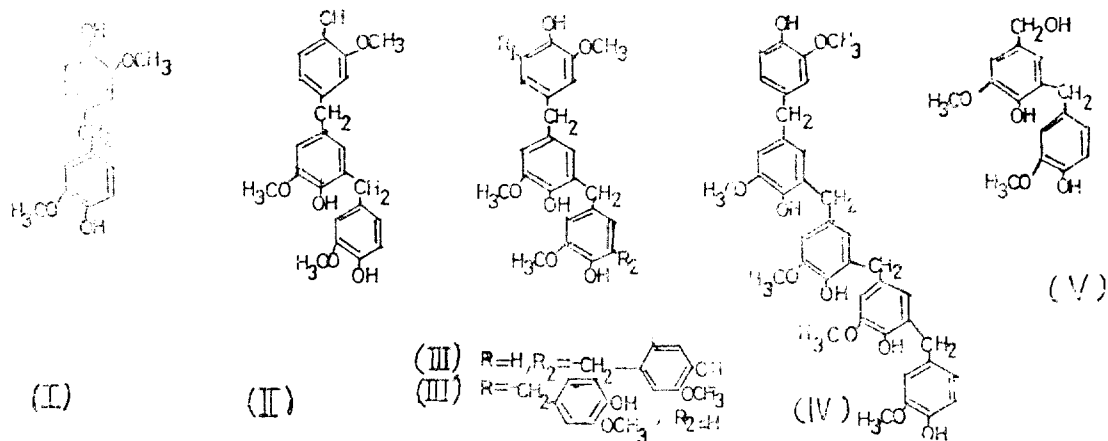


Fig. 1. Compounds isolated from vanillyl alcohol treated with alkaline solution

Mass spectrum of compound I had molecular ion at 260. The compound indicated to be eliminated two hydroxylmethylene from vanillyl alcohol of two molecule. m/e 229 was a cation given by demethylation and m/e 137 was a cation occurred by elimination of guaiacol radical. m/e 124 was a peak given by loss of benzyl type structure and it was shown as a guaiacol. In NMR spectrum of compound in $CDCl_3(\delta)$. 8 protons containing 2 methoxyl groups and one methylene group were resonated at 3.72 and aromatic ring resonance was 5.36 and 6.40-6.81. The compound was coincided with diguaiacyl methane, bp. 109 reported by I. A. Pearl³⁾.

COMPOUND II.

Mass spectrum of compound II had molecular ion 396. The compound had more equivalent weight 136 than compound I. It means that the compound II

were added guaiacyl methylene to compound I. m/e 272 was a ion peak shown by loss of guaiacyl from molecular ion and m/e 259 was accounted for a cation occurred by dissolving of benzylum radical. In NMR spectra of compound II in $CDCl_3(\delta)$, 3.69 and 3.72 are assigned as 13 protons including three methoxyl and two methylene groups. The signal at 6.26 to 6.31 and 5.47 were three protons of phenolic hydroxyl group. As the identified above, compound II are illustrated 1,4-dibenzyl benzene type structure as shown in II of Fig. 1. The compound are reported by Nakano⁴⁾ in terms of treatment of methanol and alkaline solution from vanillyl alcohol.

COMPOUND III.

In mass spectrum of compound III as shown in Fig. 2, molecular ion was 532. The compound had more molecular ion 136 than compound II. The compound

