

## ORIGINAL ARTICLE

Yoshihiro Sano · Shu Shimamoto · Makiko Enoki  
Haruo Konno

## Fractionation of woody biomass with boiling aqueous acetic acid containing a small amount of mineral acid at atmospheric pressure: Reactivity of arylglycerol- $\beta$ -aryl ethers in lignins with aqueous acetic acid containing $H_2SO_4$

Received: August 22, 1997 / Accepted: December 19, 1997

**Abstract** To characterize the mechanism of the reaction of lignin with aqueous acetic acid (AW) containing a small amount of  $H_2SO_4$ , guaiacylglycerol- $\beta$ -guaiacyl ether (GOG), and guaiacylglycerol- $\beta$ -syringyl ether (GOS) were refluxed in 90% AW with 0.28%  $H_2SO_4$  for 0–120 min. Reaction products and their silylated derivatives were characterized by analytical methods such as gas chromatography–mass spectrometry and nuclear magnetic resonance. When the model compounds were allowed to react at boiling temperature for 0 min (heat-up time 30 min), most of their primary alcohol groups and some of their secondary alcohol groups were acetylated, but their phenolic groups were not. About 90% of GOG was degraded, polymerized, or both during boiling for at least 15 min, yielding guaiacol and isocoumaran compounds (GOG-e and GOG-f) in addition to homovanillin (II) as guaiacylvinyl alcohol (I) and other minor products. GOS yielded syringol, homovanillin (II), and a novel compound (V) together with unknown products but not the corresponding isocoumaran compounds.

**Key words** Fractionation of biomass · Atmospheric AcOH pulping · Degradation of  $\beta$ -Ethers · Sulfuric acid · Lignin model compounds

### Introduction

Delignification of hardwoods and some softwoods by refluxing in aqueous acetic acid (AW) with a mineral acid as a catalyst at atmospheric pressure has generated increasing

interest as an alternative pulping process. It is a simpler, less energy-intensive, more economical method than the conventional pulping processes.<sup>1,2</sup> The strength of the resulting acetic acid pulps has been compared favorably to that of kraft pulps.<sup>1,2</sup> Moreover, hemicellulose is recovered as monosaccharides in large amounts, and acetic acid lignin (AcL) is prepared easily and quantitatively for conversion to low-molecular-weight phenols,<sup>3</sup> carbon fibers,<sup>4</sup> active carbon fibers,<sup>5</sup> adhesives,<sup>6</sup> cation-exchange resins,<sup>7</sup> and so forth. The pulp can be bleached with nonchloride agents to a brightness of more than 80%.<sup>2</sup>

In this study the mechanism of delignification by boiling in AW containing a small amount of  $H_2SO_4$  was investigated using lignin model compounds with  $\beta$ -0–4 linkages to establish satisfactory pulping conditions and to obtain information on the chemical structure of AcL.

### Experimental

Guaiacylglycerol- $\beta$ -guaiacyl ether (GOG) and guaiacylglycerol- $\beta$ -syringyl ether (GOS) were synthesized as lignin model compounds by the methods described in previous reports.<sup>8,9</sup> Both GOG and GOS were mixtures of *erythro* and *threo* isomers at a molar ratio of 4:1. A 50-mg sample of each compound was dissolved in 5 ml of 90% aqueous acetic acid (AW) containing 0.28%  $H_2SO_4$ , and the mixture was then heated at the boiling temperature of 90% AW for 0–120 min. The heat-up time was 30 min. The reaction solution was adjusted to 25 ml with dioxane. A 10-ml aliquot of the solution, to which 0.1 mg of  $\beta$ -naphthol was added as an internal standard, was analyzed for the determination of guaiacol and syringol by gas chromatography (GC).<sup>8</sup> Another 10-ml aliquot of the solution was evaporated to dryness, and the residue was dissolved in 1 ml pyridine. The material in 50  $\mu$ l of the resultant solution was silylated by heating with 40  $\mu$ l of bis-(trimethylsilyl)-acetoamide for 30 min at 70°C. The silyl ethers of the products were analyzed by GC, or GC mass spectrometry according to the procedure described previously.<sup>8</sup>

