

SUPPLEMENTARY MATERIAL

Neuroprotective triterpene saponins from the leaves of *Panax notoginseng*

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Abstract: Two new triterpene saponins, namely notoginsenoside Ng5 (**1**) and notoginsenoside Ng6 (**2**) were isolated from the leaves of *Panax notoginseng*, along with five known ones. Their structures were determined by chemical methods, NMR and X-ray experiments. The absolute configuration of compound **3** with four sugar units was confirmed by single crystal X-ray analysis. Compounds **2–4** and **6** inhibited PC12 cell damage induced by serum deprivation, and increased cell viability from $58.7 \pm 6.7\%$ to $66.7 \pm 4.5\%$, $76.1 \pm 6.1\%$, $64.7 \pm 5.2\%$ and $67.2 \pm 5.0\%$ at 10 μM , respectively.

Keywords: *Panax notoginseng* leaves; triterpene saponins; neuroprotective

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SI-1. Instruments and chemicals.

Column Chromatography (CC) was performed with 200-300 mesh silica gel, D101 macroporous resin, diatomite, PRP-512B and Sephadex LH-20 gel. Thin layer chromatography (TLC) was conducted on prefabricated silica gel plate HSGF₂₅₄, and visualized by spraying *n*-butanol solution (0.93 mL aniline, 1.66 g phthalic acid, 100.0 mL *n*-butanol) followed by heating (Zhao et al. 1987). A JASCO V-650 spectrophotometer was used to record UV spectra (Japan). Optical rotations were taken with a JASCO P2000 digital polarimeter (Japan). IR (microscope) spectra were conducted by a Nicolet 5700 instrument (USA). HR-ESI-MS were recorded using an Agilent 1100 series LC/MS ion trap mass apparatus (USA). VNS-600 (USA) was used to acquire NMR spectra. The sugars determinations were performed on Agilent 7890A GC apparatus (Germany). Single-crystal X-ray diffraction data were taken with an Agilent Xcalibur Eos Gemini diffractometer (USA) with Cu K α radiation.

SI-2. Extraction and isolation.

The air-dried leaves of *P. notoginseng* (25 kg) were successively extracted with ethyl alcohol and water. The ethanolic extract, was applied to a diatomite column [PE, CHCl₃, ACTN, ACTN/EtOH (4:1, v/v), ACTN/EtOH (1:1, v/v), EtOH, MeOH] to obtain 7 fractions: F1–F7. The water extract was loaded to a D101 column (100 cm × 20 cm), eluting with EtOH/H₂O (gradient: 0:1→95:5) to afford 4 fractions: W1–W4.

F6 (1336 g) was loaded to a D101 column [alcohol solvent (0, 30%, 50%, 95%)] and divided into 4 sub-fractions (F6.1–F6.4). F6.4 (360 g) was divided into 26 additional fractions (F6.4.1–F6.4.26) by silica gel column (EtOAc/MeOH/H₂O, 9:1:0.5 → 2:1:0.5). F6.4.3 (12.0 g) was separated into 30 parts (F6.4.3.1–F6.4.3.30) by C18 MPLC (30–70–100% MeOH, 0–5–9 h). F6.4.3.24 was purified by p-HPLC, eluting with MeCN-H₂O (24:76, v/v) to obtain compound **4** (18 mg). Compound **5** (6 mg) was isolated from F6.4.3.25 by p-HPLC with MeOH-H₂O (55:45, v/v). F6.4.14 (18.0 g) was separated into 45 parts (F6.4.14.1–F6.4.14.45) by C18 MPLC (50–70% MeOH, 9h). Compounds **3** (25 mg) was prepared from F6.4.14.18 with MeCN-H₂O (20:80, v/v). Compounds **6** (10 mg) was isolated from F6.4.14.33 by p-HPLC (MeCN-H₂O, 20:80, v/v). Compound **7** (8 mg) was obtained from F6.4.14.40 by p-HPLC with MeOH-H₂O (65:35, v/v).

W4 (90.0 g) was carried out on a PRP-512B column [alcohol solvent (10%, 30%, 50%, 60%, 80%, 95%)] and divided into 6 fractions: W4.1–W4.6. W4.2 (13.0 g) was divided into 5 sub-fractions (W4.2.1–W4.2.5) by Sephadex LH-20 gel CC, eluted with methanol. W4.2.5 (5.0 g) was separated into 50 additional fractions (W4.2.5.1–W4.2.5.50) by C18 MPLC (60–60–80% MeOH, 0–10–13h). Compound **2** (8 mg) was isolated from W4.2.5.21 by p-HPLC with 30% MeCN-H₂O (30:70, v/v). In a similar way, W4.4 (16 g) was separated into 33 sub-fractions (W4.4.1–W4.4.33) by C18 MPLC (75% MeOH-H₂O, 10h), and compound **1** (20 mg) was prepared from W4.4.4 by p-HPLC with 40% MeCN-H₂O (40:60, v/v).

SI-3. Acid hydrolysis of new saponins (1 and 2).

Compounds **1** and **2** (3 mg each) were heated with 3.0 mL HCl (2.5 N) at 90 °C for 12 h. After cooling, 3.0 mL water was added into each reaction mixture and then extracted by ethyl acetate (6.0 mL × 3). Then the aqueous layer residues were compared with authentic sugars through TLC. The sugars were determined as glucose and xylose in compound **1**; glucose, xylose and arabinose in compound **2**.

SI-4. Absolute configuration of sugars.

The sugar components were obtained as described above. According to the literature reported (Ma et al. 2017), 2.0 mg L-cysteine methyl ester hydrochloride and 1.0 mL superdry pyridine were added into the residues at 60 °C, and stirring for 2 h. As soon as the reaction mixture was dried under N₂, 0.4 mL *N*-trimethylsilylimidazole was treated and heated at 60 °C for another 2 h. Then water (2 mL) and *n*-hexane (4 mL × 3) were used to extract the reaction mixture. The supernatant was injected into GC and analyzed with selected conditions: HP-5 capillary column; carrier gas, nitrogen, 1.5 mL/min; H₂ flame ionization detector; injector and detector temperature, 300 °C; injection volume, 2.0 µL; initial temperature at 200 °C, and raised to the final temperature at 280 °C with a speed at 10 °C/min, maintaining the final temperature for 35 min.

References

- Ma J, Li CJ, Yang JZ, Li Y, Bao XQ, Chen NH, Zhang DM. 2017. Three new coumarin glycosides from the stems of *Hydrangea paniculata*. *J Asian Nat Prod Res.* 19(4):320-326.
- Zhao PP, Li BM, He LY. 1987. Studies on the method of determination of combined sugars in glycosides. *Acta Pharm Sin.* 22(1):70-74.

Table S1. ^{13}C and ^1H NMR (150 MHz, 600 MHz in $\text{C}_5\text{D}_5\text{N}$) data of compounds **1** and **2**.

