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ORIGINAL ARTICLE

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Preparation of anion-exchange resins from pine sulfuric acid lignin, one of the acid hydrolysis lignins

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Abstract To utilize acid hydrolysis lignin effectively, chemical conversion to anion-exchange resin was investigated by two methods. Sulfuric acid lignin (SAL) was selected as a typical acid hydrolysis lignin in this experiment. Because it is less reactive, SAL was phenolated with sulfuric acid catalyst to yield reactive phenolized SAL (P-SAL) with *p*-hydroxyphenyl nuclei. One method was the restricted resinification of P-SAL followed by the Mannich reaction with formaldehyde and dimethylamine to yield a weakly basic anion-exchange resin with an ion-exchange capacity of 2.4 mEq/g. Another method was to react resinified P-SAL with glycidyltrimethylammonium chloride to yield a strongly basic anion-exchange resin with an ion-exchange capacity of 2.0 mEq/g. The reaction of a simple P-SAL model compound with an epoxide suggested that the phenolic hydroxyl group of the *p*-hydroxyphenyl nucleus had slightly higher reactivity than that of the guaiacyl nucleus.

Key words Lignin · Acid hydrolysis lignin · Mannich reaction · Epoxy reagents · Anion-exchange resin

Introduction

Recently, much attention[1–6] has been paid to hydrolysis of cellulose and hemicellulose of biomass resources with enzyme and acid from the standpoint of suppressing carbon dioxide evolution from fossil resources, production of industrial organic resources, production of liquid fuel, conservation of the global environment, and so on. In each case, polysaccharides of cellulose and hemicellulose are first hydrolyzed with enzyme or sulfuric acid to monosaccharides and then converted to ethanol by fermentation. It was also reported that the sulfuric acid used as a catalyst for saccharification was recovered with an anion-exchange resin.[7]

There are two major methods for converting lignocellulosic biomass into monosaccharides. One is enzymatic hydrolysis. This method has an advantage in that special instruments are not needed owing to the moderate reaction condition. However, it has disadvantages, such as the need for pretreatment (e.g., explosion to facilitate enzyme attack) and selecting a species for high yield. Another method is acid hydrolysis, which does not require species selection and can produce monosaccharides at high yield. Its drawbacks are the need for acid-resistant instruments and the production of less reactive acid lignin. One of the key considerations when developing acid saccharification is to find effective ways to utilize acid lignin.

There have been many investigations on the utilization of acid lignin. Arbuzov and Ovchinnikov[8] studied the utilization of acid lignin for manufacturing boards, Tzolova and Christov[9] studied the conversion of chlorinated acid lignin to anion-exchange resin, and Tsolova and Todorov[10] investigated the substitution of carbon black as a filler for phosphorylated hydrolytic lignin for rubber production. The preparation of anion-exchange resins from acid lignin also has been attempted. Enkvist et al.[11] attempted to introduce amino groups into saccharification lignin, but the ion-exchange capacity reached no more than 0.55 mEq/g. Tai et al.[12] prepared an anion-exchange resin by chloromethylation of sulfuric acid lignin and subsequent amination to obtain resin with an ion-exchange capacity of 1.97 mEq/g. However, an intermediate of chloromethylation was unstable because of hydrolysis of the chloride.

Recently, Yasuda et al.[13,14] investigated the structure of sulfuric acid lignin (SAL), which is characterized by condensed structures formed by intermolecular dehydration between the benzylic carbons and the six positions of the guaiacyl nuclei. Thus, SAL has extremely low reactivity

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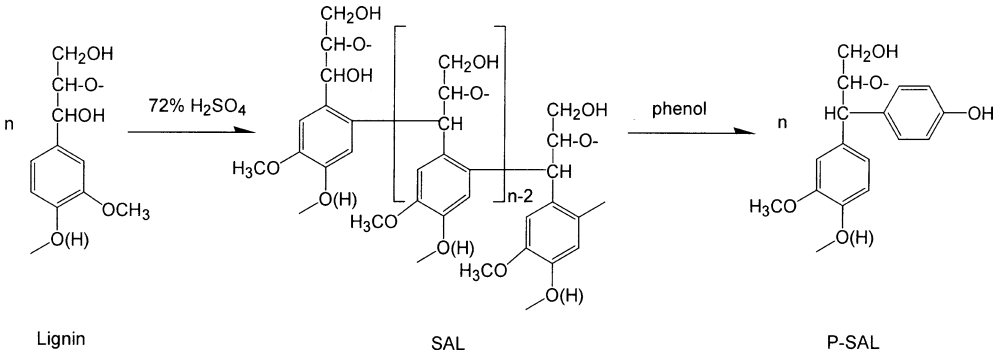

