Chemistry of Natural Compounds, Vol. 29, No. 4, 1993

TRITERPENE GLYCOSIDES OF *Hedera taurica*. XI. STRUCTURES OF TAUROSIDES St-G_1, St-H_1, and St-H_2 FROM THE STEMS OF CRIMEAN IVY

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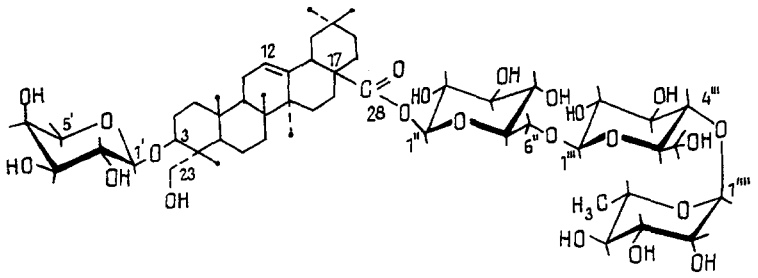
UDC 547.918:543.422

The previously known glycosides 3-O-α-L-arabinopyranosyl-28-O-[α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl]hederagenin and 3-O-[α-L-rhamnopyranosyl-(1→2)-O-α-L-arabinopyranosyl]-28-O-[α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl]hederagenin and the new triterpene glycoside tauroside St-H_1 — 3-O-β-D-glucopyranosyl-28-O-[α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl]hederagenin — have been isolated from the stems of Hedera taurica *Carr.*

In continuation of a study of the triterpene glycosides of Crimean ivy, we have analyzed the composition of the stems of this plant. TLC analysis of an ethanolic extract showed the presence of at least ten glycosides, which have been called St-A, -B, -C, -D, -E, -F, -G, -H, -I, -J, and -K (St- from stem). They were isolated by extracting the stems with hot ethanol, concentrating, diluting with water, and extracting successively with benzene (to eliminate fats and waxes), chloroform (extraction of St-A–St-F), and butanol (St-G–St-K).

In the present paper we describe the determination of the structures of St-G_1, St-H_1, and St-H_2. Separation of the butanol extract was achieved on silica gel with elution by the solvent system chloroform–ethanol–water. This yielded narrow fractions of glycosides G, H, I, J, and K.

Analysis of fraction G in the chloroform–methanol–ammonia system showed that it consisted of four glycosides, which were called St-G_0, -G_1, -G_2, and -G_3, and of which the second (St-G_1) greatly predominated and was obtained in the pure form by rechromatography. According to TLC, it was identical with hederoside G from the berries of Crimean ivy [1] and tauroside G_1 from the leaves [2]. The structure of tauroside St-G_1 was additionally confirmed by the results of acid and alkaline hydrolyses, and also by a comparison of the ^{13}C NMR spectrum with that published previously [1, 2]. Consequently, tauroside St-G_1 is 3-O-α-L-arabinopyranosyl-28-O-[α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl]hederagenin.



TLC analysis of fraction H showed the presence in it of two glycosides, which were called St-H_1 and St-H_2. They were separated preparatively by rechromatography on silica gel. The chromatic mobility of the predominating glycoside, St-H_2 coincided with that of hederoside St-H_1 from ivy berries [1] and that of tauroside St-H_2 from the leaves [2]. The structure of

M. V. Frunze Simferopol' State University. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 571-579, July-August, 1993. Original article submitted December 28, 1992.

