# **Supporting information**

# Inhibitory activity of amyloid β aggregation of triterpene saponins

from cactus, Stenocereus pruinosus

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Figure 66. NOESY spectrum of stenoside A (7) in DMSO-d<sub>6</sub>.

#### **Extraction and isolation**

Aerial parts of *S. pruinosus* were dried, and the dry powder (639.1 g) was extracted three times with CHCl<sub>3</sub> and then extracted three times with MeOH. The MeOH extract (144.2 g) was applied to a Diaion HP-20 column, which was successively eluted with H<sub>2</sub>O, 30% MeOH (MeOH-H<sub>2</sub>O 30:70, v/v), 70% MeOH, and 100% MeOH to give 4 fractions [H<sub>2</sub>O-eluted fraction (disposal), 30% MeOH-eluted fraction (15.0 g), 70% MeOH-eluted fraction (60.3 g), and 100% MeOH-eluted fraction (106.5 g)], respectively.

The 70% MeOH-eluted fraction (60.3 g) was subjected to silica gel column chromatography (Si. C. C.) using a stepwise gradient (CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O 60:14:1  $\rightarrow$ 150:50:4  $\rightarrow$  150:60:4  $\rightarrow$  30:15:1  $\rightarrow$  30:18:1  $\rightarrow$  30:20:1  $\rightarrow$  6:4:1  $\rightarrow$  MeOH) to give 10 fractions (Fr. A: 0.1 mg, Fr. B: 2.3 mg, Fr. C: 1.0 mg, Fr. D: 620.1 mg, Fr. E: 409.0 mg, Fr. F: 2.6 g, Fr. G: 4.6 g, Fr. H: 10.3 g, Fr. I: 26.0 g, Fr. J: 10.9 g). Fr. H (10.3 g) was subjected to Si. C. C. using a stepwise gradient (CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O 30:18:1  $\rightarrow$  30:20:1  $\rightarrow$  6:4:1  $\rightarrow$  MeOH) to give 3 fractions (Fr. Ha: 0.1 mg, Fr. Hb: 7.5 g, Fr. Hc: 1.0 g). Fr. Hb (7.5 g) was subjected to Si. C. C. using a stepwise gradient (CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O 75:30:2  $\rightarrow$  30:15:1  $\rightarrow$  30:18:1  $\rightarrow$  30:20:1  $\rightarrow$  6:4:1  $\rightarrow$  MeOH) to give 5 fractions (Fr. Hb1: 29.2 mg, Fr. Hb2: 853.5 mg, Fr. Hb3: 886.0 mg, Fr. Hb4: 5.0 g, Fr. Hb5: 315.7 mg). Fr. Hb4 (5.00 g) was subjected to Si. C. C. using a stepwise gradient (CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O 75:30:2  $\rightarrow$  30:15:1  $\rightarrow$  30:18:1  $\rightarrow$  30:20:1  $\rightarrow$  6:4:1  $\rightarrow$  MeOH) to give 3 fractions (Fr. Hb4-1: 770.2 mg, Fr. Hb4-2: 4.1 g, Fr. Hb4-3: 21.6 mg). Fr. Hb4-2 (4.1 g) was subjected to octadecyl silylated silica gel column chromatography (ODS C. C.) using a stepwise gradient (MeOH-H<sub>2</sub>O 30:70  $\rightarrow$  50:50  $\rightarrow$  60:40  $\rightarrow$  70:30  $\rightarrow$  80:20  $\rightarrow$  90:10  $\rightarrow$  MeOH) to give 5 fractions (Fr. Hb4-2a: 213.1 mg, Fr. Hb4-2b: 93.6 mg, Fr. Hb4-2c: 1.8 g, Fr. Hb4-2d: 1.0 g, Fr. Hb4-2e: 644.5 mg). Fr. Hb4-2b (93.6 mg) was subjected to ODS C. C. using a stepwise gradient (MeOH-H<sub>2</sub>O 40:60  $\rightarrow$  50:50  $\rightarrow$  60:40  $\rightarrow$  70:30  $\rightarrow$  MeOH) to give 3 fractions (Fr. Hb4-2b-1: 2.4 mg, Fr. Hb4-2b-2: 48.3 mg, Fr. Hb4-2b-3: 48.3 mg). Fr. Hb4-2b-2 (48.3 mg) was further separated by Si. C. C. using a stepwise gradient (CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O 75:30:2  $\rightarrow$  30:15:1  $\rightarrow$  30:18:1  $\rightarrow$  30:20:1  $\rightarrow$  6:4:1  $\rightarrow$  MeOH) to afford chichipenoside D (1, 16.7 mg, 0.003%, Fr. Hb4-2b-2d).

