

深海来源真菌 *Penicillium* sp. F00120 代谢产物的研究田永奇<sup>1,2</sup>, 林秀萍<sup>1\*</sup>, 刘娟<sup>1</sup>, 王俊峰<sup>1</sup>, 杨斌<sup>1</sup>, 鞠志冉<sup>1</sup>, 陶华明<sup>3</sup>, 刘永宏<sup>1\*</sup><sup>1</sup>中国科学院南海海洋研究所 中国科学院热带海洋生物资源与生态重点实验室, 广州 510301;<sup>2</sup>中国科学院大学, 北京 100049; 南方医科大学中医药学院, 广州 510515

**摘要:** 利用硅胶柱色谱、凝胶柱、反向柱色谱和高效液相色谱等手段对深海来源的真菌 *Penicillium* sp. F00120 在高盐培养基中的代谢产物进行分离纯化, 从中分离得到了 9 个化合物。通过理化性质、波谱分析方法结合文献对照, 鉴定了化合物的结构分别为: 麦角甾醇(1)、4-methyl-5, 6-dihydro-2-pyranone(2)、citreoahyridonol(3)、1-linoleoylglycerol(4)、5 $\alpha$ , 6 $\alpha$ -Epoxy-(22*E*, 24*R*)-ergosta-8(14), 22-diene-3 $\beta$ , 7 $\beta$ -diol(5)、macrophorin(6)、purpurogenmutantin(7)、3-(2*S*, 4*S*-dihydroxypentyl)-6, 8-dihydroxyisocoumarin(8)、5-hydroxy-7-(2'-hydroxypropyl)-2-methylchromone(9)。化合物 2~4, 6~9 均为首次从深海沉积物真菌中分离得到。

**关键词:** 深海真菌; *Penicillium* sp. F00120; 波谱分析; 次生代谢产物

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Metabolites of *Penicillium* sp. F00120 from a Deep Sea Sediment SampleTIAN Yong-qi<sup>1,2</sup>, LIN Xiu-ping<sup>1\*</sup>, LIU Juan<sup>1</sup>, WANG Jun-feng<sup>1</sup>,YAN Bing<sup>1</sup>, JU Zhi-ran<sup>1</sup>, TAO Hua-ming<sup>3</sup>, LIU Yong-hong<sup>1\*</sup>

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**Abstract:** To study the chemical constituents of deep-sea fungus *Penicillium* sp. F00120, nine compounds were isolated from its EtOAc extract using silica gel, Sephadex LH-20, ODS and HPLC methods. Based on the spectroscopic analysis, their structures were identified as ergosterol (1), 4-methyl-5, 6-dihydro-2-pyranone (2), citreoahyridonol (3), 1-Linoleoylglycerol (4), 5 $\alpha$ , 6 $\alpha$ -Epoxy-(22*E*, 24*R*)-ergosta-8(14), 22-diene-3 $\beta$ , 7 $\beta$ -diol (5), macrophorin (6), purpurogenmutantin (7), 3-(2*S*, 4*S*-dihydroxypentyl)-6, 8-dihydroxyisocoumarin (8), 5-hydroxy-7-(2'-hydroxypropyl)-2-methylchromone (9). Compounds 2-4, 6-9 were isolated from *Penicillium* sp. F00120 for the first time.

**Key words:** deep-sea fungus; *Penicillium* sp. F00120; spectroscopic analysis; secondary metabolites

经过 60 多年的不懈努力, 海洋天然产物研究已经有了长足的进步, 药学家们不断地从海洋生物中分离出结构新颖, 活性良好的化合物, 超过 0.1% 的化合物已作为新药的先导化合物。镇痛药物 Ziconotide、抗肿瘤药物 ET-743 和抗肿瘤药物 Halichondrin B 等海洋药物的相继上市标志着海洋天然产物在新药研发中占据了重要的位置<sup>[1]</sup>。海洋微生物与海绵、珊瑚并列成为海洋天然产物的三大来源<sup>[2]</sup>。由于海洋真菌具有次级代谢产物丰富、活性