Fig. 1. Basic structures of surfuric acid lignin (*SAL*) and phenolated SAL (*P-SAL*)

Table 1. Mannich reaction of RHP-SAL (50 mg)

Trial	Reaction conditions			Ion-exchange capacity (mEq/g)
	50% $HN(CH_3)_2$ (ml)	37% HCHO (ml)	Time (h)	
1	1620	1460	4	1.1
2	1620	1460	18	2.4

RHP-SAL, resinified phenolized sulfuric acid lignin

because of the disappearance of the reactive benzylic hydroxyl and/or ether groups. During basic studies on the chemical structures of SAL, they also found that condensed aromatic nuclei of SAL with a diarylmethane structure are selectively exchanged with phenol in the presence of a sulfuric acid catalyst.[15] As a result, the reactivity of phenolized sulfuric acid lignin (P-SAL), which is soluble in a dilute alkaline solution and in organic solvents, is enhanced because a reactive *p*-hydroxyphenyl moiety is introduced at the side chain α-position instead of condensed-type aromatic nuclei (Fig. 1). P-SAL could be converted to water-soluble lignosulfonate,[16,17] a strongly acidic cation-exchange resin[18] and cationic surfactant.[19] In this study, the chemical conversion of P-SAL to an anion-exchange resin was investigated using the Mannich reaction and reaction with an epoxy reagent.

Experimental

Sulfuric acid lignin

Sulfuric acid lignin was prepared from red pine (*Pinus densiflora* Sieb. et Zucc) by treating it with 72% sulfuric acid in the usual manner.[20]

Phenolation of SAL

A mixture of 1.0 g of SAL and 6.3 g of phenol in 15 ml of 72% sulfuric acid was stirred at 60°C for 6 h. After quenching by dilution with 560 ml of water, the suspension was boiled for 3 h. The solids were filtered out with a glass filter and were thoroughly washed with warm water to give P-SAL.[15]

Hydroxymethylation of P-SAL

To a solution of 100 mg of P-SAL in 5 ml of 1 N NaOH was added 0.3 ml of 37% formaldehyde; it was stirred at 50°C for 2 h. After acidification with 1 N HCl, the hydroxymethylated product (HP-SAL) was separated by centrifugation. The number of hydroxylmethyl groups introduced was 0.5 per phenolated phenylpropane unit (C_9-C_6), on the assumption that all of the weight gain of the reaction product is attributed to the hydroxymethyl group.[16]

Resinification of HP-SAL

A 100-mg sample of HP-SAL was added to 1 ml of 72% sulfuric acid at room temperature. After 2 h the reaction products were filtered with a glass filter, washed with water, and then dried to give 97 mg of resinified HP-SAL (RHP-SAL).

Mannich reaction of P-SAL

A 100-mg aliquot of P-SAL in 10 ml of 80% aqueous dioxane, 0.15 ml of 37% formaldehyde, and 0.18 ml of 50% dimethylamine was stirred for 4 h at 60°C. The reaction mixture was dialyzed with a cellulose tube to remove the excess reaction reagents, and the reaction products were lyophilized to yield the Mannich reaction products. The number of dimethylaminomethyl groups introduced to the MP-SAL was calculated by elemental analysis to be 0.7 per phenolated phenylpropane unit on the assumption that all of the nitrogen atoms in the reaction product are attributed to the dimethylaminomethyl group.[19]

Mannich reaction of RHP-SAL

A 50-mg sample of RHP-SAL in 1 ml of 80% aqueous dioxane was reacted, as described above, with formaldehyde and dimethylamine under various conditions at 60°C, as shown in Table 1. The reaction mixture was filtered off with a glass filter, washed with water, and then dried to give the Mannich reaction products (MRHP-SAL) (weakly basic anion-exchange resin).

