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Effects of aromatic ring type on reactions subsequent to the *β-O*-4 bond cleavage of non-phenolic lignin model compounds under alkaline pulping conditions

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Abstract

The reaction products of an alkaline treatment of non-phenolic *β-O*-4-type lignin model compounds (C_6–C_2-type) consisting of *p*-hydroxyphenyl (H), guaiacyl (G), and/or syringyl (S) nuclei were identified and quantified. This was performed to examine how the type of H, G, or S nucleus affect the reaction product profiles. The major identified and quantified reaction products were phenol derivatives that were liberated from the aryl sides of the *β-O*-4 ether bonds of the lignin model compounds. Other products included derivatives of phenylethane-1,2-diol (glycol-type), benzaldehyde, and acetophenone, which originated from the alkyl sides of the *β-O*-4 ether bonds of the lignin model compounds. Although the type of aromatic nucleus of the aryl side of the *β-O*-4 ether bond of the lignin model compounds did not significantly affect the profile of the reaction products, the type of the alkyl side nucleus was influential. The glycol-type compound was the exclusive major reaction product when the S nucleus was on the alkyl side of the *β-O*-4 ether bond. On the other hand, when the H or G nucleus was present, a benzaldehyde derivative was the other major reaction product.

Keyword *β-O*-4 bond cleavage · Cooking · Delignification · Side-chain

Introduction

Preparation of pulp for paper production is the biggest biomass conversion process on earth. In the chemical pulping process, wood chips are delignified under relatively severe alkaline conditions (*ca*. 1–2 mol/L NaOH, 150–170 °C, 2–6 h). The delignification is mainly controlled by progress of the *β-O*-4 bond cleavage in non-phenolic lignin moieties. This is because the *β-O*-4 bond is the most common linkage between subunits in native lignin and exists primarily in non-phenolic moieties. The mechanism of the *β-O*-4 bond cleavage has been extensively studied (Fig. 1) [1–9]. The
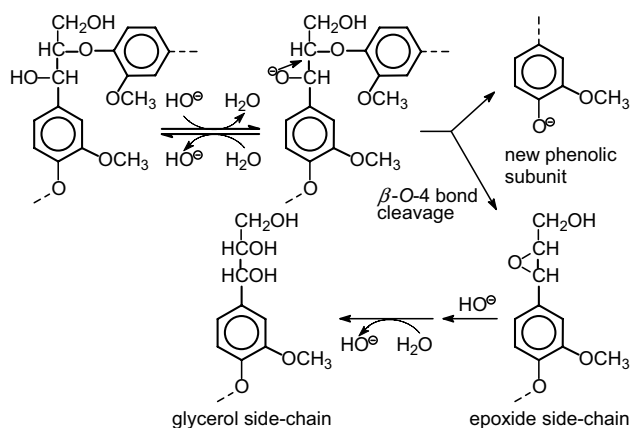
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α-alkoxide generated by dissociation attacks the neighboring *β*-carbon, resulting in the *β-O*-4 bond cleavage and the formation of a new phenolic subunit and another with an epoxide side-chain as an intermediate. This cleavage is an intramolecular S_N2-type neighboring group participation reaction. The epoxide side-chain intermediate is converted to a glycerol side-chain through the action of the hydroxide anion (Fig. 1) [4–6, 10–16]. However, the proportion of the epoxide side-chain intermediate that is converted to the glycerol side-chain and structures other than the glycerol side-chain that may be formed have not been investigated. Thus, it is meaningful to examine the entire profile of the reaction products obtained from a *β-O*-4-type substructure to further understand the alkaline pulping reaction.

In this study, eight dimeric non-phenolic *β-O*-4-type lignin model compounds with *p*-hydroxyphenyl (H), guaiacyl (G), and/or syringyl (S) nuclei (Fig. 2) were reacted under alkaline pulping conditions to identify and quantify their respective reaction products. The purpose of this study is to understand the dependence of the reaction product profile on the type of aromatic nucleus contained within the lignin model compounds. The lignin model compounds were not common C_6–C_3-types with

Fig. 1 The mechanism of the *β-O*-4 bond cleavage of a non-phenolic lignin substructure under alkaline pulping conditions
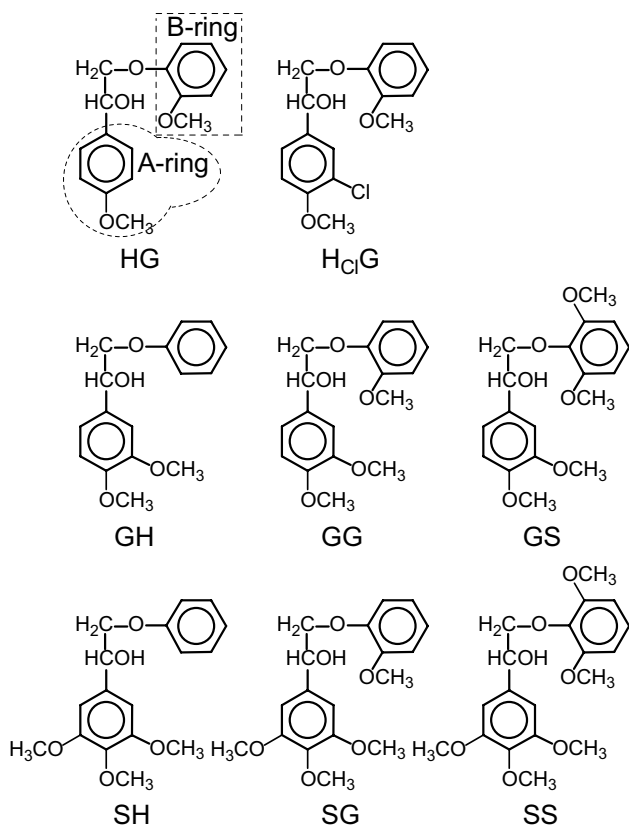
Fig. 2 Structure of the *β-O*-4-type lignin model compounds used in this study

a 2-aryloxy-1,3-dihydroxypropyl side-chain, but C_6–C_2-types with a 2-aryloxy-1-hydroxyethyl side-chain. The C_6–C_2-type compounds were used due to their lack of a *γ*-hydroxymethyl group. This lack limits the possible reaction routes of the epoxide side-chain intermediate, which is advantageous for analyzing the reactions of the intermediate.

Materials and methods

Materials

All chemicals used in this study except for the compounds described below were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), or Sigma-Aldrich Japan K. K. (Tokyo, Japan) and used without further purification. Water was deionized and thoroughly degassed before use.

