Supplementary Materials: Phytoconstituents with Radical Scavenging and Cytotoxic Activities from *Diospyros shimbaensis*

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1. NMR and Mass Spectra of 8,8′-Oxo-biplumbagin (1)

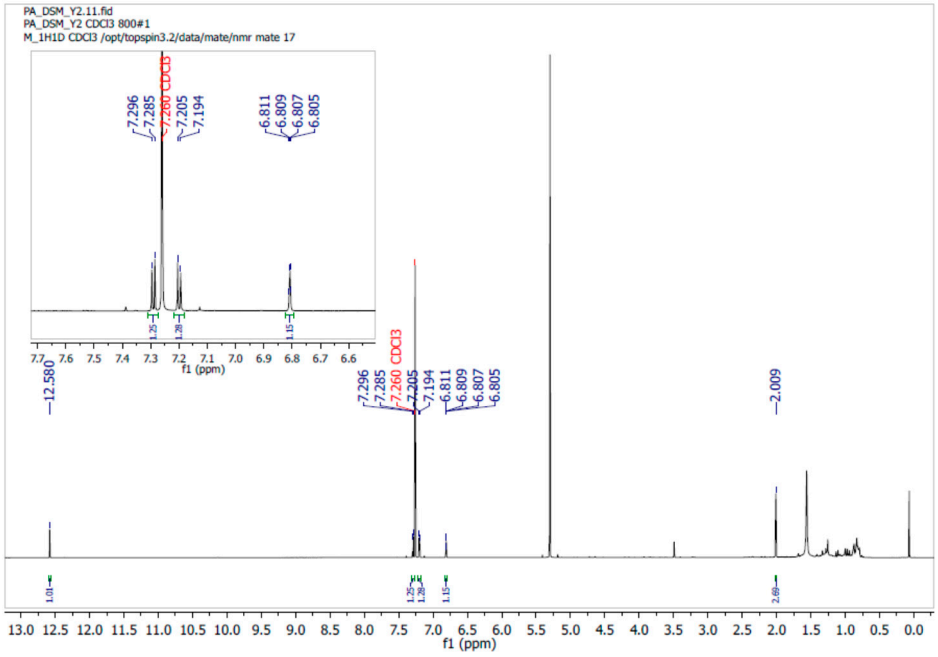

Figure S1. The ^{1}H-NMR spectrum of 8,8′-oxo-biplumbagin (**1**, $CDCl_3$, 25 °C, 799.88 MHz).

