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ORIGINAL ARTICLE

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Ready chemical conversion of acid hydrolysis lignin into water-soluble lignosulfonate III: Successive treatment of acid hydrolysis lignin and a lignin model compound by phenolation and arylsulfonation*

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Abstract The chemical conversion of red pine sulfuric acid lignin (Klason lignin) (SAL) as an acid hydrolysis lignin sample to water-soluble arylsulfonates of lignin derivation (i.e., phenolized SAL) was investigated. Treatment of phenolized SAL with chlorosulfonic acid followed by alkali hydrolysis gave water-soluble sulfonated products with a sulfonic acid group on their aromatic nuclei quantitatively. The products possess 2.0 SO_3Na/C_9–C_6. In contrast, the content of sulfuric acid group in sulfonated SAL was only $0.33/C_9$. Chlorosulfonation of 1-guaiacyl-1-*p*-hydroxyphenylethane as a phenolized guaiacyl lignin model compound revealed that the sulfonyl chloride group was introduced at the *para* position of an aromatic methoxyl group, the *ortho* position of a phenolic hydroxyl group, or both.

Key words Lignin · Lignin model compounds · Sulfonation · Lignosulfonate

Introduction

Lignosulfonates, as one of the functional materials derived from lignin, have excellent dispersing and caking properties. They are roughly divided into aryl- and alkylsulfonates, depending on the aromatic and aliphatic carbon, respectively, where the sulfonic acid group is attached.

An effective way of utilizing acid lignin with a highly condensed structure may economically develop acid saccharification industries with woody materials. One of the most practical methods for this purpose is simple conversion of acid lignins to soluble lignosulfonates. Quantitative conversion[1] of red pine Klason lignin (sulfuric acid lignin, SAL), as an example of acid hydrolysis of lignin into soluble alkylsulfonates of SAL derivation, has been achieved by hydroxymethylation with formalin and subsequent neutral sulfonation (the two-step method) and by hydroxymethylsulfonation (the one-step method) of activated SAL derivative, (i.e., phenolized SAL). In a separate experiment, the detailed reaction mechanisms[2] of the hydroxymethylation and subsequent sulfonation were investigated with phenolized guaiacyl lignin model compounds. Recently, soluble arylsulfonates were prepared from acid hydrolysis lignins (birch Klason lignin and spruce dilute acid hydrolysis lignin) by radical sulfonation[3] in 55% and 60% yields, respectively.

In this study chemical conversion of red pine SAL to soluble arylsulfonate was investigated. In addition, a phenolized guaiacyl lignin model compound was chlorosulfonated to determine the active position of *p*-hydroxyphenyl and guaiacyl nuclei in phenolized SAL.

Experimental

Phenolation of red pine SAL

A suspension of 0.21 g red pine (*Pinus densiflora* Sieb. et Zucc) Klason lignin (SAL) and 1.25 g phenol in 3 ml 72% sulfuric acid was stirred at 60°C for 6 h. After quenching by dilution with water until the sulfuric acid concentration reached 3%, the reaction solution was boiled for 3 h, as for the Klason lignin determination. The solids were separated by centrifugation and were washed with water to give 0.24 g phenolized SAL (P-SAL).

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Table 1. Sulfonation of P-SAL and SAL

Reaction condition			Product			
Sample (mg)	$ClSO_3H$ (mg)	Temp. (°C)	Residue (mg)	Solubilization (%)	S (%)	SO_3Na/C_9–C_6
P-SAL						
199	175	rt	0	100	9.8	1.17[a]
200	350	rt	0	100	10.6	1.31[a]
200	525	rt	0	100	9.8	1.17[a]
150	350	50	0	100	11.3	1.45[a]
150	350	100	0	100	14.0	2.03[a]
SAL						
259	350	rt	291	0	4.9	0.33[b]

rt, room temperature

[a] Number of introduced sulfonate groups per C_9–C_6 unit[1] of soluble sulfonated phenolized sulfurie acid lignin (SP-SAL)

[b] Number of introduced sulfonate groups per C_9 unit of insoluble sulfonated sulfurie acid lignin (S-SAL)