Y. Sano (✉) · S. Shimamoto<sup>1</sup> · M. Enoki<sup>2</sup> · H. Konno<sup>3</sup>  
Faculty of Agriculture, Hokkaido University, Sapporo 060-0809,  
Japan

<sup>1</sup> Present address: Daicel Chemical Industries, Himezi 671-12, Japan

<sup>2</sup> Present address: Wood Research Institute, Kyoto University, Uji,  
611-0011, Japan

<sup>3</sup> Present address: Iwakuni Research Laboratory of Technology,  
Nippon Paper Industries, Iwakuni 740-0003, Japan

GOG-a: GC-retention time (RT) 32 min; GC-MS (m/z) 536 ( $M^+$ ), 446, 416, 386, 356. GOG-b: RT 35 min; GC-MS (m/z) 506 ( $M^+$ ), 511, 297 (100%), 223, 209, 181, 166. GOG-c: RT 36 min; GC-MS (m/z) 506 ( $M^+$ ), 446, 340, 310, 225 (100%, 267–42), 166 (239–73). GOG-d: RT 38 min; GC-MS (m/z) 476 ( $M^+$ ), 267, 225 (100%), 209. GOG-e: RT 34.5 min; GC-MS (m/z) 446 ( $M^+$ ), 401, 386, 356 (100%), 326 (90%), 315, 283, 209. GOG-f: RT 37 min; GC-MS (m/z) 416 ( $M^+$ ), 401, 356 (80%), 341, 326 (100%), 315, 283.

GOS-a: RT 34 min; GC-MS (m/z) 566 ( $M^+$ ), 476, 436, GOS-b: RT 38 min; GC-MS (m/z) 536 ( $M^+$ ), 323, 297 (100%), 211. GOS-c: RT 38.5 min; GC-MS (m/z) 536 ( $M^+$ ), 323, 297 (100%), 267, 225, 179. GOG-d: RT 42 min; GC-MS (m/z) 506 ( $M^+$ ), 386, 309, 294, 251, 250, 239, 225, 153 (100%).

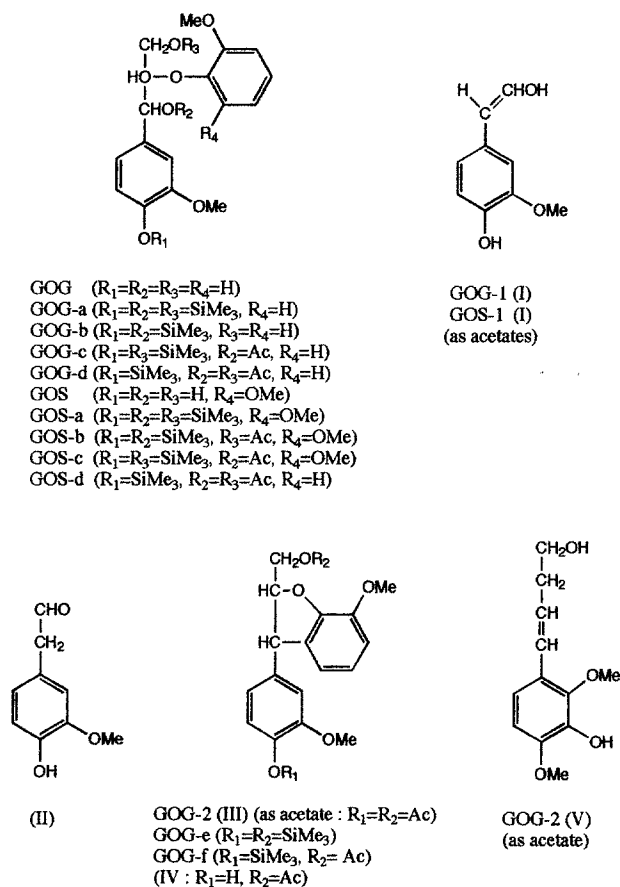
Reaction products obtained by treatment of GOG and GOS (0.5 g each) in boiling AW with 0.28%  $H_2SO_4$  for 3 h were acetylated according to the conventional procedure with pyridine-acetic anhydride and then isolated by column chromatography on silica gel with a mixture of *n*-hexane and ethylacetate (EtOAc) (3:1). Crude isolated compounds were purified by preparative thin-layer chromatography (TLC) with the same solvent system. GOG-1 and GOG-2, and GOS-1 and GOS-2, were isolated as acetates from the products of GOG and GOS, respectively.