Synthesis of 5-(N,N-dimethylaminomethyl) creosol (**1**)

To a stirred mixture of 2 g of creosol in 50 ml of dioxane, 1.5 ml of 37% aqueous solution of formaldehyde, and 10 ml of acetic acid below 0°C plus 1.7 ml of 50% aqueous solution of dimethylamine were added. The mixture was then heated at 50°C for 4 h. After adding 2 N NaOH until pH 9, the reaction mixture was extracted with ethyl acetate. The ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure. Products were purified by silica-gel column chromatography with *n*-hexane and acetone (9:1, v/v) as an eluent to give 2.3 g (81.4% from creosol) of **1**.

1: ^{1}H-NMR [$(CD_3)_2CO$ –D_2O (9:1, v/v) ppm]: δ 2.21 (3H, s, CH_3), 2.29 [6H, s, $N(CH_3)_2$], 3.57 (2H, s, CH_2), 3.80 (3H, s, OCH_3), 6.47 (1H, d, J = 3 Hz, Ar-H), 6.70 (1H, d, J = 2 Hz, Ar-H). ^{13}C-NMR [$(CD_3)_2CO$ –D_2O (9:1, v/v) ppm]: δ 20.9 (CH_3), 44.6 [$N(CH_3)_2$], 56.2 (OCH_3), 62.2 (CH_2), 113.3, 122.1, 123.3, 128.7, 145.5, 148.5. MS *m/z*: 195 (M^+).

Reaction of compound **1** with formaldehyde in acidic condition

To a solution of 50 mg of **1** in 0.5 ml of 36% sulfuric acid, 0.5 ml of 37% formaldehyde was added. The solution was heated at 70°C for 24 h. After it was neutralized with 3 N NaOH, the reaction mixture was extracted with ethyl acetate. The ethyl acetate solution was dried over sodium sulfate and then concentrated under reduced pressure to give products. The reaction products were purified by silica-gel column chromatography with benzene and methanol (9:1, v/v) to give 8 mg (13.9%) of **2**.

2: ^{1}H-NMR [$(CD_3)_2CO$ –D_2O (9:1, v/v) ppm]: δ 2.26 [6H, s, $N(CH_3)_2$], 2.29 (3H, s, CH_3), 3.72 (2H, s, CH_2), 3.80 (3H, s, OCH_3), 4.50 (2H, s, CH_2OH), 6.71 (1H, s, Ar-H). ^{13}C-NMR [$(CD_3)_2CO$ –D_2O (9:1, v/v) ppm]: δ 19.5 (CH_3), 44.5 [$N(CH_3)_2$], 56.1, 56.3, 59.0, 113.9, 124.2, 127.5, 133.3, 145.8, 147.3. MS *m/z*: 225 (M^+).

Synthesis of 1-guaiacyl-1-p-hydroxyphenylethane (**3**)

Compound **3** was prepared as previously described.[21]

3: ^{1}H-NMR ($CDCl_3$, ppm): δ 1.57 (3H, d, J = 7 Hz, CH_3), 3.82 (3H, s, OCH_3), 4.02 (1H, q, J = 7 Hz, CH), 4.87 (1H, s, OH), 5.51 (1H, s, OH), 6.66 (1H, d, J = 2 Hz, Ar-H), 6.72 (1H, dd, J = 2 and 8 Hz, Ar-H), 6.74 (2H, d, J = 8 Hz, ArH), 6.84 (1H, d, J = 8 Hz, Ar-H), 7.02 (2H, d, J = 8 Hz, Ar-H). ^{13}C-NMR ($CDCl_3$, ppm): δ 22.3 (CH_3), 43.6 (CH), 55.9 (OCH_3), 110.4, 114.2, 115.3, 120.1, 128.8, 139.0, 139.2, 143.9, 146.5, 153.8. MS *m/z*: 194 (M^+).

Reaction of compound **3** with propylene oxide

To a stirred 1 N NaOH solution of 500 mg of **3**, 1.4 ml of propylene oxide (PO) was added at 50°C for 3 h. After neutralization with 1 N HCl, the reaction mixture (pH 4) was extracted with ethyl acetate. The ethyl acetate solution was dried over sodium sulfate and then concentrated under reduced pressure. Products were separated by silica-gel column chromatography with *n*-hexane and ethyl acetate (5:1, v/v) to give three compounds (**4**, **5**, **6**).

