extracted with diethyl ether (3 × 100 ml). The extract was dried over $MgSO_4$, the solvent was evaporated off in vacuum, and the residue (700 mg) was chromatographed on a column containing 21 g of silica gel. Elution of the column with hexane–ethyl acetate (2:3) yielded the colorless crystalline substance (5), with the composition $C_{18}H_{22}O_3$, mp 142-144°C (from ether), $[\alpha]_D^{21.5}$ −25.2°, (c 0.003), R_f 0.65 (ether). Yield 300 mg (52%). IR spectrum (ν_{max}, cm^{-1}): 3030, 2945, 2870, 1790, 1680, 1650, 1630, 1470, 1420, 1390, 1310, 1230, 1200, 1180, 1120, 1050, 1005, 980, 920. Mass spectrum (m/z, %): 286 (M^+, 72), 271(76), 245(100), 215(13.8), 201(18), 189(47), 173(48), 161(16.6), 149(43), 135(86), 128(13.8), 122(36), 115-(13.8), 107 (16.6), 91(55.5), 77(36), 67(57), 55(57), 42(80.5).

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TRITERPENE GLYCOSIDES OF *Hedera taurica*

IX. STRUCTURES OF TAUROSIDES G_1, G_2, T_3, H_1, AND H_2 FROM THE LEAVES OF CRIMEAN IVY

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From the leaves of Crimean ivy we have isolated the previously known glycosides 3-O-α-L-Ara_p-28-O-[O-α-L-Rha_p-(1→4)-O-β-D-Glc_p-(1→6)-β-D-Glc_p]hederagenin, 3-O-[O-α-L-Rha_p-(1→2)-α-L-Ara_p]-28-O-[O-α-L-Rha_p-(1→4)-O-β-D-Glc_p-(1→6)-β-D-Glc_p]oleanic acid and -hederagenin, and 3-O-[O-α-L-Rha_p-(1→2)-α-L-Ara_p]-28-O-[O-β-D-Glc_p-(1→6)-β-D-Glc_p]hederagenin and a new one: tauroside H_1 – 3-O-[O-α-L-Rha_p-(1→2)-O-α-L-Ara_p]-28-O-[O-α-L-Rha_p-(1→4)-O-β-D-Glc_p-(1→6)-β-D-Glc_p]echinocystic acid.

Continuing a study of the leaves of Crimean ivy *Hedera taurica* Carr., family Arialaceae, we have isolated glycosides of medium polarity, which have been called taurosides G_1–G_3 and H_1 and H_2. For their isolation, the plant raw material, after enzyme inactivation by boiling, was dried and was extracted successfully with chloroform and with mixtures of chloroform and ethanol (6:1 and 3:2). The chloroform extract contained chlorophyll, carotenoids, resins, and other substances of low polarity; the following extract contained low-polarity glycosides; and the last extract a mixture of medium-polarity glycosides.

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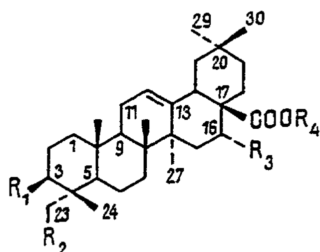
TLC analysis of the medium-polarity glycosides in the chloroform–ethanol–water system showed the presence of four components, designated as taurosides G, H, I, and J. Their preparative separation was achieved on silica gel with elution by chloroform–ethanol–water. The TLC analysis of component G in the chloroform–ethanol–ammonia system showed that it consisted of three glycosides, which were called taurosides G_1, G_2, and G_3 in order of increasing polarity. Their preparative separation was carried out on silica gel with elution by chloroform–ethanol–ammonia, which enabled the individual glycoside G_1 and a poorly separable mixture of G_2 and G_3 to be obtained. The pair G_2 and G_3 was separated on silica gel with grafted-on heptyl groups [1] by reversed-phase chromatography with elution by aqueous ethanol. The TLC analysis of component H in the chloroform–methanol–ammonia system showed that it consisted of two glycosides, which were called taurosides H_1 and H_2. The most suitable solvent system for their separation proved to be a mixture of butanol, ethyl acetate, and water. The further purification of components G_1–G_3 was performed by chromatography on silica gel in the butanol–ethyl acetate–water system, and that of components H_1 and H_2 in the chloroform–ethanol–ammonia system. Glycosides G_2 and H_1 were additionally purified through their full acetates.

