AN INVESTIGATION OF THE HYDROCHLORIC ACID LIGNIN OF COTTON STEMS

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UDC 547.621:032.11

In the present work, the hydrochloric acid lignin from cotton stems is being isolated and characterized. For the investigation we took the cotton plant (*Gossypium hirsutum*) of variety 108-F in the last period of its vegetation (after the harvesting of the cotton).

The hydrochloric acid lignin was isolated by Willstätter's method [1]. The yield was 27% of the weight of the initial plant. The lignin consisted of an amorphous powder, dark brown with a pinkish tinge, insoluble in water and organic solvents and sparingly soluble in dimethyl sulfoxide and alkali. A quantitative determination by Bertrand's method [2] showed the absence of sugars from it. The elementary composition and content of main functional groups in the lignin were calculated in percentages and as atomic units (AUs) per phenylpropane structural unit of the lignin (PPSU).

From the results obtained we calculated the empirical (I) and semiempirical (Ia) formulas of the phenylpropane structural unit (mol. wt. 186.5).

$$\text{WL}\quad C_9H_{9.11}O_{3.72}(OCH_3)_{0.45} \qquad \text{I}$$

$$C_9H_{8.43}O_{2.39}(OCH_3)_{0.45}(OH\ ph)_{0.52}(OH\ aliph.)_{0.14}(O_{CO})_{0.43}(O_{COOH})_{0.22} \qquad \text{Ia}$$

$$\text{DLA}\quad C_9H_{10}O_{3.28}(OCH_3)_{1.0} \qquad \text{II}$$

$$C_9H_{8.86}O_{1.62}(OCH_3)_{1.0}(OH\ ph.)_{0.40}(OH\ aliph.)_{0.99}(O_{CO})_{0.21}(O_{COOH})_{0.045} \qquad \text{IIa}$$

On comparing the empirical and semiempirical formulas I, Ia, and II, IIa, it can be seen that hydrochloric acid lignin differs from dioxane lignin under nitrogen (DLA) [3] by a smaller content of methoxy and alcoholic hydroxy groups and a larger content of carbonyl and carboxyl groups. Consequently, the hydrochloric acid lignin proved to be modified as compared with the DLA.

The UV spectrum of the Willstätter lignin taken in ethanol has a band characteristic for an aromatic ring (λ_{max} 280 nm). The IR spectrum shows absorption bands characteristic of a benzene ring with substituents (1615, 1520, 1450 cm^{-1}), hydroxy groups (3400 cm^{-1}), carbonyl groups (1710 cm^{-1}), and ether groups (1280, 1230, 1040 cm^{-1}). For a more complete characterization of the lignin and to determine the degree of its condensation, we used the nitrobenzene oxidation method [4].

In the reaction products vanillin, syringaldehyde, and ferulic and p-hydroxybenzoic acids were found by the GLC method (Table 1). However, some of the peaks remained unidentified.

The yield of vanillin, which is a quantitative measure of the content of uncondensed structural elements [5] in the hydrochloric acid lignin was almost 3.4 times smaller than in the DLA.

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Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 648-650, September-October, 1975. Original article submitted July 8, 1974.

TABLE 1

Lignin	Vanillin	Ferulic acid	Aceto-vanillin	p-Hydroxybenzaldehyde	p-Hydroxybenzoic acid	Syringaldehyde
Hydrochloric acid	5,33	0,021	—	—	0,32	0,21
DLA	18,00	0,310	0,73	0,58	0,34	10,30

Note. The yields of aldehydes are given as percentages of the initial weight of the lignin.

EXPERIMENTAL

Isolation of the Hydrochloric Acid Lignin [1]. A 0.5-liter conical flask was charged with 10 g of finely ground sawdust which had been previously extracted with ethanol–benzene (1:1) and with hot water, and this was covered with 200 ml of superconcentrated hydrochloric acid (d 1.21) at –5°C. The contents of the flask were shaken at room temperature for 2.5 h. Then 65 ml of ice water was added and the mixture was left for 18 h. It was diluted with the same amount of water again, and the solid matter was filtered off with suction and washed with 200 ml of hydrochloric acid (1:1) and then repeated by with water. To purify the product obtained, it was boiled for 10 min with 200 ml of water with the addition of sodium carbonate to neutrality and was then washed with water.

Nitrogenzene Oxidation of the Willstätter Lignin [4]. A mixture of 1 g of the lignin, 1 ml of nitrobenzene, and 10 ml of 8% caustic soda solution was heated in an autoclave at 180°C for 2 h. After cooling, the reaction mixture was centrifuged, and the precipitate was washed with 10 ml of water and 20 ml of ether. The solution with the wash waters was extracted with ether (3 × 50 ml), and the ethereal layer was discarded. The aqueous layer was acidified to pH 2.5 with concentrated hydrochloric acid and extracted with ether. The ethereal extract was dried over anhydrous sodium sulfate and evaporated to dryness. The dry residue was dissolved in 5 ml of ethanol, and samples of this solution were taken for analysis by GLC [6].

Methods of Analysis. The amount of OCH_3 groups was determined by the Zeisel method, the total content of OH groups by the Verley method [7], and CO groups by the method of Gierrer and Söderberg [8].

SUMMARY

1. The lignin has been isolated from the stems of the cotton plant of a late period of vegetation by the hydrochloric acid method. The elementary composition and functional groups have been determined. The mean composition for a C_6–C_3 structural unit has been determined.

2. By the oxidation of a powder of the stems of the cotton plant with nitrobenzene in the presence of alkali it has been established that the hydrochloric acid lignin is more condensed than the DLA.

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