The lignin model compounds are shown in Fig. 2: 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanol (HG), 1-(3,4-dimethoxyphenyl)-2-phenoxyethanol (GH), 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol (GG), 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl) ethanol (GS), 1-(3,4,5-trimethoxyphenyl)-2-phenoxyethanol (SH), 2-(2-methoxyphenoxy)-1-(3,4,5-trimethoxyphenyl) ethanol (SG), 2-(2,6-dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethanol (SS), and 1-(3-chloro-4-methoxyphenyl)-2-(2-methoxyphenoxy)ethanol ($H_{Cl}G$, H_{Cl}: 3-chloro-4-methoxyphenyl aromatic nucleus). The compounds were abbreviated according to the types of aromatic A- and B-rings in this order (see HG in Fig. 2 for definition). All the lignin model compounds except HG and $H_{Cl}G$ were the same as those used in our previous reports [17, 18]. HG and $H_{Cl}G$ were synthesized, following the methods described by Alder et al. [19] and in our previous reports [17, 18]. Their structures and purities were confirmed by proton nuclear magnetic resonance spectroscopy (1H-NMR, JNM-A500, 500 MHz, JEOL Ltd., Tokyo, Japan).

Four derivatives of 1-phenylethane-1,2-diol (glycol side-chain-types), 1-(4-methoxyphenyl)ethane-1,2-diol (H_{-gly}, Fig. 3), 1-(3,4-dimethoxyphenyl)ethane-1,2-diol (G_{-gly}, Fig. 3), 1-(3,4,5-trimethoxyphenyl)ethane-1,2-diol (S_{-gly}, Fig. 3), and 1-(3-chloro-4-methoxyphenyl)ethane-1,2-diol (H_{Cl-gly}, Fig. 3), were synthesized as authentic compounds for identifying the reaction products obtained from the lignin model compounds with H, G, S, and H_{Cl-gly} aromatic nuclei in the A-ring, respectively. The synthetic method used was similar to that described by Ek et al. [20] and in our previous report [21]. The structures and purities of the compounds were confirmed by 1H-NMR.

Another compound, 3,4-dimethoxyphenylacetaldehyde (homoveratraldehyde, G_{-CH_2CHO}, Fig. 3), was prepared using the method described in our previous report [22] to examine its formation and conversion in the reactions of the lignin model compounds. The structure was confirmed by gas chromatography/mass spectrometry (GC/MS, GC-2010/ PARVUM2, Shimadzu Co., Kyoto, Japan).
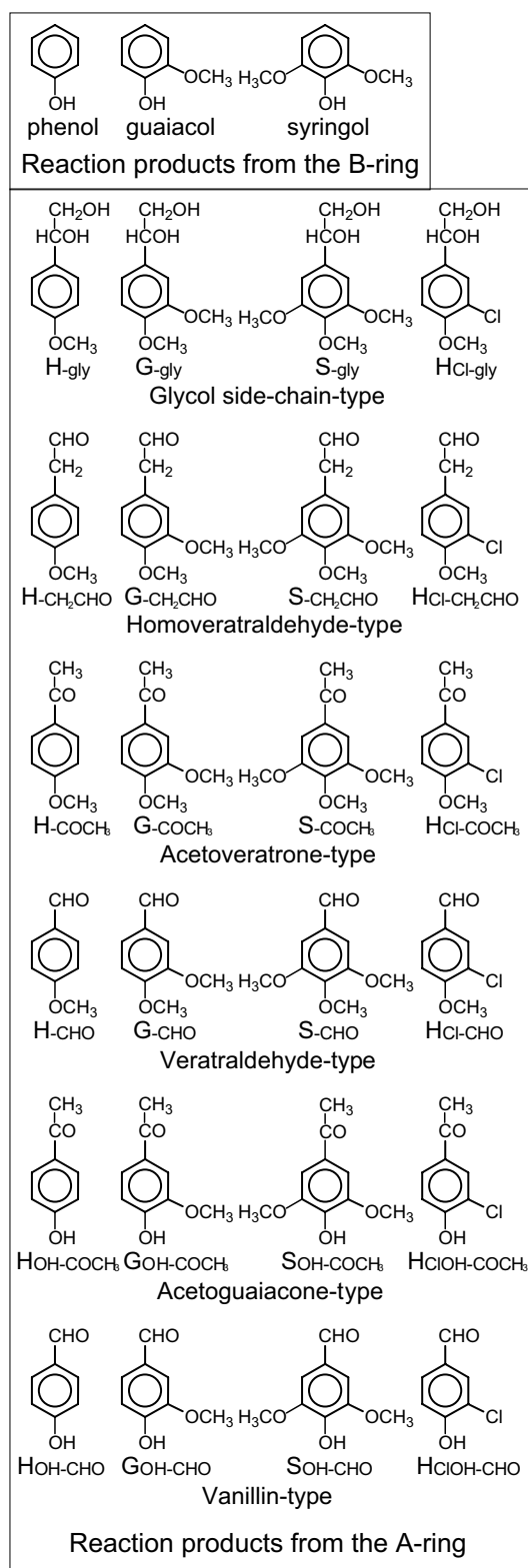
Fig. 3 Structure of the targeted reaction products in this study

Alkaline treatment of the lignin model compounds

Each lignin model compound was individually reacted in a stainless-steel autoclave (10 mL volume, Taiatsu Techno Co., Tokyo, Japan) after thorough degassing of the reaction solution and replacement of the air in the head space with nitrogen gas. Reaction conditions were: concentration of NaOH 1.0 mol/L, initial concentration of the lignin model compound 1.2 mmol/L, temperature 150 °C, volume of the solution 5.0 mL. All procedures were identical to those described in our previous reports [17, 18]. Each lignin model compound was reacted at least twice to confirm the reproducibility of the results.

Each of the possible reaction products originating from the lignin model compounds with G nucleus as the A-ring, G_{-gly}, 1-(3,4-dimethoxyphenyl)ethanone (acetoveratrone, G_{-COCH_3}, Fig. 3), 3,4-dimethoxybenzaldehyde (veratraldehyde, G_{-CHO}, Fig. 3), and 4-hydroxy-3-methoxybenzaldehyde (vanillin, G_{OH-CHO}, Fig. 3), was individually reacted under identical conditions to examine its stability and conversion reaction. Another possible reaction product, G_{-CH_2CHO}, was reacted as a starting compound under conditions different from those described above. In this reaction, the solvent was not 100% water but approximately 30% 1,4-dioxane (v/v) containing G_{-CH_2CHO} with an initial concentration of 12 mmol/L at 20–25 °C for 60 min. These different reaction conditions were used, because it was difficult to isolate G_{-CH_2CHO} as a pure solid or syrup [23–25] and it was not stable enough to react under the conditions used for the other compounds.

Qualitative and quantitative analyses of the reaction products

All work-up procedures were identical to those described in our previous reports [17, 18] except those for the reaction of G_{-CH_2CHO} as a starting compound.

The reaction products were identified using high-performance liquid chromatography (HPLC, LC-10A, Shimadzu Co.) with a photodiode array detector (SPD-M10A, Shimadzu Co.) based on the following observations. (1) The retention time and UV–visible spectrum from 190 to 800 nm of the peak of a suspected compound on the HPLC chromatogram of a neutralized reaction solution were matched to the corresponding authentic compound. (2) When an authentic compound was added to the neutralized reaction solution, the obtained HPLC chromatogram was identical to that of the original solution without adding the authentic compound except for the area of the corresponding peak.

