中山大学学报 (自然科学版)
第 36卷 第 5期 ACTA SCIENTIARUM NATURALIUM Vol. 36 No. 5
1997年 9月 UNIVERSITATIS SUNYATSENI Sep. 1997

Ceramide from the Marine Sponge *Phyllospongia* sp.*

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Abstract Phylloamide A, has been isolated from the marine sponge *Phyllospongia* sp. Its structure was deduced by spectroscopic and chemical methods.

Keywords sponge, ceramide, *Phyllospongia*

Classificational number O 629.2

1 Results and Discussion

Ceramide is one of the important class of sphingolipids which constituted abroad class of biologically important compounds[1]. Very recently, a number of unusual ceramides or ceramidelike compounds having a spohingosine moiety by longer carbon-chain and/or additional functionalities (double bond or OH) have been isolated from marine organism[2-6].

In this paper the isolation and the structural determination of a new ceramide, named Phylloamide A (**1**), were described. **1** was isolated from the marine sponge *Phyllospongia* sp. collected from the South China Sea. The structure of **1** differs from the normal ceramide in the two long chains, each possessing one more methyl group instead of straight chains.

The ethanol extract of the sponge *Phyllospongia* sp. was chromatographed on silica gel using petroleum ether with increasing amounts of ethyl acetate as eluent. **1** was afforded as an amorphous white powder from the fraction elted by petroleum ether/ethyl acetate, 40/60, θ_{mp}: 85~86℃. FABMS showed the molecular ion peak at *m/z* 678 $(M+H)^+$. Elemental analysis (*w*/%) found C, 78.05; H, 12.89; N, 2.07 (calcd. C, 77.95; H, 12.93; N, 2.07). The molecular formula of **1** was thus established as $C_{44}H_{87}NO_3$. IR ν_{max}/cm^{-1}: 3 303, 1 644, 1 546 and ^{1}HNMRδ_H ($CDCl_3$, TMS) /ppm 6.33 (1H, d, *J* = 7.5 Hz exchangeable) and ^{13}CNMRδ_C ($CDCl_3$) /ppm 173.97 suggested **1** containing a -CO-NH- moiety. ^{1}HNMRδ_H/ppm 3.69 (s, OH, exchangeable), 3.98 (s, OH, exchangeable) and the ^{13}CNMR DEPTδ_C/ppm 62.37 (t) and 74.29 (d) revealed the presence of a primary hydroxyl group and a secondary hydroxyl group in **1**. Furthermore, δ_H/ppm 4.30 (1H, dd, *J*= 7.5, 4.9 Hz), 6.20 (1H, dd, *J*= 13.6, 6.1 Hz), 5.78 (1H, m) and δ_C/ppm 134.10, 128.84 indicated that a CH-OH moiety connected with a double

* 国家自然科学基金 (19572077) 资助项目
收稿日期: 1996-10-03 万一千, 男, 34岁, 讲师

bond which was in E configuration[5,6]. W_H/ppm 3.89 and W_C/ppm 54.68 indicating a CH–NH– unit was presented in **1**[5~7]. The double resonance experiment revealed that decoupling the one-proton multiplet at W_H 3.89 ppm partly collapsed the multiplet at W_H 4.30 ppm and caused a doublets at W_H 3.79 ppm to sharp singlet; decoupling the one-proton multiplet at W_H 4.30 ppm partially collapsed the multilet at W_H 3.89 ppm and caused multiplet at W_H 6.20 ppm to doublet, thus the double resonance experiment confirmed the presence of moiety such as – CONHCH (CH_2OH) CH (OH) – CH= CH– .

The presence of two long carbon side chains in **1** was suggested by W_H 1.64 ppm (br, s, 64 H) and ^{13}C NMR and DEPT at W_C 29.49 (vs). ^{13}C NMR DEPT at W_C/ppm 14.05, 22.61, 25.75, 27.37 revealed that there were two more methyl groups in the long carbon chains. The carboxylic acid moiety of the **1** was deduced as C_7H_{15} (CH_2)$_{16}$CO– from the peak of FABMS at *m*/*z* 351 and 323. The rest moiety should be – NH– CH (CH_2OH) – CH– (OH) – CH= CH– $C_{15}H_{31}$.

