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Two New Steroid Glycosides from the Far East Starfish *Hippasteria kurilensis*

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Abstract—Two new steroid glycosides were isolated from the Far East starfish *Hippasteria kurilensis* collected in the Sea of Okhotsk. They were characterized as (22*E*,24*R*)-3-*O*-(2-*O*-methyl-β-*D*-xylopyranosyl)-24-*O*-[2-*O*-methyl-β-*D*-xylopyranosyl-(1⟶5)-α-*L*-arabinofuranosyl]-5α-cholest-22-ene-3β,4β,6α,7α,8,15β,24-heptaol (kurilensoside I) and (24*S*)-3-*O*-(2-*O*-methyl-β-*D*-xylopyranosyl)-24-*O*-(α-*L*-arabinofuranosyl)-5α-cholestane-3β,4β,6β,15α,24-pentaol (kurilensoside J). In addition, the earlier known glycosides linkosides F and L1, leviusculoside G, forbeside L, desulfated echinasteroside, and granulatoside A were isolated and identified. The structures of the new compounds were established with the help of two-dimentional NMR spectroscopy and mass- spectrometry.

Key words: starfish, Hippasteria kurilensis, glycosides, polyhydroxysteroids, and NMR spectra

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INTRODUCTION

Highly oxidized steroids and related glycosides are the most widespread secondary metabolites of starfish. Usually, they are present in animal extracts as complex mixtures of structurally close substances, which are difficultly separated into individual components. As a rule, for the isolation of these substances in each concrete case, careful selection of the optimum conditions of division with the help of column chromatography on various sorbents and HPLC is required. The oxidation degree of steroid compounds from starfish frequently exceeds those of such highly oxidized natural steroids as fito- and zooecdysones and some steroid polyols of sea sponges and soft corals [1]. The highly oxidized steroid compounds of starfish are of scientific interest not only due to their unusual chemical structure, but also due to various biological properties, including embriotoxic, antifungal, antiviral, antibacterial, neuritogenic, and other kinds of activity [2].

Earlier, we isolated four new glycosides: triosides kurilensosides A. B. and C and bioside D. as well as one known and two new polyhydrohysteroids [3] as a result of study of Far East starfish *Hippasteria kurilensis* Fisher, 1911 (family Goniasteridae, order Valvatida), collected in the Sea of Okhotsk (Kuriles). Later, five new monosides (kurilensosides E, F, G, H, and 15-*O*-sulfate of echinasteroside C) and known echinasteroside C were found in the same starfish [4]. Continuing the study of the steroid composition of sea starfish *H. kurilensis*, we isolated eight additional steroid compounds, including two new steroid glycosides, kurilensosides I (**I**) and J (**II**), and six earlier known glycosides (**III**)–(**VIII**). The structures of the new compounds were established mainly with the help of ^{1}H-^{1}H-COSY, HSQC, HMBC and DEPT NMR experiments. The new compounds (**I**) and (**II**) have a 2-*O*-methyl-β-*D*-xylopyranose residue at C3 of polyhydroxylated steroid aglycone. Kurilensoside I (**I**) is a trioside and contains an additional disaccharide fragment in the side chain of aglycone at C24. Kurilensoside J (**II**) belongs to biosides and additionally contains an α-*L*-arabinofuranose moiety in the side chain of aglycone at C24.