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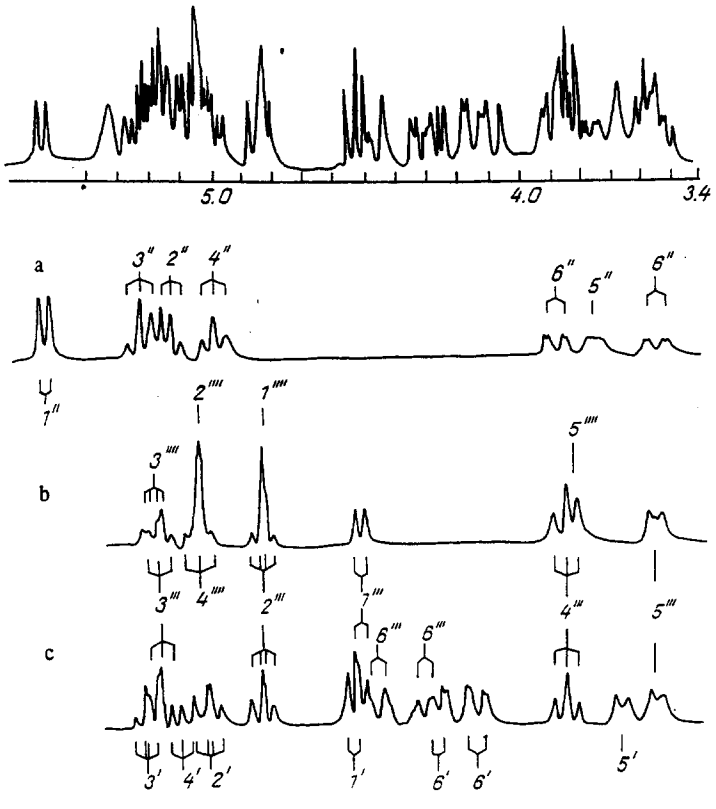
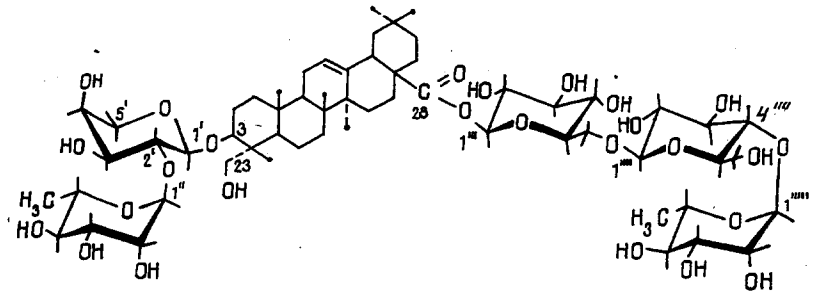


Fig. 1. Weak-field part of the PMR spectrum of the acetate of tauroside St-H_1 and one-dimensional HOHAHA spectra obtained on excitation of the following protons: a) H-1″; b) H-1‴″ and H-2′″; c) H-1′ and H-1′″.

tauroside St-H_2 was additionally confirmed by the results of acid and alkaline hydrolyses and by a comparison of its ^{13}C NMR spectrum with literature information [1, 2]. Consequently, tauroside St-H_2 is 3-O-[α-L-rhamnopyranosyl-(1→2)-O-α-L-arabino-pyranosyl]-28-O-[α-L-rhamnopyranosyl-(1→4)-O-β-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl]hederagenin.



Tauroside St-H_1 was not present in either the berries or the leaves of Crimean ivy. In the products of acid hydrolysis we identified glucose and rhamnose and, as the aglycon, hederagenin. Alkaline hydrolysis yielded a progenin identical with hederoside B from ivy berries [3], which is 3-O-β-D-glucopyranosylhederagenin. The further investigation of the structure of St-H_1 was carried out with the use of a number of variants of NMR spectroscopy.

The assignment of the signals of the carbohydrate residues in the PMR spectra of tauroside H-St_1 and its full acetate was made with the one-dimensional variant of a HOHAHA experiment in a rotating system of coordinates (RSC) [4]. Figure 1 shows HOHAHA spectra for the acetate of St-H_1. Thus, on excitation of the anomeric proton of the glucose residue Glc″, the signal of which does not overlap with any others, it was possible to reveal all the protons of this residue (Fig. 1a). Here, the assignment of the signals of the H-5″ and H-6″ protons gave no difficulty in view of their characteristic splitting, while

