Potent Cytotoxic Arylnaphthalene Lignan Lactones from *Phyllanthus poilanei*

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Figure S18. COSY (—) and the key HMBC (↷) NMR correlations of compounds 2–8.

Figure S19. Selected NOESY ($\curvearrowright$, $^1\text{H} \rightarrow ^1\text{H}$) correlations of compounds **2–5** and **7**.

Table S1. ¹H NMR Spectroscopic Data of Compounds 3–5^a

position	3 ^b	4 ^c	5 ^d
3	7.00 s	6.98 br s	7.11 br s
6	8.17 s	8.18 br s	8.28 s
9	5.40 d (8.4 ^e)	5.47 d (15.2)	5.45 dd (15.0, 3.0 ^e)
	5.51 d (7.8 ^e)	5.55 d (15.2)	5.77 dd (15.0, 3.0 ^e)
2'	6.94 s	6.93 br s	6.90 dd (15.6 ^e , 1.2)
5'	7.06 d (12.0 ^e)	7.05 d (8.0)	6.99 dd (7.8, 1.8)
6'	6.81 d (12.0 ^e)	6.81 dd (8.0, 1.6)	6.85 m
1''	4.84 t (10.2)	4.81 t (6.8)	4.95 d (7.8)
2''	3.88 br d (19.2 ^e)	3.86 m	3.71 m
3''	3.80 m	3.52 m	3.56 m
4''	4.99 br s	3.71 br s	3.50 m
5'' _{ax}	3.68 overlapped	3.46 d (11.2)	3.42 m
5'' _{eq}	3.96 overlapped	3.79 m	
6''			3.85 m
			3.97 br d (10.2)
MeO-4	3.68 overlapped	3.67 s	3.74 s
MeO-5	3.96 overlapped	3.95 s	4.01 s
OCH ₂ O-3',4'	6.14 s	6.13 br s	6.09 s
	6.14 s		6.10 s
AcO-4''	2.12 s		

^aChemical shifts were assigned based on the analysis of 1D- and 2D-NMR spectra. The overlapped signals were determined by analysis of the ¹H–¹H COSY, HSQC, and HMBC spectra without designating multiplicity (s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, dd = double doublet, t = triplet, m = multiplet). Proton coupling constant *J* (in parentheses) values are presented in Hz and were omitted if the signals overlapped as multiplets.

^bData (δ) recorded at 600.2 MHz in DMSO-*d*₆ and referenced to the solvent residual peak at δ 2.50.³⁴

^cData (δ) recorded at 400.1 MHz in DMSO-*d*₆ and referenced to the solvent residual peak at δ 2.50.³⁴

^dData (δ) measured at 600.2 MHz in acetone-*d*₆ and referenced to the solvent residual peak at δ 2.05.³⁴

^eThe unusual value may result from the rotation conformation of the D ring.

Table S2. ^{13}C NMR Spectroscopic Data of Compounds of 3–5^a

position	3 ^b	4 ^c	5 ^d
1	126.6 C	126.6 C	128.2 C
2	129.8 C	129.7 C	131.3 C
3	105.5 CH	105.4 CH	106.6 CH
4	150.0 C	150.0 C	151.4 C
5	151.5 C	151.4 C	153.0 C
6	101.7 CH	101.9 CH	102.6 CH
7	144.7 C	144.6 C	146.15/146.14 ^f C
8	129.4 C	128.98/128.81 ^f C	131.59/131.56 ^f C
9	67.0 CH ₂	67.1 CH ₂	68.1 CH ₂
1'	128.2 C	128.3 C	129.8 C
2'	110.86/110.76 ^f CH	110.91/110.83 ^f CH	111.76/111.69 ^f CH
3'	146.9 C	146.9 C	148.3 C
4'	146.9 C	146.9 C	148.2 C
5'	108.0 CH	108.0 CH	108.6 CH
6'	123.59/123.55 ^f CH	123.6 CH	124.5 CH
7'	134.9 C	134.55/134.50 ^f C	136.4 C
8'	118.7 C	118.7 C	120.1 C
9'	169.0 C	169.1 C	169.9 C
1''	105.14/105.06 ^f CH	104.90/104.78 ^f CH	106.3 CH
2''	71.2 CH	70.8 CH	75.2 CH
3''	70.4 CH	72.3 CH	78.1 CH
4''	70.7 CH	67.32/67.27 ^f CH	71.4 CH
5''	63.7 CH ₂	65.79/65.73 ^f CH ₂	78.2 CH
6''			62.8 CH ₂
MeO-4	55.2 CH ₃	55.2 CH ₃	55.7 CH ₃
MeO-5	55.8 CH ₃	55.9 CH ₃	56.4 CH ₃
OCH ₂ O-3',4'	101.1 CH ₂	101.1 CH ₂	102.1 CH ₂
AcO-4''	170.1 C		
	21.1 CH ₃		

^aChemical shifts were assigned based on the analysis of 1D- and 2D-NMR spectra. CH₃, CH₂, CH, and C multiplicities were determined by DEPT 90, DEPT 135, and HSQC experiments.

