ESTABLISHMENT OF AN ESTER BOND IN KENAF LIGNINS

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It is known that p-coumaric acid (p-CA) is bound to bamboo lignin and the lignin of herbaceous plants through an ester bond [1, 2]. It has also been reported that some lignins of hard woods, mainly pine lignins, contain esterified p-hydroxybenzoic acid [3, 4], but it has been assumed that it is preferentially bound with aliphatic hydroxyls and not with phenolic hydroxyls.

The aim of the present work was to determine the presence of an ester bond in the dioxane lignins of kenaf.

The dioxane lignins of the bast DLALK, and the two, (DLAKK) of kenal and also DLAK-I (fraction I in time) and DLAK-II (fraction II in time) [5] were subjected to alkaline hydrolysis, after which the hydrolyzates were studied by gas—liquid chromatography (Fig. 1). The yields of the hydrolyzates were as follows: 2.74, 0.53, 0.20, and 0.07% from the DLAK-I, DLAK-II, DLALK, and DLAKK lignins, respectively. The highest yield of the ether-soluble material was found in DLAK-I and the lowest in DLAKK.

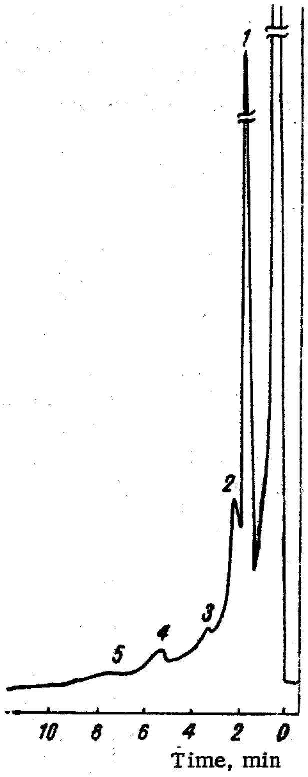

Fig. 1. Chromatogram of the products of the alkaline hydrolysis of DLALK: 1) p-coumaric acid; 3) vanillin; 5) p-hydroxybenzoic acid.

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Below we give the results of the quantitative gas-chromatographic analysis of the hydrolyzates obtained (% on the lignin):

Substance	DLAK-I	DLAK-II	DLALK	DLAKK
p-Coumaric acid	4,09	2,55	4,86	2,76
Vanillin	—	0,28	0,24	0,053
Acetovanillone	0,33	0,30	0,78	—
p-Hydroxybenzoic acid	4,09	0,64	—	0,12
Unidentified compounds	5,77	1,21	1,98	0,59

Thus, the largest amount of ester-bound p-coumaric acid was present in the DLALK. At the same time, in the DLAK-I the amounts of p-coumaric and p-hydroxybenzoic acids bound to the lignin by ester bonds were the same, together making up 8.18%. Consequently, the DLAK-I had a larger amount of ester bonds than the other lignins studied. On passing from DLAK-I to DLAK-II the amount of esterified p-coumaric and p-hydroxybenzoic acids fell sharply — it was 2.6 times less in the latter than in the former. An increase in the time of extraction in the isolation of the dioxane lignin apparently leads to a reduction in the number of ester bonds in the lignin.

The p-coumaric acid most probably esterifies the γ-OH group in the side chains of the lignin. Experiments on models have shown that it is just this type of bond that is predominating [6]. It is not excluded that part of the p-coumaric and p-hydroxybenzoic acids are bound to the α-OH groups of the lignin side chain.

In addition to the gas—liquid analysis of the hydrolyzates, we recorded the UV spectra of the DLAK-I and DLAK-II before and after alkaline hydrolysis and studied them. The kenaf lignins gave two absorption maxima — at 275-277 nm, due to an aromatic system, and at 315 nm in the form of a shoulder. The latter absorption was shifted to 360 nm in alkaline solution [+) in methylcellosolve and ++) in a mixture of methylcellosolve and 0.1 N NaOH (1:1)]:

Sample	Neutral medium^{+}		Alkaline medium^{++}	
	λ_{max}	λ_{min}	λ_{max}	λ_{min}
DLAK-I before hydrolysis	315	260	360	320
DLAK-II before hydrolysis	315	260	360	320
DLAK-I after hydrolysis	281	260	—	—
DLAK-II after hydrolysis	280	260	—	—
p-Coumaric acid [6]	309	246	336	260

A similar shift in the absorption maximum in the long-wave direction has been detected in experiments with model α- and γ-esters [6]. The peaks of the dioxane lignins at 315 nm in neutral solution and 360 nm in alkaline solution (Fig. 2) disappear on alkaline hydrolysis. This shows that the p-coumaric acid is bound by an ester bond with the aliphatic hydroxyls of the side chain of the lignin macromolecule.

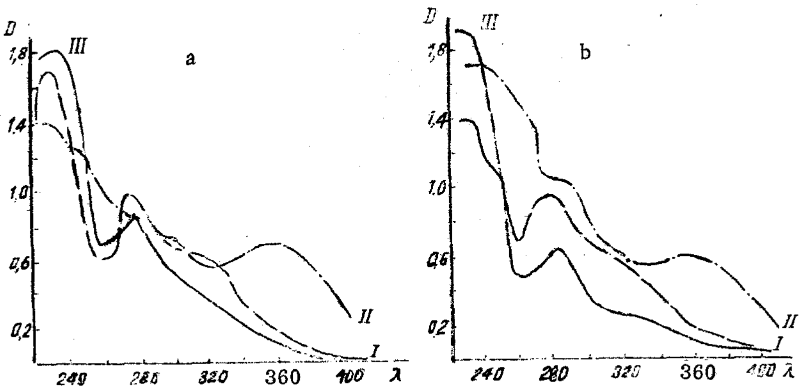

Fig. 2. UV spectra of DLAK-I (a) and DLAK-II (b): I) in methylcellosolve; II) in a mixture of methylcellosolve and 0.1 N NaOH (1:1); III) spectrum after alkaline hydrolysis (in methylcellosolve).

EXPERIMENTAL

Alkaline Hydrolysis. A solution of 500 mg of DLALK in 25 ml of 1 N NaOH was kept at 25°C for 24 h and was then acidified (pH 4) with 1 N HCl. The precipitate of lignin that deposited was filtered off and washed with a small amount of hot water. The filtrate and wash-waters were combined and extracted with ether (4 × 100 ml). The extract was shaken with saturated sodium bicarbonate solution (5 × 100 ml), and the aqueous layer was acidified with concentrated HCl and was reextracted with ether (4 × 100 ml). The ethereal fraction was washed with a saturated solution of NaCl and dried over $MgSO_4$. The ether was distilled off in vacuum and the residue, after drying over P_2O_5, was dissolved in ethanol and was studied by the GLC method.

The GLC conditions were similar to those used in the analysis of the product of nitrobenzene oxidation [7].

The UV spectra were taken on a SF-4 instrument. Methylcellosolve and also a mixture of methylcellosolve and 0.1 N NaOH (1:1) were used as solvents.

SUMMARY

Four dioxane lignins from kenaf have been subjected to alkaline hydrolysis, and the presence of esterified p-coumaric and p-hydroxybenzoic acids in them has been shown.

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