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# HYDROGENOLYSIS OF RICE HUSK LIGNINS

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*The hydrogenolysis of the protolignin, the hydrolysis lignin, and the dioxane lignin of rice husks in the presence of demethylated lignin as catalyst has been studied. The breakdown of the lignins into low-molecular-mass compounds took place with yields comparable with those obtained by hydrogenolysis using other catalysts.*

Interest in the processes taking place in the reductive degradation of lignin macromolecules catalyzed by various catalysts is due, on the one hand, to the possibility of their use for structural investigations and obtaining information on the nature of the bonds between the units of the lignin molecule and, on the other hand, to the search for possibilities of obtaining valuable low-molecular-mass compounds from lignin [1].

The choice of catalyst plays an important role in the study of the characteristic features of lignin hydrolysis. A large number of publications are known in which the influence of the composition and amount of catalyst on the yield and qualitative composition of the products of the cleavage of lignin by hydrogenolysis have been considered. We have also studied the influence of catalysts on the course of this reaction for rice husk lignin [2-5]. For a catalyst to work in our system it must either possess redox properties or form transition complexes stabilizing the intermediate products of the breakdown of the lignin. The catalysts that we have used previously – salts of metals with variable valence (copper chromite), anthraquinone, and fused oxide catalysts provided for us by workers of the catalysis laboratory of VNIKhTIMP — satisfy these requirements. We have now turned our attention to studies in which, with some method or other of cleaving lignin, demethylated lignin (DML) was used as catalyst [6-8]. The catalytic activity of DML is probably connected with the presence of a considerable amount of quinoid structures, which are initiators of the cleavage of the ether bonds of lignin. We therefore decided to use DML as catalyst in the hydrogenolysis of some rice husk lignins, namely: protolignin, hydrolysis lignin, and dioxane lignin.

**The hydrogenolysis of rice husk protolignin** was carried out under conditions analogous to those of hydrogenolysis using anthraquinone as catalyst [3], this being replaced by DML. The total yield of lignin cleavage products amounted to 74.3% of the Komarov lignin, and of these 7.0% passed into an ether (pH 8) extract, 17.2% into an ether (pH 2) extract, and 31.4% into an ethyl acetate extract, while 18.7% was hydrol lignin. Of the extracts obtained, the richest in phenolic ethers was the ether (pH 8) extract, and its composition was studied by GLC and is given in Table 1.

The amounts of *p*-coumaryl [sic]; and guaicyl structures were approximately the same. The absence of syringyl structures is connected with demethoxylation taking place under the given conditions. The formation of alcohol groups in the side chains is explained by the cleavage of ether bonds under the action of the catalyst and the subsequent reduction of benzyl alcohols, leading to propanol and ethanol derivatives. The formation of propane and ethane derivatives proceeds through the formation of quinone methides, the loss of $H_2O$, and subsequent reduction [9].

The ethyl acetate extract consisted of a mixture of monomeric and oligomeric lignin cleavage products. Of monomeric phenols we determined phenol, cresol, guaiacol, and *p*-hydroxyphenylpropane. The composition of the hydrol lignin was calculated from the results of elementary analysis: $C_9H_{9.82}O_{2.94}(OCH_3)_{1.11}$. The increased $H_2$ content showed the hydrogenation taking place under the given conditions. The fairly high content of $OCH_3$ groups indicated that the hydrol lignin was formed from the natural protolignin, which also has a high content of methoxy groups.

**The hydrogenolysis of the rice husk hydrolysis lignin** in the presence of DML was conducted under conditions analogous to those for the hydrolysis of rice husk protolignin. The total yield of cleavage products amounted to 29.0%, of

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TABLE 1. Phenolic Composition of the Products of the Cleavage of Lignin by Hydrogenolysis, % of the Total

| Compound | RL | HLRL | | DLARL |
|---|---|---|---|---|
| | ethereal extract, pH | | | |
| | 8 | 8 | 2 | 8 |
| Phenol | 6.8 | 13.1 | 20.6 | 0.5 |
| Guaiacol | 18.1 | 41.9 | 4.5 | 1.6 |
| Cresol | 12.0 | 2.1 | 3.1 | — |
| Creosol | 7.5 | — | — | — |
| *p*-Hydroxyphenylethane | 21.3 | 2.4 | 6.0 | 23.8 |
| *p*-Hydroxyphenylpropane | 4.8 | — | 6.2 | — |
| Guaiacylethane | 5.0 | 4.4 | — | 34.1 |
| Guaiacylpropane | — | — | 59.6 | 3.1 |
| 1-Guaiacylethanol | 9.4 | — | — | 3.2 |
| 1-Guaiacylpropan-1-ol | 4.9 | 10.4 | — | 5.0 |
| 3-Guaiacylpropan-1-ol | 10.2 | 25.7 | — | 17.4 |
| Syringylpropane | — | — | — | 5.3 |

which 4.4% passed into an ether (pH 8) extract, 8.3% into an ether (pH 2) extract, and 9.2% into an ethyl acetate extract, while 7.1% was hydrol lignin. In contrast to the preceding case, on extraction with ether at pH 8 and 2 a redistribution of the phenols took place: at pH 8 the total included a considerable amount of guaiacol, and at pH 2 more than half the ethereal extract consisted of guaiacylpropane. The hydrol lignin obtained in the course of the isolation of the products of the hydrogenolysis of the HLRL had the following formula: $C_9H_{10.43}O_{4.24}(OCH_3)_{0.78}$. Here, again, hydrogenation had taken place, and the fairly high $OCH_3$ group content, uncharacteristic of natural lignins, is possibly connected with the secondary methylation by $CH_3OH$ of the hydroxy groups liberated in the hydrogenolysis process.

**The hydrogenolysis of the rice husk dioxane lignin** was conducted in the presence of DML as catalyst under conditions analogous to the preceding ones. Under these conditions, the dioxane lignin was cleaved almost completely. An ether (pH 8) extract amounted to 28.0%, an ether (pH 2) extract to 20.0%, and an ethyl acetate extract to 26.0%, and there was 26.0% of hydrol lignin. The composition of the extracts of phenolic cleavage products was established by GLC analysis.

The most diverse in composition was the ether (pH 8) extract of phenols. With a predominance of guaiacyl derivatives, here a small amount of syringyl structures was even found. In the initial dioxan lignin, the closest to natural lignin, the content of $CH_3O$ groups was fairly high, which presupposed the presence of syringyl structures in it and also, quite probably, that a small part of them was retained even under the conditions of hydrogenolysis, although a demethoxylation process was observed in this case, also: a comparison of the formulas of the initial dioxane lignin and the hydrol lignin obtained by its hydrogenolysis showed a considerable decrease in the amount of $CH_3O$ groups: $C_9H_{10.92}O_{3.45}(OCH_3)_{0.75}$.

Thus, on the use of DML as catalyst in hydrogenolysis the cleavage of lignin takes place with yield comparable to those obtained by the use of other catalysts, and since it is simple and cheap to obtain DML from hydrolysis lignin — a waste product of the hydrolysis industry — the use of DML as a catalyst is completely acceptable.

## EXPERIMENTAL

Demethylated lignin was obtained by the procedure described in [10]. The hydrogenolysis of the rice husk protolignin, hydrolysis lignin, and dioxane lignin was conducted by the procedure described in [3], with the replacement of anthraquinone by demethylated lignin in an amount of 1% on the initial raw material.

The extracts of low-molecular-mass phenolic substances were analyzed by GLC on a Chrom-4 instrument under the conditions described in [11].

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