

ISOLATION AND STUDY OF INDIVIDUAL FRACTIONS  
OF DIOXANE LIGNIN FROM COTTON-PLANT STEMS

N. A. Veksler, L. S. Smirnova,  
and Kh. A. Abduazimov

UDC 547.621:032.11

We have previously obtained dioxane lignin (DLA) from ripe stems of the cotton plant of variety 108-F by Pepper's method [1]. On the basis of a study of this fraction alone erroneous conclusions were drawn concerning the total lignin of the stems. Consequently, for the more complete extraction of the lignin we have increased the time of extraction to 3 h and the amount of solvent by a factor of 2.5. So that the lignin being isolated should not undergo additional changes in the course of extraction because of its lability, we changed the solvent every hour. In this way we obtained three lignin fractions: F-I (extraction for 1 h), F-II (2 h), and F-III (3 h).

With an increase in the time of extraction, the color of the lignins became darker and their solubility in dioxane fell. Consequently, a further increase in the time of extraction may be considered undesirable from the point of view of isolating little-modified lignin. As can be seen from Table 1, about half the lignin (42.1%) can be isolated from the cotton-plant stems by using relatively mild conditions of isolation. The remainder is obviously less labile and is not extracted under conditions of mild acidolysis.

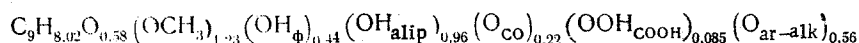
The opinion has been expressed previously that in the stems of the cotton plant [2], as in coniferous wood [3], the lignin exists in two forms: hemilignin (a mixture of low-molecular-weight phenylpropene derivatives) and ordered, high-molecular-weight lignin. In the delignification of the stems of the cotton plant with solutions of alkalis, the hemilignin fraction passes into the solution first and then, but not completely, the lignin proper does so. In the case of mild acetolysis in an aqueous dioxane medium, a complex pattern is observed.

Each of the three fractions isolated was studied separately. On the basis of functional-group analyses and determinations of elementary composition (Table 1) we calculated the semiempirical formula for each fraction per elementary C<sub>9</sub> unit with correction for the carbohydrate content.

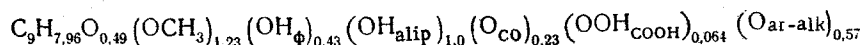
It must be observed that with an increase in the time of extraction the amount of carbohydrates bound to the lignin decreased (F-I 3.05%, F-II 1.0%), and F-III contained none.

The semiempirical formulas of the lignin fractions were as follows:

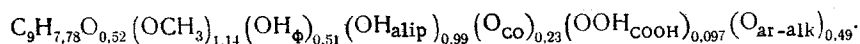
F-I:



F-II:



F-III:



It follows from Table 1 and the semiempirical formulas that F-I and F-II were almost identical. As compared with the other two, F-III contained a smaller amount of methoxy groups and a larger amount of phenolic hydroxyl and carboxy groups. It is obvious that the more prolonged acetolysis of the woody matter causes demethylation in the lignin, which leads to an increase in the number of phenolic hydroxyls. The increase in the number of carboxy groups is apparently connected with the saponification of ester groups of the lignin during the acidolysis process. Taking these differences into account, the compositions and numbers of functional

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Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from *Khimiya Prirodnikh Soedinenii*, No. 1, pp. 122-125, January-February, 1978. Original article submitted October 14, 1977.

TABLE 1. Yields and Chemical Compositions of the Fractions of Dioxane Lignin, %

Fraction	Yield on the Komarov lignin	C	H	OCH <sub>3</sub>	OH <sub>tot</sub>	OH <sub>phe</sub>	CO	COOH
F-I	21,7	60,60	6,52	18,86	11,75	3,69	3,15	1,86
F-II	13,0	60,92	6,54	18,91	11,91	3,66	3,18	1,04
F-III	7,4	60,90	6,40	17,68	12,77	4,31	3,25	2,17

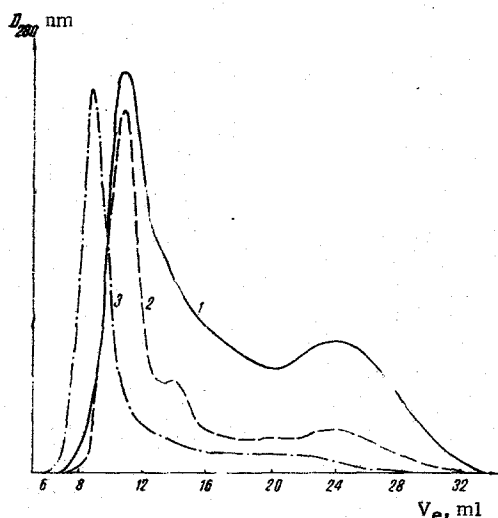


Fig. 1. Gel chromatography of the three fractions of dioxane lignin: 1) Fraction I; 2) II; 3) III.