position	1		2	
	δ_{C}	δ_{H}	δ_{C}	δ_{H}
1	39.2	1.54 (o), 0.75 (t, 12.0)	39.2	1.53 (o), 0.76 (t, 12.0)
2	26.6	1.84 (o), 1.36 (o)	26.8	2.18 (m), 1.83 (o)
3	89.2	3.26 (m)	88.9	3.29 (dd, 11.4, 4.2)
4	39.7		39.7	
5	56.4	0.69 (d, 12.0)	56.4	0.69 (d, 11.4)
6	18.5	1.56 (o), 1.38 (o)	18.5	1.52 (o), 1.37 (o)
7	35.1	1.49 (m), 1.20 (m)	35.1	1.46 (o), 1.20 (d, 12.0)
8	40.0		40.1	
9	50.2	1.37 (o)	50.1	1.37 (o)
10	36.9		36.9	
11	30.8	1.98 (o), 1.54 (o)	30.9	2.01 (m), 1.86 (o)
12	70.1	4.24 (o)	70.5	4.02 (m)
13	49.4	1.99 (o)	49.5	2.04 (m)
14	51.4		51.5	
15	30.7	1.54 (o), 1.00 (m)	30.5	1.39 (o), 0.96 (m)
16	26.8	2.20 (o), 1.84 (o)	26.4	1.78 (o), 1.47 (o)
17	51.6	2.58 (o)	52.0	2.46 (m)
18	16.0	0.96 (s, 3H)	16.0	1.00 (s, 3H)
19	16.2	0.83 (s, 3H)	16.3	0.83 (s, 3H)
20	83.5		83.4	
21	22.2	1.64 (s, 3H)	23.3	1.61 (s, 3H)
22	36.1	2.39 (o), 1.81 (o)	39.8	3.11 (dd, 14.4, 8.4) 2.88 (dd, 14.4, 8.4)
23	23.1	2.61 (o), 2.34 (o)	122.7	6.22 (m)
24	125.9	5.31 (o)	142.4	6.10 (d, 15.6)
25	131.0		69.9	
26	25.8	1.61 (s, 3H)	30.7	1.57 (s, 3H)
27	17.9	1.65 (o, 3H)	30.7	1.57 (s, 3H)
28	28.0	1.32 (s, 3H)	28.1	1.29 (s, 3H)
29	16.5	1.11 (s, 3H)	16.7	1.11 (s, 3H)
30	17.4	0.98 (s, 3H)	17.2	0.89 (s, 3H)
	3- <i>O</i> -Glc		3- <i>O</i> -Glc	
1'	104.9	4.90 (d, 7.2)	104.8	4.95 (d, 6.3)
2'	84.2	4.15 (o)	83.0	4.11 (o)
3'	77.8	4.23 (o)	78.7	4.37 (m)
4'	71.4	4.16 (o)	71.2	4.12 (o)
5'	78.0	3.91 (o)	78.3	3.97 (o)
6'	62.8	4.55 (d, 10.8), 4.32 (o)	63.0	4.60 (d, 11.4), 4.37 (o)
	2'- <i>O</i> -Glc		2'- <i>O</i> -Glc	
1''	106.2	5.32 (d, 7.8)	103.2	5.54 (d, 7.8)
2''	76.8	4.14 (o)	84.5	4.22 (o)
3''	78.4	4.30 (o)	77.8	3.88 (m)
4''	70.9	4.19 (o)	71.8	4.24 (o)
5''	75.4	4.03 (o)	78.0	4.31 (o)
6''	64.3	4.99 (d, 11.4), 4.88 (m)	62.8	4.49 (o), 4.37 (o)
	20- <i>O</i> -Glc		2''- <i>O</i> -Xyl	
1'''	98.0	5.12 (d, 7.2)	106.4	5.44 (d, 6.3)
2'''	74.8	3.91 (o)	76.0	4.14 (o)
3'''	79.2	4.17 (o)	77.9	4.14 (o)
4'''	71.4	4.05 (o)	70.7	4.15 (o)
5'''	76.8	4.05 (o)	67.5	4.32 (o), 3.70 (m)
6'''	69.9	4.71 (d, 10.8), 4.28 (o)		
	6'''- <i>O</i> -Xyl		20- <i>O</i> -Glc	
1''''	105.7	4.97 (d, 7.2)	98.3	5.19 (d, 7.8)
2''''	74.8	4.02 (o)	75.1	3.95 (o)
3''''	77.9	4.13 (o)	78.8	4.18 (m)
4''''	71.0	4.19 (o)	71.8	4.24 (o)

position	1		2	
	δ_C	δ_H	δ_C	δ_H
5'''	66.9	4.32 (o), 3.67 (t, 10.2)	76.7	4.08 (m)
6'''			69.1	4.72 (d, 9.0), 4.23 (o)
	6''-O-Crotonyl group		6'''-O-Ara(p)	
1''''	166.6		104.3	5.01 (d, 6.0)
2''''	123.2	5.97 (d, 15.4)	72.1	4.46 (o)
3''''	144.7	7.06 (dq, 15.4, 7.2)	74.0	4.26 (o)
4''''	17.8	1.65 (o, 3H)	68.4	4.38 (o)
5''''			65.3	4.34 (o), 3.85 (m)

chemical shifts (δ) in ppm; coupling constants (J) in hertz; s, singlet; d, doublet; t, triplet; m, multiplet; o, overlapped signals; dd, double doublet; td, triple doublet; dq, double quartet; Glc, β -D-glucopyranosyl; Xyl, β -D-xylopyranosyl; Ara (p), α -L-arabinopyranosyl.

Table S2. Crystal data for quinquefoloside-L_b (**3**).

Empirical formula	C ₅₃ H ₈₈ O ₂₂ ·15.8H ₂ O
Formula weight	1361.90
Temperature/K	108.6(3)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å, b/Å, c/Å	11.7835(3), 49.4514(9), 12.2525(2)
α/°, β/°, γ/°	90, 90, 90
Volume/Å ³	7139.7(3)
Z	4
ρ _{calc} /mg mm ⁻³	1.267
μ/mm ⁻¹	0.914
F(000)	2834
Crystal size/mm ³	0.340 × 0.250 × 0.130
2Θ range for data collection	9.226 to 142.488 °
Index ranges	-9 ≤ h ≤ 14, -51 ≤ k ≤ 60, -14 ≤ l ≤ 13
Reflections collected	26321
Independent reflections	13498[R(int) = 0.0368 (inf-0.9Å)]
Data/restraints/parameters	13498/54/901
Goodness-of-fit on F ²	1.113
Final R indexes [I>2σ (I) i.e. F _o >4σ (F _o)]	R ₁ = 0.0761, wR ₂ = 0.1841
Final R indexes [all data]	R ₁ = 0.0824, wR ₂ = 0.1880
Largest diff. peak/hole / e Å ⁻³	0.522/-0.364
Flack Parameters	0.03(8)
Completeness	0.9982

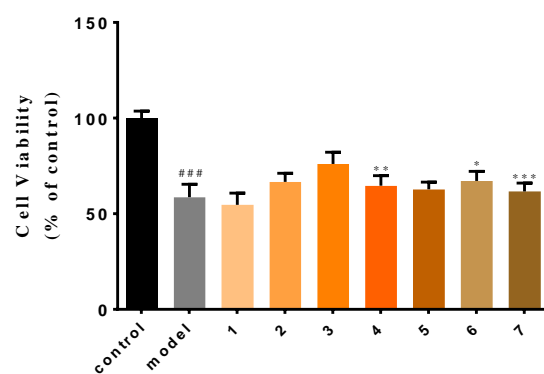


Figure S1. Neuroprotective effects of compounds **1–7** against serum deprivation injury in PC12 cell (10 μ M, means \pm SD, n=9). ### p < 0.001 vs control, * p < 0.05 vs model, ** p < 0.01 vs model, *** p < 0.001 vs model.

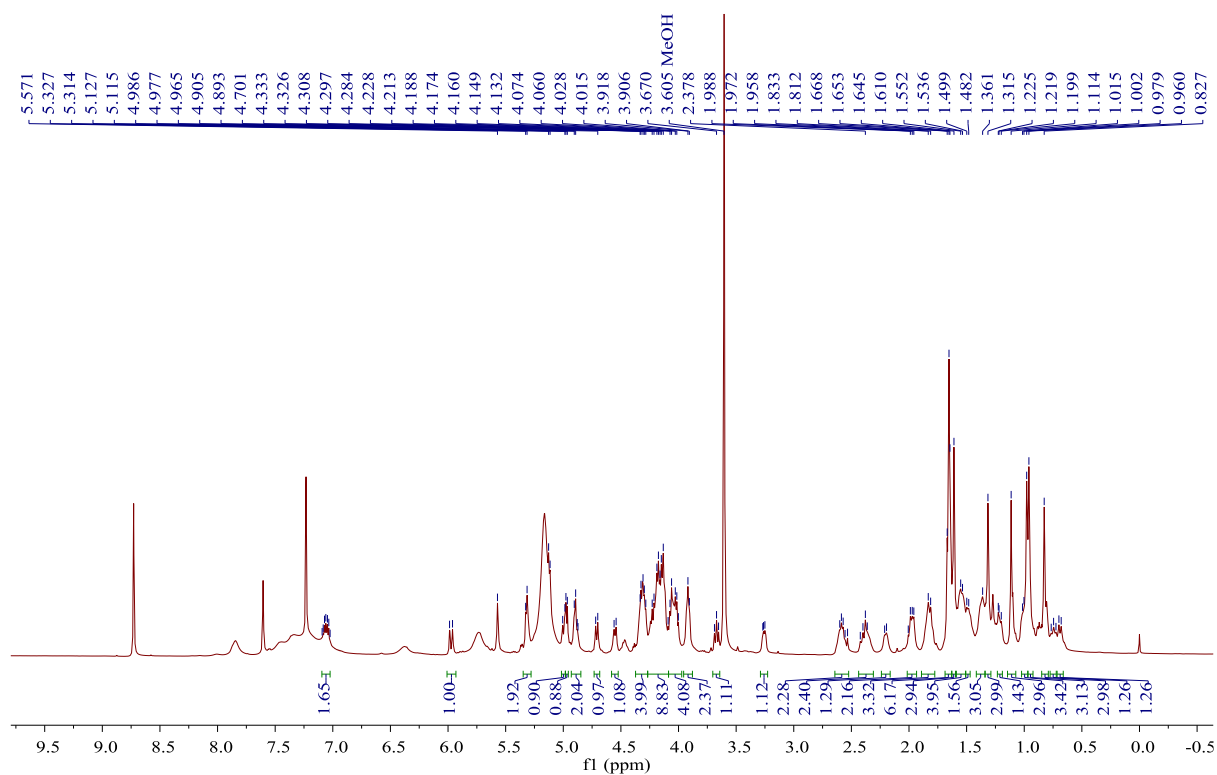


Figure S2. ¹H NMR spectrum (600 MHz, C₅D₅N) of compound **1**.

