TRITERPENE GLYCOSIDES OF LADYGINIA BUCHARICA

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The roots of Ladyginia bucharica Lipsky, family Umbelliferae, contain a considerable amount of saponins [1, 2] which have not previously been studied chemically. We have investigated the plant collected by S. A. Khamidkhodzhaev in the valley of the River Obikhangau (Darvaza range). The comminuted air-dried roots were defatted with petroleum ether and the glycosides were extracted with methanol. The yield of methanolic extract was 33% of the weight of the initial raw material. To remove the accompanying substances, the methanolic extract was dissolved in water and the combined glycosides were exhaustively extracted with n-butanol. A chromatographic study of the butanolic extract showed that it contained at least five substances of a glycoside nature, which we have called, in order of increasing polarity, "ladyginosides" A, B, C, D, and E.

The most effective systems of solvents for the chromatographic separation of the glycosides of L. bucharica proved to be: 1) butan-1-ol–ethanol–conc ammonia (10 : 2 : 5) and (7 : 2 : 5), and 2) chloroform–methanol–water (65 : 35 : 10).

The combined saponins, purified by reprecipitation, were hydrolyzed with 18% HCl at 70° C for 5 hr. On chromatography in system 3 [chloroform–ethanol (25 : 1)] in a thin layer of silica gel, two products were detected. Column chromatography with elution by the same system of solvents yielded in the individual state a substance with mp 306–308° C, $[\alpha]_D^{20}$ +79° (c 2.5, pyridine). The two products were identified by their chromatographic behavior and IR spectra in comparison with authentic samples of oleanolic acid and hederagenin. The identities were confirmed by the preparation of derivatives, acetates and their methyl ethers, whose constants coincided with literature data [3].

By repeated chromatography of the combined glycosides on columns of silica gel in systems 1 and 2 we succeeded in obtaining two individual products, ladyginosides C and D.

Ladyginoside C. Crystalline substance with mp 224–226° C, $[\alpha]_D^{20}$ –17° (c 1.8, methanol), readily soluble in water, methanol, and aqueous ethanol, and sparingly soluble in 96% ethanol and butanol. The acid hydrolysis of ladyginoside C with Kiliani's mixture yielded oleanolic acid. A chromatographic study of the aqueous part of the hydrolysate on paper in system 4 [butan-1-ol–acetic acid–water (4 : 1 : 5)] showed the presence of D-glucose, L-arabinose, and D-glucuronic acid.

Gas-liquid chromatography showed that the monosaccharides were present in a ratio of 1 : 1 : 1 [4].

Ladyginoside D. White amorphous powder with mp 202–206° C, $[\alpha]_D^{20}$ +5° [c 1.5, methanol–water (1 : 1)]. When this glycoside was subjected to acid hydrolysis, hederagenin was identified as the aglycone, and D-glucuronic acid and D-glucose were found in the hydrolysate.

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