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红树来源真菌 *Daldinia eschscholtzii* HJ004 发酵产物中三个新的次级代谢产物

王 斌[a,b] 曾尾女[a,b] 李杲钰[a,b] 肖 媚[a,b] 韦方芳[a,b]
罗由萍[a,b] 钮智刚[a,b] 黄国雷[a,b] 郑彩娟*[,a,b]
([a]海南师范大学化学与化工学院 热带药用资源化学教育部重点实验室 海口 571158)
([b]海南师范大学化学与化工学院 海南省热带药用植物化学重点实验室 海口 571158)

摘要 从红树来源真菌 *Daldinia eschscholtzii* HJ004 中分离得到 3 个新化合物以及 8 个已知化合物. 通过高分辨质谱、一维和二维核磁共振波谱以及 X 射线单晶衍射数据确定了 8-乙基-7-羟基-5-羧基-2,3-二甲基色酮(**1**)的结构. 通过电子圆二色谱(ECD)量子化学计算以及圆二色谱(CD)数据与文献进行比较, 确定了 felinone C (**2**)和螺旋霉素 G (**3**)的绝对构型. 利用总抗氧化能力检测试剂盒(ABTS 快速法)测试了所得 11 个化合物的自由基清除能力, 其中 4 个化合物表现出显著的抗氧化活性, IC_{50} 值的范围为 5.57～195.03 μmol/L, 强于阳性对照水溶性维生素 E (trolox)的抗氧化活性(IC_{50}=292.12 μmol/L), 具有开发为抗氧剂的潜力.

关键词 *Daldinia eschscholtzii*; 色原酮; 内酯类化合物; 抗氧化活性

Three New Secondary Metabolites from the Mangrove-Derived Fungus *Daldinia eschscholtzii* HJ004

Wang, Bin[a,b] Zeng, Weinv[a,b] Li, Gaoyu[a,b] Xiao, Mei[a,b] Wei, Fangfang[a,b]
Luo, Youping[a,b] Niu, Zhigang[a,b] Huang, Guolei[a,b] Zheng, Caijuan*[,a,b]
([a] *Key Laboratory of Tropical Medicinal Resource Chemistry of Ministry of Education, College of Chemistry and Chemical Engineering, Hainan Normal University, Haikou 571158*)
([b] *Key Laboratory of Tropical Medicinal Plant Chemistry of Hainan Province, College of Chemistry and Chemical Engineering, Hainan Normal University, Haikou 571158*)

Abstract Three new compounds, together with eight known compounds, were isolated from the mangrove-derived fungus *Daldinia eschscholtzii* HJ004. The structure of 8-ethyl-7-hydroxy-5-carboxyl-2,3-dimethylchromone (**1**) was extensively elucidated and characterized by HRESIMS, 1D and 2D NMR, and single-crystal X-ray crystallography. The absolute configurations of felinone C (**2**) and helicascolide G (**3**) were determined by using electronic circular dichroism (ECD) method or comparing circular dichroism (CD) data with the literature. The radical scavenging capabilities of the 11 compounds obtained were tested by total antioxidant capacity assay kit with a rapid ABTS method. Among them 4 compounds exhibited stronger antioxidant activity with IC_{50} values range from 5.57 μmol/L to 195.03 μmol/L, than the positive control trolox (IC_{50}=292.12 μmol/L). These results indicate that chromones have the potential values of developing antioxidants.

Keywords *Daldinia eschscholtzii*; chromone; lactone; antioxidant activity

1 Introduction

The mangrove ecosystem is an important biodiversity hotspot for prospecting new bioactive and chemical scaffolds, including those with potential medicinal application.[1-2] Moreover mangrove-derived fungi have repre-