Reaction products were quantified by HPLC based on the absorbance of the eluents at 280 nm. A calibration curve was prepared for each reaction product and lignin model compound with an internal standard compound, 4-chlorophenol.

Conditions of the HPLC were as follows: column: Luna 5u C18 (2) 100A (150 mm × 4.6 mm, Phenomenex Inc., Torrance, CA, USA); oven temperature: 40 °C; flow rate: 1.0 mL/min; solvent system in the reactions of HG, GH, GG, GS, SG, and SS: gradient CH_3OH/H_2O (v/v) from 25/75 to 60/40 for 30 min and maintained for 5 min for a total time of 35 min; solvent system in the reaction of SH: gradient CH_3OH/H_2O (v/v) from 28/72 to 60/40 for 30 min and maintained for 5 min for a total time 35 min; solvent system in the reaction of $H_{Cl}G$: gradient CH_3CN/H_2O (v/v) from 15/85 to 60/40 for 35 min and maintained for 10 min for a total time of 45 min.

For the reaction of G_{-CH_2CHO}, the completed reaction solution was neutralized with acetic acid and extracted with dichloromethane containing 3,4,5-trimethoxybenzaldehyde as an internal standard compound, and then twice with fresh dichloromethane. The combined organic layer was analyzed by GC (GC-2010, Shimadzu Co.) equipped with a flame ionization detector (FID) after drying with anhydrous sodium sulfate. Conditions of the GC were as follows: carrier gas: helium; injector temperature: 240 °C; detector temperature: 250 °C; column: TC-17 (a fused-silica capillary column, 30 m × 0.25 mm × film thickness 0.25 μm, GL Sciences Inc., Tokyo, Japan); temperature program: from 150 °C (5 min) to 210 °C with a rate of 2 °C/min, and immediately to 240 °C with a rate of 5 °C/min (4 min) for a total time of 45 min.

Results and discussion

Reaction of HG and $H_{Cl}G$

Our previous reports showed that phenol (Fig. 3), 2-methoxyphenol (guaiacol, Fig. 3), or 2,6-dimethoxyphenol (syringol, Fig. 3), which is an H, G, or S nucleus, respectively, is liberated almost quantitatively from the aromatic B-ring of lignin model compounds with H (GH and SH), G (GG and SG), or S nucleus as the B-ring (GS and SS), respectively. This was observed under identical reaction conditions as those employed in this study [17, 18]. In this study, it was examined whether or not guaiacol is quantitatively liberated from the B-rings of HG and $H_{Cl}G$.

Figure 4a, b shows the time courses of the changes in the recovery yields of HG and $H_{Cl}G$, respectively, and the formation of guaiacol from HG and $H_{Cl}G$, respectively. The disappearance of these compounds was accompanied by the almost quantitative formation of guaiacol and could be approximated to a pseudo-first-order reaction. The pseudo-first-order reaction rate constants were determined to be 0.0158 and 0.0177 min^{-1}, respectively. Those of the other compounds were determined in our previous reports [17, 18, 26].
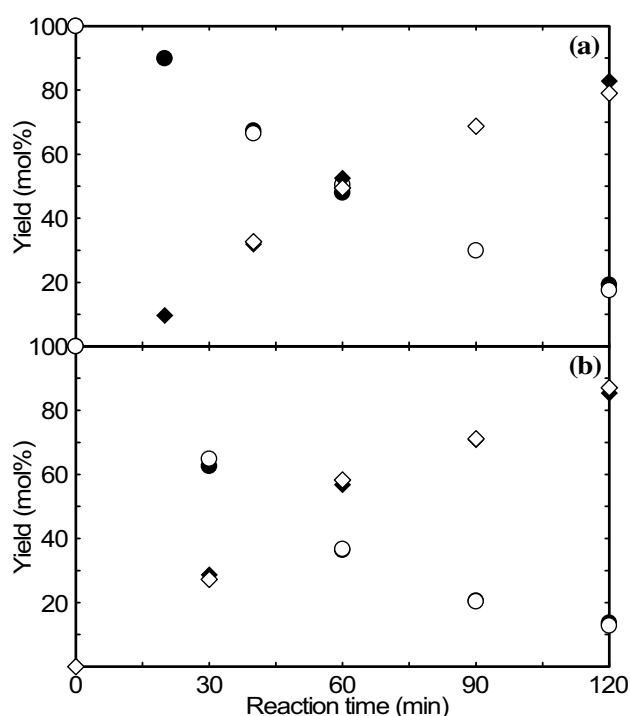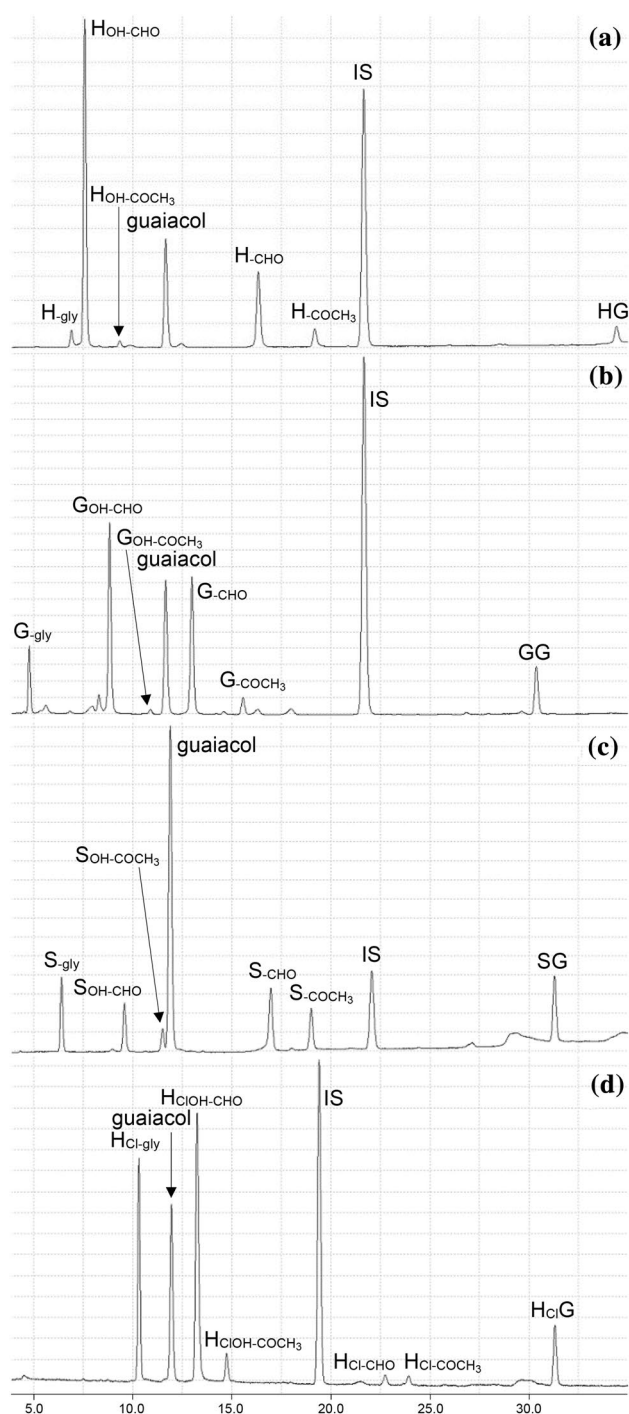

