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ALKALINE HYDROLYSIS OF THE NATURAL LIGNIN OF COTTONPLANT STEMS IN THE PRESENCE OF ANTHRAQUINONE

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The study of a three-stage alkaline hydrolysis of the natural lignin of cottonplant stems has shown that the bulk of the lignin undergoes fragmentation during stage I. The addition of anthraquinone leads to an appreciable increase in the yield of low-molecular-mass hydrolysis products.

A large number of publications has been devoted to the investigation of the hydrolysis of lignin in an alkaline medium [1-3]. This is connected with the fact that alkaline hydrolysis is used for the study of the structure of lignin and for obtaining derivatives of it, and also in the delignification of plant materials.

We have studied the transformation of the natural lignin of cottonplant stems in a three-stage process of alkaline hydrolysis. Alkaline hydrolysis was conducted in an 8% solution of sodium hydroxide in an atmosphere of nitrogen at various temperatures, with and without the addition of 0.1% of anthraquinone (AQ). To facilitate the identification of the low-molecular-mass products formed, the reaction mixture was then reduced with Raney nickel [4]. After acidification of the hydrolysate to pH 7-8, the monomeric fraction of hydrolysis products was extracted with ether, while the other low-molecular-mass products were extracted with ether at pH 2 (Table 1).

The second and third stages, in which the solid plant residues remaining from the preceding stages were subjected to hydrolysis, were conducted analogously.

It can be seen from Table 1 that in all cases a rise in the temperature and the addition of AQ led to an increase in the total yield of low-molecular-mass hydrolysis products, as has been shown previously [5]. The maximum yield of low-molecular-mass products (23.3% on the Komarov lignin) was observed as a result of the three-stage hydrolysis of cottonplant stem lignin in the presence of 0.1% of AQ.

The composition of ethyl acetate extracts was investigated by gel chromatography on Sephadex LH-20 (solvent: ethanol–water (9:1)). A comparison of the curves of the gel eluograms showed that the MMDs of the total ethyl acetate phenolic products of the alkaline hydrolysis of cottonplant stem lignin obtained after stage I at temperatures of 60, 100, and 160°C, both in the absence and presence of AQ, were more pronounced than those obtained after stages II and III (Fig. 1).

On comparing the MMD curves of the total ethyl acetate products after stages II and III, it is possible to see a shift of the maximum in the direction of higher molecular masses, which witnesses an increase in the proportion of higher-molecular-mass hydrolysis products (Fig. 2 and 3)

The monomeric fractions of the products of the hydrolysis of natural cottonplant stem lignin were investigated by gas-liquid chromatography. The qualitative composition and the quantitative levels of monomeric phenols in ethereal extracts are given in Table 2. Analysis of the figures of Table 2 shows that the total monomeric products of the hydrolysis of natural cottonplant stem lignin contained a large amount of *p*-coumaryl structures, while, in the main, the addition of AQ led to an increase in their amount. This statement is valid for the experiments performed at 60°C (stages I and III) and 160°C (stages I, II, and III). In the experiments at 100°C with the addition of AQ, on passing from stage I to stage III no economic increase in the level of *p*-coumaryl structures was observed, but their level was high (% in the mixture):

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TABLE 1. Yields of Low-Molecular-Mass Products of the Hydrolysis of Cottonplant Stem Lignin (% on the Komarov lignin)

Stage of alkaline hydrolysis	Monomeric total, pH 8	Other phenolic compounds, pH 2	Total yield
T=60°C, Without AQ			
1. I	1.80	2.10	3.90
2. II	0.90	1.00	1.90
3. III	0.31	0.97	1.28
			Σ=7.08
T=100°C, Without AQ			
4. I	2.40	2.50	4.90
5. II	0.40	0.90	1.30
6. III	0.30	0.10	0.40
			Σ=6.60
T=160°C, Without AQ			
7. I	5.10	5.60	10.70
8. II	1.40	3.10	4.50
9. III	0.80	1.30	2.10
			Σ 17.30
T=60°C, +AQ			
10. I	2.80	3.60	6.40
11. II	1.20	1.30	2.50
12. III	0.40	0.90	1.30
			Σ=10.20
T=100°C, +AQ			
13. I	3.40	3.90	7.30
14. II	1.20	1.10	2.30
15. III	0.20	0.30	0.50
			Σ=10.10
T=160°C, +AQ			
16. I	7.20	10.30	17.50
17. II	1.10	2.60	3.70
18. III	0.80	1.20	2.00
			Σ=23.20

