Bioactive α -pyrone meroterpenoids from mangrove endophytic fungus *Penicillium* sp.

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Five α -pyrone meroterpenoids, including one new 3-epiarigsugacin E (**1**) and four known compounds, arisugacin D (**2**), arisugacin B (**3**), territrem C (**4**) and terreulactone C (**5**) were obtained from marine fungus *Penicillium* sp. SK5GW1L. Their structures were identified by MS and NMR experiments, and the absolute configuration of compound **1** was further confirmed by low temperature (150 K) single crystal X-ray diffraction with Cu K α radiation. Compounds **3**, **4** and **5** showed strong inhibitory activities against acetylcholinesterase (AChE) with IC₅₀ values of 3.03 μ M, 0.23 μ M and 0.028 μ M, respectively.

Support Information

Table S1 ^1H NMR (500 MHz), ^{13}C NMR (125M), and 2D- NMR data for compound **1** (ppm from TMS, J = Hz, in CDCl_3).

Table S2. The single crystal parameters of compound **1**

Figure S1. The single crystal structure of compound **1**

Figure S2. ^1H and ^{13}C NMR, HSQC, and HMBC data for compound **1**

Figure S3. UV of compound **1**

Figure S4. IR of compound **1**

Figure S5. ESIMS of compound **1**

Figure S6. HRESIMS of compound **1**

The single crystal cif file of compound **1**

Table S1 ^1H NMR (500 MHz), ^{13}C NMR (125M), and 2D- NMR data for compound **1** (ppm from TMS, $J = \text{Hz}$, in CDCl_3).

No.	δ_{C}	δ_{H}	^1H - ^1H COSY	HMBC(H $\rightarrow$ C)
1	30.9	1.67-1.65, m 1.45, dd (8.5, 2.3)		2, 10, 19, 3, 5
2	27.4	1.79-1.76, m 1.68-1.65, m	H-3	1, 10, 4, 3
3	73.8	3.88, dd (11.0, 5.7)	H-2	17, 18
4	43.9			
5	78.1			
6	25.3	1.91-1.87, m 1.71-1.69, m	H-7	7, 5, 8
7	33.9	2.18-2.14, m 1.89-1.86, m	H-6	20, 6, 9, 8
8	80.2			
9	43.1	2.46, dd (13.1, 4.7)	H-11	20, 11, 1, 10, 8
10	40.6			
11	17.4	2.39, dd (16.7, 4.7) 2.21-2.24, m	H-9	9, 8, 12, 13
12	98.8			
13	163.7			
14	97.0	6.24, s		12, 1', 15, 13
15	158.4			
16	164.8			
1'	124.2			
2'	127.1	7.73, d (8.8)	H-3'	15, 4', 6'
3'	114.3	6.93, d (8.8)	H-2'	1', 4', 2'
4'	158.4			
5'	114.3	6.93, d (8.8)	H-6'	1', 4', 6'
6'	127.1	7.73, d (8.8)	H-5'	15, 2', 4'
17	17.6	0.96, s		18, 4, 3, 5
18	22.8	1.09, s		17, 4, 3, 5
19	18.4	1.06, s		1, 10, 9, 5
4'-OCH ₃	55.6	3.86, s		4'
20	21.2	1.28, s		8, 9, 7, 10, 6

Table S2. The single crystal parameters of compound **1**

crystallographic data of compound 1			
parameter	parameter values	parameter	parameter values
Empirical formula	C ₂₇ H ₃₄ O ₆	Reflections	15932/4078[R(int)=0.02
Formula weight	454.54	collected/unique	48]
Temperature	150(2) K		
Wavelength	1.54178 Å	Absorption correction	Semi-empirical from
Crystal system, space group	Orthorhombic, P 21 21 21		Equivalents
Unit cell dimensions		Max./min.transmission	0.8726 / 0.7470
a	10.70160(10) Å	Refinement method	Full-matrix
b	10.75190(10) Å, $\alpha=90^\circ$		least-squares on F ²
c	20.1484(2) Å, $\beta=90^\circ$	Data/restraints/parameters	4078 / 0 / 305
Volume	2318.33(4) Å ³	Goodness-of-fit on F ²	1.093
Z, calculated density	4, 1.302 mg/m ³	Final R indices	R1=0.0297WR2=0.0742
Absorption coefficient	0.737 mm ⁻¹	[I>2sigma (I)]	
F (000)	976	R indices (all data)	R1=0.0320 R2=0.0765
Crystal size	0.40×0.32×0.19 mm	Absolute structure parameter	-0.13 (13)
Theta range for data collection	4.39-66.91°		
Limiting indices	-12≤h≤12, -12≤k≤12, -23≤l≤22	Largest diff. peak and hole	0.133 and -0.196 e. Å ⁻³
completeness to theta=62.77	99.3%		