Fig. 4 Time courses of the changes in the recovery yields of HG and $H_{Cl}G$ and in the yields of guaiacol liberated from the B-rings of HG and $H_{Cl}G$ based on the initial amounts of HG and $H_{Cl}G$, respectively, in the reaction of: **a** HG and **b** $H_{Cl}G$. HG and $H_{Cl}G$: white and black circles, guaiacol: white and black diamonds. The white and black points represent the data obtained from the first and second trials, respectively

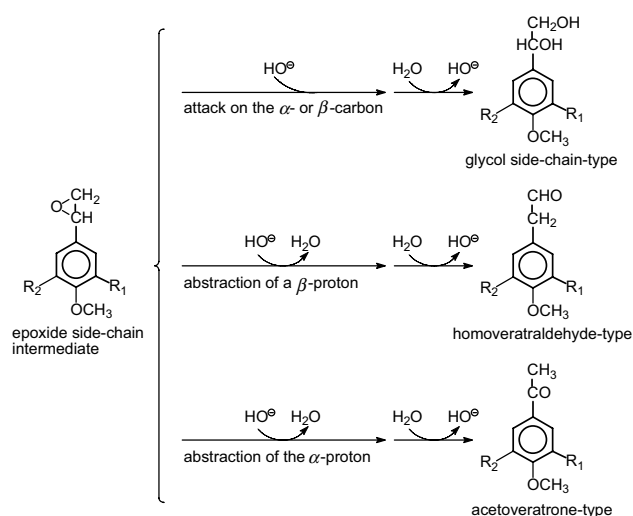### Qualitative analysis of the reaction products

Figure 5a–d shows the HPLC chromatograms of the neutralized reaction solutions of HG, GG, SG, and $H_{Cl}G$, respectively, obtained at reaction times of 150, 120, 90, and 120 min, respectively, when each of their recovery yields reached less than 15%. Because the chromatograms were not significantly different between GH, GG, and GS and between SH, SG, and SS, only representative chromatograms are shown. Most peaks other than those of the phenol derivatives liberated from the B-rings, the surviving lignin model compounds, and internal standard compounds are those of the reaction products of the original A-rings of the lignin model compounds. Figure 6 shows the theoretical reaction routes of the intermediate with the epoxide side-chain, which afforded three theoretical reaction products. The attack of the hydroxide anion on the α- or β-carbon as a nucleophile affords the glycol side-chain-type compounds H_{-gly}, G_{-gly}, S_{-gly}, and H_{Cl-gly} (Fig. 3). The attack on a β-proton as a base affords the homoveratraldehyde-type compounds H_{-CH_2CHO}, G_{-CH_2CHO}, S_{-CH_2CHO}, and H_{Cl-CH_2CHO} (Fig. 3). The attack on the α-proton as a base affords the acetoveratrone-type compounds H_{-COCH_3}, S_{-COCH_3}, and $H_{Cl-COCH_3}$

Fig. 5 HPLC chromatograms of the neutralized reaction solutions of: **a** HG, **b** GG, **c** SG, and **d** $H_{Cl}G$ at reaction times of 150, 120, 90, and 120 min, respectively

Fig. 6 Theoretical reaction routes of the intermediate with the epoxide side-chain

and vanillin-type compounds H_{OH-CHO}, G_{OH-CHO}, S_{OH-CHO}, and $H_{ClOH-CHO}$ (Fig. 3), was performed.

In the reaction of HG (Fig. 5a), H_{-gly}, H_{-COCH_3}, H_{-CHO}, $H_{OH-COCH_3}$, and H_{OH-CHO} were identified as reaction products of the original A-ring. H_{-CH_2CHO} was not detected, but most of the major peaks were identified.

In the reaction of GH, GG (Fig. 5b), or GS, G_{-gly}, G_{-COCH_3}, G_{-CHO}, $G_{OH-COCH_3}$, and G_{OH-CHO} were identified as reaction products of the original A-ring. G_{-CH_2CHO} was not detected, but most of the major peaks were identified. In addition, 3,4-dimethoxybenzyl alcohol (veratryl alcohol), 3,4-dimethoxytoluene, 1,2-dimethoxybenzene (veratrol), 4-hydroxy-3-methoxybenzyl alcohol (vanillyl alcohol), 3,4-dihydroxytoluene, and benzene-1,2-diol (pyrocatechol) were not detected.

In the reaction of SH, SG (Fig. 5c), or SS, S_{-gly}, S_{-COCH_3}, S_{-CHO}, $S_{OH-COCH_3}$, and S_{OH-CHO} were identified as reaction products of the original A-ring. S_{-CH_2CHO} was not detected, but most of the major peaks were identified.

In the reaction of $H_{Cl}G$ (Fig. 5d), H_{Cl-gly}, $H_{Cl-COCH_3}$, H_{Cl-CHO}, $H_{ClOH-COCH_3}$, and $H_{ClOH-CHO}$ were identified as reaction products of the original A-ring. H_{Cl-CH_2CHO} was not detected, but most of the major peaks were identified.

These identifications can be summarized as follows. Most of the major peaks were identified in the reactions of the *β-O*-4-type lignin model compounds. The five targeted types, the glycol side-chain type (H_{-gly}, G_{-gly}, S_{-gly}, and H_{Cl-gly}), acetoveratrone type (H_{-COCH_3}, G_{-COCH_3}, S_{-COCH_3}, and $H_{Cl-COCH_3}$), veratraldehyde type (H_{-CHO}, G_{-CHO}, S_{-CHO}, and H_{Cl-CHO}), acetoguaiacone type ($H_{OH-COCH_3}$, $G_{OH-COCH_3}$, $S_{OH-COCH_3}$, and $H_{ClOH-COCH_3}$), and vanillin type (H_{OH-CHO}, G_{OH-CHO}, S_{OH-CHO}, and $H_{ClOH-CHO}$), were consistently identified in all the reactions of the *β-O*-4-type lignin model

(Fig. 3). In all the reactions, identification of the six targeted compounds, which are the previously listed three types as well as the veratraldehyde-type compounds H_{-CHO}, G_{-CHO}, S_{-CHO}, and H_{Cl-CHO} (Fig. 3), acetoguaiacone-type compounds $H_{OH-COCH_3}$, $G_{OH-COCH_3}$, $S_{OH-COCH_3}$, and $H_{ClOH-COCH_3}$ (Fig. 3),

compounds. The other targeted homoveratraldehyde-type compounds (H_{-CH_2CHO}, G_{-CH_2CHO}, S_{-CH_2CHO}, or H_{Cl-CH_2CHO}) were not detected in any of the reactions. Thus, it was confirmed that the reaction product profile is not dependent on the type of aromatic nucleus in the lignin model compounds, based on qualitative analysis.