多样和易于发酵培养等优点, 成为发现新的海洋活性天然产物的宝库。迄今为止, 已经从海洋真菌的发酵产物中发现了 1000 多个新化合物。这些代谢产物都表现出良好的抗肿瘤、抗菌、抗病毒和神经心血管等活性<sup>[3]</sup>。

深海的高压、低温等极端环境赋予了深海真菌独特的个性。深海真菌的次级代谢产物以结构新颖, 活性良好著称, 目前已经成为药学家们关注的热点。2012 年, 本学科组从深海沉积物来源的真菌 *Penicillium* sp. F00120 中分离得到了一个结构新颖的倍半萜醌类化合物 penicilliumin A<sup>[4]</sup>。该化合物具有抗肿瘤活性, 是迄今为止报道的少数几个来源于微生物的倍半萜醌类化合物之一。本文作为此工作的延续, 采用高盐培养基进行发酵, 从 *Penicillium*

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sp. F00120 的发酵产物中分离得到了 9 个化合物, 通过核磁共振、文献对照等方法鉴定了这些化合物的结构, 其中化合物 **6** 和 **7** 为 penicilliumin A 的同系物。

## 1 仪器与材料

核磁共振波谱仪: Bruker Avance DRX500 型 (500/125 MHz, TMS 为内标)。HR-ESI-MS: Bruker micro TOF-QII mass spectrometer (Bruker, Fällanden, Switzerland)。EYELAN-1000 型旋转蒸发器。高效液相色谱仪: Agilent 1200 (泵型号: G1212C, 紫外检测器型号: G1315D), YMC-Pack (C8 250 × 10 mm I. D. S-5 μm, 12 nm)。TLC: 高效薄层层析板 (HPTLC) 为德国 Merck 公司产品和烟台江友硅胶开发有限公司产品。显色剂: 10% 硫酸香兰素溶液。常用有机试剂均为国产的分析纯产品。

海洋真菌菌株 F00120 从采自中国南海北部 (Lat. 22°6.017'N, Long119°17.440'E) 1300 m 的海底沉积物样品分离得到, 经形态特征和分子生物学鉴定, 确定其属于青霉属, 并命名为 *Penicillium* sp. F00120<sup>[4]</sup>。该菌株现保存于中国科学院南海海洋研究所热带海洋生物资源与生态重点实验室。

## 2 真菌发酵

将保藏于 4 °C 斜面的 *Penicillium* sp. F00120 接种到 MB 固体培养基 (麦芽浸膏 1.5 g, 粗海盐 1 g, 琼脂粉 1.5 g, 蒸馏水 100 mL, pH 7.4 ~ 7.8) 平板上, 于 25 °C 培养箱中培养 7 d。将活化后的菌株转接到装有 10 mL MB 液体培养基 (麦芽浸膏 1.5 g, 粗海盐 1 g, 蒸馏水 100 mL, pH 7.4 ~ 7.8, 加玻璃珠) 的 100 mL 三角瓶中, 于 28 °C、180 rpm 摇床培养 2 d。将 10 mL 种子培养液转接入装有大米固体培养基 (大米 200 g, 粗海盐 6 g, 自来水 200 mL) 的 1000 mL 三角瓶中, 于 25 °C 静置培养 60 d, 共发酵培养 30 瓶。

## 3 提取与分离

*Penicillium* sp. F00120 的固体发酵物用丙酮浸泡过夜, 搅拌粉碎, 超声提取 15 min。提取物抽滤, 蒸去丙酮, 水层浓缩体积, 用乙酸乙酯萃取 2 次, 收集上清液。固体残渣再用乙酸乙酯浸提 3 次, 每次浸泡过夜, 抽滤, 收集上清液。将 5 次得到的上清液合并, 减压旋转蒸发, 共得浸膏 47.6 g。粗浸膏以 1

