FRACTIONAL COMPOSITION OF KENAF DIOXANE LIGNIN

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The fractionation of kenaf dioxane lignin according to molecular weights has been carried out. The six fractions obtained differ by their molecular masses and chemical compositions. Semiempirical formulas of all the fractions have been deduced. The relative optical densities have been calculated on the basis of the IR spectra of the fractions.

It is known [1] that kenaf dioxane lignin (KDL) is polydisperse. For a more detailed study of its composition and polydispersity, we have performed the fractionation of KDL with respect to molecular weights by fractional precipitation from dioxane solution using the triangle method [2]. By means of this method it is possible to obtain a small number of fractions with comparatively narrow molecular weight distributions.

We obtained six fractions (I-VI) with successively decreasing molecular weights (with the exception of fraction V). Fractions III and VI had comparatively high yields. The efficacy of separation was checked by subjecting the fractions obtained to gel chromatography in an analytical column of Sephadex G-75 with dimethyl sulfoxide as solvent and eluent. Molecular weights were calculated on the basis of the results of gel chromatography. Eluograms of all six fractions and of the initial lignin are given in Fig. 1. From these eluograms we plotted integral curves of molecular weight distribution (MWD), using the coefficients found previously [3]. The weight-average ($\overline{M}_w$) and number-average ($\overline{M}_n$) molecular weights were calculated from the integral MWD curves.

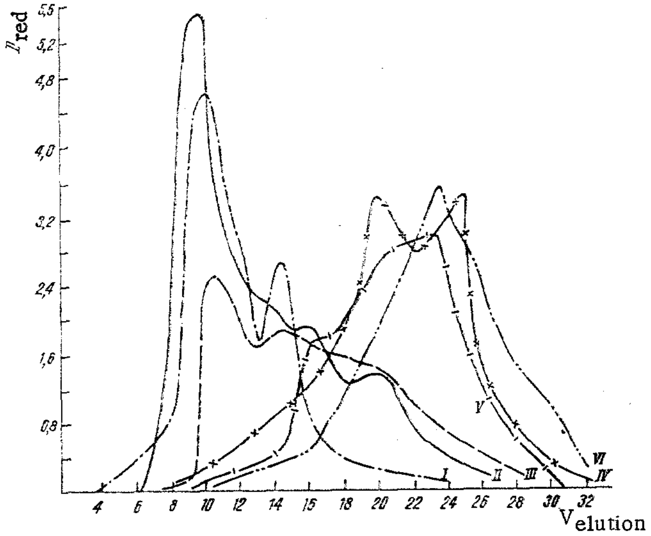

Fig. 1. Gel eluograms of the KDL fractions.

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Fraction	Yield, %	M_w	M_n	M_w / M_n
Init. lignin	100	8500	4600	1,85
I	3,18	18000	10700	1,68
II	7,46	17000	10100	1,68
III	11,81	13400	8000	1,67
IV	10,55	5000	3600	1,28
V	6,35	5700	3900	1,46
VI	21,31	4200	2800	1,50

The values of $\overline{M}_w/\overline{M}_n$, which characterize a degree of polydispersity of the fractions, were not identical. As can be seen from the results given, they range from 1.68 to 1.28. The most homogeneous was fraction IV ($\overline{M}_w/\overline{M}_n$ = 1.28); and fractions I, II, and III had the greatest degrees of polydispersity (1.68, 1.68, and 1.67, respectively). A wide polydispersity is generally characteristic for nonlinear polymers [4], and the high degree of polydispersity of the first three fractions shows that they are more heterogeneous than the others.

The fractions isolated differed both in molecular weight and in chemical composition, as can be seen from the results of elementary analysis and quantitative analysis of functional groups (%):

Fraction	C	H	OCH_3	OH_{tot}	CO	OH_{ph}	$COOH$	Carbohydrates
init. KDL	60,01	6,28	19.73	9,95	4,13	2,95	0.18	6,29
I	60.10	6,38	19.69	13.92	3,18	4.00	0,13	5,13
II	58,85	6.99	18,23	11.03	3.48	3,72	0,12	6,62
III	59,48	6,38	19,24	9.26	3.40	3.26	0,09	7,78
IV	60.81	6,50	19,19	10.48	2.86	3,16	0,04	7.86
V	60,24	6,33	19,76	8,61	2,89	5,29	0,07	5,41
VI	60,81	6.42	21,04	10,17	3.04	3,73	0.06	8,18

As for cotton-plant dioxane lignin [5], the low-molecular-weight fractions contained a relatively larger amount of carbohydrates than the high-molecular-weight fractions. On the basis of the results of elementary and functional analyses taking the presence of the carbohydrates into account, we calculated the semiempirical formulas for one phenylpropane structural unit, C_9. For the initial KDL, mol. wt. = 204.76.

$$C_9H_{7,56}O_{1,16}(OCH_3)_{1,39}(OH_{ph})_{0,36}(OH_{al})_{0,67}(O_{CO})_{0,32}(OOH_{COOH})_{0,0031}(O_{ar-al})_{0,64}$$

