

## HYDROGENOLYSIS OF RICE HUSK LIGNIN. IV

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*The hydrogenolysis of rice husk protolignin and of rice husk hydrolysis lignin in the presence of catalyst D-101, which is used in the hydrocracking of petroleum, has been studied. A substantial amount of products with syringyl structures has been found in the lignin cleavage products. The hydrogen content of the hydrol lignins isolated was considerably higher than that of the analogous lignins obtained on hydrogenolysis with the use of other catalysts.*

Hydrogenolysis is the process of cleaving — in the present case — lignin under the action of  $H_2$ . In it the rupture takes place not only of  $\beta$ -alkylaryl ether bonds but also of C—C bonds, as we have shown previously on compounds modeling lignin [1]. Partial hydrogenation takes place in parallel.

We have previously studied the hydrogenolysis of rice husks (as a source of lignin) in the presence of various catalysts, such as copper chromite, D-48, anthraquinone, and D-70 [1–3]. The action of these catalysts on the process of hydrogenolysis differs. Depending on the properties of the catalyst, the products can be used in different ways. If the catalyst has a powerful action with the cleavage of a large amount of lignin and a high yield of low-molecular-mass substances but, at the same time, secondary structural changes take place in the substances obtained [1, 3], it is desirable to use this catalyst for the purpose of obtaining the total phenols with their subsequent use for the production of, for example, phenol-formaldehyde resins. If, on the other hand, the use of the catalyst leads to a good yield of low-molecular-mass products and the structures of these substances are preserved, hydrogenolysis with this catalyst may be suitable for determining structural fragments of lignin [5]. The search for new catalysts for the hydrogenolysis of lignin and the study of their properties is therefore a fairly urgent problem.

In the present paper we consider the process of hydrogenolysis in the presence of the new catalyst D-101, which consists of a mixture of polyvalent metals modified by additions of alkaline-earth metals. With the aid of this catalyst we have carried out the hydrogenolysis of the protolignin of rice husks (RHs) and of rice husk hydrolysis lignin (RHHL). The reaction was performed in dioxane, so that the cleavage products passed directly into solution.

On the hydrogenolysis of RHs, 26.9% of the cleavage products passed into the dioxane, but only some of them were of phenolic nature. After treatment with alkali and successive extraction with hexane and ether, we isolated the phenolic substances produced by the cleavage of the lignin; the total hexane-soluble phenols — 7.7% from the Komarov lignin (KL); the total ether-soluble phenols — 30.7% on the KL; and the hydrol lignin — 31.2% on the KL. Thus, the yield of split-out phenolic substances after the hydrogenolysis of the RHs amounted to 69.6% of the KL. On comparing these results with those of hydrogenolysis using catalyst D-70, which is a catalyst of the same type as the one we have used in this case [1], we see a considerable decrease in the amount of lignin cleaved (it was 99%).

The ether and hexane extracts were analyzed by GLC (Table 1). As can be seen from Table 1, the total phenols had a fairly rich composition and, in contrast to the total phenols obtained by hydrogenolysis with the catalyst D-70, they contained a considerable amount of guaiacyl and syringyl components (in the preceding case, no syringyl components whatsoever were observed). Consequently, it may be assumed that, under these conditions, using D-101, syringyl structures behave in a fairly stable manner. The presence, in the hydrogenolysis cleavage products, of such substances as cresol and creosol indicates a

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TABLE 1. Products of the Hydrogenolysis of the RH Protolignin

Substance	Amount, % of total	
	ether	hexane
Phenol	5,0	0,5
Cresol	7,4	0,7
Guaiacol	5,2	3,9
p-Hydroxyphenylethane	11,5	26,1
Creosol	2,6	5,1
p-Hydroxyphenylpropane	3,5	—
Guaiacylethane	5,7	42,5
Guaiacylpropane	1,9	10,0
Guaiacylpropan-1-ol	11,5	6,3
Syringylpropane	28,0	5,0
Unidentified	17,7	—
p-Coumaryl:guaiacyl:syringyl	1,02:1:1,04	0,40:1:0,07