: 1 的比例与 100 ~ 200 的硅胶 H 拌匀, 待干燥后填入中压正相硅胶柱分离, 石油醚-乙酸乙酯 (1:0 ~ 0:1) 梯度洗脱, TLC 薄层检测后合并, 得到 8 个馏分 Fra. 1 ~ 8。Frs. 4 经重结晶得到化合物 **1** (200 mg); Frs. 5 经液相制备 (CH<sub>3</sub>OH: H<sub>2</sub>O = 6:4) 得到化合物 **2** (25 mg); Fra. 7 经 Sephadex LH-20 凝胶柱 (甲醇) 分离, 得到 5 个馏分 Fra. 7a ~ Frs. 7e, 其中 Fra. 7c 经正相硅胶柱分离, 二氯甲烷-甲醇 (1:0 ~ 0:1) 洗脱, 得到 8 个馏分 Fra. 7c1 ~ Fra. 7c8。Fra. 7c3 重结晶得到化合物 **3** (27 mg)。Fra. 7c5 经正相硅胶柱分离, 二氯甲烷-甲醇 (1:0 ~ 0:1), 得到化合物 **4** (3 mg)、**5** (15 mg)。Fra. 7d 经 ODS 柱分离, 甲醇-水 (1:9, 1:1, 7:3, 9:1) 得到 4 个馏分 Fra. 7d1 ~ Fra. 7d4。Fra. 7d3 经液相制备 (CH<sub>3</sub>OH: H<sub>2</sub>O = 6:4) 得到化合物 **6** (5.3 mg)、**7** (4.7 mg)、**8** (10 mg)、**9** (20 mg)。

## 4 结构鉴定

化合物 **1** 白色针状结晶 (CH<sub>3</sub>OH), 254 nm 处有紫外吸收。<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 5.59 (1H, brm, H-6), 5.39 (1H, brm, H-7), 5.22 (2H, m, H-22, 23), 3.67 (1H, m, H-3), 1.04 (3H, d, *J* = 6.5 Hz, H<sub>3</sub>-21), 0.97 (3H, s, H<sub>3</sub>-10), 0.93 (3H, d, *J* = 6.5 Hz, H<sub>3</sub>-28), 0.83 (6H, t, *J* = 7.5 Hz, H<sub>3</sub>-26, H<sub>3</sub>-27), 0.65 (3H, s, H<sub>3</sub>-18); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 141.4 (C, C-8), 139.8 (C, C-5), 135.6 (CH, C-21), 132.0 (CH, C-22), 119.6 (CH, C-6), 116.3 (CH, C-7), 70.5 (CH, C-3), 55.8 (CH, C-17), 54.6 (CH, C-14), 46.3 (CH, C-9), 42.8 (CH, C-13), 40.8 (CH<sub>2</sub>, C-4), 40.4 (CH, C-24), 39.1 (CH<sub>2</sub>, C-12), 38.4 (CH<sub>2</sub>, C-1), 37.1 (C, C-10), 33.1 (CH, C-25), 32.0 (CH<sub>2</sub>, C-2), 28.3 (CH<sub>2</sub>, C-16), 23.0 (CH<sub>2</sub>, C-15), 21.1 (CH<sub>3</sub>, C-21), 19.9 (CH<sub>3</sub>, C-26), 19.6 (CH<sub>3</sub>, C-27), 17.6 (CH<sub>3</sub>, C-28), 16.3 (CH<sub>3</sub>, C-19), 12.1 (CH<sub>3</sub>, C-18)。以上数据与文献<sup>[5]</sup>对照, 基本一致, 确定化合物结构为 ergosterol。

化合物 **2** 淡黄色油状物, 254 nm 处有紫外吸收。EI-MS: 112 [M]<sup>+</sup>; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) δ<sub>H</sub>: 5.73 (1H, m, H-3), 4.34 (2H, t, *J* = 10 Hz, H<sub>2</sub>-6), 2.41 (2H, t, *J* = 5 Hz, H<sub>2</sub>-5), 1.99 (3H, brs, H<sub>3</sub>-7); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 125 MHz) δ<sub>C</sub>: 167.33 (C=O,

C-2), 162.10 (C, C-4), 116.63 (CH, C-3), 67.63 (CH<sub>2</sub>, C-6), 30.32 (CH<sub>2</sub>, C-5), 23.11 (CH<sub>3</sub>, C-7)。以上数据与文献<sup>[6]</sup>对照,基本一致,确定化合物结构为 4-methyl-5,6-dihydro-2-pyranone。

