LIGNIN OF THE COTTON PLANT OF VARIETY TASHKENT 6

E. N. Yanishevskaya, B. Kh. Pulatov,
and Kh. A. Abduazimov

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The comminuted (0.25 mm) green stems of the cotton plant of variety Tashkent 6 were extracted with ethanol—benzene (1:2) and with hot water. The total acids and aldehydes (5.8 and 3.5% of the total material, respectively) were extracted from the ethanol—benzene extract (yield 4.08%) as described previously [1]. Of lignin precursors, vanillic, syringic, and ferulic acids and vanillin and p-hydroxybenzaldehyde were detected in them by the GLC method. The Komarov lignin content was 25.47% and the cellulose content 35.65%, the amount of lignin being greater than in a cotton plant of variety Tashkent 1, but smaller than in the subspecies *Gossypium mexicanium* [1, 2].

The dioxane lignin (DLA) isolated by Peper's method with a yield of 10.76% on the Komarov lignin had the following elemental and functional [3] compositions (%): C 59.06; H 6.52; O 34.42; OCH_3 15.5; OH_{tot} 13.45; OH_{phen} 2.32; COOH 1.28; CO 4.30. There were no carbohydrates bound to the lignin. We calculated the formula of a phenylpropane structural unit of the DLA:

molecular mass 203.20

$$C_9H_{7.96}O_{0.62}(OCH_3)_{0.99}(OH_{ph})_{0.28}(OH_{ph})_{1.33}(O_{CO})_{0.31}(OOH_{COOH})_{0.06}(O_{al-ar})_{0.72}.$$

The amount of aliphatic OH groups and of methoxyls was higher than in the lignins of variety Tashkent 1 and in *G. mexicanium* and the amount of phenolic groups was lower [1, 2].

The molecular mass distribution of the DLA was determined by the method of Alekseev et al [4]. It proved to be polydisperse with number-average, mass-average, and mean molecular masses of 4400, 9700, and 17,800, respectively. The UV spectrum of DLA taken in dioxane—water (9:1) had a maximum at λ 280 nm, log ε 3.9360 ($C = 0.65 \cdot 10^{-4}$ M). The IR spectrum had all the bands characteristic for lignins. Calculation of the PMR spectrum of acetylated DLA as described by Veksler et al. [5] showed that the total number of protons per structural unit (12.64) agreed well with the semiempirical formula (12.60). There were 0.26 phenolic OH groups and 1.31 aliphatic OH groups (in the formula: 0.28 and 1.33).

To elucidate the features of the structure of the macromolecule of the native lignin and the DLA, nitrobenzene oxidation and cleavage with sodium in liquid ammonia and with thioacetic acid were performed [6].

The oxidation products were found by the GLC method [7] to contain p-hydrobenzaldehyde, vanillin, syringaldehyde, guaiacol, acetoguaiacol, and p-hydrobenzoic, p-coumaric, vanillic, and syringic acids; their yields amounted to 43% of the Komarov lignin, or 36% of the DLA. The ratio between the structural units — p-coumaryl, guaiacyl, and syringyl — was 0.30:1:0.62 for the native lignin and 0.07:1:0.61 for the DLA.

On cleavage with sodium and liquid ammonia, p-hydroxyphenylpropane, guaiacol, guaiacylethane, guaiacylpropane, vanillin, guaiacylpropan-1-ol, and syringylpropane were detected by GLC [8]. The yields of the ethereal fractions [6] were 4 and 5%, and the ratios of the structural units 0.043:1:1.04 and 0.06:1:0.70 for the native lignin and the DLA, respectively.

In the products of cleavage by thioacetic acid (yields of monomeric fractions 28.7% of the Komarov lignin and 50% of the DLA) we identified [8] phenol, p-hydroxyphenylethane, p-hydroxyphenylpropane, guaiacol, guaiacylethane, guaiacylpropane, guaiacylpropan-1-ol, guaiacylpropan-3-ol, syringylpropane, and syringylpropan-1-ol, the ratios of the structural units being (0.25:1:0.48 and 0.06:1:0.20. The higher (66%) yield of the products of the

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

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

B. Kh. Pulatov and Kh. A. Abduazimov

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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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