Chemistry of Natural Compounds, Vol. 31, No. 2, 1995

STUDY OF THE DIOXANE LIGNIN OF A COTTON PLANT OF THE VARIETY NAMANGAN-77

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UDC 547.992.002.61

Dioxane lignin isolated from the stems of a cotton plant of the variety Namangan-77 has been studied. Its structure differs from that of the DLAs of other varieties, being of lower molecular weight and more highly oxidized.

Over a number of years, the study has been carried on of the lignins isolated from cotton plants of different varieties in the laboratory of lignin chemistry of IKhRV Akad. Nauk RUz. In continuation of these investigations, we have isolated dioxane lignin (DLA) by Pepper's method [1] from ripe stems of a cotton plant of the variety Namangan-77 free from bark. Namangan-77, derived by selective breeding from the variety S-6524, is a promising wilt-resistant variety and has been sown since 1992 [2]. The amount of total lignin (Komarov lignin) in the stems was 23.96%. The yield of DLA was 3.71% (on the weight of the plant).

The dioxane lignin was an amorphous light brown powder readily soluble in the usual solvents for lignin: dioxane, dimethyl sulfoxide, dimethylformamide, methylcellosolve. The DLA was purified by reprecipitation from aqueous dioxane (1:9 by volume) solutions in absolute ether.

The empirical formula of the DLA was calculated on the basis of the results of elementary analysis, functional-group analysis, and PMR spectroscopy of the O-acetyl derivative. It is given without taking into account the carbohydrates bound with the lignin, since their amount in the DLA was negligible: $C_9H_{7.13}O_{1.77}(OCH_3)_{1.23}(OH_{ph})_{0.22}(OH_{al})_{0.91}(O_{ar\text{-}al})_{0.78}$.

In its content of functional groups and, consequently, its chemical structure, this DLA differed from the lignins isolated from the stems of cotton plants of varieties 108-F and S-6524. Variety 108-F was the initial variety for S-6524.

Developed empirical formula of the DLA from a S-6524 cotton plant [3]: $C_9H_{7.82}O_{1.48}(OCH_3)_{1.28}(OH_{ph})_{0.28}$-$(OH_{al})_{0.48}(O_{CO})_{0.24}(OOH_{COOH})_{0.02}(O_{ar\text{-}al})_{0.72}$.

Developed empirical formula of the DLA from a 108-F cotton plant [4]: $C_9H_{8.02}O_{0.58}(OCH_3)_{1.23}(OH_{ph})_{0.44}$-$(OH_{al})_{0.96}(O_{CO})_{0.22}(OOH_{COOH})_{0.085}(O_{ar\text{-}al})_{0.56}$.

It can be seen from the formulae that the Namangan-77 DLA was the most oxidized (4.85 O/C_9) and the most highly hydroxylated (1.13 OH/C_9).

Additional characterization was provided by the PMR spectrum of the acetylated DLA. The assignment of the signals in the spectrum and their quantitative evaluation were carried out as in the consideration of the PMR spectra of the DLAs isolated from the stems of the 108-F and S-6524 cotton plants [5]. The characteristics of the PMR spectra of the three DLAs, which are given in Table 1, confirmed the different contents of protons of aromatic nuclei and functional groups in the DLAs of the three varieties of cotton plant.

The UV spectrum of the DLA, taken in ethanol, was characteristic for lignins and had a maximum at 280 nm and a minimum at 260 nm.

The IR spectrum contained all the bands characteristic for lignins.

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 0009-3130/95/3102-0246$12.50

TABLE 1

Protons	Number of protons per C_9 in the DLA		
	108-F	S- 6524	Namangan-77
Aromatic	2.34	1.81	1.89
β-Vinyl and benzyl at acetate groups	0.58	0.22	0.38
Of coumarin structures	0.32	0.16	0.30
Methoxyl and in the C_3 side-chain	6.12	6.25	5.37
Methoxyl	3.69*	3.84*	3.70*
Aromatic acetoxy groups	0.95	0.55	0.66
Aliphatic acetoxy groups	2.90	2.19	2.74
Highly screened CH_3 and CH_2 groups	0.36	0.33	0.57

A study of the molecular-mass distribution by column gel chromatography on Sephadex G-75 with dimethyl sulfoxide as eluent and solvent and of the coefficients found previously [6] showed that it was polydisperse, with $\overline{M}_w/\overline{M}_n = 2$, and had $\overline{M}_n$ 2900, $\overline{M}_w$ 5800. $\overline{M}_z$ 13800. Molecular masses were calculated by the method of [9]. It can be seen from the molecular mass of one phenylpropane structural unit of the DLA that its molecule consisted of 29 phenylpropane structural units.

By gas–liquid chromatography, in the products of the complete nitrobenzene oxidation of the DLA we identified vanillin, syringaldehyde, and *p*-hydroxybenzaldehyde. The amount of *p*-coumaryl structures in the DLA was insignificant.

EXPERIMENTAL

DLA was obtained from cottonplant stems that had been ground, exhaustively extracted with alcohol–benzene (1:1), and washed with hot water [1], and it was purified as described in [3].

Elementary composition (%): C 61.38; H 6.0; OCH_3 19.14.

Functional groups were determined by standard methods [7].

UV spectra were taken on a SF-26 spectrophotometer in ethanol, and IR spectra on a UR-20 instrument in potassium bromide tablets. The PMR spectrum was recorded on an IMH-4H-100/100 MHz spectrometer at room temperature, $C = 10\%$ (by weight), τ scale, solvent deuterochloroform, 10 – HMDS.

The gel chromatography of the DLA was conducted as described in [6].

Alkaline nitrobenzene oxidation and the GLC of the oxidation products of the DLA were carried out by the method of Novikov and Khokholko [8].

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