Supporting Information

Sumalactones A–D, Four New Curvularin-type Macrolides from a Marine Deep Sea Fungus *Penicillium Sumatrense*

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S1. The NMR data assignments of 1–4



No.	$\delta_{\mathrm{C},}$ mult.	$\delta_{ m H} \left(J ext{ in Hz} ight)$	¹ H- ¹ H COSY	HMBC		
1	171.8, qC					
2	41.3, CH ₂	3.44, d (18.3), a	H-2b	C-1, 3, 4, 8		
		3.96, d (18.4), b	H-2a	C-1, 3, 4, 5, 7, 8		
3	136.3, qC					
4	110.6, CH	6.12, d (1.8)	Н-6	C-2, 5, 6, 8		
5	161.0, qC					
6	102.4, CH	6.24, d (2.0)	H-4	C-4, 5, 7, 8, 9		
7	158.8, qC					
8	122.6, qC					
9	211.6, qC					
10	46.7, CH ₂	2.70, m, a	H-10b, 11	C-9, 11,12		
		3.06, m, b	H-10a, 11	C-9, 11, 12		
11	23.4, CH ₂	1.87, m	H-10a, 10b, 12a, 12b	C-9, 10, 12, 13		
12	35.4, CH ₂	1.47, overlapped, a	H-11, 12b, 13	C-10		
		1.95, m, b	H-11, 12a, 13	C-10		
13	76.3, CH	4.91, m	H-12a, 12b, 14a, 14b	C-1, 12		
14	45.3, CH ₂	1.47, overlapped, a	H-13, 14b, 15	C-12, 13, 15, 16		
		1.70, ddd (6.6, 7.5, 14.1), b	H-13, 14a, 15	C-12, 13, 15, 16		
15	65.5, CH	3.69, m	H-14a, 14b, 16	C-13, 14		
16	23.9, CH ₃	1.12, d (6.2)	H-15	C-14, 15		



Table S2 ¹³ C NMR (125 MHz) and ¹ H NMR (500 MHz) data of 2in CD ₃ OD										
No.	$\delta_{\mathrm{C},}$ mult.	$\delta_{ m H} (J { m in} { m Hz})$	¹ H- ¹ H COSY	HMBC						
1	172.7, qC									
2	41.3, CH ₂	3.49, d (18.5), a	H-2b	C-1, 3, 4, 8						
		3.98, d (18.4), b	H-2a	C-1, 3, 4, 5, 7, 8						
3	136.2, qC									
4	110.6, CH	6.13, d (1.6)	Н-6	C-2, 5, 6, 8						
5	161.0, qC									
6	102.4, CH	6.24, d (2.0)	H-4	C-4, 5, 7, 8, 9						
7	158.9, qC									
8	122.6, qC									
9	211.5, qC									
10	46.6, CH ₂	2.70, ddd (2.1, 7.7, 15.9), a	H-10b, 11	C-9, 11,12						
		3.06, ddd (2.2, 10.5, 15.4), b	H-10a, 11	C-9, 11, 12						
11	23.4, CH ₂	1.87, overlapped	H-10a, 10b, 12a, 12b	C-9, 10, 12, 13						
12	36.3, CH ₂	1.47, overlapped, a	H-11, 12b, 13	C-11						
		1.87, overlapped, b	H-11, 12a, 13	C-11						
13	76.3, CH	4.90, m	H-12a, 12b, 14a, 14b	C-1, 15						
14	45.9, CH ₂	1.47, overlapped, a	H-13, 14b, 15	C-12, 13, 15, 16						
		1.56, ddd (3.8, 7.9, 14.2), b	H-13, 14a, 15	C-12, 13, 15, 16						
15	65.1, CH	3.65, m	H-14a, 14b, 16							
16	23.6, CH ₃	1.09, d (6.2)	H-15	C-14, 15						



