Supplementary Information

Chroman-4-one and pyrano[4, 3-b]chromenone derivatives from the mangrove endophytic fungus *Diaporthe phaseolorum* SKS019

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Elemental Composition Report
Single Mass Analysis
Tolerance = 4.0 PPM / DBE: min = -1.5, max = 50.0
Elements Used:
C: 0-50 H: 0-100 O: 0-50

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Figure S2 $^1$H NMR spectrum (500 MHz, CDCl$_3$) of diaporchromanone A (1)

A (d) 6.46  
B (d) 6.38  
C (dd) 4.55  
D (ddd) 4.49  
E (dd) 4.42  
F (s) 3.93  
G (dt) 2.90  
J (s) 2.19  
H (dd) 2.74  
I (dd) 2.74  

Figure S3 $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of diaporchromanone A (1)

C13CPD CDCl3 (E:\Data\2016) nmrsu 1

31.03 46.91 49.60 53.35 66.50 68.55 104.68 110.44 112.02 136.27 163.03 163.95 170.50 190.96 209.22
Figure S4 DEPT NMR spectrum (125 MHz, CDCl$_3$) of diaporchromanone A (1)

Figure S5 $^1$H- $^1$H COSY spectrum (500 MHz, CDCl$_3$) of diaporchromanone A (1)
Figure S6 HSQC spectrum (500 MHz, CDCl₃) of diaporchromanone A (1)

Figure S7 HMBC spectrum (500 MHz, CDCl₃) of diaporchromanone A (1)
Figure S8 HRESIMS of diaporchromanone B (2)

Elemental Composition Report
Single Mass Analysis
Tolerance = 4.0 PPM / DBE: min = -1.5, max = 50.0
Elements Used:
C: 0-50  H: 0-100  O: 0-50

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Figure S9 $^1$H NMR spectrum (500 MHz, acetone-$d_6$) of diaporchromanone B (2)

Figure S10 $^{13}$C NMR spectrum (125 MHz, acetone-$d_6$) of diaporchromanone B (2)
Figure S11 $^1$H- $^1$H COSY spectrum (500 MHz, CDCl$_3$) of diaporchromanone B (2)

Figure S12 HSQC spectrum (500 MHz, CDCl$_3$) of diaporchromanone B (2)
Figure S13 HMBC spectrum (500 MHz, CDCl₃) of diaporchromanone B (2)

Elemental Composition Report
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Elements Used: C: 0-50 H: 0-100 O: 0-50

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Figure S15 $^1$H NMR spectrum (500MHz, CDCl$_3$) of diaporchromanone C (3)

Figure S16 $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of diaporchromanone C (3)
Figure S17 $^1$H-$^1$H COSY spectrum (500 MHz, CDCl$_3$) of diaporchromanone C (3)

Figure S18 HSQC spectrum (500 MHz, CDCl$_3$) of diaporchromanone C (3)
Figure S19 HMBC spectrum (500 MHz, CDCl$_3$) of diaporchromanone C (3)

Figure S20 HRESIMS of diaporchromanone D (4)

Elemental Composition Report
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Elements Used: C: 0-50 H: 0-100 O: 0-50
Mass Calc. Mass mDa PPM DBE Formula
321.0973 321.0974 -0.1 -0.3 8.5 C$_{16}$H$_{17}$O$_7$
Figure S21 $^1$H NMR spectrum (500 MHz, CDCl$_3$) of diaporchromanone D (4)

Figure S22 $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of diaporchromanone D (4)
Figure S23 $^1$H-$^1$H COSY spectrum (500 MHz, CDCl$_3$) of diaporchromanone D (4)

[Image of the COSY spectrum]

Figure S24 HSQC spectrum (500 MHz, CDCl$_3$) of diaporchromanone D (4)

[Image of the HSQC spectrum]
Figure S25 HMBC spectrum (500 MHz, CDCl₃) of diaporochromanone D (4)

