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Phomactins K–M, three novel phomactin-type diterpenes from a marine-derived fungus

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ABSTRACT

Three novel diterpenes, phomactins K–M (**1**–**3**), were isolated from the cultures of an unidentified marine-derived fungus. The structures of **1**–**3** were elucidated from spectroscopic data (NMR, MS, IR), and the absolute configurations of **1**, **2**, and the relative configuration of **3** were determined by X-ray diffraction analysis.

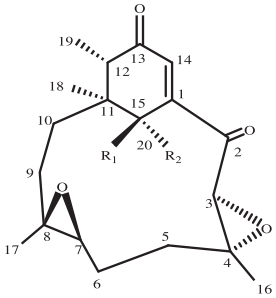
1. Introduction

Marine-derived fungi have different characteristic from the terrestrial fungi, such as salt tolerance, and yield many unique secondary metabolites. Therefore, we think marine-derived fungi to be promising as medical resources. We previously reported novel phomactin derivatives, which were isolated from marine-derived fungi found in brown algae.[1,2]

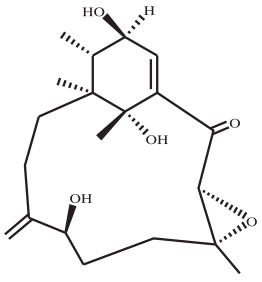
Here, we describe the isolation and structural elucidation of novel phomactins K–M (**1**–**3**). An unidentified fungus (MPUC046) was isolated from the surface of the marine brown alga *Ishige okamurae*, collected at Tateishi, Kanagawa Prefecture, Japan, in September 2000.[1,2] The D1/D2 26S rDNA and internal transcribed spacer regions, including 5.8S rDNA in the rRNA gene of the isolate, were directly sequenced using PCR. The sequence data (approximately 1200 bp long) were searched using the BLAST system (http://www.ncbi.nlm.nih.gov/BLAST/) at GenBank. The isolate was not assigned to any known species, but phylogenetically belongs to Dothideales. MPUC046 was not closely related to *Phoma* sp., which produces phomactins,[3–8] on a molecular phylogenetic tree.[9]

2. Results and discussion

Phomactin K (**1**) was obtained as a white powder that was recrystallized as colorless needles. The molecular formula for **1** was determined to be $C_{20}H_{26}O_4$ (8 degrees of unsaturation) by HR-EIMS analysis (330.1831: M^+ calcd for 330.1831). The IR spectrum of **1** indicated the presence of hydroxyl (3450 cm^{-1}) and carbonyl (1710, 1680 cm^{-1}) groups.



Phomactin K (**1**) : R_1=R_2=CH_2
Phomactin L (**2**) : R_1=H, R_2=CH_3



Phomactin M (**3**)

The ^{13}C NMR and DEPT data of **1** (Table 1) indicated the presence of two ketones (δ_C 202.1, C-13; 197.4, C-2), four olefinic carbons (δ_C 153.3, C-1; 143.3, C-15; 123.5, C-14; 123.4, C-20), three singlet methyl carbons (δ_C 21.0, C-18; 18.9, C-17; 13.9, C-16), a doublet methyl carbon (δ_C 13.5, C-19), four methylene carbons (δ_C 35.5, C-5; 29.8, C-9; 29.0, C-10; 24.3, C-6), two oxymethine carbons (δ_C 64.6, C-3; 55.3, C-7), a methine carbon (δ_C 54.2, C-12), two quaternary

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oxycarbons (δ_C 63.6, C-4; 58.4, C-8), and a quaternary carbon (δ_C 46.3, C-11). ^{1}H NMR, HMQC, and DQF-COSY data of **1** (Tables 1 and 2) showed the presence of two fragments, C5–C6–C7, and C9–C10. Further information regarding the skeletal framework was obtained from HMBC (Table 3). The HMBC correlations between H-17/C-7, C-8, C-9, and H-10/C-8 showed connections among C5–C6–C7–C8–C9–C10.

