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TRITERPENE GLYCOSIDES OF *Hedera taurica* XV. STRUCTURES OF GLYCOSIDES St-I_3, St-I_{4a}, St-I_{4b}, and St-I_5 FROM THE STEMS OF CRIMEAN IVY

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From the stems of Crimean ivy Hedera taurica *Carr. (fam. Araliaceae) we have isolated the new triterpene glycosides St-I_3, St-I_5, and St-I_{4a}, which are, respectively, the 3-O-β-D-glucopyranoside 28-O-[O-α-L-rhamnopyranosyl-(1→4)-O-(6-O-acetyl-β-D-glucopyranosyl)-(1→6)-O-β-D-glucopyranosides] of oleanolic acid and of hederagenin and the 3-O-β-D-glucopyranuronoside 28-O-β-gentiobioside of oleanolic acid, and also the previously known 3-O-[O-β-D-galactopyranosyl-(1→2)-β-D-glucopyranuronoside 28-O-β-D-glucopyranoside] of oleanolic acid (glycoside Rb-4).*

In the isolation from fraction St-I of the glycosides St-I_1 and St-I_2 described previously [1], we also eluted fractions designated as St-I_3, St-I_4, and St-I_5. TLC analysis of fractions St-I_3 and St-I_5 showed that they consisted of individual glycosides, St-I_3 (**1**) and St-I_5 (**2**). For additional purification, (**1**) and (**2**) were converted into the methyl esters (**1a**) and (**2a**) by treatment with an ethereal solution of diazomethane, and these were chromatographed on silica gel (SiO_2). TLC analysis of similarly methylated fraction St-I_4 in the solvent system chloroform–methanol–ammonia showed that it consisted of two glycosides with very close chromatographic mobilities, St-I_{4a} (**3**) and St-I_{4b} (**4**). Their separation was achieved by the chromatography of their full acetates on SiO_2, followed by deacetylation.

In complete acid hydrolysates of (**1a**) and (**2a**) we identified the monosaccharides glucuronic acid, glucose, and rhamnose, and the aglycons oleanolic acid, in (**1a**), and hederagenin, in (**2a**). Progenins obtained from (**1a**) and (**2a**) by alkaline hydrolysis were identical with the 3-O-β-*D*-glucopyranuronosides of oleanolic acid and of hederagenin (the progenins of glycosides St-J and St-K [2]).

When (**1a**) and (**2a**) were chromatographed in solvent systems containing ammonia, the partial formation from them of the more polar glycosides St-J and St-K [2] was observed, which permitted the assumption of the presence of (an) acyl group(s) in (**1a**) and (**2a**). The deacetylation of (**1a**) and (**2a**) by catalytic amounts of sodium methanolate in methanol gave, in quantitative yield, the previously described esters of glycosides St-J (from **1a**) and St-K (from **2a**) [2], which are the 3-O-β-*D*-glucopyranuronoside 28-O-[O-α-*L*-rhamnopyranosyl-(1→4)-O-β-*D*-glucopyranosyl-(1→6)-glucopyranoside]s of oleanolic acid and of hederagenin.

The types of bonds and the linkage sequence of the monosaccharide residues in the trisaccharide fragment $Rha \xrightarrow{\alpha 4} Glc \xrightarrow{\beta 6} Glc^{\beta}$ were additionally confirmed for (**1a**) by the PMR spectrum of the full acetate (**1b**) and its two-dimensional ROESY spectrum (Fig. 1), in which we observed characteristic cross-peaks between H-1 of the glucuronic acid residue and H-3 of the aglycon, and also between H-1 of Rha'''' and H-4 of Glc''' and between H-1 of Glc''' and H-6 of Glc''. The ROESY spectrum of the full acetate of (**2a**), (**2b**) was completely identical with that of the full acetate of glycoside St-K [2].