Fr. Hb4-2d (1.0 g) was subjected to ODS C. C. using a stepwise gradient (MeOH-H<sub>2</sub>O  $30:70 \rightarrow 50:50 \rightarrow 60:40 \rightarrow 70:30 \rightarrow 80:20 \rightarrow 90:10 \rightarrow MeOH$ ) to give 3 fractions (Fr. Hb4-2d-1: 10.8 mg, Fr. Hb4-2d-2: 905.5 mg, Fr. Hb4-2d-3: 118.9 mg). Fr. Hb4-2d-2 (905.5 mg) was subjected to Si. C. C. using a stepwise gradient (CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O 75:30:2  $\rightarrow$  30:15:1  $\rightarrow$  30:18:1  $\rightarrow$  30:20:1  $\rightarrow$  6:4:1  $\rightarrow$  MeOH) to give 3 fractions (Fr. Hb4-2d-2a: 247.3 mg, Fr. Hb4-2d-2b: 202.3 mg, Fr. Hb4-2d-2c: 195.8 mg). Fr. Hb4-2d-2b (202.3 mg) was further separated by ODS C. C. using a stepwise gradient (MeCN-

H<sub>2</sub>O 20:80 → 30:70 → 40:60 → MeOH) to afford oleanolic acid 3-*O*-β-D-xylopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-β-D-glucuronopyranosyl-28-*O*-β-Dglucopyranoside (**6**, 72.0 mg, 0.011%, Fr. Hb4-2d-2b-9).

Fr. Hb2 (853.5 mg) was subjected to ODS C. C. using a stepwise gradient (MeOH-H<sub>2</sub>O 30:70  $\rightarrow$  40:60  $\rightarrow$  50:50  $\rightarrow$  60:40  $\rightarrow$  70:30  $\rightarrow$  90:10  $\rightarrow$  MeOH) to afford 4 fractions (Fr. Hb2-1: 77.2 mg, Fr. Hb2-2: 86.5 mg, Fr. Hb2-3: 79.9 mg, Fr. Hb2-5: 86.6 mg) and oleanolic acid 3-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- $\beta$ -D-glucuronopyranosyl-28-*O*- $\beta$ -Dglucopyranoside (**8**, 440.3 mg, 0.069%, Fr. Hb2-4).

Fr. Hb2-2 (86.5 mg) was subjected to Si. C. C. using a stepwise gradient (CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O 75:30:2  $\rightarrow$  30:15:1  $\rightarrow$  30:18:1  $\rightarrow$  30:20:1  $\rightarrow$  6:4:1  $\rightarrow$  MeOH) to afford cochalinoside C (5, 27.5 mg, 0.004%, Fr. Hb2-2e).

The 100% MeOH-eluted fraction (94.5 g) was subjected to Si. C. C. using a stepwise gradient (CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O 60:14:1  $\rightarrow$  75:25:2  $\rightarrow$  75:30:2  $\rightarrow$  30:15:1  $\rightarrow$  30:18:1  $\rightarrow$ 30:20:1  $\rightarrow$  6:4:1  $\rightarrow$  MeOH) to give 8 fractions (Fr. 1: 105.7 mg, Fr. 2: 199.3 mg, Fr. 3: 1.0 g, Fr. 4: 1.9 g, Fr. 5: 15.9 g, Fr. 6: 11.5 g, Fr. 7: 1.1 g, Fr. 8: 6.1 g). Fr. 4 (1.9 g) was subjected to ODS C. C. using a stepwise gradient (MeCN-H<sub>2</sub>O 20:80  $\rightarrow$  30:70  $\rightarrow$  40:60  $\rightarrow$  50:50  $\rightarrow$  60:40  $\rightarrow$  MeOH) to give 3 fractions (Fr. 4A: 690.1 mg, Fr. 4B: 1.2 g, Fr. 4C: 501.6 mg). Fr. 4B (1.2 g) was subjected to Si. C. C. using a stepwise gradient (CHCl<sub>3</sub>- MeOH-H<sub>2</sub>O 75:30:2  $\rightarrow$  30:15:1  $\rightarrow$  30:18:1  $\rightarrow$  30:20:1  $\rightarrow$  6:4:1  $\rightarrow$  MeOH) to afford oleanolic acid 3-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 3)-6'-*O*-methyl- $\beta$ -D-glucuronopyranosyl-28-*O*- $\beta$ -D-glucopyranoside (**9**, 40.5 mg, 0.006%, Fr. 4B-2).

