Biochemical Systematics and Ecology 51 (2013) 203–206

Contents lists available at ScienceDirect

Biochemical Systematics and Ecology

journal homepage: www.elsevier.com/locate/biochemsyseco

# Chemical constituents of the starfish *Asterias rollestoni* Bell

Gai-yun Zhang*, Hui-Hui Ren, Yu-Bian Zhang, Ling-Qi Ma, Yan-Liu Yang, Shuang Wang

*Key Laboratory of Marine Biogenetic Resources, Third Institute of Oceanography, State Oceanic Administration, Xiamen 361005, China*

ARTICLE INFO

*Article history:*
Received 3 July 2013
Accepted 24 August 2013
Available online 24 September 2013

*Keywords:*
Starfish
α-Glycone
*Asterias rollestoni*
Asteriidae
Sacchride

ABSTRACT

Two new tetrasaccharides, β-D-quinovopyranosyl-(1→2)-β-D-fucopyranosyl- (1→4)-[β-D-fucopyranosyl-(1→2)]-α-D-quinovopyranose (**1**) and methyl β-D-quinovopyranosyl-(1→2)-β-D-fucopyranosyl-(1→4)-[β-D-fucopyranosyl-(1→2)]-α-D-quinovopyranoside (**2**), were obtained from the starfish *Asterias rollestoni* Bell, along with four known compounds: adenosine (**3**), lycoperodine 1 (**4**), forbeside E (**5**), and amurensoside D (**6**). Their structures were established mainly on detailed analysis of the 1D and 2D NMR spectroscopic data. Compounds **1** and **2** were rarely found α-guinovopyranosyl derivates among starfish, thus they have important chemotaxonomic significance for *A. rollestoni* Bell.



## 1. Subject and source

Starfish are invertebrates belonging to the Asteroidea Class, Echinodermata Phylum. There are over 1500 species universally found in all oceans of the world. Up to now, over 700 compounds were isolated with various bioactivities including cytotoxicity, antivirus, antifungal, hemolytic, and antimicrobial (Dong et al., 2011). *Asterias rollestoni* Bell belongs to the Family of Asteriidae (Forcipulatida Order). It is one of the most commonly distributed starfish in China. The sample of *A. rollestoni* was bought from Xiamen the 8th Seafood Market in June 2010, and was identified by Dr Jianjun Wang in the Third Institute of Oceanography, State Oceanic Administration. The voucher specimen (2010SF02) was deposited at the Key Laboratory of Marine Biogenetic Resources, Third Institute of Oceanography, State Oceanic Administration.

## 2. Previous work

Previous chemical composition investigations on starfish of the genus of *Asterias* have afforded several kinds of secondary metabolites including cerebrosides (Higuchi et al., 1991; Park et al., 2011), steroids and their glycosides (Burnell et al., 1984; Findlay and He, 1991; Findlay et al., 1989; Hwang et al., 2011; Ivanchina et al., 2001; Liu et al., 2008; Riccio et al., 1988), saccharides (Liu et al., 2010; Okinaga et al., 1992), and gangliosides (Chekareva et al., 1996; Muralikrishna et al., 1992). From *A. rollestoni*, it yielded triterpene glycosides (Zhan et al., 2006), ceramides (Zhang et al., 2006), cerebrosides (Liu et al., 2007; Zhang et al., 2007, 2008), steroids (Zhang et al., 2005b), amino acid, nucleoside (Li et al., 2004; Zhang et al., 2005a), *p*-hydroxybenzoic acid and fatty acids (Li et al., 2004).

* Corresponding author. Tel.: +86 592 2195833; fax: +86 592 2085376.
*E-mail address:* zhanggyun@126.com (G.-y. Zhang).