* Corresponding author. E-mail: caijuan2002@163.com
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sented a significant and potential source in the search of structurally diverse and biologically active natural products.[2-5] Especially, the genus of *Daldinia* has been found to produce various secondary metabolites, such as the immunosuppressive dalesconols A and B,[6] antifibrotic (−)-galewone,[7] antioxidant daldinone B,[8] antibacterial dalesindoloids A and B,[9] and cytotoxic concentricolide.[10] In our ongoing research on mangrove-derived fungi,[11-14] some new bioactive compounds from the mangrove-derived fungus *Daldinia eschscholtzii* HJ004 have been found.[13-14] In order to further explore bioactive compounds from the fungus *D. eschscholtzii* HJ004, we changed culture media and further conducted a chemical investigation of this strain cultured, which led to the characterization of three new compounds, chromone 8-ethyl-7-hydroxy-5-carboxyl-2,3-dimethylchromone (**1**), *O*-containing heterocyclic compound felinone C (**2**) and lactone helicascolide G (**3**), together with eight known compounds (**4**～**11**) (Figure 1). The structure of **1** was determined by its NMR spectral data and single-crystal X-ray diffraction analysis. The absolute configuration of **2** was determined by experimental and calculated electronic circular dichroism (ECD) method. The absolute configuration of **3** was established by comparing its circular dichroism (CD) data with the literature. Herein, we report the isolation, structure elucidation, and bioactivities of these compounds.

2 Results and discussion

2.1 Structure elucidation

Compound **1** was obtained as yellowish crystals, the molecular formula of **1** was established as $C_{14}H_{14}O_5$ by its HRESIMS data with eight degrees of unsaturation. The ^{1}H NMR data (Table 1) displayed the presence of one aromatic proton at δ_H 6.92 (s), one methylene signal at δ_H 2.75 (q, J=7.2 Hz) and three methyl signals at δ_H 2.41 (s), 1.90 (s) and 1.11 (t, J=7.2 Hz). The ^{13}C NMR data together with the HSQC spectrum indicated the presence of three methyl groups (δ_C 9.6, 13.3 and 18.1), one methylene group (δ_C 15.9), six aromatic carbons (δ_C 111.0, 113.0, 117.5, 154.8, 154.8 and 159.0), two olefinic carbons (δ_C 114.9 and 161.3) and two carbonyl carbons (δ_C 169.6 and 175.8). The above ^{1}H NMR and ^{13}C NMR data (Table 1) suggested that compound **1** was a chromone derivative.[14] The COSY correlation displayed one coupling system CH_2(12)-CH_3(13). The whole structure of **1** was deduced by HMBC correlations from H-9 to C-2 and C-3, from H-10 to C-2 and C-4, from H-6 to C-4a, C-8 and C-11, from H-12 to C-7 and C-8a, from H-13 to C-8 (Figure 2). These HMBC correlations established the positions of two methyl groups connected at C-2 and C-3, one carboxyl group at C-5, one hydroxyl group at C-7, and one ethyl group at C-8. Thus, compound **1** was named as 8-ethyl-7-hydroxy-5-carboxyl- 2,3-dimethylchromone.

Furthermore, the structure of **1** was established by single-crystal X-ray diffraction analysis (Figure 3). Crystallographic data for the structure of **1** have been deposited with the Cambridge Crystallographic Data Centre (deposition no. CCDC 2128434).

Compound **2** was obtained as a yellowish oil, and the molecular formula was determined as $C_{12}H_{14}O_3$ (six degrees of unsaturation) by HRESIMS data. The ^{1}H NMR data (Table 1) of **2** showed the presence of three aromatic