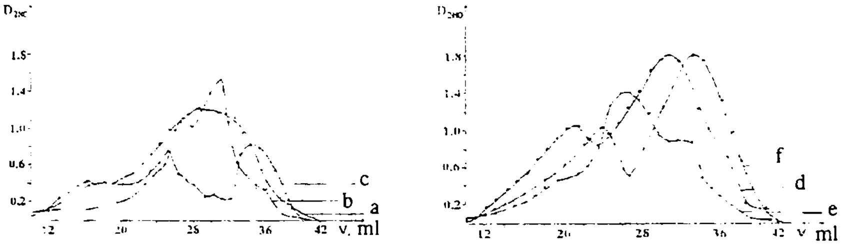

Fig. 1. Curves of the gel filtration of the total ethyl acetate phenolic products of the alkaline hydrolysis of natural cottonplant stem lignin (first stage): *a*) hydrolysis at 60°C without AQ; *b*) hydrolysis at 100°C without AQ; *c*) hydrolysis at 160°C without AQ; *d*) hydrolysis at 60°C + AQ; *e*) hydrolysis at 100°C + AQ; *f*) hydrolysis at 160°C + AQ.

T = 100°C	Without AQ	In the presence of AQ
Stage I	24.4	23.6
Stage II	35.7	29.1
Stage III	46.9	37.5

On the other hand, the proportion of syringyl derivatives was small in comparison with that found in an earlier investigation of the structure of cottonplant lignin [6]. It is likely that the lignin experienced demethoxylation under the conditions of alkaline hydrolysis in the presence of AQ. Here, syringyl derivatives proved to be far less stable than guaiacol derivatives. Literature information also indicates partial demethoxylation of lignin and its model compounds on heating with alkali [1, 7].

According to the literature, the alkaline hydrolysis of α-aryl ether bonds in structures with free phenolic hydroxyls takes place readily [8], since the formation of intermediate quinone methides is possible. In connection with this, the formation of

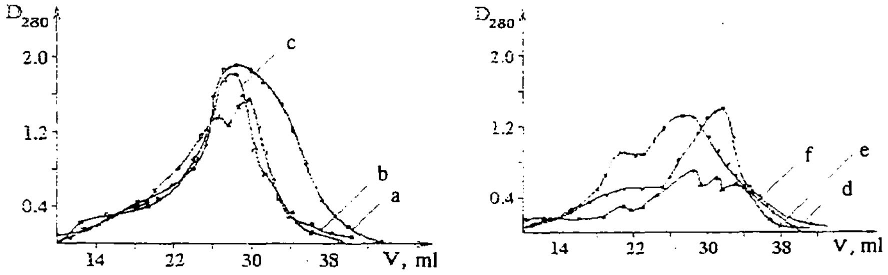

Fig. 2. Curves of the gel filtration of the total ethyl acetate phenolic products of the alkaline hydrolysis of natural cottonplant stem lignin (second stage): *a*) hydrolysis at 60°C without AQ; *b*) hydrolysis at 100°C without AQ; *c*) hydrolysis at 160°C without AQ; *d*) hydrolysis at 60°C + AQ; *e*) hydrolysis at 100°C + AQ; *f*) hydrolysis at 160°C + AQ.