GOG-1 (acetate): HRMS (m/z)  $C_{13}H_{14}O_5$  (1.2% error); MS (m/z) 250 ( $M^+$ ), 208, 166 (100%), 151;  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  2.20 (*E*-type, aryl-CH=CH-OCOCH<sub>3</sub>, 1.5H, s), 2.26 (*Z*-type, aryl-CH=CH-OCOCH<sub>3</sub>, 1.5H, s), 2.31 (phenolic COCH<sub>3</sub>, 1.5H, s), 2.32 (phenolic COCH<sub>3</sub>, 1.5H, s), 3.84 (OCH<sub>3</sub>, 1.5H, s), 3.85 (OCH<sub>3</sub>, 1.5H, s), 5.68 (*Z*-type, aryl-CH=CH-, 0.5H, d, *J* = 7.3 Hz), 6.36 (*E*-type, aryl-CH=CH-, 0.5H, d, *J* = 12.8 Hz), 6.87–7.25 (aromatic 3H, m), 7.29 (*Z*-type, aryl-CH=CH-, 0.5H, d, *J* = 7.3 Hz), 7.81 (*E*-type, aryl-CH=CH-, 0.5H, d, *J* = 12.8 Hz). GOG-2 (acetates): HRMS (m/z)  $C_{21}H_{22}O_7$  (1.4% error); MS (m/z) 386 ( $M^+$ ), 326, 284 (100%), 269;  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  2.08 (alcoholic COCH<sub>3</sub>, 3H, s), 2.31 (phenolic COCH<sub>3</sub>, 3H, s), 3.76 (OCH<sub>3</sub>, s), 3.96 (OCH<sub>3</sub>, s), 4.41 ( $\gamma$ -CH<sub>2</sub>, d, *J* = 4.81 Hz), 4.45 ( $\alpha$ -CH, d, 8.4 Hz), 4.85 ( $\beta$ -CH, dd), 6.61–7.00 (aromatic 6H, m). GOS-1 (acetate): the same parameters as those for GOG-1. GOS-2 (acetate): MS (m/z) 308 ( $M^+$ ), 248, 206 (100%);  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  2.05 (alcoholic COCH<sub>3</sub>, 3H, s), 2.36 (phenolic COCH<sub>3</sub>, 3H, s), 2.54 ( $\gamma$ -CH<sub>2</sub>, dt, *J* = 6.6 and 7.0 Hz), 3.76 (OCH<sub>3</sub>, s), 3.82 (OCH<sub>3</sub>, s), 4.18 ( $\omega$ -CH<sub>2</sub>, t, *J* = 6.6 Hz), 6.09 (*E*-type, aryl-CH=CH-, dt, *J* = 7.0 Hz and 16.2 Hz), 6.62 (*E*-type, aryl-CH=CH-, d, *J* = 16.2 Hz), 6.71 (aromatic H, d, *J* = 8.8 Hz), 7.26 (aromatic H, d, *J* = 8.8 Hz).

## Results and discussion

Degradation of lignin model compounds with  $\beta$ -0–4 linkages by refluxing in aqueous acetic acid with  $H_2SO_4$

Lignin model compounds, GOG and GOS were refluxed in 90% aqueous AW containing 0.28%  $H_2SO_4$  for 120 min for aqueous acetic acid (AcOH) pulping. From reaction prod-



**Fig. 1.** Reaction products obtained by atmospheric acetic acid (AcOH) pulping with  $H_2SO_4$  of lignin model compounds: guaiacylglycerol- $\beta$ -guaiacyl ether (GOG) and guaiacylglycerol- $\beta$ -syringyl ether (GOS). *SiMe*<sub>3</sub>, Si (CH<sub>3</sub>)<sub>3</sub>; *OMe*, OCH<sub>3</sub>; *Ac*, COCH<sub>3</sub>

ucts of GOG acetylated according to the conventional procedure, the acetates of GOG-1 and GOG-2 were isolated in yields of 3.8 and 5.6 mol%, respectively; from those of GOS the acetates of GOS-1 and GOS-2 were isolated in small quantities. Each structure was characterized by high-resolution MS (HRMS), MS, and  $^1H$ -nuclear magnetic resonance (NMR) as shown in Fig. 1.

