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SEPARATION OF THE LIGNOCELLULOSE OF NONWOODY PLANTS INTO ITS MAIN COMPONENTS AND STUDY OF THEIR PROPERTIES. 1. THE CELLULOSE AND THE LIGNOCARBOHYDRATE MIXTURE

G. N. Dalimova,[a] N. D. Burkhanova,[b] and G. V. Nikonovich[b]

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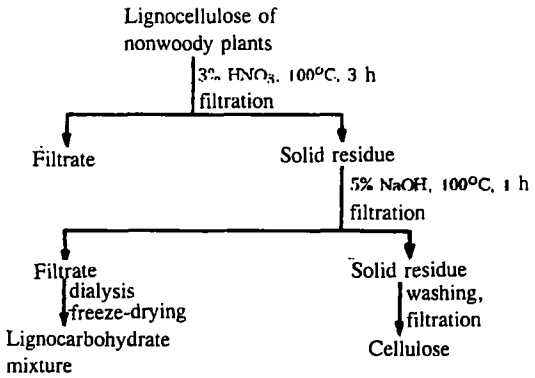
It has been shown that as a result of preliminary acid hydrolysis followed by alkaline treatment there is a separation of the lignocellulose of nonwoody plants (cotton plant stems, kenaf tow) into the structural substances of the cell wall. The nature of the separated components has been established as cellulose and a lignocarbohydrate mixture.

The dry matter of plants consists mainly of cell walls, which include structural substances: cellulose, hemicelluloses, and lignin. The separation of the lignocellulose of nonwoody plants into its main components without damage for determining their qualitative compositions and quantitative levels is an urgent problem that is difficult to solve.

We have investigated the separation of the lignocellulose of nonwoody plants (cotton plant stems and kenaf tow) by preliminary acid hydrolysis followed by alkaline treatment with the aim of obtaining valuable chemical products.

The amounts of cellulose and lignin in the cotton plant stems and kenaf tow were 37.0 and 25.0% and 48.0 and 20.0%, respectively. As can be seen from the scheme given below and Table 1, the main product of this separation was cellulose formed as a result of the hydrolytic decomposition of the natural lignocellulose. We have studied the structure and properties of the cellulose samples obtained from cotton plant stems and kenaf tow.

The supermolecular structure of the cellulose samples was studied by x-radiography, electron microscopy, and IR-spectral analysis. The x-radiographic results (Fig. 1) showed that both samples of cellulose gave the diffractogram of cellulose-I, but with a more defective structure. In place of the maxima from 101, $10\bar{1}$, 002, and 040 reflections at the corresponding angles 2θ = 14, 16, 21.5, and 34° that are characteristic for cellulose-I, an isolated maximum was observed in the 2θ = 14-16° region and weaker broadened peaks at 2θ = 21.5 and 34°.



a) Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (3712) 40 64 75; b) Institute of the Physics and Chemistry of Polymers, Academy of Sciences of the Republic of Uzbekistan, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 118-122, January-February, 1998. Original article submitted April 28, 1997.

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TABLE 1. Separation of the Lignocellulose of Nonwoody Plants into Its Main Components

Sample	HNO_3:NaOH ratio	Time of treatment, h	Yield, %	
			cellulose	lignocarbohydrate mixture
Cotton plant stems	1:1	2.0	22.6	3.9
	1:1	3.0	28.0	6.0
Kenaf tow	1:1	2.0	27.5	3.0
	1:1	3.0	32.0	5.7

TABLE 2. Characteristics of Samples of Cellulose from Cotton Plant Stems and from Kenaf Tow

Sample	DC, %	L, (Å)
Cotton plant stem cellulose	62.6	36.1
Kenaf tow cellulose	57.9	30.8

The calculated values of the degrees of crystallinity (DC) and the dimensions of the crystals (L) of the samples investigated are given in Table 2.

The values of the DC and L found for the samples investigated (Table 2) were characteristic for low-quality wood cellulose. The comparatively high values of the DC and L for the cotton plant stem cellulose showed its more perfect structure.

Microscope studies (Fig. 2) of the cellulose samples were made with a MBI-6 optical microscope in transmitted and polarized light. In these we determined the external appearance, form, presence of optical anisotropy, and the degrees of homogeneity and of the swelling of the samples in cadoxene. We determined the dimensions of the samples with the aid of an ocular micrometer and took their mean value from two parallel estimates of 30 measurements each. It was established that the cellulose samples consisted of fairly coarse agglomerates of particles adhering to one another, and we determined their dimensions and shape after separation.

The samples of cotton plant stem cellulose consisted of fine powder-like anisodiametric particles (mean dimensions 240 × 60 μm) and those from kenaf tow of rounded particles (mean dimensions 71 μm). The cellulose samples investigated fluoresced in polarized light, which showed their crystalline nature. In cadoxene the cellulose from cotton plant stems swelled greatly and dissolved slowly, while that from kenaf tow also swelled greatly but dissolved immediately. This showed a more defective structure of the latter, which correlated with the x-radiographic results.

The IR spectra of the cellulose samples had absorption bands due to the stretching and deformation vibrations of the functional groups characteristic for cellulose [1], such as bands at 2800 cm^{-1} (stretching vibrations of CH− groups), 1340-1430 cm^{-1} (deformation vibrations of C−OH, −CH, and $-CH_2$ groups), and 1000-1200 cm^{-1} (stretching vibrations of C−O groups), and in the so-called structurally sensitive region at 400-700 cm^{-1}.