The connection of C-10, C-11, and C-15 was confirmed by the HMBC correlations between H-10/C-11, C-15, C-18. The HMBC correlations between H-19/C-11, C-12, C-13, and H-14/C-2, C12, C-15 as well as H-20/C-1, C-11, C-15 showed connections among C15–C11–C12–C13–C14–C1 (cyclohexene ring), and C1–C2. The connections of C2–C3–C4–C5, and C4-C16 were confirmed by the HMBC correlations between H-5/C-4, C-16, and H-3/C-2, C-4, C-5. These data established the skeletal framework of **1** as consisting of a cyclohexene and a cyclododecane ring, which suggested that **1** was a phomactin derivative.[1–8] Compound **1** contains four oxygen atoms, including two ketones (δ_C 202.1, 197.4), but also included four oxycarbons (δ_C 64.6, 63.6, 58.4, 55.3). Comparison of the NMR data of **1** with those of phomactin I and J revealed that **1** has two epoxy groups (C-3/C-4 and C-7/C-8).[2] Single-crystal X-ray diffraction analysis was conducted to determine the absolute configuration (Fig. 1). The absolute configurations of C3, C4, C7, C8, C11, and C12 were determined to be *S*, *R*, *S*, *S*, *S*, and *R*, respectively, which were deduced from the Flack parameter, −0.0 (3), refined using 1585 Friedel pairs.[10]

Table 1
^{13}C and ^{1}H NMR spectra of **1**, **2**, and **3** in $CDCl_3$ (δ ppm)

Position	1		2		3	
	δ^{13}C	δ^1H	δ^{13}C	δ^1H	δ^{13}C	δ^1H
1	153.3 s		162.4 s		149.5 s	
2	197.4 s		198.2 s		199.8 s	
3	64.6 d	3.79 (1H, s)	66.5 d	3.73 (1H, s)	66.1 d	3.62 (1H, s)
4	63.6 s		63.4 s		65.1 s	
5	35.5 t	1.10 (1H, m)	35.3 t	129 (1H, m)	30.71	1.29 (1H, m)
		2.29 (1H, m)[a]		2.32 (1H, m)		2.03 (1H, m)
6	24.3 t	1.43 (1H, m)	24.4 t	1.50 (1H, m)	30.1 t	1.64 (1H, m)
		2.15 (1H, m)		2.17 (1H, m)		2.08 (1H, m)
7	55.3 d	2.70 (1H. dd. 10.8. 4.0)	57.2 d	2.93 (1H, dd, 10.5, 3.9)	72.5 d	4.19 (1H, brs)
8	58.4 s		59.9 s		150.0 s	
9	29.8 t	1.54 (1H, m)	30.2 t	1.79 (1H, m)	28.8 t	2.15 (2H, m)
		2.10 (1H, m)		2.09 (1H, m)		
10	29.0 t	1.15 (1H, m)	30.0 t	124(1H, m)	38.8 t	1.60 (1H, m)
		1.25 (1H, m)		1.53 (1H, m)		1.71 (1H, m)
11	46.3 s		42.5 s		43.0 s	
12	54.2 d	2.28 (1H, m) [a]	54.7 d	2.12 (1H, m)	42.9 d	1.64 (1H, m)
13	202.1 s		201.4 s		72.3 d	4.41 (1H, brs)
14	123.5 d	5.64 (1H, brs)	126.0 d	5.80 (1H, dd, 3.2, 0.9)	139.1 d	6.02 (1H, d, 2.0)
15	143.3 s		36.2 d	3.13 (1H, dq, 7.9, 3.1)	74.9 s	
16	13.9 q	1.31 (3H, s)	14.9 q	1.38 (3H, s)	16.1 q	1.28 (3H, s)
17	18.9 q	1.26 (3H, s)	18.3 q	1.27 (3H, s)	109.1 t	5.06 (1H, s)
						5.20 (1H, s)
18	21.0 q	1.12 (3H, s)	23.4 q	1.11 (3H, s)	18.9 q	1.14 (3H, s)
19	13.5 q	1.01 (3H,d, 7.4)	11.6 q	1.07 (3H, d, 7.7)	17.4 q	1.23 (3H, d, 7.1)
20	123.4 t	5.58 (1H, d, 1.4)	13.8 q	1.47 (3H, d, 7.9)	22.6 q	1.52 (3H s)
		5.82 (1H, brs)				

[a] Maybe interchanged.