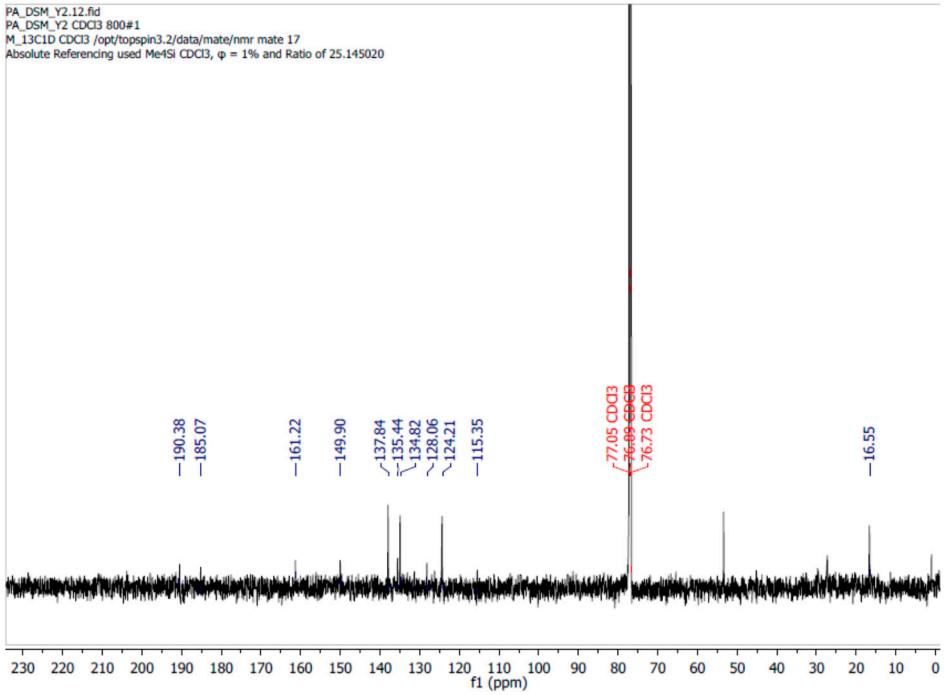

Figure S2. The ^{13}C-NMR spectrum of 8,8′-oxo-biplumbagin (**1**, $CDCl_3$, 25 °C, 201.20 MHz).

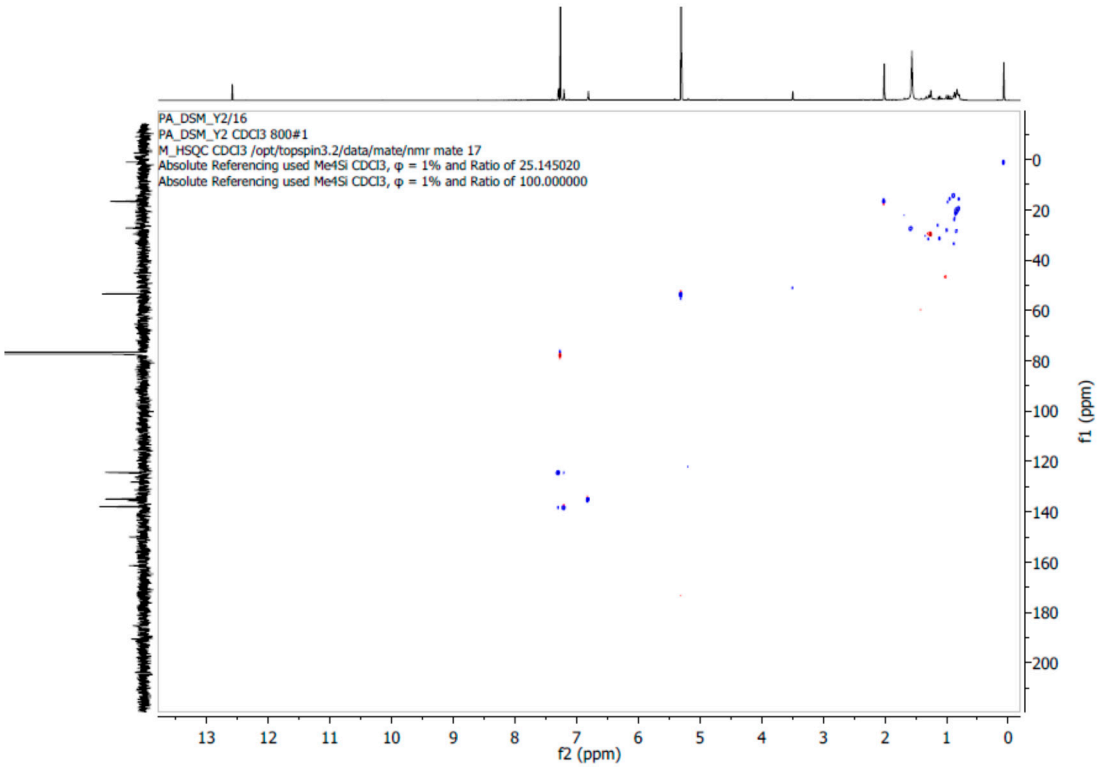

Figure S3. The ^{1}H-, ^{13}C-HSQC spectrum of 8,8′-oxo-biplumbagin (**1**, $CDCl_3$, 25 °C, 201.20 MHz).