^bData (δ) measured at 150.9 MHz in DMSO-*d*₆ and referenced to the solvent residual peak at δ 39.52.³⁴

^cData (δ) measured at 100.6 MHz in DMSO-*d*₆ and referenced to the solvent residual peak at δ 39.52.³⁴

^dData (δ) measured at 100.6 MHz in acetone-*d*₆ and referenced to the solvent residual peak at δ 29.84.³⁴

^fExist in pairs.

Table S3. ¹H NMR Spectroscopic Data of Compounds 6–8^a

position	6 ^b	7 ^b	8 ^c
3	7.21 s	7.07 s	7.09 s
6	7.56 s	7.54 s	7.70 s
9	5.55 br s	5.50 d (15.6)	5.37 s
		5.44 dd (14.8, 1.6)	
2'	6.78 overlapped	6.82 overlapped	6.85 d (1.2)
5'	6.95 d (7.6)	6.97 d (8.0)	6.97 d (8.0)
6'	6.78 overlapped	6.82 overlapped	6.82 dd (8.0, 1.6)
1''		5.10 d (7.2)	
2''		5.72 dd (9.6, 7.2)	
3''		5.19 dd (9.6, 3.6)	
4''		5.38 br s	
5'' _{ax}		3.73 br d (12.8)	
5'' _{eq}		4.21 dd (13.2, 2.8)	
MeO-4		3.81 s	3.73 s
MeO-5	4.10 s	4.09 s	4.00 s
MeO-7	4.13 s		
OCH ₂ O-3',4'	6.05 s	6.05 s	6.08 s
	6.06 s	6.10 s	6.09 s
AcO-2''		^d 2.08 s	
AcO-3''		^d 2.12 s	
AcO-4''		^d 2.22 s	
HO-4	5.96 s		

^aChemical shifts were assigned based on the analysis of 1D- and 2D-NMR spectra. The overlapped signals were determined by analysis of the ¹H–¹H COSY, HSQC, and HMBC spectra without designating multiplicity (s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, dd = double doublet, m = multiplet). Proton coupling constant *J* (in parentheses) values are presented in Hz and were omitted if the signals overlapped as multiplets.

^bData (δ) recorded at 400.1 MHz in CDCl₃ and referenced to the solvent residual peak at δ 7.26.³⁴

^cData (δ) measured at 400.1 MHz in acetone-*d*₆ and referenced to the solvent residual peak at δ 2.05.³⁴

^dInterchangeable signals.

Table S4. ^{13}C NMR Spectroscopic Data of Compounds of 6–8^a

position	6 ^b	7 ^b	8 ^c
1	125.8 C	126.3 C	124.5 C
2	131.4 C	130.9 C	131.1 C
3	109.9 CH	106.4 CH	106.8 CH
4	146.8 C	150.5 C	151.3 C
5	149.4 C	152.1 C	152.1 C
6	100.3 CH	100.6 CH	101.3 CH
7	148.0 C	144.3 C	145.7 C
8	123.9 C	127.4 C	122.8 C
9	66.8 CH ₂	67.0 CH ₂	67.0 CH ₂
1'	128.5 C	128.3 C	130.2 C
2'	111.0 CH	110.8 CH	112.0 CH
3'	147.5 C	147.7 C	148.3 C
4'	147.5 C	147.7 C	148.0 C
5'	108.3 CH	108.4 CH	108.6 CH
6'	123.8 CH	123.69/123.67 CH ^e	124.8 CH
7'	134.8 C	136.4 C	131.6 C
8'	119.6 C	119.4 C	120.0 C
9'	169.7 C	169.6 C	170.2 C
1''		101.6 CH	
2''		69.5 CH	
3''		70.3 CH	
4''		67.39/67.01 CH ^e	
5''		64.1 CH ₂	
MeO-4		56.0 CH ₃	55.7 CH ₃
MeO-5	56.4 CH ₃	56.4 CH ₃	56.1 CH ₃
MeO-7	59.8 CH ₃		
OCH ₂ O-3',4'	101.3 CH ₂	101.4 CH ₂	102.1 CH ₂
AcO-2''		^f 170.4 C	
		^g 20.9 CH ₃	
AcO-3''		^f 170.3 C	
		^g 21.1 CH ₃	
AcO-4''		^f 169.6 C	
		^g 21.1 CH ₃	

^aChemical shifts were assigned based on the analysis of 1D- and 2D-NMR spectra. CH₃, CH₂, CH, and C multiplicities were determined by DEPT 90, DEPT 135, and HSQC experiments.