Phomactin L (**2**) was obtained as a white powder that was recrystallized as colorless platelets. The molecular formula for **2** was determined to be $C_{20}H_{28}O_4$ (seven degrees of unsaturation) by HR-EIMS analysis (332.1991: M^+ calcd for 332.1988). The IR spectrum of **2** indicated the presence of hydroxyl (3450 cm^{-1}) and carbonyl (1700, 1660 cm^{-1}) groups. The ^{13}C NMR and DEPT data of **2** (Table 1) indicated the presence of two ketones (δ_C 201.4, C-13; 198.2, C-2), two olefinic carbons (δ_C 162.4, C-1; 126.0, C-14), three singlet methyl carbons (δ_C 23.4, C-18; 18.3, C-17; 14.9, C-16), two

Table 2
DQF-COSY correlations of **1**, **2**, and **3** in $CDCl_3$

Position	1	2	3
H-5	H-6	H-6	H-6
H-6	H-5, 7	H-5, 7	H-5, 7
H-7	H-6	H-6	H-6
H-9	H-10	H-10	H-10
H-10	H-9	H-9	H-9
H-12	Overlapped.	H-19	H-13, 19
H-13	—	—	H-12
H-14	—	—	n. o.
H-15	—	H-20	—
H-19	Overlapped.	H-12	H-12
H-20	—	H-15	—

n. o.=not observed.

Table 3
HMBC correlations of **1**, **2**, and **3** in $CDCl_3$

Position	1	2	3
H-3	C-2,4,5	C-2,4,5	C-2,4,5
H-5	C-4,16	C-3,4,6, 7, 16	C-16
H-6	C-5	C-5	C-8
H-7	C-6	C-6	—
H-9	C-7, 8, 10	C-7, 8, 10, 11, 17	C-8
H-10	C-8, 11, 15, 18	C-8, 9, 11, 12, 15, 18	C-9, 11, 12, 15
H-12	Overlapped.	C-10, 11, 13, 14, 15, 19	C-10, 13, 19
H-13	—	—	n. o.
H-14	C-2, 12, 15	C-2, 12, 15	C-2, 15
H-16	C-4, 5	C-3, 4, 5	C-4, 5
H-17	C-7, 8, 9	C-7, 8, 9	C-7, 9
H-18	C-10, 11, 12, 15	C-10, 11, 12, 15	C-10, 11, 12, 15
H-19	C-11, 12, 13	C-11, 12, 13	C-11, 12, 13
H-20	C-l, 11, 15	C-l, 11, 15	C-l, 11, 15

n. o.=not observed.