Figure S26 HRESIMS of (−) phomopsichin A (5a)

Elemental Composition Report
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

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Figure S27 $^1$H NMR spectrum (500 MHz, acetone-$d_6$) of (−)-phomopsichin A (5a)

Figure S28 $^{13}$C NMR spectrum (125 MHz, acetone-$d_6$) of (−)-phomopsichin A (5a)
Figure S29 $^1$H-$^1$H COSY spectrum (500 MHz, acetone-$d_6$) of (−)-phomopsichin A (5a)

Figure S30 HSQC spectrum (500 MHz, acetone-$d_6$) of (−)-phomopsichin A (5a)
Figure S31 HMBC spectrum (500 MHz, acetone-$d_6$) of (−)-phomopsichin A (5a)

Figure S32 HRESIMS of (+)-phomopsichin B (6a)

Elemental Composition Report
Single Mass Analysis
Tolerance = 4.0 PPM DBE: min = -1.5, max = 50.0
C: 0-50    H: 0-100    O: 0-50

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Figure S33 $^1$H NMR spectrum (500MHz, CDCl$_3$) of (+)-phomopsichin B (6a)

Figure S34 $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of (+)-phomopsichin B (6a)
Figure S35 $^1$H-$^1$H COSY spectrum (500 MHz, CDCl$_3$) of (+)-phomopsichin B (6a)

Figure S36 HSQC spectrum (500 MHz, CDCl$_3$) of (+)-phomopsichin B (6a)
Figure S37 HMBC spectrum (500 MHz, CDCl$_3$) of (+)-phomopsichin B (6a)

Figure S38 HRESIMS of (±)-diaporchromone A (7)

Elemental Composition Report
Single Mass Analysis
Tolerance = 4.0 PPM / DBE: min = -1.5, max = 50.0
Monoisotopic Mass, Even Electron Ions
Elements Used:
C: 0-50 H: 0-100 O: 0-50
Mass Calc. Mass mDa PPM Formula

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1603A01157_S-8a3
HMBCGPND CDCl3 [E:\Data\2016] nmrsu 6

SYNAPT G2-SiHGA489
160422-S-9c 31 (0.134) Cm (29/35)
Figure S39 $^1$H NMR spectrum (500 MHz, CDCl$_3$) of (±)-diaporchromone A (7)

Figure S40 $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of (±)-diaporchromone A (7)
Figure S41 HSQC spectrum (500 MHz, CDCl$_3$) of (±)-diaporchromone A (7)

Figure S42 HSQC spectrum (500 MHz, CDCl$_3$) of (±)-diaporchromone A (7)
Conformational analysis was initially performed using Confab [1] at MMFF94 force field for one of the relative configurations for each compound. The conformers with Boltzmann-population of over 1% were chosen for ECD calculations. The energies and populations of all dominative conformers were provided in Table 1. The theoretical calculation was carried out using Gaussian 09 [2]. First, the chosen conformer was optimized at B3LYP/6-311+g(2d,p) level, and conformers with low Boltzmann-populations were filtered. Then, the remaining conformers were further optimized at B3LYP/6-311+g(2d,p) in MeOH using the IEFPCM polarizable conductor calculation model. The theoretical calculation of ECD was conducted in MeOH using Time-dependent Density functional theory (TD-DFT) at the CAM-B3LYP/6-311+g(2d,p) level for compound 1. Rotatory strengths for a total of 50 excited states were calculated. ECD spectra were generated using the program SpecDis 1.6 (University of Würzburg, Würzburg, Germany) and GraphPad Prism 5 (University of California San Diego, USA) from dipole-length rotational strengths by applying Gaussian band shapes with sigma = 0.2 eV [3]. All calculations were performed with the High-Performance Grid Computing Platform of Sun Yat-sen University.

**Table 1** The low energy conformers of the compound 1.

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RR-1-a

RR-1-b

SR-1

SS-1-a

SS-1-b

References

