EXPERIMENTAL

The dioxane lignin preparations were acetylated for 24 h with a tenfold amount of an equimolar mixture of acetic anhydride and pyridine at room temperature. The acetylated lignins were precipitated in water and, after drying, were purified by reprecipitation from dioxane solutions in ether. The preparations obtained were carefully dried in a vacuum desiccator over P_2O_5.

All the PMR spectra were taken on a JNM-4H-100/100 MHz spectrometer at T_{room} = 22-24°C, c 10-12% by weight, 10 — HMDS, τ-scale, solvent deuterochloroform.

SUMMARY

On the basis of an analysis of the PMR spectra of cotton-plant dioxane lignins collected in various vegetation periods, it has been found that they have different degrees of substitution of the C_3 side chain and different degrees of condensation through the aromatic nuclei. The most highly condensed is the dioxane lignin of the early vegetation period, and the least, the DLA of the ripe stems.

It has been established that with an increase in the time of extraction, condensation takes place through the aromatic nuclei.

It has been shown that the number of α-alcoholic groups in the dioxane lignins studied are different.

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A STUDY OF THE STRUCTURE OF LIGNINS OF HEALTHY AND WILT-AFFECTED COTTON PLANTS OF THE VARIETY TASHKENT-1

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Continuing a study of the dioxane lignins of healthy and wilt-affected cotton plants of variety Tashkent-1 (DLCT) according to vegetation period, we have performed nitrobenzene oxidation and cleavage with sodium in liquid ammonia of the natural and isolated dioxane lignins. It has been established that in the wilt-affected samples of cotton-plant stems the amount of guaiacyl and syringyl structural units increases.

In a preceding communication [1] we described the isolation and characteristics of the dioxane lignins (DLs) of healthy cotton plants of the variety Tashkent-1 and of plants affected by wilt (*Verticillium dahliae* Kleb.) according to vegetation period. Continuing an investigation of the lignins isolated from stems of the early period (DLCT-I, 7-8 cotyledons)

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TABLE 1. Products of the Nitrobenzene Oxidation of Healthy and Wilt-Affected Stems and Bolls of Cotton Plants of Variety Tashkent-1 (I-VI) and of the Dioxane Lignins Isolated from them (DLCT-I–VII) (% in the mixture)

Substance	Stems										Bolls			
	early period		flowering				late period							
	healthy		healthy		diseased		healthy		diseased		healthy		diseased	
	I	DLCT-1	II	DLCT-II	III	DLCT-III	VI	DLCT-VI	VII	DLCT-VII	IV	DLCT-IV	V	DLCT-V
p-Hydroxybenzaldehyde	5,71	4,11	2,97	0,75	2,65	0,22	—	—	—	—	2,73	5,84	2,87	9,80
p-Hydroxybenzoic acid	—	—	—	—	—	—	5,24	4,18	0,55	2,12	—	—	—	—
Guaiacol	—	—	—	2,85	—	—	—	—	—	—	—	—	—	—
Vanillin	59,11	27,27	22,25	39,45	24,23	68,1	40,79	39,25	30,82	51,21	65,36	14,61	74,35	20,6
Acetovanillin	4,93	—	—	0,81	40,21	—	1,27	0,67	0,41	2,28	—	51,61	—	50,17
Ferulic acid	2,96	15,15	—	0,12	—	—	13,81	0,45	5,63	3,84	—	0,19	—	—
Syringaldehyde	3,45	24,24	3,74	28,56	9,52	31,13	43,0	19,55	41,27	28,70	11,94	11,39	10,92	16,93
Sinapic acid	—	—	—	—	—	—	—	0,3	—	2,28	—	—	—	—
Ratio: p-coumaryl	1	1	1	1	1	1	1	1	1	1	1	1	1	1
guaiacyl	11,76	10,3	7,4	57,6	16,76	309,5	10,0	9,6	156,4	27,0	23,9	11,3	25,9	7,3
syringyl	0,6	5,9	1,1	38,0	3,59	141,5	8,0	4,7	78,9	14,6	4,37	1,9	3,8	1,7

TABLE 2. Products of the Cleavage of Healthy and Wilt-Diseased Stems and Bolls of Cotton Plants of Variety Tashkent-1 (I-VII) and of the Dioxane Lignins Isolated from them (DLCT-I–VII) with Sodium in Liquid Ammonia (% on the mixture)