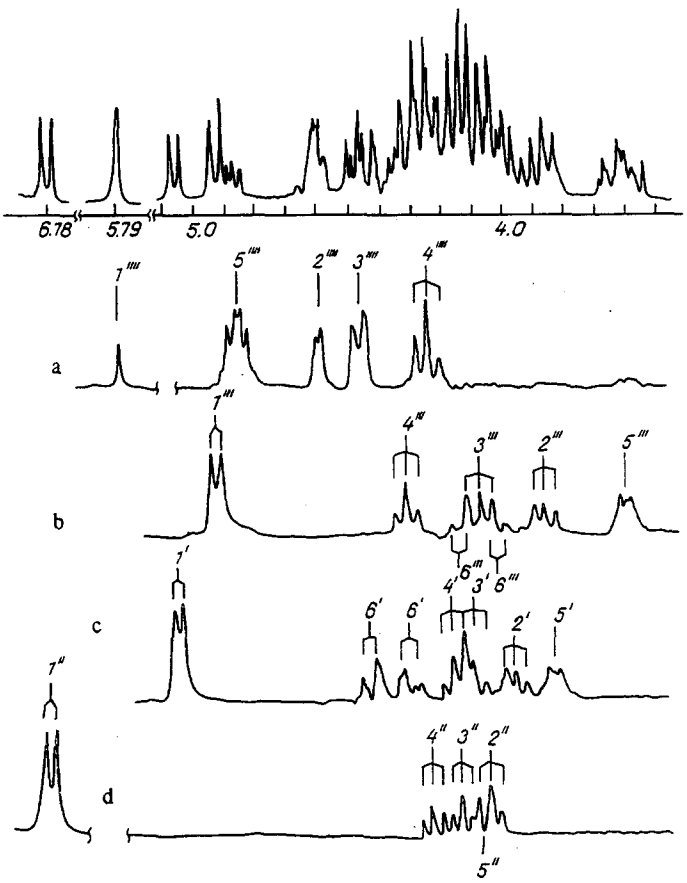


Fig. 2. Weak-field part of the PMR spectrum of tauroside St-H_1 and the one-dimensional HOHAHA spectra obtained on the excitation of the following atoms: a) H-5‴; b) H-1′‴; c) H-1′ d) H-1″.

the assignment of the signals of the H-2″, H-3″, and H-4″ protons was made with the aid of double homonuclear resonance. The interpretation of the HOHAHA spectra in Fig. 6b, c, was made by comparing these two spectra: in both, subspectra of the Glc′″ residue were present — in the first (Fig. 1b) because of the simultaneous excitation of H-1‴ of Rha‴ and H-2′″ of Glc′″, and in the second (Fig. 1c) because of the simultaneous excitation of the anomeric protons of Glc′ and of Glc′″. The assignment of the signals of the Rha‴ residue in the subspectrum of Fig. 1b was easy to make because of their characteristic splitting. Homonuclear double resonance was used for the assignment of the signals of the H-2, H-3, and H-4 protons in the subspectra of Glc′ and Glc′″. We may note that the use of a HOHAHA experiment substantially facilitates the complete identification of the signals, since the use of homonuclear double resonance alone becomes inefficient in the case of three and more sugars because of the unavoidable overlapping of the multiplets.

After the interpretation of the carbohydrate part of the acetate of St-H_1 its monosaccharide composition became obvious — three β-glucopyranose and one rhamnopyranose residues — and so also did the types of substitution in the sugar residues and the aglycon. Thus, a downfield shift of the H-1″ signal of Glc″ showed the presence of an acyl glycosidic bond at this residue (addition to the carboxy group of the aglycon). It followed from the strong-field positions of the H-4′″ atom of Glc′″ and of the H-6″ atom of Glc″ that the hydroxy groups at the corresponding carbon atoms did not bear acyl (acetyl) substituents; i.e., they were glycosylated. The weak-field positions of the signals of H2‴—H-4‴ of Rha‴ and of H-2′—H-4′ and H-6′ of Glc′ showed the absence of substitution in these sugar residues and their terminal positions.

