ISOLATION OF INDIVIDUAL FRACTIONS OF DIOXANE LIGNIN FROM KENAF STEMS AND THEIR STUDY

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Kenaf — an annual plant widely cultivated in Uzbekistan — belongs like mallow and the cotton plant to the family Malvaceae [1]. To isolate and study kenaf lignin we used the most widespread variety "Uzbekskii 15-74" of the last vegetation period collected in the territory of the Ya. M. Sverdlov collective farm in the Tashkent oblast.

To isolate the lignin we used the method of acidolysis in aqueous dioxane, the so-called Pepper method [2]. For the more complete extraction of the lignin, the time of extraction was increased from 0.5 h to 2 h 15 min, with a change of the solvent every 45 min. As a result of the extraction performed, three fractions of kenaf dioxane lignin were obtained: DLAK-I, DLAK-II, and DLAK-III, with yields of 5.0, 1.64, and 0.27%, respectively, of the organic matter of the absolutely dry plant.

The dioxane lignins were purified by the Bjorkman method [3]. The isolated kenaf dioxane lignins (DLAK-I and DLAK-II) formed light-brown amorphous powders readily soluble in absolute and aqueous dioxane, dimethyl sulfoxide (DMSO), 90% ethanol, and aqueous solutions of alkalis, and sparingly soluble in ethanol and water. An increase in the time of extraction intensified the color of the lignin and decreased its solubility. Thus, the DLAK-III differed from the two preceding fractions by poor solubility in the solvents mentioned. Consequently, a further increase in the time of extraction is undesirable.

The amount of lignin isolated by Komarov's method in kenaf stems, in contrast to that in cotton stems, proved to be very small. Below we give the yields and chemical compositions of the fractions of kenaf dioxane ligins.

Fraction	Yield on the Komarov lignin %	C	H	OCH_3	OH_{tot}	OH_{ph}	CO	COOH
DLAK-I	33.3	61.13	5.88	20.21	10.58	2.13	2.30	0.44
DLAK-II	10.9	59.50	5.51	19.91	10.34	3.24	3.30	0.25
DLAK-III	18.0	59.20	5.52	17.50	9.39	6.62	4.10	0.58

On the basis of these results for the three fractions of kenaf dioxane lignins we calculated the semiempirical formulas per elementary C_9 unit taking the presence of carbohydrates into account. As in the case of the dioxane lignin from the spruce [4], with an increase in the time of extraction the amount of carbohydrates bound to the lignin fell (DLAK-I — 3.16%; DLAK-II — 1.57%), and carbohydrates were absent from the DLAK-III.

Semiempirical formulas of the fractions of kenaf lignin:

DLAK-I

$$C_9H_{6.90}O_{0.90}(OCH_3)_{1.34}(OH_{ph})_{0.25}(OH_{alip})_{1.01}(O_{aralk})_{0,75}(O_{CO})_{0.17}(OOH_{COOH})_{0,02}$$

DLAK-II

$$C_9H_{6,12}O_{1.55}(OCH_3)_{1.32}(OH_{ph})_{0.39}(OH_{alip})_{0.87}(O_{aralk})_{0,61}(O_{CO})_{0.25}(OOH_{COOH})_{0,04}$$

DLAK-III

$$C_9H_{6.66}O_{1.68}(OCH_3)_{1.16}(OH_{ph})_{0.86}(OH_{alip})_{0.34}(O_{aralk})_{0.20}(O_{CO})_{0.30}(OOH_{COOH})_{0,07}$$

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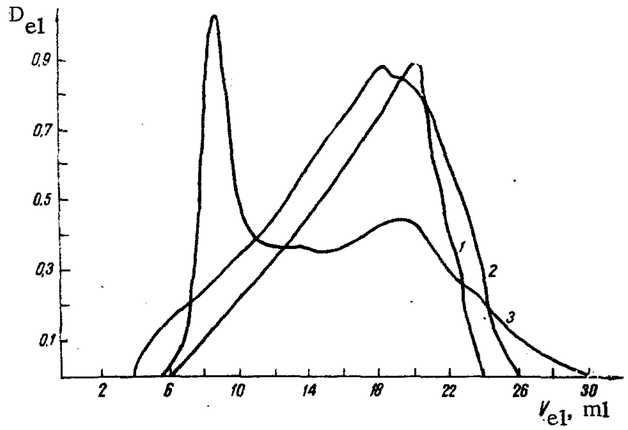

Fig. 1. Gel chromatograms of the fractions of kenaf dioxane lignin: 1) DLAK-I; 2) DLAK-II; 3) DLAK-III.

