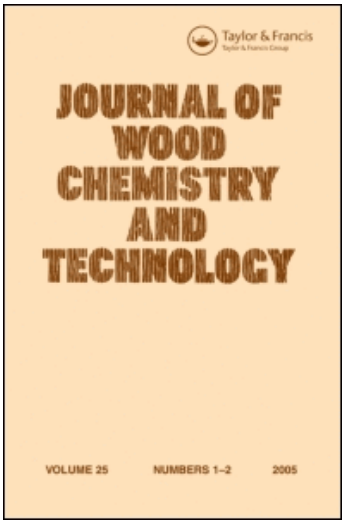

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REACTION OF SYRINGYLGLYCEROL-β-SYRINGYL ETHER TYPE OF LIGNIN MODEL COMPOUNDS IN ALKALINE MEDIUM

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To the memory of Dr. Kyosti V. Sarkanen

ABSTRACT

Reactions of three kind of syringylglycerol-β-syringyl ether type model compounds under alkaline medium were investigated. Sinapyl alcohol and β-hydroxypropiosyringone were formed as phenyl propanoid moieties from syringylglycerol-β-(methyl-syringyl) ether 1 by the β-aryl ether cleavage under soda treatment, while only sinapyl alcohol was formed from syringylglycerol-β-syringyl ether 2. The formation of both two degradation products are quite interesting because there is no nucleophilic additives in soda liquor. A possible reaction mechanisms for the β-aryl cleavage of syringylglycerol-β-syringyl ether type is homolytical cleavage via quinone methide.

INTRODUCTION

In our previous kinetic study[1], it was reported that both consumption of starting materials and β-aryl ether cleavage were

much faster for a syringylglycerol-β-syringyl ether type of lignin model compound than for a guaiacylglycerol-β-guaiacyl ether type model compound under soda and kraft systems. Even by soda treatment, significant cleavage of the syringyl ether was observed, while the cleavage of guaiacyl ether was negligible under the same conditions. Furthermore, when the syringylglycerol-β-syringyl ether type model compound was treated, both the consumption of substrate and cleavage of β-aryl ether were faster under soda treatment than kraft treatment. However, detailed reaction mechanisms have not been discussed.

Most model studies on the reaction mechanisms of lignin fragmentation during alkaline pulping have focused on softwood lignin, which is almost solely composed of the guaiacyl structure units. Although guaiacyl lignin models have been used for these studies, only Miksche[2] has employed syringyl type model compounds.

In order to understand precisely the reactions of the syringyl lignin, we have subjected three kinds of syringylglycerol-β-syringyl ether lignin model compounds (Fig. 1) to soda treatment and the degradation products were investigated.

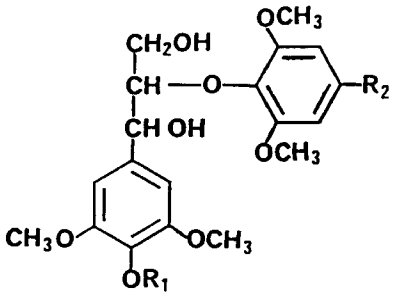
RESULTS

Syringylglycerol-β-(methylsyringyl) Ether (1)

Identification of Degradation Products

Compound 1 was treated in soda, kraft and soda/AQ liquors at 120 ℃ for 60 min. Fig. 2 shows HPLC chromatograms of their reaction mixtures. The soda treatment gave a larger number of the reaction products.

The soda treatment products of compound 1 were characterized by GC-MS analysis after acetylation. The degradation products were



(1) R_1=H R_2=CH_3

(2) R_1=H R_2=H

(3) R_1=C_2H_5 R_2=H

FIGURE 1. Model compounds employed.

listed in Fig. 3. The analysis indicated the presence of sinapyl alcohol (8), syringaldehyde (5), acetosyringone (6) and methylsyringol (4) as major reaction products, beside the remaining compound 1. These were confirmed by the comparison of retention times and fragmentation patterns of synthesized or authentic specimens by GC-MS and also by means of co-chromatography in HPLC analysis of the reaction mixture.