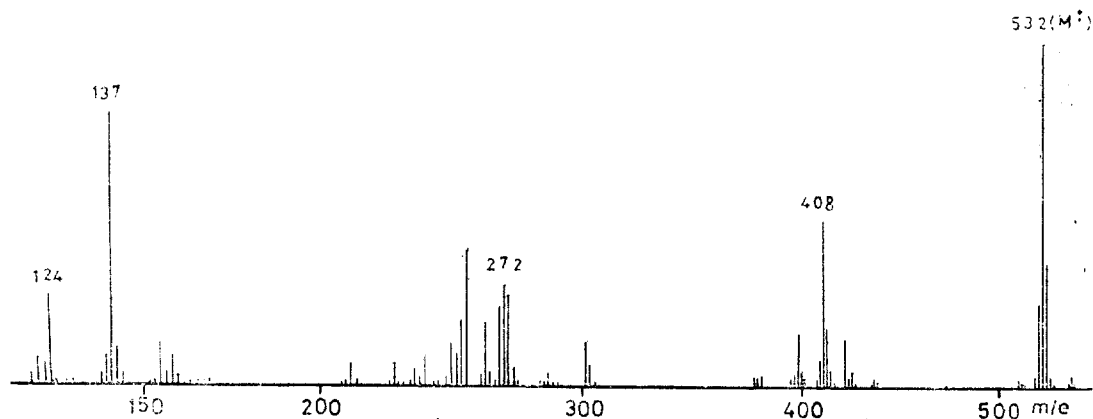


Fig. 2. Mass spectrum of compound III.

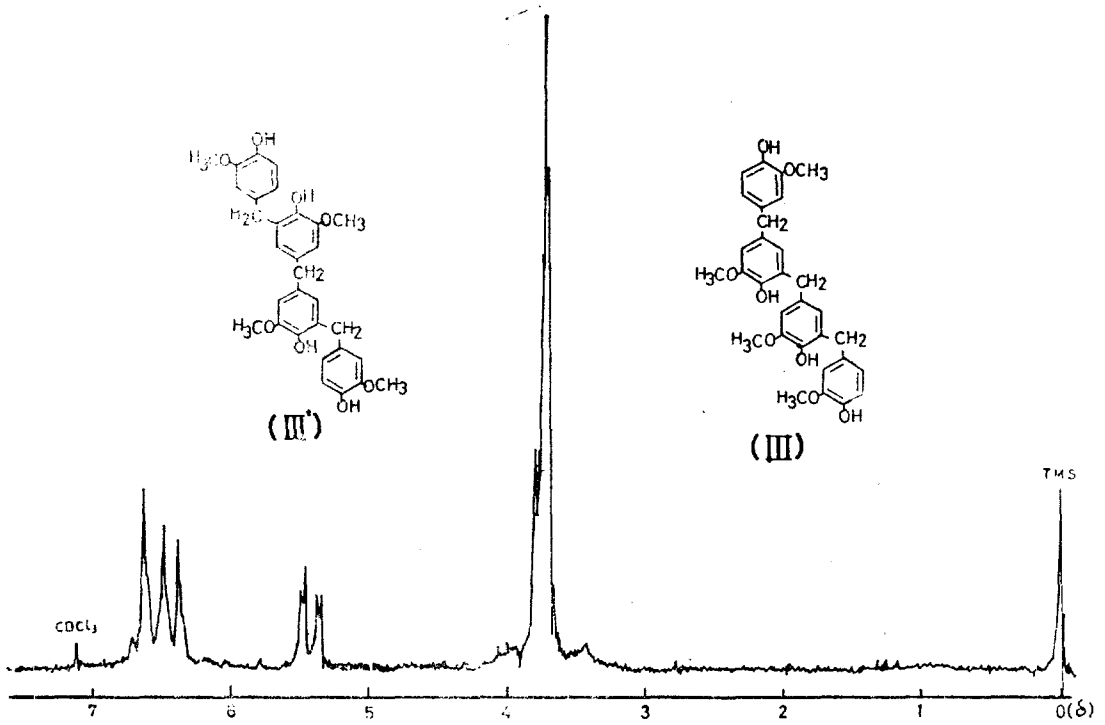


Fig. 3 NMR spectrum of compound III.