4: ^{1}H-NMR ($CDCl_3$, ppm): δ 1.26 (3H, d, J = 6 Hz, CH_3), 1.57 (3H, d, J = 7 Hz, CH_3), 2.50 (1H, s, OH), 3.76 (1H, dd, J = 8 and 9 Hz, OCH_2), 3.80 (3H, s, OCH_3), 3.90 (1H, dd, J = 3 and 9 Hz, OCH_2), 4.03 (1H, q, J = 7 Hz, CH), 4.15 (1H, m, CHOH), 5.60 (1H, s, OH), 6.66 (1H, d, J = 2 Hz, Ar-H), 6.71 (1H, dd, J = 2 and 8 Hz, Ar-H), 6.82 (2H, d, J = 8 Hz, Ar-H); 6.83 (1H, d, J = 8 Hz, Ar-H); 7.11 (2H, d, J = 8 Hz, Ar-H). ^{13}C-NMR ($CDCl_3$, ppm): δ 18.8 (CH_3), 22.3 (CH_3), 43.6 (CH), 55.9 (OCH_3), 66.4(CHOH), 73.5 (OCH_2), 110.5, 114.3, 114.6, 120.2, 128.6, 138.9, 139.6, 144.0, 146.6, 157.0. MS *m/z*: 302 (M^+).

5: ^{1}H-NMR ($CDCl_3$, ppm): δ 1.21 (3H, d, J = 6 Hz, CH_3), 1.56 (3H, d, J = 7 Hz, CH_3), 3.75 (1H, dd, J = 8 and 9 Hz, OCH_2), 3.77 (3H, s, OCH_3), 3.97 (1H, dd, J = 3 and 9 Hz, OCH_2), 4.02 (1H, q, J = 7 Hz, CH), 4.14 (1H, m, CHOH), 6.71 (1H, d, J = 2 Hz, Ar-H), 6.73 (1H, dd, J = 2 and 8 Hz, Ar-H), 6.74 (2H, d, J = 8 Hz, Ar-H); 6.82 (1H, d, J = 8 Hz, Ar-H); 7.02 (2H, d, J = 8 Hz, Ar-H). ^{13}C-NMR ($CDCl_3$, ppm): δ 18.2 (CH_3), 22.3 (CH_3), 43.6 (CH), 55.9 (OCH_3), 66.2 (CHOH), 75.9(OCH_2), 111.9, 115.0, 115.4, 128.7, 138.3, 141.1, 146.4, 149.5, 154.4. MS *m/z*: 302 (M^+).

6: ^{1}H-NMR ($CDCl_3$, ppm): δ 1.20 (3H, d, J = 6 Hz, CH_3), 1.23 (3H, d, J = 6 Hz, CH_3), 1.56 (3H, d, J = 7 Hz, CH_3), 3.74 (1H, dd, J = 7 and 9 Hz, OCH_2), 3.75 (3H, s, OCH_3), 3.77 (1H, dd, J = 7 and 9 Hz, OCH_2), 3.83 (1H, dd, J = 3 and 9 Hz, OCH_2), 3.88 (1H, dd, J = 3 and 9 Hz, OCH_2), 4.01 (1H, q, J = 7 Hz, CH), 4.13 [2H, m, CH(OH)], 6.69 (1H, d, J = 2 Hz Ar-H), 6.72 (1H, dd, J = 2 and 8 Hz, Ar-H), 6.78 (1H, d, J = 8 Hz, Ar-H); 6.79 (2H, d, J = 8 Hz, Ar-H), 7.08 (2H, d, J = 8 Hz, Ar-H). ^{13}C-NMR ($CDCl_3$, ppm): δ 18.6 (CH_3), 19.1 (CH_3), 22.2 (CH_3), 43.5 (CH), 55.9 (OCH_3), 65.9 [CH(OH)], 66.1 [CH(OH)], 73.4 (OCH_2), 75.5 (OCH_2), 111.8, 114.4, 114.5, 119.7, 128.5, 139.1, 140.5, 146.6, 149.5, 157.1. MS *m/z*: 360 (M^+).

