SUPPLEMENTARY MATERIAL

Three new triterpenoid saponins from the roots of *Ardisia crenata* and their cytotoxic activities

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Abstract

Three new triterpenoid saponins, ardisicrenoside **O** (**1**), ardisicrenoside **P** (**2**) and ardisicrenoside **Q** (**3**) together with three known compounds, 3 β ,16 α -dihydroxy-30-methoxy-28, 30-epoxy-olean-12-en, cyclamiretin A 3-O- β -D-glucopyranosyl-(1 $\rightarrow$ 2) - α -L-arabinopyranoside and cyclamiretin A 3-O- β -D-glucopyranosyl-(1 $\rightarrow$ 4) - α -L-arabinopyranoside were isolated from the roots of *Ardisia crenata* Sims. Their structures were determined by one- and two-dimensional NMR techniques, including HSQC, HMBC and TOCSY experiments, as well as acid hydrolysis and GC analysis. All isolates were evaluated for the cytotoxic activities on two human cancer cell lines and compound **3**, **5** and **6** showed significant cytotoxicity.

Keywords: *Ardisia crenata* Sims; Oleanane; triterpenoid saponins; cytotoxicity

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compound 1	$R_1 = \text{Xyl}$	$R_2 = \text{Glc}$
compound 2	$R_1 = \text{Rham}$	$R_2 = \text{Glc}$
compound 3	$R_1 = \text{H}$	$R_2 = \text{H}$

Figure S1 the structures of compound 1, 2 and 3

Figure S2 the key HMBC correlations of compound 1

Table S1

¹H NMR (400MHz) and ¹³C NMR (100MHz) data of compound **1**, **2** and **3** in C₅D₅N (δ in ppm, *J* in Hz).

1			2			3		
Position	¹ H ^a	¹³ C ^b	Position	¹ H ^a	¹³ C ^b	Position	¹ H ^a	¹³ C ^b
1	1.44(<i>o</i>), 0.92 (<i>o</i>)	38.6 t	1	1.46(<i>o</i>), 0.86 (<i>o</i>)	38.6 t	1	1.54 (<i>o</i>), 0.96 (<i>o</i>)	38.7 t
2	1.96 (<i>o</i>), 1.74 (<i>o</i>)	26.4 t	2	1.98 (<i>o</i>), 1.78 (<i>o</i>)	26.3 t	2	2.12 (<i>o</i>), 1.86 (<i>o</i>)	26.6 t
3	3.14 (dd, <i>J</i> =11.6, 4.4)	88.9 d	3	3.13 (dd, <i>J</i> =11.6, 4.4)	88.9 d	3	3.30 (dd, <i>J</i> =11.8, 3.7)	88.6 d
4		39.5 s	4		39.4 s	4		39.5 s
5	0.70 (d, <i>J</i> =11.4)	56.0 d	5	0.68 (<i>o</i>)	55.9 d	5	0.80 (d, <i>J</i> =11.7)	56.0 d
6	1.47 (<i>o</i>), 1.30 (<i>o</i>)	18.3 t	6	1.45 (<i>o</i>), 1.28 (<i>o</i>)	18.3 t	6	1.48 (<i>o</i>), 1.28 (<i>o</i>)	18.3 t
7	1.45 (m), 1.38 (<i>o</i>)	32.6 t	7	1.45 (m), 1.31 (<i>o</i>)	32.6 t	7	1.47 (m), 1.43 (<i>o</i>)	32.7 t
8		40.2 s	8		40.2 s	8		40.2 s
9	1.53 (<i>o</i>)	47.2 d	9	1.52 (<i>o</i>)	47.2 d	9	1.58 (<i>o</i>)	47.3 d
10		36.9 s	10		36.9 s	10		36.8 s
11	1.85 (2H, <i>o</i>)	23.6 t	11	1.86 (2H, <i>o</i>)	23.6 t	11	1.88 (2H, <i>o</i>)	23.6 t
12	5.34 (t, <i>J</i> =2.9)	121.7 d	12	5.32 (<i>o</i>)	121.7 d	12	5.36 (t, <i>J</i> =2.9)	121.8 d
13		143.3 s	13		143.3 s	13		136.1 s
14		43.2 s	14		43.2 s	14		43.3 s
15	2.24 (<i>o</i>), 1.68 (m)	37.0 t	15	2.23 (<i>o</i>), 1.66 (t, <i>J</i> =13.1)	36.9 t	15	3.25 (<i>o</i>), 1.70 (m)	36.9 t
16	3.56(m)	70.9 d	16	3.54(m)	70.9 d	16	3.58 (m)	70.9 d
17		41.6 s	17		41.6 s	17		41.6 s
18	3.23 (t, <i>J</i> =10.5)	47.2 d	18	3.20 (m)	47.1 d	18	3.23 (t, <i>J</i> =10.5)	47.2 d
19	2.21 (<i>o</i>), 1.32 (<i>o</i>)	43.1 t	19	2.19 (<i>o</i>), 1.32 (<i>o</i>)	43.1 t	19	2.21 (<i>o</i>), 1.34 (<i>o</i>)	43.1 t
20		38.9 s	20		38.9 s	20		38.9 s
21	2.06 (<i>o</i>), 1.31(<i>o</i>)	31.6 t	21	2.05 (<i>o</i>), 1.31(<i>o</i>)	31.6 t	21	2.04 (<i>o</i>), 1.30 (<i>o</i>)	31.6 t
22	2.31 (<i>o</i>), 2.19(<i>o</i>)	20.2 t	22	2.28 (<i>o</i>), 2.17(<i>o</i>)	20.2 t	22	2.28 (<i>o</i>), 2.16(<i>o</i>)	20.2 t
23	1.21 (s)	28.0 q	23	1.16 (s)	28.0 q	23	1.26 (s)	28.1 q
24	1.08 (s)	16.8 q	24	1.02 (s)	16.6 q	24	0.97 (s)	16.9 q
25	0.82 (s)	15.5 q	25	0.82 (s)	15.5 q	25	0.88 (s)	15.6 q
26	0.91 (s)	16.0 q	26	0.86 (s)	16.0 q	26	0.89 (s)	16.1 q
27	1.38 (s)	28.1 q	27	1.36 (s)	28.1 q	27	1.40 (s)	28.2 q
28	4.68 (d, <i>J</i> =10.6), 3.73(<i>o</i>)	78.6 t	28	4.66 (d, <i>J</i> =10.6), 3.72(<i>o</i>)	78.6 t	28	4.68 (<i>o</i>), 3.74(<i>o</i>)	78.6 t
29	0.98 (s)	28.2 q	29	0.99 (s)	28.2 q	29	0.99 (s)	28.3 q
30	4.43 (s)	110.1 d	30	4.44 (s)	110.1 d	30	4.45 (s)	110.2 d
30-OCH ₃	3.44 (s)	55.6 q	30-OCH ₃	3.44 (s)	55.6 q	30-OCH ₃	3.45 (s)	55.6 q
3- <i>O</i> -sugars			3- <i>O</i> -sugars			3- <i>O</i> -sugars		
chain Ara-1	4.76 (d, <i>J</i> =5.9)	104.6 d	chain Ara-1	4.91 (br. s)	104.3 d	chain Ara-1	4.69(d, <i>J</i> =5.5)	107.2 d
2	4.56 (<i>o</i>)	79.7 d	2	4.53 (<i>o</i>)	80.7 d	2	4.38 (<i>o</i>)	73.5 d
3	4.26 (m)	73.2 d	3	4.46 (m)	72.3 d	3	4.15 (m)	74.5 d

