TRITERPENE GLYCOSIDES OF *Silphium perfoliatum*

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Silphium perfoliatum L. (cup rosinweed), family Asteraceae (Compositae) is a valuable fodder crop [1]. Di- and sesquiterpenes [2] and polysaccharides [2] have been isolated from the plant. No saponins have previously been detected.

The air-dry epigeal part of *Silphium perfoliatum* (1.7 kg) collected in the flowering stage in August, 1981, in Stavropol krai was extracted with ether and then, exhaustively, with hot methanol. The methanolic extracts were concentrated and the saponins were precipitated with ether. The precipitate was dissolved in water and the solution was treated successively with ethyl acetate and n-butanol. Evaporation of the ethanolic extract yielded 92 g of crude total saponins (5.4%; the yield here and below is calculated on the air-dry material), the chromatography of which in a thin layer of silica gel showed the presence of not less than eight glycosides, which we have called silphiosides and have designated in the sequence of increasing polarity as A, B, C, D, E, F, G, and H. Glycosides B, C, E, and G predominated quantitatively.

The combined saponins were chromatographed on a column of silica gel using the chloroform–methanol–water (85:25:3) system. The fractions enriched with compound B were rechromatographed [chloroform–methanol (4:1) system]. This led to the isolation of 3.6 g (0.21%) of glycoside B in the individual form.

Silphioside B (I), $C_{42}H_{68}O_{13}$, consists of a white crystalline substance with mp 200–201°C (from aqueous ethanol), $[\alpha]_D^{24}$ +24.3 ± 2° (c 1.1; methanol). From the products of the acid hydrolysis of (I) (5% H_2SO_4 solution, 90°C, 5 h) an aglycone was isolated which was identified as oleanolic acid (M^+ 456, mp 305–307°C), $[\alpha]_D^{20}$ +80.0° (c 1.0; methanol), and of the sugars glucose was identified with the aid of GLC.

The IR spectrum of compound (I) had absorption bands at 1750 and 1240 cm^{-1} (ester), which suggests the presence of a sugar residue linked to the carboxy group of the aglycone. The alkaline hydrolysis of glycoside (I) (5% KOH solution, 70°C, 1 h) led to a progenin which, by means of its physical constants (mp 239–242°C; $[\alpha]_D^{20}$ + 53.2 ± 2° (c 0.9; methanol)), IR spectrum, and the products of acid hydrolysis, was characterized as oleanolic acid 3-O-β-D-glucopyranoside.

The Hakomori methylation [4] of silphioside B led to an octamethyl derivative (II) with the composition $C_{50}H_{84}O_{13}$, M^+ 892. The PMR spectrum of the permethylate (II) ($CDCl_3$, δ, ppm, HMDS) contained signals at (ppm): 0.70–1.03 (7 × CH_3, overlapping singlets) and 3.25–3.53 (3H × 8, s, OCH_3).

After the methanolysis of the permethylate (II), 2,3,4,6-tetra-O-methyl-D-glucopyranose was detected by the GLC method.

In the PMR spectrum (C_5D_5N, δ, HMDS) of glycoside (I) there were two doublets at 4.72 and 6.06 ppm with the same spin-spin coupling constant, J = 7 Hz. This permits the assumption that both pyranose residues have the C1 conformation and are attached to the aglycone by β-glycosidic bonds. The presence in the PMR spectrum of the octamethyl ether of (II) of, in addition to those mentioned above, the signals of anomeric protons at 4.18 and 5.26 ppm with spin-spin constants of 8.0 and 7.5, respectively, confirms the hypothesis put forward. A calculation of the molecular rotation differences led to the same conclusion.

Consequently, the glycoside that we isolated was oleanolic acid 3,28-di-O-β-D-glucopyranoside.

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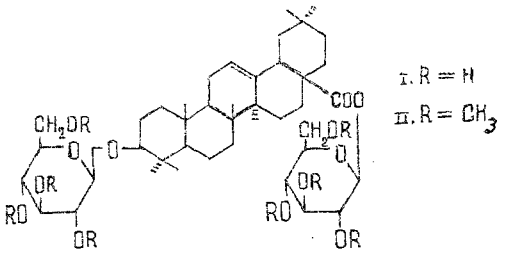

We are the first to have obtained this bisdesmoside from a natural material: It has previously been obtained by partial synthesis from oleanolic acid and α-D-glucopyranosyl bromide benzoate [5]. It must be mentioned that a glycoside close in structure has been isolated from *Anchusa officinalis* L. (Boraginaceae) — anchusoside I, to which the structure of oleanolic acid 28-O-α-D-glucopyranoside 3-O-β-D-glucopyranoside was assigned.

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SYNTHESIS OF ACETYLATED GLYCOSIDES OF 2,3-DIHYDROXY-1,4-NAPHTHOQUINONE

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We have previously reported an autocatalytic method of glycosylating hydroxynaphthoquinones with sugar 1,2-orthoesters [1]. In studying the possibilities of this method, 2,3-dihydroxy-1,4-naphthoquinone (III) [2] was glycosylated with orthoesters of D-glucose (I) [3] and of maltose (II) [4]. Boiling equimolar amounts of (I) and (III) in absolute chlorobenzene for 1 h led to a mixture of (IV) and (V) (20% and 40%, respectively, calculated on the orthoester). The orthoester of maltose (II) reacted completely with an equimolar amount of the quinone (III) in 5 h to form (VI) (48%) and (VII) (32%). The predominant formation of the bisglucoside (V) is apparently due to the electron-accepting effect of the glycosidic radical R_3 of the monoglucoside (IV), which causes an increase in the affinity and nucleophilicity of the neighboring hydroxy group and thereby increases the reactivity of (IV) as compared with the initial quinone (III). When (III) was glycosylated with the orthoester (II), the steric effect of the disaccharide radical R_4 directed the course of the reaction predominantly to the formation of the monomaltoside (VI). Glycosylation by the orthoesters (I) (1 h) and (II) (11 h) at a quinone:orthoester ratio of 1:2 led to mixtures of (IV) (4%) and (V) (83%) and of (VI) (52%) and (VII) (41%), respectively, which also confirms the conclusion that we drew concerning the influence of the radicals R_3 and R_4 on the reactivities of the monoglycosides (IV) and (VI).

The structures of the glycosides (IV-VII) were confirmed by the results of IR and ^1H and ^{13}C NMR spectroscopic studies and of elementary analysis. The signals of the anomeric carbon atoms of a D-glucose residue attached to the aglycone appeared at 98-100 ppm, which shows the β-configuration of the glycosidic bond [1]. All the newly obtained glycosides consisted of light yellow amorphous powders.

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