SUMMARY

A comparative study of the dioxane lignins isolated from healthy and wilt-affected stems of the cotton plant of variety S-6030 has shown that Fusarium fungi demethylate the lignin of cotton-plant stems and make it more oxidized as compared with the lignin from healthy stems.

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THE REACTION OF NITROLIGNIN WITH AMMONIA

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The reaction of nitrolignin with ammonia has been studied. It has been established that it takes place mainly through the carbonyl and carboxy groups of the lignin. A dark brown product with a high nitrogen content readily soluble in water and exhibiting biological activity was obtained. On the basis of the results of elementary and functional analyses, a semiempirical formula has been calculated for the substance obtained, and its viscosity and electrical conductivity have been determined. The molecular weight, determined by the sedimentation method in an ultracentrifuge, was more than 60,000. It was established by gel chromatography that the product of the interaction of nitrolignin with ammonia was polydisperse.

Nitrolignin (NL), obtained by nitrating hydrolysis lignin from cottonseed husks at the Andizhan hydrolysis factory is used in the drilling of deep wells as a viscosity-lowering agent [1], and it is biologically active [2] and possesses a limited solubility in water.

In the nitration process, the functional composition of the macromolecule of lignin undergoes considerable changes: the amount of OCH_3 and OH groups falls and the amount of carboxy and carbonyl groups increases greatly. New functional groups (NO_2, etc.) are introduced into the lignin molecule [3, 4]. The introduction of nitrogen into the lignin macromolecule leads to an increase in its solubility.

The aim of our work was to increase the solubility of nitrolignin in water, to raise its biological activity, and to study the changes taking place in the lignin macromolecule on its reaction with ammonia.

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We studied the reaction of nitrolignin with 25% aqueous ammonia. As is well known, at room temperature lignin reacts with ammonia mainly through the carbonyl and carboxy groups, forming imines and ammonium salts [3]. By varying the ratio of the reactants, the temperature, and the time of the reaction we found the following optimum conditions: ratio of NL to ammonia 4:1; time 15 min; temperature 25-30°C. The reaction took place vigorously, with the evolution of heat. As a result a dark brown powder (NA) completely soluble in water was obtained.

The semiempirical formula of one phenylpropane structural unit of the NA was calculated on the basis of elementary and functional analyses. In spite of the fact that the semiempirical formulas for isolated and modified lignins are regarded as extremely arbitrary, they permit the changes in the functional groups taking place in the course of various modifications of lignin to be followed:

$$\overset{NL}{C_9H_{10.23}O_{3.73}(OCH_3)_{0.19}(OH_{tot})_{0.45}(O_{CO})_{0.97}(OOH_{COOH})_{0.44}N_{0.34}}$$

$$\overset{NA}{C_9H_{10.68}O_{3.71}(OCH_3)_{0.09}(OH_{tot})_{0.51}(O_{CO})_{0.42}(OOH_{COOH})_{0.03}(N_{NH_2})_{0.58}(N_{NO_2})_{0.33}(N_{res})_{0.26}}$$

A comparison of the semiempirical formulas of the initial NL and of the NA obtained showed that the amount of hydrogen per C_9 had increased slightly and the amounts of oxygen and hydroxy groups had scarcely changed. The decrease in the amount of methoxy groups is normal, since ammonia, being a base, is capable of splitting out alkoxy groups [3]. The amount of carbonyl groups per phenylpropane structural unit had more than halved, while carboxy groups had disappeared almost completely. This was confirmed by the results of IR spectroscopy. When the spectra of the initial NL and NA obtained were compared it could be seen as a result of the reaction the intensity of the absorption band in the 3400 cm^{-1} region (OH and N–H) had increased, the band at 1730 cm^{-1} (COOH) had disappeared, and the shoulder at 1720 cm^{-1} (β-C=O) had remained. The absorption band at 1625 cm^{-1} relating to the stretching vibrations of an aromatic nucleus, and the shoulders at 1560 and 1330 cm^{-1} ($-NO_2$) had not changed. A new absorption band had appeared in the 1660 cm^{-1} region (–C=N–).

On the basis of the facts given above, it is possible to put forward the following scheme for the reactins of NL with ammonia:

$$\text{NL}-COOH+NH_4OH \rightarrow \text{NL}-COONH_4+H_2O$$

$$\text{NL}-C=O+NH_4OH \rightarrow \text{NL}-\underset{\displaystyle OH}{\overset{\displaystyle NH_2}{\overset{|}{\underset{|}{C}}}}+H_2O$$

$$\text{NL}-C=O+NH_2OH \rightarrow \text{NL}-C=NH+H_2O$$

The molecular weight of the NA determined by sedimentation in an ultracentrifuge [5] was ≈70,000. The degree of polydispersity was established by gel chromatography on Sephadex G-75. Water was used as the eluent and solvent. The eluogram showed that the NA was polydisperse.

On the basis of its viscosity and electrical conductivity, the polymer NA that we obtained can be assigned to the class of polyelectrolytes.

It was established in the phytotoxicology laboratory of the Institute of the Chemistry of Plant Substances of the Academy of Sciences of the USSR that NA stimulates the growth of plants, but its activity is no better than that of the commonly used stimulator, succinic acid.

EXPERIMENTAL

Preparation of the Products of the Interaction of Nitrolignin with Ammonia. With stirring, 25 ml of 25% aqueous ammonia was added over 15 min to 100 g of nitrolignin. The reaction took place with the evolution of heat and with the formation of a past product which, after drying (up to temperatures of 100°C) was converted into a dark brown powder in 100% yield. Elementary and functional comositions of the NA obtained (%): C–50.78; H–5.38; N–8.39; OCH_3–1.29; OH_{tot}–4.44; CO–3.51; COOH–0.7; N_{NH_2}–4.17; N_{NO_2}–2.35; N_{res}–1.87. THe functioonal-group analysis was performed by a standard method [6].

Determination of Amine Nitrogen [7]. To a solution containing 2-5 ml of the substance under investigation were added 15 ml of 25% CH_3COOH solution and then 1.5 ml of 30% $NaNO_2$ solution. The evolution of oxides of nitrogen began. Shaking the reaction mixture intensified

the reaction, and after 3 min the deamination process was practically complete. To determine the oxides of nitrogen and to neutralize them, they were passed over 10-15 ml of a solution of potassium permanganate. The end of the reaction was judged from the color of the permanganate (decoloration). The nitrogen content was calculated from the amount of gas evolved [8].

Viscosity and electrical conductivity were determined by literature methods [9, 10].

The IR spectrum was taken on a UR-20 instrument under identical conditions (sample weight 2 mg) in tablets with KBr.

SUMMARY

The product of the interaction of nitrolignin with ammonia has been obtained. Its semiempirical formula has been calculated.

It has been established by sedimentation and gel chromatograhy that the compound is polydisperse with a molecular weight of approximately 70,000.

The substance is distinguished by a high nitrogen content and complete solubility in water, and it is biologically active.

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