Quantitative analysis of the reaction products

The identified reaction products were quantified to determine their profile dependency on the type of aromatic nucleus of the β-O-4-type lignin model compounds on a quantitative basis. Figure 7 shows the time courses of the changes in the yields of the reaction products for the reaction of each β-O-4-type lignin model compound. Because the disappearance of each β-O-4-type lignin model compound was quantitatively accompanied by the liberation of the corresponding phenol derivative from the B-ring, as described above, the recovery yield is not shown.

In the reaction of HG, GH, GG, or GS (the left 4 figures in Fig. 7), guaiacol, phenol, guaiacol, or syringol, respectively, was liberated from the B-ring with a yield of 91, 92, 98, or 88%, respectively, at a final reaction time of 150, 300, 180, or 50 min, respectively, based on the initial amount of reactant. The total yield of the identified reaction products of the original A-ring was 62, 61, 60, or 42%, respectively, indicating that the amount of the identified reaction products were roughly two-thirds of the original A-ring, except for the reaction of GS. The glycol side-chain-type compound monotonically increased and became a major reaction product at the final reaction time in all the reactions. The veratraldehyde- and vanillin-type compounds were the other major reaction products at the end of the reaction of HG, GH, or GG. The veratraldehyde-type compound increased in the first half of the reaction, and subsequently decreased. The vanillin-type compound did not initially form during the reaction, but subsequently gradually increased. In the reaction of GS, the veratraldehyde-type compound was the other major reaction product with the glycol side-chain-type compound by the end, and the vanillin-type compound was a minor reaction product. The acetoveratrone- and acetoguaiacone-type compounds formed as minor reaction products in all the reactions.

In the reaction of SH, SG, or SS (the right 3 figures except for the top figure in Fig. 7), phenol, guaiacol, or syringol, respectively, was liberated from the B-ring with a yield of 94, 94, or 95%, respectively, at a final reaction time of 240, 120, or 50 min, respectively, based on the initial amount of reactant. The total yield of the identified reaction products of the original A-ring was 77, 93, or 90%, respectively, at the final reaction time. Thus, most reaction products of the original A-ring were identified except for the reaction of SH. The glycol side-chain-type compound monotonically increased in all reactions and became the exclusive major reaction product. The acetoveratrone-, veratraldehyde-, acetoguaiacone-, and vanillin-type compounds formed as minor products in all the reactions.

The glycol side-chain-type compound was the exclusive major reaction product formed with a high yield in the reaction of SH, SG, or SS, which consists of an S nucleus as the A-ring. On the other hand, it was one of a few major reaction products in the reaction of HG, GH, GG, or GS, which consists of an H or G nucleus as the A-ring. Thus, it was confirmed that the type of aromatic nucleus of the A-ring affects the reaction product profile on a quantitative basis. The S nucleus has two methoxy groups at the *meta*-position of the side-chain, exerting an electron-withdrawal effect on chemical reactions occurring at the benzyl position (α-position) in the side-chain (Hammett substituent constant: $\sigma = +0.115 \times 2$). This electron-withdrawal effect is stronger than that of the H nucleus with no methoxy group or G nucleus with only one methoxy group. It is anticipated that this relatively strong electron-withdrawal effect on the α-position results in the formation of the glycol side-chain-type compound as the exclusive major reaction product in the reaction of SH, SG, or SS.

$H_{Cl}G$ was used to examine this anticipation. The A-ring of $H_{Cl}G$, 3-chloro-4-methoxyphenyl nucleus, has an electron-withdrawing chloro group at the *meta*-position of the side-chain ($\sigma = +0.373$). In the reaction of $H_{Cl}G$ (the top right figure in Fig. 7), guaiacol was liberated from the B-ring with a yield of 88% at a final reaction time of 120 min based on the initial amount of $H_{Cl}G$. The total yield of the identified reaction products of the original A-ring was 83% at the final reaction time. Thus, many of the reaction products consisting of the original A-ring were identified. The glycol side-chain-type compound monotonically increased during the reaction, and as expected, was the exclusive major reaction product.

These results suggest that the relatively strong electron-withdrawing effect of the two methoxy groups of the S nucleus or of the chloro group of the H_{Cl} nucleus on the benzyl position (α-position) results in the formation of a glycol side-chain-type compound as the exclusive major reaction product. The strong electron-withdrawing effect increases the partial positive charge ($\delta+$) of the α-carbon of the intermediate with an epoxide side-chain (Fig. 6). This increase would lead hydroxide anion to the attack on the α-carbon to afford a glycol side-chain-type compound rather than to the attack on the α- or a β-proton to afford an acetoveratrone-type or homoveratraldehyde-type compound, respectively (Fig. 6).
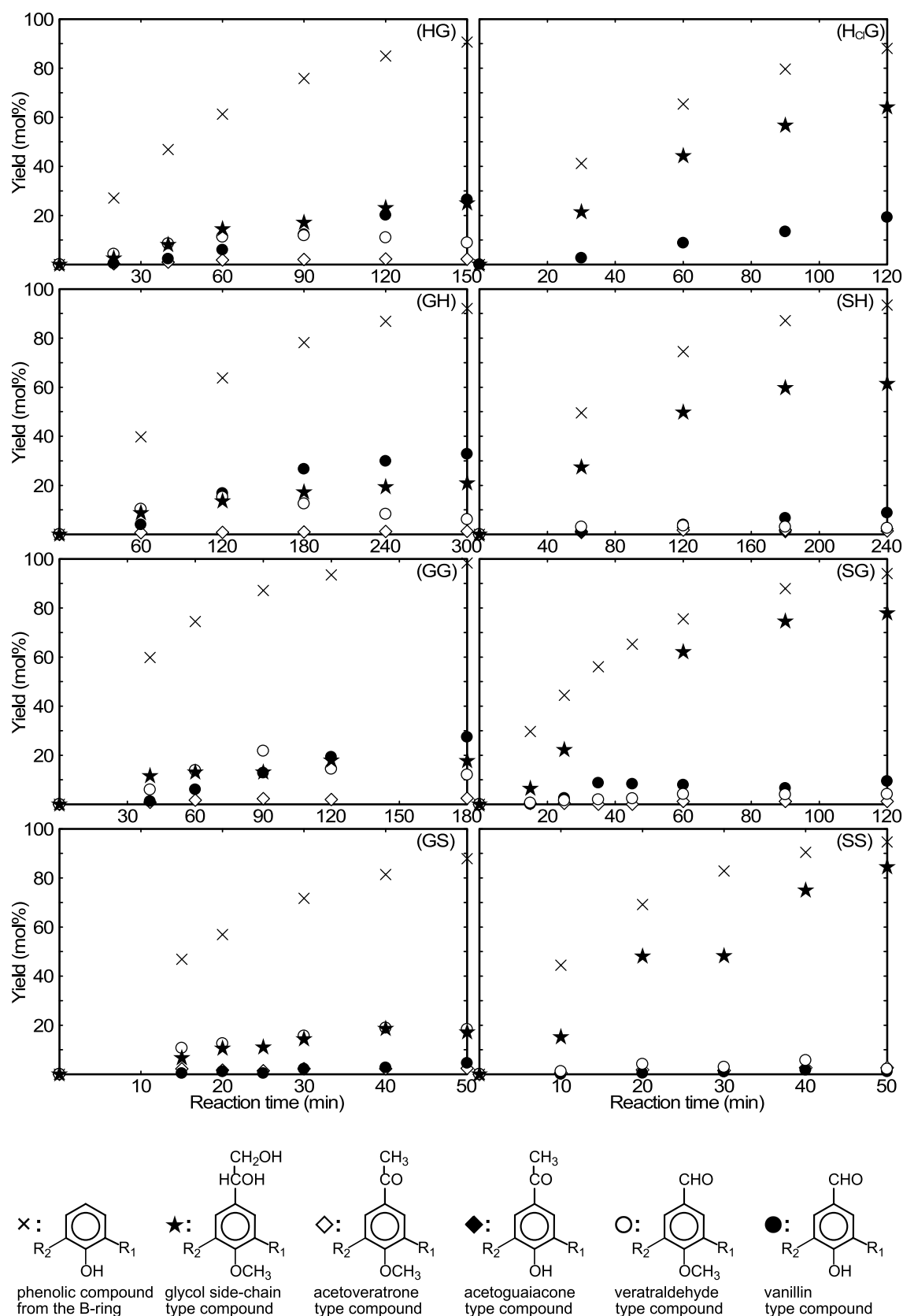
Fig. 7 Time courses of the changes in the yields of the identified reaction products, when each *β-O*-4-type lignin model compound was individually reacted. The white and black marks represent the data obtained from the first and second trials, respectively. Reaction products are not illustrated, when their yields were very low (< 1%)

