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HYDROGENOLYSIS OF RICE HUSK PROTOLIGNIN. II

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It has been established that the partial hydrogenolysis of rice husk protolignin (RHP) takes place at a temperature of 180°C and an initial hydrogen pressure of 10 atm in an alkaline medium. Conditions have been selected under which the greatest yield of low-molecular-weight products (91% on the Komarov lignin) is obtained: hydrogenolysis in an alkaline medium in the presence of an anthraquinone (AQ) catalyst. The addition of AQ increases the yield of low-molecular-weight products by a factor of 1.8. Semiempirical formulas have been derived for incompletely hydrolyzed lignin residues. A study of the molecular-weight distribution of these lignins has shown that they are polydisperse. It has been established that in the process of hydrogenolysis AQ promotes the demethoxylation of structural units with syringyl nuclei.

It is known that the presence of anthraquinone (AQ) in the alkaline hydrolysis of lignin intensifies the breakdown of the macromolecule to low-molecular-weight products [1, 2]. By catalyzing the cleavage of β-alkyl aryl ether bonds, AQ, in addition, is capable of interacting with certain structural fragments of the lignin (of the p-hydroxybenzyl alcohol type), thereby decreasing the process of condensation. However, in this case it behaves not as a catalyst but as a reagent that is consumed in the course of the reaction [3].

The presence of oxygen lowers the concentration of active reduced forms of AQ and has an adverse effect on the course of delignification [1]. Therefore, by excluding the action of oxygen and performing the reaction in hydrogen which, by exerting a reducing action, also prevents condensation, one may expect an increase in the yield of low-molecular-weight products [4]. A number of investigations devoted to the hydrogenolysis of lignins have been reported in the literature. Some of them were directed to studying the structure of lignin while others had an applied nature — the preparation of the products of the degradation of lignin that may be a source of liquid fuel, chemical reagents, biologically active substances, etc. [5].

The aim of the present work was to study the alkaline hydrogenolysis of rice husk lignin in the presence of AQ and without it in hydrogen in order to obtain information on the structure of this lignin and to reveal biologically active substances among the combined products.

The results obtained when the reaction was performed in an atmosphere of hydrogen in the presence of AQ (I) were compared with those of alkaline hydrolysis without AQ in hydrogen (II) and without AQ in air (III). The yields of low-molecular-weight lignin degradation products are given below (% on the Komarov lignin).

Conditions of extraction	Reaction conditions		
	I	II	III
pH 8, ethereal extract	34.1	19.5	8.3
pH 2, ethereal extract	26.5	27.9	34.5
pH 2, ethyl acetate extract	30.8	15.2	8.3
Total low-molecular-weight products	91.4	62.6	51.1

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As we see, alkaline hydrolysis in hydrogen is accompanied by a 1.2-fold increase in the yield of low-molecular-weight lignin degradation products, i.e., it is possible to speak of a cleaving action of hydrogen on the lignin macromolecule under these conditions. The addition of AQ affects the degradation of lignin still more strongly — the yield of low-molecular-weight compounds increased by a factor of 1.8 in comparison with an alkaline cook (III) and exceed 90% on the Komarov lignin.

The nature of the molecular-weight distribution curves of ethereal extracts at pH 8 and 2 and of ethyl acetate extracts obtained with the aid of gel chromatography on Sephadex LH-20 (ethanol—water (9:1)) shows that the extracts obtained at pH 8 consisted mainly of monomers with a small amount of dimers. On extraction from an acidified solution (pH 2) both in the ethereal and in the ethyl acetate extracts an increase in the proportion of products with higher molecular weights (dimers, trimers, oligomers) was observed in the experiment with the addition of AQ (I).

