thioacetic acid cleavage of the DLA than in the case of the dioxane lignin from *G. mexicanium* (48%) corresponds to the greater amount of alkyl—aryl bonds in the semiempirical formula.

LITERATURE CITED

1. E. N. Yanishevskaya, B. Kh. Pulatov, and Kh. A. Abduazimov, Khim. Prir. Soedin., 755 (1982).
2. B. Kh. Pulatov and Kh. A. Abduazimov, Khim. Prir. Soedin., 260 (1978).
3. G. F. Zakis, L. N. Mozheiko, and G. M. Telysheva, Methods of Determining the Functional Groups of Lignin [in Russian], Riga (1975).
4. A. D. Alekseev, V. M. Reznikov, B. D. Bogomolov, and O. M. Sokolov, Khimiya Drevesiny, 4, 49 (1969).
5. N. A. Veksler, K. L. Seitanidi, L. S. Smirnova, Kh. A. Abduazimov, and M. R. Yagudaev, Khim. Prir. Soedin., 388 (1979).
6. E. N. Yaishevskaya, B. Kh. Pulatov, and Kh. A. Abduazimov, Khim. Prir. Soedin., 758 (1982).
7. B. Leopold, Acta Chem. Scand., 4, 1532 (1950).
8. A. A. Geronikaki and Kh. A. Abduazimov, Khim. Prir. Soedin., 93 (1977).

DIOXANE LIGNIN OF THE STEMS OF THE COTTON PLANT OF VARIETY TASHKENT 1 WHOLLY AFFECTED BY WILT

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Continuing a study of the dioxane lignins of wilt-affected stems of the cotton plant of variety Tashkent 1 (DLKhT), we have isolated the dioxane lignin from ripe stems wholly affected by wilt (DLKhT-VIII) with a yield of 5.1% on the Komarov lignin. The isolated dioxane lignin had the following elemental and functional [1] compositions (%): C 60.16; H 6.00; O 33.84; OCH_3 17.27; CO 7.12; OH_{tot} 9.52; OH_{phen} 3.67. One phenylpropane structural unit (one PPSU) of DLKhT-VIII had the semiempirical formula $C_9H_{7.22}O_{1.14}(OCH_3)_{1.12}(OH_{ph})_{0.42}$-$(OH_{al})_{0.82}(O_{CO})_{0.46}(OH_{COOH})_{0.24}(O_{al-ar})_{0.58}$.

It can be seen from a comparison of the semiempirical formulas of DLKhT-VI and -VII with DLKhT-VIII that the amount of methoxy and carboxy groups in the DLKhT-VIII was higher.

The UV spectrum of DLKhT-VIII taken in aqueous dioxane (1:9) had a maximum at λ 280 nm, log ε 3.5086 ($C = 2 \cdot 10^{-4}$ M). The IR spectrum had the absorption bands characteristic for lignins [2]. A calculation of the relative optical densities of the absorption bands by the baseline and the internal-standard methods [3] likewise showed an increase in the amount of methoxy and carboxy groups in the DLKhT-VIII as compared with DLKhT-VI and -VII.

The GLC analysis of the products of alkaline nitrobenzene oxidation (NBO), and also the cleavage with sodium in liquid ammonia of the natural lignin and the DLKhT-VIII showed the presence in them of phenols which have been identified previously in the products of the degradation of the lignin of healthy and wilt-affected samples [4]. The ratios of p-coumaryl, guaiacyl, and syringyl units for the natural lignin and the DLKhT-VIII in the products of NBO were 0.16:1:0.62 and 0.03:1:0.34 and in the products of cleavage with sodium in liquid ammonia they were 0.01:1:0.73 and 0.01:1:0.51. The yields of the products of NBO and of cleavage with sodium and liquid ammonia in the natural lignin were 10.4 and 11.9% on the Komarov lignin and in the DLKhT-VIII 21 and 13%, respectively.

We studied the PMR spectra of the dioxane lignins isolated from healthy and wilt-affected stems collected in the flowering period (DLKhT-II and -III) [2] and also from healthy and partially and wholly wilt-affected ripe stems (DLKhT-VI, -VII, and -VIII). The spectra were interpreted and were calculated quantitatively according to literature methods [5, 6]. The numbers of protons per 1 PPSU are given below (A represents the percentage strength of the signal and B the number of protons per C_9):

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Zone	Zone boundaries,ppm	DLKhT—*II*		DLKhT-*III*		DLKhT—*IV*		DLKhT—*VII*		DLKhT—*VIII*	
		A	B	A	B	A	B	A	B	A	B
I	2,0—3,7	10,69	1,95	12,92	2,78	12,93	1,66	13,40	2,19	14,20	1,79
II	3,7—4,2	1,98	0,35	2,88	0,62	3,12	0,40	2,88	0,47	3,66	0,46
III	4,2—4,8	0,99	0.18	1,49	0,32	1,56	0,20	1,47	0,24	1,56	0,20
IV	4,8—7,5	39,31	7,18	43,82	9,44	44,56	5,74	39,69	6,50	45,95	5,79
IV^a	5,9—6,8	12,82	2,34	12,12	2,61	19,07	2,46	18,50	3,03	26,67	3,36
Residual		26,49	4,44	31,70	6,83	25,49	3,28	21,19	3,47	19,28	2,43
V	7,5—7,9	7,48	1,36	7,43	1,60	8,13	1,04	7,37	1,20	6,53	0,82
VI	7,9—8,4	19,08	3,48	22,06	4,75	20,32	2,62	16,96	2,78	20,25	2,55
VII	8,4—9,5	7,63	1,39	9,40	2,02	9,38	1,21	18,20	2,98	6,75	0,85
Sum		100	15,89	100	21,53	100	12,87	100	16,36	100	18,25

As we see, in the DLKhT-VI, -VII, and -VIII the content of aromatic protons (zone I) has decreased in comparison with DLKhT-II and -III. The number of aromatic protons in the DLKhT-VIII has decreased in comparison with DLKhT-VI, which can be explained by the occurrence of condensation processes in the lignin molecule under the action of the phenol-oxidizing enzymes of the wilt fungi in the concluding stage of fungal attack.

The numbers of β-vinyl protons (zone II), of coumaran protons (zone III), of methoxy protons (zone IV^a), and of α-, β-, and γ-protons of the side chain (zone IV without IV^a) and of strongly screened protons of methyl and methylene groups (zone VII) has also increased in the spectra of DLKhT-III, -VII, and -VIII. Thus, the results of a calculation of the PMR spectra show that the distribution of the protons in dioxane lignins changes both during the growth of the plants and under the action of the wilt fungi, which indicates their chemical inhomogeneity and different degrees of condensation.

LITERATURE CITED

1. G. F. Zakis, L. N. Mozheiko, and G. M. Telysheva, Methods of Determining the Functional Groups of Lignin [in Russian], Riga (1975).
2. B. Kh. Pulatov and Kh. A. Abduazimov, Khim. Prir. Soedin., 620 (1978).
3. V. B. Karklin' and P. P. Érin'sh, Khimiya Drevesiny, 7, 83 (1971).
4. B. Kh. Pulatov and Kh. A. Abduazimov, Khim. Prir. Soedin., 392 (1979).
5. C. H. Ludvig, B. J. Nist, and J. L. McCarthy, J. Am. Chem. Soc., 86, 1186 (1964).
6. N. A. Veksler, K. L. Seitanidi, L. S. Smirnova, Kh. A. Abduazimov, and M. R. Yagudaev, Khim. Prir. Soedin., 388 (1979).