However, product A, which had the shortest retention time on a HPLC chromatogram in Fig. 2, was not identified by GC-MS analysis of the acetylated reaction mixture. However, one of major products possessed a mass spectrum indicative of the acetate of 1-syringyl-2-propen-1-one (13) (data in Experimental section). Such a compound would be expected to appear at a much longer retention time on HPLC than A in Fig. 2. Structure of this propenone acetate suggested that the product A was β-hydroxypropiosyringone (7), which was presumably dehydrated to form the propenone (13) acetate during acetylation procedure. Thus, the product A was isolated by

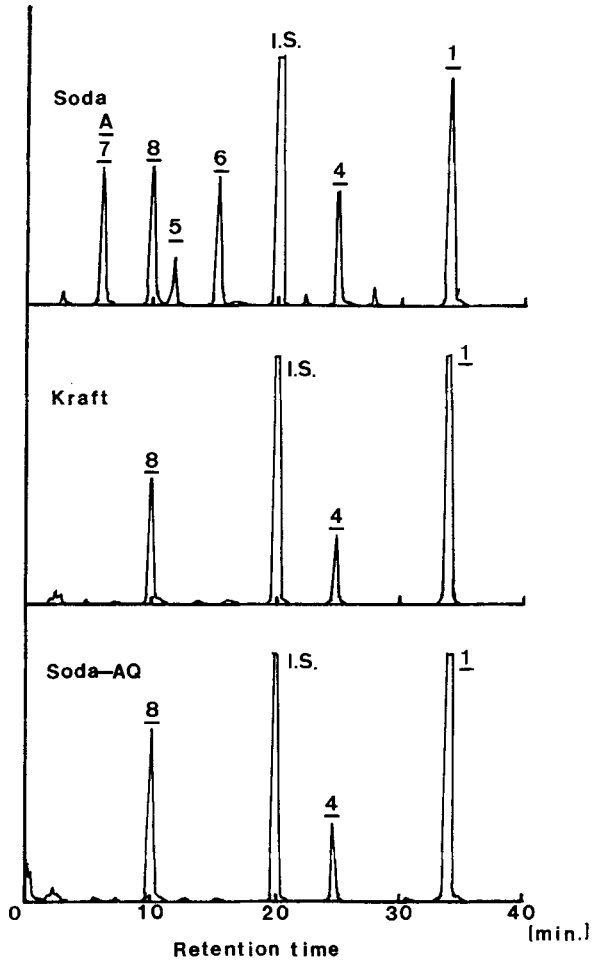
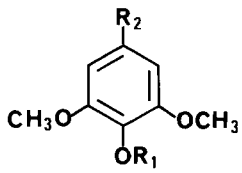


FIGURE 2. HPLC chromatograms of reaction mixtures of model compound 1 after treatment for 60 min at 120 ℃ under soda, kraft and soda/AQ conditions.

Note: See FIGURE 1 and 2 for product numbers; veratraldehyde was the internal standard (I.S.).



(4) R_1=H R_2=CH_3
(5) R_1=H R_2=CHO
(6) R_1=H R_2=$COCH_3$
(7) R_1=H R_2=$COCH_2CH_2OH$
(8) R_1=H R_2=$CH=CHCH_2OH$
(9) R_1=H R_2=H
(10) R_1=C_2H_5 R_2=CHO
(11) R_1=C_2H_5 R_2=CH_2OH
(12) R_1=C_2H_5 R_2=$CHOHCHOHCH_2OH$
(13) R_1=H R_2=$COCH=CH_2$

FIGURE 3. Degradation products.

preparative HPLC and trimethylsilylated prior to GC-MS analysis. Its mass spectrum and retention time were identical to those of the trimethylsilyl derivative of synthesized β-hydroxypropiosyringone (7). Acetylation of both the isolated and synthesized sample of 7 yielded the propenone (13) acetate which did not regenerate the ketol (7) on saponification. Thus, β-hydroxypropiosyringone (7) is one of the major products by the soda treatment of compound 1, whereas 13 acetate was an artifact of the acetylation.

