CALENDULOSIDE A FROM CALENDULA OFFICINALIS

L. P. Vecherko, E. P. Zinkevich, N. I. Libizov, and A. I. Ban'kovskii

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 1, pp. 58-59, 1969

The epigeal part of <u>Calendula officinalis</u> 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-CH₃COOH-H₂O (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-CH₃OH, 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.

REFERENCES

- 1. Z. Kasprzykowna, Prace Glownego Inst. Chemii Przemysl., 1, 39, 1966.
- 2. S. Kasprzyka and Z. Wojciechowski, Phytochemistry, 6, 69, 1967.
- 3. N. K. Kochetkov and A. Ya. Khorlin, Arzneimittel-Forsch., 16, 101, 1966.

14 June 1968

All-Union Scientific-Research Institute for Medicinal Plants

UDC 574.913+547.917

THE STRUCTURE OF HELIANTHOSIDE A

P. L. Cheban, V. Ya. Chirva, and G. V. Lazur'evskii

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 1, p. 59, 1969

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-