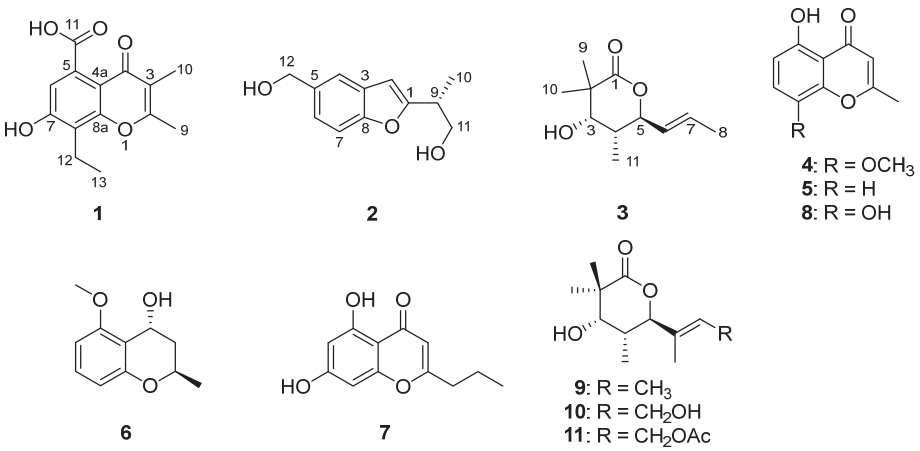

Figure 1 Structures of compounds **1**～**11**

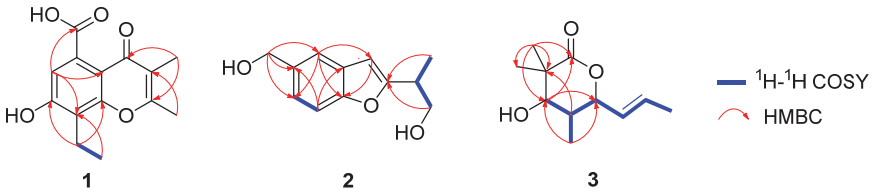

Figure 2 ^{1}H-^{1}H COSY correlations and key HMBC correlations of compounds **1**～**3**

Table 1 NMR data for compounds **1**, **2** and **3** (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz)

No.	**1** (in DMSO-d_6)		**2** (in $CDCl_3$)		**3** (in $CDCl_3$)	
	δ_H (J in Hz)	δ_C (type)	δ_H (J in Hz)	δ_C (type)	δ_H (J in Hz)	δ_C (type)
1				161.3 (C)		176.9 (C)
2		161.3 (C)	6.48 (s)	102.5 (CH)		44.2 (C)
3		114.9 (C)		128.9 (C)	3.51 (d,1.6)	77.3 (CH)
4		175.8 (C)	7.50 (s)	119.4 (CH)	2.12 (ddq, 1.6, 6.8, 10.8)	34.4 (CH)
4a		111.0 (C)				
5		154.8 (C)		135.6 (C)	4.68 (dd, 8.4, 10.8)	82.8 (CH)
6	6.92 (s)	113.0 (CH)	7.23 (d,8.4)	123.2 (CH)	5.44 (ddd, 1.6, 8.4, 15.2)	128.6 (CH)
7		159.0 (C)	7.40 (d,8.4)	111.1 (CH)	5.79 (dq, 6.8, 15.2)	131.9 (CH)
8		117.5 (C)		154.5 (C)	1.73 (dd, 1.6, 6.8)	17.8 (CH_3)
8a		154.8 (C)				
9	2.41 (s)	18.1 (CH_3)	3.13～3.21 (m)	36.8 (CH)	1.27 (s)	26.6 (CH_3)
10	1.90 (s)	9.6 (CH_3)	1.37 (d, 6.8)	15.2 (CH_3)	1.33 (s)	22.7 (CH_3)
11		169.6 (C)	3.80～3.89 (m)	66.4 (CH_2)	1.00 (d, 6.8)	14.0 (CH_3)
12	2.75 (q, 7.2)	15.9 (CH_2)	4.74 (s)	65.8 (CH_2)		
13	1.11 (t,7.2)	13.3 (CH_3)				