TABLE 2. Products of the Hydrogenolysis of the RHHL

Substance	Amount, % on the total	
	ether	hexane
Phenol	10,4	0,6
Cresol	3,6	—
Guaiacol	7,2	4,5
p-Hydroxyphenylethane	21,2	23,6
Creosol	—	7,4
p-Hydroxyphenylpropane	5,5	6,0
Guaiacylethane	4,9	24,8
Guaiacylpropane	3,1	2,5
Guaiacylethan-1-ol	2,3	10,7
Guaiacylpropane-1-ol	9,0	9,2
Syringylpropane	10,3	8,0
Unidentified substances	22,5	2,7
p-Coumaryl:guaiacyl:syringyl	1,53:1:0,40	0,51:1:0,14

destruction of the lignin components at the  $\alpha,\beta$ -C—C bonds of the side chain, as well. The hydrol lignin that precipitated during the isolation of the low-molecular-mass phenols and consists of a product of the incomplete degradation of the lignin was analyzed. It was found that its hydrogen content was far higher than in the analogous lignin obtained on hydrogenolysis with the catalyst D-70. The catalyst that we used probably promotes hydrogenation, in the main.

On the basis of its elementary composition we calculated a short semiempirical formula for the hydrol lignin obtained:  $C_9H_{13.65}O_{3.49}(OCH_3)_{0.42}$ . From this it is possible to judge the processes that occurred on hydrogenolysis. In the first place there was hydrogenation; in the second place the presence of a fairly high level of  $OCH_3$  groups indicates that the syringyl structures present in the lignin, which are usually demethoxylated under severe conditions, behaved in relatively stable fashion in the present case. This is in harmony with the presence of a considerable amount of syringylpropanol in the ether and hexane extracts.

When the rice husk hydrolysis lignin was hydrogenolyzed, it was found that 15.4% of the initial raw material passed into the dioxane. After treatment of the dioxane-soluble products, the phenolic substances were isolated: total hexane-soluble phenols — 2.0% on the KL; total ether-soluble phenols — 8.0% on the KL; hydrol lignin — 8.0% on the KL.

Thus, the total yield of phenolic substances obtained as a result of the hydrolysis of the RHHL was 18.0% of the KL. The compositions of the hexane and ether extracts are given in Table 2.

In these totals, it is true, syringyl components were again present less intensively than in the products of the hydrogenolysis of the RHs. Here, p-coumaryl structures predominated. A short semiempirical formula of the hydrolysis lignin isolated was calculated on the basis of the results of elementary analysis:  $C_9H_{8.52}O_{2.77}(OCH_3)_{0.87}$ . The high content of  $CH_3O$

groups in the hydrol lignin is possibly connected with a secondary methylation of the liberated hydroxy groups by the methyl alcohol formed as the result of hydrogenolysis from the lignin itself.

On the basis of the results of the hydrogenolysis of RHs using the new catalyst D-101 it may be concluded that, although the degree of cleavage of the lignin had decreased in comparison with the action of the catalyst D-70, at the same time the process took place more mildly, with the retention of syringyl structures. Consequently, the low-molecular mass phenolic substances obtained and identified can be used for creating fragments of the lignin structure.

## EXPERIMENTAL

**Hydrogenolysis of Rice Husks.** A 1-liter autoclave was charged with 50 g of rice husks that had been extracted with a mixture of alcohol and benzene and had been washed with hot water, and, after the addition of 10 g of catalyst D-101 and 500 ml of dioxane, H<sub>2</sub> was pumped in to a pressure of 5.0 Pz MPa and the whole was heated at 250°C for 2 h. After the end of the reaction, the residue was separated off and was washed with dioxane. The dioxane solution was evaporated. The resulting resinous product was dissolved in 2% aqueous NaOH, and the solution was acidified with HCl to pH 3 and extracted with hexane and ether. The hexane and ether extracts were analyzed by GLC under the conditions described in [4].

The hydrogenolysis of the RHHL and the treatment of the hydrogenolysis products were carried out similarly.

Elementary composition of the hydrol lignins, %: RHs — C, 58.34; H, 7.84; O, 33.82; OCH<sub>3</sub>, 9.22; RHHL — C, 62.93; H, 5.95; O, 31.12; OCH<sub>3</sub>, 14.69

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