The assignment of the signals in the PMR spectrum of the initial St-H_1 (solution in pyridine-d_5) was made analogously. The results of HOHAHA experiements are shown in Fig. 2. Only for the Glc″ residue was it impossible to find the position of the H-6″ protons in view of the remoteness of the signal of the anomeric proton undergoing excitation from the signals of the other protons, which is unfavorable for the transfer of polarization in the spin system under the conditions of a HOHAHA

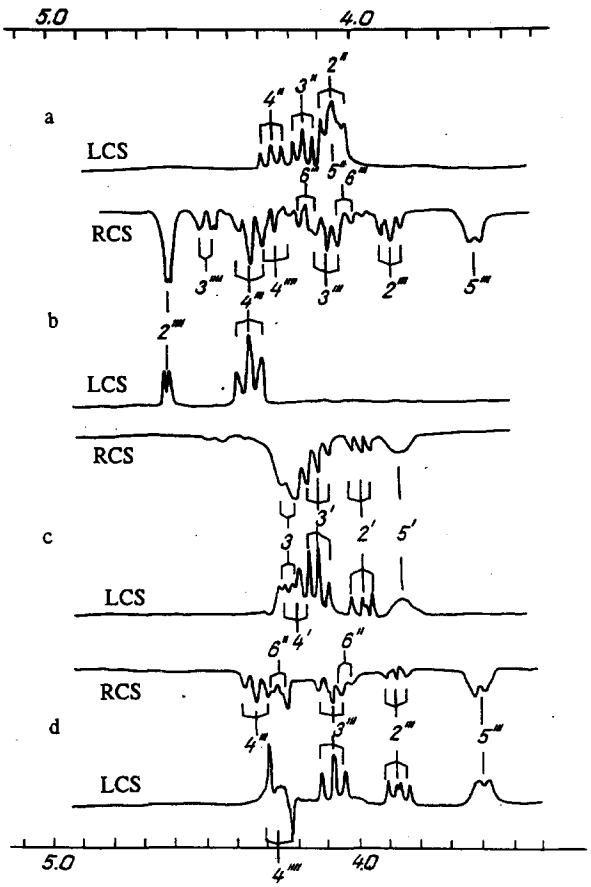


Fig. 3. Weak-field part of the different NOE spectra of tauroside St-H_1 in laboratory and rotating systems of coordinates (LSC and RSC) obtained on the preirradiation of the following atoms: a) H-1″; b) H-1‴″; c) H-1′; d) H-1′″.

experiment [4]. The selection of a different protons of this residue for excitation (such as H-5‴″ for Rha‴″) did not appear possible because of overlapping with other signals.

The sequence of linkage of the carbohydrate residues was additionally confirmed with the aid of the difference variant of nuclear Overhauser effect (NOE) spectroscopy in the laboratory system of coordinates (LSC) with the preirradiation of each anomeric proton. Preiradiation of the H-1″ proton of Glc″ (Fig. 3a) caused the appearance in the difference NOE spectrum of the signals of the protons of this residue alone, which is natural for its acyl glycosidic link with the aglycon. An analogous experiment with H-1′ of Glc′ led to the appearance in the difference spectrum of signals from H-2′, H-3′ and H-5′ of this residue (axial H-1′ proton) and also of a signal from H-3 of the aglycon (Fig. 3c). The preirradiation of H-1‴″ of Rha‴″ (Fig. 3b) led to the appearance in the difference spectrum of a signal from H-2‴″ of this residue, which showed the equatorial orientation of the H-1‴″ proton and, consequently, the α-configuration of the rhamnose residue, and of a signal from from H-4′″ of the Glc′″ residue. The latter confirmed the presence of a 1→4 bond between the terminal rhamnose residue and the Glc′″ residue. An experiment with the preirradiation of H′″ of Glc′″ (Fig. 3d) did not reveal the expected signals of a glycosylated sugar (H-6″ of Glc″) possibly because of an unfavorable correlation time for the protons close to the 1→6 bond and, as a consequence of this, zero NOEs for an instrument with a working frequency of 250 MHz. The presence in the spectrum (Fig 3d) of the signals of H-4‴″ of Rha‴″ is the result of the interference of the components of the H-5‴″ multiplet of Rha‴″ on the preirradiation of H′″ of Glc′″ (PSEUDOINDOR).