Fr. 5 (15.9 g) was subjected to Si. C. C. using a stepwise gradient (CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O 30:12:1  $\rightarrow$  20:10:1  $\rightarrow$  20:15:1  $\rightarrow$  6:4:1  $\rightarrow$  MeOH) to give 6 fractions (Fr. 5A: 49.1 mg, Fr. 5B: 186.1 mg, Fr. 5C: 211.0 mg, Fr. 5D: 391.3 mg, Fr. 5E: 300.8 mg, Fr. 5F: 604.5 mg). Fr. 5-E (300.8 mg) was subjected to ODS C. C. using a stepwise gradient (MeOH-H<sub>2</sub>O 70:30  $\rightarrow$  80:20  $\rightarrow$  90:10  $\rightarrow$  MeOH) to give 2 fractions (Fr. 5E-1: 235.2 mg, Fr. 5-E2: 336.4mg). Fr. 5E-1 (235.2 mg) was partially (46.0 mg) subjected to ODS C. C. using a stepwise gradient (MeCN-H<sub>2</sub>O 30:70  $\rightarrow$  40:60  $\rightarrow$  50:50  $\rightarrow$  MeOH) to afford longispinoside A (**2**, 16.0 mg, 0.003%, Fr. 5E-1e).

Fr. 5B (186.1 mg) was subjected to ODS C. C. using a stepwise gradient (MeCN-H<sub>2</sub>O  $40:60 \rightarrow 50:50 \rightarrow 60:40 \rightarrow 70:30 \rightarrow MeOH$ ) to give 3 fractions (Fr. 5B-1: 8.1 mg, Fr. 5B-2: 51.4 mg, Fr. 5-B-3: 26.5 mg). Fr. 5B-2 (51.4 mg) was subjected to ODS C. C. using a stepwise gradient (MeOH-H<sub>2</sub>O  $60:40 \rightarrow 70:30 \rightarrow 80:20 \rightarrow 90:10 \rightarrow MeOH$ ) to afford longispinoside A methyl ester (**3**, 24.2 mg, 0.004%, Fr. 5B-2c).

Fr. 5D (391.3 mg) was subjected to ODS C. C. using a stepwise gradient (MeOH-H<sub>2</sub>O  $70:30 \rightarrow 80:20 \rightarrow 90:10 \rightarrow MeOH$ ) to give 3 fractions (Fr. 5D-1: 22.2 mg, Fr. 5D-2: 54.3

mg, Fr. 5D-3: 191.0 mg). Fr. 5D-2 (54.3 mg) was subjected to ODS C. C. using a stepwise gradient (MeOH-H<sub>2</sub>O 80:20  $\rightarrow$  90:10  $\rightarrow$  MeOH) to give 2 fractions (Fr. 5D-2a: 1.1 mg, Fr. 5D-2b: 40.3 mg). Fr. 5D-2b (40.3 mg) was subjected to ODS C. C. using a stepwise gradient (MeCN-H<sub>2</sub>O 60:40  $\rightarrow$  MeOH) to afford erythronoside A methyl ester (4, 9.3 mg, 0.001%, Fr. 5D-2b-6).

Fr. 8 (6.1 g) was subjected to Si. C. C. using a stepwise gradient (CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O  $25:12:1 \rightarrow 15:12:1 \rightarrow 13:12:1 \rightarrow MeOH$ ) to give 2 fractions (Fr. 8A: 28.9 mg, Fr. 8B: 1.6 g). Fr. 8B (1.6 g) was subjected to ODS C. C. using a stepwise gradient (MeOH-H<sub>2</sub>O  $30:70 \rightarrow 50:50 \rightarrow MeOH$ ) to afford stenoside A (7, 28.9 mg, 0.005%, Fr. 8B-3).