^bData (δ) measured at 100.6 MHz in CDCl₃ and referenced to the solvent residual peak at δ 77.16.³⁴

^cData (δ) measured at 100.6 MHz in acetone-*d*₆ and referenced to the solvent residual peak at δ 29.84.³⁴

^eExist in pairs.

^fInterchangeable signals.

^gInterchangeable signals.

Analytical data of known compounds (**3–8**) isolated from *Phyllanthus poilanei*.

Phyllanthusmin B (**3**): Amorphous colorless powder showing a blue color under UV light at 365 nm; $[\alpha]_D^{20} -6$ (*c* 0.1, CHCl₃); UV (MeOH) $\lambda_{\max}$ (log ϵ) 260 (4.62) nm; ECD (MeOH, nm) $\lambda_{\max}$ ($\Delta\epsilon$) 297 (–4.12); IR (dried film) $\nu_{\max}$ 3364, 1723, 1615, 1505, 1480, 765 cm^{–1}; ¹H and ¹³C NMR data, see Tables S1 and S2; positive-ion HRESIMS *m/z* 577.1317, calcd for C₂₈H₂₆O₁₂Na, 577.1316.

Phyllanthusmin C (**4**): Amorphous colorless powder showing a blue color under UV light at 365 nm; $[\alpha]_D^{20} -8$ (*c* 0.1, CHCl₃); UV (MeOH) $\lambda_{\max}$ (log ϵ) 260 (4.35) nm; ECD (MeOH, nm) $\lambda_{\max}$ ($\Delta\epsilon$) 292 (–3.19); IR (dried film) $\nu_{\max}$ 3373, 1734, 1619, 1507, 1480, 767 cm^{–1}; ¹H and ¹³C NMR data, see Tables S1 and S2; positive-ion HRESIMS *m/z* 535.1237, calcd for C₂₆H₂₄O₁₁Na, 535.1210.

Cleistanthin B (**5**): Amorphous colorless powder showing a blue color under UV light at 365 nm; $[\alpha]_D^{20} -53$ (*c* 0.1, MeOH); UV (MeOH) $\lambda_{\max}$ (log ϵ) 260 (4.73) nm; ECD (MeOH, nm) $\lambda_{\max}$ ($\Delta\epsilon$) 301 (–4.94); IR (dried film) $\nu_{\max}$ 3390, 1739, 1713, 1622, 1506, 1481, 770 cm^{–1}; ¹H and ¹³C NMR data, see Tables S1 and S2; positive-ion HRESIMS *m/z* 565.1321, calcd for C₂₇H₂₆O₁₂Na, 565.1316.

Phyllanthusmin A (**6**): Amorphous colorless powder showing a blue color under UV light at 365 nm; UV (MeOH) $\lambda_{\max}$ (log ϵ) 262 (4.61) nm; IR (dried film) $\nu_{\max}$ 3447, 1766, 1716, 1597, 1508, 1480, 752 cm^{–1}; ¹H and ¹³C NMR data, see Tables S3 and S4; positive-ion HRESIMS *m/z* 403.0794, calcd for C₂₁H₁₆O₇Na, 403.0788.

7-*O*-[(2,3,4-tri-*O*-acetyl)- α -L-arabinopyranosyl]diphyllin (**7**): Amorphous colorless powder showing a blue color under UV light at 365 nm; $[\alpha]_D^{20} -12$ (*c* 0.1, CHCl₃); UV (MeOH) $\lambda_{\max}$ (log ϵ) 260 (4.45) nm; ECD (MeOH, nm) $\lambda_{\max}$ ($\Delta\epsilon$) 295 (–3.87); IR (dried film) $\nu_{\max}$ 1749, 1619,

1506, 1480, 770 cm^{-1} ; ^1H and ^{13}C NMR data, see Tables S3 and S4; positive-ion HRESIMS m/z 661.1553, calcd for $\text{C}_{32}\text{H}_{30}\text{O}_{14}\text{Na}$, 661.1527.

Diphyllin (**8**): Amorphous colorless powder showing a blue color under UV light at 365 nm; UV (MeOH) λ_{max} ($\log \epsilon$) 267 (4.59) nm; IR (dried film) ν_{max} 1705, 1615, 1506, 1489, 774 cm^{-1} ; ^1H and ^{13}C NMR data, see Tables S3 and S4; positive-ion HRESIMS m/z 403.0797, calcd for $\text{C}_{21}\text{H}_{16}\text{O}_7\text{Na}$, 403.0788.