A STUDY OF THE POLYSACCHARIDES, HYDROLYSATES, AND SULFURIC-ACID LIGNIN OF COTTONPLANT STEMS

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A comparative investigation of the acid hydrolysis of the guza-paya [stems and bolls] and seed husks of the cotton plant has shown that the hydrolysates differ in their quantitative levels of monosaccharides, but in the pentose hydrolysates xylose predominates in both cases. The extracts after the preliminary enrichment of the raw material contain a large amount of xylose. The sulfuric-acid lignin obtained from the guza-paya contains a far smaller amount of unhydrolyzed polysaccharide and a larger amount of functional groups than the lignin from the husks.

In the republics of Central Asia the raw material for obtaining xylitol and furfural in biochemical factories consists of cottonseed husks, which are a valuable fodder for animal husbandry. Therefore the search for new types of pentosan-containing raw material is urgent. Some aspects of the chemical treatment of guza-paya (the stems and bolls of the cotton plant after harvesting) have been considered previously [1], and the results of a study of the polysaccharides of the cotton plant have been presented in [2-6].

In the present paper we give the results of an investigation of the polysaccharides and acid hydrolysis of cottonplant stems. We have studied the qualitative and quantitative compositions of the carbohydrates of the initial raw material and of hydrolysates obtained and also of the sulfuric acid lignin of the guza-paya.

Samples of guza-paya from the variety Tashkent-1 gathered in the Tashkent province were investigated. The ground ($\leq$1 mm) raw material contained: 31.8% of cellulose; 29.5% of pentosans; 22.9% of Komarov lignin; 5.4% of ash; and 6.7% of moisture [7].

To study the carbohydrate components, the air-dry comminuted raw material was extracted with 82% ethanol. This led to the isolation of the ethanol-soluble sugars (3.4%), which were found by paper chromatography to contain glucose, arabinose, and xylose.

The carbohydrates were then analyzed by fractional extraction successively with water, a mixture of oxalic acid and ammonium oxalate, and caustic soda of various concentrations [8].

After the complete acid hydrolysis of the polysaccharide fractions, their qualitative carbohydrate compositions were determined. The amounts of polysaccharides and their monosaccharide compositions, determined from the results of PC and GLC, are given below:

Extractant	Yield of polysaccharide, % on the raw material	Ratio of the sugars					
		Gal	*Glc*	*Man*	*Ara*	*Xyl*	*Rha*
Water, 20°C	0.8	Tr.	3.9	Tr.	2	1	1.2
0.5 % $C_2H_2O_4$ + $+C_2O_4(NH_4)_2$, 70°C	4.2	1	7.0	Tr.	1	3.8	1.7
7% and 15% NaOH	19.8	3	9.3	1	2.6	44.3	3.6

The water-soluble polysaccharides possess no reducing capacity and did not give reactions with iodine, i.e., they did not contain a glucan of the starch type. The acid extracts gave a positive reaction for starch with iodine. The alkali-soluble polysaccharides (hemicellulose) were present in considerably larger amounts than the other polysaccharides. Xylose predomi-

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nated in their composition, which permits the conclusion that this fraction consisted mainly of a xylan [9].

In industry a valuable food product — xylitol — is obtained by the catalytic reduction of hydrolysates containing xylose. We studied the products of the hydrolysis of guza-paya under laboratory conditions in the regime of a pentose-hexose cook. For comparison, the hydrolysis of cottonseed husks was performed under similar conditions.

The plant material was first enriched by being boiled with water followed by treatment at 100°C with 10% sulfuric acid. Pentose hydrolysates 1, 2, and 3 were obtained successively by heating in a rotating autoclave with a 0.5% solution of sulfuric acid at 125°C. The residue after pentose hydrolysis was then subjected to a hexose cook with acid of the same concentration at temperatures of 150, 170, and 190°C, and hexose hydrolysates 4, 5, and 6, respectively, were obtained.

We give the yields of hydrolysates and extracts obtained after the enrichment of the raw material (%):

Hydrolysate		Cottonseed husks	Guza-paya
Extract after enrichment		23.5	20
Pentose hydrolysate	1	5	2.4
	2	2	2
	3	2	1.6
Hexose hydrolysate	4	2.5	4
	5	9	3.5
	6	11	13
Residue (lignin)		25	23

As we see, the yields from the pentose and hexose hydrolysates from the digestion of cottonseed husks were greater than in the case of the guza-paya. In both cases xylose predominated in the pentose hydrolysates, while rhamnose, arabinose, mannose, glucose, and, in small amounts, galactose were also present. The hexose hydrolysates contained mainly glucose with a small amount of xylose, rhamnose, and mannose.

