NITROGEN-CONTAINING DERIVATIVES OF LIGNIN. II

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UDC 634.0.813.11.0.813.1

Chlorine- and nitrogen-containing derivatives of lignin are biologically active substances [1]. In order to obtain new biologically active derivatives of lignin we have studied the reaction of chlorolignin with urea, thiourea, and m-phenylenediamine (m-PDA).

The reactions of chlorolignin with urea, thiourea, and m-PDA were performed in various solvents: benzene, toluene, dioxane, and dimethylformamide. In a series of experiments we found the optimum reaction conditions: solvent — dimethylformamide at a ratio of 2:1, heating for 4-6 h at 145-148°C.

The reaction of chlorolignin with urea probably takes place through the active chlorine and the carbonyl groups of the lignin like the reaction of lignin with hexamethylenediamine [2]:

$$\text{Lign}-\text{Cl}+\text{H}_2\text{N}-\text{CO}-\text{NH}_2\rightarrow \text{Lign}-\text{HN}-\text{CO}-\text{NH}_2+\text{HCl}.$$

If two molecules of chlorolignin react directly, the formation of a dimer Lign—HN—CO—NH—Lign is possible.

Urea may also react in the iso form:

$$\text{Lign}-\text{Cl}+\text{HO}-\text{C}(=\text{NH})-\text{NH}_2 \rightarrow \text{Lign}-\text{O}-\text{C}(=\text{NH})-\text{NH}_2.$$

On reaction with the carbonyl group:

$$\text{Lign}-\text{C}=\text{O}+\text{H}_2\text{N}-\text{CO}-\text{NH}_2\rightarrow \text{Lign}-\text{C}=\text{N}-\text{CO}-\text{NH}_2.$$

2. Thiourea reacts with chlorolignin like urea in the iso form [3].

3. m-PDA reacts with chlorolignin also through the active chlorine and through carbonyl groups.

The chemical characteristics of the lignin derivatives obtained are given in Table 1.

TABLE 1

Preparation	C	H	O	N	S	Cl	Functional groups		
							OH	OCH_3	CO
Chlorolignin (CL)	53,50	5,00	31,5	—	—	10,0	5,6	4,87	7,28
Product of the reaction of CL with urea (PCLU)	56,20	5,52	32,17	5,57	—	0,54	3,15	4,71	4,92
Product of the reaction of CL with thiourea (PCLTU)	55,54	4,87	29,17	4,12	4,55	1,65	3,10	4,8	7,165
Product of the reaction of CL with m-PDA (PCLU-PDA)	56,7	5,84	31,46	5,0	—	1,0	3,725	4,68	3,33

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Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 540-541, July-August, 1975. Original article submitted June 6, 1974.

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The semiempirical formulas per C_6–C_3 unit for the initial chlorolignin and the derivatives obtained from them have been calculated:

CL $C_9H_{8.52}O_{2.47}(OCH_3)_{0.3}(OH)_{0.67}(CO)_{0.53}Cl_{0.56}$

PCLU $C_9H_{10.07}O_{3.09}(OCH_3)_{0.31}(OH)_{0.37}(CO)_{0.32}N_{0.8}Cl_{0.031}$

PCLTU $C_9H_{9.1}O_{2.95}(OCH_3)_{0.32}(OH)_{0.39}(CO)_{0.57}N_{0.62}S_{0.30}Cl_{0.098}$

PCL-m-PDA $C_9H_{10.43}O_{2.96}(OCH_3)_{0.3}(OH)_{0.42}(CO)_{0.24}N_{0.72}Cl_{0.056}$.

In the reaction of chlorolignin with urea, one nitrogen atom reacts with 1.22 PPU [Propylphenyl unit] of lignin, or one molecule of urea with 2.5 PPU.

In the product of the reaction with thiourea, there is one nitrogen atom to 1.66 PPU and one molecule of thiourea to 3.6 PPU. In the product of the reaction of chlorolignin with m-PDA there is one nitrogen atom to 1.35 PPU and 1 mole of m-PDA to 2.8 PPU.

All the preparations that we have obtained are being tested by phytotoxicologists as biostimulators of plant growth in cotton-growing.

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