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CALENDULOSIDE A FROM CALENDULA OFFICINALIS

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The epigeal part of Calendula officinalis has been studied previously [1, 2]. We have investigated the roots of this plant collected in September 1967 by P. N. Kibal'chich in the Moscow region.

By the usual method for isolating triterpene glycosides [3], we obtained a mixture of substances consisting, according to thin-layer chromatography, of eight glycosides which we named, in increasing order of polarity, calendulosides A, B, C, D, E, F, G, and H.

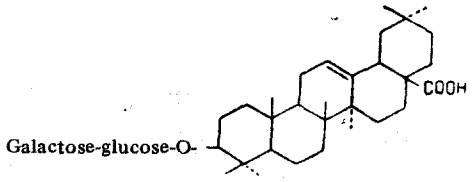
On complete acid hydrolysis of the combined calendulosides A—H with Kiliani's mixture (concentrated HCl—CH_3COOH—H_2O (10 : 35 : 55)), we obtained a genin which from its R_f values, IR spectrum, melting point (306-308° C) and a mixed melting point test with an authentic sample was identified as oleanolic acid. Glucose and galactose were also found in the hydrolysis products. Glucuronic acid, which is present in all the glycosides of Calendula flowers [2], was absent.

Column chromatography with the combined triterpene glycosides gave calenduloside A with the composition $C_{42}H_{68}O_{13}$, mp 260-262° C (decomp.), $[\alpha]_D^{20}$ +71 ± 2° (c 0.1; methanol). The substance is practically insoluble in water but dissolves readily in alkalis, which shows the presence in it of a free carboxy group. This corresponds to information obtained from the IR spectrum.

The melting point of the pentaacetate of calenduloside A is 154-156.5° C. Found, %: C 62.58; 62.47; H 7.86; 7.78. Calculated for $C_{56}H_{82}O_{20}$, %: C 62.58; H 7.69.

The complete acid hydrolysis of calenduloside A with Kiliani's mixture yielded oleanolic acid, glucose, and galactose (1 : 1 : 1). The molecular weight found from the yield of genin also corresponded to a bioside. On stepwise hydrolytic cleavage with 5% HCl—CH_3OH, in addition to oleanolic acid a monooside was obtained (mp 240-242° C), the complete hydrolysis of which with Kiliani's mixture gave oleanolic acid and glucose.

Thus, calenduloside A has the structure 3-galactosylglucosyloleanolic acid.



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THE STRUCTURE OF HELIANTHOSIDE A

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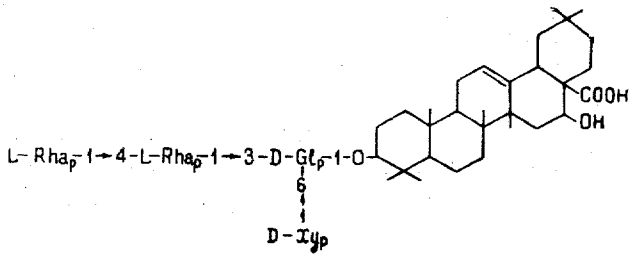
Helianthoside A, a triterpene glycoside that we have found in the petals of the sunflower [1], was isolated by chromatography on silica gel in preparative amounts and was subjected to acid hydrolysis. Echinocystic acid was identi-

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.