Taurosides G_1 and H_2 coincided in their chromatographic mobilities with hederosides G and H_1 from the berries of Crimean ivy [2]. Their identity was further confirmed by the results of acid hydrolysis, by a comparison of their progenins after alkaline hydrolysis, and by the complete identity of their ^{13}C NMR spectra. Consequently, substances G_1 and H_2 were 3-O-α-L-arabinopyranosyl-28-O-[O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl]hederagenin (I) and 3-O-[O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl]-28-O-[O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl]-hederagenin, respectively:



	R_1	R_2	R_3	R_4
I	$Ara_p \xrightarrow{\alpha}$	OH	H	$Rha_p \xrightarrow{\alpha 4} Glc_p \xrightarrow{\beta 6} Glc_p \xrightarrow{\beta}$
II	$Rha_p \xrightarrow{\alpha 2} Ara_p \xrightarrow{\alpha}$	OH	H	$Rha_p \xrightarrow{\alpha 4} Glc_p \xrightarrow{\beta 6} Glc_p \xrightarrow{\beta}$
III	$Rha_p \xrightarrow{\alpha 2} Ara_p \xrightarrow{\alpha}$	OH	H	$Glc_p \xrightarrow{\beta 6} Glc_p \xrightarrow{\beta}$
IV	$Rha_p \xrightarrow{\alpha 2} Ara_p \xrightarrow{\alpha}$	H	H	$Rha_p \xrightarrow{\alpha 4} Glc_p \xrightarrow{\beta 6} Glc_p \xrightarrow{\beta}$
V	$Rha_p \xrightarrow{\alpha 2} Ara_p \xrightarrow{\alpha}$	H	OH	$Rha_p \xrightarrow{\alpha 4} Glc_p \xrightarrow{\beta 6} Glc_p \xrightarrow{\beta}$

The acid hydrolysis of tauroside G_3 permitted the identification in its composition of rhamnose, arabinose, and glucose residues, with hederagenin as the aglycon. Alkaline hydrolysis gave a progenin identical with tauroside E, having the structure of 3-O-[O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl]hederagenin. Analysis of the ^{13}C NMR spectrum of tauroside G_3 revealed the signals of four anomeric C atoms in the 90-100 ppm region. Consequently, a disaccharide fragment was attached to the carboxy group. The assignment of the signals of the O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl fragment was made by comparison with literature information [2-4]. The remaining 12 signals of carbohydrate C atoms must have belonged to the disaccharide fragment at the carboxy group. In the light of the results of acid hydrolysis, these must have been two glucose residues. A comparison of the chemical shifts of these signals with literature figures for a β-gentiobiose residue [2, 5] showed their complete agreement, while the signals of the aglycon moiety of glycoside G_3 agreed with those given in the literature for a 3,28-diglycosylated hederagenin [2]. Thus, tauroside G_3 was 3-O-[O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl]-28-O-[O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl]hederagenin (III). A glycoside with this structure has previously been isolated from *Dipsacus aureus* [6].

TABLE 1. Chemical Shifts of the Signals of the ^{13}C Atoms of the Aglycon Moieties of Taurosides G_1 (I), H_2 (II), G_3 (III), G_2 (IV), and H_1 (V) (δ, ppm; 0 – TMS; C_5D_5N)

C atom	Compound					Atom	Compound				
	I	II	III	IV	V		I	II	III	IV	V
1	39,0	39,2	39.2	38,9	39.2	16	23,9	23,8	23,9	23.8	74,4
2	26;3	26,2	26,1	26,6	26,7	17	46,4	46,3	46,5	46,3	49,3
3	82,2	81,2	81,4	88,8	89,0	18	41,8	41,8	41,9	41,7	41,4
4	43,6	43.6	43.6	39.5	39,6	19	47,2	47,2	47,3	47,1	47.3
5	47,7	47,8	48,0	56,0	56.2	20	30,9	30,9	30,8	30,8	30.9
6	18,3	18,0	18,4	18.6	18,7	21	34,1	34.1	34,3	34,0	36,1
7	32,6	32,3	32,8	32.5	33 6	22	32,9	32.9	33,0	33,1	32.3
8	40,1	40,0	40,2	39,9	40,2	23	64,6	64,1	64,5	28,1	28,2
9	48,3	48,3	48,4	48.1	47,3	24	13.7	14.1	14,0	17,0	17,1
10	37,1	37,0	37,1	37.0	37.2	25	16,4	16,3	16,3	15,7	15,9
11	23,5	23,5	23,6	23,4	24.0	26	17,7	17,7	17,7	17,5	17.7
12	122,9	123.1	123,1	122,9	122,9	27	26.3	26,2	26,1	26,1	27,3
13	144,4	144,3	144.3	144.2	144,6	28	176,8	176,7	176.6	176,7	176,2
14	42,3	42,3	42,4	42,2	42,2	29	33,3	33,3	33,1	33,1	33,3
15	28,4	28.4	28,5	28,3	36,2	30	23.9	23,8	24,0	23,7	24,8

