

The considerable decrease in the intensity of the 1275-cm^{-1} band shows a demethyloxylation of the lignin, while the accumulation of phenolic OH groups is confirmed by an increase in the intensity of the band in the 1220-cm^{-1} region. A new band is observed in the 682 cm^{-1} -region the appearance of which can probably be referred to the formation during the electrooxidation of lignin of structures of the type of 1,3,5-trisubstituted aromatic systems [8].

Thus, it may be concluded that the medium (solvent) has a substantial influence on the electrooxidation of lignin.

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A STUDY OF DIOXANE AND HYDROLYSIS LIGNINS FROM THE SEED HULLS OF THE COTTON PLANT

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The seed hulls of the cotton plant are a raw material for the hydrolysis industry. At the present time, investigations are being performed on the use of hydrolysis lignin in the national economy [1].

Natural lignin from the seed hulls of the cotton plant has been little studied chemically [2]. The investigation of this lignin is of interest because its formation takes place without a direct connection with the cambial layer of the plant. The functions that this lignin fulfills—the protection of the seed kernel from mechanical damage and its capacity for swelling during growth—are different from the functions of the lignin in the stems and pods of the cotton plant.

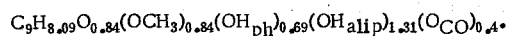
From the comminuted (0.25 mm) seed hulls of the cotton plant of variety 108-F which had previously been extracted with a mixture of ethanol and benzene (1:1), we isolated the dioxane lignin (DLA) by a modification of Pepper's method [3] with a yield of 3.8% on the initial material (about 17% on the Komarov lignin).

After purification by Björkman's method, the DLA contained 2.8% of carbohydrates and consisted of an amorphous powder soluble in the usual solvents for lignins and readily soluble in water. Its UV spectrum, taken in aqueous dioxane, was typical for cotton lignins: λ_{max} 280 nm and 330 nm (shoulder) ($\log \epsilon$ 3.5; c $2.675 \cdot 10^{-4}$ M). The IR spectrum (tablets of KBr) had absorption bands at (cm^{-1}) 3400 (OH), 1710 (carbonyls), 1620, 1530 (benzene rings), and 1470 (methoxyls).

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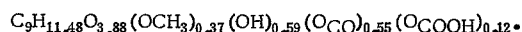
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On the basis of functional-group and elementary analyses, the following formula of the C₆-C₃ unit of the DLA was calculated (with a correction for the carbohydrates):



Gel chromatography of the DLA on a column of Sephadex G-75 with DMSO as eluent and solvent showed that it is monomodal and of high molecular weight (mol. wt. 28,000-26,000).

When the DLA was compared with the hydrolysis lignin obtained in the Yangiyul' Hydrolysis Plant it was found that in the latter the content of methoxy and hydroxy groups had fallen sharply and the amount of carbonyl groups and oxygen had risen:



The hydrolysis lignin is an almost black amorphous powder sparingly soluble in all solvents. In its IR spectrum the main absorption bands are resolved less sharply than in the lignins isolated under mild conditions: 3250 cm⁻¹ (OH), 1720, 1690 cm⁻¹ (carbonyls), 1600 cm⁻¹ (aromatic rings), 1450 cm⁻¹ (methoxyls).

The fraction of the hydrolysis lignin soluble in DMSO (3.8%) was, as shown by gel chromatography, poly-disperse with a wide range of molecular weights from 26,000 to 1000. The fraction insoluble in DMSO probably has a molecular weight greater than 26,000.

It is obvious that, under severe conditions of hydrolysis, processes of cross-linking [4] and of the degradation of the lignin molecule take place. The decrease in the amount of methoxy and hydroxy groups shows that in hydrolysis both the aromatic nucleus and the C₃ side chain in the lignin molecule are affected and the increase in the number of carbonyls and in the amount of oxygen shows the oxidative processes taking place on hydrolysis.

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REDUCTIVE DEGRADATION BY METALLIC SODIUM IN LIQUID AMMONIA OF THE NATURAL LIGNIN OF *Althaea spens*

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In the present paper we consider the results of a study of the decomposition by metallic sodium in liquid ammonia of the natural lignin of the stems of two species of *Althaea*: *Althaea rhyticarpa* and *A. nudiflora*. The products obtained on decomposition by this method [1-4] were extracted from the aqueous alkaline solutions at pH 8 with ether and then at pH 2. The concentrated and dried ethereal extract (pH 8; 1.27% and 1.42% of the initial raw material, respectively) was chromatographed on a "Khrom-4" chromatograph with a flame-ionization detector and a 370 × 0.3-cm stainless steel column filled with 15% of Apiezon L on Chromaton NAW DMCS (0.16-0.20 mm). The temperature of the column was 205°C, that of the evaporator was 255°C, and the rate of flow of the carrier gas (helium) was 40 ml/min. On the chromatograms the decomposition products (Table 1) were identified from their retention times and by the addition of standard substances. Quantitative estimation was performed by the method of normalizing areas [5].

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