0305-1978/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.bse.2013.08.031

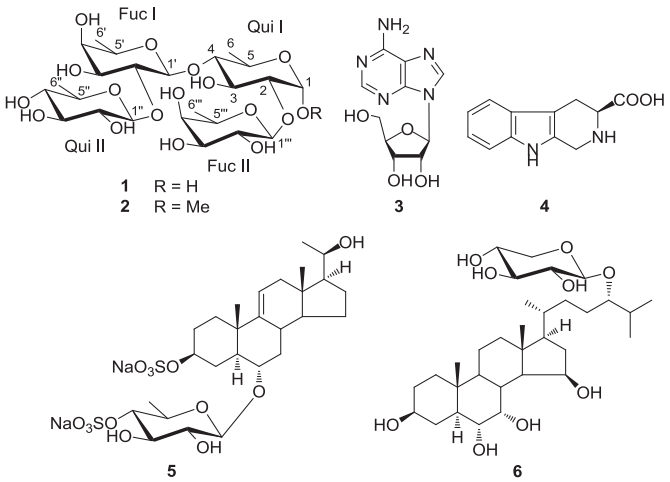


**Fig. 1.** Compounds isolated from the starfish *Asterias rollestoni* Bell.

## 3. Present study

The dried and powdered material of *A. rollestoni* (1 kg) was extracted with 70% ethanol for 24 h at room temperature for three times. The extract was then concentrated to a small volume and partitioned with $CHCl_2$ (2 L) and *n*-BuOH (2 L). The *n*-BuOH extract (30 g) was subjected to column chromatography (CC) over silica gel using gradient $CH_2Cl_2$–MeOH (0–100%) to give four fractions (Fr.1–Fr.4). Fraction Fr.1 was further purified by CC over Sephadex LH-20 using $CHCl_3$–MeOH and MeOH as eluant to afford **6** (68.3 mg). Fraction Fr.2 was subjected to repeated CC over silica gel ($CH_2Cl_2$–MeOH, 10:1) and Sephadex LH-20 (MeOH) to give **4** (12.0 mg). By similar procedures, **5** (14.0 mg) was obtained from fraction Fr.3. Fraction Fr.4 was firstly subjected to CC over ODS to give three subfractions (Fr.4.1–Fr.4.3). By repeated CC over silica gel ($CH_2Cl_2$–MeOH, 5:2) and Sephadex LH-20 (MeOH), **1** (50.9 mg), **2** (56.3 mg), and **3** (120.0 mg) were purified from subfraction Fr.4.1, Fr.4.2, and Fr.4.3, respectively.

By comparing the NMR and MS data with the referenced data, four known compounds were identified as: adenosine (**3**) (Breitmai et al., 1972), lycoperodine 1 (**4**) (Li et al., 2004; Yahara et al., 2004), forbeside E (**5**) (Findlay et al., 1989), and amurensoside D (**6**) (Riccio et al., 1988) (Fig. 1).

Compound **1** was assigned a molecular formula of $C_{24}H_{42}O_{17}$ on the basis of its positive HR-ESI-MS at *m/z* 625.2303 $[M + Na]^+$. The $^1H$ NMR showed four anomeric protons in the lowfield at $\delta_H$ 5.28 (1H, d, $J = 3.6$ Hz), 4.56 (1H, d, $J = 7.8$ Hz), 4.55 (1H, d, $J = 7.8$ Hz), and 4.53 (1H, d, $J = 7.8$ Hz). In the highfield, four methyl doublets were found at $\delta_H$ 1.18 (3H, d, $J = 6.5$ Hz), 1.19 (3H, d, $J = 6.4$ Hz), 1.22 (3H, d, $J = 6.2$ Hz), and 1.30 (3H, d, $J = 6.2$ Hz). The $^{13}C$ and DEPT NMR spectra exhibited 24 carbons including four methyls [$\delta_C$ 15.2, 15.4, and 16.7 ($\times 2$)] and 20 oxygenated methines of which four were anomeric carbons ($\delta_C$ 91.2, 100.8, 103.6, and 104.1). Altogether, the 1D NMR spectra indicated **1** could be a tetrasaccharide. In the $^1H$–$^1H$ COSY spectrum, four spin systems were found which constructed four similar segments (Fig. 2). Based on the HMBC correlations of four anomeric protons of H-1 to C-5, H-1′ to C-5′/C-4, H-1″ to C-5″/C-2′, and H-1‴ to C-5‴/C-2, these four fragments could easily be connected, which established the planar structure as shown in Fig. 2. For the relative structure of glycone A, the small coupling constant of the anomeric proton ($J = 3.6$ Hz) and the large coupling constants of H-3 (t, $J = 9.4$ Hz), H-4 (t, $J = 9.4$ Hz), and H-5 (dd, $J = 9.8$, 6.2 Hz) suggested α-configuration for the C-1 position while β-form for the other positions of C-2/3/4/5. This indicated glycone A might be an α-quinovose. Similarly, the other three glycones B, C, and D were deduced as β-fucose, β-quinovose, and β-fucose, respectively. After acid hydrolyses according to the reported protocol (Yang et al., 2006), followed by purification using preparative TLC, the glycones were determined to be D-configuration by measurement of their optical rotation values. Therefore, compound **1** was assigned as β-D-quinovopyranosyl-(1→2)-β-D-fucopyranosyl-(1→4)-[β-D-fucopyranosyl-(1→2)]-α-D-quinovopyranose.

Compound **2** gave a molecular formula of $C_{25}H_{44}O_{17}$ on the basis of the positive HR-ESI-MS at *m/z* 639.2447 $[M + Na]^+$. Its $^1H$ and $^{13}C$ NMR spectra were very similar to those of **1**, except for an additional methoxyl ($\delta_H$ 3.27 s; $\delta_C$ 54.8 q) in **2**. Close

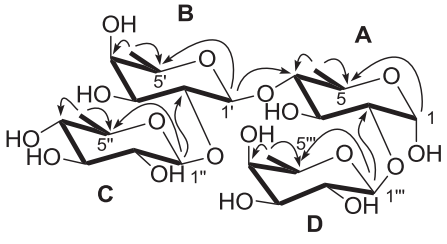


**Fig. 2.** Key $^1H$–$^1H$ COSY (bold) and HMBC (arrow) correlations for **1**.