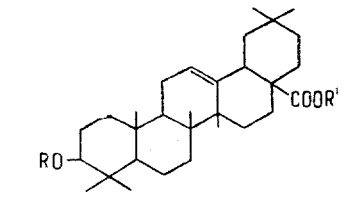
group of oleanolic acid has the structure L-Rha-1→4-D-Gl-1→4-D-Gl-1→6-D-Gl-1→.

In the reduced glycoside of the erythrodiol there was no 2,3,6-tri-O-methyl-D-glucose as there is in the reduced erythrodiol from clematoside B. Clematoside A lacks one of the molecules of glucose located at the end of the carbohydrate chain attached to the carboxy group of oleanolic acid.

A possible structure of clematoside A is expressed by the formula



R'=L-Rha-1→4-D-Gl-1→4-D-Gl-1→6-D-Gl-1→

R=D-Gl-1→4-D-xy-1→2-L-Ar-1→2-L-Ar-1→4-L-Rha-1→

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STRUCTURE OF CLEMATOSIDE B

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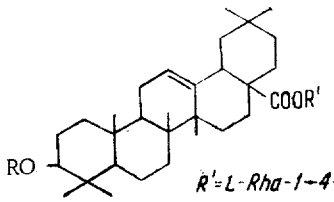
According to refined data, clematoside C [1,2] – a triterpene oligoside from Clematis manshurica Rupr. – must be assigned to the following structure:



R'=L-Rha-1→4-D-Gl-1→4-D-Gl-1→6-D-Gl-1→

R=L-Rha→1-6-D-Gl-1→4-D-Gl-1→4-D-xy-1→2-L-Ar-1→2-L-Ar-1→4-L-Rha-1 (clematoside C)

R=D-Gl-1→4-D-Gl-1→4-D-xy-1→2-L-Ar-1→2-L-Ar-1→4-L-Rha-1→ (clematoside B)

The chromatography on silica gel in the 1-butanol–ethanol–water (10:2:5) system of a butanolic extract of the saponins obtained in the isolation of clematoside C yielded clematosides A', A, and B.

The aglycone of clematoside B (mp 200–202° C, acetate mp 159–161° C) was identified from its melting point, a mixed melting point, and its chromatographic behavior as oleanolic acid, and the carbohydrate fraction was found to contain glucose, arabinose, xylose, and rhamnose. Photocolorimetry of the paper chromatogram showed that these sugars are present in the saponin in a molar ratio of 5:2:1:2. A determination of the molecular weight from the yield of genin gave a figure of 1950, which corresponds approximately to a decaoside of oleanolic acid.

When clematoside B and its acetate were treated with diazomethane with subsequent acid hydrolysis, oleanolic acid and its methyl ester were isolated, which shows the presence of a O-acyl glycoside bond in the saponin.

On periodate oxidation, all the sugars were destroyed.

The data obtained permit the conclusion that the structure of clematoside B is close to that of clematoside C except that a rhamnose residue is lacking from one of the carbohydrate chains.

In actual fact, the aluminum hydride cleavage of methylated clematoside B gave a methylated oligosaccharide which was identified from its constants and its monomeric composition as the oligosaccharide of clematoside C, while the glycoside of the erythrodiol contained 2,3,4,6-tetra-O-methyl-D-glucose, 2,3,6-tri-O-methyl-D-glucose, 2,3,di-O-methyl-L-xylose, 2,3-di-O-methyl-L-rhamnose, and 2 moles of 3,4-di-O-methyl-L-arabinose. The sugars were identified by paper and gas-liquid chromatography.

It is not difficult to see that as compared with the methylated sugars of the erythrodiol glycoside from clematoside C, the analogous product from clematoside B lacks completely methylated rhamnose, while a completely methylated molecule of glucose appears. Apparently the sequence of monosaccharides attached to the hydroxy group of the aglycone in the two glucosides is the same, but clematoside B lacks the terminal rhamnose molecule attached to the hydroxyl at C-3 of oleanolic acid. It is possible that clematoside B is a genetic precursor of clematoside C in the plant.

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