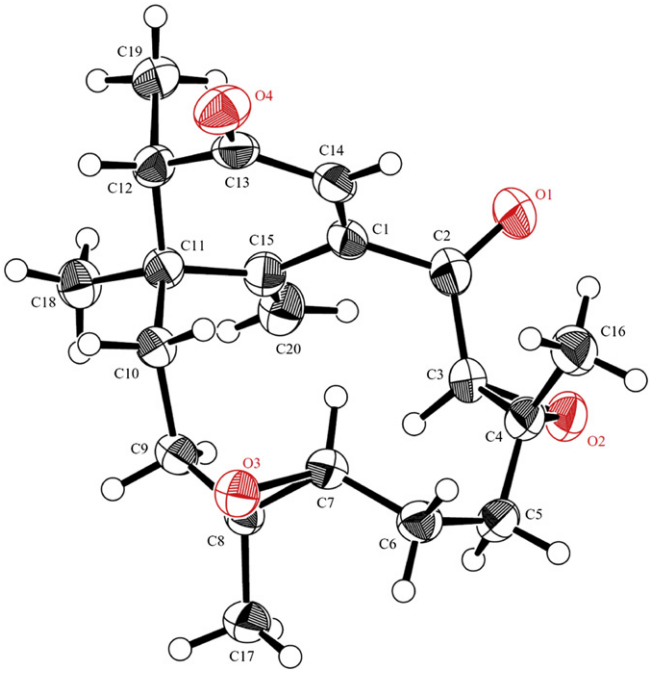

Fig. 1. ORTEP drawing of **1**.

doublet methyl carbons (δ_C 11.6, C-19; 13.8, C-20), four methylene carbons (δ_C 35.3, C-5; 30.2, C-9; 30.0, C-10; 24.4, C-6), two oxymethine carbons (δ_C 66.5, C-3; 57.2, C-7), two methine carbons (δ_C 54.7, C-12; 36.2, C-15), two quaternary oxycarbons (δ_C 63.4, C-4; 59.9, C-8), and a quaternary carbon (δ_C 42.5, C-11). ^{1}H NMR, HMQC, DQF-COSY data (Tables 1 and 2), and HMBC data (Table 3) of **2** suggested that **2** was a phomactin derivative similar to **1** except for the bonding pattern at C15-C20. Single-crystal X-ray diffraction analysis was conducted to determine the absolute configuration (Fig. 2). The absolute configurations of C3, C4, C7, C8, C11, C12, and C15 were determined to be *S*, R, *S*, *S*, *R*, *S*, and *S*, respectively, which were deduced from the Flack parameter, −0.1 (2), refined using 1431 Friedel pairs.[10]

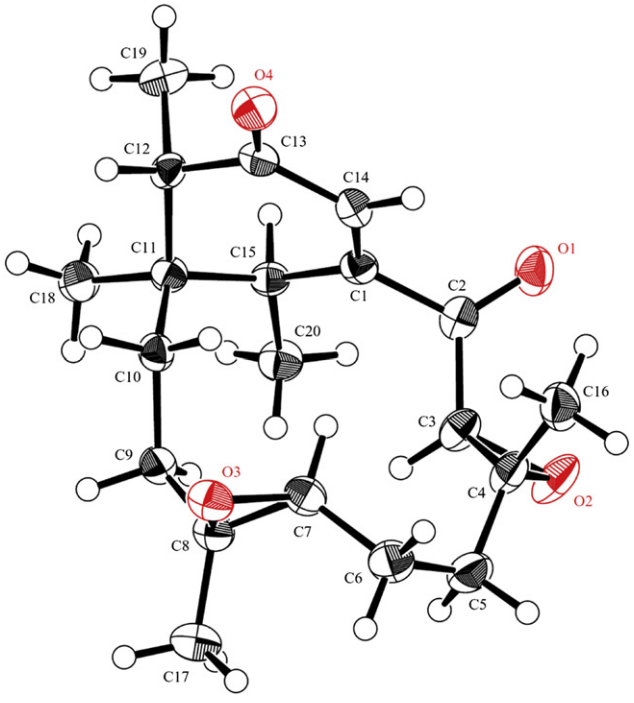

Fig. 2. ORTEP drawing of **2**.

