TRITERPENE GLYCOSIDES OF Ladyginia bucharica

V. THE STRUCTURE OF LADYGINOSIDE E

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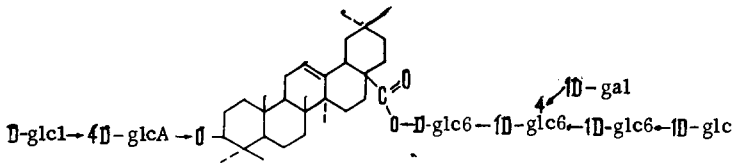
Ladyginoside E, with mp 200-202°C, $[\alpha]_D^{20}$ +6 ± 2° (aqueous methanol, 1 : 1) and ladyginoside F are the most polar triterpene glycosides of the roots of Ladyginia bucharica Lipsky [1]. The structure of ladyginoside F has been established previously [2].

On acid hydrolysis, ladyginoside E forms oleanolic acid, D-glucose, D-glucuronic acid, and D-galactose in a ratio of 1 : 5 : 1 : 1. There are two carbohydrate chains in the glucoside, one of which is split off on saponification with AV-17 anion-exchange resin (OH^- form) with the formation of ladyginoside A [3]. When ladyginoside E was subjected to periodate oxidation, not one of its monosaccharides escaped degradation, which excludes the possibility of 1 → 3 bonds between them.

When glycoside E was subjected to stepwise hydrolysis with 2% H_2SO_4, among the reaction products we found gentiobiose and a glycoside the sugar composition of which was the same as for ladyginoside D [2]. The exhaustive methylation of ladyginoside E yielded its permethylate. The acid hydrolysis of the latter led to oleanolic acid, 2,3,4,6-tetra-O-methyl-D-glucose, 2,3-di-O-methyl-D-glucuronic acid, 2,3,4-tri-O-methyl-D-glucose, 2,3-di-O-methyl-D-glucose, and 2,3,4,6-tetra-O-methyl-D-galactose. Thus, the qualitative and quantitative composition of the methylated sugars present in ladyginoside E and ladyginoside F proved to be identical. The first two methylated sugars are formed from the carbohydrates of the O-glycosidic moieties of the molecules of the glycosides being compared and correspond to the sugars of ladyginosides A and B [3], and the others must be assigned to the carbohydrates of the O-acyl moiety.

In order to determine the nature of the sugar attached to the carboxy group of the aglycone, the permethylated glycoside E was subjected to reductive cleavage with lithium tetrahydroaluminate, and the reduced products of the methylated bioside and pentasaccharide were isolated. The bioside yielded erythrodiol, 2,3,4,6-tetra-O-methyl-D-glucose and 2,3-di-O-methyl-D-glucose, and the pentasaccharide yielded 2,3,4-tri-O-methyl-D-glucose, 2,3-di-O-methyl-D-glucose, 2,3,4,6-tetra-O-methyl-D-glucose, 2,3,4,6-tetra-O-methyl-D-galactose, and 2,3,4-tri-O-methyl-D-sorbitol.

The results obtained show that the carbohydrate chains in the acyloside moieties of the molecules of ladyginosides E and F have the same structure. The glycosides differ only in their aglycones: the first is a pentaoside of oleanolic acid and the second a pentaoside of hederagenin. Ladyginoside E is represented by the following structural formula:



We have not yet detected an oleanolic acid pentaoside identical with ladyginoside D in the structure of the sugar moiety or a hederagenin trioside corresponding to ladyginoside C [4]. It is not excluded that in a more careful investigation glycosides of such structures may be found.

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LITERATURE CITED

1. M. Patkhullaeva, L. G. Mzehl'skaya, and N. K. Abubakirov, Khim. Prirodn. Soedin., 485 (1970).
2. M. Patkhullaeva, L. G. Mzhel'skaya, and N. K. Abubakirov, Khim. Prirodn. Soedin., 733 (1973).
3. M. Patkhullaeva, L. G. Mzhel'skaya, and N. K. Abubakirov, Khim. Prirodn. Soedin., 466 (1972).
4. M. Patkhullaeva, L. G. Mzehl'skaya, and N. K Abubakirov, Khim. Prirodn. Soedin., 36 (1973).