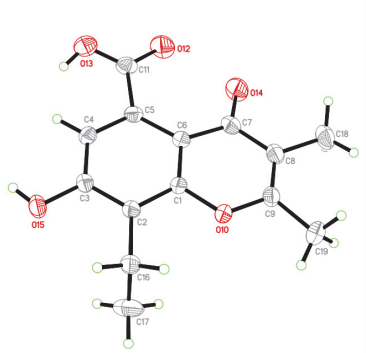

Figure 3 X-ray crystal structure of compound **1**

proton signals at δ_H 7.50 (s), 7.40 (d, J=8.4 Hz) and 7.23 (d, J=8.4 Hz), indicating the presence of one 1,2,4-trisubstituted benzene. One olefinic proton signal at δ_H 6.48 (s), and two oxygenated methylene signals at δ_H 4.74 were also observed in the ^{1}H NMR spectrum. The ^{13}C NMR and DEPT-135 data revealed the presences of one methyl group (δ_C 15.2), one methine group (δ_C 36.8), two oxygenated methylene groups (δ_C 66.4 and 65.8), six aromatic carbons (δ_C 154.5, 135.6, 128.9, 123.2, 119.4 and 111.1) and two olefinic carbons (δ_C 161.3 and 102.5). On the basis of these NMR data, the structure of **2** was similar to felinone B.[15] The major differences were the appearance of one oxygenated methylene signal [δ_H 3.80～3.88 (m), δ_C 66.4 (C-11)] and one methine group [δ_H 3.15～3.19 (m), δ_C 66.4 (C-9)], and the absence of one methyl group [δ_H 1.61 (s), δ_C 27.6 (CH_3)] at C-9 for **2** in the ^{1}H NMR and ^{13}C NMR spectra. The COSY correlations displayed two coupling systems CH(6)-CH(7) and CH_3(10)-CH(9)-CH_2(11). Meanwhile, the HMBC correlations from H-12 to C-4 and C-6, from H-6 to C-4 and C-8, from H-7 to C-5 and C-3, from H-4 to C-2, C-6 and C-8, and from H-10 and H-11 to C-1, suggesting that one oxygenated methylene group connected at C-5, and C-9 connected at C-1, respectively (Figure 2). Therefore, the planar structure of **2** was established as shown in Figure 1.

To determine the absolute configuration of **2**, the ECD calculation method was applied. The configurations (9*R*)-**2** and (9*S*)-**2** were calculated using time-dependent density functional theory (TDDFT) at PBE1PBE/6-311 G* level, with the polarized continuum model (PCM) in methanol. A comparison of the experimental ECD spectrum of **2** and the calculated ECD spectra of (9*R*)-**2** and (9*S*)-**2** showed that the experimental ECD spectrum of **2** was consistent with the calculated ECD spectrum of (9*R*)-**2** (Figure 4). Thus, the absolute configuration of **2** was assigned as 9*R*, and named as felinone C.

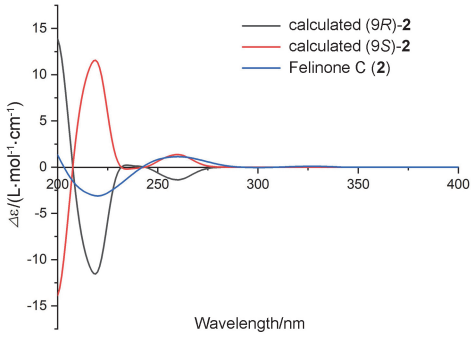

Figure 4 Experimental and calculated ECD spectra of **2**

Compound **3** was isolated as a colorless oil, with the molecular formula of $C_{11}H_{18}O_3$ (three degrees of unsaturation) determined by HRESIMS data. The ^{1}H NMR data of **3** showed the presence of two olefinic proton signals at δ_H 5.79 (dq, J=6.8, 15.2 Hz) and 5.44 (ddd, J=1.6, 8.4, 15.2 Hz), two oxygenated methine proton signals at δ_H 4.68 (dd, J=8.4, 10.8 Hz) and 3.51 (d, J=1.6 Hz), one methine group at δ_H 2.12 (ddq, J=1.6, 6.8, 10.8 Hz), and four methyl groups at δ_H 1.73 (dd, J=1.6, 6.8 Hz), 1.33 (s), 1.27 (s) and 1.00 (d, J=6.8 Hz). These spectroscopic features combined with the ^{13}C NMR data suggested that **3** was closely resembled of helicascolide A (**9**),[16] except for the

absence of one methyl signal at [δ_H 1.60 (s), δ_C 10.3 (CH_3)], and the presence of an olefinic proton signal at δ_H 5.79 (dd, J=6.4, 15.2 Hz) for C-6 in **3**. The COSY correlations displayed one coupling system CH(3)-CH(4)-CH(5)-CH(6)-CH(7)-CH_3(8). Additionally, the HMBC correlations from H-9 and H-10 to C-1, C-2 and C-3, from H-3 to C-1 and C-5, from H-11 to C-3 and C-5, indicating that two methyl groups were attached to C-2 and a methyl group connected at C-4, respectively (Figure 2). Hence, the planar structure of **3** was established.

