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Cleavage of  $\beta$ -Aryl Ether Bonds in Lignin  
by Trimethylsilyl Iodide

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ABSTRACT

Trimethylsilyl iodide (TMSiI) is a novel reagent to cleave ether bonds selectively under very mild reaction conditions. The authors applied the reagent for the cleavage of the arylglycerol- $\beta$ -aryl ether bond using a guaiacylglycerol- $\beta$ -guaiacylether as a model compound. Under the optimum conditions, the above ether bond was cleaved almost quantitatively, and the reaction mechanism turned out not to be direct cleavage proposed by Jung et al., but to be the iodination of the benzyl carbon followed by the formation of a  $\alpha$ - $\beta$  double bond and the cleavage of the  $\beta$ -aryl ether bond.

It was also found that TMSiI reagent is able to depolymerize a milled wood lignin very effectively to a range of Mw 400-800.

INTRODUCTION

As is well known, lignin is a polymeric substance of phenylpropane structural units, namely syringyl, guaiacyl and *p*-hydroxyphenyl units for hardwood lignin and the latter two units for softwood lignin. Those units are bound together by several kinds of ether and carbon-carbon bonds without any practical regularity.

Thus, the chemical structure of lignin becomes extremely complicated and difficult to be simply visualized. In other words, most of the structural information on lignin provides only the average features of chemical structures.

Furthermore, the structural inhomogeneities of lignin in different morphological regions of the cell wall which were first indicated by Goring<sup>1)</sup> using UV-microscopy, brought about a new difficulty in preparing a representative lignin sample. That is, Bjorkman's milled wood lignin (MWL) may not be a good lignin sample representative of the whole natural lignin because of its considerably low yield. The authors<sup>2)</sup> have characterized MWLs sequentially extracted from birch wood meal and concluded that a MWL, especially extracted at the initial stage of milling, mainly originated from the compound middle lamella region. By the way, it is interesting to note that the origin of softwood MWL was reported to be secondary wall lignin by Whiting et al.<sup>3,4,5)</sup> depending on the comparison of the solubilities and chemical reactivities between MWL and gravimetrically separated lignin rich fractions.

Based on the UV-microscopic analysis, Goring et al.<sup>1)</sup> pointed out that the ratio of guaiacyl to syringyl structural units in hardwood lignin varies remarkably among the different cell wall regions, namely secondary wall,

middle lamella and cell corner. The syringyl units are rich in the secondary wall lignin whereas the lignin at the compound middle lamella and cell corner are mostly composed of guaiacyl units.

Concerning the nature of the compound middle lamella lignin, the authors have been trying to characterize the lignin in the differentiating xylem which has an extremely thin cell wall and is mainly composed of compound middle lamella. It is of great interest to note that the initially deposited lignin in the differentiating xylem has a highly condensed and guaiacyl rich nature. This is in agreement with Goring's earlier results. Terashima et al.<sup>6)</sup> have also reported the similar nature of hardwood compound middle lamella lignin based on the incorporation of 14-C labelled lignin precursors at the cambium of two different hardwood species. Of course, it is not possible at this moment to discuss whether the secondary wall lignin in hardwood is composed of a homogeneous mixture of syringyl and guaiacyl units or of syringyl-rich and guaiacyl-rich fractions. It is also very difficult to distinguish the exact nature of middle lamella, primary wall and outer layer of secondary wall(S1).

As mentioned before, lignin structural units are bound together with ether and carbon-carbon bonds. The distributions of each bond in lignin have been another

interesting target for lignin chemists, but have not yet been visualized exactly. Quantitative information on each bonding structure, at this time, is only available by the degradation of lignin using alkaline nitrobenzene oxidation and permanganate oxidation.  $^{13}\text{-C}$  NMR spectroscopy has recently improved quite remarkably, but is only semi-quantitative, although it is sure to be a most reliable method in the near future. It also must be kept in mind that structural information from degradation reactions or spectroscopic methods represent the average nature of lignin.