Fraction I, MW = 203,15

$$C_9H_{7,72}O_{1,03}(OCH_3)_{1.29}(OH_{ph})_{0,48}(OH_{al})_{1,09}(O_{CO})_{0,27}(OOH_{COOH})_{0,0064}(O_{ar-al})_{0,52}$$

Fraction II, MW = 206,73

$$C_9H_{9,36}O_{1,38}(OCH_3)_{1,30}(OH_{ph})_{0,45}(OH_{al})_{0,74}(O_{CO})_{0,28}(OOH_{COOH})_{0,0058}(O_{ar-al})_{0,55}$$

Fraction III, MW = 205,36

$$C_9H_{7,97}O_{1,69}(OCH_3)_{1,38}(OH_{ph})_{0,39}(OH_{al})_{0,53}(O_{CO})_{0,27}(OOH_{COOH})_{0,0044}(O_{ar-al})_{0,61}$$

Fraction IV, MW = 199,77

$$C_9H_{7,87}O_{1,30}(OCH_3)_{1,34}(OH_{ph})_{0,37}(OH_{al})_{0,68}(O_{CO})_{0,22}(OOH_{COOH})_{0,0018}(O_{ar-al})_{0,63}$$

Fraction V. MW = 203,37

$$C_9H_{7,79}O_{1,64}(OCH_3)_{1,37}(OH_{ph})_{0,63}(OH_{al})_{0,26}(O_{CO})_{0,22}(OOH_{COOH})_{0,0036}(O_{ar-al})_{0,37}$$

Fraction VI, MW = 202,56

$$C_9H_{7,46}O_{1,004}(OCH_3)_{1,50}(OH_{ph})_{0,44}(OH_{al})_{0,57}(O_{CO})_{0,24}(OOH_{COOH})_{0,0031}(O_{ar-al})_{0,56}$$

As we see, the fractions isolated also differed in their chemical compositions. The amounts of methoxy, hydroxy, carbonyl, and carboxy groups and also the number of aryl—alkyl ether bonds were different. The fractions of the kenaf lignin were more highly methoxylated than the fractions of cotton-plant lignin [5]; the OCH_3/C_9 ratio in fraction VI of the DLK was 1.50, while in the dioxane lignin of the cotton plant it was 1.38. The amounts of phenolic hydroxyls in fractions I, II, and VI were almost identical (averaging 0.46), which means that in 46 out of each 100 structural units the fourth position does not participate in the formation of ether bonds. The amounts of CO groups in fractions I-III were practically identical (0.27) and the same applies to fractions IV-VI (0.23). For each 100 phenylpropane structural units there were 27 and 23 fragments with such groups. The amount of acidic groups was very small in all the fractions. The amounts of aliphatic hydroxyls in fractions III and VI were almost identical: Out of 100 structures, 53-57 had a hydroxyl. Fraction V had the smallest number of aliphatic hydroxyls: Out of 100 structures, 26 had hydroxyls.

TABLE 1

Frequency, cm^{-1}	Relative optical densities of the fractions						
	init KDI	I	II	III	IV	V	VI
3450–3460	0,75	0,87	0,94	0,83	0,83	0.76	0,71
2930–2950	0,51	0,62	0,70	0,72	0,88	0,59	0,64
2850–2880	0,51	0,42	0,40	0,45	0,60	0,35	0.44
1720–1735	0,25	0,42	0,36	0,44	0,39	0.33	0.35
1595–1600	0.79	0,93	1.01	0.88	0 88	0.87	0,81
1510–1520	1.00	1,00	1,00	1.00	1,00	1.00	1,00
1460–1470	1,02	1,05	1,20	1.02	1.01	1,01	0,98
1425	0,75	0,93	0,95	0,86	0,84	0.84	0,76
1320–1330	0,77	0,86	0 89	0,83	0,82	0,81	0,76
1270–1275	1.06	0,91	1,12	0 95	0,87	0,94	0,94
1225–1230	1.13	1,03	1,24	1.13	1,06	1.13	1,09
1130–1135	1 61	1,89	1,91	1,65	1,48	1,55	1.52
1030–1040	0,94	0,95	1,11	1.03	0,95	0,95	0,88
875–880	0.18	—	—	0.19	0,39	0,19	0,27
835	0,18	0,29	0,15	0 16	0,20	—	0,10

Thus, the fractions isolated differed both in molecular weights and in the amounts of functional groups that they contained. The different amounts of unidentified oxygen (from 1.003 to 1.69) and of hydrogen (from 7.46 to 9.36) also show dissimilar structures of the fractions.

The IR spectra of the fractions and of the initial lignin were difficult to evaluate visually, since they were very similar. Consequently, for a quantitative estimation of the intensities of the absorption bands we used the relative optical densities (RODs) which were determined by the internal-standard method. As the internal standard we took the 1510-1520 cm^{-1} band corresponding to the vibrations of the benzene nuclei in lignin. The base lines were drawn through the absorption minima at 1800 and 700 cm^{-1} and at 3750 and 2800 cm^{-1}. The values of the RODs were calculated by the method of Karklin' and Érin'sh [6].

