CLEAVAGE OF DIOXANE LIGNIN OF THE COTTON PLANT WITH THIOACETIC ACID

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Previously, in a study of the natural lignin and the dioxane lignin (DLA) of the cotton plant it was established that the main structural fragments of cotton-plant lignin are guaiacyl, syringyl, and p-coumaryl units [1, 2]. When the lignins were cleaved by metallic sodium in liquid ammonia, only part of the aryl—alkyl ester bonds were broken and the yields of phenolic products were low [2, 3]. Even after nine successive treatments of spruce copper-ammonia lignin, a total of only about 30% of phenolic substances was obtained [4].

These bonds are cleaved most completely by thioacetic acid, which has been used in the study of the natural lignin of the beech [5] and poplar [6].

We have used this reaction to study the DLA of mature stems of the cotton plant of variety 108-F obtained by Pepper's method with a yield of 21.7% from the Komarov lignin [7]. On reaction with thioacetic acid, the DLA of the cotton plant was cleaved to the extent of almost 92%. The cleavage products were separated on analytical and preparative columns of Sephadex LH-20 in the methanol—water (9:1) system.

For calibrating the analytical column we used model substances with different molecular weights and different proportions of hydroxy groups. Below we give a list of these substances with their molecular weights and the distribution coefficients found (K_{av}):

Substance	Molecular weight	K_{av}
Syringaresinol	418	0,62
Eudesmin	386	0,89
1-(2-Methoxyphenoxyl)-α-propioveratrone	332	0,83
1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol	304	0,86
1-(4-Hydroxy-3,5-dimethoxyphenyl) propan-1-ol	188	0,78
3-(4-Hydroxyphenyl)propan-1-ol	152	1,00
1-(4-Hydroxy-3-methoxyphenyl) propane	150	1,08

On the basis of the results obtained we have calculated the coefficients in the basic equation of chromatography for LH-20 gel and the solvent methanol—water (9:1): $K_{av} = 2.82 - 0.815 \log M$. Then, on the eluogram (Fig. 1) of the cleavage products we delimited the regions of the oligomers, trimers, dimers, and monomers. By calculating the areas of these fractions, we found that the oligomeric products (fraction 1 in Fig. 1) amounted to 7.8% of the total, the trimers (fraction 2) to 12.7%, and dimers (fraction 3) to 21.5%, and the monomers (fraction 4) to 57.8%. From the eluogram and the calculations it can be seen that the bulk consisted of monomeric degradation products. In view of the fact that some phenolic products are capable of being adsorbed by the gel and being eluted with a large volume of solvent not corresponding to their molecular weights [8], the amount of monomers found was somewhat high (by about 0.5%). Consequently, the actual monomer content is 57.3%.

Knowing the amount of monomers and the fact that in lignin only the aryl—alkyl ether bonds relating to the C_3 side chain of the phenylpropane structures are cleaved by thioacetic acid, it is possible to state that in the cotton-plant DLA all the monomers are connected with one another only by aryl—alkyl bonds. The dimers participate in the formation of $21.5 \cdot 1/2 = 10.75\%$ of the alkyl—aryl ester bonds, and the trimers in $12.7 \cdot 1/3 = 4.23\%$.

Thus, thioacetic acid cleaves 72.3% of the alkyl—aryl ether bonds in cotton-plant DLA, i.e., almost 3/4 of the total number of bonds in the lignin are aryl—alkyl bonds. The remaining 1/4 (27.7%) are C—C bonds and, in small amounts, diaryl ether bonds. From all that has been said it can be seen that cotton-plant DLA has a low degree of condensation.

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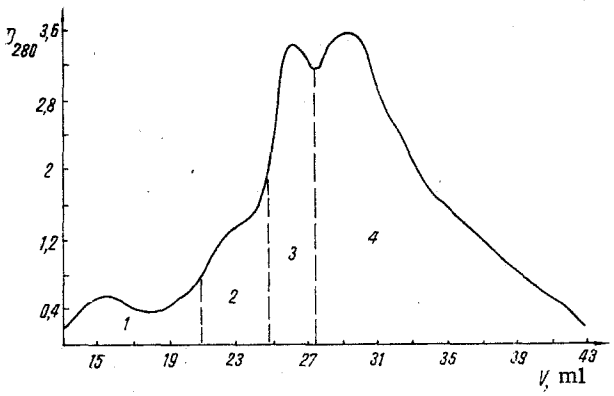

Fig. 1. Gel chromatogram of the products of the cleavage of cotton-plant dioxane lignin by thioacetic acid: 1) oligomers; 2) trimers; 3) dimers; 4) monomers.

After the isolation and rechromatography of the monomer fraction, by the GLC method we found in it the same phenols as in the products of the cleavage of the DLA by sodium in liquid ammonia [2]: phenol, guaiacol, vanillin (4-hydroxy-3-methoxyphenyl)ethane, 1-(4-hydroxy-3-methoxyphenyl)propane, 1-(4-hydroxy-3-methoxyphenyl)propan-1-ol, 3-(4-hydroxy-3-methoxyphenyl)propan-1-ol, and 1-(4-hydroxy-3,5-dimethoxyphenyl)propane. As in the case of the cleavage of DLA with sodium in liquid ammonia, the main structures were the guaiacyl, and then the syringyl structures. The p-hydroxyphenylpropane structures were present in the smallest amount. The dimeric products are being studied.

EXPERIMENTAL

The work was carried out with the DLA of mature stems of the cotton plant of variety 108-F obtained previously (fraction 1 [7]). Gel chromatography was performed on analytical (1 × 32 cm) and preparative (4 × 150 cm) columns of Sephadex LH-20, the solvent and eluent being methanol–water (9:1). The columns were calibrated by a standard method [8].

Cleavage with Thioacetic Acid. A mixture of 1 g of DLA, 24 ml of freshly distilled thioacetic acid, and 0.6 ml of the ether complex of BF_3 was shaken at room temperature for 60 h. The excess of thioacetic acid was distilled off in vacuum and the resinous residue was dissolved in 25 ml of 8% caustic soda in aqueous ethylene glycol (1:3) and heated at 60°C under a current of nitrogen for 16 h. Then 75 ml of 8% caustic soda in aqueous ethylene glycol (1:3) and the Raney nickel catalyst obtained from 20 g of aluminum–nickel alloy were added to the reaction mixture and it was boiled with the passage of nitrogen for 8 h. After the elimination of the catalyst and acidification of the reaction mixture with hydrochloric acid to pH 2, it was extracted with ethyl acetate, and the extract was dried over sodium sulfate and evaporated in vacuum. The products obtained were subjected to gel-chromatographic separation.

SUMMARY

1. It has been established that the dioxane lignin of mature cotton-plant stems is cleaved by thioacetic acid. About 3/4 of the bonds in the lignin are alkyl–aryl ether bonds and only 1/4 are C–C bonds.

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