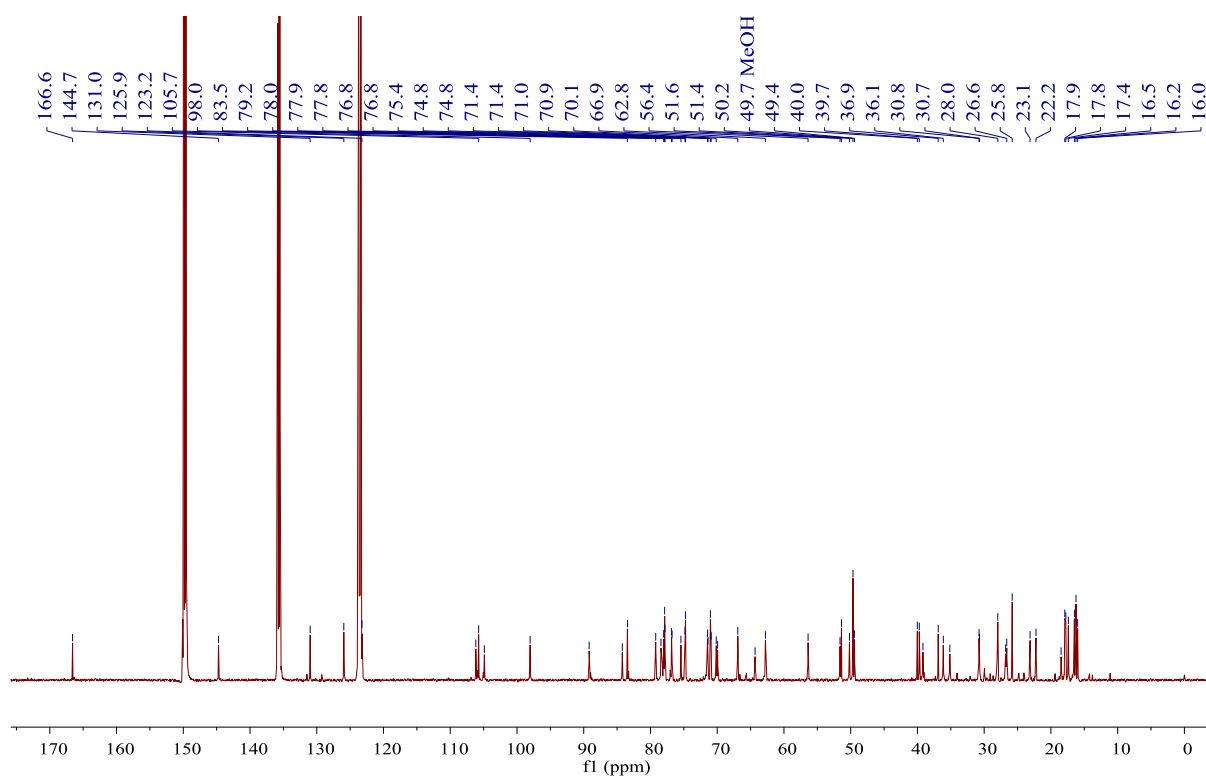


Figure S3. ¹³C NMR spectrum (150 MHz, C₅D₅N) of compound **1**.

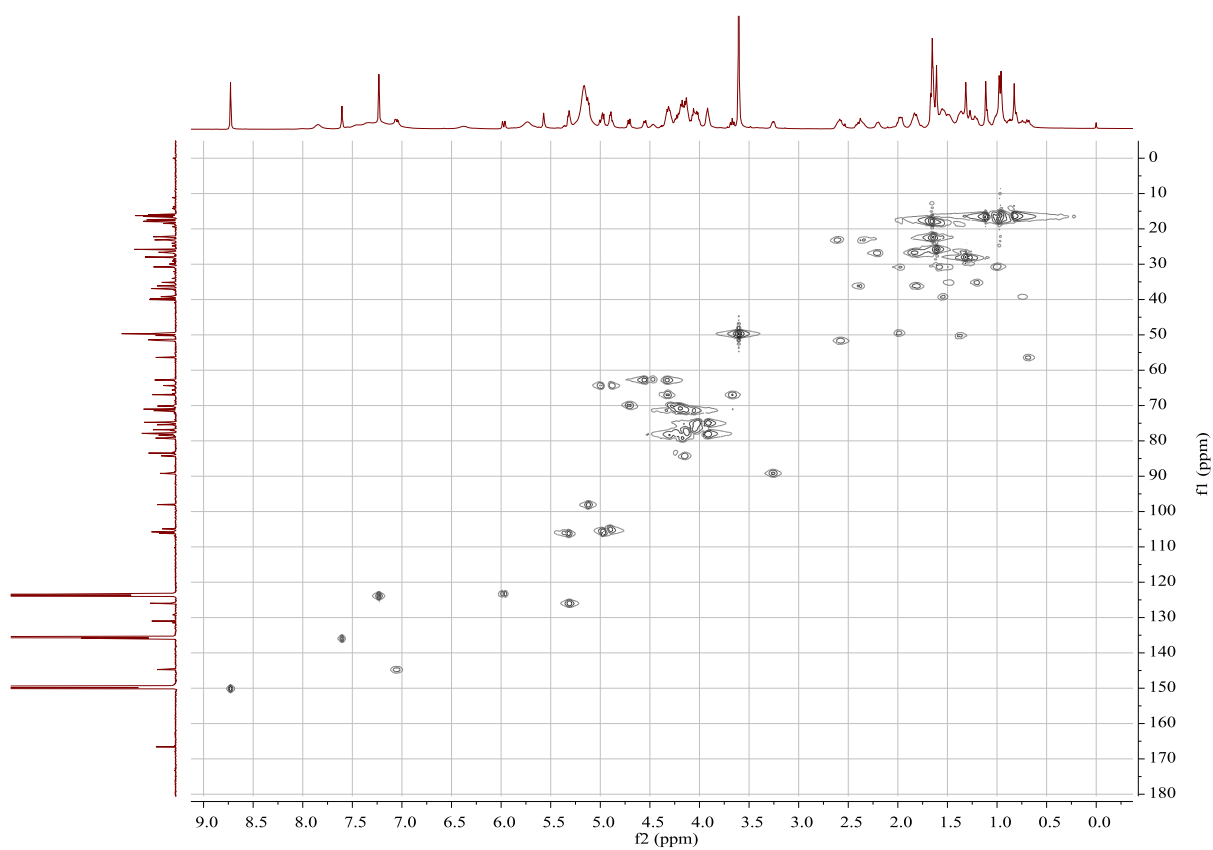


Figure S4. HSQC spectrum of compound **1**.