The main purpose of this study is to develop a new method to visualize the real distribution of carbon-carbon bonds in lignin. Trimethylsilyl iodide was found by Jung et al.<sup>8)</sup> to be a very selective reagent to cleave various kinds of ether bonds. The authors applied this reagent to a lignin model compound, guaiacylglycerol- $\beta$ -guaiacylether, to see the reactivity, the selectivity and the reaction mechanism of this reagent to the above mentioned type structural units in lignin.

## EXPERIMENT

### Sample

Guaiacylglycerol- $\beta$ -guaiacylether, threo form (GG)<sup>9)</sup> was used as a lignin model compound. A MWL was prepared

from birch wood meal according to Bjorkman's method.<sup>10)</sup>  
Yield of MWL was 19.7% based on Klason lignin content.

#### Trimethylsilyl iodide treatment

Trimethylsilyl iodide (TMSiI) was purchased from Aldrich Chemical Co., U.S.A. and was stored in a refrigerator.

a) TMSiI treatment of GG: A one milliliter of chloroform solution containing 10 mg of GG (0.03 mmole) was sealed in a glass tube with a plastic cap and cooled in a cold bath maintained at 0°C for 5 min. A 10-300  $\mu$ l of TMSiI reagent (0.07-2.19 mmole) was added quickly to the above solution which was then kept in the same cold bath for 0.5-20 hr with gentle stirring. The reaction was terminated by the addition of a small amount (5 ml) of water containing about 5% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The reaction products were extracted with chloroform exhaustively (4x30ml) and analyzed by the use of TLC, HPLC, GLC and GC-MS. For GLC and GC-MS analyses, 2,6-di-t-butyl-p-cresol was used as the internal standard.

b) TMSiI treatment of NaBH<sub>4</sub> reduced MWL: A birch wood MWL(500mg) was reduced with NaBH<sub>4</sub> (500mg) in 0.05 N-NaOH solution for about 300 hr under nitrogen atmosphere. The reduced MWL precipitated on acidification was collected quantitatively by the centrifugation. A sample of reduced MWL(100mg) suspended in 10ml chloroform was kept in a 0 °C cold bath, and TMSiI reagent(500  $\mu$ l) was added

quickly. The mixture was kept in the cold bath for 3hr with gentle stirring. The reaction was terminated by the addition of a small amount (5 ml) of water containing  $\text{Na}_2\text{S}_2\text{O}_3$ . TMSiI treated MWL immediately precipitated out in the chloroform-water system was collected and washed with water by centrifugation.

A TMSiI treated MWL was acetylated with acetic anhydride-pyridine for one day at room temperature. The molecular weight distribution of the acetylated TMSiI treated MWL was studied by a Sephadex LH-60 column (2.5cm x 44cm) using chloroform as the eluent.

#### Instrumental Analyses of Reaction Products

Silica-gel TLC was conducted using benzene/ethylacetate =10/2 as the developing solvent. Rf-values of the reaction products of the treatment at 0 °C were as follows: Rf 0.85(guaiacol), 0.72(trace), 0.62(trace), 0.41(trace), 0.29(compound A), 0.23(compound B) and 0.19(coniferyl alcohol). In the case of the treatment at -30 °C, spot at Rf 0.62 was not observed, but a new spot was appeared at the baseline.

HPLC was carried out on Shimazu LC-4A instrument with a Lichrosorb RP-18 column (4.6x300mm, Nihon Chromato Works Ltd.) using acetonitrile/water=1/1 as the developing solvent.

Mass spectra were obtained on a JEOL DX-300 instrument. Sample was introduced by a GC-MS inlet

system. The Mass spectrum of compound A showed intensive ions at  $m/e$  178 ( $M^+$ , base), 147 and 135, and the High-Mass gave a molecular formula of  $C_{10}H_{10}O_3$  (degree of unsaturation 6). Compound B gave intensive ions at  $m/e$  308 ( $M^+$ ), 181, 153 (base) and 93, and a molecular formula by High-Mass was  $C_{10}H_{13}O_3I_1$  (degree of unsaturation 4).

