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ASTEROSAPONIN OPHIDIANOSIDE F FROM GONADS OF THE FAR-EASTERN STARFISH *Aphelasterias japonica*

N. V. Ivanchina, T. V. Malyarenko, A. A. Kicha, A. I. Kalinovskii, and P. S. Dmitrenok

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Physiologically active steroidal oligoglycosides from starfish (asterosaponins) are known to fulfill protective functions and regulate maturation processes of ova in these animals [1, 2]. In continuation of research on polar steroidal compounds from the Far-Eastern starfish *Aphelasterias japonica* [3], we studied the asterosaponin fraction from gonads of animals collected in Pos′et bay of the Sea of Japan in July 2002 at a depth of 10 m.

Gonads from *A. japonica* were extracted with ethanol (70%). The aqueous alcohol solution was washed with benzene to remove nonpolar lipids and concentrated in vacuum. Column chromatography of the resulting dry solid over Amberlite XAD-2, Sephadex LH-20 (ethanol:water, 2:1), and silica gel ($CHCl_3$:C_2H_5OH, 1:1→1:10) and subsequent HPLC over Diasphere-110-C18 (5 μm, 4×250 mm, CH_3OH, 60%) isolated a pure steroidal glycoside (3 mg, 0.067% yield per dry weight of the aqueous ethanol extract). ^1H and ^{13}C NMR spectra and MALDI/TOF and LSI mass spectra established that the isolated compound was asterosaponin and had the steroidal aglycon thornasterol A and an oligosaccharide chain of five monosaccharide units including two quinovose, two xylose, and one fructose unit. Acid hydrolysis of this glycoside gave total monosaccharides that were identified as D-quinvose, D-xylose, and D-fucose (2:2:1) (TLC, GC of polyol peracetates, specific rotation). Signals of protons and C atoms in NMR spectra of the glycoside agreed completely with the corresponding signals of ophidianoside F from the starfish *Ophidiaster ophidianus* [4]. The sequence of monosaccharides in the isolated compound was also confirmed by the fragmentation in LSI mass spectra. We concluded from this that the isolated glycoside was identical to ophidianoside F and had the structure (20*R*)-6α-O-{β-D-fucopyranosyl-(1→2)-β-D-xylopyranosyl-(1→4)-[β-D-quinovopyranosyl-(1→2)]-β-D-xylopyranosyl-(1→3)-β-D-quinovopyranosyl}-20-hydroxy-23-oxo-5α-cholest-9(11)-en-3β-yl sodium sulfate. This asterosaponin was found for the first time in the Far-Eastern starfish *Aphelasterias japonica*. Its MALDI/TOF and LSI mass spectra have not been previously reported.

Ophidianoside F: amorphous compound, $[\alpha]_D$ +0.5° (*c* 0.2, CH_3OH); MALDI/TOF (+) mass spectrum (*m*/*z*): 1291 $[M_K + K]^+$, 1275 $[M_{Na} + K]^+$, 1259 $[M_{Na} + Na]^+$, 1139 $[M_{Na} + Na - 120]^+$; MALDI/TOF (-) mass spectrum (*m*/*z*): 1212 $[M_{Na} - Na]^-$, 1113 $[M_{Na} - Na - 100]^-$, 1067 $[M_{Na} - Na - 146]^-$; LSI (+) mass spectrum (*m*/*z*): 1253 $[M_K + H]^+$, 1237 $[M_{Na} + H]^+$, 1153 $[M_K + H - 100]^+$, 1137 $[M_{Na} + H - 100]^+$, 1107 $[M_K + H - Fuc]^+$, 1091 $[M_{Na} + H - Fuc]^+$, 975 $[M_K + H - Fuc - Xyl]^+$, 959 $[M_{Na} + H - Fuc - Xyl]^+$; LSI (-) mass spectrum (*m*/*z*): 1213 $[M_{Na} - Na]^-$, 1113 $[M_{Na} - Na - 100]^-$, 1067 $[M_{Na} - Na - Fuc]^-$, 935 $[M_{Na} - Na - Fuc - Xyl]^-$, 657 $[M_{Na} - Na - Fuc - Xyl - Xyl - Quin]^-$, 511 $[M_{Na} - Na - Fuc - Xyl - Xyl - (Quin) - Quin]^-$, 411 $[511 - 100]^-$.

PMR (300 MHz, CD_3OD) and ^{13}C (75.5 MHz, C_5D_5N) spectra were identical to those published previously [4].

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Pacific Institute of Bioorganic Chemistry, Far-East Division, Russian Academy of Sciences, fax 7-(4232) 31 40 50, e-mail: ivanchina@piboc.dvo.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 4, p. 392, July-August, 2005. Original article submitted April 11, 2005.

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