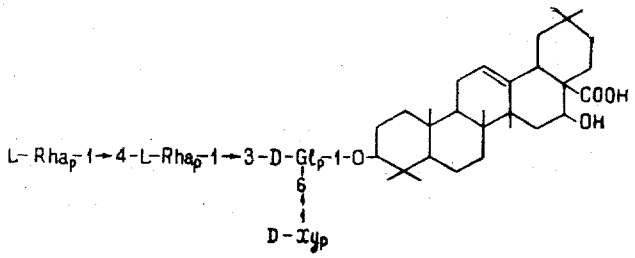
fied as the aglycone, and the monosaccharides glucose, xylose, and rhamnose were found in a ratio of 1:1:2. This amount of monosaccharides was also confirmed by a determination of the molecular weight of the glycoside from the yield of genin, which gave a figure of 1117. The saponification of helianthoside C [1] gave a glycoside with the same R_f value as helianthoside A on chromatography in a thin layer of silica gel. The following reactions were carried out to demonstrate their identity.

Helianthoside A, previously treated with diazomethane, was hydrolyzed. The resulting methyl ester of echinocystic acid showed the presence of a free carboxy group in the glycoside. Then helianthoside A was exhaustively methylated by Kuhn's method and was subjected to acid hydrolysis. This made it possible to identify by paper and gas-liquid chromatography 2,3-di-O-methyl-L-rhamnopyranose, 2,4-di-O-methyl-D-glucopyranose, 2,3,4-tri-O-methyl-L-rhamnopyranose, and 2,3,4-tri-O-methyl-D-xylopyranose. The results of methylation were confirmed completely by those of periodate oxidation. The partial hydrolysis of helianthoside A with dilute sulfuric acid gave the same mixture of glycosides as in the case of helianthoside C.

With respect to their IR spectra, specific rotations, and melting points, helianthoside A and its derivatives coincide completely with the glycoside obtained by the saponification of helianthoside C and its derivatives. Consequently helianthoside A has the structure:



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TRITERPENE GLYCOSIDES OF SAPONARIA OFFICINALIS

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We have studied the roots of Saponaria officinalis L. (bouncingbet; fuller's herb) for their content of saponins. The air-dry material was comminuted, defatted with petroleum ether, and exhaustively extracted with methanol. The yield of extract was 25% (on the weight of the initial raw material).

According to the literature [1], the saponins of S. officinalis contain gypsogenin as aglycone. When the combined saponins were hydrolyzed with 5% hydrochloric acid at 100° C for 5 hr, a substance was isolated the chromatographic behavior and melting point of which did in fact coincide with those of an authentic sample of gypsogenin.

On chromatography in a thin layer of silica gel in the 1-butanol—acetic acid—water (4:1:5) system, four glycosides were detected, which were named in order of increasing polarity saponasides A, B, C, and D.

Using the same solvents in a silica gel column, the most polar glycoside, saponaside D, was isolated; it had mp 241-244° C, $[\alpha]_D^{20}$ + 40° (c 4; water) and was subjected to a detailed chemical study. By comparing its chromatographic behavior with glycosides of known structure [2, 3], it was concluded that saponaside D contained about ten monosaccharides. In an acid hydrolysate, paper chromatography showed the presence of galactose, glucose, arabinose, xylose, fucose, rhamnose, and glucuronic acid.

When saponaside D was subjected to periodate oxidation and subsequent acid hydrolysis, only fucose, xylose, and glucuronic acid escaped destruction.

Preliminary information on the analysis of the products of the hydrolysis of the methylated glycoside has enabled us to show that it contains three monomethyl sugars, which indicates an unusually high degree of branching of the carbohydrate components of saponaside D.

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THE STRUCTURE OF CLEMATOSIDE A'

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In the present paper we report the determination of the structure of a compound that we have found in Clematis manshurica Rupr. [1-3]—clematoside A' [mp 176-179° C, $[\alpha]_D^{20}$ −31° (c 5; CH_3OH); acetate with mp 149-151° C, $[\alpha]_D^{20}$ −1.9° (c 5; CH_3OH)], which is a pentaoside of oleanolic acid.

The saponin was isolated by chromatography on silica gel by the method described previously [1, 3]. When clematoside A' was subjected to acid hydrolysis, glucose, xylose, arabinose, and rhamnose (1 : 1 : 2 : 1) were identified in the carbohydrate fraction. The monosaccharides were determined quantitatively by the paper chromatography of the hydrolysate of the glycoside and the subsequent photocolorimetric determination of the optical density of the eluates of the spots obtained on the chromatograms.

The molecular weight of the saponin (1170) was determined from the yield of genin. Hydrolysis of the glycoside after its treatment with diazomethane permitted the isolation of methyl oleanolate, which shows the absence of a carbohydrate chain from the carboxy group of the aglycone. This was also confirmed by the treatment of clematoside A' with alkali, which left the saponin unchanged.

The chromatographic behavior, IR spectra, and specific rotation, of clematoside A' was identical with that of the glycoside obtained by the alkaline hydrolysis of clematoside A. A similar comparison of their acetates showed that the latter were identical.

When methylated clematoside A' ($[\alpha]_D^{20}$ −14°) was decomposed, 1 mole each of 2,3,4,6-tetra-O-methyl-D-glucose, 2,3-di-O-methyl-D-xylose, and 2,3-di-O-methyl-L-rhamnose and 2 moles of 3,4-di-O-methyl-L-arabinose were identified by gas-liquid chromatography. This was also confirmed by paper and thin-layer chromatography. The methylated monosaccharides proved to be identical with the methylated sugars of the glycoside erythrodiol obtained from methylated clematoside A after its decomposition with lithium aluminum hydride. The results of methylation agree with those of the periodate oxidation of clematoside A'.

Thus, the carbohydrate moiety of clematoside A' is attached to the hydroxy group at C_3 of the aglycone and is identical with the corresponding carbohydrate chain of clematoside A. There is no doubt that clematoside A' is a biogenetic precursor of the saponins found in the Manchurian ground clematis.