$^1H$ -NMR spectra were obtained in  $CDCl_3$  using a Bruker AM-500 instrument. Signals of compound A were assigned as follows; 9.65ppm ( $^1H_\gamma$ , d,  $J_{\beta\gamma} = 8.1\text{Hz}$ ), 7.39ppm ( $^1H_\alpha$ , d,  $J_{\alpha\beta} = 16.1\text{Hz}$ ), 7.11ppm ( $^1H_6$ , q,  $J_{26} = 2.01\text{Hz}$ ,  $J_{56} = 8.05\text{Hz}$ ), 7.06ppm ( $^1H_2$ , d,  $J_{26} = 2.01\text{Hz}$ ), 6.95ppm ( $^1H_5$ , d,  $J_{56} = 8.05\text{Hz}$ ) and 6.58ppm ( $^1H_\beta$ , q,  $J_{\alpha\beta} = 16.1\text{Hz}$ ,  $J_{\beta\gamma} = 8.1\text{Hz}$ ). Compound A was thus identified as coniferyl aldehyde.

### RESULTS AND DISCUSSION

#### Cleavage of $\beta$ -ether bond in guaiacylglycerol- $\beta$ -guaiacyl ether

As mentioned before, Jung et al.<sup>8)</sup> have found a simple and efficient cleavage of ether linkages by the use of  $TMSiI$  reagent. The proposed mechanism for the ether cleavage is shown in Fig.1. It was reported that aryl-alkyl ethers always afford aromatic trimethylsilyl ethers and the alkyl iodides. The alkyl-alkyl ethers are generally much more susceptible to this reagent than aryl-alkyl ethers. Since  $TMSiI$  is an expensive and unstable reagent, Olah et al.<sup>11)</sup> have developed an alternative. A mixture of



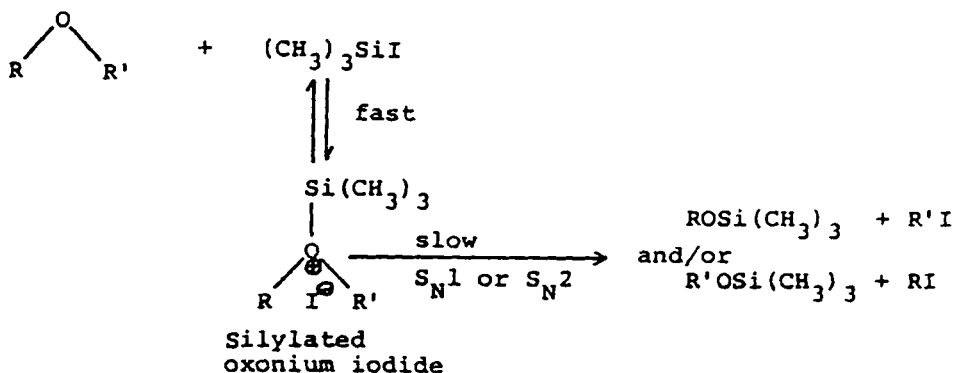


Fig. 1 Proposed Mechanism of Ether Cleavage by  $\text{TMSiI}$ <sup>8)</sup>

chlorotrimethylsilane - sodium iodide in acetonitrile was proposed instead of  $\text{TMSiI}$  reagent. In this case, the freshly generated  $\text{TMSiI}$  in the reaction mixture is responsible to the reaction. It is interesting to note the quite different efficiencies of these two methods. Namely, the methoxyl group cleaves totally by Jung's method in 25 hr at 50 °C and by Olah's method in 48hr at 82 °C. The lower efficiency of the latter method can be ascribed to adduct formation between  $\text{TMSiI}$  and acetonitrile. According to these earlier reports, we tried several kinds of solvents in preliminary experiments. Pyridine, acetonitrile, chloroform, pyridine-chloroform mixture, acetonitrile-pyridine mixture were compared in terms of the yields of guaiacol from GG and its stability. First of all, guaiacol was completely stable to  $\text{TMSiI}$  reagent in pyridine, acetonitrile, pyridine-chloroform