4	4.23 (<i>o</i>)	78.5 d	4	4.55 (<i>o</i>)	74.7 d	4	4.36 (<i>o</i>)	79.7 d
5	4.59 (d, <i>J</i> =4.0), 3.65 (<i>o</i>)	64.2 t	5	4.38 (<i>o</i>), 3.78 (<i>o</i>)	63.4 t	5	4.42 (<i>o</i>), 3.77 (<i>o</i>)	66.1 t
Terminal			Terminal					
4-Glc-1	5.48 (d, <i>J</i> =7.6)	104.9 d	Glc-1	5.33 (<i>o</i>)	105.4 d	4-Glc-1	5.25 (d, <i>J</i> =7.5)	106.8 d
2	4.07 (<i>o</i>)	76.2 d	2	4.05 (<i>o</i>)	76.3 d	2	4.03 (d, <i>J</i> =8.0)	75.8 d
3	4.01 (<i>o</i>)	77.9 d	3	4.21 (<i>o</i>)	78.0 d	3	4.22 (<i>o</i>)	78.4 d
4	4.24 (<i>o</i>)	71.8 d	4	4.22 (<i>o</i>)	71.7 d	4	4.23(<i>o</i>)	71.3 d
5	4.01 (<i>o</i>)	77.8 d	5	4.05 (<i>o</i>)	78.1 d	5	3.94(<i>o</i>)	78.7 d
6	4.39 (m), 4.54 (<i>o</i>)	63.0 t	6	4.36 (m), 4.45 (<i>o</i>)	62.8 t	6	4.52 (d, <i>J</i> =11.4), 3.58(m)	62.6 d
Inner Glc-1	4.99 (d, <i>J</i> =7.8)	104.2 d	Inner Glc-1	5.22 (d, <i>J</i> =7.8)	103.1 d			
2	3.92 (<i>o</i>)	85.4 d	2	4.24 (<i>o</i>)	77.2 d			
3	4.20 (<i>o</i>)	77.5 d	3	4.17 (<i>o</i>)	79.5 d			
4	4.21 (<i>o</i>)	71.1 d	4	4.12 (<i>o</i>)	71.8 d			
5	3.78 (<i>o</i>)	78.3 d	5	3.77 (<i>o</i>)	78.3 d			
6	4.41 (<i>o</i>), 4.29 (<i>o</i>)	62.3 t	6	4.37 (<i>o</i>), 4.27 (<i>o</i>)	62.6 t			
Xyl-1	4.90 (<i>o</i>)	107.6 d	Rham-1	6.38 (br s)	101.5 d			
2	4.02 (<i>o</i>)	76.1 d	2	4.69 (<i>o</i>)	72.3 d			
3	4.25(<i>o</i>)	78.2 d	3	4.64 (<i>o</i>)	72.7 d			
4	4.19 (<i>o</i>)	70.7 d	4	4.23 (<i>o</i>)	74.8 d			
5	4.52 (<i>o</i>), 3.68(<i>o</i>)	67.4 t	5	5.01 (<i>o</i>)	69.4 t			
			6	1.78 (d, <i>J</i> =6.2)	18.8 q			

^a 400MHz, Pyr-d₅; chemical shifts in ppm relative to TMS; coupling constants (*J*) in Hz;

^b 100MHz, Pyr-d₅; multiplicity was established from DEPT data.

¹H NMR of compound 1

¹³C NMR of compound 1

HMOC of compound 1

HMBC of compound 1

NOESY of compound 1

TOCSY of compound 1

¹H NMR of compound 2

¹³C NMR of compound 2

^1H - ^1H COSY of compound 2

DEPT135 of compound 2

NOESY of compound 2

TOCSY of compound 2

¹H NMR of compound 3

¹³C NMR of compound 3

^1H - ^1H COSY of compound 3

DEPT 135 of compound 3

HMQC of compound 3

NOESY of compound 3

TOCSY of compound 3