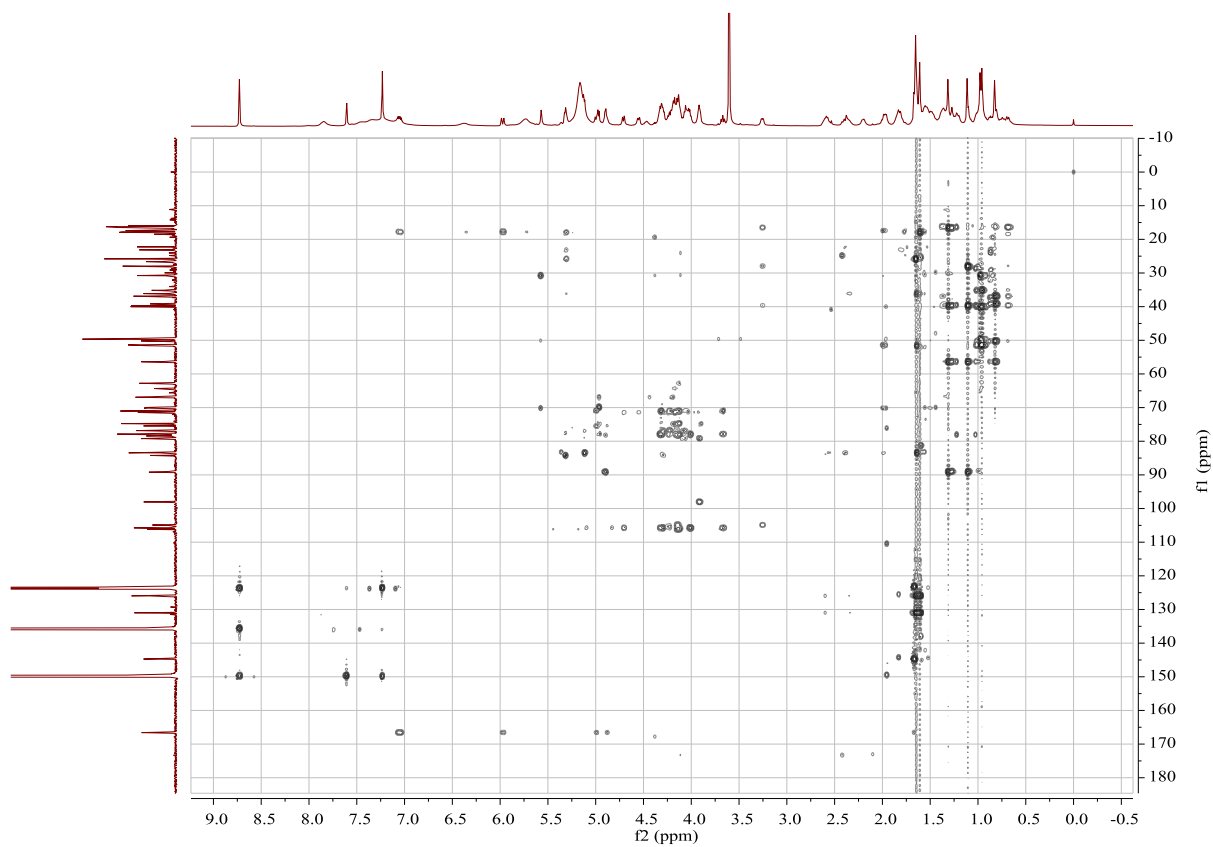


Figure S5. HMBC spectrum of compound **1**.

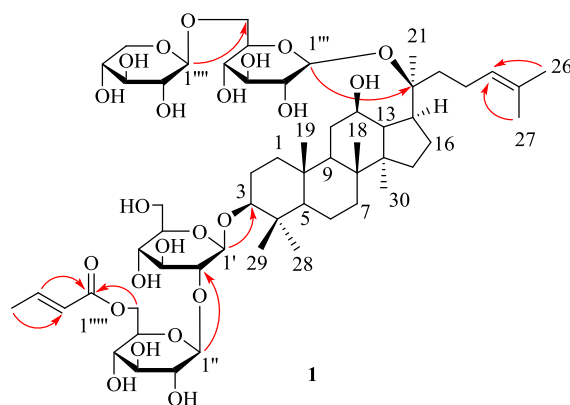


Figure S6. Key HMBC correlations of compound **1**.

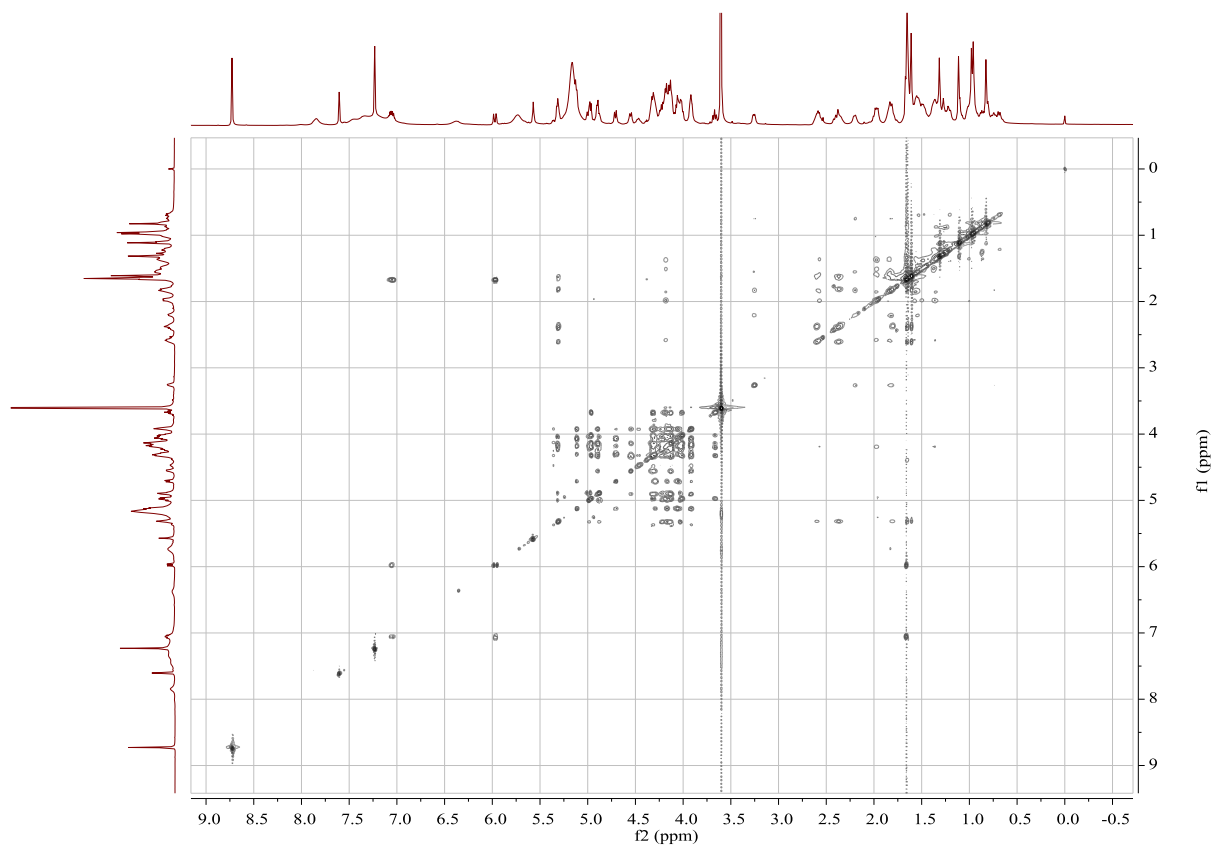


Figure S7. TOCSY spectrum of compound **1**.

MS Formula Results: + Scan (8.266 min) Sub (2017011301.d)

m/z	Ion	Formula	Abundance
1169.6099	[M+Na] ⁺	C57 H94 Na O23	267723.5

Best	Formula (M)	Ion Formula	Score	Cross Sc	Mass	Calc Mass	Calc m/z	Diff (ppm)	Alts Diff (ppm)	Mass Match	Abund Match	Spacing Match	DRE
✓	C57 H94 O23	C57 H94 Na O23	99.88		1169.6164	1169.6186	1169.6078	1.92	1.92	99.87	99.85	99.93	11
✓	C58 H96 Na O19	C58 H96 Na O19	99.78		1146.6164	1146.6199	1169.6091	3.05	3.05	99.67	99.84	99.95	16
✓	C52 H94 N2 O25	C52 H94 N2 Na O25	99.67		1146.6164	1146.6146	1169.6038	-1.61	1.61	99.91	99.06	99.94	7
✓	C56 H94 N2 O20 S	C56 H94 N2 Na O20 S	99.47		1146.6164	1146.6213	1169.6013	-3.82	3.82	99.48	99.04	99.98	11
✓	C49 H88 N2 O25 S	C49 H88 N2 Na O25 S	99.22		1146.6165	1146.6179	1169.6072	1.3	1.3	99.94	97.4	99.98	2
✓	C54 H96 O23 S	C54 H96 Na O23 S	99.19		1146.6164	1146.622	1169.6112	4.82	4.82	99.17	98.58	99.98	6
✓	C55 H94 N4 O19 S	C55 H94 N4 Na O19 S	99.14		1146.6165	1146.6233	1169.6125	5.96	5.96	98.73	99.14	99.98	11
✓	C47 H84 Na O27	C47 H84 Na Na O27	98.76		1146.6164	1146.6165	1169.5995	-5.14	5.14	99.06	97.29	99.96	3
✓	C53 H98 N2 O20 S2	C53 H98 N2 Na O20 S2	98.71		1146.6165	1146.6154	1169.6047	-6.91	6.91	99.97	99.58	99.97	6
✓	C58 H98 O18 S2	C58 H98 Na O18 S2	98.67		1146.6165	1146.6195	1169.6087	2.62	2.62	99.75	99.79	99.97	10
✓	C59 H94 N4 O14 S2	C59 H94 N4 Na O14 S2	98.67		1146.6165	1146.6208	1169.61	3.76	3.76	99.49	98.19	99.98	15
✓	C48 H88 N4 O22 S2	C48 H88 N4 Na O22 S2	98.08		1146.6165	1146.6114	1169.6006	-4.44	4.44	99.29	94.49	99.96	2
✓	C57 H98 N2 O15 S3	C57 H98 N2 Na O15 S3	97.33		1146.6165	1146.6129	1169.6022	-3.11	3.11	99.49	91.27	99.95	10
✓	C50 H102 N2 O20 S3	C50 H102 N2 Na O20 S3	97.07		1146.6165	1146.6188	1169.608	2.01	2.01	99.96	90.06	99.93	1

Figure S8. HR-ESI-MS spectrum of compound **1**.

