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STUDY OF THE LIGNIN OF COTTON PLANTS OF THE VARIETY AN BAYAUT-2. I.

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The dioxane lignin has been isolated from ripe stems of a cotton plant of the variety AN Bayaut-2. Its developed empirical formula has been derived, its UV, IR, and PMR spectra have been recorded, and its molecular weight has been determined. It has been shown that the dioxane lignins of the stems of cotton plants of different varieties differ in chemical structure.

Continuing a study of the lignin of medium-fiber varieties of the cotton plant, we have investigated the dioxane lignin (DLA) from ripe stems of a cotton plant of the variety AN Bayaut-2. The DLA was obtained by Pepper's method [1] from the stems that had previously been ground (0.2 mm), exhaustively extracted with ethanol—benzene (1:1), and washed with hot water. The yield of DLA was 6.1% (on the Komarov lignin). The total amount of lignin (Komarov lignin) in the stems was 23.01% [2]. The stem DLA consisted of a light-brown amorphous powder readily soluble in the usual solvents for lignins: dioxane, dimethyl sulfoxide, dimethylformamide, methylcellosolve, etc. The DLA was purified by two reprecipitations of its aqueous dioxane solutions in absolute diethyl ether. The developed empirical formula was calculated from the results of elementary analysis and functional group analysis. It is given without allowance for the carbohydrates bound to the lignin, since their amount in the DLA was low (less than 1%). Mol. wt. 210.66,

$$C_9H_{8.26}O_{2.31}(OCH_3)_{0.81}(OH_{ph})_{0.49}(OH_{al})_{0.55}(O_{CO})_{0.39}(O_{ar-al})_{0.51}\,.$$

When this is compared with the formula of the DLA from ripe stems of a medium-fiber cotton plant of variety 108-F [3]

$$C_9H_{8,02}O_{0,58}(OCH_3)_{1.23}(OH_{ph})_{0.44}(OH_{al})_{0.95}(O_{CO})_{0.22}$$
$$(OOH_{COOH})_{0.085}(O_{ar-al})_{0.56}$$

and the DLA from the stems of the variety Tashkent-1 [4]

$$C_9H_{6.22}O_{1.21}(OCH_3)_{0.82}(OH_{ph})_{0.63}(OH_{al})_{0.83}(O_{CO})_{0.46}$$
$$(OOH_{COOH})_{0.17}(O_{ar-al})_{0.37}$$

it can be seen that the lignins differ in the amounts of functional groups and, consequently, also in chemical structure. With respect to the degree of oxidation, the lignin of the variety AN Bayaut-2 comes first (5.06 O/C_9) and this is followed by the DLA of the Tashkent-1 variety (4.54 O/C_9). The least oxidized of all was the DLA of the 108-F variety (4.07 O/C_9).

With respect to their OCH_3/C_9 ratios, the lignins of the varieties AN Bayaut-2 and Tashkent-1 were close, but as a calculation of the numbers of aromatic protons in their PMR spec-

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tra showed, the degree of substitution of the nuclei in them differed (more will be said about this below).

The lignins from the stems of cotton plants of the varieties considered likewise differed with respect to the number of free phenolic hydroxyls and could be arranged in the sequence: Tashkent 1 > AN Bayaut-2 > 108-F. The degrees of hydroxylation of the C_3 side chains were different for all the DLAs. Here the sequence was different: 108-F > Tashkent-1 > AN Bayaut-2. The smallest amount of free hydroxyls was present in the AN Bayaut-2 DLA ($1.04/C_9$) and the largest amount in the Tashkent-1 DLA ($1.51/C_9$).

The lignins also differed with respect to the amount of carbonyl groups that they contained. Consequently, they had different degrees of substitution not only of the aromatic nuclei but also of the C_3 side chain.

The UV spectrum of the DLA of the stems of a cotton plant of the AN Bayaut-2 variety had a minimum at 260 nm ($\log \varepsilon$ 3.35) and a maximum at 280 nm ($\log \varepsilon$ 3.45). The same pattern was observed in the UV spectra of the lignins of the other two varieties of cotton plant. A calculation of the molar extinctions referred to the molecular weight of one phenylpropane structural unit (PPSU) showed their closeness: for AN Bayaut-2, $\varepsilon = 2900$; for Tashkent-1, $\varepsilon = 3100$ [5]; and for 108-F, $\varepsilon = 2900$ [3]. But, in view of the fact that the value of the molecular extinction depends on many factors (the number of guaiacyl, syringyl, and p-coumaryl nuclei in the lignin molecule, the number of aryl-aryl bonds, etc.), it is impossible to judge the similarity of the structures of these lignins from it.

The IR spectrum of the DLA under investigation contained all the absorption bands characteristic for lignins. However, their relative optical densities (ROPs) [6] showed that it was not identical with the spectra of the lignins from the stems of the other two cotton plant varieties.