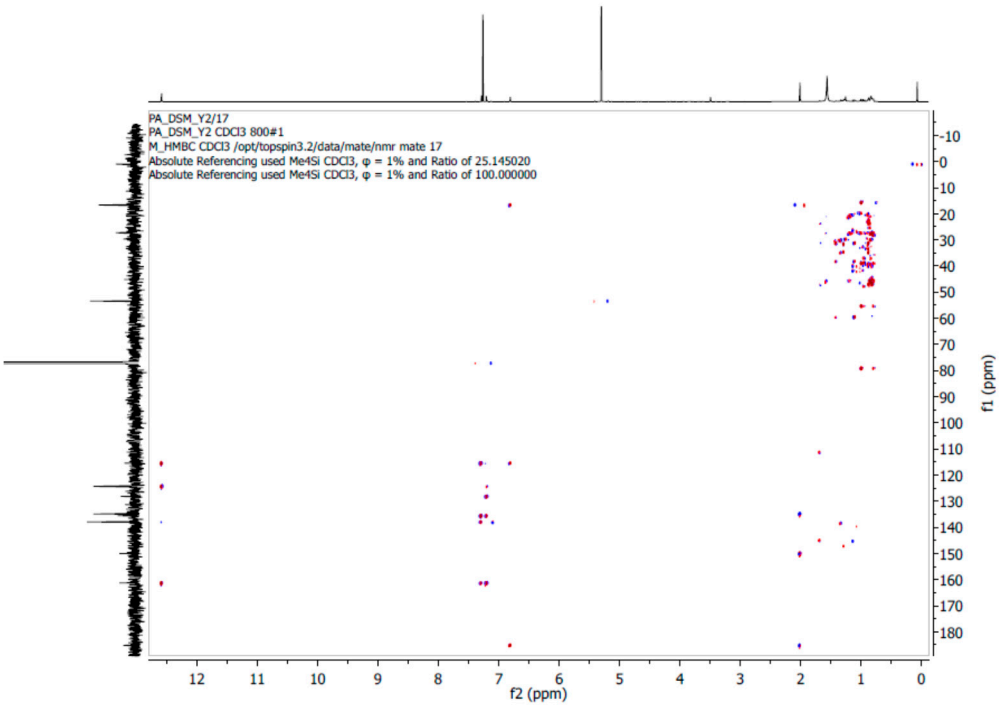

Figure S4. The ^{1}H-, ^{13}C-HMBC spectrum of 8,8′-Oxo-biplumbagin (**1**, $CDCl_3$, 25 °C, 201.20 MHz).

