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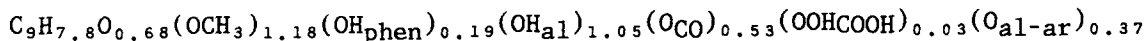
The dioxane lignin (DLA) isolated from a powder of the stems the castor-oil plant by a modification of Pepper's method has been investigated. The yield of DLA amounted to 19.85% on the Komarov lignin. On the basis of elementary and functional analysis, a developed semiempirical formula has been proposed for it from which it can be seen that the amounts of methoxy, aliphatic hydroxy, and carbonyl groups are high and that of phenolic hydroxyl low. UV, IR, and PMR spectra have been taken, and the molecular weight of the material has been determined.

Ricinus communis (castor-oil plant) [1] is one of the widely cultivated technical plants. The alkali lignins of the castor-oil plant have been studied [2, 3]. The lignin obtained was no longer the native form of lignin. The action of alkali changes the nature of the side chains, eliminating some of the important functional groups.

Continuing a study of the lignins of monocotyledonous technical plants, we have investigated the dioxane lignin (DLA) of the castor-oil plant. The dioxane lignin is close to the natural lignin. The amounts of the chemical components of the stems of the castor-oil plant were (%): Komarov lignin, 19.64; cellulose, 32.95; ethanol-benzene extract, 5.10; aqueous extract, 7.41.

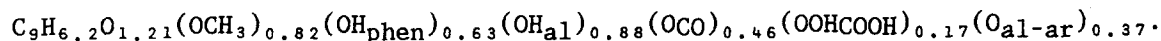
The DLA was isolated from a powder of the stems of the castor-oil plant by a modification of Pepper's method under a current of nitrogen [4]. The yield of DLA amounted to 19.85% on the Komarov lignin. The DLA purified by two reprecipitations from aqueous ethanol solution (1:9) into absolute ether consisted of an amorphous light brown powder soluble in dioxane-water (9:1), dimethyl sulfoxide, and acetic acid. The castor-oil plant DLA had the following elementary and functional composition (%): C - 59.70; H - 5.00; OCH₃ - 17.90; OH_{tot} - 10.30; OH_{phen} - 1.59; CO - 7.20.

On the basis of elementary and functional analyses, and also in the light of the molecular weight of one phenylpropane structural unit (1 PPSU), which is 206.94, the following semiempirical formula of the DLA was calculated:



As compared with the dioxane lignin of ripe stems of the cotton plant of variety (Tashkent-1 (DLCT)), which also belongs to the monocotyledonous technical plants, 1 PPSU of the castor-oil plant DNA contains more methoxy, aliphatic hydroxy, and carbonyl groups fewer phenolic hydroxy groups.

For the DLCT, the molecular weight of 1 PPSU is 200.75 [5]:



The UV and IR spectrum of the castor-oil plant DLA were the usual ones for lignin preparations.

In the UV spectrum there was a maximum at 280 nm and a weak inflection at 320 nm. The molar extinction of the DNA was 2360.

In the IR spectrum of the DLA there were all the absorption bands characteristic of lignin: bands of the absorption of OH groups with associated hydrogen bonds (3500 cm⁻¹), of the stretching vibrations of C-H bonds and of methyl and methylene groups (2950 cm⁻¹), of β-, and α-carbonyl groups (1720, 1670 cm⁻¹), of C-H bonds in methoxy groups (1470, 1430,

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1330 cm^{-1}), of the skeletal vibrations of double bonds in aromatic nuclei (1600, 1510 cm^{-1}), and of ether bonds in methoxy groups (1280 cm^{-1}).

In contrast to the spectrum of the cotton-plant lignin, the IR spectrum of the castor-oil plant lignin had absorption bands of β - and α -carbonyl groups. A calculation of the relative optical density (ROD) by the base-line method showed [6] that the optical density of the β -carbonyl groups (2.5) was greater than that of the α -carbonyl groups (2.09).

The molecular-weight distribution of the DLA was studied by gel chromatography on a column of Sephadex G-75 [7]. The number-average ($\bar{M}_n = 3900$), the weight-average ($\bar{M}_w = 9700$), and the mean ($\bar{M}_z = 19,600$) molecular weights were calculated by a standard procedure [8] and showed that the DLA was polydisperse.

The PMR spectrum of the acetylated DLA had the signals of the protons of an aromatic nuclei ($C_9/1.39$), of β -vinyl and the diphenyl ether protons of a side chain (0.18), of the protons of coumarane structures (0.07) and of methoxy groups (3.54), of the β -protons of a side chain (1.75), and of the protons of aromatic and aliphatic acetoxy groups (0.85 and 2.68), and also of the highly screened protons of methyl and methylene groups (0.15).

A calculation of the PMR spectrum confirmed the low content of phenolic hydroxy groups in the castor-oil plant DLA.

EXPERIMENTAL

The UV spectrum was taken on a SF-26 spectrophotometer in aqueous dioxane (1:9): $\log \epsilon$ 3.3727 ($C = 3.01 \cdot 10^{-4}$ M); the IR spectrum on a UR-20 instrument in tablets with potassium bromide; and the PMR spectrum of the acetylated DLA on a HNM-4M-100/100 MHz spectrometer at room temperature with $C = 10$ -12% by weight, 10 - HMDS, solvent - CDCl_3 , calculation performed in accordance with [10].

Gel chromatography was carried out on a 1.2×45 cm column filled with G-75 gel in DMSO. $V_t = 26.4$ ml, $V_0 = 9.6$ ml for dextran blue with a mol. wt. of 2,000,000 [8].

Preparation of the DLA. With constant stirring under a current of nitrogen, 50 g of air-dry castor oil plant stems that had been ground (0.25 mm), extracted with ethanol-benzene (1:2), and washed with hot water was extracted with a mixture of 900 ml of dioxane, 80 ml of water, and 18 ml of concentrated hydrochloric acid at 90°C for 0.5 h. The extract was separated from the plant material, and the latter was washed with hot aqueous dioxane (1:9), which was combined with the main extract and, after neutralization with sodium carbonate, this was evaporated in vacuum to a volume of 50-70 ml. The concentrated extract was added dropwise to cold water acidified with HCl to pH 2. The DLA that precipitated was separated off by centrifugation, washed with water, and dried over P_2O_5 . The DLA was purified by two reprecipitations in absolute ether.

Functional Group Analysis. Methoxy groups were determined by the Zeisel-Viebach-Schwappach method, carbonyl groups by the oximation method, total hydroxy groups by acetylation, and phenolic hydroxyl by the chemisorption method [9].

SUMMARY

1. The DLA of the castor-oil plant has been isolated and has been characterized by its elementary and functional composition. A semiempirical formula has been derived and a low content of phenolic hydroxy groups per phenylpropane structural unit has been found.

2. A study of the molecular-weight distribution of the DLA has shown its polydispersity.

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