Substance	Stems										Bolls			
	early period		flowering				Late period							
	healthy		healthy		diseased		healthy		diseased		healthy		diseased	
	I	DLCT-I	II	DLCT-II	III	DLCT-III	VI	DLCT-VI	VII	DLCT-VII	IV	DLCT-IV	V	DLCT-V
Phenol	9.80	0,37	4,53	—	—	—	0,06	2,98	—	—	13,35	0,58	4,70	0,94
4-Hydroxyphenylethane	—	—	—	—	—	—	—	—	—	—	13,08	—	18,33	—
4-Hydroxyphenylpropane	—	—	—	1,00	—	0,30	1,91	1,0	2,56	1,90	—	4,40	—	2,50
3-(4-Hydroxyphenyl) propan-1-ol	1,50	3.56	4,03	2.50	5.20	1,90	—	1,0	—	—	—	—	—	0.50
Guaiacol	18,07	6,00	—	9,60	—	2,11	—	—	—	3,10	3,27	—	1.41	—
Vanillin	5,44	11.18	8,40	24,90	13.00	21,90	0,78	—	8,30	0,90	—	18.18	25,30	3.38
Vanillyl alcohol	7,71	3.00	5,41	0,70	2.47	0,65	0,39	0,80	0,20	1,70	6,25	—	—	—
Guaiacylethane	4,31	—	—	—	1,96	3,11	1,17	2,82	0.90	3,10	—	—	—	—
1-Guaiacylethanol	—	3,00	—	4,80	—	—	—	--	—	1,03	—	—	—	—
Guaiacylpropane	11,90	18,20	35,3	17,70	41,5	20,25	46,70	32,53	45.2	28.40	7.17	37,8	8.81	40,00
1-Guaiacylpropan-1-ol	0,85	2.00	5,2	8.50	6,5	14,00	7,72	4,65	7,96	2,65	4,36	—	7,05	2,81
3-Guaiacylpropan-1-ol	—	—	—	2,50	—	3,00	0,47	—	2,20	5,30	1.63	4,13	1,18	5,92
Guaiacylpropane-1,3-diol	—	32,52	—	9,59	—	—	—	—	—	—	—	—	—	—
Syringylpropane	30,59	19,80	35,70	24,8	30,46	26,3	36,70	38,80	19,40	27,90	21,25	29,70	11,1	17,7
1-Syringylpropan-1-ol	—	—	—	—	—	—	3,00	—	—	—	—	4,50	—	—
3-Syringylpropan-1-ol	—	—	—	2,20	—	—	—	—	8,0	—	—	—	—	—
Ratio:														
p-coumaryl	1	1	1	1	1	1	1	1	1	1	1	1	1	1
guaiacyl	4,2	19,3	6	29	12,6	29,4	25,3	10,2	29,1	34.4	16,5	12	3,9	13.2
syringyl	2,7	5,0	3,9	7,6	5,8	13,3	11,6	9.7	20,0	14,4	1	6,8	1	4,5

of healthy and wilt-affected stems of the vegetation period and the later period (DLCT-II, -III, -IV, and -VII, after the harvesting of the crop), and bolls (DLCT-IV and -V, after the harvesting of the crop), and of healthy (I, II, IV, and VI) and wilt-infected (II, V, VII) stems and bolls and stems of the cotton plant of variety Tashkent-1, we have performed nitrobenzene oxidation in an alkaline medium and cleavage with metallic sodium in liquid ammoni The GLC analyses of the products of the nitrobenzene oxidation of the plants and of the ligni are given in Table 1.

If we compare the products of the nitrobenzene oxidation of healthy and diseased specimens, it can be seen that in the wilt-affected plants and the dioxane lignins isolated from them the amount of guaiacyl and syringyl structures has increased.

In the products of the cleavage with sodium and liquid ammonia of the plants and of the lignins isolated from them, by the GLC method we have identified sixteen phenolic compounds relating to three types of structural units (Table 2). The main cleavage products of both the healthy and the wilt-affected plants and of the lignins are guaiacylpropane and syringylpropane.

