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SULFOMETHYLATION OF LIGNINS

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Water-soluble derivatives have been obtained by the sulfomethylation of technical lignins. Their semiempirical formulas have been calculated and the introduction of a sulfomethyl group into the lignin macromolecule is discussed on the basis of these formulas.

The sulfomethylation of lignin is an electrophilic substitution reaction and takes place at various pH values, temperatures, and ratios of the reactants. This makes it possible to synthesize sulfomethyl derivatives of lignin with different degrees of substitution of the aromatic ring and the side-chain [1-4].

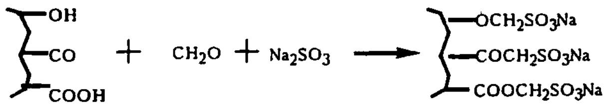
We have studied the sulfomethylation of a number of lignins with the aim of obtaining soluble derivatives. The reaction was carried out at a ratio of lignin, formaldehyde, and sodium sulfite of 1:2:1, with heating in an alkaline medium (pH 8). The reaction yielded products with water-solubilities that had increased in comparison with the initial lignin by from 1% to 89% (Table 1).

As can be seen from Table 1, lignins, the solubility of which remained low (DML, ChL, CSHHL, and NL), were the more condensed high-molecular-mass preparations requiring fragmentation to increase their solubility.

The lignins, the solubility of which increased appreciably under the conditions of sulfomethylation (DLA, SL, and NSL), were less condensed and, probably, readily underwent fragmentation followed by dissolution. Furthermore, the presence of a sulfo group (SL, NSL) also favored an increase in the solubility of the lignins. From elementary and functional analyses we calculated semiempirical formulas of the derivatives obtained (Table 2), and these show their differences from one another more clearly.

By comparing the semiempirical formulas of the initial and the sulfomethylated lignin derivatives it is possible to convince oneself of the fact that the change in the levels of the main functional groups (OH, CO, COOH) depends on the nature of initial lignin. For example, for the cotton plant stem dioxane lignin, which is a model close to natural lignin, the decrease in the level of aliphatic and phenolic hydroxy groups, and also that of carboxy groups in the soluble fraction, is equal to the number of sulfomethyl groups introduced, 66/100 C_9. This rule is not observed for the other soluble derivatives since the technical lignins investigated were highly condensed and differed sharply from the preparations of dioxane lignin.

It is known that the introduction of a sulfomethyl group into the molecule of an organic compound takes place by the replacement of a hydrogen atom [5], and the sulfomethylation of DLA can therefore be represented in the following way:



The IR spectra of the water-soluble sulfomethylated products showed more intense absorption in the regions of 1150, 1260, 1080, and 1110 cm^{-1}, corresponding to the vibrations of the C–S bond, than those of the insoluble products. These facts correlate with the results of functional analysis. In actual fact, a comparison of the semiempirical formulas of the soluble and the insoluble derivatives shows a higher level of sulfomethyl groups in the soluble products.

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TABLE 1. Solubilities of Sulfomethylated Lignin Derivatives in Comparison with the Initial Specimens

Lignin specimen	Increase in solubility, %
1. Cotton plant stem dioxane lignin (DLA)	50.0
2. Nitrolignin (NL)	25.0
3. Chlorolignin (ChL)	3.0
4. Demethylated lignin (DML)	1.0
5. Sulfate lignin (SL)	60.0
6. Nitrosulfolignin (NSL)	89.0
7. Cotton seed husk hydrolysis lignin (CSHHL)	22.0