In summarizing the identification results in Fig. 2, β-hydroxypropiosyringone (7), syringaldehyde (5) and acetosyringone (6) were characteristically formed by the soda treatment. Miksche[2] has studied the degradation products of the soda treatment of the model compound 1 in 1.0 mol/l NaOH at 140℃ for 180 min and identified several monomeric and dimeric products. However, he

did not report the production of 7 and 8, suggesting that treatment conditions are different. Their more vigorous conditions may have caused secondary reactions leading to loss of products 7 and 8.

Reaction of Compound 1 under Soda Treatment

The Effect of Alkalinity on the β-Aryl Ether Cleavage

The effect of alkalinity (0.1 mol/l and 1.0 mol/l) on β-aryl ether cleavage of the model compound 1 was investigated (Fig. 4). There was no significant difference between two alkalinity conditions for both the rates of starting material consumption and methylsyringol (4) formation, which represented the extent of the β-aryl ether cleavage.

Formation of Sinapyl Alcohol

In Fig. 5 the yield of sinapyl alcohol (8) was illustrated as a function of the yield of methylsyringol (4). By the soda/AQ treatment, yield of 8 was almost equivalent to the β-aryl ether cleavage. On the other hand, in the case of soda treatment, the yield of 8 accounts for only 25 to 30 % molar equivalent of the β-aryl ether cleavage. Ketol (7), which is observed in this case is also a β-aryl ether cleavage product.

Miksche[2] reported the isolation of isoeugenol in 43 molar % yield from the soda treatment of guaiacylpropandiol-β-(methylsyringyl) ether in 1.0 mol/l NaOH at 140 ℃ for 180 min. The formation of isoeugenol from that model compound corresponds to the formation of sinapyl alcohol (8) from compound 1. Therefore, his and our results suggest that the same reaction occurred during the soda treatment of both model compounds and that the ether-linked syringyl ring may play an important role in the formation of isoeugenol or sinapyl alcohol.

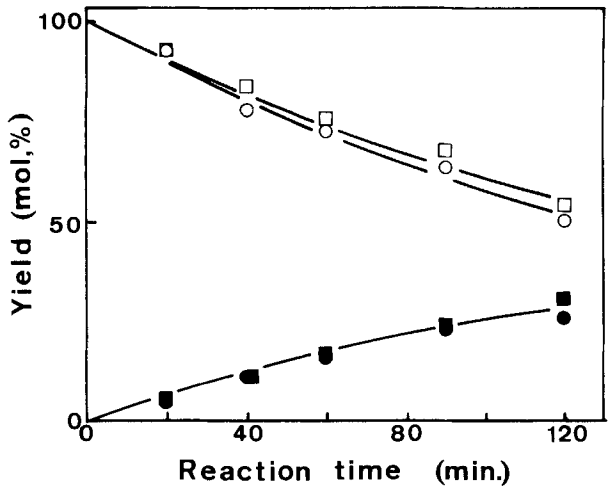


FIGURE 4. The effect of alkaline concentration on the degradation of compound 1: 0.1 mol/l NaOH(○, ●) and 1.0 mol/l NaOH(□, ■) at 110 ℃.

Recovery of 1: ○, □ ; Formation of 4: ●, ■

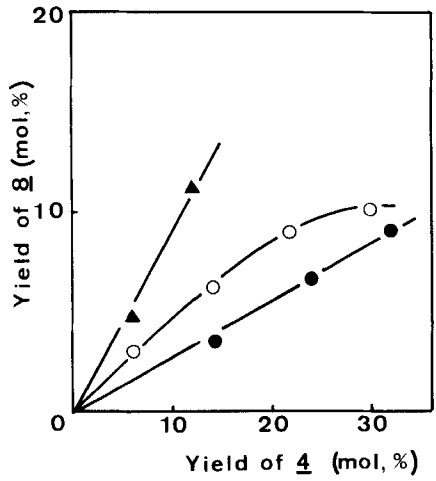


FIGURE 5. Formation of 8 from 1 under soda(●), kraft(○) and soda/AQ(▲) treatments at 120 ℃.