The assignments of the signals between atoms 17 and 19 in compounds (I)-(III) and between atoms 15 and 21 in compound (V) have been made arbitrarily.

According to the results of acid hydrolysis, taurosides G_2 and H_1 contained rhamnose, arabinose, and glucose residues and, as aglycons, oleanolic and echinocystic acids, respectively. The progenins of taurosides G_2 and H_1 were identical with taurosides C [7] and D [8] from Crimean ivy leaves and consisted of the 3-O-[O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside]s of oleanolic and echinocystic acids. The ^{13}C NMR spectrum of each of these two glycosides contained five signals of anomeric carbon atoms. Consequently, to the carboxy groups in G_2 and H_1 were attached trisaccharide fragments with the presumable structure of O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl-, which is typical for glycosides from plants of the Araliaceae family.

In the ^{13}C NMR spectra of G_2 and H_1 the signals of the C atoms of the aglycon moieties were similar to those for oleanolic and echinocystic acids [9 and 10, respectively]. The subspectra of the carbohydrate moieties of glycosides G_2 and H_1 were completely identical. For the assignment of the signals in the PMR spectra of G_2 and H_1 we used the methods of selective $\{H_i\}-\{H_j\}$ homonuclear double resonance and of two-dimensional homonuclear correlation spectroscopy. The complete assignments of the signals in the ^{13}C NMR spectra were made with the aid of two-dimensional heteronuclear correlation spectroscopy. In this way we confirmed the structure of the disaccharide fragment at the C_3–OH group, since the signal of the C2' atom of the arabinose residue had undergone a downfield shift in comparison with unsubstituted arabinose. We may note that the chemical shifts of the signals of the C atoms of the arabinose residues in glycosides G_2 and H_1 were fairly sensitive to the temperature. Thus the values of the C-1'–C-5' signals at 60°C were, respectively, 104.3, 76.3, 73.0, 68.0, and 63.8 ppm in both glycosides. This is obviously connected with the conformational mobility of the arabinose residue and with a displacement of the equilibrium $^4C_1 \rightleftarrows {}^1C_4$ to the right with a rise in the temperature. This was confirmed by a simultaneous decrease in the value of $J_{1,2}$ for the arabinose residue (6.0 Hz at 20°C; 5.3 Hz at 27°C; and 4.5 Hz at 60°C). The possibility of the presence of an arabinose residue in the $^1C_4$ conformation in an analogous disaccharide fragment has been reported in the literature [11].

An analysis of the positions of the signals of the trisaccharide carboxylic fragment in each of taurosides G_2 and H_1 showed that the glucose residue bound to the carboxy group was substituted at the C6''' atom, and the other glucose residue at the C-4'''' atom; the rhamnose residue was terminal (unsubstituted).

The types of bonds in both carbohydrate chains were additionally confirmed by an analysis of the PMR spectra of the full acetates of G_2 and H_1, in which the arabinose H-2' signals and the glucose H-4'''' and H-6''' signals were shifted upfield from their usual positions by 0.6-1.0 ppm. The β-configuration of both glucose residues and the α-configuration of the arabinose residue followed from the values of the spin-spin coupling constants (SSCCs) of the signals of the anomeric protons.

TABLE 2. Chemical Shifts of the Signals of the ^{13}C Atoms of the Carbohydrate Moieties of Taurosides G_1 (I), H_2 (II), G_3 (III), G_2 (IV) and H_1 (V) (δ, ppm; 0 — TMS; C_5D_5N).