The MS fragmentation of **1** (Fig. 1) indicated that one methyl group was attached at C_{18} and the other one was connected with C_{15}, and the gross structure of **1** could be established as Ⅰ . Hydrolysis of **1** with acid by the Gaver-Sweeley method[8] afforded the methyl 18-methyl-tricosanoate, which was identified by its FABMS at *m*/*z* 383 (M^+ + 1), 368 (M^+ –15), 323 (M^+ –COOMe), 99, 71, 74 (100%). Accordingly, the structure of **1** was proved to be Ⅰ .

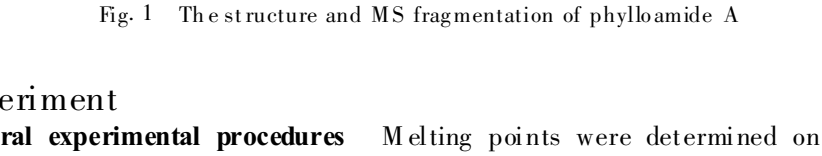

Fig. 1 The structure and MS fragmentation of phylloamide A

2 Experiment

2.1 **Gneral experimental procedures** Melting points were determined on an X4 micromelting point apparatus and are uncorrected. IR spectrum was recorded using NICOET-5DX-FT IR spectrometer. UV spectrum was taken in MeOH on a Perkin-Elmer Lambda 3 UV/VIS spectrometer. FABMS were run on a VGZAB-E mass spectrometer, and NMR spectra were recorded on JOEL-FX-90Q and VXR-400 spectrometers using $CHCl_3$ (reference to TMS as internal standard). All solvents used were analytical grade. Light petroleum refers to the 60~ 90℃ fraction. Si gel H was used for flash cc.

2.2 **Biological material** The *Phyllosponge* sp. was collected off the Nansha Island in the South China Sea in April 1993. A voucher specimen (No. 93~ 13) has been deposited in the Research Center of Organic Natural Products, Zhongshan University, Guangzhou, China.

2.3 **Extraction and isolation** The EtOH extract of the sundried specimen (dry wt. 350 g of the marine sponge *Phyllospongia* sp. was partitioned between EtOAc and H_2O. The EtOAc-soluble partion material was chromatographed repeatedly over Si gel using solvents of increasing polarity from petroleum ether to EtOAc, then was chromatographed on Al_2O_3, finally was purified on hoplc plate. The new compound **1** was obtained as an amorphous white powder from the fraction eluted by petroleum ether/ethyl acetate (40/60).

2.4 **Spectral data of Phylloamide A** W_H ($CHCl_3$, TMS) /ppm: 6.33(s), 6.20(dd), 6.13 (m), 5.78(m), 5.50~ 5.38(m), 4.30(dd), 3.98(s), 3.89(m), 3.79(d), 3.69(s), 3.68~

3.65(m), 2.80~ 2.37(m), 2.30~ 1.83(m), 1.64(br. s), 0.88~ 0.68(m). ^{13}C (CHCl$_3$, TMS) /ppm: 173.97, 134.10, 128.84, 74.29, 62.37, 54.68, 39.20, 36.80, 32.25, 31.87, 29.92, 29.65, 29.49, 29.33, 27.92, 27.37, 25.75, 22.61, 14.05. FABMS *m* /*z*: 678 [M+H]$^+$, 618, 619, 604, 466, 410, 383, 368, 366, 351, 323, 296, 283, 264, 251, 210, 99, 85, 74, 71 (100), 57. ν /cm^{-1}: 3 303, 3 078, 2 917, 2 853, 1 644, 1 546, 1 468, 1 378, 1 257, 1 064, 969, 899, 723.3.

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海绵 *Phyllospongia* sp. 中分离的神经酰胺 Phylloamide A.

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摘　要　从中国南海海绵 *Phyllospongia* sp. 中分离得到了一个神经酰胺类化合物 Phylloamide A, 它的结构通过波谱方法和化学方法确定.

关键词　海绵, 神经酰胺, 杯叶海绵, 杯叶酰胺 A
分类号　O 629.2

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