Chemistry of Natural Compounds, Vol. 29, No. 5, 1993

INTERACTION OF CHLOROLIGNINS WITH AMINO COMPOUNDS

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UDC 547.992.3

The reactions of chlorolignins with such amines as ethyleneamine, nitroaniline, urea, thiourea, etc., are known and have been studied [1-3].

With the aim of obtaining new nitrogen-containing derivatives of lignins, we have studied the reactions of chlorolignins with piperidine and dimethylamine. For the synthesis of the chlorolignins, hydrolysis lignin and cellolignin were first purified with hot water and dichloroethane, while lignosulfonates were treated with dichloroethane alone, since they are readily soluble in water. Chlorination was carried out by the passage of gaseous chlorine through suspensions of the lignins in CCl_4 at room temperature for 5 h. The characteristics of the chlorolignins synthesized are given below as percentages:

Substance	Yield of product	Solubility in water	C	H	OCH_3	Cl	CO	COOH
Chlorocellolignin	87,3	54	43,8	4,95	2,05	10,9	6,3	1,36
Chlorinated hydrolysis lignin	89,6	55	43,8	4,49	1,60	19,2	9,9	2,2
Chlorolignosulfonate	81,8	100	34,4	4,4	2,8	31,4	5,9	0,4

The reactions of the chlorolignins with piperidine and dimethylamine were conducted at ratios of the reactants of 1:1-1:4 at the boiling point of dioxane for 1-6 h. The greatest amount of chlorine was introduced into the lignin molecule at a ratio of chlorolignin to amine of 1:2 and a reaction time of 4 h.

The aminolignins obtained from cellochlorolignin and chloro(hydrolysis lignin) were purified by washing on the filter with dioxane, and the products of the interaction of chlorinated lignosulfonate with dimethylamine and piperidine were purified by dialysis.

The characteristics of the products of the interaction of chlorocellolignin, chlorinated hydrolysis lignin, and chlorinated lignosulfonate with dimethylamine (I, II, III) and with piperidine (IV, V, VI) are given below (in percentages):

Substance	Yield of product	Solubility in water	C	H	N	Cl	OCH_3	CO	COOH
I	86,0	60,0	41,0	6,4	5,7	9,9	2,0	3,6	4,0
II	83,0	65,0	52,4	4,3	4,2	14,7	1,6	6,6	6,1
III	72,0	100	38,9	6,0	4,6	30,3	3,2	2,4	1,3
IV	84,3	65	50,9	7,6	7,6	8,7	2,6	5,0	3,3
V	85,6	65	50,0	7,9	6,3	11,0	1,7	5,2	5,6
VI	77,0	100	43,3	7,4	5,9	11,6	5,7	3,9	4,0

It was established on the basis of elementary and functional [4] analyses that the reaction of chlorolignins with piperidine and dimethylamine takes place through the chlorine and the carbonyl groups of the lignins, as in the interaction of chlorolignins with hexamethylenediamine [5] and urea [6]. The nitrogen content of the amino compounds obtained was greater in those from the reactions of the chlorolignins with piperidine, which is possibly connected with the fact that the reactivity of piperidine is greater than that of dimethylamine. The increase in the amount of methoxy groups in the amino derivatives obtained from chlorinated lignosulfate is, in all probability, connected with the elimination of low-molecular-mass substances during dialysis.

The increase in the level of acid groups in the aminated lignins is possibly connected with the hydrolysis of ester bonds in the lignin macromolecule in the presence of amino compounds, as is confirmed by the literature [7, 8].

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Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 771-773 September-October, 1993. Original article submitted June 24, 1993.

0009-3130/93/2905-0695$12.50

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