Analysis of the monosaccharide composition of the extracts after enrichment showed that they contained a considerable amount of xylose and, obviously, it is more desirable to process them further into xylitol and not to use them for obtaining fodder yeast and alcohol.

The paper and gas-liquid chromatography of the reduced pentose hydrolysates and the sulfuric acid extracts showed the presence of predominating amounts of xylitol (71% in the extract after enrichment of the husks and 66% in the pentose hydrolysate; in the case of guza-paya, the amount of xylitol in the two materials was the same — 58.5%; Table 1).

Recently, interest has arisen in the use of technical lignins. The homogeneity, purity, and the presence of reactive groups in the lignin macromolecule are of great importance. In this connection, great scientific and practical interest was presented by an investigation of the sulfuric acid lignin obtained from guza-paya and a comparison of its characteristics with the lignin of the husks. It was found that in the case of the guza-paya hydrolysis took place more completely and the resulting lignin contained only 5% of polysaccharides that had not reacted, while the lignin from the husks contained 27% of this material. This is apparently connected with the looser structure and better grinding of the raw material, which facilitates the access of the digesting reagents.

Below we give the elementary and functional compositions of these lignins (%) and their semiempirical formulas calculated to C_9:

	C	H	OCH_3	OH_{phe}	OH_{alip}	OH_{acid}	CO
guza-paya lignin	63.76	5.88	8.60	3.72	5.64	0.56	8.94
	$C_9H_{9.42}O_{1.79}(OCH_3)_{0.50}(OH_{phe})_{0.39}(OH_{alip})_{0.60}(O_{CO})_{0.57}(OOH_{COOH})_{0.02}$						
husk lignin	59.32	5.90	5.57	2.52	3.85	1.53	7.10
	$C_9H_{9.27}O_{2.46}(OCH_3)_{0.34}(OH_{phe})_{0.28}(OH_{alip})_{0.43}(O_{CO})_{0.48}(OOH_{COOH})_{0.06}$						

The IR spectra of both lignins contained absorption bands characteristic for OH groups (3420 cm^{-1}), OCH_3 groups (2865, 1470, 1430, 1330 cm^{-1}), aromatic rings (1520, 1600 cm^{-1}), and

TABLE 1

Substance	Amount of polyols, %			
	guza-paya		cottonseed husks	
	sulfuric acid extract	total of the pentose hydrolysates	sulfuric acid extract	total of the pentose hydrolysates
Rhamnitol	2,4	1,5	0,5	0,8
Arabitol	19,5	7,2	9,5	15,8
Xylitol	58,5	58,7	71,1	66,6
Mannitol	2,7	7,5	14,2	4,6
Sorbitol	11,2	2,7	3,2	1,1
Ducitol	5,7	15,6	1,4	11,0

phenolic OH groups (1230 cm^{-1}). As compared with the spectrum of the husk lignin, in the spectrum of the guza-paya lignin the absorption band of β-CO groups (1725 cm^{-1}) was more intense, which agrees with the analytical results.

As we see, the guza-paya lignin was characterized by a higher content of carbon and of functional groups, except for carboxy groups, and consequently, should be more reactive.

EXPERIMENTAL

Descending chromatography was performed on type FN-11 paper (GDR) in the solvent system butan-1-ol—pyridine—water (6:4:3). The sugars and their derivatives were revealed with a solution of aniline hydrogen phthalate at 105-110°C and with a 1% solution of potassium permanganate.

For analysis, the monosaccharides were converted into the corresponding aldononitrile acetates [10], while polyols were acetylated. GLC was performed on a Chrom-41 instrument with a flame-ionization detector and a steel column (0.3 × 200 cm). The packing consisted of 5% of XE-60 on Chromaton N-AW (0.200-0.250 mm); the rate of flow of helium was 60 ml/min, the temperature of the thermostat 210°C and that of the evaporator 250°C. Paper electrophoresis was performed in a horizontal instrument at 1100 V, 7 mA, in 1% acetic acid on FN-7 paper for 4 h. All solutions were evaporated in vacuum at 45 ± 2°C. The substances obtained were dried in vacuum over P_2O_5.