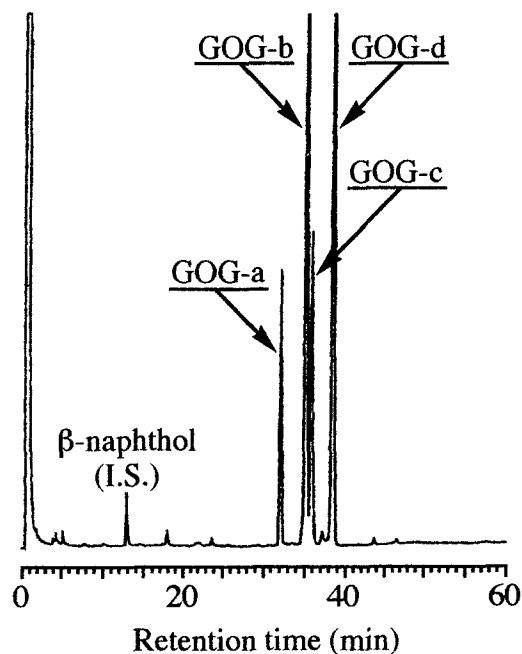
The millimass of the acetate of GOG-1 revealed the molecular formula to be  $C_{12}H_{14}O_5$ . The mass spectrum had major fragment ions at m/z 250 ( $M^+$ , 4%), 208 (11%), and 166 (100%). The  $^1H$ -NMR spectrum showed that GOG-1 had two phenolic hydroxyl groups, two alcoholic hydroxyl groups, and two methoxyl groups. The  $^1H$ - $^1H$  COSY NMR spectrum had two sets of signals at  $\delta$  5.68 and 7.29 and at 6.36 and 7.81 ppm, having two equal integrated intensities, which were assigned to aryl- $C\alpha H=C\beta H-$  of *E* and *Z* types, respectively. Therefore, GOG-1 was identified as a mixture of equal amounts of *E*- and *Z*-2-guaiacylvinyl alcohol (I). GOG-1 may be derived from homovanillin (II) during acetylation of the reaction,<sup>9</sup> as silylated GOG-1 and GOG-II were not detected by GC-MS, as discussed below.

The millimass of the acetate of GOG-2 showed the molecular formula to be  $C_{21}H_{22}O_7$ . The compound had major fragment ions at  $m/z$  386 ( $M^+$ , 20%), 326 (20%), 284 (100%), and 269 (70%).  $^1H$ -NMR showed that GOG-2 had one phenolic, one alcoholic hydroxyl, and two methoxyl groups, and  $C_\alpha H$  at 4.45 ppm,  $C_\beta H$  at 4.85 ppm, and  $C_\gamma H$  at 4.41 ppm. From these results and the  $^1H$ - $^1H$  COSY spectrum, GOG-2 was identified to be 3-guaiacyl-2,3-dihydro-7-methoxy-2-benzofuran methanol (III), as reported previously.<sup>10-12</sup> GOG-2 was isolated as a diacetoxyl derivative from the products acetylated by the conventional procedure. However, we cannot elucidate directly whether GOG-2 exists by itself or as other acetylated compounds, such as 3-guaiacyl-2,3-dihydro-7-methoxy-2-benzofuran-acetoxymethane (IV), among the reaction products of GOG. Yasuda and Ito<sup>11</sup> isolated some condensation products with  $C_6$ - $C_\alpha$  and  $C_6$ - $C_\gamma$  in high yields when they treated monolignols and arylglycerol- $\beta$ -aryl ethers in 90% AcOH at 170–180°C. We did not isolate any similar products because guaiacyl and syringyl ethers were used as  $\beta$ -ether moieties in place of *p*-creosol ether for arylglycerol- $\beta$ -aryl ethers. Davis and coworkers<sup>12</sup> showed that 90% of GOG was consumed during a 10-min reaction with 75% AcOH at 165°C to produce roughly 0.7 mol of guaiacol per mole of GOG. They did not investigate any other products from GOG. The spectroscopic results for GOS-1 were consistent with the structure (I) for GOG-1.