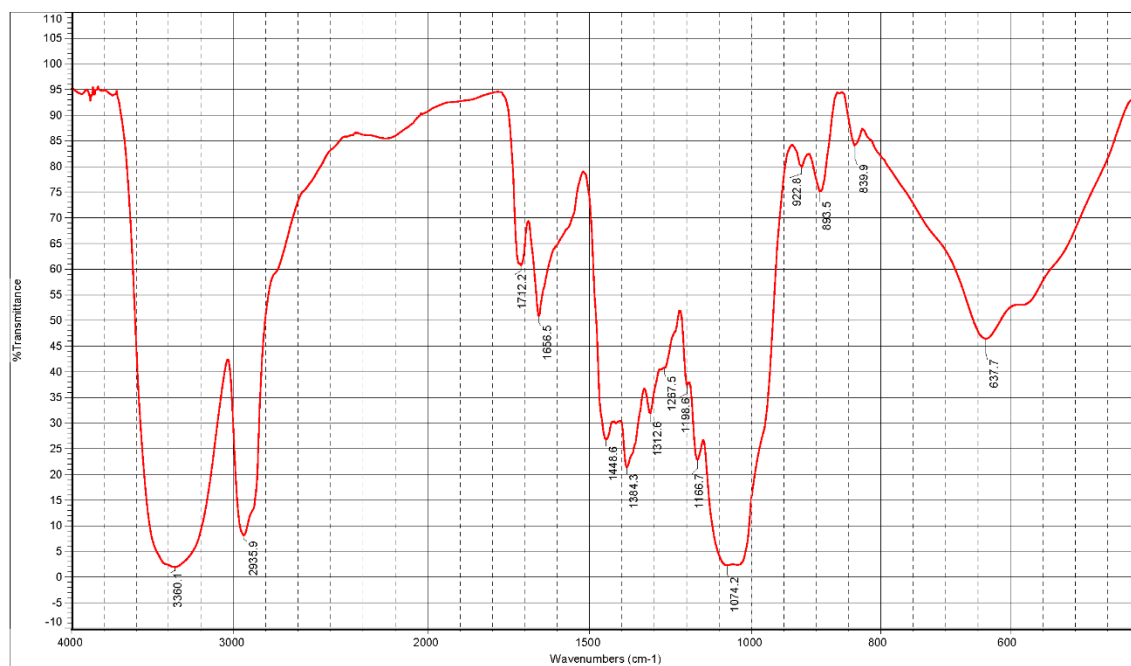


Figure S9. IR spectrum of compound **1**.

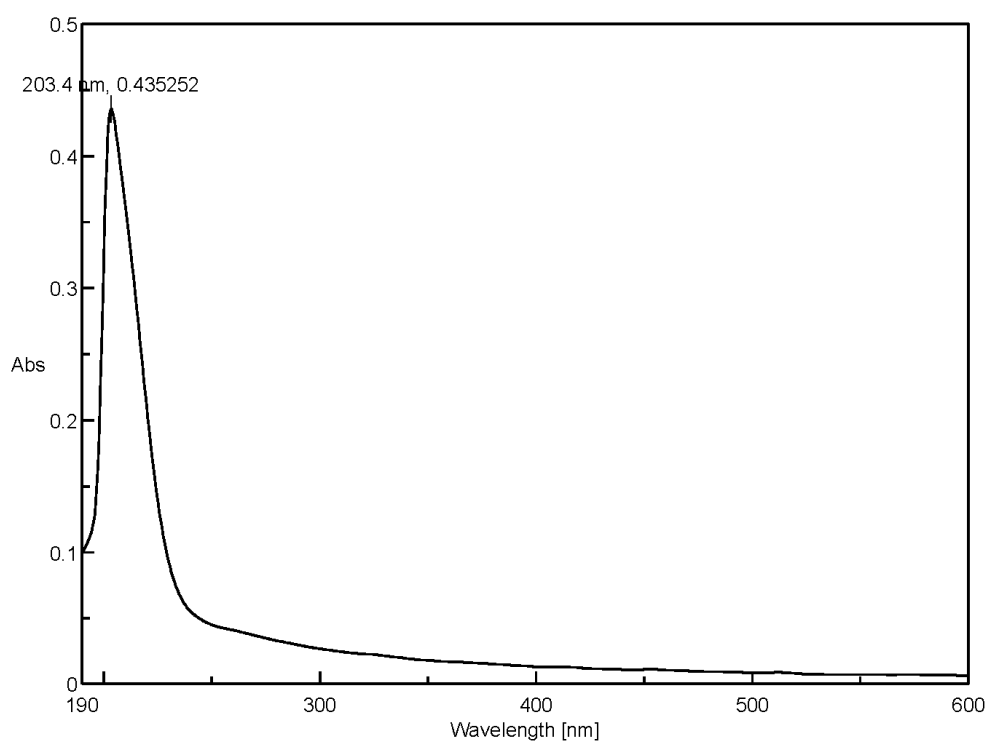


Figure S10. UV spectrum of compound **1** in MeOH.

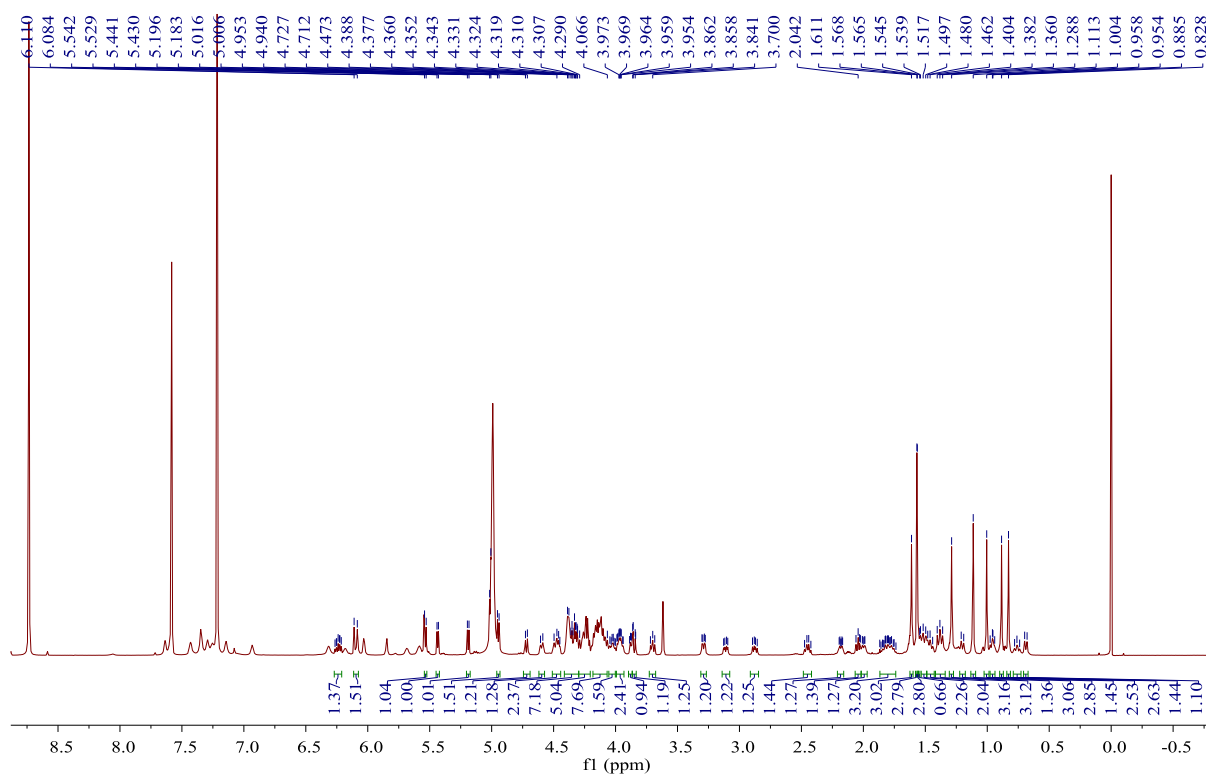


Figure S11. ¹H NMR spectrum (600 MHz, C₅D₅N) of compound **2**.

