STUDY OF THE DIOXANE LIGNIN OF THE COTTON PLANT. III

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The present paper gives the results of the isolation of dioxane lignin from the stems of the cotton plant and its characterization. For the investigation we used the cotton plant Gossypium hirsutum, variety 108-F, from the late vegetation period (after the harvesting of the cotton). The dried stems were converted into particles with a size of 0.25-0.2 mm, which were extracted with ethanol–benzene (1:1) and with hot water.

DLA-II lignin was obtained by Pepper's method in a current of nitrogen [1], the yield of dry DLA-II lignin amounting to 2.2% of the weight of the initial plant or 8.3% of the weight of the Komarov lignin [2]. The DLA-II lignin was purified by dissolving it in a mixture of dioxane and water (9:1) followed by its precipitation in dry ether. The DLA-II lignin formed a light-brown amorphous powder readily soluble in aqueous solutions of alkalis, moist dioxane, and dimethyl sulfoxide (DMSO).

In view of the fact that the DLA-II isolated may contain a certain amount of bound carbohydrates, we performed a quantitative determination of the sugars in it by Bertrand's method [3]. The DLA-II was hydrolyzed by heating on the water bath with a 2.5% solution of sulfuric acid in aqueous dioxane for 5 h. The total amount of carbohydrates calculated as glucose was 4.01%. Analysis of the hydrolyzate by the GLC method [4] gave 3.6% of total carbohydrates: 3.3% of xylose, 0.25% of glucose, and 0.05% of arabinose. Consequently, the sugars consist mainly of pentosans.

The elementary composition and amounts of the main functional groups in the DLA-II were calculated with allowance for the presence of the carbohydrates as percentages and atomic units (AU) per phenylpropane structural unit (PPSU): C 60.12; H 5.69; O 33.95:

Main functional groups	Amount, %	AU/PPSU
Methoxy groups	15,4	1
Total hydroxy group	11,7	1,37
Phenolic hydroxy groups	3,38	0,4
Aliphatic hydroxy groups	8,32	0,97
Carbonyl groups	1,7	0,21
Carboxy groups	0,36	0,045

From the results given we calculated the empirical and semiempirical formulas of the phenylpropane structural unit of the DLA-II (mol. wt. 199.6): $C_9H_{8.26}O_{3.23}$ $(OCH_3)_1$; $C_9H_{6.89}O_{1.61}$ $(OCH_3)_1$ $(OH_{phen})_{0.4}$ $(OH_{aliph})_{0.97}$ $(O_{CO})_{0.21}$ $(O_{COOH})_{0.045}$.

The composition of the DLA-II differs from that of the Bjorkman lignin obtained from the stems of the cotton plant [5] by a smaller amount of methoxy groups and larger amounts of hydroxy and carbonyl groups.

The UV spectrum of DLA-II taken in aqueous dioxane (c $3.264 \cdot 10^{-4}$ M) is similar to that of the spruce DLA [6]: λ_{max} 284 nm (log ε 3.45).

The IR spectrum of DLA-II (tablets with potassium bromide) shows the absorption bands characteristic for a benzene ring with substitutents (1610, 1520, 1450 cm^{-1}) and for hydroxyl (3400 cm^{-1}), carbonyl (1710 cm^{-1}), and ether (1280, 1250, 1080 cm^{-1}) groups.

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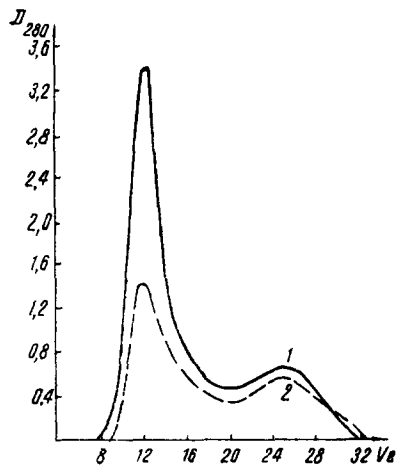

Fig. 1

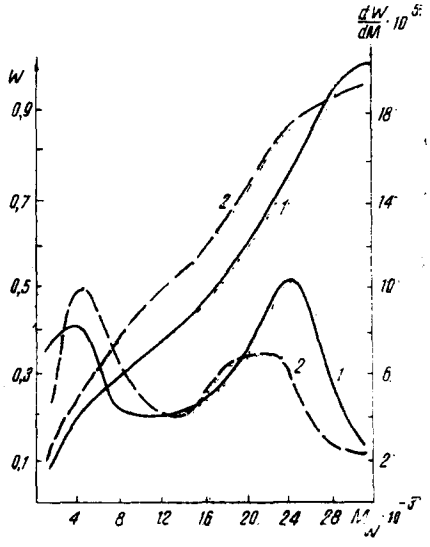

Fig. 2

Fig. 1. Gel chromatography curves of lignin preparations: 1) DLA-II; 2) DLA-I.

