A STUDY OF DIOXANE LIGNIN FROM BOLLS OF THE COTTON PLANT OF VARIETY AN BAYAUT-2 II

S. Makhamedova, L. S. Smirnova, and Kh. A. Abduazimov

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The dioxane lignin was isolated from ripe bolls of a medium-fiber cotton plant of the variety AN Bayaut-2. Its developed empirical formula was derived, its UV, IR, and PMR spectra were recorded, and its molecular weight was determined. It was shown that the boll lignin is more condensed than the stem lignin. It differs from the stem lignin by a lower content of methoxy groups and a higher content of hydroxy and carbonyl groups.

In communication I we gave the results of a study of the dioxane lignin (DLA) from ripe stems of a medium-fiber cotton plant of the variety AN Bayaut-2 [1] — a new high-yielding fast-ripening variety created on the basis of the wilt-resistant Tashkent-1 variety of cotton plant.

Continuing this investigation, from ripe bolls of the cotton plant we have isolated the DLA by Pepper's method [2] with a yield of 5.6% (on the Komarov lignin). The total amount of lignin in the bolls was 27.5% (Komarov lignin). As can be seen, in spite of the high lignin content in the bolls, its mild acidolysis liberated a smaller amount than from the stems (6.1% [1]). As compared with the stem lignin, the boll lignin had a more intense brown coloration, but their solubilities were identical. The DLA was purified by two reprecipitations of its aqueous dioxane solutions in absolute ether.

The developed formula of the DLA was calculated on the basis of elementary analysis and the analysis of functional groups. Since the amount of carbohydrates bound to the lignin was less than 1%, it was not taken into account in the drawing up of the formula.

Molecular weight 210.65

$$C_9H_{8,24}O_{2,08}(OCH_3)_{0.75}(OH_{ph})_{0.75}(OH_{al})_{0.72}(O_{CO})_{0.49}(O_{ar\text{-}al})_{0.44}$$

The boll DLA contained a smaller amount of methoxy groups and a larger amount of hydroxyls and carbonyls than the stem DLA. In their degree of oxidation (5.04 O/C_9) the two DLAs were similar. The UV spectrum of DLA taken in a mixture of methylcellosolve, water, and ethanol (2:1:1) showed the maximum characteristic for lignins (280 nm, log ε 3.48). The molar extinction was 3000, calculated to the molecular weight of one phenylpropane structural unit (PPSU), almost the same as for the stem DLA (2900).

The IR spectrum differed little from that of the stem DLA.

The PMR spectrum of the acetylated DLA showed a difference between the stem and boll lignins. The identification of the chemical shifts in the spectrum and their quantitative characterization were carried out in accordance with [3]. The results were given below (number of protons of OCH_3 groups taken from the empirical formula):

Number of the zone	Limits of the zone, ppm	Protons	Number of protons per C_9
I	2 - 3.70	Aromatic	2.25
II	3.70 - 4.2	β-Vinyl and benzyl ether protons of the C_3 side chain	0.42
III	4.2 - 4.8	Coumarane structures	0.42
IV	4.8 - 7.5	Methoxylic in the C_3 side chain	4.65
IVa	6.0 - 6.8	Methoxylic	2.25
		Other	2.40

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Number of the zone	Limits of the zone, ppm	Protons	Number of protons per C_9
V	7.5 - 7.9	Acetoxy groups	1.91
VI	7.9 - 8.4	Aliphatic acetoxy groups	2.21
VII	8.4 - 9.4	Highly screened methyl and methylene groups	1.14

In the boll DLA the aromatic nucleus was more substituted than in the stem DLA, where the number of free aromatic protons was 2.92 [1]. One aromatic proton in the boll DNA participates in the formation of a bond: 4 — 0.75 — 2.25 = 1 (calculation made as in [1]). As in the stem DLA, the number of protons in the boll DLA corresponding to benzyl acetate groups (0.42) indicates that the bulk of the aliphatic hydroxy groups occupy the α-position. The amount of coumarane structures in the boll DLA was 1.6 times less than in the stem DLA. A comparison of the number of protons in the C_3 side chain of the boll DLA (3.54) with that in the stem DLA (4.02) also indicated that the boll lignin was more condensed than the stem lignin.

A study of the molecular-weight distribution of the boll DLA by column gel chromatography [4] showed that, like the stem DLA, it was polydisperse and with respect to molecular weights scarcely differed from the stem DLA: $\bar{M}_n$ = 3000, $\bar{M}_w$ = 7000, $\bar{M}_z$ = 12,800. The degree of polydispersity $\bar{M}_w/M_n$ = 2.33.

The molecule of the boll lignin, like that of the stem lignin, consisted of 33 PSUs.

EXPERIMENTAL

The dioxane lignin was isolated by Pepper's method [2]. Functional groups were determined and the empirical formulas calculated by standard methods [5].

Analytical results (%): C 59.04; H 4.83; OCH_3 11.71; OH_{tot} 10.32; OH_{phen} 4.48; CO 6.57.

The UV spectrum was taken on a SF-26 spectrophotometer in a 2:1:1 mixture of the solvents methylcelluosolve, ethanol, and water, C = $2.230 \cdot 10^{-4}$ M. The molar extinction was calculated for the molecular weight of 1 PPSU of 210.65.

Gel chromatography was performed on an analytical column with Sephadex G-75 using dimethyl sulfoxide as eluent and solvent. Molecular weights were calculated by the method of Alekseev et al. [4] using the coefficients given in [6].

The DLA was acetylated as described in [3]. The PMR spectrum was taken on a JNM-4H-100/100 MHz spectrometer at T = 22-24°C, C = 10-12% by weight, 10 — HMDS, τ scale, with deuterochloroform as the solvent.

SUMMARY

The dioxane lignin has been isolated from the ripe bolls of a cotton plant of the variety AN Bayaut-2 and has been characterized. It has been shown that with respect to its molecular weight it is similar to the DLA from stems of the cotton plant of the same variety but contains a small amount of methoxy groups and a larger amount of hydroxy and carbonyl groups. The boll lignin is more condensed than the stem lignin.

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