A STUDY OF THE STRUCTURE OF KENAF LIGNINS BY ALKALINE NITROBENZENE OXIDATION

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Continuing an investigation of kenaf lignins [1], we have studied their structure by the method of alkaline nitrobenzene oxidation (NBO) [2]. The natural lignin of kenaf stems of the variety "Uzbeksii 15-74" (outer and inner parts) and three fractions of dioxane lignin were oxidized, the yields being given below:

Initial raw material and isolated lignin	Yield of aldehydes on the raw material, g	Yield on the Komarov lignin, %
Kenaf of the late period	0.336	18.67
Inner part	0.462	18.97
Outer part	0.204	16.35
DLKA-I (kenaf DLA, fraction I)	0.545	
DLAK-II	0.335	
DLAK-III	0.221	

It is known [3] that the best yield of aldehydes is obtained from natural lignins. The milder the methods by which the lignin has been isolated; i.e., the smaller the extent to which it has changed in comparison with natural lignin, the higher is the yield of aldehydes. It can be seen from the facts given that the yield of aldehydes decreases with a rise in the time of extraction of the lignin, being smallest for DLAK-III. It is likely that DLAK-III is more condensed than the other fractions.

So far as concerns natural lignins, the lowest yield of aldehydes was obtained from the outer part of the kenaf stems. This is possibly due to the smaller amount of lignin isolated by Komarov's method in them (10.4% as compared with 20.3% from the inner part). To identify the products of nitrobenzene oxidation of kenaf lignin, we used gas—liquid chromatography and in the choice of the conditions for their gas-chromatographic determination we started from the fact that both we and other workers have obtained better results in the separation of aromatic aldehydes on a polar stationary phase than on the nonpolar stationary phase usually used [6].

The natural lignins were oxidized by Leopold's method [2], while the DLA fractions were oxidized by a rapid method [5]. The reaction mixtures obtained were separated and identified by using a Khrom-4 chromatograph with a flame-ionization detector. The oxidation products were identified from their retention times and by the introduction of markers.

The order of issue of the homologs — vanillin, p-hydroxybenzaldehyde, and syringaldehyde (Fig. 1) — was the same as on using cyclohexanedimethanol succinate as the stationary phase [5]. Apart from the peaks of the aldehydes, the chromatograms showed the peaks of p-hydroxyacetophenone, acetovanillone, and p-hydroxybenzoic, ferulic, and p-coumaric acids.

The results of a quantitative chromatographic analysis of the products of the nitrobenzene oxidation of the natural lignins of kenaf stems and of the DLA fractions are given in Table 1.

It can be seen from Table 1 that in the kenaf lignins, as in the lignin from the mallow [7] and the cotton plant [8], there are all three types of structural units: p-coumaryl, guaiacyl, and syringyl.

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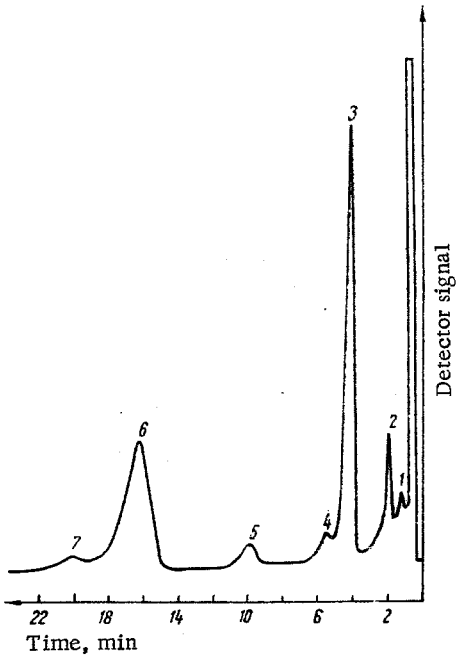

Fig. 1. Gas—liquid chromatogram of the products of the oxidation of the inner part of kenaf stems: 1) ferulic acid; 2) p-coumaric acid; 3) vanillin; 4) acetovanillone; 5) p-hydroxybenzaldehyde; 6) syringaldehyde; 7) unidentified.

In the lignin of kenaf stems, as in mallow lignin [7], the syringyl component predominates, its amount exceeding that of guaiacyl structures by factors of from 1.3 in the lignin of the inner part to two in the kenaf lignin as a whole. A comparison of the products of nitrobenzene oxidation of different parts of the stem shows that both in the outer and in the inner parts syringyl structures predominate.

Among the products of the oxidation of the free fractions of kenaf DLA the same compounds were detected as in the aldehyde mixtures from the natural lignins (see Table 1). In this case, as well, in all the fractions the syringyl component predominates (2-2.5 times exceeding the guaiacyl structures in DLAK-I and DLAK-II). In DLAK-III the amounts of guaiacyl and syringyl structures are approximately the same.

With an increase in the time of extraction, i.e., on passing from DLAK-I to DLAK-III the amounts of all the structural units decrease. The amount of syringyl structures decreases sharply, falling from 36.19% in DLAK-I to 6.75% in DLAK-III. These differences are possibly due, on the one hand, to different ratios of structural units making up the macromolecules of these lignins. On the other hand, as is well known [9], the distribution of lignin is heterogeneous. There are different lignins in different parts of the xylem tissue, namely: guaiacyl, syringyl, or guaiacyl—syringyl. In addition, the possibility is not excluded of the localization of these fractions in structural elements of the plant tissue with different accessibilities to the reagent. The decrease in the yield of aldehydes may also be connected with condensation processes which may take place on prolonged acidolysis.

In the products of the nitrobenzene oxidation of the fractions of kenaf dioxane lignin it has been possible to detect by paper chromatography dehydrodivanillin, which is a representative of structures with a biphenyl bond [10-13].