Sulfonation of P-SAL

To a suspension of 0.2g P-SAL in 1.0ml chloroform was added chlorosulfonic acid, as shown in Table 1. After stirring at room temperature for 1h, the reaction mixture was made basic with 20ml 2N NaOH, refluxed for 1h, and then adjusted with 1N HCl to pH 6.0. Insoluble sulfonation products were filtered out with a glass filter. The filtrate was concentrated under reduced pressure to 5ml, centrifuged to remove any insoluble inorganic material, and then subjected to column gel filtration chromatography (25 × 4.1cm) on a Sephadex G-25 column to remove the inorganic chemicals detecting with a 10% $BaCl_2$ solution. The combined inorganic chemical-free fraction was freeze-dried to give soluble sulfonated P-SAL (SP-SAL). Sulfonation of P-SAL (150mg) with chlorosulfonic acid (350mg) at 50° and 100°C was carried out using tetrachloroethane as the solvent.

Sulfonation of phenolized lignin model compounds

To a solution of 300mg of model compound I in 3ml chloroform, which was dried over molecular sieves, was added 500mg chlorosulfonic acid. After stirring at room temperature for 30min and at 40°C for 40min, the solution was diluted with water to decompose any excess reagent and then extracted with ethyl acetate. The ethyl acetate solution was washed with water, dried over sodium sulfate, and then concentrated under reduced pressure to give reaction products.

The products were separated by silica gel column chromatography with mixed solvents of *n*-hexane with an increasing proportion of acetone as an eluent to isolate 10mg (3.7% yield) of compound **II**, 125mg (23.1%) of **V**, and 48mg (8.9%) of **VII**.

II: MS m/z: 222 (M^+); ^1H NMR δ: 4.02 (3H, s, OCH_3), 7.26 (1H, d, J = 8Hz, aromatic H), 7.48 (1H, d. J = 2Hz, aromatic H), 7.82 (1H, dd, J = 8 + 2Hz, aromatic H); ^{13}C NMR δ: 56.9 (OCH_3), 112.4, 113.7, 121.1, 136.6, 148.1, 154.8. Anal. calcd. for $C_7H_7O_4SCl$: C, 37.76; H, 3.17; S, 14.40; Cl, 15.93. Found: C, 37.71; H, 3.15; S, 14.38; Cl, 15.90.

V: MS m/z: 441 (M^+); ^1H NMR δ: 1.78 (3H, d, J = 7Hz, CH_3), 3.93 (3H, s, OCH_3), 4.02 (1H, q, J = 7Hz, CH), 7.11 (1H, s, aromatic H), 7.23 (1H, d, J = 8Hz, aromatic H), 7.56 (1H, s, aromatic H), 7.69 (1H, dd, J = 8 + 2Hz, aromatic H), 7.91 (1H, d, J = 2Hz, aromatic H); ^{13}C NMR δ: 21.7 (CH_3), 38.7 (CH), 56.8 (OCH_3), 113.8, 115.5, 119.4, 128.1, 130.4, 134.7, 137.0, 138.2, 139.7, 145.9, 154.8, 155.4. Anal. calcd. for $C_{15}H_{14}O_7S_2Cl_2$: C, 40.77; H, 3.20; S, 14.53; Cl, 16.07. Found; C, 40.76; H, 3.18; S, 14.55; Cl, 16.02.

VII: MS m/z: 441 (M^+); ^1H NMR δ: 1.65 (3H, d, J = 8Hz, CH_3), 3.97 (3H, s, OCH_3), 4.25 (1H, q, J = 8Hz, CH), 7.07 (1H, dd, J = 8 + 2Hz, aromatic H), 7.19 (1H, d, J = 1Hz, aromatic H), 7.43 (3H, m, aromatic H); ^{13}C NMR δ: 25.7 (CH_3), 39.4 (CH), 56.5 (OCH_3), 109.7, 110.1, 112.3, 120.3, 130.0, 131.1, 134.9, 136.8, 139.4, 146.5, 151.7, 157.2. Anal. calcd. for $C_{15}H_{14}O_7S_2Cl_2$: C, 40.77; H, 3.20; S,14.53; Cl, 16.07. Found; C, 40.76; H, 3.16; S, 14.55; Cl, 16.01.