Formation of Other Degradation Products from Compound 1

After soda treatment, three major degradation products, syringaldehyde (5), acetosyringone (6) and β-hydroxypropiosyringone (7) were identified, in addition to sinapyl alcohol (8) and methylsyringol (4). Their yield profiles were investigated in order to understand more deeply the reaction mechanisms in soda treatment at two temperatures, 100 and 120℃ (Fig. 6).

The yield of ketol (7) increased rapidly to a maximum of about 6 molar %, in 30 min at 120 ℃ and 90 min at 100 ℃, respectively, and then decreased gradually suggesting that this ketol (7) was unstable at the elevated temperatures. The yield of acetosyringone (6) showed a rapid increase after an apparent induction period, especially at the higher temperature. The yield profiles of both 6 and 7 suggested that 6 is derived from 7 by a reversed aldol reaction at high temperatures in an alkaline medium. This hypothesis was confirmed by the almost quantitative liberation of 6 on a treatment of 7 in 0.1 mol/l NaOH at 110 ℃ for 30 min. Miksche[2] obtained 6 a 10% yield but no 7 by the soda treatment (1.0 mol/l NaOH at 140℃ for 180 min).

The increase of sodium hydroxide concentration from 0.1 mol/l to 1.0 mol/l resulted in increased yield of acetosyringone (6) and decreased yield of β-hydroxypropiosyringone (7), without affecting the rates of consumption of 1 or extent of β-aryl ether cleavage.

The yield of syringaldehyde (5) at 120 ℃ increased approximately three times as much as that at 100℃, whereas the yield of sinapyl alcohol (8) was smaller at the higher temperature as mentioned earlier. This data suggest that 5 was formed from 8 during soda treatment of 1. The increase of NaOH concentration slightly decreased the formation of 8 and slightly increased the formation of 5.

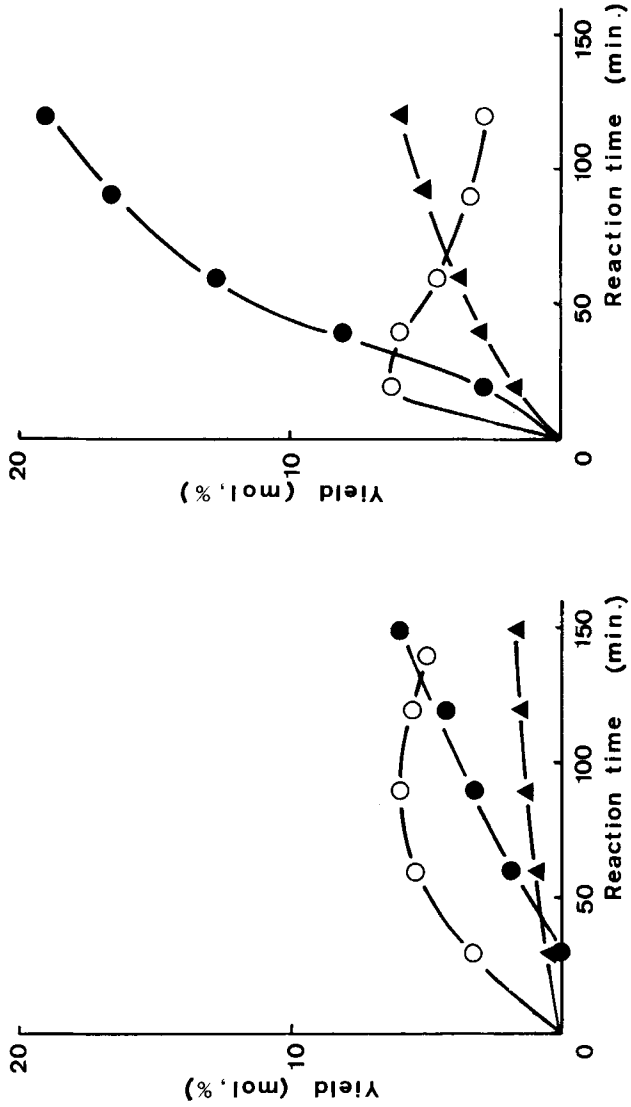


FIGURE 6. Formation of 5(▲), 6(●), 7(○) from treatment of compound 1 with soda at 100 ℃ (left) and 120 ℃ (right).