In the fractions of the kenaf dioxane lignin, dehdyrodivanillin was determined by the method of L. A. Kodina et al. [12]. The concentration of dehydrodivanillin was measured in an SF-4 spectrophotometer and its amount by means of a calibration graph plotted for an alkaline solution of pure dehydrodivanillin:

TABLE 1. Products of the Nitrobenzene Oxidation of Kenaf Lignin

Substance	Kenaf, % of the Komarov lignin			Lignin, % on the initial		
	plant as a whole	outer part	inner part	DLAK-I	DLAK-II	DLAK-III
p-Hydroxybenzaldehyde	0,75	0,51	0,80	3,55	1,14	0,28
p-Hydroxyacetophenone	0,19	0,43	—	0,17	1,66	—
p-Hydroxybenzoic acid	—	—	—	—	—	1,08
p-Coumaric acid	—	—	0,80	—	—	—
Vanillin	5,36	3,66	6,66	13,47	9,32	5.79
Ferulic acid	—	0,37	0,12	0,90	0,69	—
Acetovanillone	0,33	0,30	0,44	—	—	0,51
Syringaldehyde	11,52	6,63	9,30	36,19	20,06	6,75

Sample	Time of extraction, min	Dehydrodivanillin, μg/g of dry substance
DLAK-I	45	1650
DLAK-II	90	3700
DLAK-III	135	7400

As the figures given above show, the amount of dehydrodivanillin in the kenaf DLA fractions rises with an increase in the time of extraction, i.e., the degree of condensation rises, which is in full agreement with the semiempirical formulas of these lignins [1].

EXPERIMENTAL

Nitrobenzene oxidation was carried out by the method described previously [7]. Chromatographic analysis was performed on a Khrom-4 chromatograph with a flame-ionization detector. Conditions for chromatography: column (120 × 0.3 cm) filled with 4% of poly(ethylene glycol adipate) on Chromaton NAW (60-80 mesh), column temperature 205°C, rate of flow of the carrier gas (helium) 40 ml/min.

The peaks were identified from their retentions times and by the introduction of standards. Quantitative evaluation was performed by the area standardization method [14].

Paper Chromatography. "Leningradskaya srednyaya" ["Leningrad medium"] paper was used, with the solvent system suggested by Kodina and Generalova [12]: n-propanol—3% NH_4OH (4:1). Dehydrodivanillin was detected on a chromatogram moistened with a 0.2% solution of KOH in ethanol from its violet fluorescence in UV light.

SUMMARY

1. The nitrobenzene oxidation of the natural lignins of kenaf stems and of DLA fractions has been performed. A study of the oxidation products by gas—liquid chromatography has shown that the kenaf lignins are constructed of three types of structural units: p-coumaryl, guaiacyl, and syringyl, with the latter predominating.

2. Among the products of the nitrobenzene oxidation of fractions of kenaf dioxane lignin paper chromatography has shown the presence of dihydrodivanillin, which is a representative of structures with a biphenyl bond.

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THE LIGNIN OF THE ALGA *Fucus vesiculosus*

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Until recently, the idea of the absence of lignin from plants having no mechanical and conductive tissues was generally accepted. Starting from this basic assumption, a theory of the genesis of fossils has been developed and ideas on the role of lignin in plants has been formulated. We have previously [1, 2] given definite evidence of the presence of lignin in peat mosses. Consequently, it was natural to consider it desirable to study the question of the presence of lignin at a lower degree of evolution in the algae. By the vibromilling method we have previously [3] isolated a preparation close in its physicochemical characteristics to lignin from brown algae (*Fucus vesiculosus*). However, to obtain indisputable evidence of the presence of the latter in algae additional information was necessary concerning the lignin arylpropane nature of the aromatic component of the plant tissue of the algae.

With this aim we have used the method of decomposition with metallic sodium in liquid ammonia which is applicable to the lignin of plants with a low degree of organization. Decomposition was carried out by the method of N. N. Shorygina et al. [4].

The ethereal extract of the decomposition products, separated into phenolic and acidic fractions, was analyzed by paper chromatography. In the phenolic fraction we identified six compounds: 3-(4-hydroxyphenyl)propan-1-ol (R_f 0.2), 3-(4-hydroxy-3-methoxyphenyl)propan-1-ol (R_f 0.35), 4-hydroxy-3-methoxyphenylethane (R_f 0.46), 1-(4-hydroxy-3-methoxyphenyl)propan-1-ol (R_f 0.65), 1-(4-hydroxyphenyl)propane (R_f 0.86), and 1-(4-hydroxy-3-methoxyphenyl)propane (R_f 0.89). In the acidic fraction we identified p-hydroxybenzoic and p-coumaric acids.

The decomposition products of phenolic nature were also analyzed by gas—liquid chromatography. The phenols were identified by their retention times and by the introduction of markers. Below we give the composition and residence times of the phenols obtained as the result of the decomposition of *Fucus vesiculosus* with metallic sodium in liquid ammonia:

	Retention time, min
Phenol	5.33
Guaiacol	10.62
1-(4-Hydroxyphenyl)propane	15.5
4-Hydroxy-3-methoxyphenylethane	15.72
1-(4-Hydroxyphenyl)propan-1-ol	18.28
1-(4-Hydroxy-3-methoxyphenyl)ethanol	19.01
1-(4-Hydroxy-3-methoxyphenyl)propane	20.62
Vanillin	22.72
1-(4-Hydroxy-3-methoxyphenyl)propan-1-ol	24.00
3-(4-Hydroxyphenyl)propan-1-ol	29.21
1-(4-Hydroxy-3,5-dimethoxyphenyl)propan-1-ol	37.25
3-(4-Hydroxy-3-methoxyphenyl)propan-1-ol	41.28

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