A STUDY OF COTTON LIGNIN

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Cotton lignin has been little studied. Basically, the qualitative composition of this plant raw material is known [1-3]. For the present study we used cotton plant of the variety 108-F grown in the "Severnyi mayak" kolkhoz of the Sredne-Chirchikskii region of Tashkent oblast.

The lignin in the cotton plant was determined quantitatively by the usual Komarov method. (The lignin so obtained does not contain the carbohydrate complex.)

In a study of the cotton plant with respect to the various periods of vegetation, it was seen that the amount of extractive substances in it gradually decreases (Table 1), and the amounts of lignin, cellulose, and pentosans increase with the development of the plant. The amount of lignin reaches a maximum in the late vegetation period. The high lignin content in the early period is apparently due to its pronounced contamination with humification products [4]. The amount of mineral substances in the cotton plant gradually increases up to the budding period and then falls. This can most probably be explained by the assumption that before flowering the plant intensively absorbs mineral salts from the soil.

With the development of the cotton plant, there is an increase in its content of lignin, while the latter changes qualitatively. The lignin becomes more highly methoxylated. This has been confirmed by experiments using alkaline nitrobenzene oxidation.

The method of alkaline nitrobenzene oxidation is that generally adopted for determining the terminal aromatic structures of the lignin units [5, 6]. It provides the possibility of establishing the type of struc-

TABLE 1

Sample No.	Vegetation period	Plant organs	Extractive substances	Ash	Komarov lignin	Pentosans	Cellulose	Methoxy groups
			% on the plant					
I	2-cotyledonous leaves	Stems	16,14	9,45	23,0	12,99	12,37	1,05
II	3-4 leaves		14,50	12,66	21,0	12,62	15,63	1,13
III	7-8 leaves		13,86	20,64	20,0	13,10	14,69	1,45
IV	Budding, incipient flowering		13,70	16,45	22,4	13,53	13,59	1,45
V	Flowering		12,11	14,25	22,6	14,43	13,61	1,34
VI	Incipient fruit formation		11,13	13,19	22,7	17,52	19,15	2,5
VII	Fruit formation, incipient opening of the bolls		10,20	5,46	24,9	24,00	33,10	2,15
VIIa		Green bolls	10,00	4,83	22,5	25,42	30,68	3,04
VIII	Massive opening of the bolls	Stems	5,12	5,01	25,5	29,68	35,62	3,10
VIIIa		Green and semiripe bolls	5,00	3,76	23,1	28,22	34,99	2,93
IX	End of vegetation	Stems	3,18	4,31	26,6	29,86	38,89	3,44
IXa		Ripe bolls	2,65	5,86	27,4	27,14	30,22	3,38

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TABLE 2

Sample No.	Amt., %, of vanillin	Amt., %, of syringaldehyde	Ratio of vanillin to syringaldehyde
I	0,05	0,02	2,5 :1
II	0,09	0,07	1,3 :1
III	0,12	0,10	1,20:1
IV	0,13	0,12	1,08:1
V	0,16	0,15	1,07:1
VI	0,28	0,27	1,04:1
VII	0,19	0,16	1,18:1
VIII	0,48	0,43	1,07:1
IX	0,75	0,81	0,92:1
IXa	0,90	0,77	1,17:1

tural units present in the lignin (p-coumaric, guaiacyl, or syringyl), and also their ratio. The stems, bolls, and seed hulls of cotton have been studied by this method previously [7].

We used this method to identify the aromatic structural units of the lignin in the developing cotton plant. Since it has been established that in the alkaline nitrobenzene oxidation of the lignins the yields of aromatic aldehydes are far less than in the oxidation of the wood of plants because of condensation processes taking place during the isolation of the lignin [6], the wood of the cotton plants was oxidized.

The cotton plants of samples II-V showed only a small amount of aldehydes on alkaline nitrobenzene oxidation according to Freudenberg [8]. From sample VI onwards the amount of aldehydes in the products of nitrobenzene oxidation increased. In this case, oxidation was performed by the micro method of Stone and Blundell in Kodina's modification [9, 10]. Chromatograms of the products obtained in the oxidations showed the presence of vanillin and syringaldehyde (Table 2). No p-hydroxybenzaldehyde was found in the cotton plant during any of the vegetation periods, as is confirmed by previous results [11].

It can be seen from Table 2 that the amounts of vanillin and syringaldehyde rise with the development of the cotton plant. At the beginning of vegetation, the ratio of vanillin to syringaldehyde is 2.5 : 1 and at the end of the vegetation period it is 0.9 : 1. From the second vegetation period, when a hard stem appears in the cotton plant, the ratio of vanillin and syringaldehyde changes insignificantly.

EXPERIMENTAL

Cotton plants without leaves were used for the investigation. They were dried and were then comminuted in a ball mill, and the fraction with particle dimensions of 0.25 mm was taken.

To determine the amount of extractive substances, weighed samples of the plant were exhaustively extracted in a Soxhlet apparatus with a mixture of ethanol and benzene (1 : 1). The extract obtained was evaporated to dryness, dried further, and weighed. In all the determinations, samples extracted with the mixture of ethanol and benzene were used.

The amount of lignin was found by Koenig's method in Komarov's modification [12], the amounts of cellulose and pentosans by the method of Mozheiko and Yaunzemes [13], and the methoxy groups by the method of Vieböck and Schwappach [14].

In Table 1, all the results are given on the absolutely dry substance with the exception of the content of extractive substances, which is referred to the air-dry substance. The moisture content of the raw material was 5-6%.

Oxidation of the Cotton Plant with Nitrobenzene. The cotton-plant material (12 g) of samples I-V was mixed with 100 ml of 8% caustic soda solution and 12 ml of nitrobenzene. The mixture was heated in an autoclave at 160°C for 3 h. The products of the reduction of the nitrobenzene were distilled off with live steam (until the distillation of a yellow oil ceased). Two parallel 100-ml samples were taken from the reaction mixture. Each sample was acidified with sulfuric acid to pH 3 and then, by the gradual addition of Na_3PO_4, the pH of the solution was brought to 7.3, and it was treated with ether. The ethereal extract was evaporated almost to dryness, and the residue so obtained was dissolved in 5 ml of ethanol; 0.07-0.09 ml of the ethanolic solution was deposited on chromatograms. Chromatography on paper of type "M" ["slow"] of the Volodarskii Leningrad paper mill was performed for 4 h using the petroleum ether (70-100°C)–dibutyl ether–water (6 : 1 : 1) system. The elution and determination of the aldehydes were performed by Kodina's method [10].

The figures given in Table 2 were obtained as the result of three or four repetitions of the oxidation.

SUMMARY

1. In a study of the cotton plant with respect to its vegetation period, it has been established that as it develops the amount of extractive substances in it decreases and the amount of lignin, cellulose, and pentosans increases.

2. The ratio of the main components of the combined aldehydes obtained in the oxidation of the cotton plant material with nitrobenzene in an alkaline medium (vanillin and syringaldehyde) does not remain con-

stant. At the beginning of the vegetation period the vanillin predominates, and then the amounts of the two aldehydes become equal.

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