Determination of sulfur content

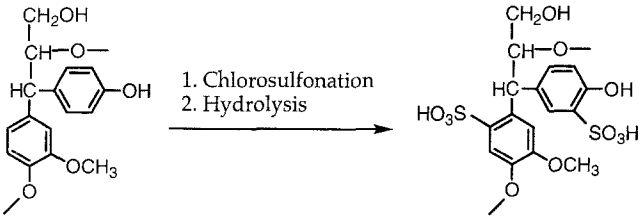
The sulfur content of sulfonated products was quantitatively determined by a combustion method.[1]

Molecular weight distribution of arylsulfonates of lignin derivatives

The molecular weight distribution of the arylsulfonates was measured on Sepharose CL-6B (51 × 1.8cm) with 0.5N NaOH as an eluent and an ultraviolet detector (280nm). Sodium polystyrenesulfonates (MW 1.8×10^3 to 1.0×10^5) were used as a standard.

Spectrometry

The ^1H and ^{13}C NMR spectra of compounds in hexadeuteroacetone were recorded with trimethylsilane (TMS) as



Phenolized SAL

Fig. 1. Sulfonation of phenolized sulfuric acid lignin (P-SAL)

an internal standard on a Jeol JNM-EX 270 FT NMR spectrometer. The mass spectrometric (MS) spectrum was recorded on a Jeol JMD D-100 mass spectrometer.

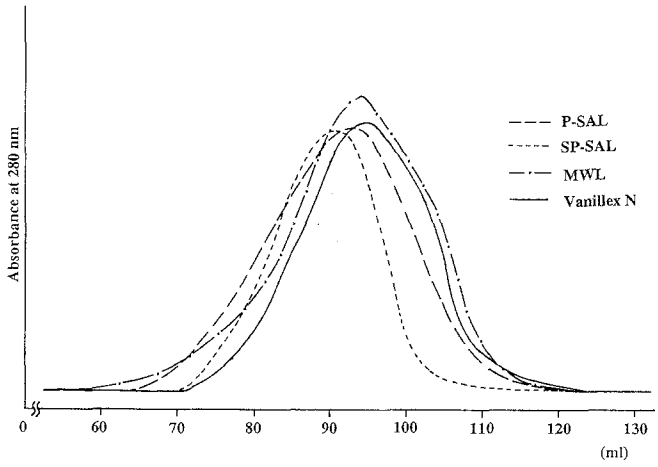


Fig. 2. Gel filtration curves of sulfonation products

Results and discussion

Sulfonation

Sulfonation of SALs was carried out by chlorosulfonation with chlorosulfonic acid, followed by alkali hydrolysis. The acid is known to be a strong sulfonation agent[4] for aromatic compounds and is used satisfactorily for technical production. Two equivalent weights of the acid are necessary for chlorosulfonation,[5] as shown in the following equation.

$$ArH + 2 \times ClSO_3H \rightarrow ArSO_2Cl + HCl + H_2SO_4$$

Sulfonation of SAL itself did not give soluble lignosulfonate. Because SAL is formed by intermolecular dehydrative condensation[6,7] between side chain benzylic carbons and aromatic nucleus carbons, the reactive *para* position of a methoxyl group in the guaiacyl nucleus toward chlorosulfonation is protected. This protection contributes to the reduced reactivity of SAL to a great extent.

