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PHOSPHORYLATION OF HYDROLYSIS LIGNIN BY DIALKYL PHOSPHOROCHLORIDATES

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It has been established that the phosphorylation of lignin by dialkyl phosphorochloridates takes place through the hydroxy groups of the lignin macromolecule.

Phosphorus-containing derivatives of technical lignins possess biological activity [1, 2]. With the aim of introducing phosphoryl groups into the lignin macromolecule we have carried out the interaction of hydrolysis lignin (HL) with dialkyl phosphorochloridates. The reactions were performed at various ratios of lignin and phosphorylating agent (PA) in boiling CCl_4 or ether for 1 h (Table 1).

As can be seen from Table 1, after the interaction of HL and DHPC, the content of functional groups in the products obtained had changed hardly at all and the amount of lignin-bound phosphorus had changed only slightly. After the interaction of DEPC with HL, the content of bound phosphorus in the products obtained had increased to 1.6% and the content of hydroxy groups had fallen. The same pattern was observed on the interaction of lignin with MECP. The phosphorus content of the products obtained reached 2.60 and 2.84%, depending on the ratio of the reactants and the nature of the solvent used. The maximum introduction of phosphorus into the HL macromolecule was achieved with the use of DMCP as phosphorylating agent.

It must be mentioned that with an increase in the phosphorus content of the products obtained the content of carboxy groups rose and that of hydroxy groups fell. The fall in the content of hydroxy groups with an increase in the phosphorus content of the products obtained shows that phosphorylation probably takes place at the hydroxy groups of the lignin.

Calculation of the semiempirical formulas of the initial HL and its phosphorylated derivatives from the results of elemental and functional analyses also showed a fall in the number of hydroxy groups and increases in the numbers of carboxy and methoxy groups and in the amount of phosphorus in comparison with those for the initial HL on passing from DECP to DMCP (Table 2).

The results of IR-spectral analysis correlate with those of the quantitative analysis of the content of hydroxy groups in the initial HL and its phosphorylated derivatives. Thus, a study of the IR spectra of the initial HL and its phosphorylated derivatives showed a decrease in the intensity of the absorption band in the 3000-3600 cm^{-1} region corresponding to the vibrations of hydroxy groups. The appearance of an absorption band at 1048 $\pm$ 5 cm^{-1}, corresponding to the vibrations of a P–O–C bond, indicated the binding of the phosphoryl groups with the hydroxy groups of the HL.

Thus, a study of the interaction of HL with some dialkyl phosphorochloridates has permitted the following conclusions to be drawn: In the phosphorylation of hydrolysis lignin it is the hydroxy groups of the latter that take part; with a decrease in the size of the alkyl radicals in dialkyl phosphorochloridates acting as phosphorylating agents their phosphorylating capacity increases.

We may note that in comparison with dimethyl phosphite and phosphorous acid, which have been used previously as lignin phosphorylating agents [3], the use of dimethyl phosphorochloridate permits the introduction of a larger amount of phosphorus into the lignin macromolecule.

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TABLE 1. Results of the Phosphorylation of Hydrolysis Lignin by Dialkyl Phosphorochloridates

Phosphorylating agent	HL:PA ratio	Medium	Content, %		
			phosphorus	COOH	OH
DHPC*	1:1	CCl_4	0.10	1.53	11.06
DHPC	1:2	"	0.30	1.49	10.97
DEPC	1:2	"	1.66	2.16	7.95
DEPC	5:1	"	1.01	2.27	8.07
MEPC	1:1	"	1.88	2.94	8.85
MEPC	1:2	"	2.60	2.97	7.02
MEPC	1:1	Ether	1.20	2.40	8.95
MEPC	1:2	"	2.84	2.60	6.28
DMPC	1:1	"	3.14	2.98	3.92
DMPC	5:1	CCl_4	6.26	7.68	0.68
Initial HL				1.53	11.07

*DHPC) dihexyl phosphorochloridate; DEPC) diethyl phosphorochloridate; MEPC) methyl ethyl phosphorochloridate; DMPC) dimethyl phosphorochloridate.

TABLE 2. Semiempirical Formulas of the Initial Hydrolysis Lignin and its Phosphorylated Derivatives

Sample No.*	Sample	Semiempirical formula
	Initial HL	$C_9H_{8.65}O_{3.02}(OCH_3)_{0.30}(OH)_{1.13}(COOH)_{0.08}$
3	HL + DECP	$C_9H_{8.91}O_{2.95}(OCH_3)_{0.37}(OH)_{0.95}(COOH)_{0.09}P_{0.006}$
8	HL + MECP	$C_9H_{9.19}O_{2.65}(OCH_3)_{0.35}(OH)_{0.78}(COOH)_{0.12}P_{0.16}$
10	HL + DMCP	$C_9H_{13.24}O_{4.64}(OCH_3)_{0.58}(OH)_{0.09}(COOH)_{0.43}P_{0.48}$

*The numbering of the phosphorylated lignin samples corresponds to the order in which they are given in Table 1.

EXPERIMENTAL

The IR spectra of the samples investigated were taken on a Perkin-Elmer model 2000 Fourier IR spectrometer (Sweden). Cottonseed husk hydrolysis lignin obtained from the Yangiyul' biochemical factory was used.

Synthesis of Dimethyl Phosphorochloridate. With constant stirring a mixture of methanol, triethylamine, and ether in a ratio of 2:2:1.5 was added through a dropping funnel to a solution of 1 mole of $POCl_3$ in ether that had been cooled to 0°C. After the end of the reaction, the excess of triethylamine and the ether were distilled off, and the triethylamine hydrochloride that had formed was filtered off. The yield of reaction product was 54% of theoretical. The other dialkyl phosphorochloridates were obtained analogously.

The interaction of the HL and the dialkyl phosphorochloridates was carried out in aprotic solvents — CCl_4 and ether — at the boiling point for 1 h with a variation in the ratio of the initial reactants (HL–phosphorylating agent) — 1:1, 1:2, and 5:1. The contents of hydroxy and methoxy groups were determined according to [4], and that of phosphorus as described in [5].

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