The combined yield of degradation products 5, 6, 7, and 8 is close to that of 4, the other component in the β-aryl ether cleavage. The quantitative investigation suggests that there might be two reaction pathways for compound (1), ketol (7) formation and sinapyl alcohol (8) formation. Under soda treatment condition, the rate of former was approximately 1.5 to 2 times faster than the latter.

Syringylglycerol-β-Syringyl Ether (2)

Compound 2 was subjected to soda treatment in order to investigate the effect of the methyl group at the para-position of the B ring on the β-ether cleavage. The reaction was carried out in 0.1 mol/l NaOH at 110 ℃ and reaction mixture was subjected to HPLC analysis. Sinapyl alcohol (8) and syringaldehyde (5), as well as syringol (9), which is the B ring β-ether cleavage product, were identified by means of co-chromatography with synthesized and authentic specimens on HPLC. Two additional components were observed in the region of retention time for dimeric compounds, but identification was not accomplished. The only phenyl propanoid moiety observed as a result of β-ether cleavage were 8; both 8 and 7 were formed by β-ether cleavage of compound 1. These results clearly indicate that the methyl group on para-position to ether linkage affected the reaction pathway of β-ether cleavage of syringyl ether type model compounds under soda treatment.

Consumption of 2 and formation of 9 were depicted in Fig. 7 as a function of time. By 60 min treatment, approximately 75% of 2 was consumed and 35% of 9 was observed; the rate of consumption 2 was about 3 times and both were much faster than those of 1. This result clearly indicates that the methyl group at para-position to the ether linkage suppresses the rate of the β-aryl ether cleavage.

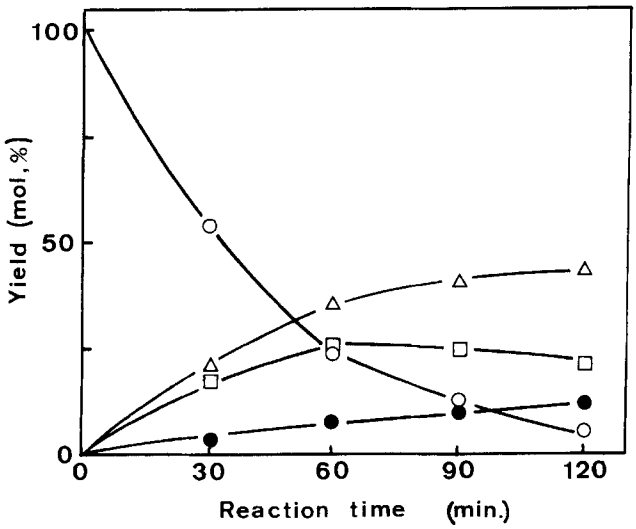


FIGURE 7. Time vs reaction profile for the consumption of 2(○) and formation of 9 (△), 8(□) and 5(●) under soda treatment with 0.1 mol/l NaOH at 110 ℃.

Yield of syringol (9) was about a half of consumption of compound 2, suggesting that other degradation pathways exist. One of such reactions might be an elimination of hydroxymethyl group at the γ -position to afford formaldehyde and a styryl ether[3]. In this connection, the HPLC chromatogram of a soda treatment mixture of compound 2 exhibited two peaks which correspond to the retention time region for dimeric compounds.

The combined yield of sinapyl alcohol (8) and syringaldehyde (5) is very consistent with the yield of syringol (9) (Fig. 7). Syringaldehyde (5) can be derived from 8 in alkaline medium at high temperature, as mentioned in earlier section. This means that the β -syringyl ether linkage in compound 2 was cleaved with only formation of 8.