	Table S3 ¹³ C NMR (125 MHz) and ¹ H NMR (500 MHz) data of 3 in CD ₃ OD											
No.	$\delta_{\mathrm{C},}$ mult.	$\delta_{ m H} \left(J ext{ in Hz} ight)$	¹ H- ¹ H COSY	HMBC								
1	172.4, qC											
2	41.1, CH ₂	3.46, d (17.2), a	H-2b	C-1, 3, 4, 8								
		4.14, d (17.1), b	H-2a	C-1, 3, 4, 7, 8								
3	136.3, qC											
4	111.5, CH	6.16, d (2.2)	Н-6	C-2, 5, 6, 8, 9								
5	160.9, qC											
6	102.6, CH	6.25, d (2.2)	H-4	C-4, 5, 7, 8, 9								
7	158.8, qC											
8	122.0, qC											
9	209.8, qC											
10	41.7, CH ₂	2.87, ddd (3.4, 6.1, 17.5), a	H-10b, 11a, 11b	C-9, 11,12								
		3.17, ddd (3.1, 11.6, 17.4), b	H-10a, 11a, 11b	C-9, 11, 12								
11	23.9, CH ₂	1.47, overlapped, a	H-10a, 10b, 11b, 12a, 12b	C-9, 10, 12, 13								
		1.89, m, b	H-10a, 10b, 11a, 12a, 12b	C-9, 10, 12, 13								
12	22.0, CH ₂	1.23, m, a	H-11a, 11b, 12b, 13a, 13b	C-10,11,13,14								
		1.66, m, b	H-11a, 11b, 12a, 13a, 13b	C-10, 11, 13, 14								
13	$26.1,CH_2$	1.47, overlapped,a	H-12a, 12b, 13b, 14a, 14b	C-12, 14, 15								
		1.75, m, b	H-12a, 12b, 13a, 14a, 14b	C-12, 15								
14	79.8, CH	4.75, ddd (3.3, 5.1, 10.5)	H-13a, 13b, 15	C-1, 12, 13, 15, 16								
15	69.4, CH	3.63, dq (5.3, 6.3)	H-14, 16	C-13, 14, 16								
16	18.7, CH ₃	0.98, d (6.4)	H-15	C-14, 15								



	Table 54.5C NIVIK (125 MHZ) and 'H NMR (500 MHZ) data of 4 in CD_3OD										
No.	$\delta_{\mathrm{C},}$ mult.	$\delta_{ m H} \left(J { m in} { m Hz} ight)$	¹ H- ¹ H COSY	HMBC							
1	172.5, qC										
2	41.1, CH ₂	3.50, d (17.1), a	H-2b	C-1, 3, 4, 8							
		4.11, d (17.1), b	H-2a	C-1, 3, 4, 8							
3	136.3, qC										
4	111.7, CH	6.17, d (2.2)	Н-6	C-2, 5, 6, 8							
5	160.9, qC										
6	102.6, CH	6.24, d (2.2)	H-4	C-4, 5, 7, 8							
7	158.7, qC										
8	122.0, qC										
9	209.9, qC										
10	41.8, CH ₂	2.86, ddd (3.3, 6.0, 17.3), a	H-10b, 11a, 11b	C-9, 11							
		3.19, ddd (3.2, 11.6, 17.3), b	H-10a, 11a, 11b	C-9, 11							
11	23.9, CH ₂	1.47, overlapped, a	H-10a, 10b, 11b, 12a, 12b	C-9, 12							
		1.89, m, b	H-10a, 10b, 11a, 12a, 12b	C-9, 12							
12	22.1, CH ₂	1.23, m, a	H-11a, 11b, 12b, 13a, 13b	C-11, 13, 14							
		1.67, overlapped, b	H-11a, 11b, 12a, 13a, 13b	C-11, 13, 14							
13	26.3, CH ₂	1.47, overlapped, a	H-12a, 12b, 13b, 14	C-11, 12							
		1.67, overlapped, b	H-12a, 12b, 13a, 14	C-11, 12							
14	79.9, CH	4.78, ddd (2.7, 6.0, 10.2)	H-13a, 13b, 15	C-1, 12, 13, 15, 16							
15	69.2, CH	3.62, p (6.4)	H-14, 16	C-13, 14, 16							
16	18.9, CH ₃	1.02, d (6.5)	H-15	C-14, 15							

d III NIMD (500 MILT) dat (125 MIL-) £ 4 : m

S2. Preparation of (S)- and (R)- MTPA esters of 1 and 3

A solution of 1/3(1.0 mg) in pyridine- $d_5(0.5 \text{ mL})$ was treated with (S)-MTPA chloride (15µL) under an atmosphere of nitrogen in an NMR tube. The mixture was stirred at room temperature for 4 h to obtain the (R)-MTPA ester (1b/3b). The same procedure was used to prepare the (S)-MTPA ester (1a/3a) with (R)-MTPA chloride.

The key $\Delta\delta$ values ($\Delta\delta_{H-11}$: +0.12, +0.18; $\Delta\delta_{H-12}$: +0.07, +0.12; $\Delta\delta_{H-13}$: +0.15; $\Delta\delta_{H-14}$: +0.07, +0.07; $\Delta\delta_{H-16}$: -0.07) of the (*S*)- and (*R*)-MTPA esters of **1** (**1a** and **1b**) indicated the *S* configuration for C-15 in **1**.

The key $\Delta \delta$ values ($\Delta \delta_{\text{H-11}}$: +0.16, +0.21; $\Delta \delta_{\text{H-12}}$: +0.08, +0.08; $\Delta \delta_{\text{H-13}}$: +0.01, +0.09; $\Delta \delta_{\text{H-14}}$: +0.02; $\Delta \delta_{\text{H-16}}$: -0.10) of the (*S*)- and (*R*)-MTPA esters of **3**(**3a** and **3b**) indicated the *S* configuration for C-15 in **3**.