The relative configuration of the lactone moiety in **3** was deduced from the coupling constants in ^{1}H NMR and 1D NOE spectra. The large coupling constant $J_{H4\text{-}H5}$=10.8 Hz indicated a *trans* orientation, and the small coupling constant $J_{H3\text{-}H4}$=1.6 Hz denoted the *cis* configuration. In the selective 1D NOE experiments, the irradiation of H-4 resulted in the enhancement of H-3 and H-6, which required that they should be on the same face of the molecule. The irradiation of H-5 resulted in the enhancement of H_3-11, indicating that H-5 should be placed on the opposite side of H-3 and H-4 (Figure 5). The positive cotton effect at 218 nm suggested that the dihedral angle C(3)-C(2)-C(1)-O is negative and that the substituents at C-4 and C-5 are in pseudoequatorial positions (Figure 6), by comparison with data for lactones described in the literature.[14] Thus, the structure of **3** was defined and named as helicascolide G.

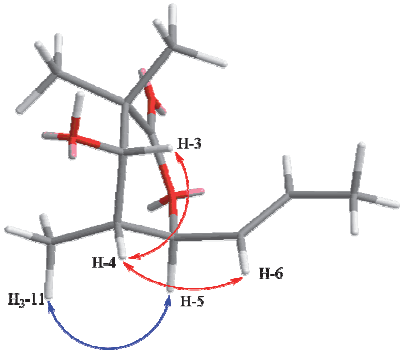

Figure 5 Key NOE correlations for compound **3**

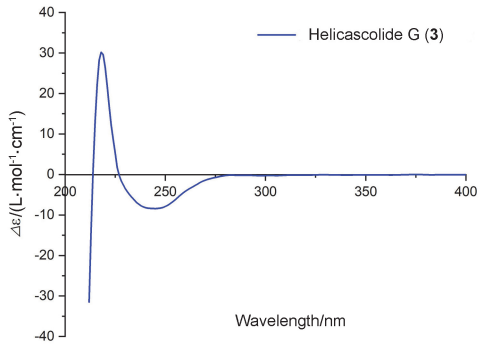

Figure 6 CD spectrum of **3**

The structures of known compounds **4**～**11** were identified by comparison of their spectroscopic data with those in the literature, and their structures were identified as 5-hydroxy-8-methoxy-2-methyl-4*H*-1-benzopyran-4-one (**4**),[17] 5-hydroxy-2-methyl-4*H*-chromen-4-one (**5**),[18] (2*R*,4*S*)-5-methoxy-2-methyl-2*H*-1-benzopyran-4-ol (**6**),[19] 5,7-dihydroxy-2-propylchromone (**7**),[20] 5,8-dihydroxy-2-methylchromone (**8**),[17] helicascolide A (**9**),[16] helicascolides D (**10**) and E (**11**).[14]

2.2 Biological activity

The antioxidant assays of the isolated compounds were carried out for their ABTS radical scavenging capacities. Compounds **1**, **5**, **7** and **8** exhibited potent antioxidant activity with IC_{50} values of 195.03, 20.79, 5.57 and 8.90 μmol/L, respectively, which stronger than the positive control trolox with the IC_{50} value of 292.12 μmol/L. All compounds exhibited no antibacterial activity against four pathogenic bacteria: *Staphylococcus epidermidis*, *S. aureus*, *Escherichia coli* and *Bacillus cereus* at the concentration of 50 μg/mL.

3 Conclusions

In summary, three new compounds, chromone 8-ethyl-7-hydroxy-5-carboxyl-2,3-dimethylchromone (**1**), *O*-containing heterocyclic compound felinone C (**2**) and lactone helicascolide G (**3**), together with eight known compounds (**4**～**11**) were isolated from the mangrove-derived fungus *Daldinia eschscholtzii* HJ004. The structure of **1** was determined by its single-crystal X-ray diffraction. The absolute configuration of **2** was determined by experimental and calculated electronic circular dichroism (ECD) methods. The absolute configuration of **3** was established by comparing its circular dichroism (CD) data with the literature. Compounds **1**, **5**, **7** and **8** showed potent antioxidant activity with IC_{50} values range from 5.57 μmol/L to 195.03 μmol/L, which stronger than the positive control trolox with the IC_{50} value of 292.12 μmol/L. These results indicate that the chromones have the potential values of developing antioxidants.