4-O-Ethylsyringylglycerol-β-Syringyl Ether (3)

Identification of Degradation Products

After the soda treatment of non-phenolic compound 3 in 1.0 mol/l NaOH at 140℃, degradation products were subjected to GC-MS analysis as trimethylsilyl derivatives. Two of the four observed products were identified as, 4-O-ethylsyringaldehyde (10) and 4-O-ethylsyringylalcohol (11) by comparing mass spectra and retention times on GC-MS with authentic specimens. The most dominant degradation product was tentatively identified as 4-O-ethylsyringylglycerol (12) based on the mass spectrum, but the confirmation with authentic specimen has not been done. Syringol (9) was identified by means of HPLC.

Reaction of Compound 3

Compound 3 was used in order to estimate the effect of a phenolic hydroxyl group. Compound 3 used in this experiment was a mixture of threo and erythro stereo isomers (about 1:3). The reactions were performed in 1.0 mol/l NaOH solution containing 25 % of dioxane because of the poor solubility of 3 in water. Therefore, the experimental conditions were somewhat different from the conditions for phenolic compound 1 and 2. Obst[4] investigated the effect of dioxane for the rate of β-aryl ether cleavage by using veratrylglycerol-β-guaiacyl ether and reported that the cleavage was not affected strongly by 30% dioxane. Therefore, it seems that the results obtained here could be compared with the compound 1.

Consumption of compound 3 and formation of 9 as a function of treatment time, are illustrated in Fig. 8. The apparent faster consumption (3-4 times) of erythro (3) than that of threo (3) was observed. Miksche[5] has investigated the β-aryl ether cleavage of both threo and erythro veratrylglycerol-β-guaiacyl ether kinetically and reported the rate constant of ether cleavage of

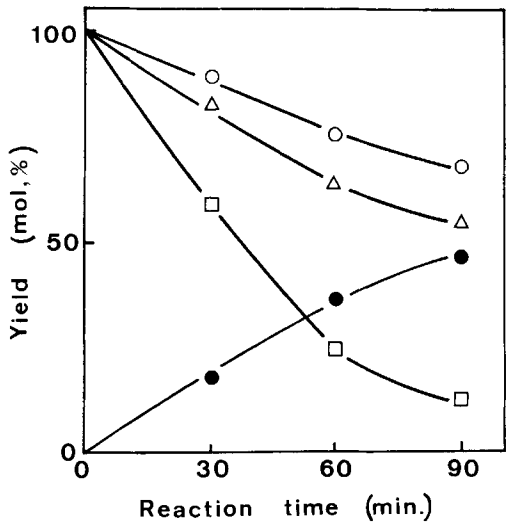


FIGURE 8. Time course of consumption of 3 and formation of 9(●). Model compound 3 was treated with 1.0 mol/l NaOH at 140 ℃. Recovery of threo 3(○), erythro 3(□) and mixture (△).

erythro was about 3.6 times greater than of threo in 1 mol/l NaOH at 140℃. Obst[4] also examined the rate of alkaline hydrolysis of the threo-erythro mixture (60:40) of veratrylglycerol-β-guaiacyl ether and found the simulated rate constants from the pure threo and erythro isomers agreed with the experimentally determined rate. Our results obtained here supported their observations. The yield of syringol (9) matched the sum of the consumption of threo and erythro forms of 3, suggesting the β-aryl ether cleavage was almost exclusive in the reaction. 4-O-ethylsyringylglycerol was the sole phenyl propanoid formed by the β-aryl ether cleavage. Therefore, the reaction of non-phenolic compound 3 can be interpreted by the pathway via oxirane intermediate proposed for guaiacyl ether models[6].

By a 90-min soda treatment in 1.0 mol/l NaOH at 120 ℃, approximately 12 % of β-aryl ether was cleaved and 13 % of 3 was consumed. On the other hand, soda treatment of 1 in 0.1 mol/l NaOH at 120 ℃ resulted in 42 % of β-aryl ether cleavage and 53 % of disappearance of 1. The comparative model studies of 1 and 3 indicated that the phenolic hydroxyl group was important for the rapid cleavage of the β-aryl ether, and led to different reaction pathways.

Miksche[2] has performed a 140 ℃ soda treatment for the methyl ether of compound 1 (threo form). Based on his data, 8.6 % of the β-aryl ether cleavage were predicted by a 60-min treatment at 140 ℃, whereas 23 % of β-ether of compound 3 (threo) was cleaved at 140 ℃ (Fig. 8). The rate of the β-aryl ether cleavage was to be reduced by the electron donating effect of the para methyl substituent on ring B.