Phomactin M (**3**) was obtained as a white powder that was recrystallized as colorless blocks. The molecular formula for **3** was determined to be $C_{20}H_{30}O_5$ (six degrees of unsaturation) by negative HR-FABMS analysis (349.1999: $[M-H]^-$ calcd for 349.2015). The IR spectrum of **3** indicated the presence of hydroxyl (3400 cm^{-1}) and carbonyl (1680 cm^{-1}) groups. The ^{13}C NMR and DEPT data of **3** (Table 1) indicated the presence of a ketone (δ_C 199.8, C-2), four olefinic carbons (δ_C 150.0, C-8; 149.5, C-1; 139.1, C-14; 109.1, C-17), three singlet methyl carbons (δ_C 22.6, C-20; 18.9, C-18; 16.1, C-16), a doublet methyl carbon (δ_C 17.4, C-19), four methylene carbons (δ_C 38.8, C-10; 30.7, C-5; 30.1, C-6; 28.8, C-9), three oxymethine carbons (δ_C 72.5, C-7; 72.3, C-13; 66.1, C-3), a methine carbon (δ_C 42.9, C-12), two quaternary oxycarbons (δ_C 74.9, C-15; 65.1, C-4), and a quaternary carbon (δ_C 43.0, C-11). ^{1}H NMR, HMQC, and DQF-COSY data of **3** (Tables 1 and 2) showed the presence of three fragments, C5-C6-C7, C9-C10, and C13-C12-C19. The HMBC correlations between H-18/C-10, C-11, C-12, C-15 identified the C9–C10–C11–C12–C19 linkage. Moreover, it was also shown that C-15 and C-18 were connected to C-11. The linkage of C7–C8–C9 was confirmed by the HMBC correlations between H-6/C-8, H-9/C-8, and H-17/C-7, C-9. The HMBC correlations between H-20/C-1, C-11, C-15 established the C1–C15–C11 linkage and that C-20 was attached to C-15. The connection of C14–C1 was confirmed by the HMBC correlation between H-14/C-15. The HMBC correlations between H-3/C-4, C-5, and H-16/C-4, C-5 showed a C3-C4-C5 linkage and C-16 attached to C-4. These data inferred the partial structure of **a** and the ketone (C-2) that remained. By comparison with other phomactin derivatives, it was postulated that compound **3** had the structural formula of **b** (Fig. 3). Single-crystal X-ray diffraction analysis was conducted to determine the relative configuration (Fig. 4). The determination of absolute configuration wasn't succeeded due to problems of the crystal structure (flack parameter; −0.1(6)). Moreover, we couldn't obtain enough amounts of **3** for Mosher's method. And, since probably the 12 member ring existed, absolute structure was not determined by CD spectrum.

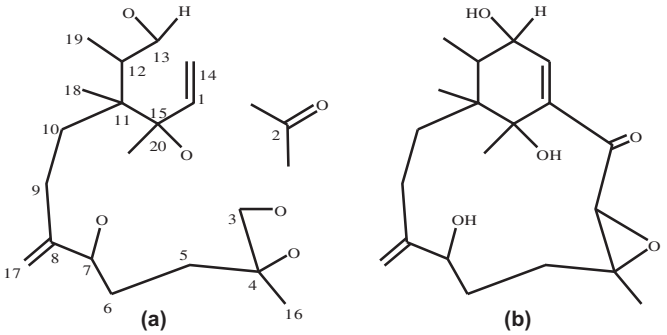

Fig. 3. The partial structure of **3**.

Sixteen phomactins [A,[3] B, B1, B2, C (Sch 47918[7]), D,[4] E, F, G,[5] H,[1] I, 13-*epi*-I, and J[2] as well as Sch 49,026, 49,027 and 49,028[8]] have been previously isolated and most of those were isolated from *Phoma* sp. It is very interesting that phomactin-type diterpenes were isolated from MPUC046, which is far from *Phoma* sp. genetically.[9] Meanwhile, those phomactins are reported to be active as platelet activating factor (PAF) antagonists.[3–8] We have performed various activity examinations about phomactins H and I with comparatively much yield in order to find out the new bioactivity for phomactins. (Inhibition of β-hexosaminidase release assay, inhibition of melanogenesis assay, HUVECs (human umbilical vein endothelial cells), NHDF (normal human dermal fibroblasts) cells,

