SHORT REPORT

A C G publications

*Rec. Nat. Prod.*6:4 (2012) 398-401

records of natural products

Jaspiferin A and B: Two New Secondary Metabolites from the South China Sea Sponge *Jaspis stellifera*

Shengan Tang*[1], Rong Xu[2], Wenhan Lin[3] and Hongquan Duan[1]

[1] *Tianjin Key Laboratory on Technologies Enabling Development of Clinical Therapeutics and Diagnostics (Theranostics), School of Pharmaceutical Sciences, Research Center of basic Medical Sciences, Tianjin Medical University, Tianjin, 300070, China*
[2] *Department of Pharmacy, Quanzhou Medical College, Quanzhou, 362000, China*
[3] *National Research Laboratories of Natural and Biomimetic drugs, Peking University, Beijing, 100083, China*

(Received November 7, 2011; Revised November 9, 2012; Accepted July 17, 2012)

Abstract: A chemical investigation of marine sponge *Jaspis stellifera*, collected from South China Sea, led to the isolation of two new compounds, Jaspiferin A and B (**1**-**2**), and six known compounds, gibepyrone F (**3**), *p*-hydroxy benzaldehyde (**4**), 3-Indole-3-aldehyde (**5**), Thymine (**6**), 24(28)-dehydroaplysterol (**7**), (25s)-26-methylene-cholest-4-en-3-one (**8**). Their structures were determined by extensive spectroscopic analysis in association with physical and chemical properties, as well as comparison of their spectral data with these reported in literatures. The biogenetic transformation of compound **2** was also speculated.

Keywords: *Jaspis stellifera*; marine sponge; chemical investigation.

1. Animal source

The sponge *jaspis stellifera* was collected at Guangdong, South China Sea of People's Republic of China, in June 2010. The sample was frozen immediately after collection, and was identified by Dr. R. van Soest (Institute of Systematic and Ecology, Amsterdam University) as *jaspis stellifera*. A voucher specimen (XWS-03) was deposited at the School of Pharmaceutical Sciences, Tianjin Medical University, Tianjin, People's Republic of China.

2. Previous Studies

Marine sponges of the genus *Jaspis* (family) have been shown a rich source of biologically active and structurally novel natural products, such as isomalabaricanes[1,2], jaspamides[3], jaspisamides[4], bengamides[5], bengazole alkaloid[6].

* Corresponding author: E- Mail: tangshengan@tijmu.edu.cn, Phone +86-022-23542838

The article was published by Academy of Chemistry of Globe Publications
www.acgpubs.org/RNP © Published 7/20/2012 EISSN:1307-6167

3. Present Study

The frozen sponge (2.0 kg) was homogenated and extracted with MeOH, and the extract was concentrated under reduce pressure to afford residue (150 g). The residue was dissolved in water and then partitioned between H_2O and CH_2Cl_2. The concentrated CH_2Cl_2 fraction (40.0 g) was chromatographed on a silica gel column by eluting with petroleum ether-EtOAc (4:1, 2:1) to obtain ten fractions (A-J). Fraction G (2.0 g) was further subjected to chromatography over silica gel column eluting with gradient of CH_2Cl_2: acetone, and **1** (1.5 mg), **2** (0.4 mg), **3** (8.2 mg), and **4** (10.0 mg) were yielded from the ratio 20:1, while **5** (2.1 mg) **6** (5.0 mg) were obtained from the ratio 10: 1. Compound **7** (120.0 mg) was obtained by recrystallization from fraction D, **8** (3.8 mg) was obtained by repeatedly silica gel column eluting with gradient of CH_2Cl_2: EtOAc.