**化合物 3** 白色晶体, EI-MS: 500 [M]<sup>+</sup>, 高分辨给出分子式为 C<sub>28</sub>H<sub>36</sub>O<sub>8</sub>; <sup>1</sup>H NMR (500 MHz, DMSO) δ<sub>H</sub>: 5.24 (1H, s, H-11), 4.77 (1H, d, J = 4.5 Hz, H-6), 4.48 (1H, brs, H-3), 3.89 (1H, d, J = 14.3, 4.5 Hz, H-7β), 3.40 (3H, s, H<sub>3</sub>-28), 2.48 (1H, m, H-9), 2.33 (1H, dd, J = 14.3, 4.5 Hz, H-7α), 1.99 (3H, s, H<sub>3</sub>-27), 1.90 (1H, brs, H-1), 1.88 (1H, brs, H-5), 1.74 (3H, s, H<sub>3</sub>-21), 1.57 (1H, m, H-2), 1.28 (3H, s, H<sub>3</sub>-18), 1.12 (3H, s, H<sub>3</sub>-22), 1.02 (3H, s, H<sub>3</sub>-20), 0.89 (3H, s, H<sub>3</sub>-24), 0.78 (3H, s, H<sub>3</sub>-25); <sup>13</sup>C NMR (DMSO, 125 MHz) δ<sub>C</sub>: 194.3 (C, C-15), 194.1 (C, C-17), 179.2 (C, C-23), 173.2 (C = O, C-19), 169.6 (C = O, C-26), 140.3 (C, C-12), 118.4 (CH, C-11), 103.5 (C, C-16), 77.9 (CH, C-6), 75.5 (CH, C-3), 70.0 (C, C-14), 54.8 (C, C-13), 53.8 (CH, C-5), 50.6 (CH, C-9), 50.2 (CH<sub>3</sub>, C-28), 43.2 (C, C-10), 41.1 (C, C-8), 36.4 (CH<sub>2</sub>, C-7), 33.8 (C, C-4), 25.8 (C, C-24), 24.2 (CH<sub>3</sub>, C-22), 22.0 (C, C-25), 21.7 (CH, C-2), 20.9 (CH<sub>3</sub>, C-21), 20.7 (CH<sub>3</sub>, C-27), 20.6 (CH, C-1), 17.7 (CH<sub>3</sub>, C-20), 7.9 (CH<sub>3</sub>, C-18)。以上数据与文献<sup>[7]</sup>对照,基本一致,确定化合物结构为 citreohybridonol。

**化合物 4** 白色晶体, EI-MS: 428 [M]<sup>+</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 5.27 (2H, m, H-22, H-23), 4.88 (1H, brd, J = 6.6 Hz, H-7α), 4.31 (1H, m, H-3α), 3.37 (1H, d, J = 2.5 Hz, H-6β), 2.55 (1H, dd, J = 13.2, 11.7 Hz, H-4β), 1.28 (3H, s, H<sub>3</sub>-19), 1.07 (3H, d, J = 6.6 Hz, H<sub>3</sub>-21), 0.96 (3H, s, H<sub>3</sub>-18), 0.94 (3H, d, J = 6.9 Hz, H<sub>3</sub>-28), 0.85 (6H, d, J = 6, 8 Hz, H<sub>3</sub>-26, H<sub>3</sub>-27); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 151.6 (C-14), 135.2 (C-22), 132.4 (C-23), 126.8 (C-8), 68.7 (C-3), 64.9 (C-5), 63.6 (C-7), 60.3 (C-6), 55.4 (C-17), 43.7 (C-13), 42.9 (C-24), 40.5 (C-20), 39.3 (C-9), 39.2 (C-4), 37.1 (C-12), 34.9 (C-10), 33.1 (C-25), 33.0 (C-1), 31.2 (C-2), 28.0 (C-16), 25.9 (C-15), 21.1 (C-21), 20.0 (C-27), 19.7 (C-26), 19.3 (C-11), 17.9 (C-28), 17.7 (C-28), 16.9 (C-19)。以上数