The question of the nature and localization of the acyl groups in (**1a**) and (**2a**) was answered by an analysis of PMR and ^{13}C NMR spectra. The assignment of the signals in the PMR spectrum of (**2a**) was based on sections on ν_2 of the TOCSY two-dimensional total-correlation spectrum (2D HOHAHA) [3] from the chemical shifts of H-1 of GlcUA (5.16 ppm), H-1 of Glc'' (6.16 ppm) and H-5 of Glc''' (3.78 ppm). The chemical shifts of all the skeletal protons, with the excep-

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TABLE 1. Chemical Shifts of the ^{13}C Atoms of the Aglycon Part of the Methyl Ester of Glycoside St-I_5 (**2a**) (δ, ppm, 0–TMS, C_5D_5N, 70°C)

C-Atom	2a	C-Atom	2a	C-Atom	2a
1	38.8	11	23.4	21	34.1
2	26.1	12	123.0	22	32.9
3	82.5	13	144.2	23	64.5
4	43.5	14	42.2	24	13.8
5	47.6	15	28.4	25	16.2
6	18.3	16	23.8	26	17.6
7	32.7	17	47.1	27	26.1
8	40.0	18	41.7	28	176.5
9	48.2	19	46.3	29	33.2
10	37.0	20	30.8	30	23.8

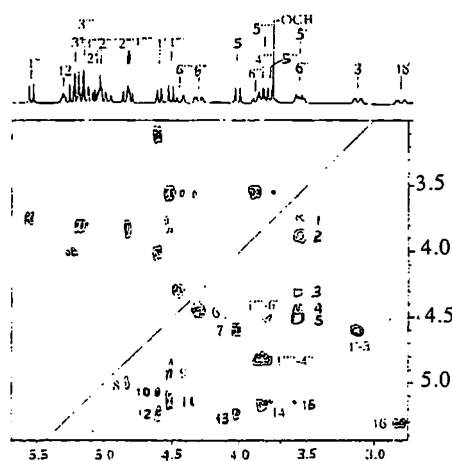
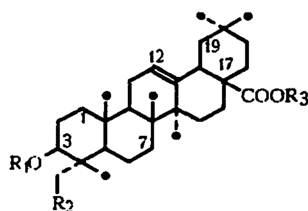


Fig. 1. Fragment of the two-dimensional ROESY spectrum of the full acetate of glycoside St-I_3. The numerals designate cross-peaks between the signals of the following protons: 1) (5–6B)″; 2) (6A–6B)″; 3) (5–6B)‴; 4) (5–6A)‴; 5) (1–5)‴; 6) (6A–6B)‴; 7) (1–5)′; 8) (1–2)⁗; 9) (1–2)‴; 10) (1–2)′; 11) (1–3)‴; 12) (1–3)′; 13) (3–5)′; 14) (3–5)⁗; 15) (3–5)‴; 16) (12–18); 17) (1–5)″.

tion of H-6 and H-5 of the Glc‴ residue, practically coincided with those for glycoside St-K [1], while the signals of H-6A,B of Glc‴ were shifted downfield by 0.2 ppm as compared with St-K. This is due to the position of the O-acyl group at C-6 of Glc‴. Analysis of the high-field region of the PMR spectrum together with the singlet signals of the six CH_3 groups of the aglycon and the singlet of the O-CH_3 of the methyl ester of the glucuronic acid residue permitted the detection of a single three-proton singlet with δ 1.88 ppm in the usual region for acetates of 1.8-2.2 ppm. Consequently the carbohydrate moiety of (**2a**) is represented by the acetylated trisaccharide $\text{Rha}\xrightarrow{\alpha 4}\text{(6-OAc-Glc)}\xrightarrow{\beta 6}\text{Glc}^{\beta}$, which has been found previously in plants of the Araliaceae family [4].

The assignments in the ^{13}C NMR spectrum of (**2a**) were made by comparison with the spectrum of the methyl ester of glycoside St-K [2]. The signal of the C-6 atom of the Glc‴ residue had experienced a downfield (2 ppm) shift, and C-5 an upfield (3.4 ppm) shift, which confirmed the PMR results on the localization of the O-acetyl group at C-6 of the internal glucose residue. The assignments made in this way agree with the literature for the 6-O-acetylated trisaccharide [4].

The assignments of the signals in the PMR spectrum of (**1a**) was made by comparison with the spectrum of (**2a**), and were practically identical for the carbohydrate components. Thus, glycosides St-I_3 and St-I_5 are the 3-O-β-D-glucopyranuronoside 28-O-[O-α-*L*-rhamnopyranosyl-(1→4)-O-(6-acetyl-β-*D*-glucopyranosyl-(1→6)-O-β-*D*-glucopyranoside]s of oleanolic acid and of hederagenin and are new compounds.