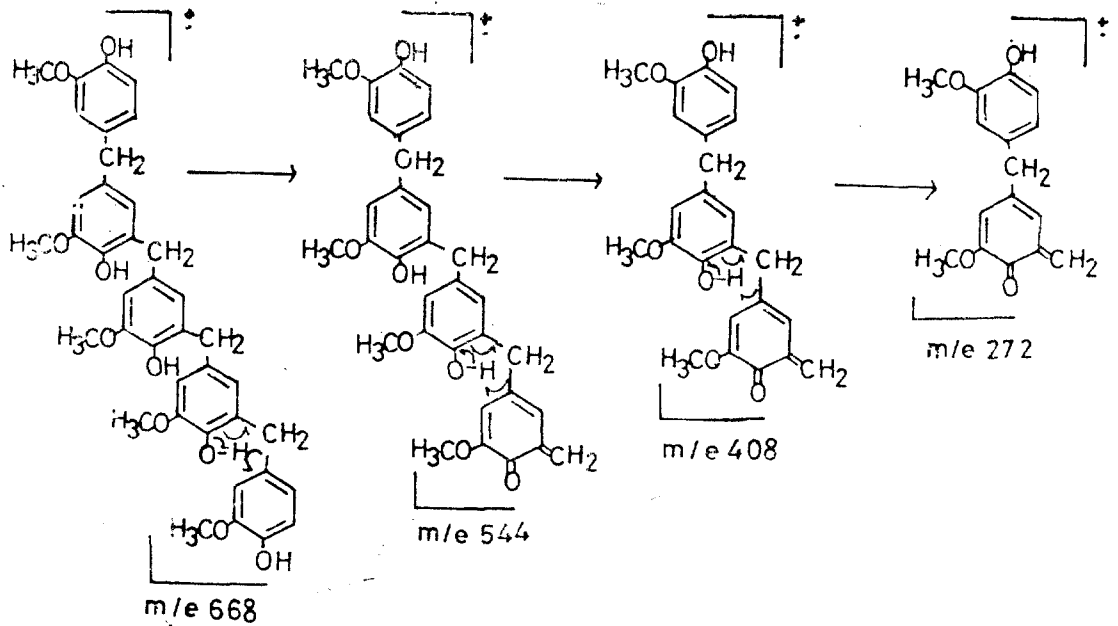


Fig. 4. Fragmentation pattern of compound IV.

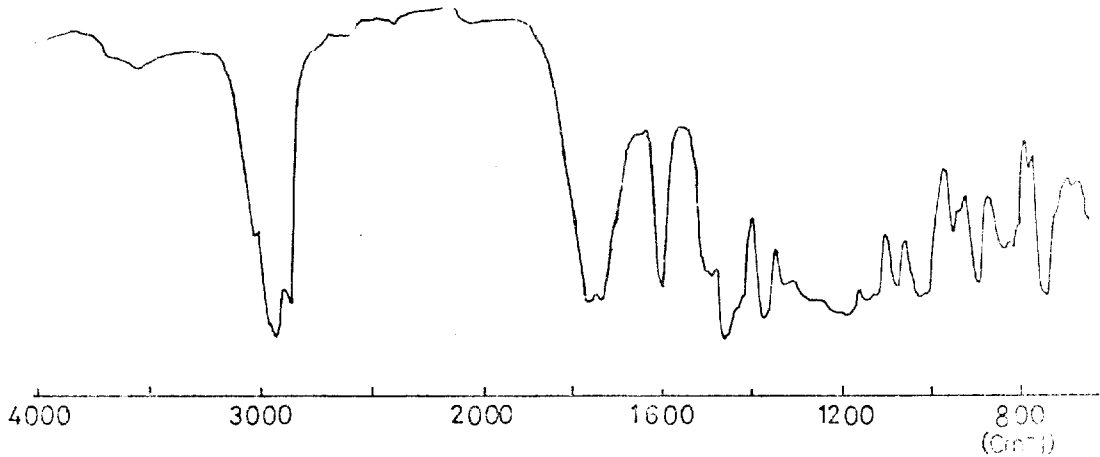


Fig. 5. IR spectrum of the acetylated compound of V.

is indicated that benzyl type structure was added to compound II. 408 ion peak was given by loss of guaiacol molecule from compound III, and 272 ion was given by elimination of benzyl units from 408 ion.

NMR spectrum of compound III was exhibited in Fig. 3 and the peaks are assigned as follows: $\delta(\text{CDCl}_3)$ ppm; 6.19–6.60 (10H, siglet, aromatic), 3.7 and 3.62 (18H, 4 methoxyl and 3 methylene), 5.28, 5.31, 5.39, 5.41 (4H, phenolic hydroxyl).