Figure S1. HRESIMS spectrum of 1

Monoisotopic Mass, Even Electron Ions 21 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass) Elements Used: C: 0-20 H: 0-30 O: 0-10 09-Mar-2017 J5-3-1-1-2 97 (6.709) 1: TOF MS ES-7.74e+007 307.1197 923.3669 977.2747 1185.2880 375.1066 457.1092 615.2449 651.2203 100 1356.3043 1284.4010 112.9864263.1299 m/z 1200 1300 1400 1500 900 100 300 500 700 200 400 600 800 1000 1100 Minimum: -1.5 2.0 10.0 50.0 Maximum: Mass DBE Calc. Mass mDa PPM i-FIT Norm Conf(%) Formula 307.1197 307.1182 1.5 4.9 7.5 837.5 n/a n/a C16 H19 O6

Figure S2. ¹H NMR spectrum of 1 in CD₃OD (500 MHz)







Figure S4. ¹H-¹H COSY spectrum of 1 in CD₃OD





Figure S5. HSQC spectrum of 1 in CD₃OD



Figure S6. HMBC spectrum of 1 in CD₃OD



Figure S7. HRESIMS spectrum of 2

Monoisotopic Mass, Even Electron Ions 21 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass) Elements Used: C: 0-20 H: 0-30 O: 0-10 09-Mar-2017 J5-3-1-2-2 100 (6.918) 306.1107 307.1193 308.1225 310.1271 314.8340 315.9572 321.0979 322 1054 323.1134 325.1244 326 9505 100- 297,2436 ----

11	301.	/186	1				314.8340 /		13	22.1054/	1	_326.9505m/z
297.5	300.0	302.5	305.0	307.5	310.0	312.5	315.0	317.5	320.0	322.5	325.0	327.5
Minimum: Maximum:		2.0	10.0	-1.5 50.0								
Mass	Calc. Ma	ss mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula	1			
307.1193	307.1182	1.1	3.6	7.5	759.2	n/a	n/a	C16 H19	06			

1: TOF MS ES-5.20e+007 Figure S8. ¹H NMR spectrum of 2 in CD₃OD (500 MHz)





Figure S9. ¹³C NMR spectrum of 2 in CD₃OD (125 MHz)

Figure S10. ¹H-¹H COSY spectrum of 2 in CD₃OD





Figure S11. HSQC spectrum of 2 in CD₃OD



Figure S12. HMBC spectrum of 2 in CD₃OD

Figure S13. HRESIMS spectrum of 3

Monoisotopic Mass, Even Electron Ions 21 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass) Elements Used: C: 0-20 H: 0-30 O: 0-10 09-Mar-2017 J5-3-1-4-1 102 (7.053) Cm (101:104)

1: TOF MS ES-4.81e+008

100	264.1	354		289.1085	308.	1250	322.10	037	344.101	10 34	54.1290	376.112	20	390.1270	4	08.0484	422.11	68 m/z
0.11	260	270	280	290	300	310	320	330	340	350	360	370 3	80	390	400	410	420	430
Minimu Maximu	am: am:			2.0	10.0	5	1.5											
Mass		Calc.	Mass	mDa	PPM	D	BE	i-FIT	Norm	Cor	nf(%)	Formula						
307.11	191	307.1	182	0.9	2.9	7	.5	1345.6	n/a	n/a	a	C16 H19	06					

Figure S14. ¹H NMR spectrum of 3 in CD₃OD (500 MHz)



Figure S15. ¹³C NMR spectrum of 3 in CD₃OD (125 MHz)



Figure S16. ¹H-¹H COSY spectrum of **3** in CD₃OD





Figure S17. HSQC spectrum of 3 in CD₃OD





Figure S19. HRESIMS spectrum of 4

307.0818

19.6

Monoisotopic Mass, Even Electron Ions 13 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass) Elements Used: C: 14-18 H: 0-50 O: 4-8 08-Nov-2016 1108-J5-3-1-5-1 80 (3.102) Cm (79:81) 1: TOF MS ES-6.46e+007 263.1024 307.1014 108 615.2509 967,3849,1012.3167 1284.50631323.4640 467.9517 740.1312 m/z 600 500 700 800 900 1000 1400 400 1200 100 200 300 1100 1300 1500 Minimum: -1.5 Maximum: 20.0 10.0 50.0 Mass Calc. Mass PPM DBE i-FIT mDa Norm Conf(%) Formula 307.1014 307.1182 -16.8 -54.7 7.5 1092.4 0.592 55.31 C16 H19 06

1092.6 0.805 44.69 C15 H15 07

8.5

63.8

Figure S20. ¹H NMR spectrum of 4 in CD₃OD (500 MHz)







Figure S22. ¹H-¹H COSY spectrum of **4** in CD₃OD





Figure S23. HSQC spectrum of 4 in CD₃OD



Figure S24. HMBC spectrum of 4 in CD₃OD