1-5

	R_1	R_2	R_3
1	GlcUA'β	H	βGlc" ←6β— Glc‴ (6 ← OAc) ←4α— Rha""
2	GlcUA'β	OH	βGlc" ←6β— Glc‴ (6 ← OAc) ←4α— Rha""
3	GlcUA'β	H	βGlc" ←6β— Glc‴
4	Gal" —β2→ GlcUA'β	H	βGlc"
5	Gal" —β2→ GlcUA'β	H	H

In an acid hydrolysate of the methyl ester of St-I_{4a} (**3a**) we identified glucuronic acid, glucose, and oleanolic acid. A progenin from (**3a**) was identical with an authentic specimen of oleanolic acid 3-O-*β-D*-glucopyranuronoside (a progenin of tauroside St-J) [2]. The further determination of the structure of this glycoside was achieved by analyzing the PMR spectrum of (**3b**), the full acetate of (**3a**), the assignment of the signals in which was made by the method of selective homonuclear double resonance. In this, we identified in the spectrum the signals of three anomeric protons (doublets with SSCCs of about 8 Hz) and the corresponding signals of the skeletal protons of three monosaccharide residues — a *β*-glucopyranuronose and two *β*-glucopyranoses, of which one was substituted in the C-6 hydroxy group, since the signals of the H-6A,B protons were present in a relatively upfield region of the spectrum at 3.5-4.0 ppm, while the other two monosaccharide residues were unsubstituted (terminal). Then, taking into account the results of acid and alkaline hydrolyses, the *β*-glucopyranuronose forms a glycosidic bond at the C-3 atom of the aglycon and the *β*-glucopyranose residues, in the form of the disaccharide *β*-gentiobiose, are attached to the aglycon through an acyl glycosidic bond.

The types of bonds of the monosaccharide residues with one another and with the aglycon were additionally confirmed by the ROESY spectrum of (**3b**) (Fig. 2), in which we identified structurally informative cross-peaks between the protons H-1 of GlcUA′ and H-3 of the aglycon, and between H-1 of Glc‴ and H-6 of Glc″, and other cross-peaks corresponding to 1,3-diaxial interactions of skeletal protons in individual monosaccharide residues. Thus, glycoside St-I_{4a} is oleanolic acid 3-O-*β-D*-glucopyranuronoside 28-O-*β*-gentiobioside and is a new triterpene glycoside.

In the products of the complete acid hydrolysis of the methyl ester of glycoside St-I_{4b} (**4a**) we identified glucose, galactose, and glucuronic and oleanolic acids. The alkaline hydrolysis of (**4a**) gave progenin (**5**), the acid hydrolysis of which formed galactose and glucuronic and oleanolic acids. The partial acid hydrolysis of (**5**) led to galactose and oleanolic acid 3-O-*β-D*-glucopyranuronoside [2]. Thus, the carbohydrate chain at the C3−OH group of the aglycon is represented by the disaccharide Gal→GlcUA, and glucose forms an acyl glycosidic bond with the aglycon.

Analysis of the PMR spectrum of (**4b**), the full acetate of (**4a**), the assignments in which were made in a similar way to those for (**3b**), permitted the identification of the signals of three monosaccharide residues, two of which (*β*-galactopyranose and *β*-glucopyranose), from the positions of their signals, were terminal, while the third was substituted at C-2 (H-2 signal in the 3.5-4.0 ppm region). Consequently, glucoside St-I_{4b} was oleanolic acid 3-O-[O-*β-D*-galactopyranosyl-(1→2)-*β-D*-glucopyranuronoside 28-*β*-glucopyranoside]. Glycosides of similar structure have been isolated previously from *Aralia cordata* (udosaponin B) [5] and *Tetrapanax papyriferum* (saponin R-1c) [6].

EXPERIMENTAL

For general observations and procedures for acetylation, deacetylation, and acid and alkaline hydrolysis, see [1].