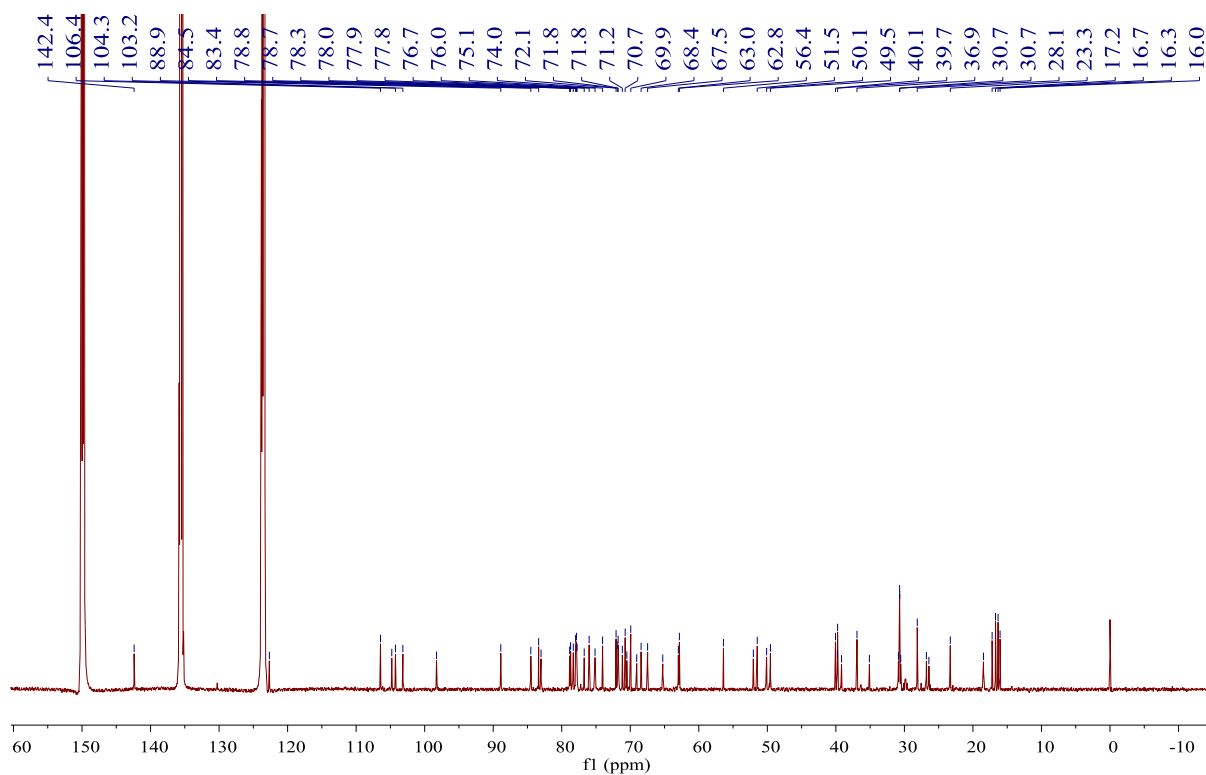


Figure S12. ¹³C NMR spectrum (150 MHz, C₅D₅N) of compound **2**.

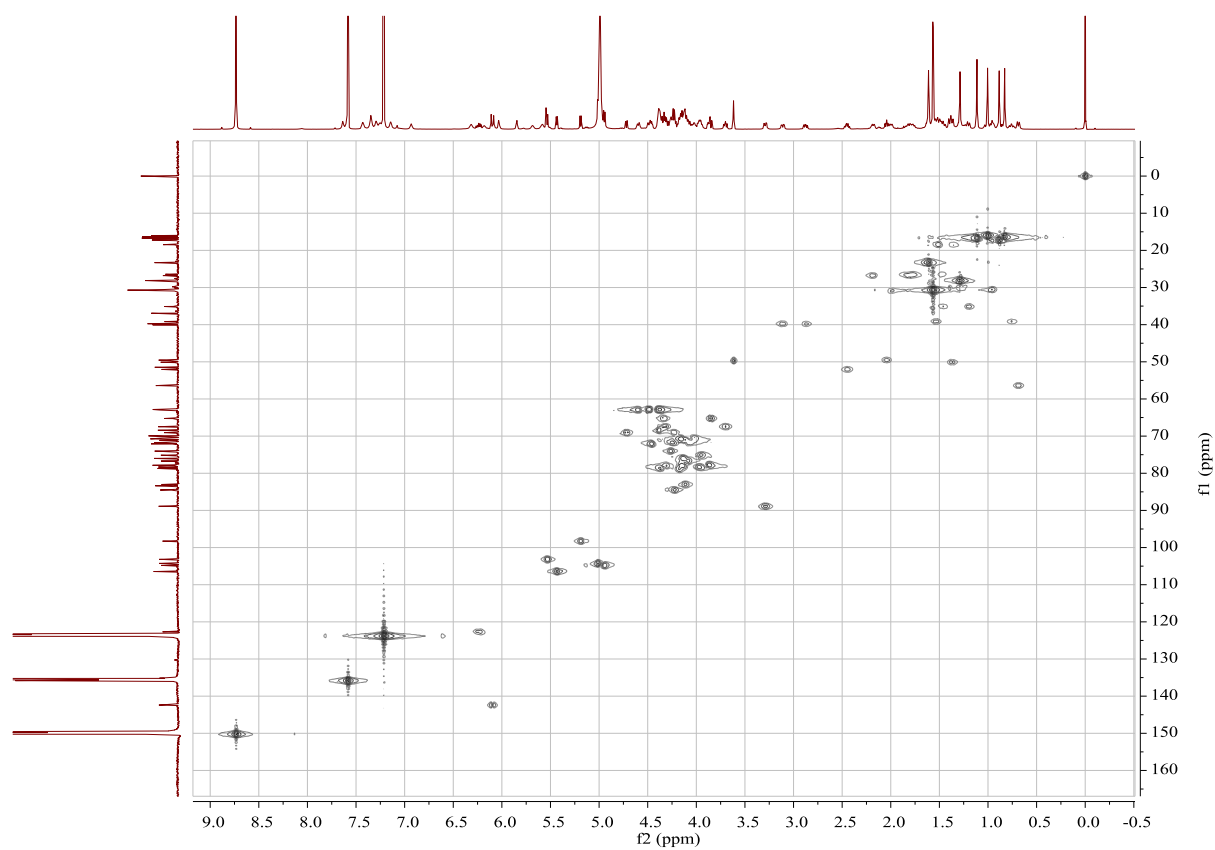


Figure S13. HSQC spectrum of compound **2**.

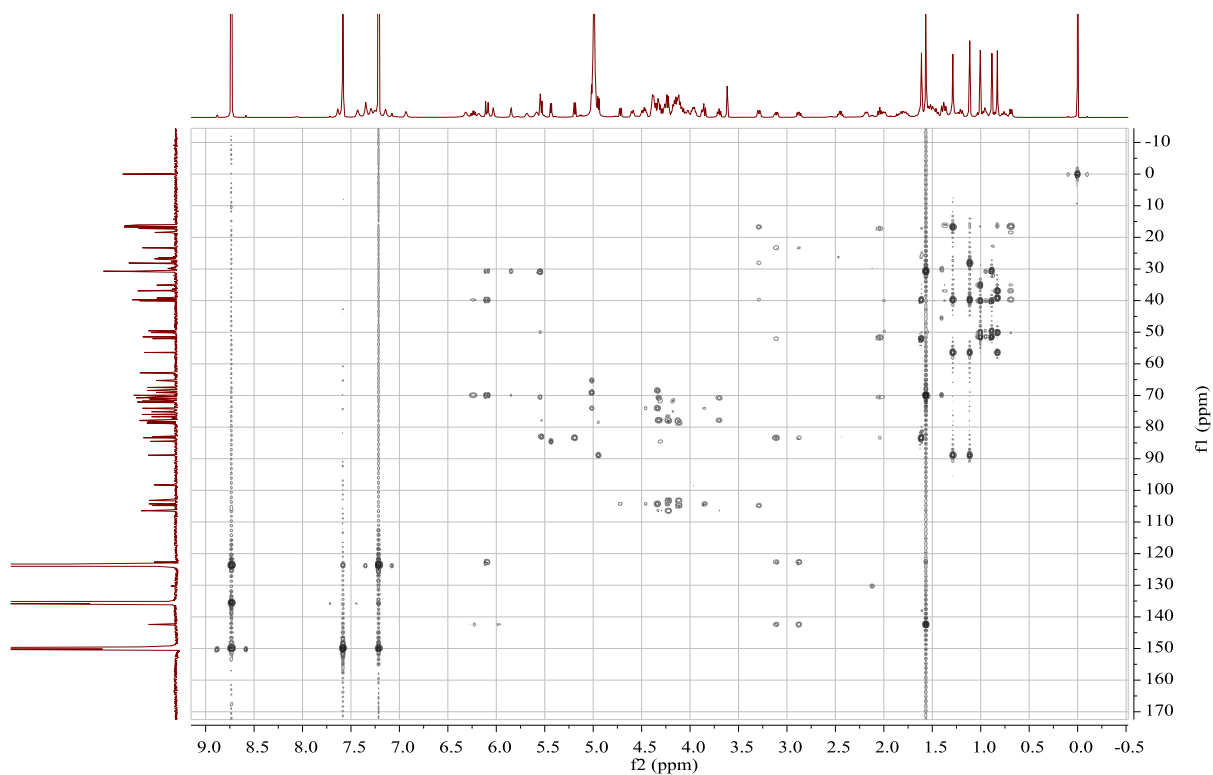


Figure S14. HMBC spectrum of compound **2**.