**Table 1.** <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopic data for compounds **6** (500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C, in DMSO- $d_6$ ).

Position				6
1 05111011	39.1	Сн	~	0.86 (0)
1	38.1	$CH_2$	u p	1.47(0)
2	25.6	CU	р	1.47(0)
2	23.0	$CH_2$	α	1.70 (010, 10.0)
2	000	CU	β	1.32(0)
5	88.9	СН		5.01 (ad, 10.6, 3.8)
4	58.8	C <sup>II</sup>		0.67(a)
5	55.0	CH		0.67 (0)
6	17.8	$CH_2$	α	1.43 (0)
			β	1.27 (t, 12.0)
7	32.3	$CH_2$	α	1.35 (0)
			β	1.19 (o)
8	39.0	С		
9	47.1	CH		1.45 (o)
10	36.3	С		
11	23.0	$CH_2$		1.76 (brs)
12	121.7	CH		5.14 (brs)
13	143.5	С		
14	41.3	С		
15	27.2	$CH_2$	α	0.93 (o)
			β	1.70 (brt, 10.4)
16	22.5	$CH_2$	α	1.92 (brt, 10.4)
			β	1.57 (o)
17	46.0	С		
18	40.8	CH		2.72 (dd, 13.4, 3.0)
19	45.6	$CH_2$	α	1.60 (t, 13.4)
		-	β	1.05 (o)
20	30.3	С	'	
21	33.3	$CH_2$	α	1.32 (0)
		2	ß	1 13 (brd 9 6)
22	31.6	CH	P M	1.57 (o)
22	51.0		ß	1.37(0) 1.47(0)
22	27.2	CU	р	1.47(0)
23	27.3	CH <sub>3</sub>		0.94 (s)
24	15.9	$CH_3$		0.72 (s)
25	15.2	$CH_3$		0.83 (s)
26	16.7	$CH_3$		0.66 (s)
27	25.4	CH <sub>3</sub>		1.05 (s)
28	175.3	C		
29	32.8	CH		0.86(s)
30	23.4	CU		0.85 (s)
50	25.4 Cla	СП3		0.03(8)
11	102.4			
1	105.4	СП		4.41 (0, 8.0)
2	82.2	СН		3.47(1, 8.0)
5 1'	02.3 70.2	СЦ		3.33(1, 0.0)
4 5'	70.2	СЦ		3.44(0)
5	170.3	Сп		5.09 (u, 9.7)
0	170.5	C		
	Xvl			Xvl
1"	102.8	CH		4.35 (d. 7.7)
2"	74.0	CH		2.93 (0)
3"	76.6	CH		3.07 (o)
4"	69.7	CH		3.21 (o)
5"	65.8	CH-	α	2.96 (t. 11.9)
ĩ	00.0	2.12	ß	3 61 (0)
	Rhe		Ч	Rha
1'''	101.0	СН		4.93 (d. brs)
2""	70.6	CH		3.77 (0)
3"	70.6	CH		3.44 (o)
4'''	72.0	CH		3.19( o)
5'''	68.7	CH		3.79 (o)
6'''	17.8	CH-		1.07 (d. 6 0)
0	Glo	<b>C</b> 113		Glc
1''''	Q/ 1	СН		5 22 (d 8 2)
2""	72 /	СН		3.22(0, 0.2)
2 3''''	767	СН		3.19 (0)
4""	69.6	CH		3.11 (0)
	77 7	CH		3.12 (0)
6""	60.7	CH.		342(0)
0	00.7	$CH_2$		3.72(0)
				5.00 (0)

Figure 1. HMBC, COSY, and Key NOESY Correlations of **3**.



Figure 2. HMBC, COSY, and Key NOESY Correlations of 6.



Figure 3. HMBC, COSY, and Key NOESY Correlations of 7.





Figure 4. <sup>1</sup>H NMR spectrum (500 MHz) of chichipenoside D (1) in DMSO-*d*<sub>6</sub>.

Figure 5. <sup>13</sup>C NMR spectrum (125 MHz) of chichipenoside D (1) in DMSO- $d_6$ .



#### Figure 6. DEPT 90 and 135 pulse NMR spectra of chichipenoside D (1) in DMSO-d<sub>6</sub>.



#### Figure 7. DQF-COSY spectrum of chichipenoside D (1) in DMSO-d<sub>6</sub>.



#### Figure 8. HMQC spectrum of chichipenoside D (1) in DMSO-d<sub>6</sub>.



Figure 9. HMBC spectrum of chichipenoside D (1) in DMSO-d<sub>6</sub>.