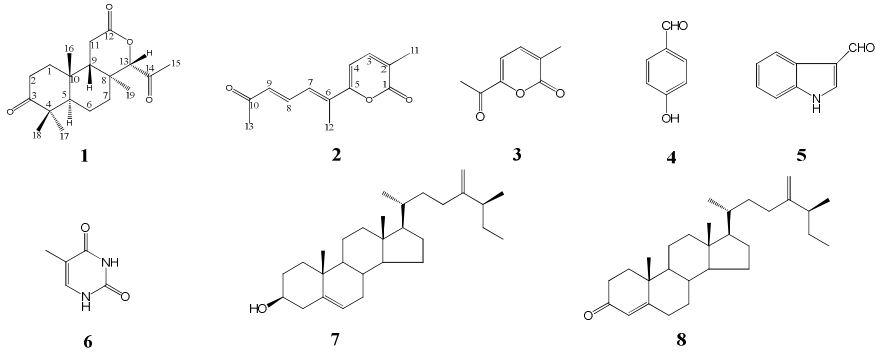


Figure 1. Structures of 1-8 isolated from J. stellifera

Compound **1**, colorless solid, $[\alpha]^{25}_{,D}$ –3.7° (*c* 0.01, acetone), has a formula $C_{19}H_{29}O_4$ as determined by HR-FAB-MS (*m/z* 321.2067 $[M+H]^+$, Calcd:321.2060), ^{1}H- and ^{13}C-NMR data. The ^{1}H NMR spectra exhibited 6 prominent signals at δ_H 4.31 (H-13), 2.32 (CH_3-15), 1.24 (CH_3-19), 1.12 (CH_3-17), 1.08 (CH_3-18), 0.89 (CH_3-16), ^{13}C NMR spectra exhibited nineteen carbons in the molecule. The low field region of the ^{13}C NMR spectrum revealed the presence of two carbonyl carbons [δ_C 218.0 (C-3), 206.0 (C-14)], one carboxyl carbon [δ_C 171.0 (C-12)]. The three carbonyl groups derived from ^{13}C NMR analysis accounted for 3 of the 6 degrees of unsaturation, thus implying a polycyclic nature for **1**.

The gross structure of **1** was established on the basis of extensive 2D NMR analysis. In the HMBC spectrum, five long-range coupling systems of methyl group can be observed, they were δ_H 2.32 / (δ_C 206.0), δ_H 1.24 / (δ_C 92.6, 44.7, 34.5), δ_H 1.12 / (δ_C 218.0, 46.8, 46.6, 19.6), δ_H 1.08 / (δ_C 218.0, 46.8, 46.6, 29.0), δ_H 0.89 / (δ_C 46.6, 44.7, 35.1, 33.3); one oxygenated methine proton signal at δ_H 4.31 has long-range correlation with δ_C 206.0, 44.7, 34.5, 18.5. A comparative analysis of the remaining data in the two-dimensional NMR spectra (COSY, HMQC, and HMBC) allowed us to assign all the resonances of the complete planar structure of **1**.

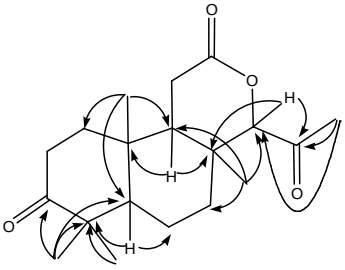


Figure 2. the selected HMBC correlations of **1**

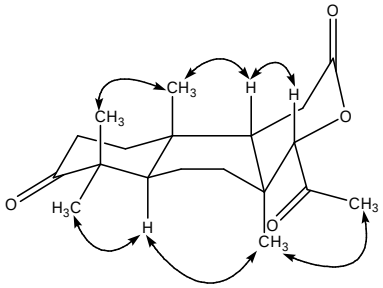


Figure 3. the selected NOESY correlations of **1**

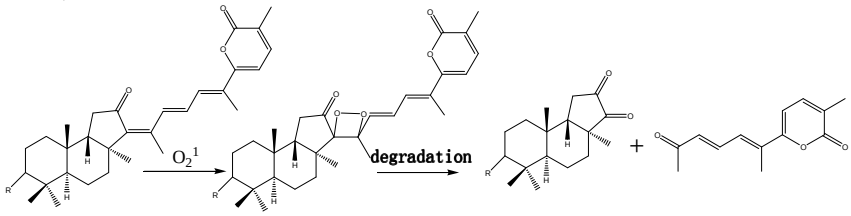
The 2D-NOESY cross peaks between H-5 / H-17, H-5 / H-19, H-9 / H-16, H-9 / H-13, H-16 / H-18 indicated a trans-syn-trans stereochemistry of the tricyclic system. The geometry of H-13 was assigned as β-orientation since NOE correlation was observed between H-13 / H-9, and H-15 / H-19. Therefore, compound **1** was determined to be Jaspiferin A.

Table 1: ^{1}H-, ^{13}C-NMR data of compound **1** (in $CDCl_3$)

position	^{1}H	^{13}C	position	^{1}H	^{13}C
1	1.58(m), 2.25(m)	33.3(t)	11	2.62(m)	28.0(t)
2	2.40(m), 2.73(m)	33.4(t)	12		171.0(s)
3		218.0(s)	13	4.31(s)	92.6(d)
4		46.8(s)	14		206.0(s)
5	2.07(m)	46.6(d)	15	2.32(s)	28.7(q)
6	1.39(m)	19.2(t)	16	0.89(s)	22.8(q)
7	2.27(m)	37.0(t)	17	1.12(s)	29.0(q)
8		34.5(s)	18	1.08(s)	19.6(q)
9	1.83(m)	44.7(d)	19	1.24(s)	18.5(q)
10		35.1(s)			

Compound **2**, yellow solid, has a formula $C_{13}H_{14}O_3$ as determined by HR-EI-MS (*m/z* 218.0945 $[M]^+$, Calcd: 218.0943). In ^{1}H NMR spectra, an ABX coupling system of olefinic protons at δ_H 6.45 (1H, d, *J* =15.2 Hz), 7.55 (1h, dd, *J* =11.9, 15.2 Hz), and 7.20 (1h, d, *J* = 11.9 Hz) were attributed to the proton signals at H-9, H-8, and H-7 of side chain, respectively, while an AB coupling system at δ7.18(1H, d, *J* = 6.8 Hz) and 6.33 (1H,d, *J* = 6.8 Hz) were due to the olefinic protons of H-3 and H-4 at the terminal unsaturated δ- lactone. There were three methyl signals in ^{1}H NMR spectrum, of which they were assigned to position at C-11, C-12, and C-13 [δ_H 2.16 (3H, br s), 2.13 (3H, br s), and 2.35 (3H, s)], respectively.

