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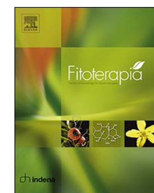

Spongian diterpenes from Chinese marine sponge *Spongia officinalis*

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ABSTRACT

3-Nor-spongiolide A (**1**), belonging to the extremely rare 3-nor-spongian carbon skeleton, and spongiolides A (**2**) and B (**3**), having γ-butenolide instead of furan ring as usual for ring D, together with six related known metabolites were isolated from South China Sea sponge *Spongia officinalis* as its metabolic components. Their structures were elucidated on the basis of extensive spectroscopic analysis. The absolute configurations of three new compounds **1–3** were determined by ECD calculations.

1. Introduction

Spongian diterpenes are a family of isoprenoid natural products displaying parent 6,6,6,5-tetracyclic ring system, despite the fact that they could be integrated into two main groups: I - compounds with the intact spongiane skeleton, and II - compounds with an incomplete or rearranged skeleton [1]. Interestingly, they shared the same joint stereochemistry of rings A, B and C in the spongiane skeleton for group I, which have been proven by a series of X-ray diffraction analyses [1–5] and synthetic studies [6]. Aside from their role as eco-physiological mediators, a broad range of pharmaceutically relevant biological activities such as cytotoxic, antifungal, antiviral, as well as anti-inflammatory activity have been reported for spongian diterpenes, making them attractive targets for chemical synthesis [6–9]. Although spongian diterpenes could be found from a wide variety of sources including marine invertebrates, sponges have been the richest source of this kind of marine natural products [2], especially for its genus *Spongia* [10,11].

In the course of our ongoing screening program for novel and biologically active natural products from Chinese marine flora and fauna [12–15], we collected the samples of sponge *Spongia officinalis* (order Dictyoceratida, family Spongidae), a widespread member of the South China Sea coral reef. The animals have been well recognized for the production of various secondary metabolites, such as diterpenes, sesterterpenes, sesquiterpene quinoenes, sterols, *etc.* [10]. In the early chemical investigation on this species by our group [16], one sesterterpene and three C_{21} furanoterpenoids have been reported. Inspired by the previous work, a further research for the minor components was carried out on the title animals, leading to the isolation of three new diterpenes, named 3-nor-spongiolide A (**1**) and spongiolides A (**2**) and B (**3**), as well as six related known metabolites **4–9** (Fig. 1). Compound **1**, a ring-A-contracted norditerpenoid, represented the second report of 3-nor-spongian, whereas the isolates **2** and **3** displayed γ-butenolide instead of furan ring as usual for ring D. Details of the isolation and structure elucidation for these secondary metabolites are reported herein.

2. Experimental

2.1. General methods

Optical rotations were measured in $CHCl_3$ on a Perkin-Elmer 241MC polarimeter (Perkin-Elmer, Waltham, MA, USA). UV spectra were recorded in MeOH on an Cary 300-Bio UV–Visible spectrometer (Varian, Palo Alto, CA, USA); peak wavelengths are reported in nm. IR spectra were recorded on a Nicolet 6700 spectrometer (Thermo Scientific, Waltham, MA, USA) with KBr pellets; peaks are reported in cm^{-1}. 1D and 2D NMR spectra were measured on a Bruker DRX-400 or Bruker

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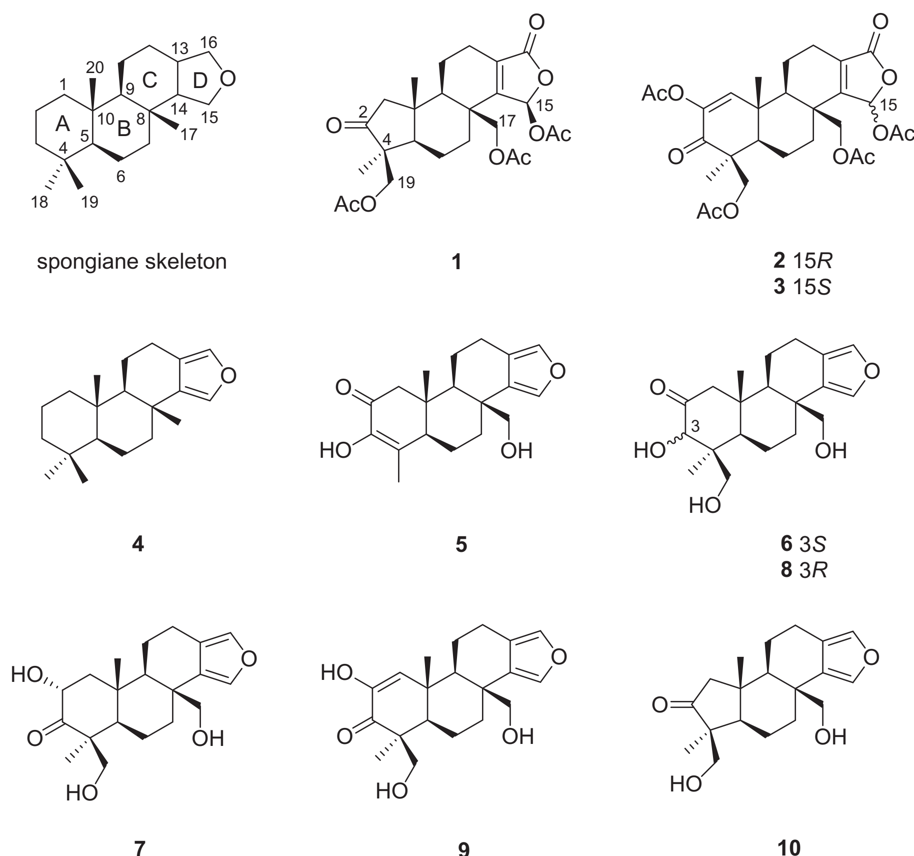

Fig. 1. Chemical structures of compounds **1**–**10**.

