STRUCTURE OF VITALBOSIDE D FROM Clematis vitalba

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In the triterpene glycosides from Clematis vitalba L. we have found L-ribose and have established the structure of the main saponin [1, 2]. The present paper gives results going to prove the complete structure of vitalboside D from this plant.

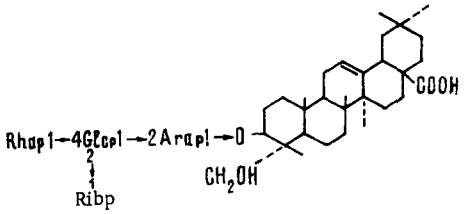
Vitalboside D – mp 180-182°C, $[\alpha]_D^{20}$ –53° (c 1.14; methanol) – is split on acid hydrolysis into glucose, arabinose, ribose, and rhamnose. Gas–liquid chromatography of the aldononitrile acetates estbalished their ratio as 1:1:1:1. Hederagenin, with mp 330-332°C $[\alpha]_D^{20}$ +79° (c.08; pyridine), was identified as the aglycone. Literature data for hederagenin – mp 332-334°C, $[\alpha]_D^{20}$ +81°. Its structure was confirmed additionally by mass spectrometry. On alkaline hydrolysis, vitalboside D underwent no change. Consequently, it is not a O-acyl glycoside.

To determine the types of bonds between the monosaccharides, we methylated vitalboside D by the methods of Kuhn and Purdie [3, 4]. In a methanolizate of the completely methylated saponin – mp 128-130°C, $[\alpha]_D^{20}$ –60° (c 1.15; methanol) – by thin-layer and gas–liquid chromatography we identified methyl 3,4-di-O-methyl-L-arabinoside, 3,6-di-O-methyl-D-glucoside, 2,3,4-tri-O-methyl-L-rhamnoside, and 2,3,4-tri-O-methyl-L-riboside.

After the oxidation of the glucoside by Smith's method, only the glucose residue prove to be undestroyed. The complete structure of the saponin was determined by partial hydrolysis, as a result of which we obtained a monoside (III) with mp 226-228°C, $[\alpha]_D^{20}$ +58° (c 1; methanol); a bioside (IV) with mp 135-136°C, $[\alpha]_D^{20}$ +40° (c 0.37; methanol); and a trioside of hederagenin (V) with mp 140-142°C, $[\alpha]_D^{20}$ +51° (c 1.5; methanol). In the products of the hydrolysis of (III) only arabinose was detected, in the case of (IV) arabinose and glucose, and in the case of (V) rhamnose in addition to these.

The positions of the attachment of the terminal rhamnose and ribose residues with respect to the glucose were established by the methanolysis of a permethylate of the progenin (V). By the GLC method we found methyl 2,3,4-tri-O-methyl-L-rhamnoside, 2,3,6-tri-O-methyl-D-glucoside, and 3,4-di-O-methyl-L-arabinoside. Thus, the terminal ribose in the saponin can be attached only at C_2 of the glucose. The mass spectrum of the vitalboside revealed fragments corresponding to the terminal monosaccharides, to possible di- and trisaccharides, and also to hederagenin arabinoside.

The facts presented show that the structure of vitalboside D is as follows:



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