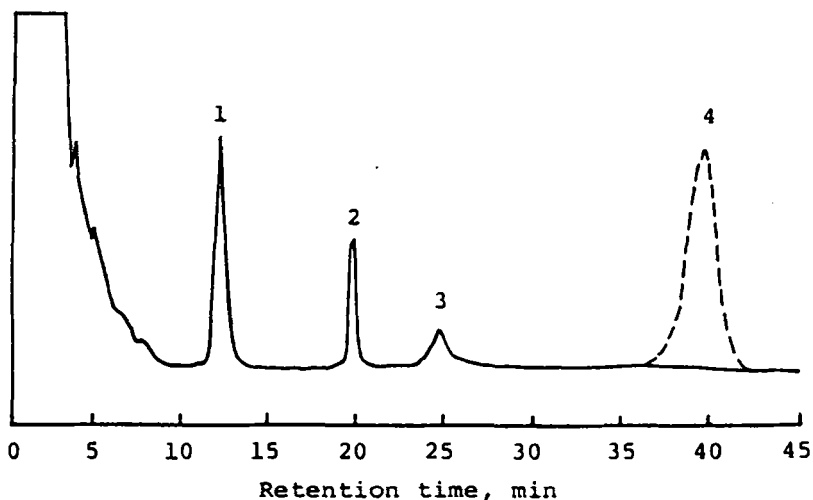


Fig. 2 GLC of Reaction Products of Guaiacylglycerol- $\beta$ -guaiacyl ether by TMSiI

Column: OV 101, Temp.: 100-250°C

Rate: 5°C/min

Peak 1: guaiacol

Peak 2: 2,6-di-*t*-butyl-*p*-cresol  
(internal standard)

Peak 3: coniferyl alcohol

Peak 4: GG (not appeared after the treatment)

mixture and acetonitrile-chloroform mixture even at the room temperature. In the case of chloroform, however, the reaction temperature had to be kept around 0 °C to avoid the formation of catechol by demethylation.

The order of the guaiacol yield was as follows: Pyridine < Acetonitrile << Chloroform. For example, the maximum guaiacol yield in pyridine was only 5-10% of the theoretical value in 6hr at 60-90°C. In the case of acetonitrile, the guaiacol yield was about 50% in 6 hr at 60-80°C. On the other hand, a higher than 70% yield of

guaiacol was attained by the use of chloroform in 3hr at 0°C. The lower efficiencies in pyridine or acetonitrile confirmed the earlier results. This is why chloroform was used as the solvent in this experiment.

However, such a facile cleavage of the  $\beta$ -ether bond is not in good agreement with the behavior of several aryl ethers, such as aryl-methyl ether, aryl-ethyl ether and aryl-n-butyl ether, none of which gave any significant amount of phenol under the same reaction conditions as applied for GG. In other words, the cleavage of the  $\beta$ -ether bond in GG is not dependent on the direct cleavage mentioned above, but some other reaction mechanism must be involved. Fig.2 shows a typical GLC chromatogram of the reaction products as the TMS derivatives. Peak 1 and 4 are guaiacol and starting material, respectively. Peak 2 is the internal standard, 2,6-di-t-butyl-p-cresol which was added after the reaction.

The height of peak 3 is dependent on the reaction conditions. Namely, it was quite strong in the case of the chloroform system at -30°C or the pyridine system at 60 C, but was quite small in the case of chloroform at 0 °C, regardless of the amounts of guaiacol seen on the GLC. These findings strongly suggest the highly labile nature of the compound at peak 3 which was shown to be coniferyl alcohol by GLC and GC-MS. The formation of coniferyl alcohol does not agree with the mechanism for direct ether cleavage mentioned before.