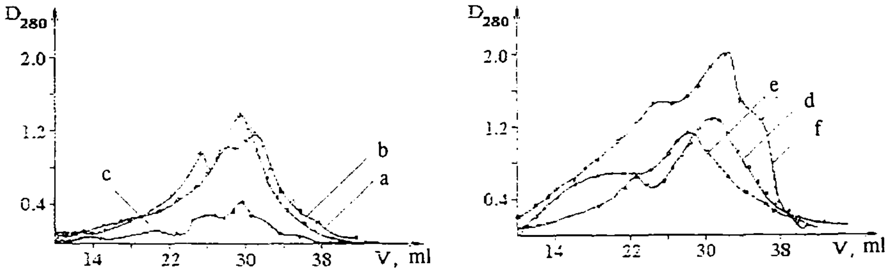

Fig. 3. Curves of the gel filtration of the total ethyl acetate phenolic products of the alkaline hydrolysis of natural cottonplant stem lignin (third stage): *a*) hydrolysis at 60°C without AQ; *b*) hydrolysis at 100°C without AQ; *c*) hydrolysis at 160°C without AQ; *d*) hydrolysis at 60°C + AQ; *e*) hydrolysis at 100°C + AQ; *f*) hydrolysis at 160°C + AQ.

α-alcohols (1-guaiacylethanol, 1-guaiacylpropanol) as the result of alkaline hydrolysis indirectly shows the hydrolysis of structural units of lignin having α-O-4 bonds and free phenolic hydroxyls.

The cleavage of β-O-4 ether bonds is one of the most important reactions of alkaline delignification. It is known that structural units of lignin of the nonphenolic β-ether type are capable of undergoing alkaline hydrolysis when free hydroxyls are present on neighboring α- or γ-carbon atoms or if there is a CO group in the α-position [9]. The formation of guaiacylpropane, 3-guaiacylpropanol, and *p*-hydroxyphenylpropane as a result of alkaline hydrolysis indirectly shows the presence of structural units with β-O-4 bonds in cottonplant stem lignin.

The formation of guaiacol may be a consequence of the hydrolysis of units with β-O-4 bonds having free phenolic hydroxyls. Such a phenomenon has been observed previously on lignin model compounds [10-12].

Because of the complexity of the structure of the initial lignin, it is difficult to envisage all the transformations during an alkaline cook, but, nevertheless, the investigation of the stagewise hydrolysis of natural cottonplant stem lignin showed that, in all variants of the experiments on alkaline hydrolysis, on passing from stage I to stage III the yields of low-molecular-mass products decreased and, consequently, the bulk of the lignin underwent fragmentation during stage I. The subsequent action of alkali on the residual plant material led to the liberation of relatively small amounts of low-molecular-mass products. The addition of AQ led to an appreciable increase in the yield of low-molecular-mass products of the alkaline hydrolysis of cottonplant lignin. The high level of *p*-coumaryl structures in the monomeric fractions may be due to the demethoxylation of the lignin under the conditions described.

EXPERIMENTAL

Three-stage Alkaline Hydrolysis of Natural Cottonplant Stem Lignin. Powdered cottonplant stem lignin (10 g) was treated with 100 ml of 8% NaOH solution and with AQ in an amount of 0.1% on the weight of the plant, and the mixture was heated at 60, 100, or 160°C with stirring in an atmosphere of nitrogen for 4 h. After the lapse of this time, the solid matter

TABLE 2. Compositions of the Monomeric Products of the Alkaline Hydrolysis of Cottonplant Stem Lignin (% in the mixture) in the Three (I-III) Stages of Hydrolysis