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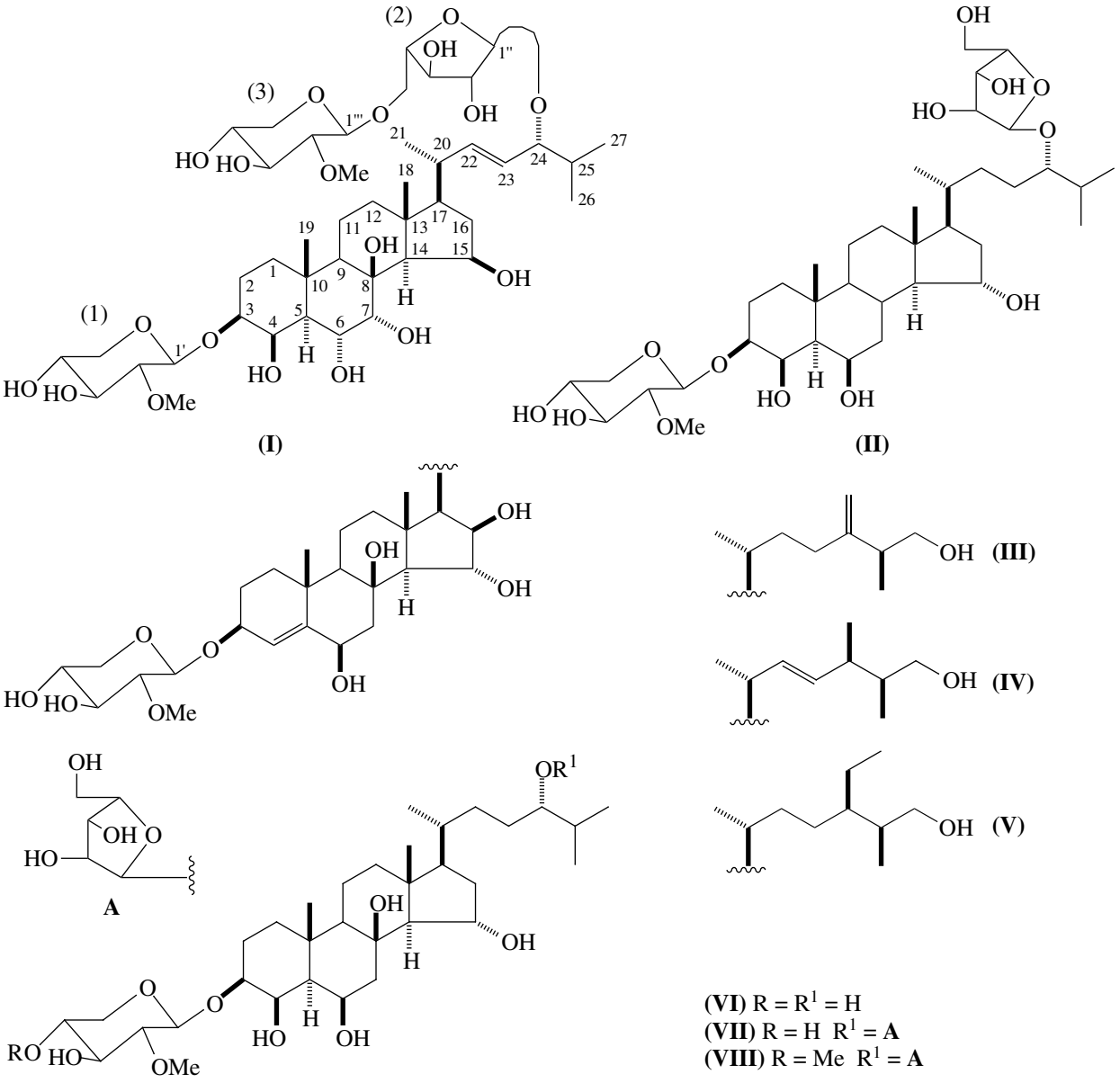

RESULTS AND DISCUSSION

The fractions of highly oxidized steroid compounds were isolated from an ethanolic extract of the starfish *H. kurilensis* with the help of column chromatography on an Amberlite XAD-2, silica gel, and Florisil. The use of HPLC on the semipreparative and analytical columns of Diasphere-110-C18 allowed us to isolate two new glycosides, (**I**) and (**II**), and six known compounds (**III**)–(**VIII**) from these fractions. The results of the chromatographic separation of the steroid fractions are given in Table 1. The known glycosides were identified by a comparison of their spectra, ^{1}H- and ^{13}C-NMR, and mass spectra with the corresponding data for these substances found in published works.

The mass spectrum HR-ESI (registration of cations) of kurilensoside I (**I**) contained the peak of a pseudomolecular ion with *m/z* 929.4711 $[M + Na]^+$ corresponding to the molecular formula $C_{44}H_{74}O_{19}$. It followed from the spectra ^{1}H-, ^{13}C-, and DEPT NMR that glycoside (**I**) contains 44 carbon atoms, including carbons of five methyl, eight methylene, and 24 methine groups; and three quaternary carbon atoms, including one oxygenated, two protonated olefin carbon atoms, and two methoxyl groups (Table 2). Three anomeric protons (at δ 4.45, 4.91, and 4.33 ppm) are exhibited in the ^{1}H-NMR spectrum of (**I**); they were bound in a HSQC spectrum with three signals of carbon atoms at δ 102.3, 109.0, and 105.3 ppm, respectively. In the mass spectrum, there were peaks of fragment ions at *m/z* 783

