TRITERPENE GLYCOSIDES OF *Silphium perfoliatum*. II

É. S. Davidyants, Zh. M. Putieva,
V. A. Bandyukova, and N. K. Abubakirov

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We have previously reported the isolation from the epigeal part of *Silphium perfoliatum* L. of silphioside B [1]. On further chromatographic purification of the total extractive subsubstances on a column of silica gel (in the chloroform—methanol—water (85:35:3) system), we isolated a glycoside G, more polar than the preceding compound.

Initially, this substance was obtained in the form of a salt with mp 260-262°C (decomp.). Its IR spectrum showed the absorption band of a carboxylate ion at 1610 cm^{-1}. After desalting with a 5% solution of acetic acid (25°C, 30 min) and recrystallization from aqueous methanol, the pure crystalline compound G had mp 197-200°C (decomp.), $[\alpha]_D^{25}$ +6.0 ± 3° (c 1.0; methanol), composition $C_{42}H_{66}O_{14}$.

The acid hydrolysis of glycoside G gave oleanolic acid with mp 305-307°C, $[\alpha]_D^{25}$ +78.6° (c 0.9; methanol). D-Glucose and D-glucuronic acid were identified in the hydrolysate with the aid of TLC 1-butanol—methanol—water (5:3:1) system) and GLC.

The alkaline saponification of glycoside G gave a monoglycoside with mp 214-216°C, $[\alpha]_D^{25}$ +17.0 ± 3° (c 0.44; methanol). On hydrolysis (5% H_2SO_4, 85°C, 4 h), this compound was cleaved to form oleanolic acid and D-glucose. The monoglycoside was identified as oleanolic acid 3-O-β-D-glucuronopyranoside, which has been described repeatedly [2].

The Hakomori methylation of glycoside G led to the formation of an octa-O-methyl derivative with the composition $C_{50}H_{82}O_{14}$, M^+ 906. PMR spectra ($CDCl_3$, ppm, HMDS): 0.74-1.09 (21 H, s, 7 × CH_3); 3.30-3.75 (24 H, s, 8 × OCH_3); 4.28 (1 H, d, J = 7.5 Hz, anomeric proton); 5.26-5.29 (2 H, m, $>C{=}C{-}H$ and the anomeric proton).

In the products of the methanolysis of the permethylate methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside and methyl (methyl 2,3,4-tri-O-methyl-β-D-glucosid)uronate were detected by GLC.

It follows from what has been said that the glycoside was a bisdesmoside in which a D-glucuronic acid residue was attached to the hydroxy group at C-3, and a D-glucose residue to the carboxy group of oleanolic acid.

The configurations of the glycosidic bonds were determined from molecular rotation differences and also with the aid of the PMR spectrum. The signals of the anomeric protons appeared at 4.73 and 6.05 ppm in the form of two doublets with spin-spin coupling constants of 7.5 Hz.

Thus, glycoside G had the structure of oleanolic acid 28-O-β-D-glucopyranoside 3-O-β-D-glucuronopyranoside.

A glycoside of this structure was first isolated from *Calendula officinalis* L. and was called calenduloside F [3]. It was later found in the roots of *Panax pseudoginseng* (Naga) (saponin C) [4] and of *Panax japonicum* A. Mayer (chikusetsusaponin IVa) [5].

LITERATURE CITED

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