DIOXANE LIGNIN FROM SHOOTS OF THE COTTON PLANT OF VARIETY 108-F. I

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The dioxane lignin has been isolated by Pepper's method from two-week shoots of the cotton plant of variety 108-F and has been separated into two fractions — insoluble and soluble in ether — DLA-A and DLA-B, respectively. It has been shown that in the early stage of development of the cotton plant a low-molecular-weight lignin with a low degree of methoxylation and distinctly different from the lignin from ripe stems of the same cotton plant is synthesized.

Continuing a study of the dioxane lignin (DLA) of the cotton plant of variety 108-F, we have investigated two-week shoots. The DLA was obtained by Pepper's method [1] from the comminuted shoots that had first been extracted with ethanol-benzene and washed with hot water. On purifying the DLA by precipitating its aqueous dioxane solution absolute diethyl ether, we obtained an ether-insoluble fraction DLA-A, and an ether-soluble fraction, DLA-B. Both fractions were reprecipitated from their aqueous dioxane solutions: DLA-A into absolute ether, and DLA-B into acidified water. The amount of DLA-A (on the weight of the plant) was 0.3% and of DLA-B 1.1%.

The UV spectrum of DLA-A showed a maximum at 270-275 nm, which is characteristic for lignins, and that of the DLA-B a shoulder at 270-300 nm.

The IR spectra of the two fractions showed the presence of absorption bands characteristic for the functional groups of lignin. The spectra were interpreted by the method of Karklin' and Érin'sh [2] on the basis of the relative optical densities (RODs):

Frequency cm^{-1}	DLA-A	DLA-B	Assignment of the absorption bands
3400	0,92	1,16	Stretching vibrations of O–H bonds of hydroxyls and hydrogen bonds
3080	0.53	0.78	
2960	0,68	1,36	
2930	0,78	2,53	Stretching vibrations of C–H bonds in CH_2 and CH_3 groups
2880	0,60	—	
2860	0.61	1,51	Stretching vibrations of C–H bonds in CH_2 and in CH_3 of OCH_3 groups
1730	0,69	1,34	Stretching vibrations of carbonyl groups
1620	1,11	1,63	Stretching vibrations of double bonds in aromatic rings
1520	1,00	1.00	
1560	—	1,03	
1460	0,94	1,34	Deformation vibrations of C–H bonds in OCH_3 groups
1380	—	1,31	
1340	0,88	—	
1300	—	1.63	
1280	0,96	1,05	Stretching vibrations of C–O–C bonds in OCH_3 groups
1250	—	1 40	
1230	0,99	1,36	Stretching vibrations of C–O–C bonds in ethers
1130	1,12	1,19	Wagging vibrations of OCH_3 groups
1070	—	1.09	
1040	0,82	0,92	Symmetrical stretching vibrations of C–O–C bonds in OCH_3 groups
990	—	0 93	

As we see, the spectra of both fractions consist of a large set of absorption bands. The fractions differed both in the number of bands and in their relative densities.

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On the basis of the results of elementary analysis and the analysis of functional groups we calculated developed empirical formulas for the DLA-A and DLA-B, and these are given without taking into account the carbohydrates bound to the lignin, since their amount was small in both fractions:

DLA-A, mol. mass = 188.43

$$C_9H_{9.24}O_{1.51}(OCH_3)_{0{,}53}(OH_{ph})_{0{,}78}(OH_{al})_{0{,}48}(O_{CO})_{0{,}36}(O_{ar\text{-}al})_{0{,}22}$$

DLA-B, mol. mass = 158.07

$$C_9H_{9{,}67}O_{0{,}5}(OCH_3)_{0{,}12}(OH_{ph})_{0{,}52}(OH_{al})_{0.39}(O_{CO})_{0{,}34}(O_{ar\text{-}al})_{0.48}$$

It can be seen from the empirical formulas that the fractions differed sharply by their content of the main functional groups, particularly methoxyl. The amount of them in the DLA-B was four times less than in the DLA-A. On comparing these formulas with the formula for the DLA from ripe stems of the same cotton plant [3]

$$C_9H_{8{,}02}O_{0{,}74}(OCH_3)_{1{,}33}(OH_{ph})_{0.42}(OH_{al})_{0{,}85}(O_{CO})_{0{,}22}(OOH_{COOH})_{0{,}06}(O_{ar\text{-}al})_{0.58}$$

