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THE SAPONINS OF THE SUNFLOWER

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We have studied the yellow petals of the sunflower (Helianthus annuus) collected in the flowering period. So that the saponins should not undergo degradation during the process of air drying, the petals were fixed with 70% methanol immediately after gathering.

A chromatographic study of a methanol extract of the sunflower petals in the 1-butanol–acetic acid–water (4:1:5) system showed the presence of three saponins, which we have called in order of polarity helianthosides A, B, and C. By paper chromatography, among the reducing sugars galactose, glucose, and arabinose have been found.

After evaporation of the extract, the residue was dissolved in water and exhaustively extracted with ether and then with chloroform. To eliminate the reserve sugars, the aqueous extract after defatting was subjected to gel filtration on Sephadex G-25. Chromatography on silica gel in the 1-butanol–acetic acid–water (4:1:5) system yielded helianthoside C with mp 215–217° C.

The acid hydrolysis of this saponin gave an aglycone coinciding in R_f value and melting point with echinocystic acid. The derivatives of the aglycone obtained–acetate, methyl ester, and acetate of the methyl ester–were fully identical with the corresponding derivatives of echinocystic acid. Z. Kasprzyk (Warsaw) provided a sample of echinocystic acid for comparison, and A. A. Ryabinin and L. G. Matyukhina (Leningrad) provided a sample of the diacetate of this acid.

Glucose, arabinose, xylose, and rhamnose were identified in the carbohydrate fraction of helianthoside C.

The results obtained do not agree with the results of the Polish chemists. They showed the presence in the methanolic extract of two saponins, the carbohydrate components of which included only glucose and arabinose [1].

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STRUCTURE OF CLEMATOSIDE A

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Using the methods described in preceding communications [1,2] and taking the structures of the other clematosides into consideration, we propose a possible structure for clematoside A – a nonaoside of oleanolic acid. The glycoside was isolated by means of chromatography on silica gel in a similar manner to clematoside B [2].

The acid hydrolysis of clematoside A yielded oleanolic acid as the aglycone. Glucose, xylose, arabinose, and rhamnose were identified in the hydrolyzate. A quantitative determination of the monosaccharides by densitometry of the chromatograms showed that their ratio in the glycoside is 4:1:2:2. A determination of the molecular weight from the yield of the genin gave 1740.

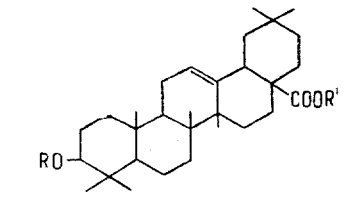
On hydrolysis of the fully methylated glycoside, the following sugar derivatives were isolated and identified by paper and gas-liquid chromatography: 2,3,6-tri-O-methyl-L-rhamnose (1 mole), 2,3,6-tri-O-methyl-D-glucose (2 moles), 2,3,4-tri-O-methyl-D-glucose (1 mole), 2,3,4,6-tetra-O-methyl-D-glucose (1 mole), 2,3-di-O-methyl-D-xylose (1 mole), 3,4-di-O-methyl-L-arabinose (2 moles), and 2,3-di-O-methyl-L-rhamnose (1 mole). On periodate oxidation of clematoside A, not one of the monosaccharides was unaffected.

The cleavage of the methylated glycoside with aluminum hydride yielded an oligosaccharide identical with the oligosaccharide obtained analogously from clematosides B and C. Thus, the carbohydrate chain connected to the carboxy

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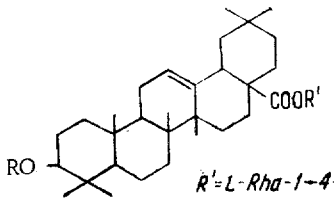
According to refined data, clematoside C [1,2] – a triterpene oligoside from Clematis manshurica Rupr. – must be assigned to the following structure:



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.