Table 1 gives the RODs of the initial KDL and of fractions I–VI of the kenaf lignin.

The IR spectra contain all the main bands, but their ROD values differ, which indicates different amounts of the functional groups corresponding to these bands in the fractions. The 3450-3460 cm^{-1} band characterizes the absorption of hydroxy groups. The greatest value of the ROD (0.94), which means the greatest intensity of this band, is observed for fraction II of the KDL. The 1720-1735 cm^{-1} band characterizes the absorption of β-carbonyl and carboxy groups, the vibrations of a guaiacyl ring with the stretching vibrations of the CO group characterized by the 1220-1230 cm^{-1}, and the stretching vibrations of the carbonyl groups of aliphatic ethers and alcohols by the band at 1030-1040 cm^{-1}. All these bands are fairly well-defined and have high values of their RODs in comparison with the values for other groups.

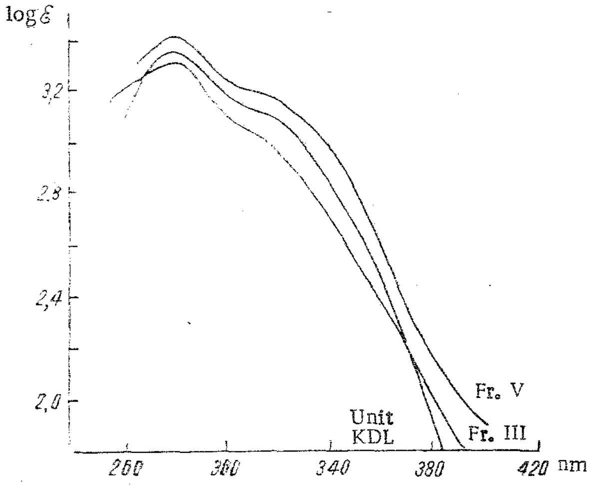


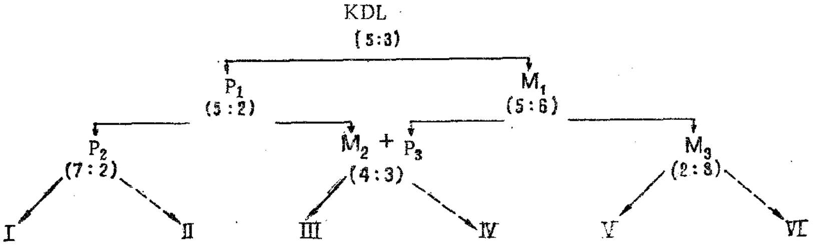
Fig. 2. UV spectra of the initial KDL and of the lignin fractions.

The UV spectra of the initial KDL and of the lignin fractions recorded in aqueous dioxane are characteristic for the natural lignins and each has a maximum at 280 nm and a shoulder at 300-360 nm. Figure 2 shows the spectra of fractions III and V and of the initial KDL. We do not give the spectra of the other fractions because of their similarity.

The results of gel chromatography, quantitative analysis of the functional groups, and calculations of ROD values of the individual KDL fractions showed that they differed from one another not only by their molecular weights but also by their molecular structures.

EXPERIMENTAL

Dioxane lignin was obtained from the stems of the kenaf variety Uzb. 15-74 by Pepper's method [1]. Fractionation was performed in a three-necked round-bottomed flask placed in a thermostat (25°C) and fitted with a mechanical stirrer, a bubbler for the passage of nitrogen, a reflux condenser, and a dropping funnel. With vigorous stirring and the passage of nitrogen, 600 ml of absolute diethyl ether was added to a solution of 10 g of kenaf lignin in 1000 ml of dioxane. The first ratio of solvent to precipitant (dioxane to ether) was 5 : 3. The subsequent ratios are given in the scheme



The precipitate that deposited (P_1), was dissolved in aqueous dioxane (1 : 100), and after precipitation with ether the precipitate P_2 and the mother liquor M_2 were obtained; the latter was concentrated in vacuum and subjected to further separation. The scheme shows the course of fractionation where P represents precipitates and M mother liquors. The dashed lines denote the production of mother solutions concentrated for subsequent precipitations. The fractions isolated were purified by reprecipitation from dioxane solutions into absolute ether. The yields of the purified fractions have been given above.

Gel chromatography was carried out in an analytical column (1.0 × 40.0 cm) containing Sephadex G-75 with DMSO as eluent and solvent. The values of $\bar{M}_w$ and $\bar{M}_n$ were calculated by standard methods [2]. IR spectra were taken on a UR-20 spectrophotometer in tablets with potassium bromide, and UV spectra on an SF-4 spectrophotometer in dioxane—water (9 : 1) as solvent.

SUMMARY

1. Kenaf dioxane lignin has been separated according to molecular weight into six fractions which were fairly homogeneous and differed considerably in molecular weights.

2. The different amounts of functional groups in the phenylpropane structural units and a comparison of the ROD values of the main bands in the IR spectra have shown the chemical nonidentity of the fractions isolated.

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