The acetate of GOS-2 had the molecular formula  $C_{16}H_{20}O_6$  from the millimass. The major fragment ions were observed at  $m/z$  308 ( $M^+$ ), 248, 206, and 191.  $^1H$ -NMR revealed the presence of one phenolic, one alcoholic hydroxyl, and two methoxyl groups. The  $^1H$ - $^1H$  COZY spectrum of acetylated GOS-2 showed that signals at  $\delta$  2.54, 4.16, 6.09, 6.62, 6.71, and 7.26 ppm were assigned to  $C_\gamma H$ ,  $C_\omega H$ ,  $C_\beta H$ ,  $C_\alpha H$ , aromatic  $C_5 H$ , and aromatic  $C_6 H$ , respectively. The coupling constant  $J_{\alpha\beta}$  was 16.2 Hz, indicating that the configuration of the olefin bond was E-type. Therefore, the structure of GOS-2 was identified as 1-(2,4-dimethoxy-3-hydroxyphenyl)-1-buten-4-ol (V). GOS-2, which is 3-alkylsyringol with a butenol side chain, is a novel compound; the mechanism of its formation is unclear at present. The isolation of GOG-2 indicates that the intermolecular condensation between  $C_6$  sites on syringyl moieties and side chains in lignin may take place to a significant degree during atmospheric AcOH pulping.

#### Time course of formation of reaction products by atmospheric AcOH pulping of lignin model compounds

Both GOG and GOS were subjected to refluxing in a 90% AW with 0.28%  $H_2SO_4$  for 0–120 min for an examination of the time course of the formation of the reaction products. The products and their silylated derivatives were analyzed by GC-MS. After reaction for 0 min when the solution began to boil, the GC chromatogram of the silylated products of GOG had four main peaks, designated GOG-a through GOG-d, as shown in Fig. 2. GOG-a was the silylated start-

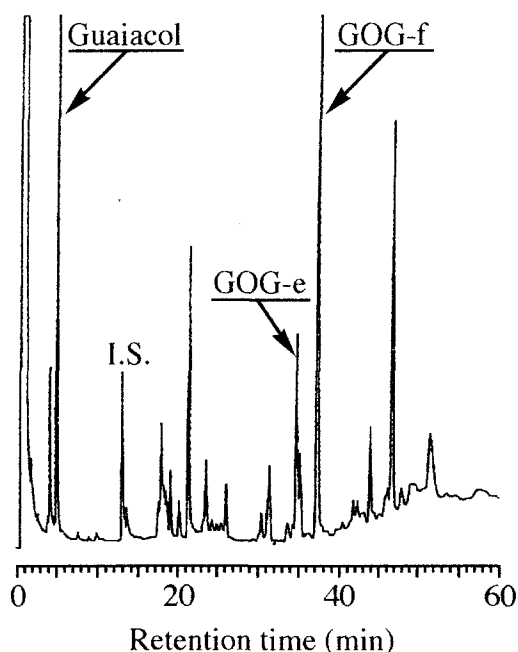


**Fig. 2.** Gas chromatogram of silylated derivatives of reaction products obtained from GOG by refluxing in 90% aqueous AcOH with 0.28%  $H_2SO_4$ . Heating-up time 40 min; refluxing time 0 min