Fig. 2. Integral and differential curves of the MWD of lignin preparations: 1) DLA-II; 2) DLA-I.

To investigate the polydispersity of the DLA-II we used gel filtration on Sephadexes with DMSO as the eluent. The results of a comparison of the elution curves obtained by fractionating the same sample of DLA-II on Sephadexes G-75 and G-100 showed that on G-75 there is a sharper separation in the low-molecular-weight region. Consequently, for the quantitative experiments we chose the G-75 gel.

It can be seen from the chromatograms (Fig. 1) that DLA-II consists of two fractions (Fig. 1). The high-molecular-weight fraction (mol. wt. 18,000-24,000) makes up 29.14% and the low-molecular-weight fraction (mol. wt. 3000-6000) 28.81% of the lignin. The differential and integral curves of molecular-weight distribution (MWD) were plotted using the coefficients found previously [7] (Fig. 2).

Natural lignins are polydisperse, and the severity of the methods for their isolation leads to an increase in their polydispersity [6]. In view of the fact that the preliminary treatment of plant material with hot water could change the properties of the natural DLA, we obtained DLA-I from the raw material unextracted by hot water. Gel chromatograms of this lignin taken under the same conditions show that it also consists of high-molecular-weight (mol. wt. 20,000-26,000) and low-molecular-weight (mol. wt. 3000-6000) fractions, the former amounting to 50.7% and the latter to 20% of the lignin. Consequently, in the DLA-I there is 2.5 times more of the high-molecular-weight fraction. When the plant material is extracted with water, the MWD in the DLA-II changes, since the amount of low-molecular-weight fraction increases.

EXPERIMENTAL

Methods for Determining Functional Groups. Methoxy groups were determined by the method of Viebock and Schwappach [8] and the total hydroxy groups by acetylation according to Verley and Bolsing in Mozheiko's modification [9]. The phenolic hydroxy groups were found by difference between their total amount of acid groups determined by the chemosorption method in Enkvist's modification and the strongly acidic groups [10] obtained by the calcium acetate method [11]. The aliphatic hydroxy groups were calculated by difference between the total hydroxy groups and the phenolic. The carbonyl groups were determined by oximation in the modification of Bogomolov et al. [12].

Isolation of the Dioxane Lignin. The systems for the isolation of the DLA consisted of three units connected in series with one another: extraction, neutralization, and concentration, and also precipitation. All the operations were performed in a current of nitrogen. The extraction flask was charged with 25 g of the comminuted cotton-plant stems previously treated with ethanol–benzene (1:1) and with hot water, and they were extracted with 200 ml of dioxane–water (9:1) containing 0.7% of hydrochloric acid at 90°C for 0.5 h. Then, in the second unit, the dioxane extract was neutralized with a solution of sodium bicarbonate

and concentrated under vacuum at 40°C to 50 ml. The concentrated extract was precipitated in 500 ml of ice-water in the third unit. The lignin precipitated was separated off and was washed several times with distilled water. Yield 0.6 g. The DLA obtained was purified by being dissolved in aqueous dioxane and reprecipitated in absolute ether. The preparation dried over phosphorus pentoxide was then studied.

Gel Chromatography. A sample of 0.3-0.5 ml of a 0.5% solution of DLA in DMSO was charged onto a column (1.2 × 50 cm) of Sephadex G-75 equilibrated with DMSO. The rate of elution was 6-8 ml/h. Fractions amounting to 1 ml were collected, and the lignin concentrations in them were measured on an SF-4 spectrophotometer at 280 nm. To determine the "free" volume (the volume of the solvent between the granules of gel) a solution of dextran blue with mol. wt. 3,000,000 in DMSO was passed through the column. The volume of DMSO that eluted the dextran blue was taken as the "free" volume V_0. The calculations were made by the basic formula of chromatography using the coefficients found previously [7].

SUMMARY

1. Dioxane lignin has been isolated from mature stems of the cotton plant Gossypium hirsutum by mild acidolysis in an atmosphere of nitrogen.

2. Its expanded semiempirical formula has been established by elementary and functional analyses.

3. The molecular-weight distribution of the dioxane lignin has shown that it consists of high-molecular-weight and low-molecular-weight fractions.

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