TABLE 2. Chemical Shifts of the ^{13}C Atoms of the Carbohydrate Parts of the Methyl Ester of Glycoside St-I_5 (**2a**) (δ, ppm, 0−TMS, C_5D_5N, 70°C)

C-Atom	2a	C-Atom	2a	C-Atom	2a	C-Atom	2a
GlcUA′		Glc″		Glc‴		Rha⁗	
1	106.4	1	95.6	1	104.7	1	103.0
2	75.4	2	73.8	2	75.0	2	72.3
3	77.8	3	78.7	3	76.3	3	72.6
4	73.1	4	71.0	4	79.3	4	73.8
5	77.3	5	78.1	5	73.7	5	70.7
6	170.8	6	69.4	6	63.7	6	18.5
				-CO-CH_3	170.7		
				-CO-CH_3	20.7		

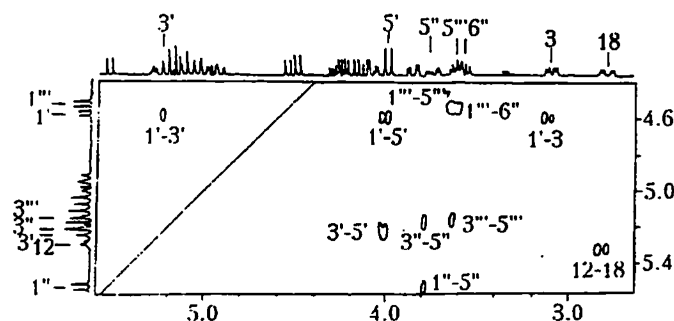


Fig. 2. Fragment of the ROESY two-dimensional spectrum of the full acetate of glycoside St-I_{4a}.

Separation of Fraction St-I. The preparative separation of 4 g of fraction St-I [1] on SiO_2 with elution by the solvent system water-saturated chloroform−ethanol (1:1) led to 0.9 g of St-I_1 and 0.4 g of St-I_2 [1], and also 0.1 g of glycoside St-I_3 (**1**), 0.1 g of fraction St-I_4, and 0.8 g of glycoside St-I_5 (**2**).

Separation of Glycosides St-I_{4a} (3) and St-I_{4b} (4). Fraction St-I_4 was successively esterified with an ethereal solution of diazomethane and acetylated with acetic anhydride in pyridine. The mixture of acetates of methyl esters so obtained (0.25 g) was separated on SiO_2 with elution by benzene−chloroform (3:7). This gave 40 mg of (**3b**) and 40 mg of (**4b**).

Methyl Ester of Glycoside St-I_3 (1a). For additional purification, 0.1 g of (**1**) was esterified with an ethereal solution of diazomethane and the product was chromatographed on SiO_2 with elution by the water-saturated chloroform−ethanol (2:1) system. This gave 50 mg of pure (**1a**), $[\alpha]_D$ −7° (*c* 0.5; pyridine). In an acid hydrolysate of (**1a**) we identified glucuronic acid, glucose, rhamnose, and oleanolic acid. A progenin from (**1a**) obtained by alkaline hydrolysis was identified by TLC as oleanolic acid 3-O-*β*-*D*-glucopyranuronoside [2]. The deacetylation of (**1a**) gave a product identical (TLC) with the methyl ester of glycoside St-J [2].

^1H NMR spectrum of (**1a**) (δ, ppm, 0−TMS, C_5D_5N): 4.97 (d, H-1′, $J_{1,2}$ 8.0); 4.08 (t, H-2′, $J_{2,3}$ 8.5); 4.18 (t, H-3′, $J_{3,4}$ 9.0); 4.48 (t, H-4′, $J_{4,5}$ 9.0); 4.54 (d, H-5′); 6.21 (d, H-1″, $J_{1,2}$ 8.0); 4.05-4.20 (m, H-2″, H-3″, H-4″); 4.04 (m, H-5″); 4.66 (dd, H-6″A, $J_{5,6A}$ 2.0; $J_{6A,6B}$ 12.0); 4.33 (dd, H-6″B, $J_{5,6B}$ 5.0); 4.98 (d, H-1‴, $J_{1,2}$ 8.0); 3.93 (t, H-2‴, $J_{2,3}$ 8.0); 4.05-4.15 (m, H-3‴, H-4‴); 3.81 (m, H-5‴); 4.62 (H-6‴A); 4.50 (H-6‴B); 5.51 (d, H-1⁗, $J_{1,2}$ 1.5); 4.61 (dd, H-2⁗, $J_{2,3}$ 3.0); 4.49 (dd, H-3⁗, $J_{3,4}$ 9.0); 4.31 (t, H-4⁗, $J_{4,5}$ 9.0); 4.85 (dq, H-5⁗); 1.69 (d, H-6⁗, $J_{5,6}$ 6.0); 3.33 (dd, H-3, $J_{2e,3}$ 4.0, $J_{2\alpha,3}$ 12.0); 3.15 (dd, H-18, $J_{18,19e}$ 4.0; $J_{18,19\alpha}$ 13.0); 1.27; 1.23; 1.05; 0.96; 0.90; 0.88; 0.82 (all s, 7 CH_3); 3.72 (s, O-CH_3); 1.90 (s, O-CO-CH_3).