it can be seen that both fractions differed sharply from the DLA from the ripe stems of the cotton plant. The amount of OCH_3 groups in the DLA-A was 2.5 times and in the DLA-B 11 times smaller than in the DLA from the ripe stems. Consequently, weakly methoxylated lignin is synthesized in the early period. In both fractions the amount of phenolic OH groups was higher and that of aliphatic OH groups lower than in the DLA of the ripe stems. The amounts of the two types of hydroxyl in the DLA-A and the DLA of the ripe stems were the same ($1.26/C_9$) and the DLA-B lower ($0.91/C_9$). The amounts of carbonyl groups in the two fractions was higher than in the DLAs of the ripe stems. The total amount of oxygen in the DLA-A, expressed as O atoms per C_9 unit, was 3.56, in the DLA-B 2.35, and in the DLA of the ripe stems 4.14. It can be seen from this that the lignin of the cotton plant in the early stage of development is impoverished in oxygen because of its low content of OCH_3 groups and aliphatic hydroxyls. On the whole, in the early stage of development of the cotton plant a lignin sharply differing from the lignin of the ripe stems is synthesized.

On comparing the empirical formulas of fractions A and B with the formulas for the MWL from higher plants [4], it can be seen that they have much in common: In the lignin obtained by mechanical grinding (MWL) from lower plants the amount of OCH_3 groups is low (MWL of *Fucus*, $0.15/C_9$, of *Equisetum* $0.13/C_9$, and of *Lycopodium* $0.43/C_9$). At the same time, the amount of phenolic OH groups was far higher than the amount of alcoholic hydroxyls. In many of its indices, DLA-A is comparable with the *Lycopodium* MWL: They have identical or very similar amounts of total oxygen, OCH_3 groups, phenolic OH groups, carbonyl, and total hydrophilic groups.

Fraction B is untypical for lignins: It has no clear maximum in the UV spectrum, a molecular mass of 1 PPCE that is uncharacteristic for lignins, and a small amount of total oxygen.

A study of the molecular-mass distribution by gel chromatography of both fractions showed that they were monomodal, of low molecular weight, and more homogeneous than the DLA from the ripe stems of the cotton plant:

	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w / \overline{M}_n$
DLA-A	4900	3200	1,53
DLA-B	2700	1900	1,42
DLA	12000	4200	2,90

Consequently low-molecular-weight lignin is synthesized in the early stage.

EXPERIMENTAL

Dioxane lignin was obtained by Pepper's method [1] from cotton-plant shoots that had been ground (0.1 mm), exhaustively extracted with ethanol—benzene (1:1 by volume), washed with hot water, and dried. The yield was 1.5% on the weight of the plant.

Fractionation of the DLA. A solution of 1 g of the DLA in 20 ml of a mixture of dioxane and water (9:1) was added dropwise with stirring to 200 ml of absolute ether. The resulting precipitate, after drying and reprecipitation, from aqueous dioxane solution into absolute ether formed DLA-A. Yield 0.21 g.

After the separation of the DLA-A, the ethereal mother solution was evaporated to dryness, the dark resinous residue was dissolved in dioxane—water (9:1), and the solution added dropwise with stirring to water acidified to pH 2. A brown amorphous precipitate of DLA-B deposited. It was purified by reprecipitation under the same conditions. Yield 0.59 g.

UV spectra were taken on an SF-26 spectrophotometer in ethanol, and IR spectra on a UR-20 instrument in tablets with potassium bromide. The interpretation of the spectra was carried out by the method of Karklin' and Érin'sh [2].

Elementary Analysis (%). DLA-A: C, 61.06; H, 5.88; OCH_3, 8.72; OH_{tot}, 10.9; OH_{phen}, 6.8; CO, 5.43; carbohydrates 1.2; DLA-B: C, 69.38; H, 6.8; OCH_3, 2.3; OH_{tot}, 9.74; OH_{phen}, 5.6; CO, 6.09; carbohydrates, 0.5. OCH_3 was determined by the Vieböch-Schwappach method, OH_{tot} by acetylation, OH_{phen} by a chemosorption method, carbonyls by oximation [5], and carbohydrates as described by Somogyi [6].

Gel chromatography was performed in an analytical column (V_t = 31 ml) filled with Sephadex G-75, with DMSO as eluent and solvent. The free volume was determined with dextran blue with a molecular mass of 2,000,000. To calculate the molecular masses we used the coefficients found by Babikova et al. [7] and the method of calculation given by Rafikov et al. [8].

SUMMARY

The dioxane lignin has been obtained from shoots of the cotton plant of variety 108-F and has been separated into two fractions. It has been shown that in the early stage of development of the cotton plant a lignin is synthesized which differs sharply with respect to molecular mass and amount of functional groups from the lignin of the ripe stems.

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