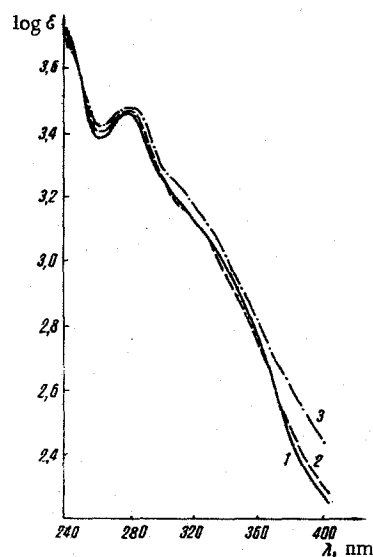


Fig. 2. UV spectra of the dioxane lignin fractions: 1) fraction I; 2) II; 3) III.

groups in the three fractions are very similar and, consequently, their fundamental chemical natures are the same. A similar conclusion has been made in relation to the dioxane lignins isolated from fractions of ailanthus and willow woods [4].

To study the molecular-weight distribution (MWD) of the dioxane lignin fractions, they were passed through a column of Sephadex G-75. Figure 1 shows gel-chromatograms of the fractions. As can be seen from them, only in F-I are two peaks corresponding to the high-molecular-weight and low-molecular-weight fractions of the lignin clearly defined. In F-II and F-III there is an insignificant amount of low-molecular-weight lignin. From the positions of the peaks corresponding to the high masses, it can be seen that in F-III the lignin has higher molecular weights than in F-I and F-II.

By using for calculating the molecular weights and for plotting the MWD curves the coefficients found by Alekseev et al. [5] and performing a statistical treatment of the MWD curves we determined the number-average, weight-average, and mean molecular weights for each fraction.

Fraction	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$
F-I	5620	12800	18880	2,28
F-II	8370	16730	21380	2,00
F-III	13900	20000	23560	1,44

It is well known, that the ratio of the weight-average molecular weight ( $\bar{M}_w$ ) to the number-average molecular weight ( $\bar{M}_n$ ) characterizes the degree of polydispersity of a preparation. It can be seen from the facts given above that with an increase in the time of extraction the molecular weights of the fractions isolated rise and the degree of polydispersity falls from 2.28 to 1.44 because of the absence from F-III of low-molecular-weight lignins. Thus, the low-molecular-weight fractions of the lignin, as the most soluble, are extracted first. The high-molecular-weight fractions become soluble in the later stages of isolation. It is not excluded that the increase in the molecular weight may be the consequence of the polymerization of the lignin being isolated under the fairly prolonged action of an elevated temperature and of acid under the acidolysis conditions.

The successive fractionation during the isolation of spruce dioxane lignin and the determination of the molecular weights of the fractions isolated [6] showed that they increased from 4300 to 85,000. Consequently, in the case of the dioxane lignin of cotton-plant stems the extraction process takes place similarly.

The UV spectra of the three fractions taken in dioxane-water (9:1) solution each have a maximum at 280 nm and a shoulder in the 300-360 nm region. The differences are observed for F-III, in which the shoulder in the 300-360 nm region is less well defined and which absorbs more strongly in the long-wave region. The latter fact is obviously connected with the increase in the degree of condensation in F-III (Fig. 2).

The values of the molecular extinctions at  $\lambda = 280$  nm calculated to the molecular weight of a phenyl-propane structural unit are 2900, 2970, and 3020 for F-I, F-II, and F-III, respectively, i.e., they increase very slightly. This is also connected with the increase in the degree of condensation of F-III.

The IR spectra of the three fractions are characteristic for the natural lignins, contain the same bands, and differ little from one another.

Thus, the results obtained enable us to state that the soluble fractions of the lignin from ripe cotton-plant stems differ mainly in molecular weight while differences in chemical composition are very slight and may, on the one hand, be caused by the heterogeneity of the initial lignin in the wood and, on the other hand, be the result of prolonged acidolysis. The different solubilities may be explained by a morphological distribution of the lignin in the wood complex and by the dimensions of its macromolecules.

## EXPERIMENTAL

Isolation of the Dioxane Lignin Fractions. Cotton-plant stems comminuted (0.25 mm) and pre-extracted with ethanol-benzene (1:1) (50 g) were covered with 1000 ml of dioxane-water (9:1) containing 0.7% HCl and were heated in the apparatus [1] at 90°C in a current of nitrogen with stirring for 1 h. After the separation of the solvent, the plant material was washed with 250 ml of aqueous dioxane and the solution was combined with the main extract. The concentration and precipitation of this in water yielded F-I. The same plant material was covered with fresh extraction mixture and was heated for another 1 h. The concentrated extract yielded F-II. Fraction F-III was obtained similarly.

The dioxane lignin fractions were analyzed by methods described previously [1].

Gel chromatography was performed in analytical columns of Sephadex G-75 using dimethyl sulfoxide as solvent [1].

The UV spectra were recorded on an SF-16 spectrophotometer in dioxane-water (9:1) as solvent.

## SUMMARY

1. By stepwise extraction with aqueous dioxane containing HCl, three fractions of dioxane lignin have been isolated from ripe stems of the cotton plant of variety 108-F with a total yield of 42.1%.
2. On the basis of chemical analysis, semiempirical formulas of the fractions have been deduced, and their UV and IR spectra have been reported. The results show the closeness of the structures of the free fractions.
3. With an increase in the time of extraction the molecular weights of the fractions increase and their degree of polydispersity decreases.

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