Figure S1. The single crystal structure of compound **1**

Figure S2. ^1H and ^{13}C NMR, COSY, HSQC, HMBC and NOE data for compound **1**

^1H -NMR

^{13}C NMR

^1H - ^1H COSY

HSQC

HMBC

NOE

Figure S3. UV of compound **1**

Figure S4. IR of compound **1**

Figure S5. ESIMS of compound **1**

Figure S6. HRESIMS of compound **1**

D:\Data\2014\05\Dingbo\H-19
LTQ Orbitrap Elite

5/13/2014 7:27:48 PM

H-19 #12-16 RT: 0.08-0.11 AV: 5 NL: 7.41E5
T: FTMS + c ESI Full ms [200.00-1000.00]

SPECTRUM - simulation :

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
455.24319	455.24282	0.82	10.5	C27 H35 O6

Limits:

- (1) Charge: 1
- (2) Nitrogen-Rule: Do not use
- (3) Mass tolerance: 10.00 ppm
- (4) Elements in use: ^{12}C (0~30), ^1H (0~60), ^{16}O (0~15);

The single crystal cif file of compound **1**

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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

;

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O5 C16 1.3867(16) . ?

O2 C5 1.4532(16) . ?

O2 H2 0.8200 . ?

O3 C13 1.3412(18) . ?

O3 C8 1.4862(16) . ?

O4 C16 1.2267(18) . ?

O1 C3 1.4326(17) . ?

O1 H1 0.8200 . ?

O6 C20 1.3651(18) . ?

O6 C26 1.430(2) . ?

C11 C12 1.5015(19) . ?

C11 C9 1.5339(19) . ?

C11 H11A 0.9700 . ?

C11 H11B 0.9700 . ?

C12 C13 1.369(2) . ?

C12 C16 1.421(2) . ?

C13 C14 1.425(2) . ?

C10 C1 1.5412(19) . ?

C10 C25 1.5433(18) . ?

C10 C9 1.5584(18) . ?

C10 C5 1.5722(19) . ?

C6 C5 1.534(2) . ?

C6 C7 1.5350(19) . ?
C6 H6A 0.9700 . ?
C6 H6B 0.9700 . ?
C7 C8 1.512(2) . ?
C7 H7A 0.9700 . ?
C7 H7B 0.9700 . ?
C5 C4 1.5715(19) . ?
C18 C19 1.383(2) . ?
C18 C17 1.392(2) . ?
C18 H18 0.9300 . ?
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C3 C4 1.545(2) . ?
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C9 C8 1.5384(19) . ?
C9 H9 0.9800 . ?
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C22 C21 1.385(2) . ?
C22 C17 1.397(2) . ?
C22 H22 0.9300 . ?
C8 C32 1.530(2) . ?
C2 H2A 0.9700 . ?
C2 H2B 0.9700 . ?
C25 H25A 0.9600 . ?
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C25 H25C 0.9600 . ?
C19 H19 0.9300 . ?
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C23 H23A 0.9600 . ?
C23 H23B 0.9600 . ?
C23 H23C 0.9600 . ?
C24 C4 1.543(2) . ?
C24 H24A 0.9600 . ?
C24 H24B 0.9600 . ?
C24 H24C 0.9600 . ?
C21 H21 0.9300 . ?
C32 H32A 0.9600 . ?
C32 H32B 0.9600 . ?

C32 H32C 0.9600 . ?
C26 H26A 0.9600 . ?
C26 H26B 0.9600 . ?
C26 H26C 0.9600 . ?

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C13 O3 C8 115.73(11) . . ?
C3 O1 H1 109.5 . . ?
C20 O6 C26 117.57(14) . . ?
C12 C11 C9 109.93(12) . . ?
C12 C11 H11A 109.7 . . ?
C9 C11 H11A 109.7 . . ?
C12 C11 H11B 109.7 . . ?
C9 C11 H11B 109.7 . . ?
H11A C11 H11B 108.2 . . ?
C13 C12 C16 118.42(13) . . ?
C13 C12 C11 122.59(13) . . ?
C16 C12 C11 118.98(13) . . ?
O3 C13 C12 123.27(12) . . ?
O3 C13 C14 115.67(13) . . ?
C12 C13 C14 121.06(13) . . ?
O4 C16 O5 115.96(13) . . ?
O4 C16 C12 125.57(13) . . ?
O5 C16 C12 118.47(13) . . ?
C1 C10 C25 107.90(12) . . ?
C1 C10 C9 108.85(11) . . ?
C25 C10 C9 110.50(11) . . ?
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C9 C10 C5 107.53(11) . . ?
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C7 C6 H6A 109.3 . . ?
C5 C6 H6B 109.3 . . ?
C7 C6 H6B 109.3 . . ?