Reaction of RHP-SAL with glycidyltrimethylammonium chloride

A lignin sample (RHP-SAL) was reacted with glycidyltrimethylammonium chloride (GTA) under various conditions at 60°C, as shown in Table 2. The reaction mixture was filtered off with a glass filter, washed with water, and then dried to give the quaternary ammonium chloride products (GRHP-SAL) of RHP-SAL (strongly basic anion-exchange resin).[22]

Table 2. Reaction of RHP-SAL (30 mg) with GTA at 60°C

Trial	Reaction conditions			Ion-exchange capacity (mEq/g)
	GTA (ml)	Time (h)	NaOH	
1	5	12	0.1 N (0.5 ml)	1.3
2	5	12	1 N (0.5 ml)	1.8
3	5	12	4 N (0.5 ml)	1.8
4	5	12	10 N (0.5 ml)	0.2
5	1	12	4 N (1.0 ml)	0.4
6	2	3	1 N (0.5 ml)	2.0

GTA, glycidyltrimethylammonium chloride

Measurement of ion-exchange capacity

A 50-mg sample of each weakly anion-exchange resins (MRHP-SAL) was suspended in 2 ml of 1 N NaOH solution at room temperature for 2 h and washed with water until the washing was neutral using phenolphthalein as the indicator. After drying in vacuo, a 2-ml aliquot of 0.05 N HCl solution was added and allowed to stand at room temperature for 1 day with stirring at intervals. After filtering out the resin with a glass filter and washing with water, the combined solution of filtrate and washings was titrated with 0.05 N NaOH solution using phenolphthalein as the indicator.[23]

For strongly basic anion-exchange resin (GRHP-SAL), a 50-mg sample was stirred in 2 ml of 1 N NaOH at room temperature for 2 h. After filtration, the resin was washed with 20 ml of 0.05 M NaCl solution and then with water until the washing fluid was neutral using phenolphthalein as the indicator. After suspending in 2 ml of 1 N NaOH solution at room temperature for 2 h and washing with water until the washing fluid was neutral using phenolphthalein as the indicator, the resin was suspended in 5 ml of 0.05 M NaCl solution at room temperature for 1 h. After filtering out the resin with a glass filter, the combined solution of the filtrate and the washings was titrated with 0.05 N HCl using methyl red-methylene blue solution as an indicator.

High-performance liquid chromatography analysis

High-performance liquid chromatography (HPLC) analysis of reaction products (compounds **4** and **5**) were run on a GL Sciences Unisil Pack 5C18-300B with the following elution conditions: linear gradient 50%–60% solvent B; solvent A, H_2O-MeOH-H_3PO_4 (940:50:1, v/v/v); solvent B, MeOH-H_3PO_4 (990:1, v/v); gradient duration 30 min; flow rate 1.5 ml/min; detection: ultraviolet (UV) 280 nm. Retention times were as follows: compound **4** 18.9 min, compound **5** 16.7 min.

Spectrometry

The ^{1}H- and ^{13}C-nuclear magnetic resonance (NMR) spectra of compounds were recorded with trimethysilane (TMS) as an internal standard on a JEOL TNM-EX 270 FT NMR spectrometer. The mass spectrometric (MS) spectra were recorded on a JEOL D-300 mass spectrometer.

Results and discussion

Preparation of weakly basic anion-exchange resin by Mannich reaction

At first, preparation of an anion-exchange resin by chloromethylation and subsequent amination from P-SAL according to Tai et al.[12] was attempted. However, only anion-exchange resin with low ion-exchange capacity was obtained, probably because of rapid condensation of the chloromethylated P-SAL. Therefore, the amino group could not be introduced to the chloromethylated products.

The aminomethyl group is introduced by the Mannich reaction at the *ortho* position of the phenolic hydroxyl group in good yield.[24] To enhance reactivity, SAL was transformed to P-SAL, in which was substituted condensed-type aromatic nuclei formed during sulfuric acid treatment by phenol. In fact, it was found that the Mannich reaction was useful for introducing aminomethyl groups on P-SAL, which has one *p*-hydroxyphenyl nucleus per phenylpropane unit.[19] Introduction of 1.0 dimethylaminomethyl group per phenolized phenylpropane unit (C_9-C_6) of P-SAL leads to water solubility. In this study, the Mannich reaction with dimethylamine and formaldehyde was applied to P-SAL to prepare anion-exchange resins.