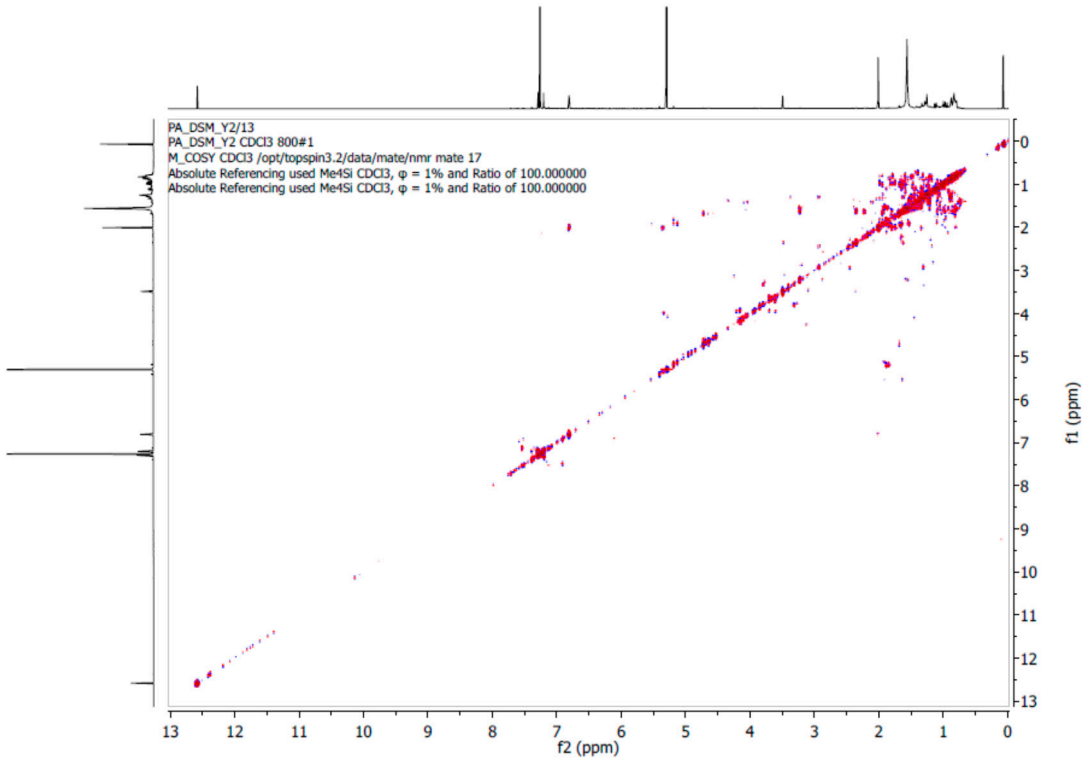

Figure S5. The ^{1}H-^{1}H COSY spectrum of 8,8′-oxo-biplumbagin (**1**, $CDCl_3$, 25 °C, 799.88 MHz).

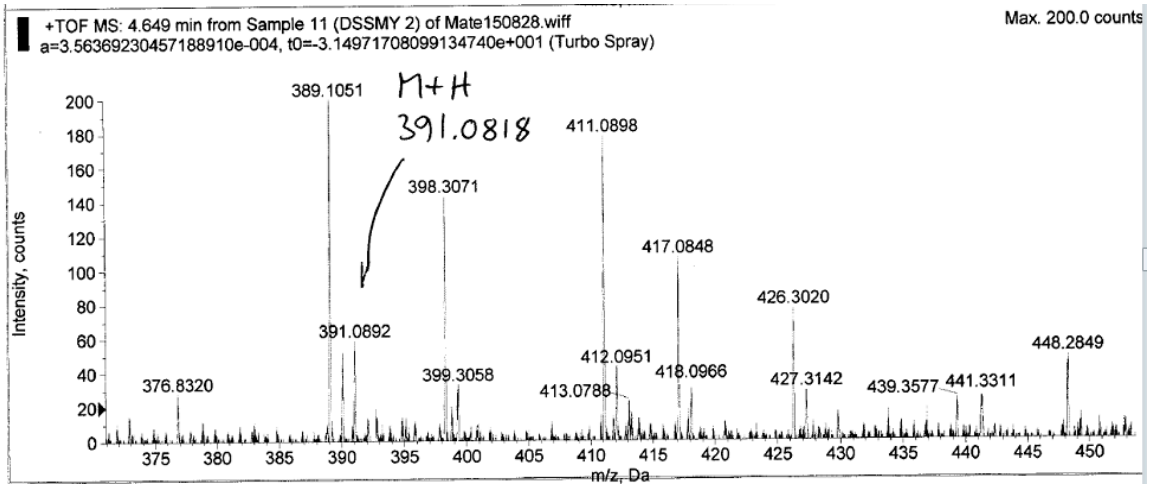

Figure S6. The HR (ESI) mass spectrum of 8,8′-oxobiplumbagin (**1**).

2. Spectroscopic Data of the Known Compounds 2–5

trans-Isoshinanolone (**2**) [1]. White amorphous solid. ^{1}H-NMR ($CDCl_3$, 25 °C) δ (799.88 MHz, ppm): 1.19 (3H, *d*, *J* = 6.6 Hz, C-11), 1.92 (1H, *d*, *J* = 6.6 Hz, 1-OH), 2.29 (1H, *dddq*, *J* = 10.1, 7.3, 6.6, 4.1 Hz, H-2), 2.44 (1H, *dd*, *J* = 17.4, 10.1 Hz, H-3a), 2.93 (1H, *dd*, *J* = 17.4, 4.2 Hz, H-3b), 4.51 (1H, *brt*, *J* = 6.9 Hz, H-1), 6.94 (1H, *dd*, *J* = 8.4, 0.9 Hz, H-6), 7.12 (1H, *t*, *J* = 8 Hz, H-8), 7.51 (1H, *dd*, *J* = 8.4, 7.6 Hz, H-7), 12.48 (1H, *s*, 5-OH); ^{13}C-NMR ($CDCl_3$, 25 °C) δ (201.20 MHz, ppm), 18.0 (C-11), 37.7 (C-2), 43.6 (C-3), 73.9 (C-1), 115.5 (C-10), 117.3 (C-8), 117.5 (C-6), 137.2 (C-7), 146.0 (C-9), 162.7 (C-5), 204.8 (C-4). IR ($CHCl_3$) cm^{-1}: 3620, 1617. GC-MS (70 eV): *m*/*z* 192 $[M]^+$ (100), 177 (25), 150 (45), 121 (90).