It can be seen from the figures given that the amount of methoxy and aliphatic hydroxy groups gradually decreases, reaching their smallest values in DLAK-III, while the amount of phenolic hydroxyls and carbonyl and hydroxy groups rises.

The kenaf lignin contains "guaiacyl" and "syringyl" fractions. The latter are condensed to a smaller degree, are more difficult to cross-link in an acid medium and pass into solution first. The "guaiacyl" fraction is very readily condensed in the solid phase and slowly passes into solution in cross-linked form. This is obviously explained by the gradual decrease in the amount of methoxy groups in the fractions of kenaf lignin studied. However, it is not excluded that these lignin fractions are localized in structural elements of the plant tissue that differ in their accessibility to the reagent. An increase in the amount of phenolic hydroxy groups can be explained by the cleavage of benzyl aryl ether bonds [5]. The increase in the amount of carboxy groups is obviously connected with the saponification of the ester groups of the lignin in the process of acidolysis.

To study the molecular-weight distribution of the kenaf lignin we used gel chromatography in Sephadex G-75 with DMSO as solvent and eluent. As can be seen from the gel chromatograms (Fig. 1) the kenaf lignin of the three fractions is polydisperse with a predominance of the low-molecular-weight fraction. Only in DLAK-III are two peaks corresponding to high- and low-molecular-weight fractions of lignin well-defined.

The positions of the peaks on the gel chromatograms shows that DLAK-III has a higher molecular weight than the other two fractions [6]. This apparently is due to secondary condensation processes [7]. To calculate the MWD curves we used the coefficients found by Alekseev and Reznikov [8]. As a result of a statistical treatment of the MWD curves we determined the weight-average ($\bar{M}_W$), number-average (M_n), and mean (M_Z) molecular weights for each fraction [9]:

Time of extraction, min	Lignin fraction	M_W	M_n	M_Z	M_W/M_n
45	DLAK-I	6511	2530	11,074	2.57
90	DLAK-II	4946	3255	11,559	2.19
135	DLAK-III	13,245	6046	19,873	1.52

The degree of polydispersity of a preparation is, as is well known, determined by the ratio M_W/M_n. An increase in the time of extraction leads to a rise in the molecular weights of the fractions isolated. Simultaneously, the degree of polydispersity decreases from 2.57 to 1.52. It is considered that the increase in molecular weights may be a consequence of the condensation of the lignin being isolated under the prolonged action of temperature and acid under acidolysis conditions. In the case of the kenaf dioxane lignin, the extraction process takes place similarly to the extraction of spruce wood [10].