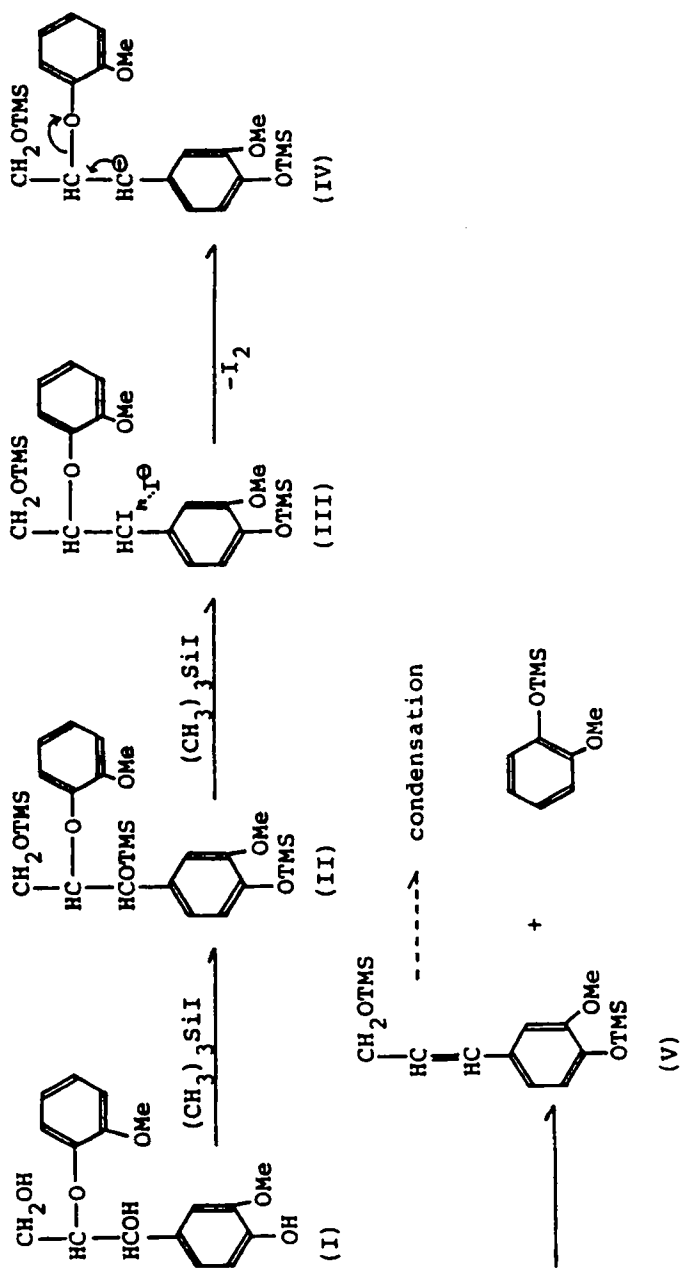


Fig. 3 Tentative Mechanism of Ether Cleavage by TMSiI

The authors propose a new mechanism for the  $\beta$ -ether cleavage in the arylglycerol- $\beta$ -aryl ether structural unit in lignin (Fig.3). The formation of compound (III) from compound (II) is a simple substitution of a TMS ether group with iodine as previously reported by Jung et al.<sup>8)</sup> Although the substitution reaction can be expected at both  $\alpha$  and  $\gamma$  carbon ultimately, it should be reasonable to expect initial substitution at the  $\alpha$  carbon because of its higher susceptibility to a nucleophilic reagent. The benzylic iodine atom will be removed as an iodine molecule in cooperation with an excess amount of TMSiI reagent, and then spontaneously changed to a coniferyl alcohol structure (V) with the release of guaiacol.

Fig.4 shows the yields of guaiacol under different reaction temperatures. Maximum yields of guaiacol at 0 °C, -10 °C and -30 °C were 71%, 73% and 79%, respectively. It is interesting to note that at the lower reaction temperature, a higher maximum yield was obtained with a longer reaction time. The reaction times, 6hr and 20hr, required for -10°C and -30°C, respectively, were too long. Thus, the authors decided to focus on the reaction at 0 °C and further modify the reaction conditions in order to increase the guaiacol yield at least up to 90%. By the way, it is not clear why the yields of guaiacol decreased markedly with time. It might be attributable to the reaction between guaiacol and I<sub>2</sub> formed by the reaction proposed in Fig. 3.