Full Acetate of the Methyl Ester of Glycoside St-I_3 (1b). The acetylation of 40 mg of (**1a**) gave 45 mg of (**1b**), $[\alpha]_D$ −5° (*c* 0.5; chloroform). Lit. $[\alpha]_D$ −6°(chloroform) [2]. According to TLC, (**1b**) was identical with the full acetate of the methyl ester of glycoside St-J [2].

^1H NMR spectrum (δ, ppm, 0−TMS, $CDCl_3$): 4.58 (d, H-1′, $J_{1,2}$ 8.0); 5.04 (t, H-2′, $J_{2,3}$ 10.0); 5.24 (t, H-3′, $J_{3,4}$ 10.0); 5.18 (t, H-4′, $J_{4,5}$ 9.5); 3.99 (d, H-5′); 5.53 (d, H-1″, $J_{1,2}$ 8.0); 5.11 (t, H-2″, $J_{2,3}$ 9.5); 5.21 (t, H-3″, $J_{3,4}$ 9.0); 4.97 (dd, H-4″, $J_{4,5}$ 11.0); 3.72 (m, H-5″); 3.86 (dd, H-6″A, $J_{5,6A}$ 3.0; $J_{6A,6B}$ 10.0); 3.54 (dd, H-6″B, $J_{5,6B}$ 5.0); 4.50 (d,

H-1‴, $J_{1,2}$ 8.0); 4.81 (t, H-2‴, $J_{2,3}$ 9.5); 5.14 (t, H-3‴, $J_{3,4}$ 8.5); 3.81 (t, H-4‴, $J_{4,5}$ = 9.5); 3.55 (m, H-5‴); 4.43 (dd, H-6‴A, $J_{5,6A}$ 2.5, $J_{6A,6B}$ 12.0); 4.28 (dd, H-6‴B, $J_{5,6B}$ 4.0); 4.80 (d, H-1⁗, $J_{1,2}$ 2.0); 5.01 (dd, H-2⁗, $J_{2,3}$ 3.5); 5.16 (dd, H-3⁗, $J_{3,4}$ 10.0); 5.02 (t, H-4⁗, $J_{4,5}$ 10.0); 3.81 (m, H-5⁗); 1.12 (d, H-6⁗, $J_{5,6}$ 6.0); 5.29 (bt, H-12, $J_{11,12}$ 3.5); 3.10 (dd, H-3, $J_{2e,3}$ 5.0, $J_{2\alpha,3}$ 12.0); 2.79 (dd, H-18, $J_{18,19e}$ 4.0; $J_{18,19\alpha}$ 13.0); 1.25; 1.13; 0.91; 0.90; 0.90; 0.73; 0.73 (all s, 7-CH_3).

Methyl Ester of Glycoside St-I$_5$ (2a). The esterification of **(2)** and the chromatographic purification of **(2a)** were carried out in a similar way to the case of **(1a)**. From 100 mg of **(2)** we obtained 80 mg of **(2a)**, $[\alpha]_D$ −10° (*c* 1.1; pyridine). In an acid hydrolysate of **(2a)** we identified glucuronic acid, glucose, rhamnose, and hederagenin. A progenin from **(2a)** was identical (TLC) with hederagenin 3-O-*β*-*D*-glucopyranuronoside [2]. The deacetylation of **(2a)** gave a product identical according to TLC with the methyl ester of glycoside St-K [2].