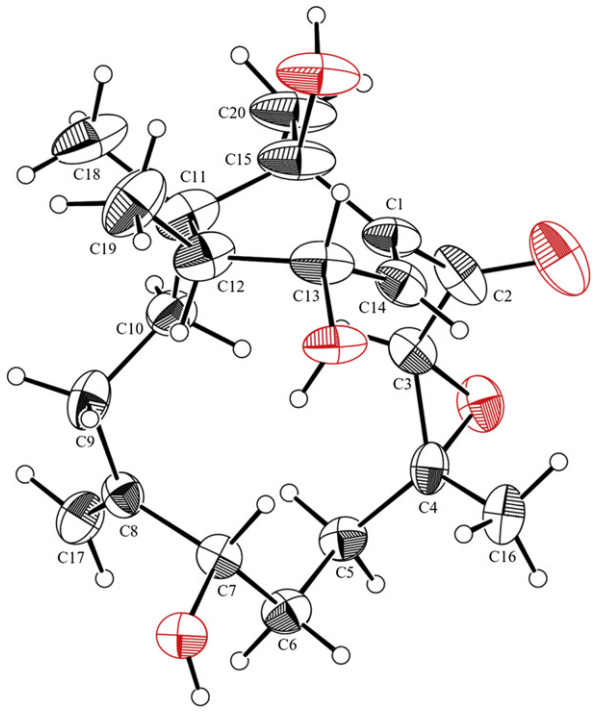

Fig. 4. ORTEP drawing of **3**.

and HeLa cells growth inhibition assay, and HUVECs migration assay). But those results only showed very weak activity or inactivity. Even cytotoxicity was not observed. Therefore, if new biological activity is observed for phomactin, it will be said that the biological activity is high specificity. By the above-mentioned reason, it is thought that there is possibility of the seed compound of pharmaceutical products in phomactin.

3. Experimental

3.1. General

Melting points were determined with a Yanagimoto MP micromelting point apparatus. UV spectra were recorded on a Shimadzu UV-240 spectrophotometer. The IR spectra were measured with a JASCO IR Report-100 infrared spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded with JEOL JNM-AL-400 (^{1}H 400 and ^{13}C 100 MHz) and JEOL JNM-LA500 (^{1}H 500 and ^{13}C 125 MHz) spectrometers, using the solvent is $CDCl_3$ as the internal standard. The $[\alpha]_D$ values were determined with a JASCO DIP-370 digital polarimeter and a HORIBA SEPA-300 polarimeter. The MS spectra were obtained using a JEOL JMS-700 spectrophotometer. Column chromatography was carried out on 70–230 mesh silica gel (Merck) and a Sephadex LH-20 column. HPLC was performed with a JASCO PU 980 unit and a JASCO UV 970 (Gulliver) detector using a PEGASIL Silica 60–5 (10ϕ, 250 mm) column. Flash column chromatography was carried out on a YFLC-AI-580 instrument with a Hi-Flash 3L (SiOH, 46ϕ, 130 mm) column and a Hi-Flash L (SiOH, 26ϕ, 100 mm) column.