cis-Isoshinanolone (**3**) [28]. White amorphous solid. ^{1}H-NMR ($CDCl_3$, 25 °C) δ (799.88 MHz, ppm): 1.2 (3H, *d*, *J* = 6.9 Hz, 2-CH_3), 2,4 (1H, *dddq*, *J* = 11.0, 7.0, 4.2, 2.8 Hz, H-2), 2.9 (1H, *J* = 17.5 11.0·Hz, H-3a), 2.6 (1H, *dd*, *J* = 17.5, 4.3·Hz, H-3b), 4.8 (1H, *d*, *J* = 2.8 Hz, H-1), 6.9 (1H, *dd*, *J* = 8.5 1.1·Hz, H-6), 6.9 (1H, *d*, *J* = 7.4 Hz, H-8); 7.5 (1H, *dd*, *J* = 8.4, 7.4· Hz), 12.4 (1H, *s*, 5-OH). ^{13}C-NMR ($CDCl_3$, 25 °C) δ (201.20 MHz,

ppm): 16.3 (C-11), 34.6 (C-2), 40.9 (C-3), 71.3 (C-1), 115.1 (C-10), 118.4 (C-8), 118.8 (C-6), 137.1 (C-7), 145.1 (C-9), 162.9 (C-5), 204.9 (C-4). IR ($CHCl_3$) cm^{-1}: 3619, 1619. GC-MS (70 eV): *m/z* 192 $[M]^+$ (50), 177 (10), 150 (25), 121 (100).

Plumbagin (**4**) [21]. Yellow armophous solid. ^{1}H-NMR ($CDCl_3$, 25 °C) δ (799.88 MHz, ppm): 2.19 (3H, *d*, *J* = 1.6 Hz, 2-CH_3), 6.81 (1H, *q*, *J* = 1.6Hz, H-3), 7.25 (1H, *d*, *J* = 1.2 Hz, H-6), 7.60 (1H, *t*, *J* = 7.9 Hz, H-7), 7.64 (1H, *dd*, *J* = 7.5, ·1.2 Hz), 11.98 (1H, s, 5-OH). ^{13}C-NMR ($CDCl_3$, 25 °C) δ (201.20 MHz, ppm): 16.7 (C-11), 115.3 (C-10), 119.5 (C-8), 124.3 (C-6), 132.2 (C-9), 135.6 (C-3), 136.3 (C-7), 149.8 (C-2), 162.0 (C-5) 185.0 (C-1), 190.4 (C-4). IR ($CHCl_3$) cm^{-1}: 3611, 1584. GC-MS (70eV): *m/z* 188 $[M]^+$ (100), 173 (25), 131 (45), 92 (25).

3,3′-Biplumbagin (**5**) [21]. Yellow armophous solid. ^{1}H-NMR ($CDCl_3$, 25 °C) δ (799.88 MHz, ppm): 2.08 (6H, s, 2-CH_3), 7.30 (2H, *dd*, *J* = 1.3, 8.4 Hz, H-6 and H-6′), 7.67 (2H, *t*, *J* = 8.0 Hz, H-7 and H-7′), 7.77 (2H, *dd*, *J* = 1.3, 7.5 Hz, H-8 and H-8′), 11.81 (2H, *s*, 5-OH and 5′-OH). ^{13}C-NMR ($CDCl_3$, 25 °C) δ (201.20 MHz, ppm): 16.7 (C-11 and C-11′), 115.3 (C-10 and C-10′), 119.5 (C-8 and C-8′), 124.3 (C-6 and C-6′), 132.2 (C-9 and C-9′), 135.6 (C-3 and C-3′), 136.3(C-7 and C-7′), 149.8 (C-2 and C-2′), 161.3 (C-5 and C-5′), 184.9 (C-1 and C-1′), 190.4 (C-4 and C-4′). GC-MS (70eV): *m/z* 374 $[M]^+$ (96), 331 (47), 303 (75), 278 (47), 250 (47).