DISCUSSION

The reaction pathway of lignin in alkaline systems summarized by Gierer[6] was based on the phenolic guaiacyl type lignin model studies. A rate determining step in the reactions is the formation of quinone methide (QM). In the case of soda treatment, the elimination of hydroxymethyl group from γ-position as formaldehyde is dominant and the β-aryl ether cleavage is very slow. In the case of kraft and soda/AQ treatments, SH^- or AHQ^{2-} attack to α-position of quinone methide, resulting in β-aryl ether cleavage.

The appearance of styrene-type products is apparent in the soda reactions of syringyl-syringyl dimmer models. In the reaction of compound 1 under soda treatment, the β-aryl ether cleavage is

rapid and sinapyl alcohol (8) and ketol (7) are formed from 1. This type of product is generally only seen with β-ring models having guaiacyl units in the presence of SH^- or AHQ^{2-}. The β-aryl ether cleavage of 3 is much slower than that of 1 and only arylglycerol (12) was obtained as a phenyl propanoid. These results suggest that the QM formation is required for the rapid cleavage and formations of 7 and 8. A possible explanation for the rapid β-aryl ether cleavage and formation of 8 and 7 is homolytical fragmentation of β-aryl ether. Miksche[2] has performed the soda treatment of guaiacylpropandiol-β-(methylsyringyl) ether and obtained isoeugenol and propioguaiacone which are corresponding to 8 and 7, respectively. The ether linked syringyl ring strongly affects the rate of β-aryl ether cleavage and reaction mechanism, which may be due to the electron density and rigidity of β-aryl ether linkage exerted by two methoxyl group on the ring B.

EXPERIMENTS

Model Compounds

Compounds 1, 2 and 3 were synthesized by reported methods (Kirk et al.[7], Hosoya et al.[8]). The threo stereoisomer for compound 1 and the erythro stereoisomer for compound 2 were used, respectively. In the cases of compound 3, the threo and erythro mixture (about 1:3) was used.

Authentic specimens used for product identification as shown in Fig. 3, syringaldehyde (5), acetosyringone (6) and 2,6-dimethoxyphenol (10; syringol) were purchased and purified by recrystallization if necessary. Sinapyl alcohol (8) was synthesized by $LiAlH_4$ reduction of 4-O-acetyl-ethylsinapate according to the method of Freudenberg[9]. 2,6-Dimethoxy-4-methylphenol (4; methyl-

syringol) were synthesized by the hydrogenation (H_2: 5 kg/cm^2) of syringaldehyde in acetic acid with palladium-charcoal (5%) for 30 hr. The reaction mixture was evaporated under reduced pressure after filtration. The pale yellow residue was distilled and a fraction with bp.116-117 ℃ (2 mmHg) was collected. The obtained colorless oil was crystallized after standing allow in refrigerator for 2 hr (mp. 38.5-39.5 ℃, 70.3% yield). β-Hydroxypropiosyringone (7) was prepared by aldol condensation of paraformaldehyde and acetosyringone in the alkaline medium. Acetosyringone and five molar equivalent of paraformaldehyde was dissolved in 0.1 mol/l NaOH. The solution was sealed in stainless steel bombs and heated in glycerol bath at 110 ℃ for 40 min. The reaction mixture was extracted with $CHCl_3$ and the organic layer was dried over Na_2SO_4. 7 was purified by silica gel column chromatography and recrystallized in $CHCl_3$-hexane. (mp. 111-112.5 ℃)

Alkaline Treatment of Model Compounds and Quantitative Analysis of Reaction Products by HPLC

The soda, kraft and soda/AQ treatments in this paper denote treatment in an aqueous NaOH solution containing no additive, 0.015 mol/l of NaSH, and anthraquinone (1.0 mmol/l) and 10 mmol/l glucose, respectively. Concentration of NaOH was 0.1 mol/l unless otherwise noted. A dioxane-water mixture (1:3) was used to dissolve the compound 3.