Table 1. Steroid glycosides isolated from the starfish *H. kurilensis*

Compound	Quantity, mg	R_f^*	(+)-MALDI–TOF mass spectrum $[M + Na]^+$	Starfish from which the compound was first isolated [reference]
Kurilensoside I (**I**)	1.5	0.17	929**	
Kurilensoside J (**II**)	3.2	0.39	753	
Lincoside F (**III**)	1.0	0.52	647	*Linckia laevigata* [5]
Echinasteroside A desulfated (**IV**)	1.5	0.54	647	*Henricia downeyae* [6]
Forbeside L (**V**)	0.5	0.50	663**	*Asterias forbesi* [7]
Linckoside LI (**VI**)	1.0	0.54	637	*Linckia laevigata* [8]
Granuloside A (**VII**)	17.4	0.33	769	*Choriaster granulatus* [9]
Leviusculoside G (=Forbeside J) (**VIII**)	1.0	0.46	783**	*Henricia leviuscula* [10], *Asterias forbesi* [7]

Notes: * It is determined in a toluene–ethanol system (9 : 5);
** (+)-ESI mass spectrum

$[(M + Na) - 146]^+$, corresponding to a loss of the terminal residue of *O*-methylpentose, and at *m/z* 651 $[(M + Na) - 146–132]^+$, corresponding to a loss of the *O*-methylpentose and pentose residues. The data indicate the presence in the glycoside molecule (**I**) of three pentosyl monosaccharide residues and a heptasubstituted cholestane aglycone.

A comparison of the chemical shifts of carbon atoms and protons and the corresponding coupling constants in the ^{1}H- and ^{13}C-NMR spectra of glycoside (**I**) and kurilensoside C from the same starfish [3] showed that both compounds have 3β,4β,6α, 7α,8,15β,24-heptahydroxy-5α-cholestane aglycone with 2-*O*-methyl β-*D*-xylopyranose residues at C3 and 2-*O*-methyl β-*D*-xylopyranosyl-(1⟶5)-α-*L*-arabinofuranose residue at C24. However, unlike kurilensoside C, the NMR spectra of (**I**) contained signals of a double bond in the side chain of aglycone and its molecular mass was, respectively, smaller by two mass units. According to ^{13}C-NMR spectra, in the side chain of glycoside (**I**) were three methyl groups (δ 20.8, 19.1, and 18.5 ppm); three methine groups, one of which was attached to oxygen atom (δ 40.9, 33.8, and 86.2 ppm); and two carbon atoms of a double bond (δ 140.6 and 128.3 ppm). ^{1}H-^{1}H-COSY, HSQC, and HMBC NMR experiments allowed for the determination of signals of all protons and carbon atoms of the steroid nucleus, the side chain of aglycone, and three monosaccharide residues of glycoside (**I**) (Table 2). On the basis of the data, it was established that glycoside (**I**) has a cholestane side chain with a 22(23)-double bond glycosylated in position C24. The value of the coupling constant $J_{22,23}$ 15.3 Hz corresponds to a trans configuration of the 22(23)-double bond [11].

The attachment of the carbohydrate fragments in the molecule and the presence of (1⟶5)-glycoside bond between monosaccharide residues in the disaccharide chain of glycoside (**I**) were confirmed by HMBC correlations of the corresponding anomeric protons and carbon atoms—H1'(2-*O*-Me-Xyl)/C3, H1'''(2-*O*-Me-Xyl)/C5''(Ara), H1'(Ara)/C24—and also by the presence of the cross-peak H24/C1''(Ara). By analogy with kurilensoside C, the *R*-configuration was suggested for chiral center C24. The *L*-configuration was ascribed to the arabinose residue, and the *D*-configuration to the 2-*O*-methylxylose, since only such forms of monosaccharide units have been found earlier in steroid glycosides of starfish [1, 2]. On the basis of available data, the structure of kurilensoside I was determined as (22*E*,24*R*)-3-*O*-(2-*O*-methyl-β-*D*-xylopyranosyl)-24-*O*-[2-*O*-methyl-β-*D*-xylopyranosyl-(1⟶5)-α-*L*-arabinopyranosyl]-5α-cholest-22-ene-3β,4β,6α,7α,8,15β, 24-heptaol. Thus, it was established that glycoside (**I**) represents a Δ^{22}-analogue of kurilensoside C [3].