C atom	Compound					C atom	Compound				
	I	II	III	IV	V		I	II	III	IV	V
Ara 1′	106,7	104,4	103.8	104,9	104,9	Glc 1‴	95,7	95,8	95,7	95,7	95,9
2′	73,2	75,9	76,3	75,9	76,1	2‴	74,0	74,0	73,7	73,8	74.0
3′	74 8	74 6	74.2	73,8	73,7	3‴	78,7	78,8	78,8	78.7	78,7
4′	69,7	69,4	68 6	68,7	68,6	4‴	70,8	70,7	71,4	70,8	70,9
5′	67,0	65,6	64,6	64.8	64,6	5‴	78,1	78,1	77,9	78,1	78,2
						6‴	69,2	69 4	69,8	69,2	69,4
Rha 1″		101,7	101.8	101.9	101.9	Glc 1⁗	104,8	104,9	105.2	104,9	105,0
2″		72,4	72,3	72,4	72.4	2⁗	75,4	75.4	75,2	75,3	75,4
3″		72,6	72,6	72,6	72,6	3⁗	76,6	76.6	78,2	76,5	76.5
4″		74·2	74.0	74,1	74,1	4⁗	78,4	78,4	71,9	78,3	78.5
5″		69,9	69,8	69,9	70,0	5⁗	77,2	77,2	78.4	77,2	77,2
6″		18.5	18,4	18,6	18,6	6⁗	51,4	61,4	63,0	61.3	61.4
						Rha 1′′′′′	102,8	102,8		102,8	102,9
						2′′′′′	72.6	72,6		72,6	72,6
						3′′′′′	72,8	72,8		72,7	72,8
						4′′′′′	74,0	74,0		73,9	74,0
						5′′′′′	70.4	70,4		70,4	70,4
						6′′′′′	18.6	18,6		18,6	18,6

Thus taurosides G_2 and H_1 are 3-O-[O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl]-28-O-[O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyloleanolic and -echinocystic acids, (IV) and (V), respectively. Glycosides analogous to tauroside G_2 have previously been isolated from the following plants of the Arialaceae family: Acanthopanax senticosus [12], Eleutherococcus senticosus [13], and Hedera helix [14].

EXPERIMENTAL

NMR spectra were obtained on Bruker WM-250 and AM-300 instruments. Two-dimensional spectra were taken with the use of the standard procedures of the mathematical provision of the Bruker firm as applied to ASPECT 2000 and 3000 computers. Solutions in pyridine-d_5 were used for the glycosides, and solutions in $CDCl_3$ for the acetates. Specific rotations were measured on a SU-4 saccharimeter at λ 589 nm.

TLC monitoring was carried out on Silufol plates. Preparative separation was effected on silica gel L (40-100 μm). The following solvent systems were used: 1) chloroform—methanol—water (15:5:1); 2) chloroform—methanol—ammonia (15:5:1); 3) chloroform—ethanol (4:1 → 2:1), saturated with water; 4) chloroform—ethanol (4:1 → 2:1), saturated with 25% ammonia; 5) 35% aqueous ethanol; 6) butanol—ethyl acetate—water (10:5:1); 7) carbon tetrachloride—acetone (10:1). We have described the conditions for acetylation, deacetylation, and acid and alkaline hydrolysis previously [2].

Isolation of the Glycosides. Leaves of Crimean ivy gathered in May, 1990, in the region of the village of Pereval'nyi in an amount of 10 kg were boiled in water for 20 min, and were dried, comminuted, and extracted successively with chloroform and with mixtures of chloroform and ethanol (6:1 and 3:2). According to TLC, the chloroform extract contained chlorophyll, carotenoids, and other substances of low polarity; the 70 g of extract obtained with chloroform—ethanol (6:1) consisted of a mixture of glycosides of low polarity and other substances; and the 100 g of extract obtained with chloroform—ethanol (3:2) contained triterpene glycosides of medium polarity, designated as G, H, I, and J. The preparative separation of 50 g of this extract in system 3 yielded 7 g of component G, 25 g of H, 1 g of I, and 0.1 g of J.