At first, resinification was investigated by two pathways (Fig. 2). One was resinification of P-SAL after the Mannich reaction and the other was before the Mannich reaction. To confirm the ability of the first pathway, we used the model compound **1** in an attempt at resinification with formaldehyde in 36% sulfuric acid at 70°C (Fig. 3). This compound has the dimethylaminomethyl group at the *ortho* position of the phenolic hydroxyl group. ^{1}H-NMR and ^{13}C-NMR of reaction products showed that the main product was compound **2**, with a hydroxymethyl group at the *meta* position against the phenolic hydroxyl group. Furthermore, increasing the sulfuric acid concentration (72%) or the reaction temperature (to >120°C) caused degradation of the dimethylaminomethyl group. These findings indicate that it is difficult to resinify the Mannich reaction products (MP-SAL) of P-SAL under acidic conditions. We tried to resinify MP-SAL under acidic conditions but could not prepare resin (RMP-SAL) with the amino group. Resinification of MP-SAL in 3 N NaOH at 130°C was also tried, but degradation of the group occurred.

Hydroxymethylation in alkali medium and subsequent polymerization using the second pathway (P-SAL → HP-SAL → RHP-SAL) were adopted for this study (Fig. 4). As the *ortho* position of the phenolic hydroxyl group of the *p*-hydroxyphenyl nucleus is concerned with both the Mannich reaction and formation of a crosslinked structure, the number of the introduced hydroxymethyl groups per C_9-C_6 unit should affect the ion-exchange capacity of prepared resins to a large extent. Therefore, as it is preferable to use one