4 Materials and methods

4.1 General experimental procedures

Melting points were determined on a WRX-4 micro melting point apparatus (Shanghai YiCe Apparatus and Equipment Co., Ltd., Shanghai, China) and uncorrected. Optical rotations were measured on a JASCO P-1020 digital polarimeter (JASCO, Tokyo, Japan). IR spectra were recorded on a Thermo Scientific Nicolet 6700 (using KBr disks) spectrophotometer (Thermo Scientific, Madison, WI, USA). CD spectra were recorded on a Mos-450 spectrometer. HR-ESIMS spectra were obtained on a Bruker Daltonics Apex-Ultra 7.0 T (Bruker Corporation, Billerica, MA, USA). Single-crystal data were measured by an Agilent Gemini Ultra X-ray single crystal diffractometer (Cu Kα radiation). NMR spectra were recorded on a Bruker AV spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). HPLC were used for Agilent 1100 prep-HPLC system with an Agilent C_{18} analytical HPLC column. Se-

phadex LH-20 (Pharmacia Co. Ltd., Sandwich, UK) and silica gel (200～300 and 300～400 mesh, Qingdao Marine Chemical Factory, Qingdao, China) were used for column chromatography (CC). All solvents were purchased from Xilong Chemical Reagent Factory (Guangzhou, China).

4.2 Fungal materials

The fungus HJ004 was isolated from the stem of mangrove *Bruguiera sexangula* var. *rhynchopetala* collected in the South China Sea in August 2012. It was deposited in China General Microbiological Culture Collection Center (CGMCC), with the CGMCC number 17674. The fungus was identified according to its morphological characteristics and by comparison of the internal transcribed spacer (ITS) sequence amplification, using primer pair ITS1 and ITS4 and sequencing of the internal transcribed spacer (ITS) region. The sequence data has been submitted to GenBank, with an accession number MH059553, and the fungal strain was identified as *Daldinia eschscholtzii*.

4.3 Fermentation, extraction and isolation

The fungal strain was cultivated in rice solid-substrate medium (3 g of sea salt and 3 g of glucose in 100 mL of distilled H_2O, and 100 g of rice, in 1 L of Erlenmeyer flasks) at room temperature under static conditions and daylight for 1 month. The fermentation was extracted three times with an equal volume of EtOAc. The combined EtOAc layers were evaporated to dryness under reduced pressure to give an EtOAc extract (67 g), which was subjected to silica gel column chromatography (CC) (petroleum ether, EtOAc, CH_3OH, gradient) to generate seven fractions (Fr.1～Fr.7). Fr.2 was isolated by CC on silica gel eluting with petroleum ether/EtOAc (V∶V=9∶1～7∶3) and then subjected to repeated Sephadex LH-20 CC eluting with mixture of $CHCl_3$/CH_3OH (V∶V=1∶1) to afford three subfractions 2a ～ 2c. Subfraction 2b was further separated by Semi-Preparative HPLC (CH_3OH/H_2O, V∶V=73∶27) to obtain **5** (6 mg). Fr.3 was isolated by column chromatography (CC) on silica gel eluted with petroleum ether/EtOAc (V∶V=9∶1～1∶1) to afford four subfractions 3a～3d. Subfraction 3b was further purified by Semi-Preparative HPLC (CH_3OH/H_2O, V∶V=45∶55) to obtain **4** (4 mg) and **6** (3 mg). Subfraction 3c was further separated by Semi-Preparative HPLC (CH_3OH/H_2O, V∶V=40∶60) to obtain **3** (15 mg) and **9** (36 mg). Subfraction 3d was further separated by Semi-Preparative HPLC (CH_3OH/H_2O, V∶V=45∶55) to obtain **10** (6 mg) and **11** (21 mg). Fr.4 was isolated by CC on silica gel eluted with petroleum ether/EtOAc (V∶V=9∶1～0∶100) to afford four subfractions 4a～4d. Subfraction 4b was further purified by Semi-Preparative HPLC (CH_3OH/H_2O, V∶V=35∶65) to obtain **1** (15 mg) and **2** (9 mg). Subfraction 4c was further separated by Semi-Preparative HPLC (CH_3OH/H_2O, V∶V=30∶70) to obtain **7** (15 mg) and **8** (12 mg), respectively.