Figure 10. HSQC-TOCSY spectrum of chichipenoside D (1) in DMSO-d<sub>6</sub>.

#### Figure 11. pfg-TOCSY spectrum of chichipenoside D (1) in DMSO-*d*<sub>6</sub>.



Figure 12. NOESY spectrum of chichipenoside D (1) in DMSO-d<sub>6</sub>.





Figure 13. <sup>1</sup>H NMR spectrum (500 MHz) of longispinoside A (2) in DMSO-*d*<sub>6</sub>.

sp-8/13C JEOL RESONANCE Filename Author Experiment Sample\_Id Solvent Creation\_Time Revision\_Time Current\_Time = 15d009\_Carbon-1-10.jdf = delta = carbon.jxp = 15d009 = 15d009 = DMSO-D6 = 1-JUN-2015 16:57:28 = 5-JUN-2015 15:45:10 = 5-JUN-2015 15:58:25 = sp-8/13C = 1D REAL = 26214 = Carbon13 = [ppm] = X = ECA 500 = DELTA2\_NMR Comment Data Format Dim\_Size Dim\_Title Dim\_Units Dimensions Site Spectrometer 
 Spactromster
 DELTA2\_NER

 Field Strength
 11.62926421[7] (500

 X Acg\_Duration
 0.0386608[8]

 X Dream
 132

 X Treq
 136 0510059[RHz]

 X Treq
 136 0510059[RHz]

 X Presens
 4

 X Sweep
 39.0625[RHz]

 X Sweep
 39.0625[RHz]

 X Sweep
 31.25[RHz]

 Thr Domain
 Proton

 Irr\_Dreq
 405.13191398[MHz]

 Irr\_Offset
 5[pn]

 Clipped
 FALSE

 Stans
 20000

 Total\_Sons
 2000
 = 11.62926421[T] (500[MHz]) = 0.8388608[s] 
 10tal\_static
 - 2000

 Delaxation
 = 60

 Peop Gat
 = 23.9[dCl

 Yamp Gat
 = 03.9[dCl

 Yamp Gat
 = 30.9[dCl

 X Acq Time
 = 0.035[us]

 X Acq Time
 = 0.088608[c3]

 X Acq Time
 = 0.038608[c3]

 X Acq Time
 = 0.388608[c3]

 X Ata
 = 0.173[d3]

 Irr Ata Nee
 = 21.173[d3]

 Irr Moise
 = 40.173

 Irr Moise
 = 40.173

 Irr Moise
 = 40.173

 Irr Moise
 = 10.173

 Irr Moise
 = 10.173

 Irr Moise
 = 10.173

 Irr Moise
 = 10.173

 Irris Mait
 = 1[s]

 Nos
 = Truts
 = 92[us] = TRUE = 1[s] = TRUE Noe Noe\_Time Repetition\_Time = 2[s] = 2.8388608[s] Water Winderstein Strategie i si na palanta ina panana ka manana manana ka manana ka manana ka manana ka mana ka mana ka mana ka mana ka k while we are the second and the second and the 200.0 190.0 180.0 170.0 160.0 150.0 20.0 ò 50.0 40.0 30.0 10.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 the second second 74.324 72.122 70.599 68.024 64.500 121.605 -105.184 88.265 80.356 54.849 280 143.321 E X : parts per Million : Carbon13

Figure 14. <sup>13</sup>C NMR spectrum (125 MHz) of longispinoside A (2) in DMSO-*d*<sub>6</sub>.

#### Figure 15. DEPT 90 and 135 pulse NMR spectra of longispinoside A (2) in DMSO-*d*<sub>6</sub>.



#### Figure 16. DQF-COSY spectrum of longispinoside A (2) in DMSO-d<sub>6</sub>.



#### Figure 17. HMQC spectrum of longispinoside A (2) in DMSO-d<sub>6</sub>.



#### Figure 18. HMBC spectrum of longispinoside A (2) in DMSO-d<sub>6</sub>.



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#### Figure 19. HSQC-TOCSY spectrum of longispinoside A (2) in DMSO-d<sub>6</sub>.