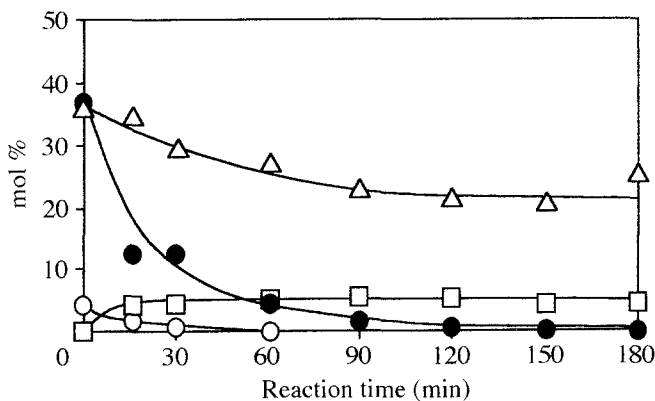
ing material. GOG-b had major fragment ions at  $m/z$  506 ( $M^+$ ), 297 (100%), and 209; so the structure of GOG-b was deduced to be the silylated compound of 3-acetoxy-2-guaiacoxy-1-guaiacyl-propanol-1. GOG-c was estimated to be the silylated derivative of 1-acetoxy-2-guaiacoxy-1-guaiacyl-propanol-3 because of the presence of the characteristic fragment ions at  $m/z$  506 ( $M^+$ ), 225 (267–42), and 149 (239–90). GOG-d had major fragment ions at  $m/z$  476 ( $M^+$ ), 267, 225, and 209. It is deduced to be the silylated derivative of 1,3-diacetoxy-2-guaiacoxy-1-guaiacylpropane. The relative peak areas for GOG-a through GOG-d demonstrated that the primary alcoholic hydroxyl group of GOG is more readily acetylated during the pulping than the secondary alcoholic hydroxyl group.

When GOG was subjected to refluxing in aqueous AcOH with  $H_2SO_4$  for 15 min, about 90% of GOG and its acetates was modified; and a large peak due to GOG-f was observed in addition to a relatively small peak for GOG-e, as shown in Fig. 3. GOG-e and GOG-f appeared to be two isophenylcoumarans, that is, 3-guaiacyl-2,3-dihydro-7-methoxy-2-benzofuran methanol trimethylsilyl ether and 3-(3-methoxy-4-trimethylsilyloxy-phenyl)-2, 3-dihydro-7-methoxyl-2-benzofuran acetoxymethane, on the basis of the parent ions with  $m/z$  446 and 416, respectively. No peaks due to derivatives of homovanillin (II) or its tautomers (I) described above could be detected by GC-MS because of instability on heating.

As expected, the GC chromatograms of trimethylsilyl ethers of products, which were obtained by the atmospheric AcOH pulping of GOS, had no peaks that corresponded to isophenylcoumarans, homovanillin (II), or GOS-2. GOS-a



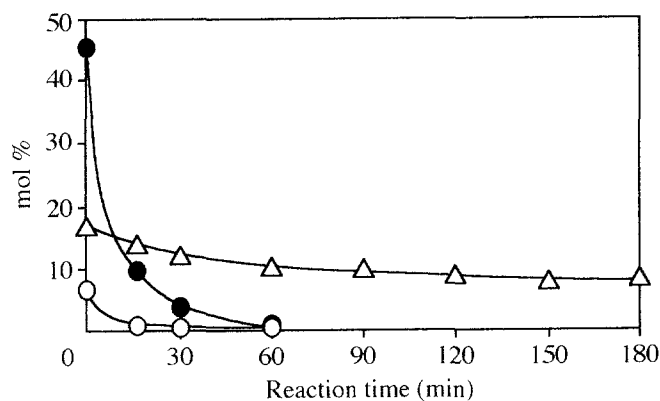
**Fig. 3.** Gas chromatogram of silylated derivatives of reaction products obtained from GOG by refluxing in 90% aqueous AcOH with 0.28%  $H_2SO_4$ . Heating-up time; 40 min; refluxing time, 120 min



**Fig. 4.** Time course of formation of reaction products obtained from GOG by treating under conditions for atmospheric AcOH pulping. Conditions were the same as those shown in Fig. 2 except the refluxing (reaction) time (0–180 min). Open circles, GOG; filled circles, GOG-b to GOG-d; triangles, guaiacol; squares, GOG-e and GOG-f

through GOS-d (Fig. 1) seemed to be the silylated derivatives corresponding to GOG-a through GOG-d, respectively, because of their similar MS fragment patterns.