An effective way of promoting chlorosulfonation of SAL consists therefore in the conversion of condensed-type aromatic nuclei formed during the acid treatment to noncondensed-type nuclei to keep an active site at the *para* position of an aromatic methoxyl group or additional introduction of another reactive aromatic nucleus (or both). The purpose can be achieved by phenolation[8] with sulfuric acid as a catalyst because of specific substitution of the condensed aromatic nuclei for phenol. Treatment of phenolized SAL (P-SAL) at room temperature with two equivalent weights of chlorosulfonic acid, as shown in Table 1, followed by alkali hydrolysis gave the soluble arylsulfonate (SP-SAL) of P-SAL, quantitatively. The content (Table 1) of the sulfonic acid group was determined by a volumetric method after purification of SP-SAL with column gel filtration chromatography on Sephadex G-25. Soluble SP-SAL possessed 1.17 SO_3Na/C_9–C_6. In contrast, the insoluble sulfonation product (S-SAL) of SAL contained only 0.33 SO_3Na/C_9. Soluble and insoluble alkylsulfonates[1] derived from P-SAL derivatives had possessed 0.76 and 0.56 SO_3Na/C_9–C_6, respectively. Attempts to introduce more of the sulfonic acid group into P-SAL at room temperature by increasing the chlorosulfonation agent was not successful, but a higher reaction temperature resulted in an increase in the number of functional groups. SP-SAL chlorosulfonated at 100°C possessed 2.03 SO_3Na/C_9–C_6.

On the basis of chlorosulfonation of a phenolized lignin model compound described later, one of two introduced sulfonic acid groups probably exists on the carbon C-6 (i.e. the *para* position of a methoxyl group of guaiacyl nuclei), and another exists on the *ortho* carbon of a phenolic hydroxyl group in *p*-hydroxyphenyl nuclei, as shown in Fig. 1.

Table 2. Average molecular weights of P-SAL, SP-SAL, MWL, and commercial ligno-sulfonate (Vanillex N)

Sample	$\overline{Mn}$	$\overline{Mw}$
P-SAL	3.3×10^3	1.0×10^4
SP-SAL (S content 9.8%)	5.7×10^3	9.9×10^3
MWL	2.9×10^3	9.7×10^3
Vanillex N	2.4×10^3	6.0×10^3

MWL, milled wood lignin; $\overline{Mn}$, number average molecular weight; $\overline{Mw}$, weight average molecular weight

Molecular weight distribution

The molecular weight distribution of the arylsulfonates was determined with Sepharose CL-6B.[1] Figure 2 shows the gel filtration curves of P-SAL, soluble arylsulfonate (SP-SAL: S content 9.8%), and commercial lignosulfonate (Vanillex N).[1] Their average molecular weights are summarized in Table 2.

Although the molecular weight of protolignin is not known, the molecular weight of P-SAL was compared with that of milled wood lignin (MWL) to obtain information on the molecular weight of P-SAL. P-SAL was found to have a molecular weight similar to MWL. This finding can be reasonably explained on the basis of the formation mechanism[6] of SAL and the reaction mechanism[8] of 72% sulfuric acid-catalyzed phenolation of SAL, because carbon–carbon link-

Fig. 3. Sulfonation of model compound I at C-1 accompanying the elimination of a side chain

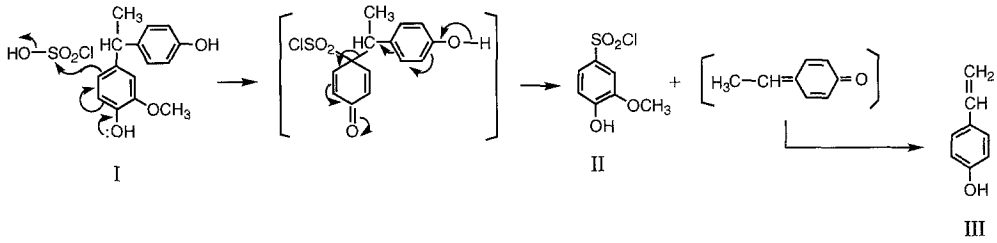
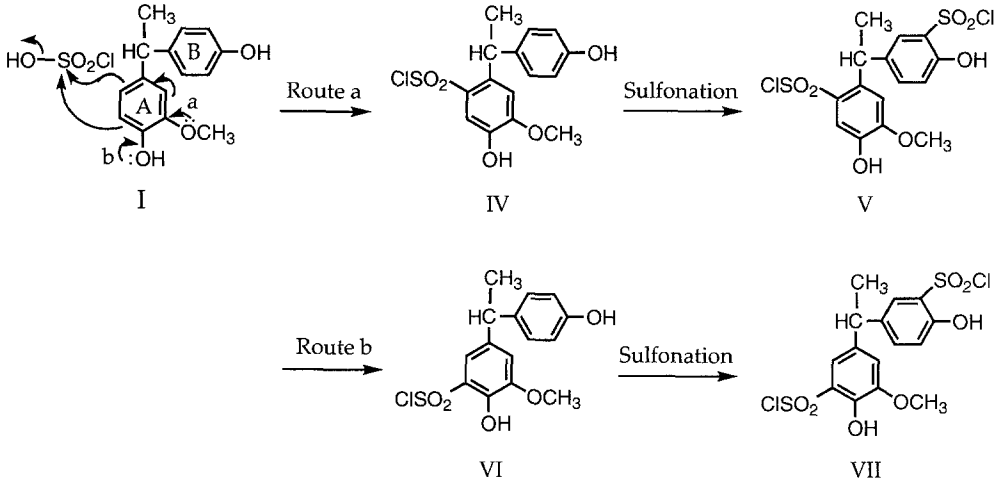