The formation of 1-guaiacylethanol, 1-guaiacylpropan-1-ol, and 1-syringylpropan-1-ol is a confirmation of the presence of free benzyl alcohol groups, and the presence of guaiacylpropane-1,3-diol in the lignins of the stems of the early period and of the lignin of healthy plants in the flowering period shows that the lignin of cotton plants of variety Tashkent-1 consists of guaiacylglycerol structural units. The absence of β-alcohols in the cleavage products can apparently be explained by the presence of β-aryl-alkyl ether bonds between the structural units of the lignin.

As in the case of the products of nitrobenzene oxidation, in the products of the cleavage with sodium and liquid ammonia of wilt-affected samples of plants and dioxane lignins, again, guaiacyl and syringyl structural units predominate.

Henderson et al. [2] have shown the capacity of the fungus *P. versicolor* for methylating phenolic hydroxy groups of certain model lignin compounds. Thus, the metabolism of guaiacylglycol β-guaiacyl ether formed veratryl alcohol. Veratraldehyde and veratric acid were also formed as a result of the metabolism of p-hydroxybenzoic acid, protocatechuic acid, vanillin, and vanillyl alcohol.

As can be seen from the results of analysis of the products of nitrobenzene oxidation and of cleavage by sodium in liquid ammonia, wilt fungi are also capable of methylating lignin, like some white-rot fungi.

EXPERIMENTAL

The nitrobenzene oxidation of healthy and wilt-affected stems and bolls of cotton plants of variety Tashkent-1 (I-VII) was performed by Leopold's method [3], and that of the isolated dioxane lignins (DLCT-I–VII) as we have described previously [4]. The products of nitrobenzene oxidation were analyzed by GLC on a Khrom-4 chromatograph with a flame-ionization detector as described by Leopold [3]. Quantitative evaluation was done as described by McNair and Bonelli [5].

The cleavage with sodium in liquid ammonia of the natural lignins and isolated dioxane lignins and the analysis of the products obtained were performed by methods described previously [6, 7].

SUMMARY

It has been established by nitrobenzene oxidation and by cleavage with sodium in liquid ammonia that in wilt-affected stems of cotton plants of variety Tashkent-1 and the lignins isolated from them the amount of guaiacyl and syringyl structural units is greater than for healthy stems and the lignins isolated from them.

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COMPOSITION OF THE RESINOUS SUBSTANCES OF CONIFER NEEDLES.

I. GROUP COMPOSITION OF THE RESINOUS SUBSTANCES OF THE NEEDLES OF THE PINE *Pinus silvestris*

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A system of solvents has been selected for the successive extraction of pine needles (benzene, isopropanol, and isopropanol + chloroform). Extraction was carried out by the steeping method at room temperature, and the yield of resinous substances was 19.4%. The extractive substances isolated consisted of neutral compounds, glycolipids, and phospholipids. The group compositions of the neutral substances have been determined by column chromatography. The predominating components in them are hydrocarbons (15.9%), diglycerides (10.7%), and waxy substances (27.6%).

The chemical composition of conifer needles is extremely complex and diverse, and it depends on many conditions; specific features of the plants, age of the plant and of the needles themselves, the environmental conditions, the type of soil, etc. [1-3]. The composition of the resinous substances may also change with the solvent with which extraction is performed, and also with a change in the conditions of extraction [4]. There is information in the literature on the chemical composition of pine needles, but this information characterizes the resinous substances of trees growing mainly in the European part of the USSR [3]. Information on the composition of the resinous substances of the needles of species growing in Siberia is practically nonexistent.

The aim of the present work was to study the group composition of the resinous substances of the needles of the pine *Pinus silvestris* obtained by extraction of the initial raw material successively with organic solvents (Table 1).

As can be seen from Table 1, with the selected method of extraction a considerable yield of resinous substances was achieved — about 19%. Furthermore, extraction at room temperature excluded the destruction of components unstable to heat. The use of isopropanol as solvent did not exclude the possibility of the extraction of water-soluble components (salts, sugars, and amino acids, etc.). To eliminate these substances from the extract, provision was made for its preliminary washing with water. After this, the group composition of the extract isolated was determined. The following groups of substances were then isolated: neutral substances, glycolipids, and phospholipids. The residue on the silica gel, the oxidized substances, was eluted with a mixture of ethanol and benzene. The results of the determination of the group compositions of the resinous substances isolated are given at the top of the next page, immediately following Table 1.

Thus, the extractive substances isolated consisted to the extent of 65% of the group of so-called neutral substances.

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