Formation mechanism of the identified reaction products

Among the five types of the identified reaction products, the glycol side-chain-type compounds (H_{-gly}, G_{-gly}, S_{-gly}, and H_{Cl-gly}) and acetoveratrone-type compounds (H_{-COCH_3}, G_{-COCH_3}, S_{-COCH_3}, or $H_{Cl-COCH_3}$) form *via* the mechanism shown in Fig. 6. Although the veratraldehyde-type compounds (H_{-CHO}, G_{-CHO}, S_{-CHO}, and H_{Cl-CHO}) and vanillin-type compounds (H_{OH-CHO}, G_{OH-CHO}, S_{OH-CHO}, and $H_{ClOH-CHO}$) would not be produced by oxidation of contaminated dioxygen owing to the following reasons. (1) The reaction solutions were thoroughly degassed before the reaction. (2) The air in the head space of the reactor (5 mL) was thoroughly replaced with nitrogen before the reaction. (3) The corresponding phenol derivative was liberated from the B-ring of any β-O-4-type lignin model compound and detected with a high yield. The derivative was potentially oxidized by dioxygen more easily than the non-phenolic compounds produced as reaction products. It cannot completely be excluded that some primary reaction products were oxidized by other products affording veratraldehyde- and vanillin-type compounds.

The formation of veratraldehyde-type, vanillin-type, and acetoguaiacone-type compounds ($H_{OH-COCH_3}$, $G_{OH-COCH_3}$, $S_{OH-COCH_3}$, and $H_{ClOH-COCH_3}$) are not shown in Fig. 6. To examine their formation, reaction, and stability, a glycol side-chain-type compound G_{-gly}, acetoveratrone-type compound G_{-COCH_3}, veratraldehyde-type compound G_{-CHO}, and vanillin-type compound G_{OH-CHO} were individually reacted under identical conditions. A homoveratraldehyde-type compound G_{-CH_2CHO} was also reacted under much milder conditions. Figure 8a–d show the time courses of the changes in the recovery yields of G_{-gly}, G_{-COCH_3}, G_{-CHO}, and G_{OH-CHO}, respectively, and the yields of the identified reaction products when each of the compounds was individually reacted.

When the glycol side-chain-type compound G_{-gly} was reacted as a starting compound, the recovery yield was 88% at a reaction time of 180 min (Fig. 8a). A veratraldehyde-type compound G_{-CHO} and vanillin-type compound G_{OH-CHO} were the major reaction products with the yields of approximately 6 and 3%, respectively, at the same reaction time and based on the initial amount of G_{-gly}. The stability of G_{-gly} confirms that the reaction products identified in the reaction of the β-O-4-type lignin model compounds is not derived from the corresponding primarily produced glycol side-chain-type compound. The stability of G_{-gly} was much higher than those of GH, GG, and GS, because the recovery yield of GH, GG, or GS was 22, 2, or 0%, respectively, under identical reaction conditions at the same reaction time (180 min). Because the reaction of G_{-gly} is presumed to follow the mechanism shown in Fig. 1, the high stability of G_{-gly} can be attributed to the leaving ability of the leaving hydroxide
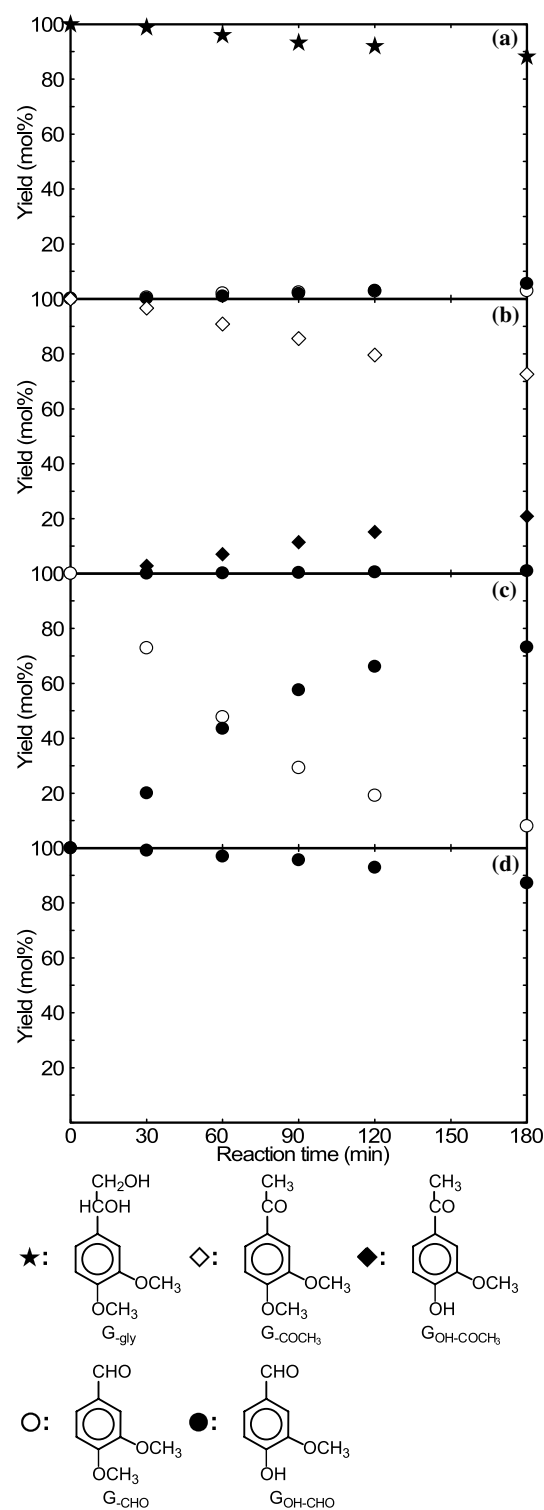
Fig. 8 Time courses of the changes in the recovery yields of: **a** G_{-gly}, **b** G_{-COCH_3}, **c** G_{-CHO}, and **d** G_{OH-CHO} and in the yields of the identified reaction products based on the initial amounts of: **a** G_{-gly}, **b** G_{-COCH_3}, **c** G_{-CHO}, and **d** G_{OH-CHO}, when: **a** G_{-gly}, **b** G_{-COCH_3}, **c** G_{-CHO}, or **d** G_{OH-CHO} was used as a starting compound

