THE STRUCTURE OF CALENDULOSIDE F FROM THE ROOTS OF *Calendula officinalis*

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UDC 547.918+547.597

In development of our investigations of the glycosides of the roots of *Calendula officinalis* [1], we report the structure of a new glycoside of oleanolic acid – calenduloside F [1].

Calenduloside F, obtained from the combined glycosides of the roots of *C. officinalis* L. by chromatography on a column of silica gel has mp 263-265°C (decomp.) and contains about 4% of incombustible residue. After desalting with cation-exchange resin (Dowex 50 W×2, 100/200, H^+ form), compound (I) was obtained with the composition $C_{42}H_{66}O_{14} \cdot 2H_2O$, mp 203-205°C (methanol), $[\alpha]_D^{20}+8°$ (c 0.5; methanol). Found: mol. wt.. 809 (spectrophotometrically) [2]. $C_{42}H_{66}O_{14} \cdot 2H_2O$. Calculated: mol. wt. 831. IR spectrum: 1740 cm^{-1} $\left(C\begin{matrix}O\\ \diagdown O-\end{matrix}\right)$ and 3450 cm^{-1} (OH).

In the products of the acid hydrolysis of (I), oleanolic acid was identified by direct comparison with an authentic sample and D-glucuronic acid and D-glucose were identified by means of PC and TLC. The stepwise hydrolytic cleavage of (I) gave a mixture of substances from which, by chromatography on a column of silica gel were isolated: a monoside (II), identical with the oleanolic acid 3-O-β-D-glucuronopyranoside acid that we have isolated previously [1] and a monoside (III) with mp 234.5-236°C (methanol); $[\alpha]_D^{20}+$ 50° (c 0.5; methanol). IR spectrum of (III): 1740 cm^{-1} $\left(C\begin{matrix}O\\ \diagdown O--\end{matrix}\right)$ and 3400 cm^{-1} (OH). The further acid hydrolysis of (III) gave oleanolic acid and D-glucose. Compound (III) with mp 241-243°C (methanol), $[\alpha]_D^{20}+$ 54.48° (c 0.78; ethanol) has been obtained previously by the microbial cleavage of chikusetsusaponin (IV) [3].

After the alkaline hydrolysis of (I) and subsequent treatment of the hydrolysis product with cation-exchange resin, we obtained (II) and D-glucose.

The treatment of (I) with an ethereal solution of diazomethane, and also the desalting of a methanolic solution of (I) by cation-exchange resin or its stepwise hydrolytic cleavage in methanol formed the monomethyl ester of (I), $C_{43}H_{68}O_{14}$ with mp 215-217°C (methanol), $[\alpha]_D^{20}+16°$ (c 0.5; methanol). Its acetate $C_{55}H_{80}O_{20}$ had mp 158-160°C (methanol), $[\alpha]_D^{20}+12°$ (c 0.25; chloroform). The NMR spectrum of the acetate showed the signal of a methoxycarbonyl group (3.68 ppm).

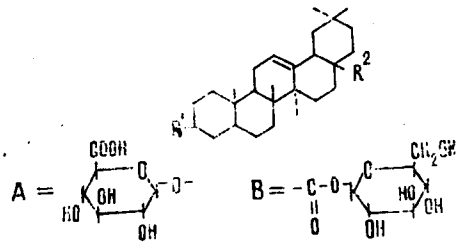
The exhaustive methylation of (I) [4] gave a permethylate $C_{50}H_{82}O_{14}$ with mp 140-142°C, $[\alpha]_D^{20}+14.3°$ (c 0.5; chloroform), and the cleavage of this with hydrochloric acid gave oleanolic acid, identified by comparison with authentic samples, and methyl 2,3,4-tri-O-methyl-D-glucuronate and 2,3,4,6-tetra-O-methyl-D-glucopyranose, identified with the aid of PC, TLC, and GLC.

The presence in the IR spectra of (I) and (III) of an absorption band at 1740 cm^{-1}, the results of alkaline hydrolysis, and the formation of oleanolic acid on the hydrolysis of the permethylate show the presence of an ester bond in the molecule. Consequently, the D-glucuronic acid is attached to the hydroxyl and the D-glucose to the carboxyl group of the genin.

The configurations of the glycosidic bonds were determined by means of Klyne's rule [5].

Thus, calenduloside F is the previously undescribed glucopyranosyl oleanolate 3-O-β-D-glucuronopyranoside.

All-Union Scientific-Research Institute of Medicinal Plants. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 561-562, July-August, 1973. Original article submitted January 31, 1973.



I. R^1 = A; R^2 = B.
II. R^1 = A; R^2 = COOH.
III. R^1 = OH; R^2 = B.

LITERATURE CITED

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