An additional characterization was given by a study of the PMR spectrum of the acetylated DLA. The assignment of the chemical shifts in the spectrum and their quantitative evaluation was carried out in accordance with [7]. The results of the calculations are given below (the numbers of protons were taken from the empirical formula):

Zone No.	Boundaries of the zone, ppm	Protons	No. of protons per C_9
I	2.0-3.8	Aromatic	2.92
II	3.8-4.2	β-Vinyl and benzyl ether C_3 side chains	0.44
III	4.2-4.8	Coumarane structures	0.71
IV	4.8-7.3	Methoxyls in the C_3 side chain	6.23
IVa	6.0-6.8	Methoxyls	2.43
		Others	3.80
V	7.3-7.8	Aromatic acetoxy groups	1.46
VI	7.8-8.3	Aliphatic acetoxy groups	1.59
VII	8.3-9.0	Highly screened methyl and methylene groups	0.22

As can be seen from the calculations, the number of free aromatic protons in the DLA is 2.92. In view of the fact that the number of free protons in each PPSU of lignin is, theoretically, $4 - 0.81$, i.e., 3.19, the deficiency of aromatic protons can be calculated as $3.19 - 2.92 = 0.27$. Consequently, in each fourth nucleus a bond is formed at the expense of one proton. The number of such bonds in the DLA from the stems of the cotton plant of variety 108-F is 0.43 and in that of the variety Tashkent-1 it is 1.52 [8].

Consequently, in spite of the similar OCH_3/C_9 ratios in the lignins of the cotton plants of varieties AN Bayaut-2 and Tashkent-1, the aromatic nuclei in them are dissimilar. In the DLA of the tashkent-1 variety of cotton plant each aromatic nucleus participates in the formation of one bond, and each second nucleus in the formation of two bonds. In the DLA from the 108-F variety of cotton plant the proton of each second aromatic nucleus participates in the formation of a bond.

The number of protons corresponding to benzyl acetate groups, $Ar{-}CH(AOc){-}C{-}C$ in the DLA of the AN Bayaut-2 cotton plant (0.44) shows that most of the aliphatic hydroxyls occupy the α positions. In the DLAs of the cotton plants of the other two varieties such OHs amount to a half of the total aliphatic hydroxyls.

From the number of protons in zones V and VI good agreement can be seen between the phenolic and aliphatic hydroxyls determined chemically and found spectrally.

An unusually large number of protons was found in zone III. These are protons of coumaran structures. In the DLAs of the cotton plants of the two other varieties their amounts are 2-3 times smaller. This can apparently be explained, in part, by the large amount of unidentified oxygen in the empirical formula of the DLA of the cotton plant under investigation.

A calculation of the protons in the C_3 side chain (zones II, III, and IV) likewise showed different degrees of substitution of this chain.

The total number of protons found from the PMR spectrum (11.54) agrees well with the amount of hydrogen in the developed empirical formula (11.73).

Thus, a study of the PMR spectrum of the lignin of the stems of a cotton plant of the AN Bayaut-2 variety has given additional information on the functional groups and nature of the structural units of the DLA.

A study of the molecular-weight distribution (MWD) of the DLA by gel chromatography [9] showed its polydispersity. Among the DLAs of medium-fiber cotton plants studied it had the lowest molecular weights: $\bar{M}_n = 3400$, $\bar{M}_w = 7000$, $\bar{M}_z = 12{,}900$. The degree of polydispersity, $\bar{M}_w/\bar{M}_n = 2.06$. In view of the molecular weight of a PPSU, it can be seen that the DLA molecule consists of 33 PPSUs.

EXPERIMENTAL

The dioxane lignin was isolated by Pepper's method [1]. The functional groups were determined and the empirical formula was calculated by standard methods [10]. Analytical figures (%): C 59.97, H 4.98, OCH_3 12.8, $OH_{tot} = 8.42$, $OH_{ph} = 3.92$, CO 5.28.

UV spectra were recorded on an SF-26 spectrophotometer in methylcellosolve—ethanol—water (2:1:1), $c = 1.257 \cdot 10^{-4}$ M. The molar extinction was calculated to the molecular weight of a PPSU.

The IR spectrum was taken on a UR-20 spectrophotometer in tablets with potassium bromide. Karklin' and Erin'sh's method was used to calculate ROPs.

Gel chromatography was performed on a column of Sephadex G-75 using dimethyl sulfoxide as solvent and eluent. The number-average, weight-average, and mean molecular weights were calculated as described in [9], using the coefficients given in [11].

To record the PMR spectrum, the DLA was acetylated as described in [7]. The spectrum was taken on a JNM-4H-10/100 MHz spectrometer $T_{room} = 22\text{-}24°C$, $c = 10\text{-}12\%$ by weight, 10 — HMDS, τ scale, solvent deuterochloroform.

SUMMARY

The dioxane lignin has been isolated from ripe stems of a cotton plant of the AN Bayaut-2 variety, its empirical formula has been derived, its UV, IR, and PMR spectra have been recorded, and its molecular weight has been determined. It has been shown that the dioxane lignins of the stems of cotton plants of different varieties have different chemical structures.

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