^{1}H NMR spectrum of **(2a)** (δ, ppm, 0−TMS, C_5D_5N): 5.16 (d, H-1′, $J_{1,2}$ 7.5); 4.03 (dd, H-2′, $J_{2,3}$ 9.5); 4.13 (t, H-3′, $J_{3,4}$ 9.0); 4.38 (t, H-4′, $J_{4,5}$ 9.8); 4.44 (d, H-5′); 6.16 (d, H-1″, $J_{1,2}$ 8.0); 4.00-4.12 (m, H-2″, H-4″); 4.18 (t, H-3″, $J_{2,3}$ = $J_{3,4}$ 9.0); 3.65 (m, H-5″); 4.62 (dd, H-6″A, $J_{5,6A}$ 2.0; $J_{6A,6B}$ 10.5); 4.29 (dd, H-6″B, $J_{5,6B}$ 6.0); 4.95 (d, H-1‴, $J_{1,2}$ 8.0); 3.89 (t, H-2‴, $J_{2,3}$ 8.0); 3.97-4.12 (m, H-3‴, H-4‴); 3.78 (m, H-5‴); 4.59 (H-6‴A, $J_{5,6A}$ 2.5; $J_{6A,6B}$ 12.00); 4.48 (dd, H-6‴B, $J_{5,6B}$ 4.5); 5.48 (d, H-1⁗, $J_{1,2}$ 1.5); 4.57 (dd, H-2⁗, $J_{2,3}$ 3.5); 4.45 (dd, H-3⁗, $J_{3,4}$ 9.5); 4.27 (t, H-4⁗, $J_{4,5}$ 9.5); 4.81 (dq, H-5⁗); 1.65 (d, H-6⁗, $J_{5,6}$ 6.5); 4.10 (dd, H-3, $J_{2e,3}$ 4.0, $J_{2\alpha,3}$ 13.0); 3.11 (dd, H-18, $J_{18,19e}$ 4.0; $J_{18,19\alpha}$ 14.0); 5.34 (bt, H-12, $J_{11,12}$ 3.5); 3.66 (s, O-CH_3); 1.88 (s, O-CO-CH_3); 1.14; 1.05; 0.90; 0.89; 0.86; 0.83 (all s, 6-CH_3).

Full Acetate of the Methyl Ester of Glycoside St-I$_{4a}$ (3b), $[\alpha]_D$ +12° (*c* 0.3; chloroform).

^{1}H NMR spectrum of **(3b)** (δ, ppm, 0−TMS, $CDCl_3$): 4.59 (d, H-1′, $J_{1,2}$ 8.0); 5.06 (t, H-2′, $J_{2,3}$ 9.0); 5.26 (t, H-3′, $J_{3,4}$ 9.5); 5.19 (t, H-4′, $J_{4,5}$ 9.5); 4.01 (d, H-5′); 5.55 (d, H-1″, $J_{1,2}$ 8.5); 5.12 (dd, H-2″, $J_{2,3}$ 9.5); 5.23 (t, H-3″, $J_{3,4}$ 9.5); 4.97 (t, H-4″, $J_{4,5}$ 10.0); 3.75 (m, H-5″); 3.87 (dd, H-6″A, $J_{5,6A}$ 2.5; $J_{6A,6B}$ 12.0); 3.59 (dd, H-6″B, $J_{5,6B}$ 5.5); 4.54 (d, H-1‴, $J_{1,2}$ 8.0); 4.96 (t, H-2‴, $J_{2,3}$ 9.5); 5.17 (t, H-3‴, $J_{3,4}$ 9.5); 5.05 (t, H-4‴, $J_{4,5}$ 9.5); 3.63 (m, H-5‴); 4.27 (dd, H-6‴A, $J_{5,6A}$ 4.5, $J_{6A,6B}$ 12.5); 4.10 (dd, H-6‴B, $J_{5,6B}$ 2.5); 5.31 (bt, H-12, $J_{11,12}$ 3.5); 3.10 (H-3); 2.80 (H-18); 1.26; 1.11; 0.93; 0.91; 0.75; 0.75 (all s, 7 CH_3).

Full Acetate of the Methyl Ester of Glycoside St-I$_{4b}$ (4b), $[\alpha]_D$ −4° (*c* 0.3: chloroform).