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#### Figure 21. NOESY spectrum of longispinoside A (2) in DMSO-*d*<sub>6</sub>.



K

# Figure 22. <sup>1</sup>H NMR spectrum (500 MHz) of longispinoside A methyl ester (3) in DMSO-*d*<sub>6</sub>.



Figure 23. <sup>13</sup>C NMR spectrum (125 MHz) of longispinoside A methyl ester (3) in DMSO-*d*<sub>6</sub>.



#### Figure 24. DEPT 90 and 135 pulse NMR spectra of longispinoside A methyl ester (3) in DMSO-*d*<sub>6</sub>.





Figure 25. DQF-COSY spectrum of longispinoside A methyl ester (3) in DMSO-d<sub>6</sub>.

0.8 +. JEOL RESONANCE -0.6 t. 0.4 + . abundance 0 0.2 0 = 16d001\_HMQC-1-5.jdf = delta Filename All Experiment Sample\_Id Solvent = hmqc.jxp = 16d001 = DMSO-D6 n all MARY 01 Solvent Creation\_Time Revision\_Time Current\_Time = DMSO-D6 = 19-MAY-2016 16:08:47 = 23-MAY-2016 17:22:12 = 23-MAY-2016 17:22:48 sp-9/gradient enhanced HMQC with X-decoupling 10.0 = sp-9/gradient enhanced H4Q = 20 REAL REAL = 819, 512 = Proton Carbon13 = [ppm] [ppm] = X Y = ECA 500 = DEU TR3 1 MP Comment Data Format Dim\_Size Dim\_Title Dim\_Units Dimensions 20.0 . 1 60 vito Site Spectrometer 30.0 = DELTA2\_NMR = 11.62926421[T] (500[MHz]) = 0.15024128[s] Field\_Strength X\_Acq\_Duration X\_Domain X\_Freq X\_Frints X\_Frints X\_Frints X\_Frints X\_Frints X\_Sweep X\_Sweep Y\_Demain Y\_Freq Y\_Frints Y\_Freq Y\_Fre Field Strength 40.0 0 = 1H = 495.13191398[MHz] 69 = 5[ppm] = 1024 1 0 50.0 = 1024 = 4 = 6.65596033[Hz] = 6.81570338[kHz] = 5.4525627[kHz] = 13C = 124.5010059[kHz] = 100[ppm] = 256 = 0 (1) 60.0 0 () 6 · 000 % 70.0 0 0 = 256 = 0 = 121.76589776[Hz] = 31.17206983[kHz] = Proton = 495.13191398[MHz] = 5[ppm] = FALSE = 64 = 16384 0 80.0 (h 90.06 Scans Total\_Scans 100.0 Relaxation Dolay Reave Galaxation Dolay Reave Galaxation X Aoq Time X Aoq Time X Aoq Time Y Aon Y Dolay Y Aon Y Dolay Time Dolay Dolay Time Crad 2 Amp Grad 2 Amp Grad 2 Amp Grad 2 Amp Grad 3 Amp Grad 2 Amp Grad 3 Amp Gra Lay = 1.5[s] = 50 = 23.7[dC] = 23.7[dC] = 0.15024128[s] = 3.8[dB] = 12.5[us] = 6.21248[ms] = 6.1[dB] = 10.25[us] = 27.32[dB] = MPF8 0 110.0 120.0 = MPF8 = 0.118[ms] 130.0 = 0.110[fma] = 0.0ff = PALSE = TRUE = 1.5[s] = 0.18[T/m] = 0.18[T/m] = 0.18[T/m] = 1.18[T/m] = 0.18[T/m] = 0.18[T/m] = 0.1425966[mT/m] = 1.18[ = 1.060:1.900:1 = 1.18[ = 1.060:24128[s] = 1.050:24128[s] = 1.050:24128[s] 140.0 Y : parts per Million : Carbon13 200.0.90.0 180.0 170.0 160.0 150.0 = 1.65024128[ = 1[us] = 8.1814[ms] = 1.988 = 2 πp 20.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 Ó Ó 10.0 30.0 (thousandths) X : parts per Million : Proton

Figure 26. HMQC spectrum of longispinoside A methyl ester (3) in DMSO-d<sub>6</sub>.