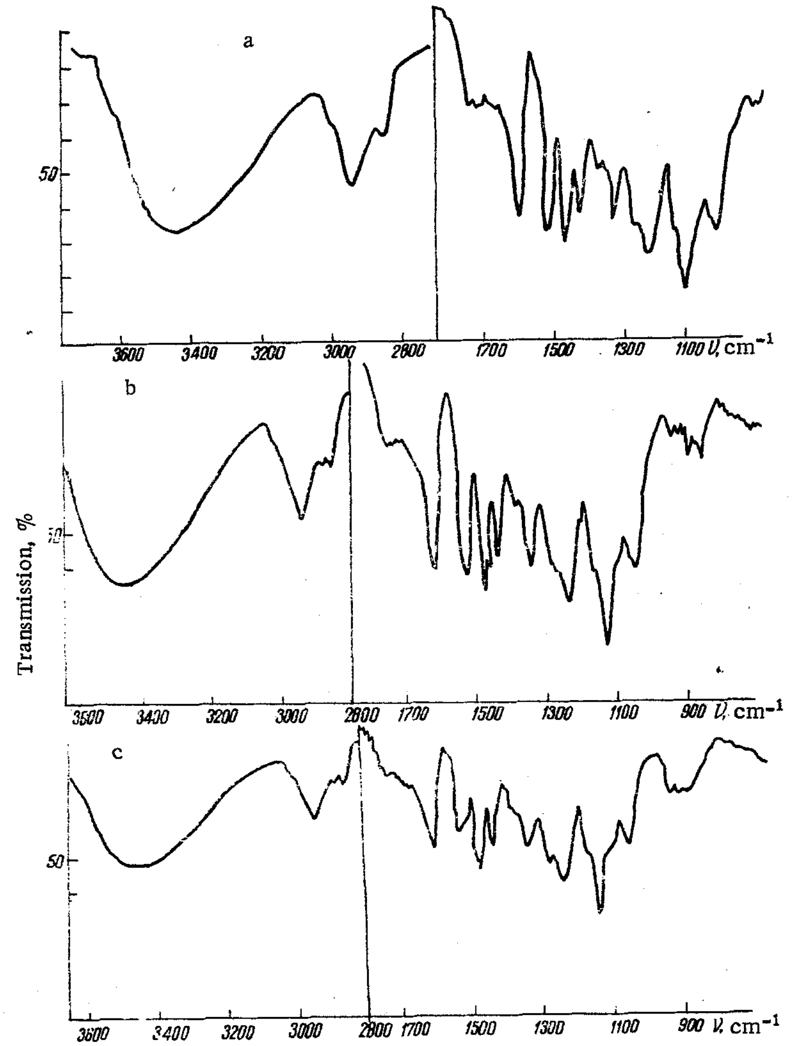

Fig. 2. IR spectra of the fractions of kenaf dioxane lignin: a) DLAK-I; b) DLAK-II; c) DLAK-III.

The UV spectra of all the fractions taken in aqueous dioxane (9:1) have absorption maxima at λ 280 nm and a shoulder in the region of 310-360 nm, which is the least pronounced in DLAK-III. The molar extinctions at λ 280 nm calculated to the molecular weight of a phenylpropane structural unit are 2600, 2750, and 2760 for DLAK-I, DLAK-II, and DLAK-III, respectively.

The IR spectra of these fractions were also recorded (Fig. 2); they show the bands characteristic for a benzene ring with substituents (1610, 1510 cm^{-1}), for hydroxy groups (3400 cm^{-1}), for carbonyl groups (1720 cm^{-1}), and for ether bonds (1230, 1040 cm^{-1}). A band at 1470 cm^{-1} relates to the deformation vibrations of C—H bonds in the methylene and methyl groups of methoxyl residues. The IR spectra of the fractions differ little from one another.

Thus, on the basis of the results obtained it can be stated that the soluble fractions of lignin isolated from kenaf stems differ basically in their molecular weight and amount of functional groups.

EXPERIMENTAL

Chemical composition of the raw material (%): lignin isolated by Komarov's method, 15.0; pentosans, 22.4; cellulose, 52.9; extractive substances, 4.6; moisture, 8.8; ash, 8.07. All the operations were performed as described by Obolenskaya et al. [11].

Isolation of the Kenaf Dioxane Lignin. The comminuted raw material (50 g), preextracted with ethanol—benzene (1:1) was covered with 1000 ml of dioxane—water (9:1) containing 0.7% of concentrated HCl, and the mixture was heated for 45 min at 90°C with stirring in a current of nitrogen. After the separation of the extracting mixture, the plant material was washed with 300 ml of dioxane—water (9:1) and this solution was combined with the main extract. When this was condensed and precipitated in water, DLAK-I was obtained. The same plant material was covered with a fresh portion of solvent and heated for another 45 min. The concentrated extract yielded DLAK-II. DLAK-III was obtained similarly. The functional groups of these fractions of kenaf dioxane lignin were determined by methods described previously [12].

Gel chromatography was performed on an analytical column of Sephadex G-75 using DMSO as solvent. The UV spectra were taken on an SF-4 spectrophotometer with dioxane—water (9:1) as solvent.

SUMMARY

1. Three fractions of dioxane lignin have been isolated from kenaf stems of the variety "Uzbekskii-15-74" by stepwise extraction with aqueous dioxane containing HCl.

2. On the basis of the results of elementary and functional analyses, semiempirical formulas of all the fractions have been derived, and their IR and UV spectra have been recorded.

3. It has been shown that an increase in the time of extraction leads to a rise in the molecular weight of the fractions and to a decrease in their degree of polydispersity.

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