3. NAMFIS Analysis

Table S1. Monte Carlo conformational analysis for compounds **2** and **3**.

***trans*-Isoshinanolone (2)**	***cis*-Isoshinanolone (3)**
M σ% = 0.979D + 02	M σ% = 0.614D + 02
Conformation 1 = 10%	Conformation 1 = 88%
Conformation 2 = 81%	Conformation 2 = 12%
Conformation 3 = 1%	
Conformation 4 = 9%	

All other molar fractions are 0.00.

Tables S2. Best fit solution for compounds **2** and **3**.

***trans*-Isoshinanolone (2)**			***cis*-Isoshinanolone (3)**		
Assign.	**Exp.**	**Calc.**	**Assign.**	**Exp.**	**Calc.**
Interproton distances (Å)			**Interproton distances (Å)**		
H1-OH	3.40	3.23	H1-2	2.10	2.40
H1-H2	2.80	2.82	H1-Me	2.80	2.85
H3a—H1	2.80	2.79	H3a-H4	3.50	3.50
H3b-H2	2.30	2.47	H3a-Me	2.60	2.79
H3b-Me	3.00	2.86	H3b-Me	2.90	2.85
H3a-Me	2.80	2.75			
RMSD = 0.40			RMSD = 0.16		
Coupling constants (Hz)			**Coupling constants (Hz)**		
H1-H2	8.2	7.6	H1-H2	2.8	2.3
H2-H3a	4.6	4.1	H2-H3a	4.3	3.5
H2-H3b	10.1	10.4	H2-H3b	10.9	10.7
RMSD = 0.47			RMSD = 0.55		

4. Antioxidant Assay

Table S3. DPPH radical scavenging activity (RSA) of compounds isolated from *D. shimbaensis*.

% RSA	Concentration (μM)			
	25.0	**12.5**	**6.25**	**3.13**
Compound **1**	41.2	38.5	34.8	32.0
Compound **2**	43.9	42.8	32.4	31.7
Compound **3**	58.7	49.1	41.5	38.1
Compound **4**	40.5	36.8	36.4	32.9
Compound **5**	42.6	38.2	35.7	30.7

5. Cytotoxicity Assay

Table S4. Cytotoxicity data of the constituents of *D. shimbaensis*, and of its crude extracts suing various solvents. The data was obtained on a MDA-MB-231 breast cancer cell assay.

Compound	IC_{50} (μg/mL)	95% Confidence Interval
2	>100	-
3	50.11848	-
4	24.62663	1.897 to 258.9
5	30.68116	6.054 to 278.4
DSLD Crude	72.97427	-
DSRM Crude	>100	-
DSLM Crude	44.74559	24.03 to 697.8
DSSM Crude	59.56605	1.951 to 148502
DSRH Crude	16.1141	1.285 to 374.6
DSRD Crude	29.74992	8.371 to 133.2

DSSM (methanol crude extract from the stem barks); **DSRH** (isohexane crude extract from the root barks); **DSRD** (dichloromethane crude extract from the root barks); **DSRM** (methanol crude extract from the root barks); **DSLD** (dichloromethane crude extract from the leaves); **DSLM** (methanol crude extract from the leaves).

References

1. Bringmann, G.; Pfeifer, R.M.; Breuning, M.; Reichert, M.; Messer, K.; Schraut, M.; Tóth, G. Structure of *trans*-isoshinanolone in the crystal and in solution. *Z. Naturforsch.* **2004**, *59*, 100–105.