Kurilensoside I (**I**) is the fourth representative of a rare structural group of polyhydroxylated steroid triglycosides of the starfish containing two carbohydrate fragments, one of which, a monosaccharide residue, is attached to C3 of the steroid nucleus, and another, a disaccharide residue, is localized at C24 of the aglycone chain. Previously, three such earlier steroid triosides have been known: kurilensosides A, B, and C; they have also been found in the starfish *H. kurilensis* [3]. Usually, the glycosides of starfish poyhydroxysteroids are monosides or biosides.

A pseudo-molecular peak with *m/z* 753.4359 $[M + Na]^+$ corresponding to the molecular formula $C_{38}H_{66}O_{13}$ was exhibited by HR MALDI–TOF mass spectrum (registration of cations) of kurilensoside J (**II**). The data of spectra ^{1}H- and ^{13}C-NMR of the compound (**II**) (Table 2) are close to the corresponding spectra of leviusculoside F from the starfish *Henricia leviuscula* [10], which proved the presence of identical 3-*O*-substituted 3β,4β,6β,15α,24-pentahydroxy-5α-cholestane aglycone with the residue of α-*L*-arabinofuranose at C24. However, unlike the spectra of leviusculoside F,

Table 2. NMR spectra of kurilensosides I (**I**) and J (**II**) (CD_3OD, δ, ppm, *J*, Hz)*

Atom number	(**I**)			(**II**)		
	δ_C**	δ_H	HMBC	δ_C**	δ_H	HMBC
1	39.7, CH_2	1.70 dt (13.4, 3.9); 0.99 m		39.4, CH_2	1.65 m; 1.00 m	
2	24.8, CH_2	1.91 m; 1.62 m		25.4, CH_2	1.93 m; 1.68 m	
3	81.2, CH	3.59 m		80.8, CH	3.59 m	
4	66.5, CH	4.41 br s	C10	74.5, CH	4.23 br s	
5	47.4, CH	1.48 dd (2.2, 11.6)	C19	50.2, CH	1.13 m	C10, C19
6	66.6, CH	4.27 dd (2.8, 11.6)	C5	74.7, CH	4.15 k (2.7)	
7	76.7, CH	3.91 d (3.1)	C5, C6, C9, C14	40.4, CH_2	2.13 m; 1.30 m	
8	79.3, C			31.8, CH	1.99 m	
9	51.2, CH	1.10 dd (3.5, 13.0)		56.1, CH	0.71 m	
10	37.9, C			36.8, C		
11	18.9, CH_2	1.82 m; 1.44 m		21.4, CH_2	1.46 m; 1.39 m	
12	42.9, CH_2	1.94 m; 1.16 m		41.4, CH_2	1.96 m; 1.21 m	
13	44.2, C			44.8, C		
14	56.7, CH	1.42 d (5.4)	C13, C17, C18	63.7, CH	1.05 dd (9.2; 10.9)	
15	71.2, CH	4.51 m	C13	74.3, CH	3.86 dt (3.3; 9.1)	
16	43.5, CH_2	2.28 dt (15.0; 7.9); 1.39 m		41.9, CH_2	1.90 m; 1.74 m	
17	57.8, CH	1.05 m		55.0, CH	1.40 m	
18	16.6, CH_3	1.30 s	C12, C13, C14, C17	13.7, CH_3	0.74 s	C12, C13, C14, C17
19	16.9, CH_3	1.17 s	C1, C5, C9, C10	18.2, CH_3	1.33 s	C1, C5, C9, C10
20	40.9, CH	2.21 m		36.8, CH	1.38 m	
21	20.8, CH_3	1.02 d (6.5)	C17, C20, C22	19.2, CH_3	0.93 d (6.2)	C17, C20, C22
22	140.6, CH	5.42 dd (8.5, 15.3)	C20, C21, C24	33.0, CH_2	1.60 m; 1.00 m	
23	128.3, CH	5.34 dd (7.4, 15.3)	C20, C22, C24	28.7, CH_2	1.60 m; 1.30 m	
24	86.2, CH	3.63 t (6.4)	C1", C26, C27	84.8, CH	3.32 m	
25	33.8, CH	1.76 m		31.8, CH	1.83 m	
26	19.1, CH_3	0.92 d (7.0)	C24, C25, C27	18.4, CH_3	0.90 d (6.8)	C24, C25, C27
27	18.5, CH_3	0.86 d (7.0)	C24, C25, C26	18.3, CH_3	0.89 d (6.8)	C24, C25, C26
2-OMe-Xyl						
1'	102.3, CH	4.45 d (7.4)	C3	102.6, CH	4.45 d (7.6)	C3
2'	84.7, CH	2.90 dd (7.6, 9.0)	C1', C3'	84.7, CH	2.90 dd (7.6, 9.0)	C1', C3', OMe
3'	77.7, CH	3.34 t (9.0)	C2', C4'	77.6, CH	3.35 t (8.9)	C2', C4'
4'	71.3, CH	3.48 m		71.2, CH	3.47 m	
5'	66.8, CH_2	3.82 dd (5.4, 12.0); 3.15 m	C1', C3', C4'; C1', C4'	66.8, CH_2	3.81 dd (5.4, 11.2); 3.16 dd (10.0, 11.5)	C1', C3', C4'; C1', C3', C4'
2'-OMe	61.0[a], CH_3	3.61 s[b]	C2'	61.0, CH_3	3.62 s	C2'
Ara						
1"	109.0, CH	4.91 d (2.1)	C24, C3", C4"	109.4, CH	4.91 d (1.8)	C24, C4"
2"	83.7, CH	3.97 dd (2.1, 4.0)		83.9, CH	3.96 dd (1.9, 4.1)	C3"
3"	78.9, CH	3.90 dd (4.0, 6.6)	C2", C5"	78.7, CH	3.83 dd (4.2, 6.7)	C2", 4"
4"	83.4, CH	4.03 m	C3"	85.0, CH	3.97 m	
5"	70.1, CH_2	3.92 dd (5.0, 11.7); 3.70 dd (3.7, 11.1)	C1'", C3", C4"; C1'", C3", C4"	62.9, CH_2	3.73 dd (3.3, 12.0) 3.63 dd (4.9, 11.8)	C3"; C3", C4"
2-OMe-Xyl						
1'"	105.3, CH	4.33 d (7.4)	C5"			
2'"	84.7, CH	2.88 dd (7.4, 9.0)	C1'", C3'"			
3'"	77.2, CH	3.32 t (9.5)	C2'", C4'"			
4'"	71.3, CH	3.48 m				
5'"	66.8, CH_2	3.85 dd (5.4, 11.8); 3.17 dd (10.2, 11.6)	C1'", C3'", C4'"; C1'"			
2'"-OMe	61.1[a], CH_3	3.58 s[b]	C2'"			

