3. The presence of gossypol and of phytates substantially changes the solubility of gossypulin.

LITERATURE CITED

1. T. S. Yunusov and M. T. Turakhozhaev, Khim. Prir. Soedin., 366 (1983).
2. K. Okubo, D. V. Myers, and G. A. Jacobucci, Cereal Chemistry, 52, 513 (1976).
3. 3. B. L. O'Dell and A. de Boland, J. Agric. Food. Chem., 24, 804 (1976).
4. T. S. Yunusov and Z. S. Yunusova, Khim. Prir. Soedin., 770 (1981).
5. R. F. Itzhaki and D. M. A. Gill, Analyt. Biochem., 9, 401 (1964).

LIGNIN OF THE FINE-FIBERED COTTON PLANT OF VARIETY S-6030 AFFECTED BY FUSARIAL WILT. II

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A comparative study of the products of cleavage by sodium in liquid ammonia of the dioxane lignins (DLAs) from healthy and fusarial-wilt-affected stems of the fine-fibered cotton plant of variety S-6030 and a study of the PMR spectra of both lignins has shown that the DLA from the healthy stems is more highly condensed than the DLA of the stems affected by wilt. The main structures of DNA wilt are of the guaiacyl type. In the DLA from the affected stems, the amount of p-coumaryl structures had increased, which confirms the demethylating action of fusarial wilt on cotton-plant lignin.

Continuing a study of the dioxane lignins (DLAs) from ripe stems of the thin-fibered cotton plant of variety S-6030, both healthy and affected by fusarial wilt [1, 2], we have cleaved the DLAs with metallic sodium and liquid ammonia by the procedures adopted for lignins [3]. The total yield of monomeric cleavage products from the DLA of the healthy plant (15.62%) was only half that from the DLA of the wilt-affected cotton plant (30.70%). This, like the yield of the product of nitrobenzene oxidation [2], indicates a greater degree of condensation of the lignin from the healthy stems. The yield of high-molecular-weight cleavage products was 33.49% from the DLA of the healthy stems and 34.97% from the DLA of the wilt-affected stems. The gel chromatography of these combined materials on a column of Sephadex LH-20 (with aqueous methanol as eluent and solvent) showed their similarity. Using the coefficients found previously [4], it was possible to delimit on the gel chromatograms the regions of oligomers (fraction 1), trimers (fraction 2),dimers (fraction 3), and monomers (fraction 4). The bulk consisted of the oligomeric and monomeric fractions.

Analysis of the total monomers on a gas-liquid chromatograph showed the presence of phenols belonging to three types of phenylpropane structural units (PPSUs): p-coumaryl, guaiacyl, and syringyl. The ratio of the p-coumaryl, guaiacyl, and syringyl components in the monomers from the healthy stems was 0.09:1:0.32, and from the affected stems 0.15:1:0.22.

Below we give the yields of monomeric products from the cleavage of lignins with metallic sodium and liquid ammonia (% on the DLA):

Substance	DLA from healthy stems	DLA from affected stems
p-Hydroxyphenylpropane	—	0,40
3-(p-Hydroxyphenyl)propanol	0,65	1,58
Guaiacol	0,26	0,26
Guaiacylethane	0,38	0,56
Guaiacylpropane	6,03	10,42
1-Guaiacylpropanol	0,90	2,25
Syringylpropane	2,92	2,86

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TABLE 1. Interpretation of the PMR Spectra of the Dioxane Lignins.

Number of the zone and its boundaries	Number of protons in the DLA of the stems		Interpretation of the protons
	healthy stems	affected stems	
I. 2,0—3,75	1,83	1,99	Aromatic protons
II. 3,75—4,2	0,46	0,38	Benzyl at acetyl groups
III. 4,2—4,8	0,33	0,45	Coumarane structures
IV. 4,8—7,5	2,06	2,87	C_3 side chain
IVa. 5,9—6,8	3,54*	2,94*	Methoxy groups
V. 7,5—7,9	1,18	1,85	Aromatic acetyl groups
VI. 7,9—8,4	3,57	2,45	Aliphatic acetyl groups
VII. 8,4—9,5	1,54	0,69	Methyl groups

*These values were taken from the empirical formulas.

As we see, in the DLA of the affected stems the proportion of p-coumaryl components had increased sharply which confirms the demethylating action of the wilt fungi. In both cases, the main structures were of the guaiacyl type.

A study of the PMR spectra (the identification and calculation of the protons was done in accordance with [5, 6]) of the DLAs from healthy and wilt-affected stems showed their nonidentity (Table 1).

An estimation of the hydroxy groups from the benzyl (αOH) and acetyl protons showed that the total amount of hydroxyls deduced from the spectrum was high in comparison with that shown in the formula. In the case of the diseased stems, because of the pronounced overlapping with the bands of aromatic and aliphatic acetyl groups the number of aromatic acetyls was very high in comparison with the given formulas.