TABLE 2. Semiempirical Formulas of the Lignins

Lignin specimen	Semiempirical formulas
1. Initial DLA	$C9\ H_{7.81}\ O_{0.58}\ (OCH_3)_{1.31}\ (OH_{ph})_{0,24}\ (OH_{al})_{0.92}\ (O_{co})_{0.56}\ (OOH_{COOH})_{0.03}$
2. Sulfomethylated DLA (sol. fr.)	$C_9H_{10.07}O_{0.89}(OCH_3)_{0.14}\ (OH_{ph})_{0.18}\ (OH_{l})_{0.76}\ (O_{co})_{0.12}\ (OOH_{COOH})_{0.03}\ (CH_2SO_3H)_{0.66}$
3. Sulfomethylated DLA (insol. fr.)	$C_9H_{6.94}O_{0.48}\ (OCH_3)_{1.05}\ (OH_{ph})_{0.22}\ (OH_{l})_{0.87}\ (O_{co})_{0.22}\ (OOH_{COOH})_{40.02}\ (CH_2SO_3H)_{0.53}$
4. Initial CSHHL (sol. fr.)	$C_9H_{48.87}O_{3.02}\ (OCH3)_{0.35}\ (OH_{ph})_{0.28}\ (OH_{l})_{0.24}\ (O_{co})_{0.51}\ (OOH_{COOH})_{0.08}$
5. Sulfomethylated CSHHL (sol. fr.)	$C_9H_{11.34}O_{1.35}\ (OCH_3)_{0.15}\ (OH_{ph})_{0.24}\ (OH_{l})_{0.24}\ (O_{co})_{0.04}\ (OOH_{COOH})_{0.02}\ (CH_2SO_3H)_{0.54}$
6. Sulfomethylated CSHHL (insol. fr.)	$C_9H_{8\cdot 27}O_{3.97}\ (OCH_3)_{0.25}\ (OH_{ph})_{0.24}(OH_{l})_{0.24}\ (O_{co})_{0.03}\ (OOH_{COOH})_{0.02}\ (CH_2SO_3H)_{0.25}$
7. Initial SL	$C_9H_{8.38}O_{1.75}\ (OCH_3)_{0.43}\ (OH_{ph})_{0.62}\ (OH_{l})_{0.46}\ (O_{co})_{0.63}\ (OOH_{COOH})_{0.13}S_{0.22}$
8. Sulfomethylated SL (sol. fr.)	$C_9H_{11.3}O_{4.09}\ (OCH_3)_{0.24}\ (OH_{ph})_{0.23}(OH_{l})_{0.12}\ (O_{co})_{0.26}\ (OOH_{COOH})_{0.03}\ (CH_2SO_3H)_{0.41}$
9. Sulfomethylated SL (insol. fr.)	$C_9H_{10.89}O_{4.09}\ (OCH_3)_{0.12}\ (OH_{ph})_{0.35}(OH_{l})_{0.22}\ (O_{co})_{0.48}\ (OOH_{COOH})_{0.05}\ (CH_2SO_3H)_{0.25}$
10. Initial NL	$C_9H_{8.12}O_{3.11}\ (OCH_3)_{0.19}\ (OH_{ph})_{0.40}\ (OH_{l})_{0.33}\ (O_{co})_{0.56}\ (OOH_{COOH})_{0.45}N_{0.66}$
11. Sulfomethylated NL (sol. fr.)	$C_9H_{10.42}O_{0.82}\ (OCH_3)_{0.16}\ (OH_{ph})_{0.22}\ (OH_{l})_{0.20}\ (O_{co})_{0.19}\ (OOH_{COOH})_{0.03}N_{0.1}\ (CH_2O_3H)_{0.26}$
12. Sulfomethylated NL (insol. fr.)	$C_9H_{9.42}O_{0.82}\ (OCH_3)_{0.}\ (OH_{ph})_{0.22}(OH_{l})_{0.20}\ (O_{co})_{0.46}\ (OOH_{COOH})_{0.18}N_{0.3}\ (CH_2SO_3H)_{0.09}$
13. Initial NSL	$C_9H_{12.24}O_{9.58}\ (OCH_3)_{0.37}\ (OH_{ph})_{0.64}\ (OH_{l})_{0.79}\ (O_{co})_{0.82}\ (OOH_{COOH})_{0.08}N_{0.7}S_{0.31}$
14. Sulfomethylated NSL (sol. tr.)	$C_9H_{9.5}O_{3.1}\ (OCH_3)_{0.27}\ (OH_{ph})_{0.33}\ (OH_{l})_{0.54}\ (O_{co})_{0.24}\ (OOH_{COOH})_{0.04}N_{0.2}\ (CH_2SO_3H)_{0.23}$
15. Sulfomethylated NSL (insol. fr.)	$C_3H_{10.66}O_{3.1}\ (OCH_3)_{0.17}\ (OH_{ph})_{0.36}\ (OH_{l})_{0.29}\ (O_{co})_{0.09}\ (OOH_{COOH})_{0.04}N_{0.37}\ (CH_2SO_3H)_{0.08}$
16. Initial SL	$C_9H_{8.58}O_{1.45}\ (OCH_3)_{0.63}\ (OH_{ph})_{0.45}\ (OH_{l})_{0.70}\ (O_{co})_{0.03}\ (OOH_{COOH})_{0.02}S_{0.46}$
17. Sulfomethylated SL (sol. fr.)	$C_9H_{9.29}O_{0.9}\ (OCH_3)_{0.63}\ (OH_{ph})_{0.33}\ (OH_{l})_{0.54}\ (O_{co})_{0.04}\ (OOH_{COOH})_{0.04}\ (CH_2SO_3H)_{0.65}$

The fall in the levels of hydroxy and carbonyl groups in the sulfomethylated products as compared with the initial lignins shows indirectly that sulfomethyl groups may be introduced not only into the aromatic nucleus but also into the propane side-chains [6].

The decrease in the level of methoxy groups in the reactions of lignin with various compounds can be judged from the number of added groups and molecules [7]. Judging from their semiempirical formulas, the soluble sulfomethylated derivatives of DLA and HL contained few methoxy groups, as compared with the initial lignin and its insoluble sulfomethylated derivatives. This may show that during sulfomethylation in an alkaline medium it is mainly the carbohydrate-containing part of the lignin that dissolves. It is known that both dioxane lignins and hydrolysis lignins contain a definite fraction of lignin-bound carbohydrates.

In the soluble fractions of the other specimens of technical lignins (SL, NL, NSL, and LS) the content of methoxy groups was greater than in the insoluble fractions. These lignins are modified materials and do not contain bound carbohydrates. It is obvious that performing the sulfomethylation reaction in an alkaline medium leads to the dissolution of the more methoxylated fractions of the lignins under investigation.

EXPERIMENTAL

Dioxane lignin (DLA) was isolated from a flour of the stems of a cotton plant of the S-4880 variety [8].

Nitro- and nitrosulfolignins (NL and NSL) were obtained as described in the literature [1, 10].

Cotton seed husk hydrolysis lignin (CSHHL) was obtained from the Yangiyul' biochemical factory.

Lignosulfonate was obtained in the Syas'kii pulp and paper combine (OST 13 183 83).

Sulfomethylation Reaction. A mixture of 10 g of lignin, 20 ml of 40% formalin, and 10 g of sodium sulfite (pH 8) was heated in a water bath at 95°C for 3 h. After the end of the reaction the soluble fraction was separated by filtration from the insoluble fraction by filtration. The soluble fraction was dialyzed against water to neutrality and was lyophilized and dried further over P_2O_5 in a vacuum desiccator. The insoluble fraction was washed with water until the wash-waters were neutral and was dried in the air and kept over P_2O_5.

The sulfomethylated derivatives of technical lignins obtained in this way were used for subsequent analyses.

The amounts of methoxy, hydroxy, carbonyl, and carboxy groups present were determined by a method given in [9]. Sulfur contents were determined as described in [11].

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