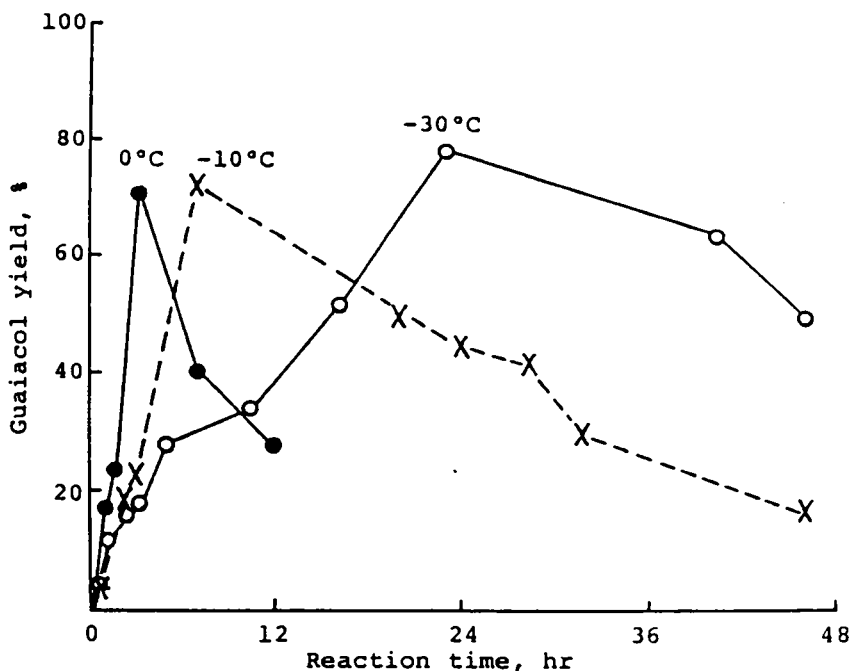


Fig. 4 Yields of Guaiacol by Treatment of Guaiacyl-glycerol- $\beta$ -guaiacyl ether with TMSiI  
Solvent:  $\text{CHCl}_3$ , GG: 53.3mg/ml

The relation between guaiacol yield and the amount of TMSiI reagent added is shown in Fig. 5. In this case, it is important that the concentration of GG is kept at about 1/5 of the case shown in Fig. 4. At the TMSiI/GG molar ratio of 10 to 18, almost quantitative amounts of guaiacol were obtained. Based on this information, the authors selected an optimal treatment condition as follows. Solvent: chloroform, treatment temp.: 0 °C, treatment time: 3hr, concentration of GG 10mg/ml, TMSiI/GG molar ratio: 10/1.