Having the possibility of performing a NOE experiment in a RSC (CAMELSPIN) [5], we compared the results obtained with those in the laboratory system of coordinates (LSC). It can be seen from Fig. 3b that excitation of the anomeric proton of the Rha‴″ residue led to the appearance in the difference spectrum not only of the H-2‴″ signal of Rha‴″ but also of a small signal from H-3‴″ of Rha‴″, which is a consequence of spin diffusion during the time of spin-locking (0.2 s). Particulary

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

C atom	Compound			C atom	Compound		
	I	II	III		I	II	III
1	38,8	38,7	39,0	16	23,8	23,7	23,7
2	26,0	26,0	26,0	17	46,2	46,2	46,2
3	82,0	82,3	80,9	18	41,6	41,6	41,5
4	43,3	43,3	43,3	19	47,0	47,0	46,9
5	47,6	47,7	47,6	20	30,7	30,7	30,6
6	18,1	18,2	18,0	21	34,0	34,0	34,0
7	32,5	32,5	32,4	22	32,7	32,8	32,5
8	39,9	39,8	39,9	23	64,6	64,7	64,0
9	48,1	48,1	48,0	24	13,5	13,5	13,8
10	36,9	36,9	36,7	25	16,1	16,2	16,0
11	23,3	23,3	23,2	26	17,5	17,5	17,4
12	122,8	122,9	122,8	27	26,0	25,8	26,0
13	144,0	144,1	144,0	28	176,4	176,5	176,4
14	42,1	42,1	42,0	29	33,0	33,0	33,0
15	28,2	28,3	28,2	30	23,6	23,7	23,6

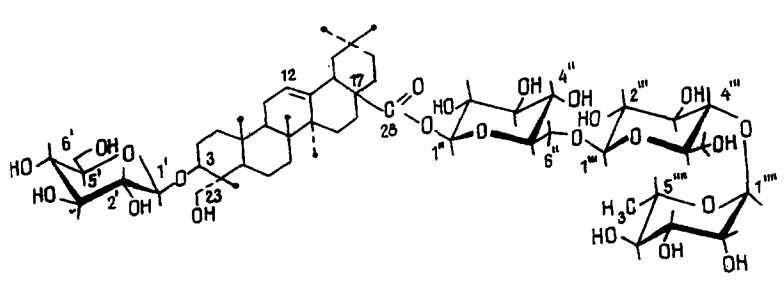
TABLE 2. Chemical Shifts of the Signals of the ^{13}C Atoms of the Carbohydate Moieties of Taurosides St-G_1 (I), St-H_1 (II), and St-H_2 (III) (δ, ppm, 0 — TMS; C_5D_5N)

C atom	I	II	C atom	I	II	C atom	III	C atom	III
	Ara	Glc		Glc	Glc		Ara		Glc
1′	106,3	105,7	1″	95,5	95,5	1′	104,1	1‴	95,5
2′	72,9	75,6	2″	73,8	73,8	2′	75,7	2‴	73,7
3′	74,5	78,4	3″	78,5	78,4	3′	74,3	3‴	78,5
4′	69,4	71,5	4″	70,8	70,7	4′	69,0	4‴	70,7
5′	66,7	78,1	5″	77,8	77,9	5′	65,3	5‴	77,9
6′		62,7	6″	69,1	69,2	6′		6‴	69,0
				Glc	Glc		Rha		Glc
			1‴	104,6	104,7	1″	101,5	1⁗	104,6
			2‴	75,1	75,1	2″	72,1	2⁗	75,1
			3‴	76,4	76,3	3″	72,4	3⁗	76,3
			4‴	78,4	78,1	4″	73,9	4⁗	78,2
			5‴	76,9	77,0	5″	69,6	5⁗	76,9
			6‴	61,3	61,2	6″	18,4	6⁗	61,1
				Rha	Rha				Rha
			1⁗	102,6	102,6			1⁗′	102,5
			2⁗	72,3	72,3			2⁗′	72,4
			3⁗	72,6	72,5			3⁗′	72,5
			4⁗	73,8	73,8			4⁗′	73,8
			5⁗	70,2	70,2			5⁗′	70,2
			6⁗	18,3	18,4			6⁗′	18,4

appreciable was spin diffusion in the neighboring residue Glc‴, for which, in the difference spectrum, signals were seen not only of the protons close to H-1⁗ of Rha⁗ (H-4‴ and H-6″ of Glc″) but also of the other signals of this residue. An experiment with the excitation of H′ of Glc′ (Fig. 3c) led to results analogous to those in the LSC. In an experiment with the irradiation of H-1‴ of Glc‴ (Fig. 3d), in addition to the H-2‴–H-5‴ protons of this residue, it was possible to reveal signals with δ 4.04 and 4.25 ppm (both doublets of doublets, the largest about 12 Hz) obviously relating to H-6A″ and H-6B″ of Glc″ (but these did not appear in the HOHAHA spectrum).

