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CLEAVAGE OF THE NATURAL LIGNIN OF COTTON-PLANT STEMS WITH THIOACETIC ACID IN THE PRESENCE OF ANTHRAQUINONE

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The influence of additions of catalytic amounts of anthraquinone on the stages of hydrolysis in the cleavage of natural lignin by thioacetic acid has been investigated. The degree of delignification does not change under these conditions, but the yield of low-molecular-weight cleavage products increases, which indicates a profound degradation of the lignin macromolecule. The qualitative and quantitative compositions of the monomeric fractions of cleavage products do not undergo appreciable changes in the presence of anthraquinone.

The presence of anthraquinone (AQ) in alkaline cooks of lignin-containing materials intensifies the breakdown of the β-O-4-alkyl aryl ether bonds in the lignin macromolecule [1]. Since under the action of thioacetic acid (TAA) the same bonds are attacked selectively, we have investigated the influence of additions of AQ in the course of the cleavage with TAA of the natural lignin of the stems of the cotton plant, ssp. mexicanium and the variety Tashkent-6, on the yield and composition of the degradation products. The catalyst (in an amount of 0.1% of the weight of the raw material) was added at the stage of alkaline hydrolysis of the S-benzyl thioacetates formed under the action of TAA [2].

It was found that the degree of delignification determined from the change in the amount of Komarov lignin in the plant raw material before and after the reaction was not affected by the presence of AQ. The yield of low-molecular-weight lignin degradation products extractable by ether and by ethyl acetate increased in the presence of AQ from 35.4% [3] to 40.0% for the mexicanium cotton plant and from 45.5% [4] to 55.8% for the variety Tashkent-6. The more appreciable increase in the yield in the latter case corresponds to the higher amount of alkyl-aryl ether bonds in the lignin molecule [4].

To facilitate the identification of the products obtained, in accordance with [3] we extracted the monomer fraction with ether at pH 8 and the remaining low-molecular-weight substances with ethyl acetate at pH 2.

Part of the reaction mixture was acidified directly to pH 2 and was extracted with ethyl acetate, which made it possible to study the molecular-weight distribution of the degradation products. The amounts of oligomeric, tetrameric, trimeric, dimeric, and monomeric fractions determined with the aid of gel chromatography on Sephadex LH-20 [with methanol—water (9:1)

Fraction	Mexicanium variety				Variety Tashkent-6			
	without AQ		0.1% of AQ		without AQ		0.1 % Of AQ	
	A	B	A	B	A	B	A	B
Oligomers	2	0,7	3	1,2	9	4,1	3	1.7
Tetramers	11	3,9	4	1.6	6	2,7	9	5 0
Trimers	14	4,9	17	6 8	10	4,6	12	6 7
Dimers	40	14,2	46	18,4	28	12,7	33	18.4
Monomers	33	11,7	30	12,0	47	21.4	43	24,0
Total		35,4		40,0		45,5		55,8

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as eluent] were (here and below, A is the amount of the fraction on the total, %, and B is the yield of the fraction on the Komarov lignin, %).

As we see, in the presence of AQ with a total absolute increase in the yield of the monomer, dimer, and trimer fractions (see the yields on the Komarov lignin), the proportion of the monomer fraction in the total fell as a result in the increase in the proportion of the dimer and trimer fractions (see the amount as a proportion of the total).

The fractions extracted with ether at pH 8, containing practically only monomeric cleavage products, were investigated by the GLC method:

Substance	Mexicanium variety				Variety Tashkent-6			
	without AQ		0.1 % of AQ		without AQ		0.1% of AQ	
	A	B	A	B	A	B	A	B
Phenol	2,35	0,50	—	—	—	—	—	—
p-Hydroxyphenylpropane	0,26	0,06	0,7	0 12	13,1	3,76	9,1	2,94
Guaiacol	0,53	0.11	0,8	0.14	1.6	0,46	1,0	0,22
Guaiacylethane	8,88	1,88	15,2	2,63	—	—	—	—
Guaiacylpropane	23,11	4,90	23.8	4,12	38,9	11,16	32,10	7,19
Vanillin	0,56	0.12	—	—	—	—	—	—
1-Guaiacylethanol	1,60	0.34	—	—	2,2	0,63	3,3	0,74
1-Guaiacylpropanol	10.80	2,30	15.6	2,70	10,0	2,87	9,9	2,22
3-Guaiacylpropanol	17 0	3,60	10.3	3,51	8,9	2,55	15,0	3,36
Syringlylpropane	26 5	5.62	24,8	4.29	25 0	7,18	22,9	5 13
3-Syringylpropanol	—	—	5,3	0,95	—	—	4,2	0,94
Ratio								
p-coumaryl units	0,04		0,01		0,21		0,14	
guaiacyl units	1		1		1		1	
syringyl units	0,42		0,45		0,41		0,44	

The qualitative and quantitative compositions of the monomeric fractions of the products of cleavage by thioacetic acid in the presence of AQ and without it were similar, and the ratios of guaiacyl and syringyl units were also close. In all cases, the amount of p-coumaryl units was low and it was even somewhat lower in the experiments performed in the presence of the catalyst.