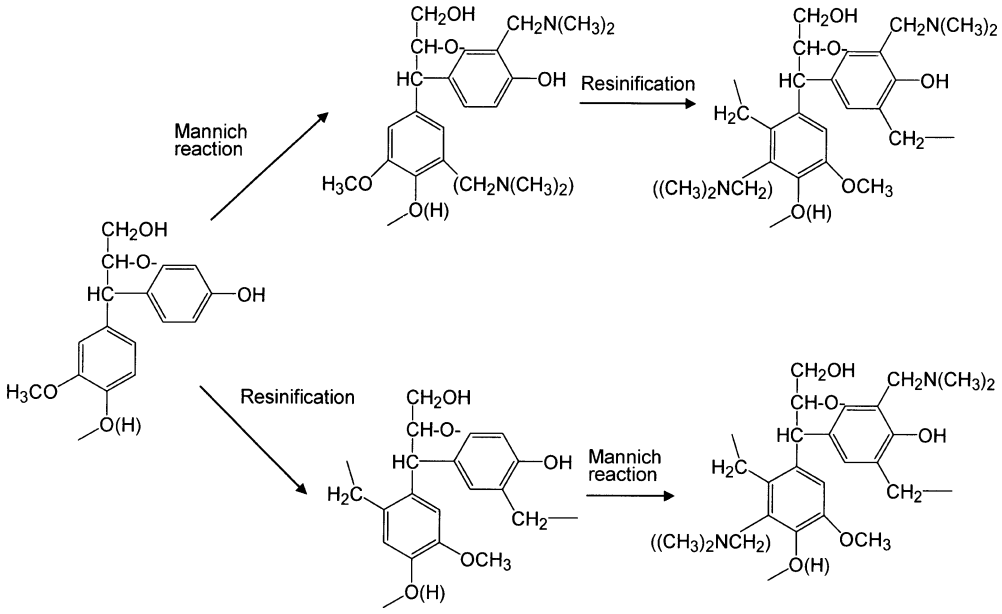

Fig. 2. Two pathways to obtain anion-exchange resin from P-SAL

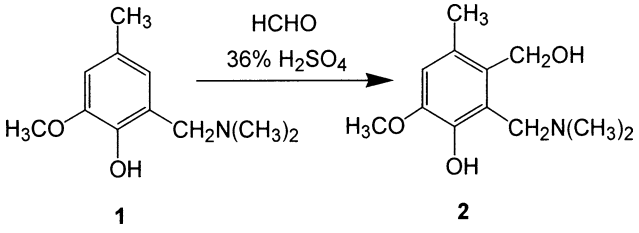

Fig. 3. Reaction of compound **1** with formaldehyde under acidic conditions

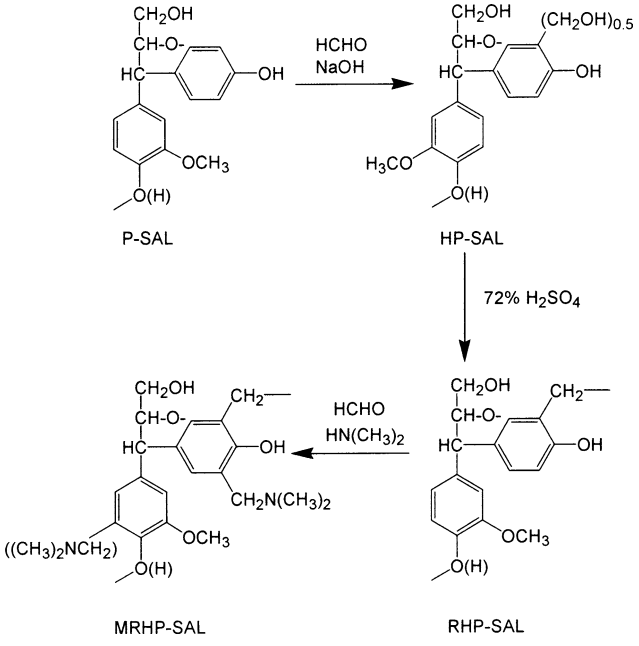

Fig. 4. Preparation of weakly basic anion-exchange resins from P-SAL. *HP-SAL*, hydroxymethylated P-SAL; *RHP-SAL*, resinified HP-SAL; *MRHP-SAL*, Mannich reaction products

ortho position for the Mannich reaction and another for the crosslinked structure, hydroxymethylated P-SAL (HP-SAL) with 0.5 CH_2OH unit per C_9-C_6 was prepared with formaldehyde in alkaline medium. Resinification of HP-SAL gave an insoluble resin (RHP-SAL), which was then reacted with formaldehyde and dimethylamine in aqueous dioxane to yield a weakly basic anion-exchange resin (MRHP-SAL) with an ion-exchange capacity of 2.4 mEq/g in a quantitative yield (Table 1). On the assumption that the molecular weight of P-SAL is 275 per C_9-C_6,[15] an ion-exchange capacity of 2.4 mEq/g means that about 0.8 dimethylaminomethyl group per C_9-C_6 was introduced to RHP-SAL.

Preparation of strongly basic anion-exchange resin by reaction of RHP-SAL with GTA

To prepare other types of anion-exchange resins, reactions of RHP-SAL with glycidyltrimethylammonium chloride (GTA) were investigated. The epoxy group of GTA is expected to react with the phenolic hydroxyl group of lignin under relatively mild conditions to introduce a quaternary ammonium salt. At the beginning, to investigate the difference in reactivity between the phenolic hydroxyl group of *p*-hydroxyphenyl unit and the guaiacyl unit in RHP-SAL and to obtain information on reaction conditions during the reaction with the epoxy reagent, 1-guaiacyl-1-*p*-hydroxyphenylethane (compound **3**) was synthesized as a simple phenolized sulfuric acid lignin model compound and reacted with propylene oxide (Fig. 5).

Three compounds (**4**–**6**) were isolated by silica-gel column chromatography of the reaction products of compound **3**. In the ^{1}H-NMR spectrum of compound **4**, the downfield shift of the *p*-hydroxyphenyl nucleus protons to 6.82 and 7.11 ppm suggests etherification of the phenolic hydroxyl group of the *p*-hydroxylphenyl nucleus. Mass and ^{13}C-NMR