anion lower than that of the phenolate anion liberated from the B-ring of the *β-O*-4-type lignin model compounds. An acetoveratrone-type compound G_{-COCH_3} was not detected, although it was always produced in the reaction of *β-O*-4-type lignin model compounds and G_{-gly} should undergo the mechanism shown in Fig. 6. The lack of G_{-COCH_3} is likely due to the small amount of disappearing G_{-gly} and further conversion of G_{-COCH_3} to G_{-CHO} and G_{OH-CHO} as described below. The total yield of G_{-CHO} and G_{OH-CHO} from G_{-gly} was roughly three-fourths of the disappearing G_{-gly} (12%) at a reaction time of 180 min. The remaining one-fourth can be explained by the formation of G_{-CH_2CHO} *via* the route shown in Fig. 6 and consecutive conversion to uncharacterized compounds as described below.

When the acetoveratrone-type compound G_{-COCH_3} was used as a starting compound, the recovery yield was 73% at a reaction time of 180 min (Fig. 8b). An acetoguaiacone-type compound $G_{OH-COCH_3}$ and vanillin-type compound G_{OH-CHO} were the only identified reaction products with yields of 21 and 1%, respectively, at the same reaction time based on the initial amount of G_{-COCH_3}. This suggests that an acetoguaiacone-type compound detected in the reaction of the *β-O*-4-type lignin model compounds was derived from the corresponding primarily produced acetoveratrone-type compound. Because the yield of the vanillin-type compound was always similar to or higher than that of the acetoveratrone-type compound in the reaction of any *β-O*-4-type lignin model compound, it is likely that the vanillin-type compound was not derived from the corresponding acetoveratrone-type compound.

When the veratraldehyde-type compound G_{-CHO} was used as a starting compound, the recovery yield was 8% at a reaction time of 180 min (Fig. 8c). The vanillin-type compound G_{OH-CHO} was the only identified reaction product with a yield of 74% based on the initial amount of G_{-CHO} at the same reaction time. This suggests that the vanillin-type compound was mostly derived from the corresponding previously produced veratraldehyde-type compound in the reaction of the *β-O*-4-type lignin model compounds. The most likely mechanism is S_NAr, where a hydroxide anion attacks the aromatic carbon at the *para*-position of the benzyl carbonyl carbon and substitutes the methoxy group. S_N2 attack on the methyl carbon of the *para*-methoxy group represents another possible mechanism owing to the relatively high leaving ability of the 4-formyl-2-methoxyphenolate (vanillate) group.

When the vanillin-type compound G_{OH-CHO} was used as a starting compound, the recovery yield was 87% at a reaction time of 180 min. No reaction products were detected. The conversion or degradation of vanillin-type compounds to unknown compounds in the reaction of *β-O*-4-type lignin model compounds partly explains the gradual decrease of the total yields of remaining *β-O*-4-type lignin model compounds and the corresponding identified reaction products of the original A-ring.

When the homoveratraldehyde-type compound G_{-CH_2CHO} was used as a starting compound even under mild conditions (1.0 mol/L NaOH in 30% 1,4-dioxane at 20–25 °C for 60 min), the conversion/degradation was rapid with a recovery yield of approximately 5%. The veratraldehyde-type compound G_{-CHO} was the only detected reaction product with a yield of approximately 5–10% based on the initial amount of G_{-CH_2CHO}. Small precipitates appeared in the reaction solution after the reaction was initiated, and gradually grew in size. These observations indicate that the homoveratraldehyde-type compound is unstable under these conditions and a small amount of the corresponding veratraldehyde-type compound (and corresponding vanillin-type compound) is produced in the reaction of *β-O*-4-type lignin model compounds. This instability and conversion to unknown compounds is likely the main reason for the observation that the total amount of remaining *β-O*-4-type lignin model compounds and all the corresponding identified reaction products of the original A-rings gradually decreased with the progress of the reaction of *β-O*-4-type lignin model compounds.

Among the six types of targeted reaction products consisting of the original A-ring (Fig. 3), the formation route of the veratraldehyde-type compounds has not yet been determined, although the homoveratraldehyde-type compounds were not detected. The veratraldehyde-type compounds may form *via* an unknown route in the reaction of the *β-O*-4-type lignin model compounds.

In the reactions of GS and SS, the yields of the veratraldehyde-type compounds were higher than those of the vanillin-type compounds, which is contrast to those of all the other *β-O*-4-type lignin model compounds (Fig. 7). These phenomena suggest that the type of the B-ring affects the formations of these type of compounds. This suggestion cannot be explained by the above discussion that the vanillin-type compounds are derived from the veratraldehyde-type compounds. Because the effect of the type of the B-ring must appear only before the *β-O*-4 bond cleavage, an unknown mechanism (different from Fig. 1) may possibly contribute to the reaction of the *β-O*-4 bond cleavage.

In the reaction of $H_{Cl}G$, the yield of the veratraldehyde-type compound was very low and the vanillin-type compound formed with the fairly large amount (Fig. 7). This result suggests that the conversion of the veratraldehyde-type- to vanillin-type compound was very rapid owing to the character of the H_{Cl} nucleus as the A-ring and/or the vanillin-type compound favourably formed *via* an unknown mechanism. It can be noted as another point in the reaction of $H_{Cl}G$ that the total yield of the glycol side-chain-type compound H_{Cl-gly} and vanillin-type compound $H_{ClOH-CHO}$ was close to the yield of guaiacol from the B-ring.

