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ON THE PINORESINOL TYPE OF STRUCTURAL UNITS IN LIGNIN

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Recent publications dealing with the isolation of *dl*-pinoresinol or *dl*-syringaresinol from acidolysis products of wood lignin by K.Freudenberg ¹⁾ and H.Nimz,²⁾ prompt us to report our results which also prove the presence of *dl*-pinoresinol-type structures in protolignin molecules through a different method.

Prior to the present paper, it has previously been reported by the authors that on the nitric acid oxidation of the ethanol-lignins prepared from several kinds of woods, di-γ-lactone of α,β-bis-(hydroxymethyl)-succinic acid (III) was detected by a thin layer chromatography.³⁾

We have now succeded in isolating the di-γ-lactone in a crystalline form.

Nitric acid oxidations of acetic acid-, dioxane-, and milled wood-lignins prepared from sugi-, red pine-, and white birch-woods were performed under the conditions described previously³⁾ and a spot of di-γ-lactone was similarly found on TLC of each degradation product. On a larger scale oxidation, sugi-dioxane-lignin afforded a crystalline compound as one of the oxidation products through a purification with silica gel column chromatography.

This had $[\alpha]_D^{20°} = 0°$(in $CHCl_3$) and m.p. 158-158.5°C, which corresponded to those of (*dl*) *cis* di-γ-lactone. Elementary analysis : C, 50.71 H, 4.44 (required for $C_6H_6O_4$: C, 50.51 H, 4.26)

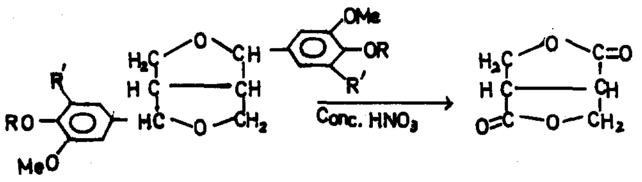
Yield : 0.5% based on the original lignin.

IR spectrum of this compound was almost identical with that of (*l*) *cis* di-γ-lactone prepared from symplocosigenol.

And further, comparison of TLC and GLC of both di-γ-lactones established that the di-γ-lactone obtained was identical with (*dl*) *cis* di-γ-lactone. Since the di-γ-lactone is known to be derived from a condensed tetrahydrofuran ring such as a series of lignan molecules, pinoresinol- and its analogous structures should also exist as *dl*-form in protolignin molecules.

FIG. 1

Nitric acid oxidation of pinoresinol-type structures



(1) R,R'=H	pinoresinol(*d*-, *dl*-) symplocosigenol(*l*-epi-)	di-γ-lactone of α,β-bis-(hydroxymethyl)-succinic acid
(11) R=H, R'=OMe	syringaresinol(*dl*-)	(*d*-, *l*-, and *dl*-)

The precise estimation of the amounts of pinoresinol-type structures in lignin failed, because yield of the di-γ-lactone mainly depends upon the stereochemical features of the original materials and upon its oxidation conditions.[4]

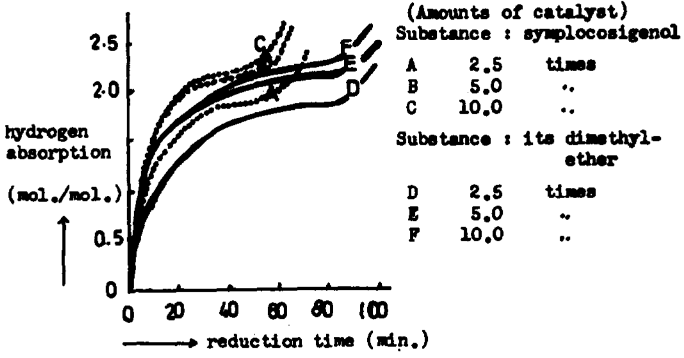
The behaviors of model substances and sugi-dioxane-lignin were examined on catalytic hydrogenation in order to further confirm the presence of pinoresinol-type structures and to estimate their amounts in lignin molecules.

