Chemistry of Natural Compounds, Vol. 30, No. 6, 1994

TRITERPENE GLYCOSIDES OF *Hedera taurica*
II. STRUCTURES OF TAUROSIDES St-G_{0-1}, St-G_2, AND St-G_3 FROM THE STEMS OF CRIMEAN IVY

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UDC 547.918:543.422

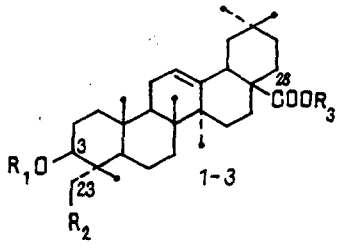
In the present communication we give the results obtained in establishing the structures of taurosides St-G_{0-1}, St-G_2, and St-G_3. We have described their isolation from the stems of Crimean ivy *Hedera taurica* previously [1]. The acetylation of St-G_0 and TLC analysis showed that it consisted of two glycosides, which we have designated as St-G_{0-1} and St-G_{0-2} and which were obtained in the individual form by the preparative separation of the mixture of acetates (170 mg) on SiO_2 in the chloroform—methanol (200:1) system in amounts of 50 and 40 mg, respectively.

As components of St-G_{0-1} (**1**), $[\alpha]_D$ +10° (*c* 0.5, methanol), lit. $[\alpha]_D$ +15° (methanol) [2] by acid hydrolysis we detected arabinose, glucose, and hederagenin. Alkaline hydrolysis gave a progenin identical with hederagenin 3-O-α-*L*-arabinopyranoside (tauroside B) [3]. The determination of the structure of (**1**) was completed by using PMR spectroscopy, which required a minimal amount of substance. PMR spectrum of the full acetate of (**1**) (δ, ppm, $CDCl_3$): 4.42 (d, H-1′, $J_{1,2}$ 7.3); 5.19 (t, H-2′, $J_{2,3}$ 9.0); 5.02 (dd, H-3′, $J_{3,4}$ 3.5); 5.24 (m, H-4′); 4.00 (dd, H-5′e, $J_{4,5e}$ 2.8 $J_{5\alpha,5e}$ 13.7); 3.60 (dd, H-5′α, $J_{4,5\alpha}$ 2.5); 5.53 (d, H-1″, $J_{1,2}$ 8.2); 5.12 (dd, H-2″, $J_{2,3}$ 9.6); 5.22 (t, H-3″, $J_{3,4}$ 9.3); 4.97 (dd, H-4″, $J_{4,5}$ 9.8); 3.75 (m, H-5″); 3.87 (dd, H−6″ A, $J_{5,6A}$ 2.5; $J_{6A,6B}$ 11.6); 3.58 (dd, H-6″B, $J_{5,6B}$ 5.5); 4.53 (d, H-1‴, $J_{1,2}$ 8.0); 4.96 (dd, H-2‴, $J_{2,3}$ 9.5); 5.16 (t, H-3‴, $J_{3,4}$ 9.4); 5.05 (t, H-4‴, $J_{4,5}$ 9.9); 3.62 (m, H-5‴); 4.26 (dd, H-6‴ A, $J_{5,6A}$ 4.8, $J_{6A,6B}$ 12.5); 4.09 (dd, H-6‴ B, $J_{5,6B}$ 2.5); 5.31 (br.t, H-12, $J_{11,12}$ 3.4); 4.09 (d, H-23A, $J_{23A,23B}$ 12.3); 3.66 (d, H-23B); 3.51 (dd, H-3, $J_{2e,3}$ 5.0; $J_{2\alpha,3}$ 11.5); 0.73; 0.74; 0.90; 0.97; 1.10; 1.26 (all s, 6 CH_3).

The signals of the skeletal protons corresponding to each monosaccharide residue were determined with the aid of the one-dimensional variant of a HOHAHA experiment in a rotating frame [4]. The complete assignments of the signals in each monosaccharide residue were made with the help of COSY homonuclear correlation spectroscopy and homonuclear double resonance. The nature of the splitting of these signals corresponded to two β-glucopyranose residues and one α-arabinopyranose residue.

It followed from the relatively strong-field positions of the signals of the H-6′′ protons in the PMR spectrum of the full acetate that the hydroxy group at C-6 of Glc′′ was glycosylated. This type of bond was additionally confirmed by the observation of NOEs in a rotating frame [5], where preirradiation of H-1′′′ caused the appearance in the difference spectrum of only the signals of the H-6′′ proton. When H-1′ was preirradiated, the H-2′, H-3′, and H-5α′ signals of the same monosaccharide residue and the signal of H-3 of the aglycon were detected in the difference spectrum.

Thus, (**1**) is the gentiobiosyl ester of hederagenin 3-O-α-*L*-arabinopyranoside. This glycoside has not previously been detected in plants of the Araliaceae family, but it has been isolated from *Akebia quinata* [2]



	R_1	R_2	R_3
1	Ara″α	OH	βGlc′ . 6β Glc′′
2	Rha‴ α2 . Ara″α	H	βGlc′ . 6β Glc′′ . 4α Pha‴
3	Rha‴ α2 . Ara″α	OH	βGlc′ . 6β Glc′′

Simferopol' State University. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 826-828, November-December, 1994. Original article submitted January 10, 1994.

0009-3130/94/3006-0772$12.50

The minor taurosides St-G_2 (**2**), $[\alpha]_D$ −25° (*c* 0.1; methanol), lit. $[\alpha]_D$ −28.8° (methanol) [6] and St-G_3 (**3**), $[\alpha]_D$ −7° (*c* 0.3; pyridine), lit. $[\alpha]_D$ −8.2° (pyridine) [6], isolated previously in the form of a mixture [1], were separated by reversed-phase gas chromatography, as described in [6]. According to TLC in various solvent systems, (**2**) and (**3**) were identical with taurosides G_2 and G_3 from the leaves of Crimean ivy [6]. For the additional identification of these glycosides, they were subjected to acid and alkaline hydrolysis, with identification of the aglycons and sugars by comparison with authentic specimens, while progenins were identical with taurosides C and E [3, 7].

Thus, (**2**) is the O-α-*L*-rhamnopyranosyl-(1→4)-O-β-*D*-glucopyranosyl-(1→6)-glucopyranosyl ester of oleanolic acid 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-α-*L*-arabinopyranoside] and (**3**) is the β-gentiobiosyl ester of hederagenin 3-O-[O-α-*L*-rhamnopyranosyl-(1→2)-glucopyranoside].

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