The structure of compound III can be supposed to be III or III' as shown in Fig. 1. Suggesting the compound is compound III, it will have two signals as a 4 phenolic hydroxy protons in comparison to compound I and II. Having four signals, the compound can be determined as a compound III.

COMPOUND IV.

NMR spectrum of the compound are assigned as the following: $\delta(\text{CDCl}_3)$ ppm; 3.6–3.7 (23H, methoxyl and methylene), 5.35–5.42 (5H, phenolic hydroxyl), 6.26–6.72 (11H, aromatic). Mass m/e : 668 (M^+), 544 ($M-124$), 408 and 272. The compound I to IV had very similar fragmentation patterns each other. Its fragmentation pattern is shown in Fig. 4.

COMPOUND V.

Compound V was acetylated by the same method as the compound 1. IR spectrum of its acetate as shown in Fig. 5 gives two infrared bands near 1760 cm^{-1} and 1730 cm^{-1} that are the positions of phenolic and alcoholic hydroxyl position substituted by acetyl group. Mass spectrum of compound V gives

molecular ion 290. It was suggested that occurred by elimination of one molecular of H_2O from two molecular of vanillyl alcohol. 166 (M -guaiacol), 124. NMR spectrum of compound V acetylated was assigned as following: $\delta(\text{CDCl}_3)$; 6.40–6.8 (5H, aromatic), 2.00 (3H, acetyl group substituted to alcoholic hydroxyl group), 2.16, 2.19 (6H, acetyl group substituted phenolic hydroxyl group), 4.82 (2H, siglet hydroxymethylene) and 3.60, 3.40 (10H, 2 methoxyl and methylene of benzyl).

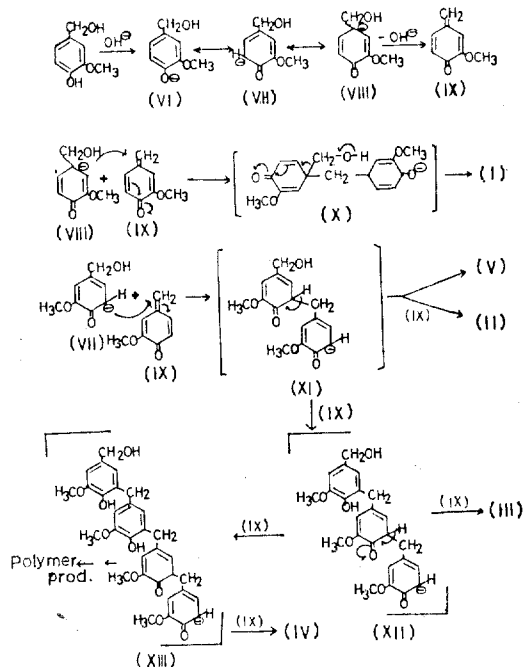


Fig. 6. Condensation mechanism of vanillyl alcohol in alkaline solution.

Condensation mechanism of vanillyl alcohol in alkaline solution are summarised in Fig. 6.

Vanillin in alkaline solution was proceeded by means of electron transfer and formed resonance-stabilised structure VIII to V. Proceedingly methylene quinone (IX) was given by loss of hydroxyl group from these. Quinone methide (IX) forming dimer intermediate was attacked to anion of structure VIII. Compound I was formed by deformatdehyde of intermediate X. IX. It becomes to be compound V by electron rearrangement. Compound II is formed by adding intermediate (XI) to compound I, compound III and IV are given by the same reaction mechanism of compound II.

Polymerization will be given arising to the same mechanism as the identified products before in order.

As described above, the reaction products yielded by alkaline treatment in nitrogen have α -1 bond structure of compound I, α -1 and α -5 bond structure of compound II, III, IV and α -1 bond structure of compound V. All of these five compounds isolated

caused to color by the oxidation of air and alkaline treatment and compounds. These color will be discussed forwards.

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