Fig. 4. Sulfonation of I at C-5 (*route b*) and C-6 (*route a*) keeping a side chain



ages formed during 72% sulfuric acid treatment are preferentially substituted by a simple nucleophile, phenol, during phenolation. In other words, the concentrated sulfuric acid treatment and the subsequent phenolation of lignin mean substitution of both hydroxyl groups and an ether bond at the benzylic position of native lignin by phenol without changing its molecular weight.

On the other hand, the average molecular weight of SP-SAL (S content 9.8%) was greater than that of P-SAL. Because SP-SAL was prepared by chlorosulfonation of P-SAL with chlorosulfonic acid and subsequent hydrolysis with dilute alkali under mild conditions, P-SAL and the reaction products are not brought to conditions that cause an increase in molecular weight. Furthermore, molecular weight distribution with gel filtration is largely influenced by the extent of swelling, hydrodynamic radius, chemical property, and adsorption on gel under the conditions used. Therefore, a comparison of the average molecular weights of P-SAL and SP-SAL seems difficult. SP-SAL has a higher average molecular weight than a purified commercial lignosulfonate, Vanillex N, but is similar to that of a crude lignosulfonate, Pearllex N.[1]

Reactivity of a lignin model compound I

To determine the active positions on the aromatic nuclei of P-SAL for chlorosulfonation, 1-guaiacyl-1-*p*-hydroxyphenylethane (compound I) was selected as the phenolized guaiacyl lignin model compound and was reacted with the reagent. The low yields of products separated by silica gel column chromatography are due to partial hydrolysis of their sulfonyl chloride groups in the column.

Three products – II, V, VII – were isolated. Six aromatic carbon signals and the absorption pattern due to three aromatic protons in ^{13}C and ^{1}H NMR spectra indicate that product II is 3-methoxy-4-hydroxy-benzenesulfonyl chloride, as shown in Fig. 3. The molecular ions in the MS spectra and 12 aromatic carbon signals in the ^{13}C NMR spectra of compounds V and VII suggest that both compounds have at least one sulfonyl chloride group on the *p*-hydroxyphenyl nucleus (B ring) and one more. Furthermore, the absorption patterns of their aromatic five protons indicate that they have the structures shown in Fig. 4.

The formation of the most minor product II can proceed via chlorosulfonation of compound I at C-1 of the guaiacyl nucleus (A-ring), followed by elimination of a side chain (Fig. 3), Isolation of compound III was not successful. The formation of compounds V and VII can be explained in the usual way; that is, the first chlorosulfonation at C-6 (route a) or at C-5 (route b) is on the A ring with higher electron density followed by the second chlorosulfonation on the B ring (Fig. 4). However, the reaction on the aromatic rings is not stepwise, such as at the first A-ring and then the B-ring; there is higher reactivity on the A-ring. The *para* and *ortho* positions of the aromatic methoxyl and hydroxyl groups, respectively, are found to be reactive during chlorosulfonation.

As described above, phenolation of acid-hydrolysis lignin with a highly condensed structure to prepare soluble arylsulfonate with an electrophilic reagent proved to be

an effective pretreatment in terms of restoration of the blocked *para* position of the aromatic methoxyl group and introduction of the reactive *p*-hydroxyphenyl group.

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