The ethereal extracts (pH 8), containing mainly monomers, were studied by the GLC method. The monomeric composition of the lignin cleavage products are given below (% on the Komarov lignin):

Substance	Retention time, min	*I*	*II*	*III*
Phenol	11	1.3	1.3	0.4
Guaiacol	18	11.1	4.7	1.8
p-Hydroxyphenylethane	22	1.7	1.3	0.4
p-Hydroxyphenylpropane	32	13.3	5.1	1.6
p-Hydroxyphenylpropan-1-ol	52	0.4	1.8	0.1
Guaiacylpropane	47	2.6	0.7	0.2
Guaiacylpropan-1-ol	77	1.9	1.8	—
Guaiacylethane	36	—	—	1.2
Syringylpropane	96	—	3.3	1.7
p-Coumaryl: guaiacyl:syringyl	—	1.07 : 1 : 0	1.30 : 1 : 0,45	0.77 : 1 :0.51

By comparing the ratios of the structural units of the monomeric fraction after an alkaline cook (III) with those of the nitrobenzene oxidation of rice husk dioxane lignin (RDL) (p-coumaryl:guaiacyl:syringyl 0.1:1:0.4 [6]) and after cleavage of the RDL with sodium in liquid ammonia (0.73:1:0.79, respectively [7]), we see that in all these cases all three types of structural units of the lignin were present, with the guaiacyl type predominating. When alkaline hydrolysis was performed in hydrogen (II), the cleavage of the lignin into low-molecular-weight products took place more profoundly. In the presence of hydrogen, the cleavage and the hydrogenation of the lignin macromolecule took place simultaneously, the hydrogen in some degree promoting the demethoxylation of the structural units of the lignin. Because of this, the proportion of syringyl components decreased and the amount of p-coumaryl components increased.

In hydrolysis, part of the lignin passed into the alkaline solution, but it precipitated on acidification. It was subjected to purification by reprecipitation in ether from aqueous dioxane solution.

The composition of the phenylpropane structural unit was calculated on the basis of elementary and functional analyses. A comparison was made of the formulas of the lignins obtained on alkaline hydrolysis under the given conditions I, II, and III with a formula close to natural rice husk dioxane lignin (RDL):

I

$$C_9H_{9,48}O_{2,50}(OCH_3)_{0.62}(OH_{al})_{0,62}(OH_{phe})_{0,51}(O_{CO})_{0,25}(OOH_{COOH})_{0,07},$$

II

$$C_9H_{8,43}O_{2,70}(OCH_3)_{0,73}(OH_{al})_{0.60}(OH_{phe})_{0,48}(O_{CO})_{0,31}(OOH_{COOH})_{0,07}$$

III

$$C_9H_{8,04}O_{1,13}(OCH_3)_{0,77}(OH_{al})_{0,69}(OH_{phe})_{0,30}(O_{CO})_{0,30}(OOH_{COOH})_{0,09}$$

RDL

$$C_9H_{7,57}O_{1.13}(OCH_3)_{0,93}(OH_{al})_{0,89}(OH_{phe})_{0,33}(O_{CO})_{0,31}$$

A comparison of the semiempirical formulas of these lignins with RDL showed an increase in the amount of hydrogen from 7.57 in the RDL to 9.45 in the lignin I. In combination with the decrease in the amount of carbonyl groups in lignin I, this fact can be explained by the

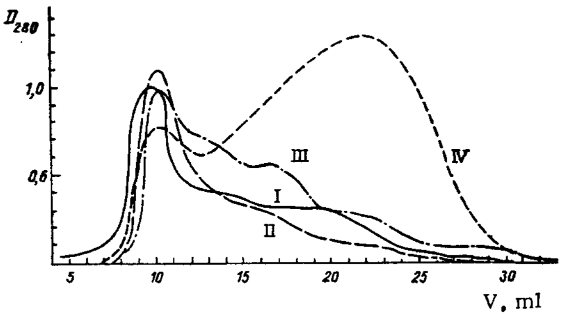

Fig. 1. Curves of the molecular-weight distribution of lignins I, II, and III, and RDL (IV).

assumption that at a high temperature under the action of hydrogen and AQ partial hydrogenolysis of the lignin took place.

The increase in the amount of phenolic hydroxyls in lignins I and II can be explained by the cleavage of β-O-4-ether bonds taking place during hydrogenolysis in an alkaline medium in the presence of hydrogen even without a catalyst: the addition of AQ intensifies this process.

The IR spectra of the lignins obtained showed bands characteristic of a benzene ring with substituents (1510, 1600, 1470 cm^{-1}) and of hydroxy (3450 cm^{-1}), carbonyl (1720 cm^{-1}), methoxy (1330 cm^{-1}), and ether (1280, 1230, 1040 cm^{-1}) groups. In the lignin obtained on alkaline hydrolysis in the presence of AQ in hydrogen a decrease was observed in the intensity of the absorption band of carbonyl groups, which is explained by the partial hydrogenation of the CO groups under these conditions.