据与文献<sup>[8]</sup>对照,基本一致,确定化合物结构为 5α, 6α-Epoxy-(22*E*, 24*R*)-ergosta-8(14), 22-diene--3β, 7β-diol。

**化合物 5** 无色油状物, EI-MS: 354 [M]<sup>+</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 5.36 (4H, m, H-9, 10, 12, 13), 4.20 (1H, dd, J = 11.5, 4.5 Hz, Ha-19), 4.16 (1H, dd, J = 11.5, 6 Hz, Hb-19), 3.93 (1H, m, H-20), 3.70 (1H, dd, J = 11.5, 4.5 Hz, H-21a), 3.60 (1H, dd, J = 11.5, 4.5 Hz, H-21b), 2.77 (2H, t, J = 6.5 Hz, H<sub>2</sub>-11), 2.35 (2H, t, J = 7.5 Hz, H<sub>2</sub>-2), 2.05 (4H, m, H<sub>2</sub>-8, H<sub>2</sub>-14), 1.64 (2H, m, H<sub>2</sub>-3), 1.25 ~ 1.40 (14H, m), 0.89 (3H, t, J = 6.5 Hz, H<sub>3</sub>-18); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.3 (C = O, C-1), 130.2 (CH, C-9), 130.0 (CH, C-13), 128.1 (CH, C-10), 127.9 (CH, C-9), 70.3 (CH, C-20), 65.2 (CH<sub>2</sub>, C-19), 63.3 (CH, C-21), 34.1 (CH<sub>2</sub>, C-2), 31.5 (CH<sub>2</sub>, C-16), 29.6 (CH<sub>2</sub>, C-7), 29.3 (CH<sub>2</sub>, C-6), 29.1 (CH<sub>2</sub>, C-17), 29.1 (CH<sub>2</sub>, C-5), 29.1 (CH<sub>2</sub>, C-4), 27.2 (CH<sub>2</sub>, C-8), 27.2 (CH<sub>2</sub>, C-14), 25.6 (CH<sub>2</sub>, C-11), 24.9 (CH<sub>2</sub>, C-3), 22.6 (CH<sub>2</sub>, C-17), 14.1 (CH<sub>3</sub>, C-18)。以上数据与文献<sup>[9]</sup>对照,基本一致,确定化合物结构为 1-Linoleoylglycerol。

**化合物 6** 白色固体, EI-MS: 360 [M]<sup>+</sup>; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) δ<sub>H</sub>: 5.91 (1H, d, J = 1.6, H-2'), 4.77 (1H, brs, Ha-12), 4.52 (2H, brs, Hb-12 and H-4'), 4.29 (1H, d, J = 17.7 Hz, H-7'a), 4.21 (1H, d, J = 17.7 Hz, H-7'b), 3.67 (1H, d, J = 2.9 Hz, H-5'), 2.33 (1H, ddd, J = 12.6, 3.9, 2.5 Hz, H-7e), 2.31 (1H, d, J = 14.0 Hz, H-11a), 1.92 (1H, td, J = 12.6, 3.9 Hz, H-7a), 1.81 (1H, dd, J = 14.0, 11.1 Hz, Hb-11), 1.76 (1H, dt, J = 12.6, 3.9 Hz, H-1e), 1.75 (1H, d, J = 11.1 Hz, H-9), 1.72 (1H, m, H-6e), 1.60 (1H, qt, J = 13.6, 3.4 Hz, H-2a), 1.49 (1H, dq, J = 13.6, 3.4 Hz, H-2e), 1.38 (1H, dm, J = 13.6 Hz, H-3e), 1.30 (1H, qd, J = 12.6, 3.9 Hz, H-6a), 1.21 (1H, td, J = 13.6, 4.6 Hz, H-3a), 1.18 (1H, td, J = 13.6, 3.4 Hz, H-1a), 1.12 (1H, dd, J = 12.6, 2.5 Hz, H-5), 0.70 (3H, s, H<sub>3</sub>-13), 0.79 (3H, s, H<sub>3</sub>-14), 0.85 (3H, s, H<sub>3</sub>-15); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD) δ<sub>C</sub>: 195.4 (C = O, C-1'), 161.2 (C, C-3'), 150.5 (C, C-8), 120.2 (CH, C-2'), 107.4 (CH<sub>2</sub>, C-12), 64.3 (CH, C-4'), 64.0 (CH<sub>2</sub>,