3.2. Extraction and isolation

Fermentation was conducted in fifty 500-mL Roux flasks, each containing 150 g of wheat. Seawater (40 mL) was added to the flasks and the contents were soaked for 40 min before autoclaving for 30 min. The flasks were inoculated with the fungus (MPUC046) and incubated at 25 °C for 30 days. The fermented wheat substrate was extracted with $CHCl_3$ (2×14 L). The extracts of each solvent were combined, filtered, and evaporated to yield 95.21 g of crude $CHCl_3$ extract. The $CHCl_3$ extract (95.21 g) was suspended in *n*-hexane, and this suspension was separated into *n*-hexane-soluble (67.44 g) and -insoluble (19.70 g) fractions using filtration. The insoluble fraction was suspended in MeOH, and separated further into MeOH-soluble (16.95 g), and -insoluble (2.75 g) fractions by filtration. The MeOH soluble fraction (16.95 g) was separated by a Sephadex LH-20 column [column A; 33×350 mm; $CHCl_3$/MeOH/H_2O (6:4:1)] into 4 fractions. Fraction A-2 (13.61 g) was applied to a Sephadex LH-20 column [column B; 33×350 mm; $CHCl_3$/MeOH/H_2O (6:4:1)] to obtain 3 fractions. Fraction B-2 (11.12 g) was subjected to silica gel column chromatography [column C; 75×220 mm; $CHCl_3$/MeOH ($CHCl_3$, 100:1, 80:1, 60:1, 40:1, 20:1, 10:1, 5:1, 1:1, MeOH)] to obtain 6 fractions. Fraction C-4 (4.14 g) was separated by a Sephadex LH-20 column [column D; 33×380 mm; $CHCl_3$/MeOH/H_2O (6:4:1)] into 3 fractions. Fraction D-2 (4.02 g) was applied to silica gel column chromatography [column E; 55×190 mm; $CHCl_3$/MeOH (50:1, MeOH)] to obtain 4 fractions. Fraction E-2 (2.60 g) was subjected to silica gel column chromatography [column F; 55×370 mm; $CHCl_3$/MeOH (80:1, MeOH)] to obtain 5 fractions. Fraction F-3 (1.19 g) was separated by flash column chromatography [column G; 26×100 mm; *n*-hexane/EtOAc (33:67, 12:88)] into 6 fractions. Fraction G-4 (462.1 mg) was applied to a Sephadex LH-20 column [column H; 24×500 mm; $CHCl_3$/MeOH/H_2O (6:4:1)] to obtain 2 fractions. Fraction H-2 (374.0 mg) was subjected to silica gel column chromatography [column I; 25×240 mm; *n*-hexane/EtOAc (2:1, 1:1, 1:2, 1:3, MeOH)] to obtain 5 fractions. Fraction I-2 (261.8 mg) was separated by silica gel column chromatography [column J; 25×225 mm; *n*-hexane/EtOAc (3:2, 1:1, 1:2)] into 3 fractions. Fraction J-2 (229.6 mg) was applied to silica gel column chromatography [column K; 25×205 mm; $CHCl_3$/MeOH ($CHCl_3$, MeOH)] to obtain 5 fractions. Fraction K-1 (8.6 mg) was further purified by HPLC [column L; 10×250 mm; *n*-hexane/$CHCl_3$ (1:3)] to yield **1** (3.2 mg) and **2** (2.6 mg).

Fraction C-5 (2.35 g) was separated by flash column chromatography [column M; 46×130 mm; $CHCl_3$/MeOH (97:3, 89:11, 70:30)] into 7 fractions. Fraction M-5 (281.2 mg) was applied to a Sephadex LH-20 column [column N; 25×500 mm; $CHCl_3$/MeOH/H_2O (6:4:1)] to obtain 2 fractions. Fraction N-2 (186.0 mg) was subjected to silica gel column chromatography [column O; 25×210 mm; $CHCl_3$/MeOH (100:1, 50:1, 10:1, 1:1)] to obtain 3 fractions. Fraction O-2 (143.4 mg) was separated by silica gel column chromatography [column P; 25×275 mm; $CHCl_3$/MeOH (100:1, 70:1, 50:1, 30:1, 20:1, 10:1, 1:1)] into 3 fractions. Fraction P-2 (91.8 mg) was applied to ODS HPLC [column Q; 10×250 mm; 60% MeOH aq] to obtain 5 fractions. Fraction Q-4 (13.1 mg) was subjected to ODS HPLC [column R; 10×250 mm; 60% MeOH aq] to obtain 3 fractions. Fraction R-2 (10.1 mg) was separated by HPLC [column S; 10×250 mm; $CHCl_3$/MeOH (30:1)] into 3 fractions. Fraction S-3 (5.6 mg) was applied to HPLC [column T; 10×250 mm; $CHCl_3$/MeOH (40:1)] to obtain 4 fractions. Fraction T-3 (2.9 mg) was subjected to HPLC [column U; 10×250 mm; *n*-hexane/EtOAc (1:3)] to obtain 4 fractions. Fraction U-2 (2.0 mg) was further purified by HPLC [column V; 10×250 mm; *n*-hexane/EtOAc (1:2)] to yield **3** (1.2 mg).