H6A C6 H6B 108.0 . . ?
C8 C7 C6 112.97(12) . . ?
C8 C7 H7A 109.0 . . ?
C6 C7 H7A 109.0 . . ?
C8 C7 H7B 109.0 . . ?
C6 C7 H7B 109.0 . . ?
H7A C7 H7B 107.8 . . ?
O2 C5 C6 107.90(11) . . ?
O2 C5 C4 106.84(11) . . ?
C6 C5 C4 113.94(12) . . ?
O2 C5 C10 103.37(10) . . ?
C6 C5 C10 109.85(11) . . ?
C4 C5 C10 114.16(11) . . ?
C19 C18 C17 120.90(14) . . ?
C19 C18 H18 119.6 . . ?
C17 C18 H18 119.6 . . ?
O1 C3 C2 110.83(12) . . ?
O1 C3 C4 108.05(12) . . ?
C2 C3 C4 113.67(12) . . ?
O1 C3 H3 108.0 . . ?
C2 C3 H3 108.0 . . ?
C4 C3 H3 108.0 . . ?
C2 C1 C10 112.50(12) . . ?
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C10 C1 H1A 109.1 . . ?
C2 C1 H1B 109.1 . . ?
C10 C1 H1B 109.1 . . ?
H1A C1 H1B 107.8 . . ?
C15 C14 C13 119.29(14) . . ?
C15 C14 H14 120.4 . . ?
C13 C14 H14 120.4 . . ?
C14 C15 O5 120.46(13) . . ?
C14 C15 C17 126.43(14) . . ?
O5 C15 C17 113.10(12) . . ?
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C8 C9 C10 114.06(11) . . ?
C11 C9 H9 105.7 . . ?
C8 C9 H9 105.7 . . ?
C10 C9 H9 105.7 . . ?
O6 C20 C21 125.06(15) . . ?
O6 C20 C19 115.06(15) . . ?
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C21 C22 C17 120.97(15) . . ?

C21 C22 H22 119.5 . . ?
C17 C22 H22 119.5 . . ?
O3 C8 C7 103.64(11) . . ?
O3 C8 C32 105.30(11) . . ?
C7 C8 C32 112.74(13) . . ?
O3 C8 C9 106.98(11) . . ?
C7 C8 C9 110.75(11) . . ?
C32 C8 C9 116.29(12) . . ?
C3 C2 C1 112.13(12) . . ?
C3 C2 H2A 109.2 . . ?
C1 C2 H2A 109.2 . . ?
C3 C2 H2B 109.2 . . ?
C1 C2 H2B 109.2 . . ?
H2A C2 H2B 107.9 . . ?
C10 C25 H25A 109.5 . . ?
C10 C25 H25B 109.5 . . ?
H25A C25 H25B 109.5 . . ?
C10 C25 H25C 109.5 . . ?
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H25B C25 H25C 109.5 . . ?
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C4 C23 H23C 109.5 . . ?
H23A C23 H23C 109.5 . . ?
H23B C23 H23C 109.5 . . ?
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C4 C24 H24B 109.5 . . ?
H24A C24 H24B 109.5 . . ?
C4 C24 H24C 109.5 . . ?
H24A C24 H24C 109.5 . . ?
H24B C24 H24C 109.5 . . ?
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C20 C21 H21 120.0 . . ?
C22 C21 H21 120.0 . . ?
C23 C4 C24 105.83(12) . . ?
C23 C4 C3 110.73(12) . . ?
C24 C4 C3 107.29(12) . . ?

C23 C4 C5 114.42(12) . . ?
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C3 C4 C5 107.76(11) . . ?
C8 C32 H32A 109.5 . . ?
C8 C32 H32B 109.5 . . ?
H32A C32 H32B 109.5 . . ?
C8 C32 H32C 109.5 . . ?
H32A C32 H32C 109.5 . . ?
H32B C32 H32C 109.5 . . ?
O6 C26 H26A 109.5 . . ?
O6 C26 H26B 109.5 . . ?
H26A C26 H26B 109.5 . . ?
O6 C26 H26C 109.5 . . ?
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H26B C26 H26C 109.5 . . ?

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C8 O3 C13 C14 162.46(11) ?
C16 C12 C13 O3 173.57(13) ?
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C16 C12 C13 C14 -6.7(2) ?
C11 C12 C13 C14 174.20(13) ?
C15 O5 C16 O4 178.27(12) ?
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C13 C12 C16 O4 -174.02(14) ?
C11 C12 C16 O4 5.1(2) ?
C13 C12 C16 O5 5.1(2) ?
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C5 C6 C7 C8 55.66(17) ?
C7 C6 C5 O2 53.23(15) ?
C7 C6 C5 C4 171.69(11) ?

C7 C6 C5 C10 -58.79(15) ?
C1 C10 C5 O2 60.71(13) ?
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C9 C10 C5 O2 -57.05(13) ?
C1 C10 C5 C6 175.65(11) ?
C25 C10 C5 C6 -64.41(15) ?
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C9 C10 C5 C4 -172.71(11) ?
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C9 C10 C1 C2 170.47(11) ?
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C13 C14 C15 O5 0.2(2) ?
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C16 O5 C15 C14 -1.7(2) ?
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C13 O3 C8 C9 51.37(14) ?
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C10 C1 C2 C3 -55.18(16) ?

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 O1 C3 C4 C5 -177.44(11) ?
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