8-Ethyl-7-hydroxy-5-carboxyl-2,3-dimethylchromone (**1**): Yellowish crystals. m.p. 163.2 ～ 164.8 ℃; UV (CH_3OH) λ_{max} [log ε/(L•mol^{-1}•cm^{-1})]: 230 (1.18) 270 (0.20) 304 (0.58) nm; ^{1}H NMR and ^{13}C NMR data see Table 1; IR (KBr) ν_{max}: 3562, 3250, 2982, 1685, 1625 cm^{-1}; HRESIMS calcd for $C_{14}H_{15}O_5$ [M+H$^+$] 263.0914, found 263.0911.

Felinone C (**2**): Yellowish oil. $[\alpha]_D^{25}$ +3.4 (c 0.2, CH_3OH); UV (CH_3OH) λ_{max} [log ε/(L•mol^{-1}•cm^{-1})]: 216 (1.63) 249 (1.26) 280 (0.38) 288 (0.39) nm; ECD (c 0.2, CH_3OH) λ_{max} [$\Delta\varepsilon$/(L•mol^{-1}•cm^{-1})]: 219 (−3.1) 260 (1.1) nm; ^{1}H NMR and ^{13}C NMR data see Table 1; IR (KBr) ν_{max}: 3550, 3017, 2981, 1638, 1617 cm^{-1}; HRESIMS calcd for $C_{12}H_{13}O_3$ (M−H$^-$) 205.0870, found 205.0867.

Helicascolide G (**3**): Colorless oil. $[\alpha]_D^{25}$ −38.5 (c 0.2, CH_3OH); UV (CH_3OH) λ_{max} [log ε/(L•mol^{-1}•cm^{-1})]: 223 (2.69) nm; ECD (c 0.2, CH_3OH) λ_{max} [$\Delta\varepsilon$/(L•mol^{-1}•cm^{-1})]: 218 (+30.2), 243 (−8.4) nm; ^{1}H NMR and ^{13}C NMR data see Table 1; IR (KBr) ν_{max}: 3549, 3473, 3414, 3020, 2980, 1717, 1460 cm^{-1}; HRESIMS calcd for $C_{11}H_{18}O_3Na$ [M+Na$^+$] 221.1148, found 221.1144.

4.4 Biological assays

4.4.1 Antioxidant activity

According to the total antioxidant capacity test kit (ABTS method), the ABTS mother liquor was prepared with equal volume of ABTS solution and oxidant solution. The ABTS working solution was stored at room temperature for 12～16 h, and then diluted into the ABTS working solution with phosphate buffer solution (PBS). After subtracting the corresponding PBS blank control from the absorbance of ABTS working solution, the absorbance at 734 nm was about 0.7. 200 μL of the ABTS working solution and 10 μL of sample were added into each detection well, mixed them gently, and incubated them at room temperature for 2～6 min. The absorbance was determined at 734 nm by full wavelength multi-functional microplate reader. PBS was used as blank control and trolox as positive control. The inhibition rate of each sample was calculated according to the following formula:

$$\text{Inhibition rate}(\%)=[(A_{blank}-A_{compound})/A_{blank}]\times 100\%.$$

Finally, the SPSS software was used to calculate the IC_{50} value.[21-22] Trolox was used as the positive control.

4.4.2 Antibacterial activity

Antibacterial activity was determined against four pathogenic bacteria, *Staphylococcus epidermidis* (ATCC 12228), *S. aureus* (ATCC 25923), *Escherichia coli* (ATCC 25922) and *Bacillus cereus* (ATCC 11778) by the microplate assay method.[23] Ciprofloxacin was used as the positive control.

Supporting Information NMR and MS spectra for new compounds **1**～**3**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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(Zhao, C.)