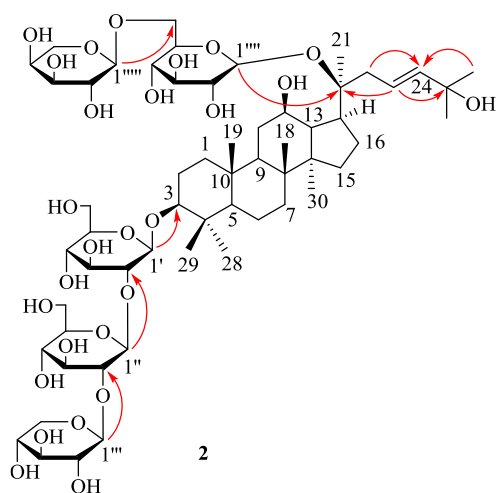


Figure S15. Key HMBC correlations of compound **2**.

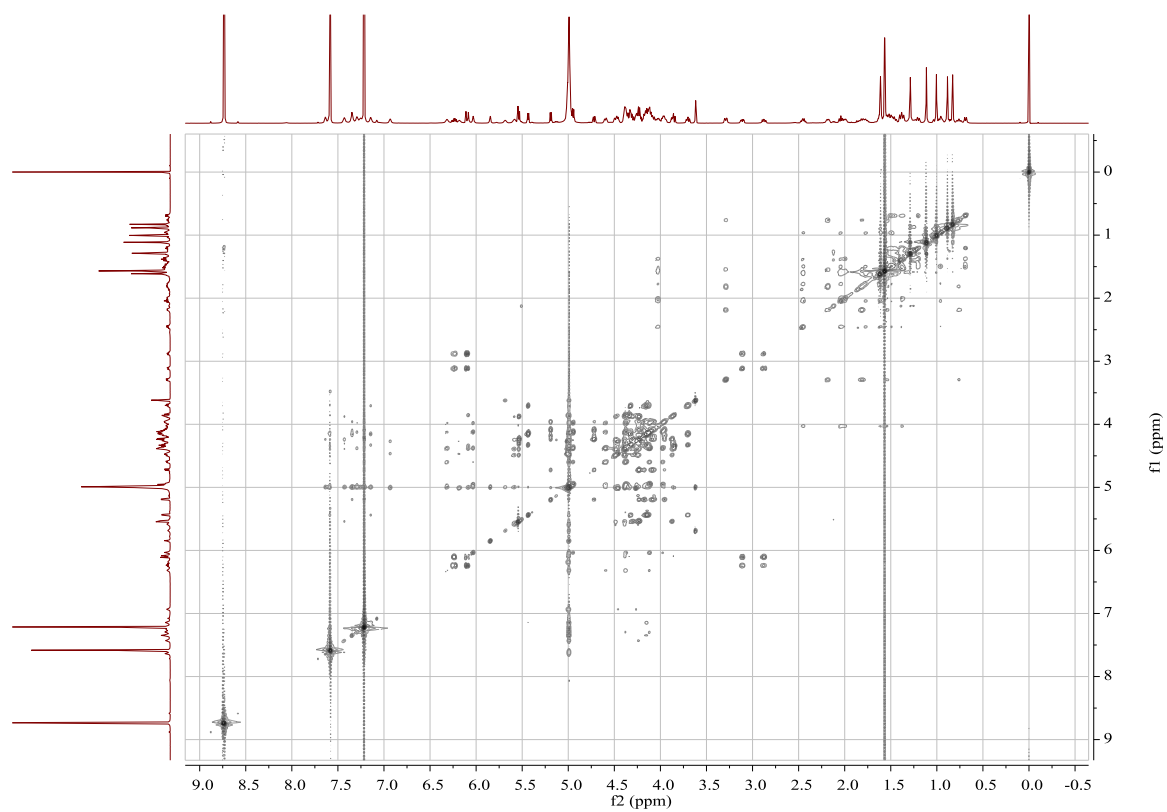


Figure S16. TOCSY spectrum of compound **2**.

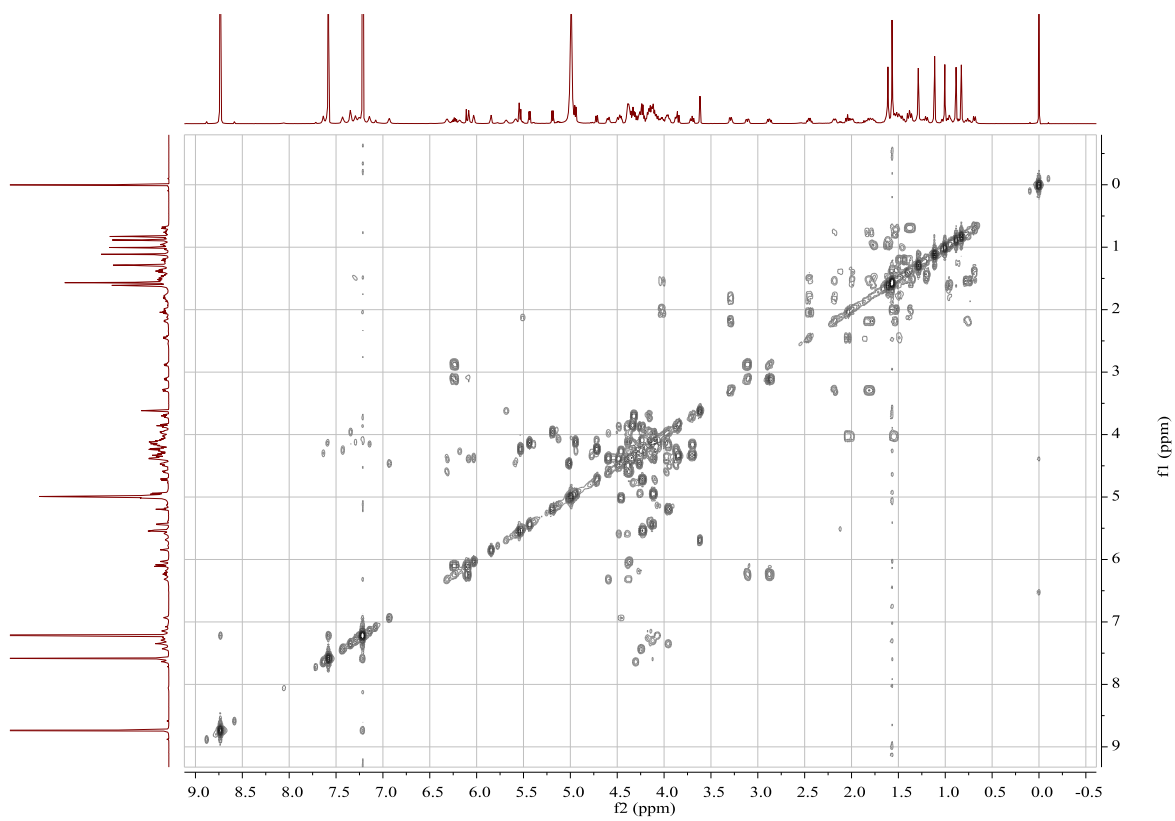


Figure S17. ^1H - ^1H COSY spectrum of compound **2**.