The structure of **2** was confirmed by compare with the MS, IR, ^{1}H NMR spectrum data of the known compound jaspolide A and B[2] which has a side chain of unsaturated δ- lactone. Therefore, compound **2** was determined to be Jaspiferin B. The hypothesis of a biogenetic pathway to generate **2** was depicted (**Scheme 1**).



Scheme 1. Proposed biogenetic pathway for **2**

The structures of known compound **3**-**8**, namely gibepyrone F (**3**)[7], *p*-hydroxy benzaldehyde (**4**)[8], 3-Indole-3-aldehyde (**5**)[9], Thymine (**6**)[10], 24(28)-dehydroaplysterol (**7**)[11], (25s)-26-methylene-cholest-4-en-3-one (**8**)[11] were elucidated by MS, NMR spectroscopies and comparison of their spectroscopic data with those report in the literatures.

Acknowledgments

This work was partially supported by the National Natural Science Foundation of China (Grant No. 81102371) and the Natural Science Foundation of Tianjin, China (Grant No. 10JCYBJC15000).

Supporting Information

Supporting Information accompanies this paper on http://www.acgpubs.org/RNP

References

[1] S. A. Tang, Z. W. Deng, P. Proksch and W. H. Lin (2007). Jaspolides G and H, unique bisisomalabaricanes from the Chinese marine sponge *jaspis* sp., *Tetrahedron Lett.* **48**, 5443-5447.
[2] S. A. Tang, Y. H. Pei, H. Z. Fu, Z. W. Deng and W. H. Lin (2006). Jaspolide A-F, six new isomalabricane-type terpenoids from the sponge *Jaspis* sp., *Chem. Pharm. Bull.* **54**, 4-8.
[3] A. Zanpella, C. Giannini, C. Debitus, C. Roussakis, and M. V. D'Auria (1999). New Jaspamide Derivatives from the Marine Sponge *Jaspis splendans* Collected in Vanuatu, *J. Nat. Prod.* **62**, 332-334.
[4] J. Kobayashi, O. Murata, H. Shigemori and T. Sasaki (1993). Jaspisamides A-C, New Cytotoxic Macrolides from the Okinawan Sponge *Jaspis* sp., *J. Nat. Prod.* **56**, 787-791.
[5] Z. Thale, F. R. Kinder, K. W. Bair, J. Bontempo, A. M. Czuchta, R. W. Versace, P. E. Phillips, M. L. Sanders, S. Wattanasin and P. Crews (2001). Bengamides Revisited: New Structures and Antitumor Studies, *J. Org. Chem.* **66**, 1733-1741.
[6] J. Rodriguez, R. M. Nieto and P. Crews (1993). New Structures and Bioactivity Patterns of Bengazole Alkaloids from a Choristid Marine Sponge, *J. Nat. Prod.* **56**, 2034-2040.
[7] A. F. Barrero, J. E. Oltra, M. M. Herrador, E. Cabrera, J. F. Sanchez, J. F. Quílez, F. J. Rojas and J. F. Reyes (1993). Gibeprones：α-Pyrones from Gibberella fujikuroi, *Tetrahedron.* **49**, 141-150.
[8] Q. Y. Yu, D. W. Zhang and S. J. Dai (2011). Isolation and Identification of Chemical Constituents from the Whole Herb of *Scutellaria Barbata*, *Mod. Chin. Med*. **13**, 25-28.
[9] W. L. Li, S. L. Mao and Y. H. Yi (2000). Studies On The Chemical Constituents Of The Sponge *Suberites Tylobtusa Levi*, *Chin. J. Mar. Drugs.* **75**, 1- 4.
[10] X. D. Peng, S. Z. Deng and D. J. Xiao (2004). Suduies on the active constituents of the marine sponge *Pseudocerati na purpurea* from the South China Sea, *Chin. J. Mar. Drugs.* **97**, 11-13.
[11] J. M. Oger, P. Richomme, J. Bruneton, H. Guinaudeau, T. Sévenet and C. Debitus (1991) . Steroids from *Neosiphonia Supertes*, A Marine Fossil Sponge, *J.Nat.Prod.* **54**, 273-275.