Thus, the NOE experiment in the RSC showed up all the spatially close atoms. On the other hand, these spectra were less characteristic than in the LSC as a consequence of the appearance of other signals due to spin diffusion.

The facts given above determined the sequence of linkage of the carbohydrate residues and the full structure of tauroside St-H_1 as 3-O-β-D-glucopyranosyl-28-O-[α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl]hederagenin.



The assignment of the signals in the ^{13}C NMR spectrum of this glycoside was made by comparing the experimental results with those given in the literature for 3-O-β-D-glucopyranosylhederagenin [3] and the trisaccharide fragment rhamnopyranosyl-(1→4)-glucopyranosyl-(1→6)-glucopyranosyl- [2, 6]. A comparison of these facts definitively confirmed the structure given above. Tauroside St-H_1 is a new triterpene glycoside.

EXPERIMENTAL

NMR spectra were otbained on a Bruker WM-250 instrument modernized for inverse procedures. One-dimensional HOHAHA experiments were conducted by the procedure of [4] using an exciting DANTE pulse [7]. One-dimensional difference NOE spectra in a RSC (CAMELSPIN) [5] were also obtained with the use of a DANTE pulse. In all the experiments the spin-locking time was 0.2 s.

Specific rotations were measured on a SU-4 polarimeter at $\lambda = 589$ nm.

TLC monitoring was conducted on Silufol plates, and preparative separation on silica gel L (40-100 μm). The following solvent systems were used: 1) chloroform–methanol–water (20:6:1); 2) chloroform–ethanol (4:1→1:1), saturated with water; and 3) chloroform–methanol–ammonia (10:4:1).

Acetylation was performed with acetic anhydride in pyridine (1:1, 20°C, 20 h) followed by evaporation to dryness with the addition of benzene and chromatographic purification on silica gel with elution by the solvent system chloroform–methanol (200:1→50:1).

Deacetylation was achieved by treating an acetate with a 0.01 N solution of sodium methanolate in absolute methanol (40°C, 5-20 h) followed by neutralization with the cation-exchange resin KU-2-8 in the H^+ form, evaporation to dryness, and chromatographic purification on silica gel in an appropriate solvent system.

Acid hydrolysis was performed with 2 N trifluoroacetic acid in a mixture of dioxane and water (1:1, 100°C, 2 h). In the hydrolysate the aglycon was identified by TLC in the solvent system benzene–acetone (5:1) and sugars in chloroform–methanol–ammonia (6:3:1).

Alkaline hydrolysis was carried out with 10% caustic potash in a mixture of methanol and water (1:1, 100°C, 2 h). After neutralization with dilute sulfuric acid to pH 5-6 the progenins were extracted with butanol.

Isolation of the Glycosides. Stems of Crimean ivy gathered in August, 1992, in the region of the village of Pereval'nii (Crimea) in an amount of 6 kg were comminuted and extracted with 70% aqueous ethanol. The extract was evaporated to 1/5 volume, diluted with water, and extracted successively with benzene, chloroform, and butanol. According to TLC in system 1, the chloroform extract (20 g) contained the weakly polar glycosides St-A–St-F. The butanol extract (50 g) contained glycosides of medium polarity, designated as St-G–St-K.

Separation of the Glycosides. The preparative separation of the medium-polarity fraction of glycosides on silica gel with elution by system 2 gave the glycoside fractions St-G (2.7 g), St-H (9.5 g), St-I (4.5 g), St-J (0.9 g), and St-K (5.5 g). The TLC analysis of fraction St-G in system 3 showed that it contained four glycosides, which were designated as St-G_0, -G_1, -G_2, and -G_3. The rechromatography of fraction St-G om silica gel in system 2 gave St-G_0 (0.3 g), St-G_1 (2.0 g), and a mixture of St-G_2 and St-G_3 (0.3 g). Rechromatography of fraction St-H on silica gel in system 2 gave St-H_1 (0.4 g) and St-H_2 (8.2 g).