C-7'), 62.2 (CH, C-5'), 59.5 (C, C-6'), 55.7 (CH, C-5), 51.5 (CH, C-9), 43.3 (CH<sub>2</sub>, C-3), 40.7 (C, C-10), 40.0 (CH<sub>2</sub>, C-1), 39.3 (CH<sub>2</sub>, C-7), 34.5 (C, C-4), 34.1 (CH<sub>3</sub>, C-13), 25.6 (CH<sub>2</sub>, C-6), 22.2 (CH<sub>3</sub>, C-14), 22.0 (CH<sub>2</sub>, C-11), 20.4 (CH<sub>2</sub>, C-2), 15.0 (CH<sub>3</sub>, C-15)。以上数据与文献<sup>[10]</sup>对照,基本一致,确定化合物结构为 Macrophorin。

**化合物 7** 无定型粉末, EI-MS: 418 [M]<sup>+</sup>; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) δ<sub>H</sub>: 6.12 (2H, brs, H<sub>2</sub>-2'), 4.90 (1H, brs, H-12a), 4.79 (1H, brs, H-12b), 4.41 (2H, brs, H-7'), 3.96 (1H, s, H-5'), 3.05 (1H, d, J = 17.2 Hz, H-8'e), 2.91 (1H, d, J = 17.2 Hz, H-8'), 2.36 (1H, ddd, J = 12.9, 3.9, 2.5 Hz, H-7b), 2.20 (1H, dd, J = 14.8, 4.6 Hz, H-11a), 2.11 (1H, td, J = 12.9, 4.8 Hz, H-7a), 1.97 (1H, m, H-11b), 1.82 (1H, m, H-9), 1.73 (1H, brd, J = 12.9 Hz, H-6b), 1.72 (1H, brd, J = 13.7 Hz, H-1b), 1.58 (1H, qt, J = 13.7, 3.4 Hz, H-2a), 1.45 (1H, qt, J = 13.7, 3.4 Hz, H-2b), 1.36 (1H, td, J = 13.7, 3.4 Hz, H-3b), 1.31 (1H, qd, J = 12.9, 3.9 Hz, H-6a), 1.17 (1H, dd, J = 12.5, 2.5 Hz, H-5), 1.14 (1H, td, J = 13.7, 3.4 Hz, H-3a), 1.12 (1H, td, J = 13.7, 3.4 Hz, H-1a), 0.84 (3H, s, H<sub>3</sub>-13), 0.78 (3H, s, H<sub>3</sub>-14), 0.70 (3H, s, H<sub>3</sub>-15); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD) δ<sub>C</sub>: 192.3 (C = O, C-1'), 167.8 (C = O, C-9'), 164.5 (C, C-3'), 150.1 (C, C-8), 120.4 (CH<sub>2</sub>, C-2'), 108.0 (CH<sub>2</sub>, C-12), 85.2 (C, C-6'), 74.7 (CH, C-5'), 71.8 (C, C-4'), 60.7 (CH<sub>2</sub>, C-7'), 56.2 (CH, C-5), 50.2 (C, C-9), 43.3 (CH<sub>2</sub>, C-8'), 42.8 (CH<sub>2</sub>, C-3), 41.0 (C, C-10), 39.3 (CH<sub>2</sub>, C-1), 38.8 (CH<sub>2</sub>, C-7), 34.2 (C, C-4), 33.8 (CH<sub>3</sub>, C-13), 25.2 (CH<sub>2</sub>, C-6), 22.2 (CH<sub>2</sub>, C-11), 22.0 (CH<sub>3</sub>, C-14), 19.9 (CH<sub>2</sub>, C-2), 15.1 (CH<sub>3</sub>, C-15)。以上数据与文献<sup>[11]</sup>对照,基本一致,确定化合物结构为 purpurogemutantin。