0.8 , . . . . iii JEOL RESONANCE 0.6 al Site 0.4 abundance 0 0.2 .... = 16d001\_HMBC-1-4.jdf = delta = hmbc.jxp = 16d001 Filename Author 4. ALL Experiment and! Sample\_Id Solvent = 16d001 = DMSO-D6 = 19-MAY-2016 23:43:42 = 23-MAY-2016 17:46:30 = 23-MAY-2016 17:47:06 0 Creation\_Time Revision\_Time Current\_Time sp-9/gradient enhanced HMBC 10.0 = sp-9/gradient enhanced HMB = 2D REAL REAL = 1638, 512 = Proton Carbon13 Comment Data Format Din Size Din Title Din Units Dimensions Site 0 ARCA . 96 20.0 = [ppm] [ppm] = X Y = ECA 500 = DELTA2\_NMR (h) () 4 00. 30.0 Speatromete = 11.62926421[T] (500[MHz]) = 0.30048256[s] 明日 40.0 0 0 0 0 = 495,13191398[MHz] 00 50.0 (1) (1) 0 60.0 = 13C = 124.5010059[MHz] = 256 = 0 = 101[ppm] = 256 = 0 = 121.75589776[Hz] = 31.17206993[kHz] = Froton = 495.13591398[MHz] = 5[ppm] = FALSE = 128 0 0 (4) 70.0 0 .0 0 0 80.0 0 0 0.06 
 Scans
 = 126

 Total\_Scans
 = 32768

 Relaxation\_Dolay
 = 1.5[s]

 Recrepted
 = 6.004205(s]

 Xymp\_Oot
 = 0.004205(s]

 Yahn
 = 0.1240[nm]

 Yahn
 = 0.125[us]

 Tri.Mode
 = 0ff

 Datay\_Time
 = 1.05[u]

 Datay\_Time
 = 1.5[u]

 Datay
 = 3.03206016[ms]

 Datain
 = 3.03206016[ms]

 Datain
 = 3.03206016[ms]

 Datain
 = 1.52[ms]

 Cand I
 = 1[ns]

 Grad J
 = 1[ns]

 Grad J
 = 0.18[T/m]

 Grad J
 = 0.18[T/m]
</t 100.0 0 0 110.0 120.0 130.0 140.0 0 0 150.0 Y : parts per Million : Carbon13 200.0190.0 180.0 170.0 160.0 0 19 7.0 10.0 9.0 5.0 3.0 1.0 Ó Ó 10.0 20.0 30.0 8.0 6.0 2.0 4.0 X : parts per Million : Proton (thousandths)

Figure 27. HMBC spectrum of longispinoside A methyl ester (3) in DMSO-d<sub>6</sub>.



Figure 28. HSQC-TOCSY spectrum of longispinoside A methyl ester (3) in DMSO-*d*<sub>6</sub>.



#### Figure 29. pfg-TOCSY spectrum of longispinoside A methyl ester (3) in DMSO-*d*<sub>6</sub>.
**Figure 30.** NOESY spectrum of longispinoside A methyl ester (**3**) in DMSO-*d*<sub>6</sub>.





Figure 31. <sup>1</sup>H NMR spectrum (500 MHz) of erythronoside A methyl ester (4) in DMSO-*d*<sub>6</sub>.

Figure 32. <sup>13</sup>C NMR spectrum (125 MHz) of erythronoside A methyl ester (4) in DMSO-*d*<sub>6</sub>.



## Figure 33. DEPT 90 and 135 pulse NMR spectra of erythronoside A methyl ester (4) in DMSO-*d*<sub>6</sub>.





### Figure 34. DQF-COSY spectrum of erythronoside A methyl ester (4) in DMSO-d<sub>6</sub>.

Figure 35. HMQC spectrum of erythronoside A methyl ester (4) in DMSO-*d*<sub>6</sub>.



Figure 36. HMBC spectrum of erythronoside A methyl ester (4) in DMSO-*d*<sub>6</sub>.





Figure 37. HSQC-TOCSY spectrum of erythronoside A methyl ester (4) in DMSO-*d*<sub>6</sub>.



Figure 38. pfg-TOCSY spectrum of erythronoside A methyl ester (4) in DMSO-d<sub>6</sub>.



Figure 39. NOESY spectrum of erythronoside A methyl ester (4) in DMSO-*d*<sub>6</sub>.



Figure 40. <sup>1</sup>H NMR spectrum (500 MHz) of cochalinoside C (5) in DMSO-*d*<sub>6</sub>.