MS Formula Results: + Scan (7.121 min) Sub (D:\...Duyiqian2017051002.d)

m/z	Ion	Formula	Abundance										
1249.6182		C58 H98 Na O27	207863.4										
Best	Formula (b)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DRE
+	C58 H98 O27	C58 H98 Na O27	99.94		1226.6286	1226.6290	1249.6201	0.76	1.82	99.88	99.79	99.96	10
+	C59 H94 Na O23	C59 H94 Na O23	99.87		1226.6286	1226.6309	1249.6201	1.82	1.82	99.88	99.79	99.96	15
+	C53 H98 N2 O29	C53 H98 N2 O29	99.71		1226.6286	1226.6255	1249.6147	-2.53	2.53	99.77	99.41	99.96	6
+	C62 H98 O22 S	C62 H98 Na O22 S	99.46		1226.6286	1226.627	1249.6161	-1.3	1.3	99.94	98.24	99.95	14
+	C63 H94 Na O18 S	C63 H94 Na O18 S	99.45		1226.6287	1226.6294	1249.6176	-0.24	0.24	100	98.11	99.96	19
+	C65 H94 O22	C65 H94 Na O22	99.45		1226.6286	1226.6237	1249.6129	-4.03	4.03	99.41	99.09	99.95	19
+	C66 H90 Na O18	C66 H90 Na O18	99.41		1226.6286	1226.625	1249.6142	-2.96	2.96	99.68	98.51	99.96	24
+	C66 H102 O27 S	C66 H102 Na O27 S	99.3		1226.6286	1226.6329	1249.6221	3.48	3.48	99.56	98.34	99.95	5
+	C64 H94 N2 O21	C64 H94 N2 Na O21	99.3		1226.6286	1226.6348	1249.6241	5.12	5.12	99.66	98.17	99.96	19
+	C56 H98 Na O23 S	C56 H98 Na O23 S	99.29		1226.6287	1226.6343	1249.6235	4.54	4.54	99.26	98.8	99.95	10
+	C50 H102 N2 O29 S	C50 H102 N2 Na O29 S	99.27		1226.6287	1226.6289	1249.6181	0.18	0.18	100	97.48	99.94	1
+	C57 H98 N2 O24 S	C57 H98 N2 Na O24 S	99.24		1226.6287	1226.623	1249.6122	-4.6	4.6	99.24	98.66	99.95	10
+	C71 H92 N2 O16	C71 H92 N2 Na O16	99.15		1226.6286	1226.626	1249.6163	0.33	0.33	100	97.69	99.96	26
+	C51 H102 O32	C51 H102 Na O32	99.09		1226.6286	1226.6364	1249.6246	5.55	5.55	98.89	98.7	99.95	1
+	C68 H94 N2 O16 S	C68 H94 N2 Na O16 S	98.92		1226.6287	1226.6324	1249.6216	3.06	3.06	99.66	96.82	99.96	23
+	C68 H98 Na O31	C68 H98 Na O31	98.84		1226.6287	1226.6215	1249.6107	-5.83	5.83	98.78	98.02	99.97	2
+	C60 H98 Na O18 S2	C60 H98 Na O18 S2	98.55		1226.6287	1226.6316	1249.621	2.48	2.48	99.78	95.37	99.93	14
+	C58 H102 O22 S2	C58 H102 Na O22 S2	98.53		1226.6287	1226.6304	1249.6196	1.42	1.42	99.93	95.05	99.92	9
+	C54 H102 N2 O24 S2	C54 H102 N2 Na O24 S2	98.51		1226.6287	1226.6364	1249.6156	-1.88	1.88	99.87	95.07	99.91	5
+	C70 H90 Na O13 S	C70 H90 Na O13 S	98.42		1226.6287	1226.6325	1249.6117	-5.02	5.02	99.69	96.03	99.96	28
+	C76 H90 O14	C76 H90 Na O14	98.42		1226.6286	1226.6311	1249.6223	3.62	3.62	99.53	95.29	99.95	37
+	C75 H90 N2 O11 S	C75 H90 N2 Na O11 S	98.25		1226.6287	1226.6265	1249.6158	-1.73	1.73	99.89	94.1	99.96	32
+	C67 H94 Na O13 S2	C67 H94 Na O13 S2	98.14		1226.6287	1226.6259	1249.6151	-2.3	2.3	99.81	93.87	99.94	23

Figure S18. HR-ESI-MS spectrum of compound 2.

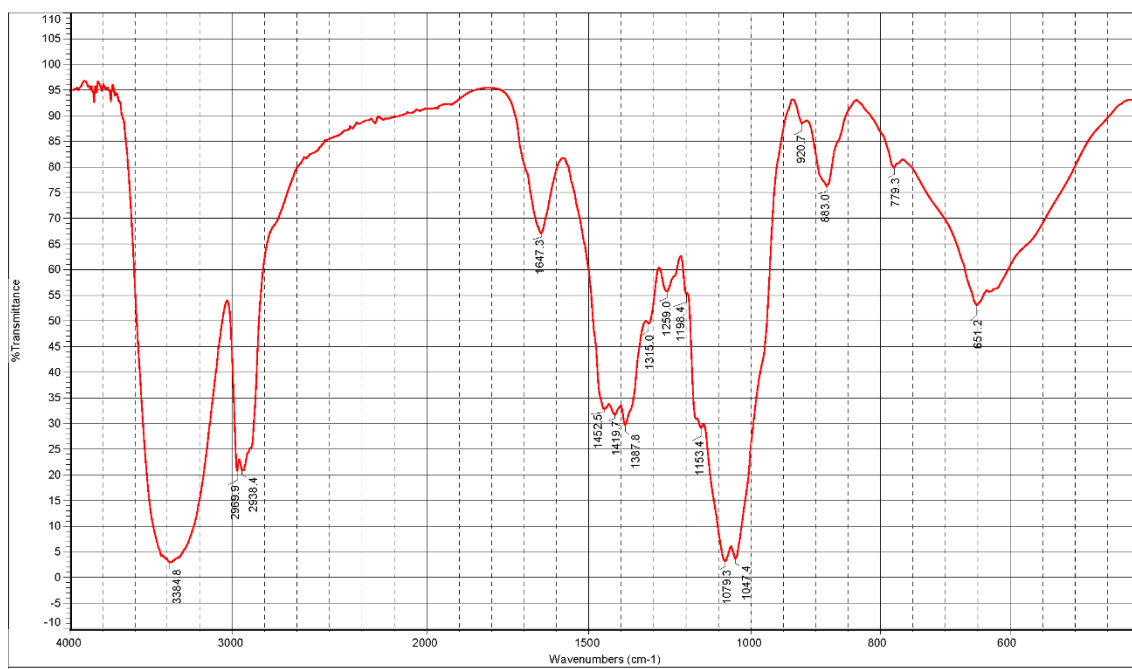


Figure S19. IR spectrum of compound 2.

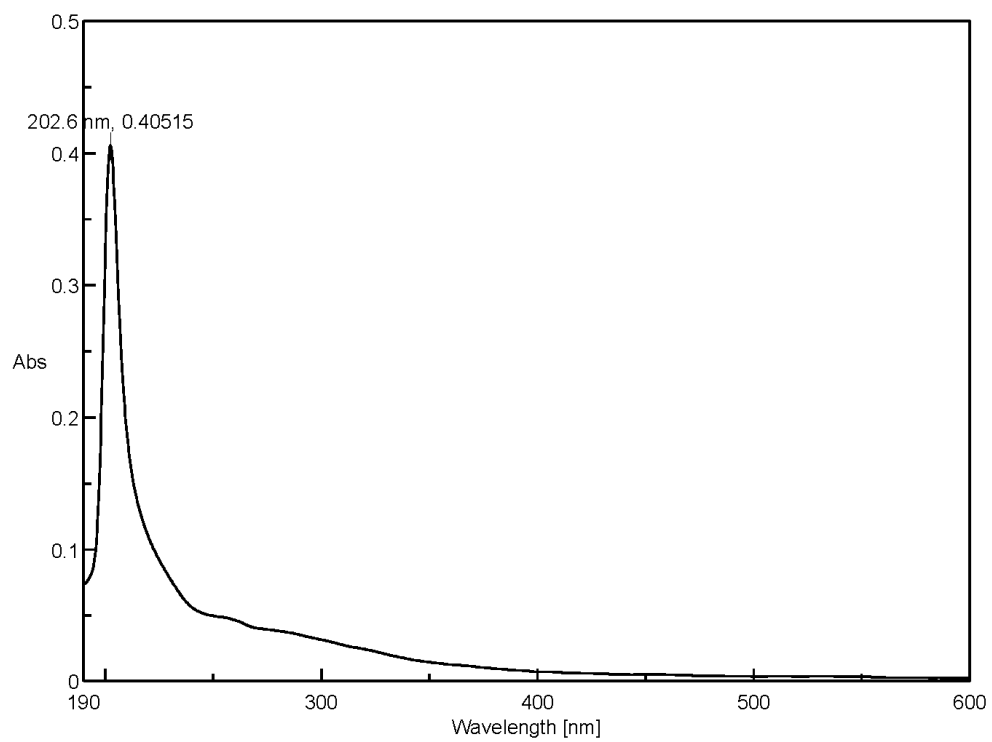


Figure S20. UV spectrum of compound **2** in MeOH.