The TLC analysis of component G in system 2 showed the presence of three glycosides, designated as G_1, G_2, and G_3 in order of increasing polarity. The preparative separation of 7 g of the mixture of G_1—G_3 was achieved in silica gel with elution by system 4. This gave 1.0 g of G_1 and 4.0 g of a mixture of G_2 and G_3. Components G_2 and G_3 were separated on silica gel with grafted-on heptyl groups using elution by system 5. This gave 0.7 g of G_3 and 2.5 g of G_2.

The TLC analysis of component H in system 6 showed the presence of two components, which were called H_1 and H_2. Preparative separation of 25 g of this yielded 3.0 g of H_1 and 18.0 g of H_2.

Tauroside G_1 (I). By the additional chromatographic purification of 1.0 g of G_1 on silica gel with elution by systems 3 and 6 we obtained 0.7 g of pure (I) $[\alpha]_D^{20}$ +3.6 (c 10.7); pyridine. According to the literature [15]: $[\alpha]_D$ +10.2 (pyridine). In an acid hydrolysate of (I) we identified rhamnose, arabinose, glucose, and hederagenin. The progenin from (I) obtained by alkaline hydrolysis was identical with tauroside B [7].

Tauroside G_2 (IV). For additional purification, 3.0 g of the full acetate of G_2 (IVa) was chromatographed on silica gel with elution by system 7. After recrystallization 1.5 g of pure (IVa) was obtained, mp 158-160°C (ethanol) $[\alpha]_D^{20}$ −5.6° (c 2.7, chloroform). PMR of (IVa) (δ, ppm; O − TMS, $CDCl_3$): 5.54 (d, $J_{1,2}$ = 7.9 Hz, H-1'''), 5.0-5.3 (m, H-2''', H-3'''), 4.97 (t, $J_{4,5}$ = 8.5 Hz, H-4'''), 3.75 (ddd, H-5'''), 3.87 (dd, $J_{6A,6B}$ = 11.0 Hz, $J_{5,6A}$ = 2.7 Hz, H-6A'''), 3.55 (dd, $J_{5,6B}$ = 5.1 Hz, H-6B'''); 4.50 (d, $J_{1,2}$ = 7.9 Hz, H-1''''), 4.82 (dd, $J_{2,3}$ = 9.0 Hz, H-2''''), 5.18 (dd, $J_{3,4}$ = 7.2 Hz, H-3''''), 3.5-3.8 (m, H-4'''', H-5''''), 4.44 (dd, $J_{6A,6B}$ = 12.5 Hz, $J_{5,6A}$ = 1.9 Hz, H-6A''''), 4.29 (dd, $J_{5,6B}$ = 3.3 Hz, H-6B''''), 4.81 (d, $J_{1,2}$ = 2.1 Hz, H-1'''''), 5.02 (dd, $J_{2,3}$ = 4.0 Hz, H-2'''''), 5.06-5.14 (m, H-3''''', H-4'''''), 3.84 (dq, H-5'''''), 1.14 (d, $J_{5,6}$ = 6.4 Hz, H-6'''''), 4.48 (d, $J_{1,2}$ = 6.5 Hz, H-1'), 3.99 (dd, $J_{2,3}$ = 9.0 Hz, H-2'), 4.99 (dd, $J_{3,4}$ = 3.0 Hz, H-3'), 5.25 (m, H-4'), 3.95 (dd, $J_{5a,5e}$ = 13.0 Hz, $J_{4,5e}$ = 3.2 Hz, H-5'e), 3.60 (dd, $J_{4,5a}$ = 2.0 Hz, H-5'a), 5.13-5.16 (m, H-1'', H-2''), 5.30 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 10.0 Hz, H-3''), 5.06 (t, $J_{4,5}$ = 10.0 Hz, H-4''), 4.25 (dq, H'5''), 1.20 (d, $J_{5,6}$ = 6.0 Hz, H-6'').