Figure 41. <sup>13</sup>C NMR spectrum (125 MHz) of cochalinoside C (5) in DMSO-*d*<sub>6</sub>.



## Figure 42. DEPT 90 and 135 pulse NMR spectra of cochalinoside C (5) in DMSO-d<sub>6</sub>.











### Figure 45. HMBC spectrum of cochalinoside C (5) in DMSO-d<sub>6</sub>.





Figure 46. HSQC-TOCSY spectrum of cochalinoside C (5) in DMSO-d<sub>6</sub>.



Figure 47. pfg-TOCSY spectrum of cochalinoside C (5) in DMSO-d<sub>6</sub>.

Figure 48. NOESY spectrum of cochalinoside C (5) in DMSO-d<sub>6</sub>.





**Figure 49.** <sup>1</sup>H NMR spectrum (500 MHz) of oleanolic acid 3-*O*- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- $\beta$ -D-glucuronopyranosyl-28-*O*- $\beta$ -D-glucopyranoside (6) in DMSO-*d*<sub>6</sub>.

**Figure 50.** <sup>13</sup>C NMR spectrum (125 MHz) of oleanolic acid 3-*O*- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- $\beta$ -D-glucuronopyranosyl-28-*O*- $\beta$ -D-glucopyranoside (6) in DMSO-*d*<sub>6</sub>.



# Figure 51. DEPT 90 and 135 pulse NMR spectra of oleanolic acid 3-*O*- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- $\beta$ -D-glucuronopyranosyl-28-*O*- $\beta$ -D-glucopyranoside (6) in DMSO-*d*<sub>6</sub>.





Figure 52. <sup>1</sup>H-<sup>1</sup>H COSY spectrum of oleanolic acid 3-*O*- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- $\beta$ -D-glucuronopyranosyl-28-*O*- $\beta$ -D-glucopyranoside (6) in DMSO-*d*<sub>6</sub>.



Figure 53. HMQC spectrum of oleanolic acid 3-*O*- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- $\beta$ -D-glucuronopyranosyl-28-*O*- $\beta$ -D-glucopyranoside (6) in DMSO-*d*<sub>6</sub>.



Figure 54. HMBC spectrum of oleanolic acid 3-*O*- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- $\beta$ -D-glucuronopyranosyl-28-*O*- $\beta$ -D-glucopyranoside (6) in DMSO-*d*<sub>6</sub>.



Figure 55. HSQC-TOCSY spectrum of oleanolic acid 3-*O*- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- $\beta$ -D-glucuronopyranosyl-28-*O*- $\beta$ -D-glucopyranoside (6) in DMSO-*d*<sub>6</sub>.



Figure 56. pfg-TOCSY spectrum of oleanolic acid 3-*O*- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- $\beta$ -D-glucuronopyranosyl-28-*O*- $\beta$ -D-glucopyranoside (6) in DMSO-*d*<sub>6</sub>.



Figure 57. NOESY spectrum of oleanolic acid 3-*O*- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- $\beta$ -D-glucuronopyranosyl-28-*O*- $\beta$ -D-glucopyranoside (6) in DMSO-*d*<sub>6</sub>.



Figure 58. <sup>1</sup>H NMR spectrum (500 MHz) of stenoside A (7) in DMSO-*d*<sub>6</sub>.



Figure 59. <sup>13</sup>C NMR spectrum (125 MHz) of stenoside A (7) in DMSO-*d*<sub>6</sub>.

# Figure 60. DEPT 90 and 135 pulse NMR spectra of stenoside A (7) in DMSO-*d*<sub>6</sub>.



Figure 61. DQF-COSY spectrum of stenoside A (7) in DMSO-*d*<sub>6</sub>.



## Figure 62. HMQC spectrum of stenoside A (7) in DMSO-d<sub>6</sub>.



Figure 63. HMBC spectrum of stenoside A (7) in DMSO-d<sub>6</sub>.



# Figure 64. HSQC-TOCSY spectrum of stenoside A (7) in DMSO-*d*<sub>6</sub>.



Figure 65. pfg-TOCSY spectrum of stenoside A (7) in DMSO-d<sub>6</sub>.


Figure 66. NOESY spectrum of stenoside A (7) in DMSO-*d*<sub>6</sub>.