Although the C_6–C_2-type dimeric lignin model compounds were employed in this study owing to simplifying the reactions and profiles of reaction products, these compounds are not the most suitable lignin model compounds. The most suitable C_6–C_3-type analogues are considered to show tendencies in the formations of the glycerol side-chain-type compounds (the derivatives of 1-phenylpropane-1,2,3-triol) similar to those of the glycol side-chain-type compounds observed in this study, because the formation mechanism of the glycerol side-chain-type compounds in the reactions of the C_6–C_3-type analogues are the same as that of the glycol side-chain-type compounds. The other minor reaction products observed in this study may also form in the reactions of the C_6–C_3-type analogues. Because the formation mechanisms of the other minor reaction products are different in the reactions between the C_6–C_2-type compounds and C_6–C_3-type analogues, however, nothing can be described on the formations of these minor reaction products in the reactions of the C_6–C_3-type analogues.

Conclusions

The identified reaction products consisted of five types, including the glycol side-chain-, acetoveratrone-, veratraldehyde-, acetoguaiacone-, and vanillin-types, in the reactions of eight non-phenolic β-O-4-type lignin model compounds with H, G, and/or S nuclei under alkaline pulping conditions. The type of aromatic nucleus of the A-ring of the lignin model compounds significantly affected the reaction product profile. The glycol side-chain-type compound is the only major reaction product in the reactions of the lignin model compounds with an S nucleus as the A-ring. This exclusive formation results from the relatively strong electron-withdrawing effect of the two methoxy groups of the S nucleus on the benzyl carbon of the epoxide intermediate. The veratraldehyde- and vanillin-type compounds are the other major reaction products in the reactions of the lignin model compounds with an H or G nucleus as the A-ring. The type of aromatic nucleus as the B-ring does not significantly affect the reaction product profile.

References

1. Hughes GK, Thompson EOP (1949) Studies in the demethylation of thioanisole. J Proc R Soc N S W 83:269–272
2. Gierer J, Kunze I (1961) Cleavage of β-hydroxyalkyl ary ethers by alkali (in German). Acta Chem Scand 15:803–807
3. Gierer J, Noren I (1962) Reactions of lignin on sulfate digestion II: Model experiments on the cleavage of aryl alkyl ethers by alkali (in German). Acta Chem Scand 16:1713–1729
4. Gierer J, Noren I (1962) Cleavage of β-hydroxyalkyl ary ethers by alkali II: the stereochemical course (in German). Acta Chem Scand 16:1976–1988
5. Gierer J, Lenz B (1965) Reactions of lignin during sulphate cooking Part 6: formation of 1,2-glycol groups in milled wood lignin on treatment with 2 N sodium hydroxide at 170 °C. Svensk Papperstidn 68:334–338
6. Miksche GE (1973) Behavior of lignins during alkali boiling IX: Alkaline decomposition of arylglycerin-β-(2,6-dimethoxy-4-alkylaryl)-ether structures (In German). Acta Chem Scand 27:1355–1368
7. Ljunggren S (1980) The significance aryl ether cleavage in kraft delignification of softwood. Svensk Papperstidn 83:363–369
8. Gierer J, Noren I (1980) On the course of delignification during kraft pulping. Holzforschung 34:197–200
9. Hubbard TF Jr, Schultz TP, Fisher TH (1992) Alkaline hydrolysis of non-phenolic β-O-4 lignin model dimers: substituent effect on the leaving phenoxide in neighboring group vs direct nucleophilic attack. Holzforschung 46:315–320
10. Lundquist K (1973) Formation of low molecular weight phenols from "milled wood lignin" during sulphate and soda cooking. Svensk Papperstidn 76:704–710
11. Löwendahl L, Petersson G, Samuelson O (1978) Phenolic compounds in kraft black liquor. Svensk Papperstidn 81:392–396
12. Niemelä K, Sjöström E (1986) Simultaneous identification of aromatic and aliphatic low molecular weight compounds from alkaline pulping liquor by capillary gas-liquid chromatography-mass spectrometry. Holzforschung 40:361–368
13. Van der Klashorst GH, Strauss HF (1987) Properties and potential utilization of industrial eucalyptus soda/anthraquinone lignin Part I: isolation and origin of the low molecular mass lignin fragments present in an industrial soda/anthraquinone spent pulping liquor. Holzforschung 41:123–131
14. Niemelä K (1988) GLC-MS studies on pine kraft black liquors Part I. Identification of monomeric products. Holzforschung 42:169–173
15. Niemelä K (1988) Gas-liquid chromatography-mass spectrometry studies on pine kraft black liquors III: the liberation of carboxylic acids in the initial phase of pulping. J Chromatogr 446:247–252
16. Lundquist K, von Unge S (2004) Stability of arylglycerols during alkaline cooking. Holzforschung 58:330–333
17. Shimizu S, Posoknistakul P, Yokoyama T, Matsumoto Y (2013) Quantitative difference in the rates of the β-O-4 bond cleavage between lignin model compounds with and without γ-hydroxymethyl groups during the alkaline pulping process. BioResources 8:4312–4322
18. Shimizu S, Yokoyama T, Matsumoto Y (2015) Effect of type of aromatic nucleus in lignin on the rate of the β-O-4 bond cleavage during alkaline pulping process. J Wood Sci 61:529–536
19. Adler E, Lindgren BO, Saeden U (1952) The β-guaiacyl ether of α-veratrylglycerol as a lignin model. Svensk Papperstidn 55:245–254
20. Ek M, Gierer J, Jansbo K (1989) Study on the selectivity of bleaching with oxygen-containing species. Holzforschung 43:391–396
21. Yokoyama T, Matsumoto Y, Meshitsuka G (2005) Characterization of active oxygen species under oxygen-alkali bleaching conditions. Holzforschung 59:269–275
22. Yokoyama T, Matsumoto Y (2008) Revisiting the mechanism of β-O-4 bond cleavage during acidolysis of lignin. Part 1: kinetics of the formation of enol ether from non-phenolic C_6-C_2 type model compounds. Holzforschung 62:164–168

23. Brunow G, Lundquist K (1984) On the synthesis and stereochemistry of certain lignin-related α-aryloxycinnamic acids and enol ethers. Acta Chem Scand B 38:323–325
24. Karlsson O, Lundquist K, Meuller S, Westlid K (1988) On the acidolysis cleavage of arylglycerol β-ethers. Acta Chem Scand B 42:48–51
25. Yokoyama T, Matsumoto Y (2010) Revisiting the mechanism of β-O-4 bond cleavage during acidolysis of lignin. Part 2: detailed reaction mechanism of a non-phenolic C_6–C_2 type model compound. J Wood Chem Tech 30:269–282
26. Shimizu S, Akiyama T, Yokoyama T, Matsumoto Y (2017) Chemical factors underlying the more rapid β-O-4 bond cleavage of syringyl than guaiacyl lignin under alkaline delignification conditions. J Wood Chem Technol 37:451–466