A study of the molecular-weight distribution of lignins I, II, and III performed on Sephadex G-75 (with dimethyl sulfoxide as solvent and eluent) (Fig. 1) showed an increase in the proportion of the higher-molecular-weight fraction in the lignins obtained by alkaline hydrolysis in hydrogen with the addition of AQ (I) and in alkaline hydrolysis in hydrogen (II) as compared with the lignin obtained in an alkaline cook in air (III), and particularly with the RDL (IV).

In all the experiments the residue after hydrolysis consisted of a yellowish powder the yield of which was always roughly the same (∿24%). After the residue had been bleached with potassium permanganate and oxalic acid, a finely disperse homogeneous cellulose was obtained with a low degree of polymerization, 95-117.

EXPERIMENTAL

Hydrogenolysis of Rice Husks. Comminuted rice husks that had been extracted with ethanol-benzene and washed with hot water (50 g) were placed in a 1-liter rotating autoclave, 500 ml of 8% aqueous NaOH solution was added, hydrogen was pumped in to a pressure of 10 atm, and the autoclave was heated at 180°C for 2 h (II). In the experiment using a catalyst, 50 mg of anthraquinone (0.1% of the weight of the raw material) was added (I). Experiment (II) was performed without a catalyst at an initial atmospheric pressure of air. The subsequent treatment of the reaction mixtures was the same for all three cases. After the end of the reaction, the residue (12 g) was separated off, washed with water to neutrality, and bleached by the method of [8]. The filtrate, combined with the wash-waters, was acidified to pH 8 and extracted with ether. Then it was acidified to pH 2 and was extracted with ether and with ethyl acetate.

The lignin that precipitated on acidification was separated by centrifugation, dried, dissolved in dioxane–water (9:1) and precipitated in absolute ether. The yields of the purified lignins obtained under conditions I, II, and III amounted to 1.0, 4.2, and 5.8 g, respectively. The purified and dried lignins were analyzed by a standard procecure [9].

The ethereal extract obtained at pH 8 was analyzed by GLC under the conditions described in [2].

CONCLUSIONS

1. Rice husk protolignin undergoes partial hydrogenolysis at a temperature of 180°C and an initial hydrogen pressure of 10 atm in an alkaline medium.

2. The maximum yield of rice husk lignin cleavage products amounted to 91% on the Komarov lignin, on the addition of 0.1% of anthraquinone referred to the initial raw material, which increases the yield of low-molecular-weight products by a factor of 1.8.

3. In the process of hydrogenolysis, anthraquinone promotes the demethoxylation of the structural units of lignin with syringyl nuclei.

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CLEAVAGE BY SODIUM IN LIQUID AMMONIA OF KENAF LIGNINS AND THE BIOLOGICAL ACTIVITY OF THE CLEAVAGE PRODUCTS

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The natural lignin of kenaf stems and fractions of the dioxane lignin of kenaf stems isolated previously were cleaved by sodium in liquid ammonia in order to study their structure. It was established that the kenaf lignins consist of three types of structural units: p-coumaryl, guaiacyl, and syringyl, with a predominance of the guaiacyl types. An antioxidation activity of the monomeric products of the degradation of the kenaf lignins has been found.

The fractionation of kenaf dioxane lignin (KDL) has been reported previously [1]. The fractions obtained were fairly homogeneous and differed considerably in molecular weight. In the present paper we give the results of the cleavage by sodium in liquid ammonia of fractions of kenaf lignin. For comparison, the natural lignin (a flour of kenaf stems) was also cleaved. The yields of cleavage products are given below (the values marked with asterisks are given as percengages of the Komarov lignin, and the others as percentages of the weight of the lignin):

Sample	Sum of the monomeric phenols, pH 8	Sum of the phenolic substances, pH 2
Natural lignin	14,6*	51,68*
KDL, initial	15,92	18,95
KDL-1F	11,39	19,83
KDL-2F	13,01	20,85
KDL-3F	13,94	14,22
KDL-4F	19,94	21,69
KDL-5F	23,39	29.90
KDL-6F	24,56	28,90

The yields of monomeric cleavage products increased on passing from KDL-1F to KDL-6F, which permits us to conclude that the degree of condensation decreases on passing from the first fraction to the sixth.

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