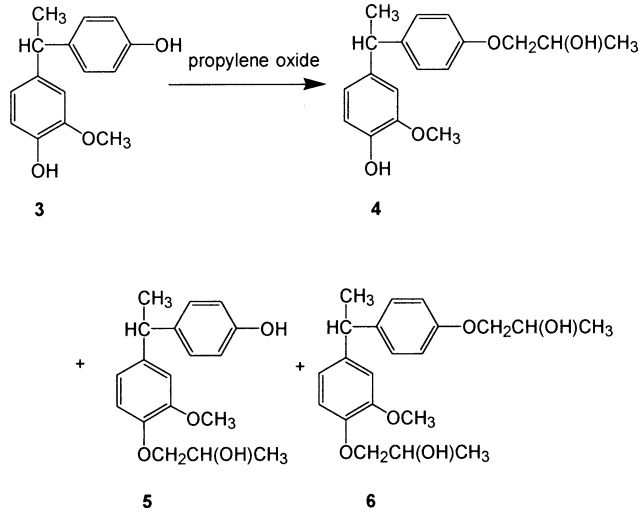

Fig. 5. Reaction of compound **3** with propylene oxide

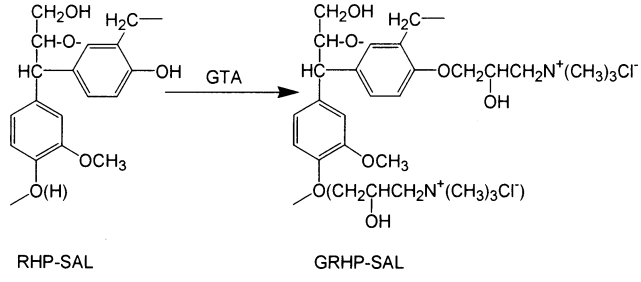

Fig. 6. Reaction of P-SAL with glycidyltrimethylammonium chloride (*GTA*). *GRHP-SAL*, guaternary ammonium chloride products of RHP-SAL

spectra supported the finding that compound **4** has the structure shown in Fig. 6. In the mass spectrum, compound **5** has the same molecular ion peak at *m/z* 302 as that of compound **4**. No shift of the *p*-hydroxyphenyl nucleus protons in the ^{1}H-NMR spectrum of compound **5** indicates etherification of the phenolic hydroxyl group of the guaiacyl nucleus. In the mass spectrum of compound **6**, a molecular ion peak at *m/z* 360 indicates introduction of two 2-hydroxylpropyl groups into compound **3**. Other compounds could not be separated from reaction products, but the ^{1}H-NMR spectrum of the reaction mixture showed an absorbance at 1.08–1.15 ppm due to methyl groups of 2-hydroxypropyl groups that seem to be introduced by the reaction with the secondary hydroxyl group generated in the epoxy ring opening.

The yields of compounds **4** and **5** were determined by HPLC analysis. As summarized in Table 3, the phenolic hydroxyl group of the *p*-hydroxyphenyl nucleus had slightly higher reactivity than that of the corresponding group of the guaiacyl nucleus. This suggests that GTA is introduced at the *p*-hydroxyphenyl nucleus prior to the guaiacyl nucleus. Compound **6** could not be determined because of the difficulty of separating fractions from compounds that had more than three 2-hydroxypropyl groups. As could be expected, the increased reaction temperature (trials 2, 4, and 5 in Table 3) brought about an increase in the 2-hydroxypropyl group content of the products.

Table 3. Reaction of compound **3** (0.2 mmol) with propylene oxide for 1 h

Trial	Reaction conditions		Yield (%)		
	PO (mmol)	Temperature (°C)	**4**	**5**	Other products
1	0.5	50	22.3	20.9	41.1
2	1	50	14.5	12.7	68.7
3	2	50	4.5	3.4	91.8
4	1	40	16.7	15.3	62.0
5	1	60	12.1	10.6	74.8

PO, propylene oxide

RHP-SAL was used for this reaction because it has one more phenolic hydroxyl group than SAL (Fig. 6). Based on the results of the model experiment outlined in Table 3, a reaction temperature of 60°C was selected. The other reaction conditions and ion-exchange capacities of the prepared ion-exchange resins (GRHP-SAL) are summarized in Table 2. The highest ion-exchange capacity of the prepared resin (GRHP-SAL) was 2.0 mEq/g (trial 6 in Table 2). As this reaction is competitive between the phenoxide and hydroxide ions for GTA, the high concentration of hydroxide ion (trial 4 in Table 2) results in the preferential degradation of GTA. Calculation of the molecular weight of RHP-SAL based on the above assumption shows that the ion-exchange capacity of 2.0 mEq/g means that $0.8/C_9$-C_6 of phenolic hydroxyl group reacted with GTA. The ion-exchange capacity of the commercial polystyrene-type, strongly basic anion-exchange resin is 2.5–3.0.

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