Substance	T 60°C, without AQ			T 100°C, without AQ			T 160°C, without AQ			T 60°C, + AQ			T 100°C, + AQ			T 160°C, + AQ		
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
1. Phenol	1.8	13.0	-	4.1	7.1	13.1	4.2	0.5	10.3	10.5	8.7	15.3	5.2	2.5	8.8	3.5	3.1	6.3
2. Guaiacol	4.9	12.1	6.4	3.6	11.9	11.3	2.6	2.0	6.2	5.8	6.3	11.6	6.7	8.0	-	2.1	3.1	3.0
3. *p*-Hydroxyphenylethane	12.4	6.3	1.9	12.0	17.8	15.0	13.3	8.9	4.6	16.7	9.6	8.2	10.1	20.7	0.9	10.6	10.2	8.5
4. *p*-Hydroxyphenylpropane	5.2	16.5	12.9	8.3	10.8	18.8	9.0	9.9	19.2	13.6	12.7	-	8.3	5.9	27.8	18.2	6.7	20.8
5. Guaiacylethane	9.0	18.8	35.1	18.0	8.8	16.1	15.1	10.5	5.5	2.9	3.3	-	12.0	2.3	15.1	16.2	7.5	6.5
6. Guaiacylpropane	5.7	13.8	46.1	3.1	7.7	-	7.5	13.5	6.9	6.9	15.6	22.1	23.8	15.9	-	8.4	4.5	11.0
7. 1-Guaiacylethanol	26.6	14.7	-	2.0	3.6	1.4	5.1	5.9	8.9	28.5	16.7	12.5	13.8	8.5	11.2	4.6	8.7	-
8. 1-Guaiacylpropanol	12.5	-	3.1	27.6	12.0	-	12.9	25.8	9.1	-	15.4	12.8	6.3	11.6	19.3	11.8	14.7	20.4
9. Syringylpropane	4.4	4.9	4.6	12.0	15.9	19.1	18.5	12.7	13.3	11.9	10.0	5.4	5.3	10.8	10.3	16.6	13.2	8.0
10. 3-Guaiacylpropanol	7.6	-	-	6.7	4.5	5.3	11.9	6.9	-	2.9	1.8	12.1	-	8.3	-	7.0	19.4	-
Ratio:																		
p-coumaryl	0.4	0.6	0.1	0.4	0.9	1.9	0.5	0.3	0.3	0.9	0.4	0.3	0.1	0.6	0.8	0.7	0.3	0.8
guaiacyl	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
syringyl	0.3	0.1	0.1	0.2	0.4	0.1	0.3	0.2	0.1	0.3	0.2	0.1	0.1	0.2	0.2	0.3	0.2	0.2

was separated off by centrifuging the hydrolysate, and it was washed first with 8% NaOH and then with water to neutrality. The combined hydrolysate and wash waters were reduced with 20 g of freshly prepared Raney nickel [4] in an atmosphere of nitrogen for 6 h.

After the separation of the reduction product by decantation, the catalyst was washed with 50 ml of 8% NaOH. The reaction mixture was acidified with dilute (1:1) HCl to pH 7-8, and the monomeric fraction of lignin hydrolysis products was extracted with ether (1.0 liter). After acidification of the residual products to pH 2, the remaining low-molecular-mass lignin hydrolysis products were extracted with ethyl acetate (1.0 liter).

The water-washed plant residue was dried, weighed, and subjected to the second stage of alkaline hydrolysis. The reaction mixture was treated in a similar way to that of the first stage. The third stage of alkaline hydrolysis – of the solid plant residue from the second stage – was carried out in the same way.

When the experiments were performed in an autoclave (T = 160°C), the reaction mixture was first purged with nitrogen for 2-3 min. The autoclave was heated to 160°C, and the reaction time was 3 h.

The alkaline hydrolysis of the natural cottonplant stem lignin without AQ was carried out under conditions analogous to those described above.

GLC analysis was conducted on a Chrom-41 chromatograph (Czechoslovakia). The total low-molecular-mass phenolic substances were analyzed in a glass column (3 mm × 2.5 m) filled with Chromaton N-AW-DMCS bearing 15% of the stationary liquid phase Apiezon-L at 180-205°C with a gas (helium) flow rate of 35-40 ml/min [13]. The hydrolysis products were identified from their retention times and by the addition of markers.

Gel chromatography was conducted on a column with Sephadex LH-20 and the eluent ethanol–water (9:1).

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