Notes: * Signal assignments was achieved by the methods of two-dimensional NMR spectroscopy ^1H-^1H-COSY and HSQC.

** Multiplicity of signals was determined from DEPT spectra.

[a, b] Signal assignment may be reversed.

containing at C3 of aglycone the residue 2,4-di-*O*-methyl-β-*D*-xylopyranose, the signals of another monosaccharide residue that practically coincided with the corresponding data for unsubstituted 2-*O*-methyl-β-*D*-xylopyranose in the NMR spectra of glycoside (**I**) were observed in the NMR spectra of glycoside (**II**).

The values of the chemical shifts for all protons and carbon atoms in glycoside (**II**) were determined with the help of ^{1}H-^{1}H-COSY, HSQC, and HMBC NMR experiments (Table 2). The attachment of the residues of 2-*O*-methyl-β-*D*-xylopyranose to C3 and α-*L*-arabinofuranose to C24 of aglycone was confirmed by the presence in HMBC spectrum of cross-peaks of anomeric protons and carbon atoms: H1'(2-*O*-Me-Xyl)/C3 and H1"(Ara)/C24. The *S* configuration was suggested for the chiral center C24 in glycoside on the basis of the coincidence of the chemical shift values of protons and carbon atoms in the NMR spectra of (**II**) and leviusculoside F. Thus, the structure of kurilensoside J (**II**) was established as (24*S*)-3-*O*-(2-*O*-methyl-β-*D*-xylopyranosyl)-24-*O*-(α-*L*-arabinopyranosyl)-5α-cholestane-3β,4β,6β,15α,24-pentaol.

The molecule of kurilensoside J contains a 3β,4β,6β,15α-tetrahydroxysteroid nucleus, which seldom occurs in polyhydroxylated steroid compounds from starfish. This structural fragment had been earlier found only in leviusculoside F [10].

