6. Z. A. Shabarova, E. M. Volkov, T. S. Oretskaya, S. I. Turkin, N. G. Dolinnaya, V. K. Kagramanova, and M. A. Prokof'ev, Dokl. Akad. Nauk SSSR, 258, 914 (1981).
7. A. M. Maxam and W. Gilbert, Methods Enzymol., 65, 499 (1980).
8. G. R. Gough, M. I. Brunden, and P. T. Gilham, Tetrahedron Lett., 24, 5317 (1983).
9. D. M. Brown, M. Fried, and A. R. Todd, J. Chem. Soc., 2206 (1953).
10. H. D. New and L. A. Heppel, J. Biol. Chem., 239, 2927 (1964).
11. J. G. Nadeau, C. H. Singleton, G. B. Kelly, H. L. Werth, and G. R. Gough, Biochemistry, 23, 6153 (1984).
12. G. S. Ti, B. L. Gaffney, and R. A. Jones, J. Am. Chem. Soc., 104, 1316 (1982).

CLEAVAGE OF THE NATURAL LIGNIN AND THE DIOXANE LIGNIN OF KENAF BY THIOACETIC ACID

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The dioxane lignin and the natural lignin of kenaf undergo 37.62% and 94.6% cleavage, respectively. The combined monomeric degradation products have been studied by the GLC method. The presence of substances relating to three types of structural units has been established: p-coumaryl, gualacyl, and syringyl. It has been shown by chromatography on Sephadex LH-20 (with ethanol–water (9:1) as solvent and eluent) that the phenolic products of degradation extracted by ethyl acetate at pH 2 consist of five fractions: oligomers, tetramers, trimers, dimers, and monomers.

The chemical structures of natural and isolated lignins have been studied previously by the method of thioacetic acid cleavage [1-5].

Continuing a study of the chemical structures of the lignins of kenaf, we have performed the cleavage of the natural lignin and the dioxane lignin of kenaf (DLAK-1; fraction I according to its time of isolation [6]) by thioacetic acid. Of the DLAK-I 37.62% underwent cleavage, and of the natural lignin of the kenaf 94.6%. The phenolic cleavage products were extracted with ether (pH 8) and with ethyl acetate (pH 2), the amounts of these products as percentages of the total phenolic substances from the natural kenaf lignin being 42.66 and 52.00 and from the kenaf dioxane lignin 25.54 and 12.08, respectively.

Chromatography on an analytical column of Sephadex LH-20 (with ethanol–water (9:1) as solvent) showed that the phenolic cleavage products extracted by ethyl acetate at pH 2 consisted of fractions of oligomers, tetramers, trimers, dimers, and monomers in the following percentages of the total for the DLAK-I and the natural kenaf lignin, respectively: 7.9, 32.7, 14.0, 31.2, and 14.3; and 20.5, 34.6, 13.60, 17.0, and 14.30. The analytical column was calibrated in a manner similar to that described previously [4].

The total of the monomeric degradation products extracted by ether at pH 8 was studied by the GLC method under conditions similar to those given in [5]. The compositions and yields of the monomeric cleavage products were as follows:

Substance	DLAK-I		Natural lignin	
	% in the mixture	% on the lignin	% in mixture	% on the Komarov lignin
Phenol	2.49	0,64	1,08	0,46
Guaiacol	5,80	1.50	4,06	1.73
p-Hydroxyphenylethane	6,33	1,69	3,52	1,46
p-Hydroxyphenylpropane	—	—	2 03	0,88
Guaiacylethane	12,15	3,08	2,03	0,88
Vanillin	1,10	0.28	—	—
1-Guaiacylethanol	—	—	2,17	0,93
Guaiacylpropane	16,57	4,18	22,73	9,7
Syringylpropane	22,10	5.57	25.58	11,06
1-Guaiacylpropanol	—	—	4,87	2.1
3-Guaiacylpropanol	11,05	2.8	7,44	3,2
Unidentified	22,10	5.57	25.75	21,3
Ratio of the p-coumaryl to guaiacyl to syringyl units	0,2:1,0:0,47		0,15:1,0:0.6	

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As we see, the phenols identified consisted of three types of structures: p-coumaryl, guaiacyl, and syringlyl. The ratio of these units shows that here, as also in the case of cleavage by sodium and liquid ammonia, guaiacyl structures predominated.

It must be mentioned that the ratio of these structures for the DLAK-I when it was cleaved with sodium in liquid ammonia was almost the same; 0.2:1.0:0.5. However, the yield of phenolic products from cleavage by sodium in liquid ammonia (21.5%) differed considerably from the yield on cleavage with thioacetic acid (37.62%), as was to be expected, since under the action of thioacetic acid on lignin a more far-reaching cleavage of alkyl-aryl ether bonds take place.

Guaiacylpropane and syringylpropane were characterized by high yields among the monomeric degradation products (as was also observed in the cleavage of these lignins by sodium in liquid ammonia). The high yield of guiacylpropane and of other compounds containing a propane side chain indicates that under the conditions used not only ether bonds but also alcoholic C—O bonds are cleaved. As shown previously [7], this phenomenon has been confirmed by experiments with model compounds [8].

The presence in the kenaf lignins of primary OH groups is shown by the finding of 1-guaiacylpropanol and 3-guaiacylpropanol among the monomeric cleavage products.

Thus, the results of the cleavage of kenaf lignins by thioacetic acid has confirmed the conclusions drawn on the basis of experiments on cleavage in liquid ammonia.

EXPERIMENTAL

The cleavage of the natural lignin and of the dioxane lignin of kepaf with thioacetic acid was performed under the conditions described in [3]. Gel chromatography was carried out in an analytical column (1.0 × 45.0 cm) of Sephadex LH-20. Ethanol—water (9:1) was used as solvent and eluent.

SUMMARY

1. The thioacetic acid cleavage of the natural and the dioxane lignins of kenaf has confirmed the presence in these lignins or three types of structural units, with a predominance of guaiacyl structures.

2. Kenaf dioxane lignin is more condensed than natural kenaf lignin, and this explains the relatively low yield of combined cleavage products (37.62% as compared with 94.6%).

LITERATURE CITED

1. H. Nimz, Chem. Ber., 102, 799 (1969).
2. H. Nimz, K. Das, and N. Minemura, Chem. Ber., 104, 1871 (1971).
3. J. Skamla and J. Rybarik, Drev. Vys., 20, Nos. 2-3, 107 (1975).
4. L. S. Smirnova and Kh. A. Abdduazimov, Khim. Prir. Soedin., 505 (1978).
5. E. N. Yanishevskaya, B. Kh. Pulatov, and Kh. A. Abduazimov, Khim. Prir. Soedin. 737, (1980).
6. N. Ya. Kul'chik, G. N. Dalimova, and Kh. A. Abduazimov, Khim. Prir. Soedin., 637 (1978).
7. G. N. Dalimova, A. A. Geronikaki, and Kh. A. Abduazimov, Khim. Prir. Soedin., 780 (1978).
8. A. Yamaguchi, Mokuzai Gakkaishi, 19, No. 3, 141 (1973).