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HYDROGENOLYSIS OF THE *G. GLABRA* LIGNIN

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Summary. *The structure of the licorice lignin was studied with the help of hydrogenolysis using polymetallic catalyst. Hexane and ether extracts of the products of the lignin hydrogenolysis were investigated with the help of GLC. The semi empiric formula of hydrolignin was calculated on the basis of elementary and functional analysis.*

Key words. *Glycyrrhiza glabra, lignin, hydrogenolysis, hydrolignin, grassy plants.*

Licorice (Glycyrrhiza glabra, local name is “boyan”) is the characteristic plant for the flora of Central Asia and known as a medicinal plant for a long time [1]. There are 13 species of licorice on the territory of CIS. [1,2]. It should be noted that the licorice root is exported to a number of countries (France, Czech Republic, Cuba, Germany, etc.) from Uzbekistan. After extraction of a licorice root at the plants there is a large number of a vegetable wastage. Based on the foregoing, a chemical study of licorice wastage is an actual.

Studying the structures of lignin – is one of the important problems in the area of the natural polymers. The structure of lignin can be elucidated by the destruction of lignin under the action of hydrogen; the method called hydrogenolysis.

There is a number of the works devoted to reaction of hydrogenolysis of a lignine in literature. One of them are directed to studying of a lignine structure, others have the applied nature of receiving products of a destruction of a lignine which can be a source of liquid fuel, chemical reagents, biologically active materials.

The Japanese scientists by method of hydrogenolysis about 28 dimer and several trimeric compounds from a spruce lignine were succeeded to isolate and prove the structures. The combination of these compounds gave a fragment which shows a possible structure of a lignin [3-4].

At hydrogenolysis the polymetallic catalyst is being used as reagent which is used also at the hydro cracking of oils. Such catalyst was used for hydrogenolysis of a lignine of a cotton [5], and in this work it was interesting to study effect of the catalyst on a glycyrrhiza lignine.

In this work hydrogenolysis of a natural (non-isolated from raw materials) lignin in the presence of the polymetallic catalyst was carried out. At the same time the dioxane-soluble product contains not only ligninic substances, but also products of a destruction of carbohydrate complexes of a licorice root. Therefore, the content of destruction products of a lignin and dioxane-soluble product is studied. To this end, the total dioxane product was dissolved in a 2% aqueous solution of NaOH and, after

acidification to pH = 3, phenols were removed with hexane and ether (Table 1).

Table 1

The yield of the hydrogenolysis destruction products of natural licorice lignin

Destruction products	Yield, %
Dioxane-soluble products*	31,6
Hexane extract**	12,3
Ether extract**	52,8
Hydrolignin**	24,5
Total % of destruction**	89,6

* - in raw materials, ** - from Komarov's lignin

Apparently from given table 1 that the destruction of native licorice root lignin by hydrogenolysis with the help of polymetallic catalyst is sufficiently deep.

With the help of GLC, hexane and ether extracts of lignin destruction products were examined. Ether extracts consisted generally of phenol and a cresol, and the hexane sums were more various on structures (table 2).

Table 2

The content of hexane licorice roots extract

Substance	**%**
phenol	8,1
cresol	0,7
guaiacol	4,8
p-oxyphenilethane	1,3
creosol	-
guaiacylethane	5,6
guaiacylpropane	2,3
guaiacylethanol-1	5,3
guaiacylpropanole-1	30,6
guaiacylpropanole-3	9,4
not identified	31,9

Guaiacyl structures are dominate in licorice roots hydrogenolysis products. Quite a lot of guaiacyl compounds with alcohol groups in the side chain, which is possible with partial hydrogenation of the available carboxyl and carbonyl groups. The presence of compounds with a shortened side chain indicates the break of the C-C side bonds. The absence of lilac structures in hydrogenolysis products indicates their instability during hydrogenolysis under these conditions using the catalyst used. Hydrgenolysis products of licorice roots can also include hydrolignins, which are the product of the inordinate destruction of lignin.

On the basis of analysis of elements and functional groups the semi-empirical formulas of the phenylpropane structural linkage of the obtained hydrolignins were calculated:

$$C_9H_{9,86}O_{1,33}(OCH_3)_{0,55}(OH_{ф})_{0,44}(OH_{ал})_{0,55}(O_{со})_{0,35}(OOH_{соон})_{0,06}$$

In hydrolignin compared with dioxane lignin, there is a significant decrease in the content of methoxyl groups and an increase in the hydrogen content. This means that in the process of hydrogenolysis using a poly-functional catalyst, demethoxylation of the lilac structures and hydrogen saturation of the resulting phenolic substances take place.

In the IR spectra of the obtained hydrolignines, bands corresponding to the benzene ring with substituents (1510, 1600, 1470 cm^{-1}), hydroxyl (3450cm^{-1}), carbonyl (1720cm^{-1}), methoxyl (1330cm^{-1}) and ether (1280, 1230, 1040 cm^{-1}) were detected.

Thus, in the hydrogenolysis of lignin in the presence of a catalyst, the alkyl-aryl-C-O-C and -C-C bonds are ruptured to structural units of lignin.

Experimental part

A licorice root (50 g), crushed, washed with hot water and extracted with an alcohol-benzene mixture was placed in a rotating autoclave in a capacity of 1 liter, a catalyst (10% by weight of the feedstock) and 500 ml of dioxane was injected, hydrogen was pressurized to 5 MPa and and media heated at 2500 ° C for 2 hours. At the end of the reaction, the mixture was cooled to room temperature, filtered off from the solid residue, and dioxane was distilled off. The dioxane-soluble resinous product was dissolved in a 2% aqueous solution of NaOH. Acidified to pH = 3 and extracted with hexane and ether. These extracts were analyzed by GLC. The precipitated hydrolignines were separated by centrifugation, dried, dissolved in a mixture of dioxane-water (9: 1) and precipitated in abs. ether.

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Rezyume. *Neft gidrokrekingida qullaniladigan gidrogenoliz usuli bilan polimetall katalizator yordamida shirinmiya ildizi ligninlari tuzilishi o‘rganildi. GSX usuli yordamida lignin gidrogenoliz maxsulotlarining geksan va efir ekstraktlari tadqiq etildi. Element va funksional analiz asosida gidroligninning poluempirik formulasi topildi.*

Резюме. *Строение лигнина солодкового корня изучено методом гидрогенолиза, с использованием полиметаллического катализатора используемого при гидрокрекинге нефти. С помощью ГЖХ исследованы гексановые и эфирные экстракты продуктов гидрогенолиза лигнина. На основании элементного и функционального анализа была рассчитана полуэмпирическая формула гидролигнина.*

Kalit so'zlar. *Glycyrrhiza glabra, lignin, gidrogenoliz, gidrolignin, o'tsimon o'simliklar*

Ключевые слова. *Glycyrrhiza glabra, лигнин, гидрогенолиз, гидролигнин, травянистые растения.*