The amounts of the main products obtained from GOG and GOS at 0–120 min were determined by GC, and the results are shown in Figs. 4 and 5, respectively. At 0 min, GOG-a (GOG) and GOS-a (GOS) were recovered at as low as 5% and 7% yields, and the recoveries of GOG-a to GOG-d and GOS-a to GOS-d with noncondensed  $\beta$ -ether moieties were only 38% and 43%, respectively. Guaiacol and syringol were obtained at a yield of 36% and 18% by



**Fig. 5.** Time course for the formation of reaction products obtained from GOS by treating under conditions for atmospheric AcOH pulping. Conditions were the same as those shown in Fig. 2 except the refluxing (reaction) time (0–180 min). Open circles, GOS; filled circles, GOS-b to GOS-d; triangles, syringol

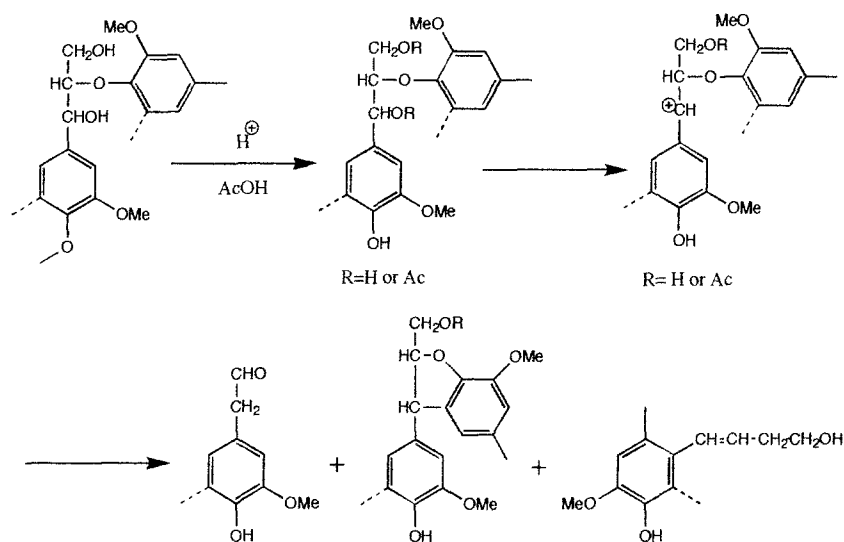
the reaction of GOG and GOS, respectively; but no Hibbert's ketones<sup>13</sup> were detected among the products. Therefore, the cleavage of  $\beta$ -ethers is accelerated to a great extent with  $H_2SO_4$  in aqueous AcOH compared to that in aqueous dioxane, but the reaction mechanism of  $\beta$ -ethers with  $H_2SO_4$  is similar in both solvents.<sup>14</sup>

The amount of guaiacol decreased with increasing reaction times and then fell to 25% at 120 min. These results demonstrate that some of the  $\beta$ -ether bonds were subject to modification during heating, and the resulting syringol condensed with the reaction products or starting materials more readily than did the guaiacol. The yields of isophenylcoumarans GOG-e and GOG-f reached a maximum of only 5% at 15 min with no further increases. Therefore, we assume that the intracondensation of arylglycerol- $\beta$ -guaiacyl ether moieties in lignin for the formation of isophenylcoumarans takes place at an early stage of the AcOH pulping at a low rate compared to the rate of cleavage of the  $\beta$ -ether linkages. The  $\beta$ -ether linkages in isophenylcoumarans seem to be not cleaved by the pulping.

#### Proposed pathways for the reaction of arylglycerol- $\beta$ -aryl ether moieties by atmospheric AcOH pulping of lignin

Based on the results obtained by AcOH pulping of lignin model compounds with  $H_2SO_4$  as a catalyst, the reaction pathways for lignin are proposed as shown in Fig. 6. At first the alcoholic hydroxyl groups, particularly the primary hydroxyl groups, are partially acetylated during the course of heating to the refluxing temperature (107°C). The resultant products are easily subject to deacetylation, followed by acidolysis such as cleavage of  $\beta$ -0-4 linkages and intracondensation. Guaiacol and syringol were obtained from GOG and GOS, respectively, together with small amounts of 2-acetoxy-1-arylethenes (acetate of I). Mixtures of equal amounts of *E*- and *Z*-isomers (I) were isolated and identified, which might be derived from their