3.3. Characteristics of each diterpenoid

*3.3.1. Phomactin K (**1**).* Colorless needles (from *n*-hexane/EtOAc); mp 175 °C; $[\alpha]_D^{27}$ +129.2 (*c* 0.21, MeOH); UV (MeOH) λ_{max} (log ε): 284 (4.14), 219 (4.19); IR ν_{max} (KBr) cm^{-1}: 3450, 2950, 1710, 1680; HR-EIMS *m*/*z*: 330.1831 (M^+, calcd for $C_{20}H_{26}O_4$: 330.1831); EIMS *m*/*z* (rel int. %): 330 (M^+, 5), 315 (10), 259 (100); ^{1}H and ^{13}C NMR, see Table 1.

*3.3.2. Phomactin L (**2**).* Colorless platelets (from *n*-hexane/EtOAc); mp 180 °C (sub.); $[\alpha]_D^{27}$ +55.0 (*c* 0.32, MeOH); UV (MeOH) λ_{max} (log

ε): 244 (3.98), 206 (3.96); IR ν_{max} (KBr) cm^{-1}: 3450, 2950, 1700, 1660; HR-EIMS *m*/*z*: 332.1991 (M^+, calcd for $C_{20}H_{28}O_4$: 332.1988); EIMS *m*/*z* (rel int. %): 332 (M^+, 21), 317 (4), 135 (100); ^1H and ^{13}C NMR, see Table 1.

*3.3.3. Phomactin M (**3**).* Colorless blocks (from *n*-hexane/EtOAc); mp 81 °C; $[\alpha]_D^{22}$ +96.3 (*c* 0.06, MeOH); UV (MeOH) λ_{max} (log ε): 238 (3.29), 205 (3.58); IR ν_{max} (KBr) cm^{-1}: 3400, 2950, 1680; negative HR-FABMS *m*/*z*: 349.1999 ($[M-H]^-$, calcd for $C_{20}H_{29}O_5$: 349.2015); negative FABMS *m*/*z* (rel int. %): 349 ($[M-H]^-$, 8), 331 (6), 183 (100); ^1H and ^{13}C NMR, see Table 1.

3.4. Single-crystal X-ray crystallographic analysis

All measurements were obtained using a Rigaku RAXIS RAPID diffractometer with graphite monochromated CuKα radiation (λ=1.54,187 Å). The structures of **1**, **2**, and **3** were solved by direct methods (SHELX97, SIR2004) and expanded using Fourier techniques.

Crystal data for **1**. Colorless needle crystal, hexagonal, $C_{20}H_{26}O_4$ (Mr=330.42), space group $P6_5$ with a=19.3421(4) Å, c=8.6231(6) Å, V=2793.8(3) $Å^3$, Z=6, D_{calcd}=1.178 g/cm^3, R=0.0469, $wR2$=0.1008.

Crystal data for **2**. Colorless platelet crystal, orthorhombic, $C_{20}H_{28}O_4$ (Mr=332.44), space group $P2_12_12_1$ with a=10.6911(2) Å, b=12.7949(3) Å, c=13.434(1) Å, V=1839.0(2) $Å^3$, Z=4, D_{calcd}=1.201 g/cm^3, R=0.0407, $wR2$=0.0925.

Crystal data for **3**. Colorless block crystal, monoclinic, $C_{20}H_{30}O_5$ (Mr=350.45), space group $P2_1$ with a=9.769(2) Å, b=8.601(1) Å, c=22.972(3) Å, β=99.618(7) °, V=1903.0(4) $Å^3$, Z=4, D_{calcd}=1.223 g/cm^3, R=0.1714, $wR2$=0.3844.

Crystallographic data for **1**, **2**, and **3** reported in this paper have been deposited at the Cambridge Crystallographic Data Centre, under the reference numbers CCDC 865628, 865629 and 865630, respectively. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK fax: +44 1223 336033 or e-mail: data_request@ccdc.cam.ac.uk.

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