Thus, under mild conditions (temperature 60°C, nitrogen atmosphere) of hydrolysis after the action of thioacetic acid on native cotton-plant lignin, the addition of catalytic amounts of AQ, while promoting a general increase in the yield of low-molecular-weight cleavage products, did not lead to appreciable structural changes in the total monomeric cleavage products.

EXPERIMENTAL

The cleavage with thioacetic acid of the native lignin of cotton-plant stems was performed as described previously [2, 3]. Anthraquinone was added at the hydrolysis stage in an amount of 0.1% of the weight of the comminuted stems that had been extracted with ethanol—benzene (1:2) and with hot water. In the case of repeated hydrolysis, the same amount of catalyst was added again. The subsequent treatment of the reaction mixture was performed with no changes.

Gel chromatography was carried out on Sephadex LH-20 using methanol—water (9:1) as solvent as eluent. Separation into fractions was effected with the aid of the coefficients given in [5]. The GLC analysis of the combined monomers was performed under the conditions described in [6].

SUMMARY

1. Additions of catalytic amounts of anthraquinone at the stage of hydrolysis in the cleavage of native cotton-plant stem lignin by thioacetic acid lead to more far-reaching degradation of the lignin macromolecule. Under these conditions the yield of low-molecular-weight cleavage products rose from 40.0 to 55.8% for the mexicanium and Tashkent-6 varieties, respectively.

2. The qualitative and quantitative compositions of the monomeric fractions of cleavage products underwent no appreciable changes in the presence of anthraquinone.

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STUDY OF THE LIGNIN OF COTTON PLANTS OF THE VARIETY AN BAYAUT-2. I.

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The dioxane lignin has been isolated from ripe stems of a cotton plant of the variety AN Bayaut-2. Its developed empirical formula has been derived, its UV, IR, and PMR spectra have been recorded, and its molecular weight has been determined. It has been shown that the dioxane lignins of the stems of cotton plants of different varieties differ in chemical structure.

Continuing a study of the lignin of medium-fiber varieties of the cotton plant, we have investigated the dioxane lignin (DLA) from ripe stems of a cotton plant of the variety AN Bayaut-2. The DLA was obtained by Pepper's method [1] from the stems that had previously been ground (0.2 mm), exhaustively extracted with ethanol—benzene (1:1), and washed with hot water. The yield of DLA was 6.1% (on the Komarov lignin). The total amount of lignin (Komarov lignin) in the stems was 23.01% [2]. The stem DLA consisted of a light-brown amorphous powder readily soluble in the usual solvents for lignins: dioxane, dimethyl sulfoxide, dimethylformamide, methylcellosolve, etc. The DLA was purified by two reprecipitations of its aqueous dioxane solutions in absolute diethyl ether. The developed empirical formula was calculated from the results of elementary analysis and functional group analysis. It is given without allowance for the carbohydrates bound to the lignin, since their amount in the DLA was low (less than 1%). Mol. wt. 210.66,

$$C_9H_{8.26}O_{2.31}(OCH_3)_{0.81}(OH_{ph})_{0.49}(OH_{al})_{0.55}(O_{CO})_{0.39}(O_{ar-al})_{0.51}.$$

When this is compared with the formula of the DLA from ripe stems of a medium-fiber cotton plant of variety 108-F [3]

$$C_9H_{8,02}O_{0,58}(OCH_3)_{1.23}(OH_{ph})_{0.44}(OH_{al})_{0.95}(O_{CO})_{0.22}$$
$$(OOH_{COOH})_{0.085}(O_{ar-al})_{0.56}$$

and the DLA from the stems of the variety Tashkent-1 [4]

$$C_9H_{6.22}O_{1.21}(OCH_3)_{0.82}(OH_{ph})_{0.63}(OH_{al})_{0.88}(O_{CO})_{0.46}$$
$$(OOH_{COOH})_{0.17}(O_{ar-al})_{0.37}$$

it can be seen that the lignins differ in the amounts of functional groups and, consequently, also in chemical structure. With respect to the degree of oxidation, the lignin of the variety AN Bayaut-2 comes first (5.06 O/C_9) and this is followed by the DLA of the Tashkent-1 variety (4.54 O/C_9). The least oxidized of all was the DLA of the 108-F variety (4.07 O/C_9).

With respect to their OCH_3/C_9 ratios, the lignins of the varieties AN Bayaut-2 and Tashkent-1 were close, but as a calculation of the numbers of aromatic protons in their PMR spec-

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