The deacetylation of 1.5 g of (IVa) and additional chromatographic purification on silica gel in system 6 yielded 0.8 g of pure (IV), $[\alpha]_D^{20}$ −28.8° (c 4.9, methanol). According to the literature [14]: $[\alpha]_D^{20}$ −22.9° (methanol). In an acid hydrolysate of (IV) we identified rhamnose, arabinose, glucose, and oleanolic acid. The progenin from (IV) was identical with tauroside C [7]. PMR of (IV) (δ, ppm; O − TMS, C_5D_5N): 4.84 (d, $J_{1,2}$ = 5.3 Hz, H-1'), 4.48 (dd, $J_{2,3}$ = 7.0 Hz, H-2'), 4.21-4.30 (m, H- , H-4', H-5'e), 3.78 (d, $J_{5a,5e}$ = 8.9 Hz, H-5'a), 6.01 (d, $J_{1,2}$ = 1.5 Hz, H-1''), 4.67 (dd, $J_{2,3}$ = 3.3 Hz, H-2''), 4.55 (dd, $J_{3,4}$ = 9.5 Hz, H-3''), 4.25 (t, $J_{4,5}$ = 9.9 Hz, H-4''), 4.50 (dq, H-5''), 1.58 (d, $J_{5,6}$ = 6.0 Hz, H-6''), 6.16 (d, $J_{1,2}$ = 8.1 Hz, H-1'''), 4.07 (t, $J_{2,3}$ = 8.5 Hz, H-2'''), 4.17 (t, $J_{3,4}$ = 8.5 Hz, H-3'''), 4.92 (d, $J_{1,2}$ = 7.9 Hz, H-1''''), 3.87 (d, $J_{2,3}$ = 8.9 Hz, H-2''''), 4.06 (t, $J_{3,4}$ = 9.0 Hz, H-3''''), 4.30 (t, $J_{4,5}$ = 9.0 Hz, H-4''''), 3.57 (H-5''''), 4.12 (H-6A''''), 4.00 (H-6B''''), 5.74 (d, $J_{1,2}$ = 1.5 Hz, H-1'''''), 4.60 (dd, $J_{2,3}$ = 3.3 Hz, H-2''''), 4.48 (dd, $J_{3,4}$ = 9.2 Hz, H-3''''), 4.27 (t, $J_{4,5}$ = 9.5 Hz, H-4''''), 4.85 (dq, H-5''''), 1.64 (d, $J_{5,6}$ = 6.1 Hz, H-6''''), 3.18 (dd, $J_{2e,3}$ = 4.0 Hz, $J_{2a,3}$ = 12.0 Hz, H-3), 5.36 (br. t., $J_{11,12}$ = 3.8 Hz, H-12), 0.6-2.3 (skeletal CH, CH_2), 1.19, 1.10, 1.03, 1.00, 0.84, 0.83, 0.81 (7 CH_3).

Tauroside G_3 (III). The additional chromatographic purification of 0.7 g of G_3 on silica gel in systems 3 and 6 gave 0.4 g of pure (III) $[\alpha]_D^{20}$ −8.2° (c 3.4, pyridine). Rhamnose, arabinose, glucose, and hederagenin were identified in an acid hydrolysate of (III). The progenin from (III) was identical with tauroside E [3].

Tauroside H_1 (V). The acetylation of 3.0 g of H_1 gave 4.0 g of the full acetate (Va). After chromatography on silica gel with elution by system 7, 2.0 g of pure (Va) was obtained, with $[\alpha]_D^{20}$ −13.2° (c 2.1; chloroform). PMR of (Va) (δ, ppm; O − TMS, $CDCl_3$): 4.49 (d, $J_{1,2}$ = 6.5 Hz, H-1'), 3.99 (dd, $J_{2,3}$ = 9.0 Hz, H-2'), 4.99 (dd, $J_{3,4}$ = 3.6 Hz, H-3'), 5.26 (m, H-4'), 3.61 (dd, $J_{5a,5e}$ = 12.5 Hz, $J_{4,5a}$ = 2.4 Hz, H-5'a), 3.96 (dd, $J_{4,5e}$ = 3.3 Hz, H-5'e), 5.14-5.18 (m, H-1'', H-2''), 5.30 (dd, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 10.0 Hz, H-3''), 5.06 (t, $J_{4,5}$ = 10.0 Hz, H-4''), 4.26 (dq, H-5''), 1.21 (d, $J_{5,6}$ = 6.2 Hz, H-6''), 5.54 (d, $J_{1,2}$ = 8.0 Hz, H-1'''), 5.08 (t, $J_{2,3}$ = 8.5 Hz, H-2'''), 5.21 (t, $J_{3,4}$ = 9.5 Hz, H-3'''), 5.00 (t, $J_{4,5}$ = 10.5 Hz, H-4'''), 3.75 (ddd, H-5'''), 3.83 (dd, $J_{6A,6B}$ = 12.5 Hz, $J_{5,6A}$ = 2.5 Hz, H-6A'''), 3.59 (dd, $J_{5,6B}$ = 5.5 Hz, H-6B'''), 4.58 (d, $J_{1,2}$ = 7.7 Hz, H-1''''), 4.83 (t, $J_{2,3}$ = 8.7 Hz, H-2''''), 5.17 (t, $J_{3,4}$ = 8.9 Hz, H-3''''), 3.85 (t, $J_{4,5}$ = 9.3 Hz, H-4''''), 3.59 (H-5''''), 4.45 (dd, $J_{6A,6B}$ = 12.3 Hz, $J_{5,6A}$ = 1.9 Hz, H-6A''''), 4.30 (dd, $J_{5,6B}$ = 4.0 Hz, H-6B''''), 4.82 (d, $J_{1,2}$ = 1.5 Hz, H-1'''''), 5.03 (dd, $J_{2,3}$ = 3.5 Hz, H-2'''''), 5.04 (t, $J_{4,5}$ = 10.2 Hz, H-4'''''), 3.83 (dq, H-5'''''), 1.15 (d, $J_{5,6}$ = 6.2 Hz, H-6'''''),