Isolation of the Polysaccharides. The polysaccharide fractions were isolated from the plant stems as described in [8].

Hydrolysis of the Polysaccharides. Each sample (0.1 g) was hydrolyzed with 2 N sulfuric acid in the boiling water bath for 10-24 h. The hydrolysates were neutralized with $BaCO_3$ and, after appropriate working up, were analyzed with the aid of PC and GLC.

Pentose-Hexose Hydrolysis of Guza-paya and the Seed Husks of the Cotton Plant. In the course of preliminary enrichment, a 100-g sample was boiled with 1 liter of water for 15 min and then with 700 ml of 10% sulfuric acid for 15 min and with 0.5 liter of water for 10 min. Acid enrichment extracts were obtained. Then the raw material was placed in a 1-liter rotating autoclave fitted with a thermocouple and pressure gauge and was covered with 0.5% sulfuric acid (the volume of acid was 300 ml in all cases) and was kept at a temperature of 125°C and a pressure of 6-7 atm for 1 h twice. This gave pentose hydrolysates 1 and 2. Pentose hydrolysate 3 was obtained by keeping the material at the same temperature and pressure with a third portion of acid for 30 min. Hexose hydrolysate 4 was obtained by keeping the material at 150°C and a pressure of 13 atm for 1 h, hexose hydrolysate 5 at 170°C and 17 atm for 1 h, and hexose hydrolysate 6 at 190°C and 20 atm for 30 min followed by washing with water at 190°C for 30 min. The acid extracts and hydrolysates obtained were neutralized with $BaCO_3$, treated with active carbon, and then evaporated in a rotary evaporator at 45°C.

The pentose hydrolysates were reduced with neutral Raney nickel at 100°C for 6 h, and the solution obtained was heated with KU-2 cation-exchange resin.

The functional compositions of the lignins obtained were determined by standard methods [11]; methoxy groups by the method of Vieböch and Schwappach, total hydroxy groups by acetylation, total acid groups by chemosorption, and carbonyl groups by the tetrahydroborate method.

IR spectra were taken in tablets with KBr on a UR-20 instrument.

SUMMARY

1. A comparative investigation of the acid hydrolysis of the guza-paya and seed husks of the cotton plant has shown that the hydrolysates differ in their quantitative compositions but xylose predominates in the pentose hydrolysates in both cases.

2. The extracts after enrichment contain a large amount of xylose, which gives xylitol on reduction.

3. The lignin obtained from the guza-paya contains a far smaller amount of unhydrolyzed polysaccharides and a larger amount of functional groups than the lignin from the husks.

LITERATURE CITED

1. Kh. U. Usmanov, V. S. Minina, and A. M. Zaripova, Prospects of the Chemical Processing of Cotton Growing Wastes [in Russian], Nauka, Tashkent, 1964.
2. V. K. Lekomtseva, L. Kh. Akhmedova, and A. S. Sadykov, Khim. Prir. Soedin., 305 (1973).
3. V. K. Lekomtseva and A. S. Sadykov, Khim. Prir. Soedin., 549 (1974).
4. D. A. Rakhimov, Z. F. Ismailov, M. T. Turakhozhaev, and T. T. Shakirov, Khim. Prir. Soedin., 131 (1977).
5. D. A. Rakhimov, N. P. Yuldasheva, S. A. Khamidkhodzhaev, and E. S. Kondratenko, Khim. Prir. Soedin., 21 (1985).
6. A. S. Sadykov, Cotton — A Wonder Plant [in Russian], Moscow (1985), p. 128.
7. B. Kh. Pulatov and Kh. A. Abduazimov, Khim. Prir. Soedin., 260 (1978).
8. A. O. Aridkhodzhaev, D. A. Rakhimov, and Z. F. Ismailov, Khim. Prir. Soedin., 246 (1980).
9. M. S. Dudkin, "Advances in xylan chemistry," Khim. Drev., No. 4, pp. 3-13 (1980).
10. D. G. Lange and L. K. N. Jones, Can. J. Chem., 45, 1995 (1967).
11. G. F. Zakis, L. N. Mozheiko, and G. M. Telysheva, Methods of Determining the Functional Groups of Lignin [in Russian], Riga (1975).