EXPERIMENTAL

Spectra ^{1}H- and ^{13}C-NMR were registered on Bruker DPX-300 (^{1}H at 300 and ^{13}C at 75.5 MHz) and Bruker DRX-500 (^{1}H at 500 and ^{13}C at 125.7 MHz, the internal standard was CD_3OD, ^{1}H, 3.30, ^{13}C, 49.0 ppm) spectrometers. The optical rotation was measured on a Perkin Elmer 343 polarimeter in MeOH. MALDI–TOF mass spectra were obtained on a Biflex III (Bruker, Germany) mass-spectrometer with laser ionization/desorption (N_2 laser, 337 nm) using α-cyano-4-hydroxycinnamic acid as a matrix. ESI mass spectra were obtained on an Agilent 6510 Q-TOF (United States) mass-spectrometer. The samples were dissolved in MeOH (*c* 0.01 mg/ml). HPLC was carried out on an Agilent 1100 Series chromatograph with a refractometric detector. TLC was carried out on Sorbfil plates with a STH-1A 5–17-μm silica gel layer fixed on a foil (Sorbpolymer, Russia). Substances were detected by spraying with concentrated H_2SO_4 with the subsequent heating of plates at 110°C for 10 min. For preparative separation, column chromatography on an Amberlite XAD-2 (20–80 mesh, Sigma Chemical Co.), silica gel KSK (50–160 μm, Sorbpolymer, Russia), and Florisil (100–200 mesh, Aldrich, U.S. Sillica Co.) were used.

Animals. Samples of starfish *H. kurilensis* were collected in July 2003 with the help of a drag from a depth of 100 m in the Sea of Okhotsk (Kuril Islands, Matua island) during the 29th scientific expedition on the research ship *Academik Oparin*. The specific definition of starfish was carried out by A.V. Smirnov (Zoological Institute of the Russian Academy of Sciences, St. Petersburg, Russia).

Isolation of compounds (I)–(VIII). The ground starfish (770 g) were twice extracted with ethanol at room temperature. The ethanol extract was concentrated in a vacuum, dissolved in water (1 l), and passed through a column (7 × 20 cm) with Amberlite XAD-2. The column was washed with water up to the absence of Cl^- ions in eluate and then ethanol. The ethanolic eluate was evaporated and the resulting gum-like total fraction of steroid compounds (3.4 g) was successively chromatographed on columns with silica gel (4 × 18 cm) in a $CHCl_3$–EtOH system (a step gradient of 4 : 1 to 1 : 6) and Florisil (2.5 × 15 cm) in a $CHCl_3$–EtOH system (a step gradient of 4 : 1 to 1 : 2). A number of fractions were obtained; they contained, according to TLC, polyhydrohylated steroid compounds (R_f values from 0.71 to 0.87 in a 4 : 1 : 2 BuOH–EtOH–H_2O system). The final purification of the substances was carried out by HPLC on a Diasphere-110-C18 column (10 μm, 15 × 250 mm, 2.5 ml/min) in a 65 : 35 EtOH–H_2O system and then on a Diaspher-110-C18 (5 μm, 4 × 250 mm, 0.5 ml/min) column in a 80 : 19 : 1 MeOH–H_2O–1 M NH_4OAc system. The results of chromatographic separation of steroid fractions with isolation of compounds (**I**)–(**VIII**) are given in Table 1.

Kurilensoside I, (22E,24R)-3-O-(2-O-methyl-β-D-xylopyranosyl)-24-O-[2-O-methyl-β-D-xylopyranosyl-(1⟶5)-α-L-arabinofuranosyl]-5α-cholest-22-ene-3β,4β,6α,7α,8,15β,24-heptaol (I); amorphous compound, $[\alpha]_D^{20}$ –14.4 (*c* 0.1, MeOH); (+)-HR ESI mass spectrum, *m/z*: 929.4711 $[M + Na]^+$ (calculated for $C_{44}H_{74}O_{19}Na$, 929.4717); (+)-ESI mass spectrum, and *m/z*: 929 $[M + Na]^+$, 783 $[(M + Na) - 146]^+$, 651 $[(M + Na) - 146 - 132]^+$, 633 $[(M + Na) - 146 - 132 - H_2O]^+$, 319 $[164 + 132 + Na]^+$. Spectra ^{1}H- and ^{13}C-NMR are given in Table 2.

Kurilensoside J, (24*S*)-3-*O*-(2-*O*-methyl-β-*D*-xylopyranosyl)-24-*O*-(α-*L*-arabinofuranosyl)-5α-cholestane-3β,4β,6β,15α,24-pentaol (II); amorphous compound; $[\alpha]_D^{20}$ –27.6 (*c* 0.2, MeOH); (+)-HR-MALDI-TOF mass spectrum, *m/z*: 753.4359 $[M + Na]^+$ (calculated for $C_{38}H_{66}O_{13}Na$, 753.4401). Spectra ^{1}H- and ^{13}C-NMR are given in Table 2.

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