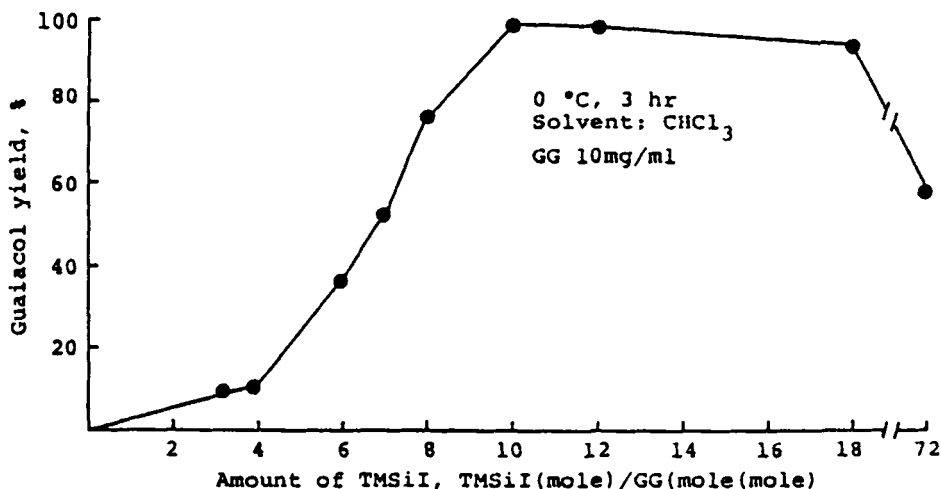


Fig. 5 Relation Between Guaiacol Yield and Amount of TMSiI Reagent Added

It is also very important to visualize how are the other parts of reaction products. Coniferyl alcohol is the only reaction product except for guaiacol appearing on GLC as mentioned before, but it cannot be a main degradation product judging from its low yield. TLC chromatograms of the reaction mixtures showed at least 6 or 7 degradation products, of which guaiacol, compound A and B for the both treatments at 0 °C and -30 °C, and product C only for -30 °C were the main products. Especially in the case of the treatment at 0 °C, compound A was really predominant. No baseline material is produced at 0 °C indicating that the reaction products have not undergone any polymerization reaction. Product C appeared at the baseline was yellowish or orange-yellowish colored,

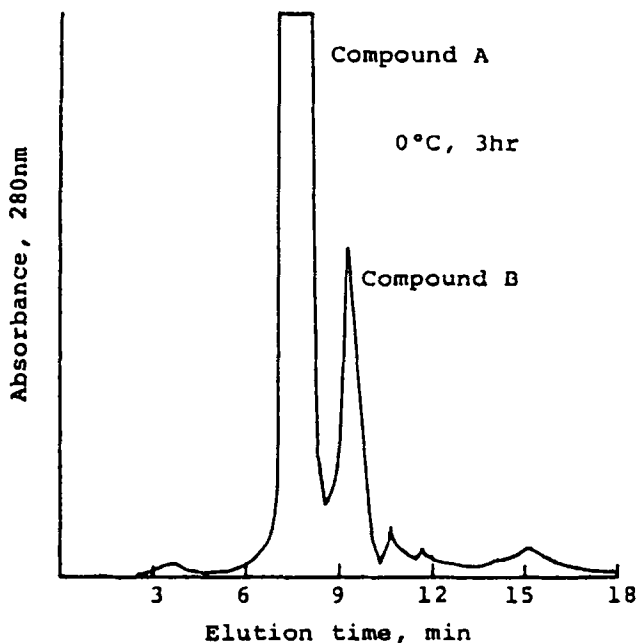


Fig. 6 HPLC of TMSiI Treatment Products from Guaiacylglycerol- $\beta$ -guaiacyl ether

Column: Lichrosorb RP-18 (4.6x300mm)  
 Solvent: Acetonitrile/H<sub>2</sub>O=1/1  
 Flow rate: 0.7ml/min

and were extremely unstable. They moved to over R<sub>f</sub> 0.6 by a mixture of benzene : ethanol : acetic acid = 10 : 4 : 1 as the developing solvent, and were composed of at least three different compounds. These facts suggest that product C is a mixture of reaction intermediates which are stable only at the reaction temperature of -30 °C.

After removing guaiacol by preparative TLC, the reaction mixture was applied to HPLC to isolate compound A and B (Fig. 6). It was determined that a rough ratio



of the yields of two compound is 4.5/1 (compound A/compound B). Compound A was confirmed to be coniferyl aldehyde by means of UV, GC-MS, High-MS and  $^1\text{H-NMR}$  spectra.

With respect to compound B, it was extremely unstable and we have not succeeded in collecting an enough sample for NMR spectrometry. Although MS and GC-MS data suggest that compound B is the product of HI addition to coniferyl alcohol, it is too early to conclude anything about its structure.

Finally, it can be concluded that GG is degraded to produce guaiacol and coniferyl alcohol which is readily converted to coniferyl aldehyde.

GG is, so far, the only compound treated by  $\text{TMSiI}$  to determine  $\beta$ -ether cleavage. The authors did not investigate the behavior of a non-phenolic model compound, veratrylglycerol- $\beta$ -guaiacylether (VG), it should be reasonable to expect a similar behavior to GG, based on the proposed mechanism. The etherification of the benzyl alcohol groups might have some effect on the B-ether cleavage, and it is now under investigation.