The model compounds (5 mmol/l) were dissolved in the treatment solution under nitrogen atmosphere and sealed in the glass ampules (about 2 ml) after flashing with nitrogen. The glass ampules were placed in stainless steel bombs and heated at the temperature ranging from 100 to 140 ℃ in a glycerol bath for a scheduled time. After the scheduled time, the bombs were cooled in water. The reaction mixture (1 ml) was neutralized with 1 ml of phosphate

buffer (0.5 mol/l, pH=3), then 2 ml of veratraldehyde solution (0.1 g/l) in acetonitrile was added as an internal standard. The samples were analyzed by Waters HPLC system with NOVA PAK C_{18} with acetonitrile and 0.01 mol/l phosphate buffer (pH=3). Detection was performed with Waters Model 481 at 272 nm. For quantitative analysis, the calibration curve was drawn with authentic specimen for each model compound and degradation product by the internal standard method.

Identification of Reaction Products by Soda Treatment by GC-MS Analysis

After compound 1 was treated by soda liquor at 110 ℃ for 40 min, the reaction mixture was acidified with HCl to pH 2-3 and extracted with $CHCl_3$ three times. The organic layer was dried over Na_2SO_4, then the solvent was removed in vacuo. The residue was acetylated with pyridine and acetic anhydride (1:1) and subjected to GC-MS analysis. β -Hydroxypropiosyringone (7) was trimethylsilylated after preparative HPLC. For the products from compound 3, the $CHCl_3$ extract was treated with N,O-bis(trimethylsilyl)-actoamide in pyridine and subjected to GC-MS analysis:

4-Methylsyringol (4) monoacetate: 210(M^+, 32%), 168(out of range), 153(100%), 139(18%), 125(86%), 124(20), 109(30%), 107(38%), 79(26%), 43(29%)

Syringaldehyde (5) monoacetate: 224(M^+, 6%), 182(100%), 181(32%), 167(19%), 153(20%), 139(17%), 125(10%), 118(19%), 93(18%), 43(24%)

Acetosyringone (6) monoacetate: 238(M^+, 7%), 198(100%), 181(out of range), 153(19%), 126(6%), 43(33%)

1-Syringyl-2-propen-1-one mono acetate: 250(M^+, 5%), 226(38%), 208(100%), 184(24%), 181(61%), 180(17%), 167(29%), 43(25%).

β -Hydroxypropiosyringone (7) diTMSi ether: 370(M^+, 67%), 355(100%), 280(18%), 265(23%), 254(24%), 253(83%), 250(24%), 196(21%), 73(52%), 44(23%).

Sinapyl alcohol (8) diacetate: 294(M^+, 27%), 253(65%), 252(out of range), 210(62%), 209(89%), 193(46%), 182(21%), 181(58%), 161(100%), 149(51%), 133(38%), 43(60%).

4-O-Ethylsyringylglycerol triTMSi ether: 488(M^+, <1%), 283(100%), 255(18%), 224(15%), 195(7%), 181(19%), 167(12%), 147(19%), 133(21%), 117(20%), 103(19%), 75(43%), 73(97%).

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REFERENCES

1. R. Kondo, Y. Tsutsumi and H. Imamura, Holzforschung, 41, 83 (1987)
2. G. E. Miksche, Acta Chem. Scand., 27, 1355 (1973)
3. J. Gierer and S. Ljunggren, Svensk Papperstidn., 82, 503 (1979)
4. J. R. Obst, Holzforschung, 37, 23-28 (1983)
5. G. E. Miksche, Acta Chem. Scand., 26, 3275 (1972)
6. J. Gierer, Wood Sci. Technol., 19, 289 (1985)
7. K. Kirk, J. Harkin and E. Cowling, Biochem. Biophys. Acta., 165, 145 (1968)
8. S. Hosoya, K. Kanazawa, H. Kaneko and J. Nakano. Mokuzai Gakkaishi 26, 118 (1980)
9. K. Freudenberg and R. Dillenberg, Chem. Ber. 84, 67 (1951)