**Fig. 6.** Main reaction mechanism of  $\beta$ -ethers in lignin by refluxing in 90% aqueous AcOH with 0.28%  $\text{H}_2\text{SO}_4$



corresponding 2-arylethanals (II) on acetylation of the reaction products with pyridine and acetic anhydride. Therefore, it seems likely that most of the  $\beta$ -ether linkages in lignin might be cleaved via hydrolysis of 1-aryl-2-aryloxyethylenes, which are formed by elimination of the  $\gamma$ - $\text{CH}_2\text{OH}$  in lignin moieties. In addition, GOG gives rise to isocoumarans as major products by intracondensation. From the results for GOS, it seems that positions *para* to methoxyl groups in aromatic rings might be much more subject to nucleophilic attack with other products or lignin moieties than others to give condensation products or substructures in lignin such as GOS-2. It is unclear at present how GOS-2 is formed.

## References

- Sano Y, Nakamura M, Shimamoto S (1990) Pulping of wood at atmospheric pressure: II. Pulping of birch wood with aqueous acetic acid containing a small amount of sulfuric acid. *Mokuzai Gakkaishi* 36:207–211
- Sano Y, Uraki Y, Kubo S, Horisaki Y, Konno H (1996) Total utilization of woody biomass by acetic acid pulping at atmospheric pressure (in Japanese). In: Proceedings of the 63rd pulp and paper research conference, pp 26–32
- Sano Y, Shimamoto S (1995) Mild hydrogenolysis of acetic acid lignin. *Mokuzai Gakkaishi* 41:1006–1011
- Uraki Y, Kubo S, Nigo N, Sano Y (1995) Preparation of carbon fibers from organosolv lignin obtained by aqueous acetic acid pulping. *Holzforchung* 49:343–350
- Uraki Y, Kubo S, Kurakami H, Sano Y (1997) Active carbon fibers from acetic acid lignin. *Holzforchung* 51:188–192
- Nakamura M, Sano Y (1990) Production of lignin adhesives: resinification of acetic acid lignin (in Japanese). *Proc Hokkaido Branch Jpn Wood Res Soc* 22:68–73
- Kanai T, Sano Y, Sasaya T (1994) Preparation of highly efficient polymers from acetic acid lignin – preparation of cation ion: exchange resin (in Japanese). In: Abstracts of the 44th annual meeting of the Japan Wood Research Society, 59
- Sano Y (1989) Reactivity of  $\beta$ -0–4 linkages in lignin during solvolysis pulping: degradation of  $\beta$ -0–4 lignin model compounds. *Mokuzai Gakkaishi* 35:813–819
- Mikshe GE (1966) Zur Synthese der beiden diastereomeren Formen des Guajacylglycerin- $\beta$ -(2-methoxyphenyl)-ethers und des Guajacylglycerins. *Acta Chem Scand* 20:1038–1043
- Ede R, Brunow G, Poppus K (1988) Formic acid/peroxyformic acid pulping: Part 1. Reactions of  $\beta$ -aryl ether model compounds with formic acid. *Nord Pulp Pap Res* 3:119–123
- Yasuda S, Ito N (1987) Behavior of lignin in organic pulping: I. Reaction of arylglycerol- $\beta$ -aryl ethers with acetic acid. *Mokuzai Gakkaishi* 33:708–716
- Davis JL, Nakatubo F, Murakami K, Umezawa T (1987) Organic acid pulping of wood: IV. Reactions of arylglycerol- $\beta$ -guaiacyl ethers. *Mokuzai Gakkaishi* 33:478–486
- Lundquist K (1970) Acid degradation of lignin: II. Separation and identification of low molecular weight phenols. *Acta Chem Scand* 24:889–907
- Karlsson O, Lundquist K, Meuller S, Westid K (1988) On the acidolytic cleavage of arylglycerol  $\beta$ -aryl ethers. *Acta Chem Scand* 42:48–51