K.Weingnes,5) R.D.Haworth and D.Woodcoch 6) have revealed that d-pinoresinol or its dimethylether is readily subjected to hydrogenolysis with formation of d-lariciresinol and l-seco-isolariciresinol or their corresponding dimethylethers on the catalytic hydrogenation. Therefore, it was presumed that on the nitric acid oxidation of these hydrogenolysis products, di-γ-lactone wouldn't be formed. Now, this assumption has been checked through the following experiment : hydrogenations were carried out in 95% aqueous acetic acid solution, at room temperature and atmospheric pressure with semi-micro apparatus.

Symplocosigenol and its dimethylether were selected as model substances and a catalyst of $PdCl_2$-$BaSO_4$(5% $PdCl_2$) prepared by the method of E.Adler and J.Marton 7) was used on the various amounts. Hydrogenation products were oxidised with conc. nitric acid, and their degradation products were examined through TLC as reported previously.

FIG. 11

Hydrogen absorption curves of model substances



Each hydrogen absorption curve of model substances revealed the existence of an equilibrium state during a period of 40~50 min. or 80~90 min. as shown in FIG. 11. On the other hand, the investigation with TLC showed that such reaction products as absorbed more than 2.0(mol./mol.) hydrogen to these plateaus did not yield the di-γ-lactone on the nitric acid oxidations.

Furthermore, it was also noted that the hydrogen consumptions after these plateaus did not directly affected the presence or absence of di-γ-lactone. The assumption mentioned before was supported with these results.

In the case of sugi-dioxane-lignin, except that the larger amounts of catalyst were charged, the procedures of the hydrogenation were almost similar to those used on the model substances.

Because, the reaction rate of the lignin polymer was expected to proceed more slowly in such a catalytic hydrogenation experiment as required the contacting role of catalyst. Therefore, the catalysts were used over 5 times the weight of the original lignin.

It was not surprising that several plateaus were observed in the hydrogenation curves of sugi-dioxane-lignin. But, their reproducibility was not good except in the first stages of the reaction. However, they became better with increase of the rates of hydrogen consumption. And, the inflections became less visible as those shown in FIG. 111. The experiment using TLC on the nitric acid oxidation products of the hydrogenated lignin, indicated that the amounts of di-γ-lactone rapidly decreased after a period of 60~70 min. and afterwords, the spot became almost constant while it could hardly be discernible. However, the di-γ-lactone did not completely disappeared even though the reaction time was prolonged to 24 hr., the amount of catalyst was increased to 20 times by the weight of lignin and hydrogen consumption amounted to 0.67(mol./OMe.) as shown in FIG. 111.

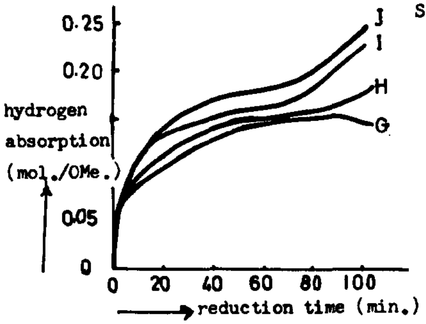
(It should also be noted that the hydrogen consumption did not stopped at a period of 24 hr. under these conditions.)

However, the most of the tetrahydrofuran rings of pinoresinol-type units in lignin would be hydrogenolysed before the first inflection and the consumptions of hydrogen after the inflection would not directly contribute to such a ring-opening reaction as recognized in model experiments. Increase of the rates of hydrogen consumption made the first inflection obscure and made the hydrogen consumption values at this time increase gradually.

These should be explained by an assumption that the increase of the catalyst mainly prompted the other reaction from the ring-opening and so that the hydrogen consumption owing to them increased even before the first inflection.

FIG. 111

Hydrogen absorption curves of sugi-dioxane-lignin



(Amounts of catalyst)

Substance : sugi-dioxane-lignin

G	5.0	times
H	10.0	"
I	15.0	"
J	20.0	"

However, the ethylenic, benzyl-aryl ether and a part of carbonyl linkages in lignin would also be hydrogenated in the first stage of the reaction.

Thus, it should be pointed out that the amounts of pinoresinol-type structures in sugi-dioxane-lignin were less than 0.15∼0.16(mol./OMe.) corresponded to the hydrogen consumption after a period of 50∼60 min. as shown in curve H in FIG. 111.

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