#### Depolymerization of $\text{NaBH}_4$ reduced birch MWL by $\text{TMSiI}$ reagent

$\text{TMSiI}$  reagent was applied to birch MWL to determine the efficiency of the B-ether cleavage on MWL. MWL suspended in chloroform dissolved gradually and only a trace of it was still suspended at the final stage of the treatment. Fig. 7 shows the gel filtration curves of

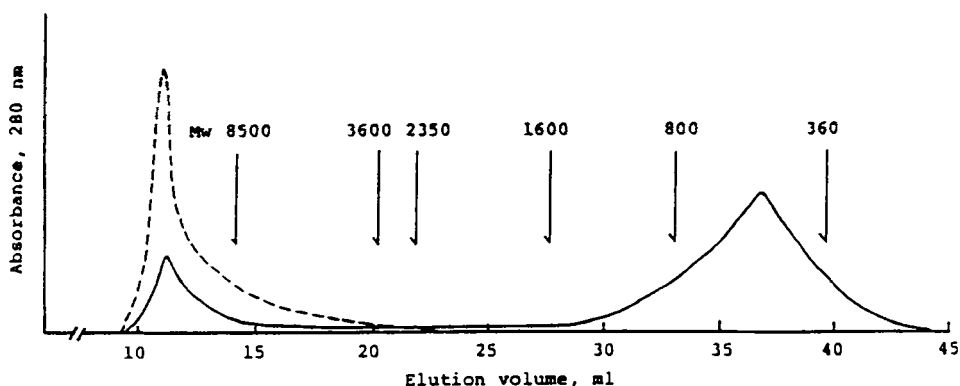


Fig. 7 Gel Filtration Curves for Acetylated Birch Wood MWL Before and After TMSiI Treatment  
 Colum: LH-60, 1.5x83 cm, Solvent:  $\text{CHCl}_3$   
 Detector: 280 nm  
 ----- : Original MWL,            ————— : TMSiI treated MWL

acetylated MWL before and after TMSiI treatment. It can be seen that the depolymerization of MWL is quite apparent and more than 80% of it shifted to the extremely low molecular weight fraction which was estimated to be about 600 at the peak position by polystyrene standard. These facts strongly suggest the efficient depolymerization of MWL by TMSiI treatment. The exact nature of the low molecular weight fraction formed now under investigation. The authors are also trying to further improve the treatment conditions to have a higher efficiency of ether bond cleavage without the artificial condensation of lignin, and to evaluate the application of this treatment for the studies of the chemical structure of lignin.

CONCLUSION

1) TMSiI reagent is able to cleave  $\beta$ -ether linkage in guaiacylglycerol- $\beta$ -guaiacylother(GG) under a mild conditions to form guaiacol and coniferyl alcohol. The latter is further converted to coniferyl aldehyde and some other reaction products.

2) Hardwood milled wood lignin is efficiently depolymerized by TMSiI reagent to give an extremely low molecular weight lignin.

REFERENCES

- 1) B.J.Fergus and D.A.I.Goring, *Holzforchung*, 24,118(1970)
- 2) Z.Z.Lee, G.Meshitsuka, N.S.Cho and J.Nakano, *Mokuzai Gakkaishi*, 27,671(1981)
- 3) P.Whiting and D.A.I.Goring, *Svensk Papperstidn.*, 84,R120(1981)
- 4) P.Whiting, B.D.Favis, F.G.T.St-Germain and D.A.I.Goring, *J.Wood Chem. Technol.*, 1, 29(1981)
- 5) P.Whiting and D.A.I.Goring, *Holzforchung* 36(6),303(1982)
- 6) G.Meshitsuka and J.Nakano, *J.Wood Chem. Technol.*, 5,391 (1985)
- 7) N.Terashima, K.Fukushima, K.Takabe, *Proceedings of 30th Lignin Symposium, Kouchi, Japan*, P9(1985)
- 8) M.E.Jung and M.A.Lyster, *J. Org. Chem.*, 42(23),3761(1977)
- 9) S.Hosoya, K.Kanazawa, H.Kaneko and J.Nakano, *Mokuzai Gakkaishi*, 26(2), 118 (1980)
- 10) A.Bjorkman, *Svensk Papperstidn.*, 59,477 (1956)
- 11) G.A.Olah, S.C.Narang, B.G.Balaram Gupta and R. Malhotra, *J. Org. Chem.*, 44(8), 1247(1979)