The appearance of asymmetry of the band in the region of 2900 cm^{-1} in the form of projections at 2870 and 2960 cm^{-1} and also the presence of a band in the 1360 cm^{-1} region, not seen in the IR spectrum of wood cellulose, showed that the samples had undergone hydrolysis.

Thus, on the basis of the results of x-radiographic, microscopic, and IR-spectral investigations, it may be concluded that the cellulose samples obtained had a microcrystalline structure.

The lignocarbohydrate mixtures from cotton plant stems and from kenaf tow were also studied by IR spectroscopy. In the IR spectra of the samples investigated there were absorption bands characteristic for lignins and carbohydrates [2]. According to their IR spectra, the lignocarbohydrate mixtures from these plants differed insignificantly from one another. The absence of a band at 3500-3700 cm^{-1} showed that there were no free hydroxy groups in the samples investigated. The presence of an ester bond between lignin and carbohydrates can be deduced from absorption in the 1730-1760 cm^{-1} region. In the samples investigated this band had shifted in the long-wave direction (1773 cm^{-1}).

With the aim of studying the chemical nature of the lignin−carbohydrate mixture, we subjected it to acid hydrolysis with 2 N sulfuric acid at 100°C for 48 h. Carbohydrates were detected in the hydrolysates by means of the phenol/sulfuric acid test. Paper chromatography was used to establish the qualitative composition of the hydrolysates. We identified glucose, arabinose, xylose, rhamnose, galactose, and uronic acids. The presence of lignin in the samples of lignocarbohydrate mixtures

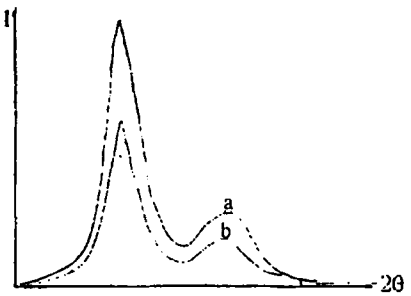

Fig. 1. Diffractograms of the MCCs from cotton plant stems (*a*) and kenaf tow (*b*).

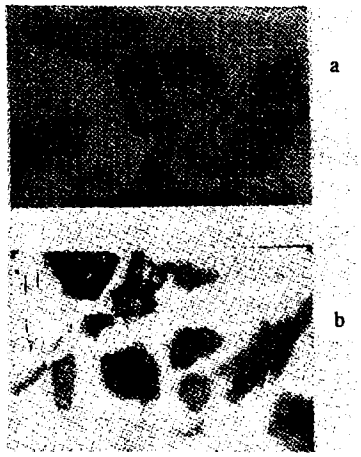

Fig. 2. Photomicrographs of MCCs from cotton plant stems (*a*) and from kenaf tow (*b*).

that we investigated was shown by the color reaction with phloroglucinol (red coloration) [3]. The molecular masses of the samples of lignocarbohydrate mixtures from kenaf tow and from cotton plant stems were determined as 65,000 and 72,000, respectively.

Thus, on the basis of the results of acid hydrolysis, a comparative study of IR spectra, and qualitative reactions for carbohydrates and lignin, it may be concluded that the samples investigated had a lignocarbohydrate nature.

EXPERIMENTAL

IR spectra of the samples of cellulose and the lignocarbohydrate mixture were taken on a Perkin-Elmer model 2000 Fourier IR spectrometer in tablets with KBr.

Preparation of the Lignocellulose Material. Ground (0.25 mm) cotton plant stems and kenaf tow were extracted with alcohol–benzene (1:2)) in a Soxhlet apparatus for 24 h and were then dried in the air. The lignocellulose material prepared in this way was used for separation.

Separation of the Lignocellulose Raw Material into its Main Components. To 25.0 g of plant material (cotton plant stems, kenaf tow) was added 250.0 ml of 3% nitric acid, and the mixture was boiled under reflux for 3 h. Then the solid residue was separated off by filtration and was boiled with 250.0 ml of 5% NaOH for 1 h. The solid residue — cellulose — was filtered off, washed with water, and dried in the air. The filtrate, containing dissolved hemicelluloses and lignin, was dialyzed against water, after which the solution was freeze-dried.

The x-radiographic investigations were conducted on a Dron-3M diffractometer with monochromatized CuK_{α} radiation at a voltage of 23 kV and a current strength of 12 mA.

The microscopic studies were made with an MBI-6 optical microscope in transmitted and polarized light.

For the **paper chromatography** of the lignocarbohydrate mixture we used FN-12 paper and the butanol–pyridine–water (6:4:3) system with acid aniline phthalate as the revealing agent.

The degrees of crystallinity of the samples were calculated from the ratios of the intensities of the peaks from the crystalline and the amorphous regions by means of Segal's formula [2]:

$$DC = \frac{J_{002} - J_a}{J_{002}} \cdot 100\%$$

where J_{002} is the intensity of the 002 reflection at $2\theta = 21.5°$, and J_a is the intensity of scattering of the amorphous halo at $2\theta = 19°$.

The half-widths of the reflections (*B*) and the dimensions of the crystallites (*L*) were calculated from Scherrer's formula:

$$L = \frac{C \cdot \lambda}{B \cdot \cos\theta},$$

where λ is the wavelength of CuK_α radiation, 1.54 Å, C is a coefficient depending on the form of the crystal and equal to 0.9 in our case, and θ is the angle of scattering.

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