^{1}H NMR spectrum of **(4b)** (δ, ppm, 0−TMS, $CDCl_3$): 4.51 (d, H-1′, $J_{1,2}$ 8.0); 3.87 (dd, H-2′, $J_{2,3}$ 9.0); 5.23 (t, H-3′, $J_{3,4}$ 9.0); 5.10 (t, H-4′, $J_{4,5}$ 10.0); 4.00 (d, H-5′); 4.66 (d, H-1″, $J_{1,2}$ 8.0); 5.11 (dd, H-2″, $J_{2,3}$ 10.5); 4.93 (dd, H-3″, $J_{3,4}$ 3.5); 5.34 (m, H-4″); 3.87 (m, H-5″); 4.10 (m, H-6″A, H-6″B); 5.58 (d, H-1‴, $J_{1,2}$ 8.0); 5.19 (dd, H-2‴, $J_{2,3}$ 9.5); 5.26 (t, H-3‴, $J_{3,4}$ 9.5); 5.13 (t, H-4‴, $J_{4,5}$ 10.0); 3.79 (m, H-5‴); 4.29 (dd, H-6‴A, $J_{5,6A}$ 4.5, $J_{6A,6B}$ 12.5); 4.05 (dd, H-6‴B, $J_{5,6B}$ 2.0); 5.33 (H-12); 3.11 (H-3); 2.82 (H-18); 1.26; 1.13; 1.06; 0.91; 0.91; 0.85; 0.73 (all s, 7 CH_3).

Methyl Ester of Glycoside St-I$_4$ (3a). The deacetylation of **(3b)** gave **(3a)** $[\alpha]_D$ +10° (*c* 0.3; pyridine). In a complete acid hydrolysate of **(3a)** we identified glucose and glucuronic and oleanolic acids. A progenin from **(3a)** obtained by alkaline hydrolysis was identical according to TLC with an authentic specimen of oleanolic acid 3-O-*β*-*D*-glucopyranuronoside (a progenin of tauroside St-J) [2].

Methyl Ester of Glycoside St-I$_{4b}$ (4a). The deacetylation of **(4b)** gave **(4a)**, $[\alpha]_D$ −6° (*c* 0.4; methanol). Lit.: $[\alpha]_D$ −8.7° (methanol) [6]; $[\alpha]_D$ −2.4° (methanol) [5]. In a complete acid hydrolysate of **(4a)** we identified glucose, galactose, and glucuronic and oleanolic acids. A progenin **(5)** was obtained from **(4a)** by alkaline hydrolysis. In a complete acid hydrolysate of **(5)** we identified galactose and glucuronic and oleanolic acids. Partial acid hydrolysis of **(5)** gave galactose and oleanolic acid glucopyranuronoside [2], identical according to TLC with an authentic specimen.

REFERENCES

1. V. I. Grishkovets, O. Ya. Tsvetkov, A. S. Shashko, and V. Ya. Chirva, Bioorg. Khim., **21**, 468 (1995).
2. V. I. Grishkovets, O. Ya. Tsvetkov, A. S. Shashko, and V. Ya. Chirva, Khim. Prir. Soedin., 397 (1997) [preceding paper in this issue].
3. L. Braunschweiler and R. R. Ernst, J. Magn. Reson., **53**, 521 (1983).
4. H. Kizu, S. Kutayama, F. Nakatani, T. Tomimori, and T. Namba, Chem. Pharm. Bull., **33**, 3324 (1985); H. Kizu, S. Hirabayashi, M. Suzuki, and T. Tomomori, Chem. Pharm. Bull., **33**, 3473 (1985); C.-J. Shao, R. Kai, J.-D. Xu, and O. Tanaka, Chem. Pharm. Bull., **36**, 601 (1988); C.-J. Shao, R. Kai, J.-D. Xu, and O. Tanaka, Chem. Pharm. Bull., **37**, 42 (1989); C.-J. Shao, R. Kasai, K. Ohtani, and O. Tanaka, Chem. Pharm. Bull., **38**, 1087 (1990).

5. H. Kawai, M. Nishida, Y. Tashiro, M. Kuroyanagi, A. Ueno, and M. Sotaka, Chem. Pharm. Bull., **37**, 2318 (1989).
6. S. Takabe, T. Takeda, Y. Chen, and Y. Ogihara, Chem. Pharm. Bull., **33**, 4701 (1985).