STRUCTURE OF VITALBOSIDE G FROM Clematis vitalba

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UDC 547.918+547.597

We have previously [1, 2] reported the isolation from Clematis vitalba (traveller's joy) of triterpene glycosides containing ribose.

Below we give results going to prove the structure of vitalboside G (I) [mp 192-194°C, $[\alpha]_D^{20}$ +60° (c 0.67; methanol)]. By gas–liquid chromatography of the sugars in the form of the aldononitrile acetates, in a hydrolyzate of (I) we identified glucose, arabinose, ribose, and rhamnose, present roughly in a ratio of 3:1:1:3.

The aglycone is hederagenin (II). The alkaline hydrolysis of (I) gave a less polar glycoside (III) (mp 228-230°C, $[\alpha]_D^{20}$ −56° (c 0.88; methanol) and an oligosaccharide (IV). Compound (III) contained one mole each of glucose, arabinose, and ribose and two moles of rhamnose. The oligosaccharide (IV) consisted of glucose and rhamnose in a ratio of 2:1. Thus, vitalboside G contains two charbohydrate chains, one of which is attached to the carboxy group and the other to one of the hydroxyls of the aglycone.

To determine the types of bonds between the monosaccharides, the saponin was methylated by Kuhn's method [3] and was further methylated by Purdie's method [4] and was then subjected to methanolysis. By thin-layer and gas–liquid chromatographies in the presence of authentic markers we identified methyl 2,3,4-tri-O-methyl-L-rhamnoside, 2,3,4-tri-O-methyl-L-riboside, 2,4-di-O-methyl-L-rhamnoside, 3,4-di-O-methyl-L-arabinoside, 2,3,6-tri-O-methyl-D-glucoside, 2,3,4-tri-O-methyl-D-glucoside, and 3,6-di-O-methyl-D-glucoside.

The lithium tetrahydroaluminate cleavage of the fully-methylated vitalboside G formed an oligosaccharide consisting of 2,3,4-tri-O-methyl-D-sorbitol, methyl 2,3,6-tri-O-methyl-D-glucoside, and methyl 2,3,4-tri-O-methyl-L-rhamnoside, and also a glycoside which decomposed on acid hydrolysis into methyl 2,3,4-tri-O-methyl-L-rhamnoside, 2,3,4-tri-O-methyl-L-riboside, 2,4-di-O-methyl-L-rhamnoside, 3,6-di-O-methyl-D-glucoside, and 3,4-di-O-methyl-L-arabinoside.

Consequently, the O-acyl glycosidic component of glycoside (I) has the structure L-Rhap-(1→4)-D-Glcp-(1→6)-D-Glcp-(1→.

The sequence of the monosaccharides in the carbohydrate chain at the hydroxy group of the aglycone was established by the partial hydrolysis of the initial saponin with oxalic acid. When the hydrolysis products were separated on silica gel in the ethyl acetate–methanol–water (10:2:3) system, a glycoside (III), a tetraoside (V) [mp 170-172°C, $[\alpha]_D^{20}$ −53° (c 1.15; methanol)]; a trioside (VI) [mp 140-142°C; $[\alpha]_D^{20}$ +50° (c 0.41; methanol)]; a bioside (VII) [mp 130-132°C, $[\alpha]_D^{20}$ +40° (c 0.37; methanol)]; a monoside of hederagenin (VIII) [mp 226-228°C, $[\alpha]_D^{20}$ +58° (c 2.5; methanol)], and hederagenin were obtained.

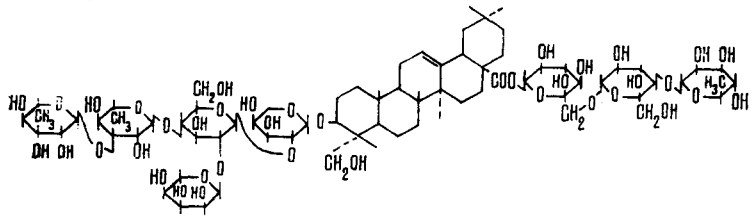
The acid hydrolysis of (VIII) yielded arabinose, and that of (VII) yielded arabinose and glucose. The acid hydrolysis of (VI) gave one mole each of arabinose, glucose, and rhamnose. Thus, the arabinose is attached directly to the aglycone and the glucose is attached to the arabinose. The gas–liquid chromatography of the aldononitrile acetates of the sugars in the hydrolyzate of (V) showed the presence of glucose, arabinose, and rhamnose in a ratio of 1:1:2. After the methanolysis of the methylated tetraoside, methyl 2,3,4-tri-O-methyl-L-rhamnoside, 2,4-di-O-methyl-L-rhamnoside, 3,4-di-O-methyl-L-arabinoside, and 2,3,6-tri-O-methyl-D-glucoside were identified. The results of the methylation of the initial saponin showed that the ribose was attached to the OH group at the C_2 atom of the glucose.

Institute of Chemistry, Academy of Sciences of the Moldavian SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 802-803, November-December, 1974. Original article submitted March 27, 1974.

Consequently, the oligosaccharide attached to one of the hydroxy groups of the hederagenin has the structure

$$\text{Rhap}1\rightarrow 3\text{Rhap}1\rightarrow 4\text{Glcp}1\rightarrow 2\text{Arap}1\rightarrow O-\text{aglycone}.$$
$$\begin{matrix}2\\ \uparrow\\ \text{Ribp}\end{matrix}$$

The results of periodate oxidation agree with those of methylation. In order to establish the localization of the carbohydrate chain attached to the hydroxyl of the aglycone, vitalboside G was oxidized with chromium trioxide as described previously [2]. After the treatment of the aglycone with diazomethane, dimethyl gypsogenate was obtained. By making use of Klyne's rule [5] to determine the configurations of the glycosidic centers, the saponin (I) can be assigned the following structure:



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