Tauroside St-G_1 (I). According to TLC in systems 1 and 3, (I) was identical with hederoside G [1] and tauroside G_1 [2]. In an acid hydrolysate of (I) we detected rhamnose, arabinose, and glucose, and the aglycon hederagenin. A progenin from (I) was identical with tauroside B [8]. The final purification of (I) was done on silica gel in system 3; $[\alpha]_D$ +9° (*c* 2.0; pyridine). According to the literature [9]: $[\alpha]_D$ +10.2° (pyridine).

Tauroside St-H_1 (II). In an acid hydrolysate of (II) we identified glucose, rhamnose, and hederagenin. A progenin from (II) was identical with hederoside B [3]. Additional chromatography on silica gel in system 3 gave pure (II): $[\alpha]_D$ +4.5° (*c* 4.3; pyridine).

PMR spectrum (II): (δ, ppm, 0 — TMS, C_5D_5N): 5.06 (d, $J_{1,2}$ = 7.8 Hz, H-1′), 3.97 (t, $J_{2,3}$ = 8.6 Hz, H-2′), 4.11 (t, $J_{3,4}$ = 7.2 Hz, H-3′), 4.18 (t, $J_{4,5}$ = 9.0 Hz, H-4′), 3.83 (H-5′), 4.45 (dd, $J_{5,6A}$ = 2.3 Hz, H-6A′), 4.32 (dd, $J_{5,6B}$ = 4.5 Hz, $J_{6A,B}$ = 12.5 Hz, H-6B′), 6.18 (d, $J_{1,2}$ = 8.0 Hz, H-1″), 4.05 (t, $J_{2,3}$ = 9.0 Hz, H-2″), 4.15 (t, $J_{3,4}$ = 8.5 Hz, H-3″), 4.24 (t, $J_{4,5}$ = 9.5 Hz, H-4″), 4.04 (H-6A″), 4.25 (H-6B″), 4.93 (d, $J_{1,2}$ = 8.0 Hz, H-1‴), 3.87 (d, $J_{2,3}$ = 8.5 Hz, H-2‴) 4.08 (t, $J_{3,4}$ = 9.5 Hz, H-3‴), 4.34 (t, $J_{4,5}$ = 9.5 Hz, H-4‴), 3.59 (H-5‴), 4.15 (dd, $J_{5,6A}$ = 3.8 Hz, H-6A‴), 4.02 (dd, $J_{5,6}$ = 5.5 Hz, $J_{6A,6B}$ = 14.0 Hz, H-6B‴), 5.79 (d, $J_{1,2}$ = 1.5 Hz, H-1⁗), 4.61 (dd, $J_{2,3}$ = 3.4 Hz, H-2⁗),

4.48 dd, $J_{3,4}$ = 9.5 Hz, H-3‴), 4.28 (t, $J_{4,6}$ = 9.5 Hz, H-4‴), 4.88 (dq, $J_{5,6}$ = 6.5 Hz, H-5‴), 1.65 (d, $J_{5,6}$ = 6.5 Hz, H-6‴).

The acetylation of (II) gave the full acetate (IIa); $[\alpha]_D$ +2.8° (*c* 3.0; chloroform).