**化合物 8** 黄色粉末, EI-MS: 218 [M]<sup>+</sup>; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) δ<sub>H</sub>: 6.37 (1H, s, H-4), 6.31 (2H, s, H-5, 7), 4.22 (1H, m, H-2'), 4.02 (1H, m, H-4'), 2.62 (1H, dd, J = 14.4, 4.9 Hz, Hb-1'), 2.55 (1H, dd, J = 14.4, 8. Hz, Ha-1'), 1.58 (1H, ddd, J = 14.2, 8.2, 7.2 Hz, Ha-3'), 1.33 (1H, ddd, J = 14.2, 4.9, 3.9 Hz, Hb-3'), 1.19 (3H, d, J = 6.3 Hz, CH<sub>3</sub>-5'); <sup>13</sup>C NMR (125 MHz,

CD<sub>3</sub>OD) δ<sub>C</sub>: 167.9 (C = O, C-1), 167.3 (C, C-6), 164.9 (C, C-8), 156.2 (C, C-3), 141.3 (C, C-10), 107.2 (CH, C-4), 103.7 (CH, C-5), 102.7 (CH, C-7), 99.9 (C, C-9), 67.1 (CH, C-2'), 65.3 (CH, C-4'), 47.0 (CH<sub>2</sub>, C-3'), 43.0 (CH<sub>2</sub>, C-1'), 24.4 (CH<sub>3</sub>, C-5')。以上数据与文献<sup>[12]</sup>对照,基本一致,确定化合物结构为 3-(2S,4S-dihydroxypentyl)-6,8-dihydroxyisocoumarin。

**化合物 9** 无色针状结晶, EI-MS: 280 [M]<sup>+</sup>; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) δ<sub>H</sub>: 6.56 (1H, d, J = 2.0 Hz, H-6), 6.53 (1H, d, J = 2.0 Hz, H-8), 5.96 (1H, s, H-2), 4.10 (1H, m, H-2'), 2.62 (1H, dd, J = 14.4, 5.1 Hz, H-1'), 2.62 (3H, s, H<sub>3</sub>-11), 2.55 (1H, dd, J = 14.4, 7.9 Hz, H-1'), 1.18 (1H, d, J = 6.2 Hz, H-3'); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD) δ<sub>C</sub>: 182.11 (C, C-4), 167.2 (C, C-5), 163.1 (C, C-9), 161.6 (C, C-2), 143.8 (C, C-7), 118.1 (CH, C-3), 118.1 (C, C-3), 116.0 (C, C-10), 112.6 (CH, C-6), 101.8 (CH, C-8), 66.5 (CH, C-2'), 44.3 (CH<sub>2</sub>, C-1'), 23.6 (CH<sub>3</sub>, C-11), 23.2 (CH<sub>3</sub>, C-3')。以上数据与文献<sup>[13]</sup>对照,基本一致,确定化合物结构为 5-hydroxy-7-(2'-hydroxypropyl)-2-methyl-chromone。

#### 参考文献

- 1 Du L (杜林). Secondary Metabolites of Five Filamentous Fungal Strains; Structures and Bioactivities. Qing dao: Ocean University of China (中国海洋大学), PhD. 2009.
- 2 Wang JF (王俊峰). Studies oil the active secondary metabolites of three marine fungal strains and the effects of alkaline stress on fungal secondary metabolites. Qingdao; Ocean University of China (中国海洋大学), PhD. 2012.
- 3 Blunt JW, Copp BR, Hu WP, *et al.* Marine natural products. *Nat Prod Reports*, 2009, 26: 170-244.
- 4 Lin XP, Zhou XF, Wang FZ, *et al.* A new cytotoxic sesquiterpene quinone produced by *Penicillium* sp. F00120 isolated from a deep sea sediment sample. *Marine Drugs*, 2012, 10: 106-115.
- 5 Li JT, Chen QQ, Zeng Y, *et al.* A new phenol compound from endophytic *Phomopsis* sp. DC01. *Nat Prod Res*, 2012, 26: 2008-2012.
- 6 Hiroko S, Yutaka S, Yoshihiro M, *et al.* A new mevalonolactone glucoside derivative from the bark of *Prunus buergeriana*. *Chem Pharm Bull*, 1989, 37: 829-830.