The DLA from the healthy stems:

$$C_9H_{8.7}O_{0.59}(OCH_3)_{1.18}(OH_{ph})_{0.29}(OH_{al})_{1.19}(O_{CO})_{0.32}(O_{ar\text{-}al})_{0.71}.$$

The DLA from the affected stems:

$$C_9H_{8.13}O_{1.77}(OCH_3)_{0.98}(OH_{ph})_{0.29}(OH_{al})_{1.05}(O_{CO})_{0.4}(O_{ar\text{-}al})_{0.71}.$$

The spectral characteristics enabled us to calculate the amounts of α- and γ-hydroxyls. In the case of the lignin from the healthy stems, αOH is $0.46/C_9$, γOH is $0.73/C_9$; and for the affected stems, αOH is $0.38/C_9$; γOH is $0.44/C_9$. In view of the increased amount of OH_{phen} in the lignin from the affected stems, the number of γOH groups in it must be far greater than 0.44. Thus, in both lignins the γ-hydroxy groups were present in the largest amount.

According to the PMR spectra, the number of protons not present in functional groups of the DLA was $5.76/C_9$ for the DLA from the healthy stems and $6.0/C_9$ for that from the affected stems. This shows the greater degree of condensation of the DLA from the healthy stems.

An estimation of the total number of protons from the spectra and a comparison of it with the formulas given show that there was a difference between them of 1.6-2.3 H/C_9. In the majority of the DLAs that we have studied [7] the amount of hydrogen found by an analytical method was higher than that calculated with the aid of PMR spectra.

EXPERIMENTAL

The cleavage of the dioxane lignins with metallic sodium and liquid ammonia and the analysis of the monomeric phenols obtained were performed as described in [3].

The DLA was acetylated for 24 h with an excess of an equimolar mixture of acetic anhydride and pyridine at room temperature. The acetylated lignin was precipitated by pouring the reaction mixture into water. After separation and drying, it was reprecipitated by pouring aqueous dioxane solutions of it into absolute ether. The preparation was dried over P_2O_5 in a vacuum desiccator.

PMR spectra were taken on a JNM-4H-100/100 MHz spectrometer at room temperature, c = 10% (by weight), τ scale, solvent deuterochloroform, 10 is HMDS.

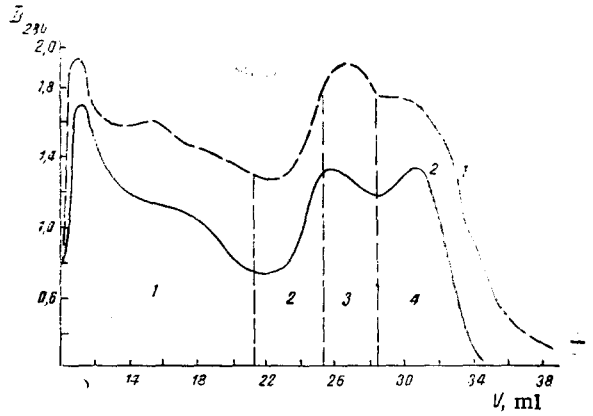

Fig. 1. Gel chromatograms of the high-molecular-weight product of the cleavage with sodium in liquid ammonia of the DLA of cotton-plant stems: 1) healthy; 2) wilt-affected.

SUMMARY

A comparative study of the products of the cleavage by sodium and liquid ammonia of the dioxane lignins of stems of the thin-fibered cotton plant of variety S-6030 in the healthy state and as affected by fusarium wilt and the study of the PMR spectra of both lignins showed that the DLA of the healthy stems was more highly condensed than the DLA of the wilt-affected stems. The main structures of both DLAs were of the guaiacyl type. The DLA of the affected stems contained a larger amount of p-coumaryl structures, which confirms the demethylating action of the fungi of fusarial wilt on cotton-plant lignin.

LITERATURE CITED

1. M. K. Mirzakhmedova, L. S. Smirnova, and Kh. A. Abduazimov, Khim. Prir. Soedin., 628 (1983).
2. M. K. Mirzakhmedova, L. S. Smirnova, S. Mukhamedova, and Kh. A. Abduazimov, Khim. Prir. Soedin., 825 (1985).
3. A. A. Geronikaki and Kh. A. Abduazimov, Khim. Prir. Soedin., 93 (1977).
4. L. S. Smirnova and Kh. A. Abduazimov, Khim. Prir. Soedin., 505 (1978).
5. C. L. Ludwig, B. J. Nist, and J. L. McCarthy, J. Am. Chem. Soc., 86, 1186, 1196 (1964).
6. N. A. Veksler, K. L. Seitanidi, L. S. Smirnova, Kh. A. Abduazimov, and M. R. Yagudaev, Khim. Prir. Soedin., 388 (1979).
7. L. S. Smirnova, G. N. Dalimova, and Kh. A. Abduazimov, Khim. Prir. Soedin., 560 (1980).