PMR spectrum (δ, ppm, 0 — TMS, $CDCl_3$): 4.52 (d, $J_{1,2}$ = 8.0 Hz, H-1′), 4.99 (t, $J_{2,3}$ = 10.0 Hz, H-2′), 5.20 (t, $J_{3,4}$ = 8.7 Hz, H-3′), 5.04 (t, $J_{4,5}$ = 9.6 Hz, H-4′), 3.69 (H-5′), 4.12 (dd, $J_{5,6A}$ = 2.7 Hz, H-6A′), 4.25 (dd, $J_{5,6B}$ = 5.3 Hz, $J_{6A,B}$ = 12.5 Hz, H-6B′), 5.53 (d, $J_{1,2}$ = 8.1 Hz, H-1″), 5.12 (t, $J_{2,3}$ = 9.1 Hz, H-2″), 5.22 (t, $J_{3,4}$ = 9.2 Hz, H-3″), 4.98 (t, $J_{4,5}$ = 9.5 Hz, H-4″), 3.77 (H-5″), 3.87 (dd, $J_{5,6A}$ = 2.5 Hz, H-6A″), 3.54 (dd, $J_{5,6B}$ = 6.0 Hz, $J_{6A,6B}$ = 11.0 Hz, H-6B″), 4.49 (d, $J_{1,2}$ = 8.0 Hz, H-1‴), 4.82 (dd, $J_{2,3}$ = 9.5 Hz, H-2‴), 5.15 (t, $J_{3,4}$ = 9.5 Hz, H-3‴), 3.82 (t, $J_{4,5}$ = 9.5 Hz, H-4‴), 3.55 (H-5‴), 4.43 (dd, $J_{5,6A}$ = 1.8 Hz, H-6A‴), 4.29 (dd, $J_{5,6B}$ = 3.8 Hz, $J_{6A,6B}$ = 12.4 Hz, H-6B‴), 4.81 (d, $J_{1,2}$ = 2.0 Hz, H-1⁗), 5.02 (dd, $J_{2,3}$ = 2.9 Hz, H-2⁗), 5.18 (dd, $J_{3,4}$ = 9.8 Hz, H-3⁗), 5.03 (t, $J_{4,5}$ = 10.2 Hz, H-4⁗), 3.82 (dq, H-5⁗), 1.14 (d, $J_{5,6}$ = 6.5 Hz, H-6⁗), 5.31 (pt, $J_{11,12}$ = 8.2 Hz, H-12), 4.05 (d, $J_{23A,23B}$ = 12.0 Hz, H-23A), 3.62 (d, H-23B), 0.72, 0.74, 0.90, 0.96, 1.106, 1.26 (all s, $-CH_3$).

Tauroside St-H_2 (III). According to TLC in systems 1 and 3, (III) was identical with hederoside H_1 [1] and tauroside H_2. In an acid hydrolysate of (III) we detected rhamnose, arabinose, glucose, and hederagenin. After additional purification on silica gel in system 3, $[\alpha]_D$ −10° (*c* 1.5; pyridine). According to the literature [9]: $[\alpha]_D$ −8° (pyridine). Progenin from (III) was identical with tauroside E [1b]. The ^{13}C NMR spectra of compounds (I), (II), and (III) are given in Tables 1 and 2.

REFERENCES

1. V. I. Grishkovets, A. A. Loloiko, A. S. Shashkov, and V. Ya. Chirva, Khim. Prir. Soedin., 779 (1990).
2. B. I. Grishkovets, N. V. Tolkachev, A. S. Shashkov, and V. Ya. Chirva, Khim. Prir. Soedin., 552 (1992).
3. A. A. Loloiko, V. I. Grishkovets, A. S. Shashkov, and V. Ya. Chirva, Khim. Prir. Soedin., 721 (1988).
4. S. Subramian and A. Bax, J. Magn. Reson.,**71**, 325 (1987).
5. A. A. Both-By, R. L. Shephens, J. Lee, C. D. Warren, and R. W. Jeanloz, J. Am. Chem. Soc., **106**, No. 3, 811 (1984).
6. V. I. Grishkovets, N. V. Tolkachev, A. S. Shashkov, and V. Ya. Chirva, Khim. Prir. Soedin., 683 (1992).
7. G. A. Morris and R. Freeman, J. Magn. Reson., **29**, 433 (1978).
8. A. A. Loloiko, V. I. Grishkovets, A. S. Shashkov, and V. Ya. Chirva, Khim. Prir. Soedin., 379 (1988).
9. M. Shimizu, M. Arisawa, N. Morita, H. Kizu, and T. Tomimori, Chem Pharm. Bull., **26**, No. 2, 655 (1978).
10 A. S. Shashkov, V. I. Grishkovets, A. A. Loloiko, and V. Ya. Chirva, Khim. Prir. Soedin., 363 (1987).