The deacetylation of 2.0 g of (Va) and additional chromatographic purification on silica gel in system (3) gave 1.1 g of pure (V), $[\alpha]_D^{20}$ −34.9° (c 3.5; pyridine). Rhamnose, arabinose, glucose, and echinocystic acid were identified in an acid hydrolysate of (V). The progenin from (V) was identical with tauroside D [8]. PMR of (V) (δ, ppm;

0 — TMS, C_5D_5N): 4.88 (d, $J_{1,2}$ = 5.3 Hz, H-1'), 4.52 (t, $J_{2,3}$ = 6.0 Hz, H-2'), 4.25 (H-3'), 6.09 (d, $J_{1,2}$ = 1.5 Hz, H-1''), 4.71 (dd, $J_{2,3}$ = 3.3 Hz, H-2''), 4.60 (dd, $J_{3,4}$ = 9.3 Hz, H-3''), 4.28 (t, $J_{4,5}$ = 9.3 Hz, H-4''), 4.56 (dq, H-5''), 1.59 (d, $J_{5,6}$ = 6.1 Hz, H-6''), 6.21 (d, $J_{1,2}$ = 8.0 Hz, H-1'''), 4.03 (t, $J_{2,3}$ = 8.6 Hz, H-2'''), 4.17 (t, $J_{3,4}$ = 8.6 Hz, H-3'''), 4.94 (d, $J_{1,2}$ = 8.0 Hz, H-1''''), 3.90 (dd, $J_{2,3}$ = 9.0 Hz, H-2''''), 4.11 (t, $J_{3,4}$ = 9.0 Hz, H-3''''), 4.38 (t, $J_{4,5}$ = 9.0 Hz, H-4''''), 3.62 (H-5''''), 5.82 (d, $J_{1,2}$ = 1.5 Hz, H-1'''''), 4.65 (dd, $J_{2,3}$ = 3.3 Hz, H-2'''''), 4.53 (dd, $J_{3,4}$ = 9.4 Hz, H-3'''''), 4.30 (t, $J_{4,5}$ = 9.4 Hz, H-4'''''), 4.94 (dq, H-5'''''), 1.67 (d, $J_{5,6}$ = 6.0 Hz, H-6'''''), 3.24 (dd, $J_{2e,3}$ = 4.0 Hz, $J_{2a,3}$ = 12.0 Hz, H-3), 5.27 (q, H-12), 5.57 (br. t., $J_{15a,16}$ = $J_{15e,16}$ = 3.0 Hz, H-16), 0.7-2.9 (skeletal CH, CH_2 of the aglycon), 1.12, 1.10, 1.04, 1.01, 0.96, 0.88, 0.85 (7 CH_3).

Tauroside H_2 (II). After the chromatographic purification of 3.0 g of H_2 on silica gel with elution by system 3, 1.5 g of pure (II) was obtained, with $[\alpha]_D^{20}$ −14.9° (c 3.5; pyridine). According to the literature [15]: $[\alpha]_D$ −8° (pyridine). Rhamnose, arabinose, glucose, and hederagenin were identified in an acid hydrolysate of (II). The progenin of (II) was identical with tauroside E [3].

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