DRX-500 spectrometer (Bruker Biospin AG, Fällanden, Germany), using the residual $CHCl_3$ signal (δ_H 7.26 ppm) as an internal standard for ^1H NMR and $CDCl_3$ (δ_C 77.00 ppm) for ^{13}C NMR. Chemical shifts are expressed in δ (ppm) and coupling constants (J) in Hz. ^1H and ^{13}C NMR assignments were supported by $^1H-^1H$ COSY, HSQC, HMBC, and ROESY experiments. EI-MS and HR-EI-MS spectra were recorded on a Finnigan-MAT-95 mass spectrometer (FinniganMAT, San Jose, CA, USA). Reversed-phase (RP) HPLC purification was carried out on an Agilent 1260 series liquid chromatography (Agilent Technologies Inc., Palo Alto, CA, USA) equipped with a DAD G1315D detector at 210 and 254 nm and with a semi-preparative ODS-HG-5 column [5 μm, 250 × 9.4 mm]. Commercial silica gel (Qingdao Haiyang Chemical Group Co., Ltd., Qingdao, China, 200–300 and 300–400 mesh) was used for column chromatography (CC), and precoated silica gel plates (Yan Tai Zi Fu Chemical Group Co., Yantai, China, G60 F-254) were used for analytical TLC. Spots were detected on TLC under UV light or by heating after spraying with anisaldehyde H_2SO_4 reagent. All the chemicals were obtained from commercial sources. All solvents used for CC were of analytical grade, and solvents used for HPLC were of HPLC grade.

2.2. Animal material

The specimens of *S. officinalis* were collected by hand using scuba at Weizhou Island, Guangxi Autonomous Region, China, in October 2015, at a depth of 20 m, and were frozen immediately after collection. It was identified by J. Li of the Institute of Oceanology, Chinese Academy of Sciences. The voucher specimen was deposited at Shanghai Institute of Materia Medica, Chinese Academy of Sciences, under registration No. 15wz-35.

2.3. Extraction and isolation

The frozen sample of *S. officinalis* (180 g, dry weight) was cut into small pieces and ultrasonically extracted with acetone (4 × 2.0 L) at room temperature. The acetone extract was concentrated under reduced pressure to give a brown residue, which was then suspended in H_2O and extracted sequentially with Et_2O and *n*-BuOH. The Et_2O extract was divided into 17 parts (Fr. A–Fr. Q) by silica gel column chromatography eluted with a gradient of Et_2O-hexane (0:1 → 1:0, v/v) followed by MeOH-CH_2Cl_2 (1:9 → 3:7, v/v). Fr. A was purified by reversed-phase HPLC eluted at 2 mL/min with MeOH-H_2O (95:5, v/v) to afford compound **4** (3.5 mg, t_R 7.8 min). Fr. O was subjected to silica gel column chromatography eluted with Et_2O–CH_2Cl_2 (3:7, v/v) to afford compound **5** (3.2 mg). Fr. Q was applied to silica gel column chromatography eluted with MeOH–CH_2Cl_2 (2:8, v/v) then further purified by HPLC (MeOH-H_2O, 30:70, v/v) to afford compounds **6** (2.8 mg, t_R 7.8 min), **7** (2.3 mg, t_R 8.8 min), **8** (1.9 mg, t_R 10.5 min), and **9** (2.1 mg, t_R 13.2 min). The *n*-BuOH extract was performed by silica gel column chromatography eluted with MeOH-CH_2Cl_2 (0:1 → 5:5, v/v), to afford 8 fractions A′–H′. Fr. D′, eluted with MeOH-CH_2Cl_2 (3:7, v/v), was a mixture, which is hardly separable by HPLC. Acetylated fraction D′ was then subjected to HPLC (MeOH-H_2O, 60:40, v/v) to afford compounds **1** (2.0 mg, t_R 10.1 min), **2** (1.4 mg, t_R 7.3 min) and **3** (2.2 mg, t_R 13.5 min).

2.4. Spectroscopic data

3-Nor-spongiolide A (**1**): white amorphous powder; $[\alpha]_D^{20}$ − 14.8 (c = 0.11, $CHCl_3$); UV λ_{max} (MeOH) (log ε): 218 (0.78) nm; ECD [MeOH, λ_{ext} ([θ])]: 302 (+12.255), 247 (−15.717), 223 (+16.463) nm; IR (KBr) ν_{max}: 1743, 1667, 1260, 1076, 750 cm^{-1}; ^1H and ^{13}C NMR data, see Table 1; HR-EI-MS m/z: 476.2035 (calcd for $C_{25}H_{32}O_9$,

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