

## New Pentacyclic Triterpenoids from *Centella asiatica*

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Three new pentacyclic triterpenoids, named centellasaponins G, H, and F (**1–3**, resp.), together with four known compounds, **4–7**, were isolated from the whole plants of *Centella asiatica*. Their structures were elucidated on the basis of chemical and spectral analysis, including 1D- and 2D-NMR and HR-MS experiments, and by comparison with literature data.

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**Introduction.** – *Centella asiatica* (L.) URBAN is a traditional herbal medicine used in Asia and Africa. The medicinal preparation obtained from the plant is widely used for wound healing and to treat hypertrophic scars [1][2]. Previous chemical studies showed that pentacyclic triterpenes were the main constituents of this plant [3]. As a part of our continuing search for bioactive components from *Centella asiatica*, our investigation now revealed the presence of three new pentacyclic triterpenoids named centellasaponins G, H, and F (**1–3**, resp.), along with four known triterpenes, **4–7** (Fig. 1) [4][5]. Centellasaponin G (**1**) is isomeric with centellasaponin H (**2**). They are the first two pentacyclic triterpenes with four sugar units. Centellasaponin F (**3**) is a new pentacyclic triterpene which bears two HOCH<sub>2</sub> groups at C(4) of the aglycon.

**Results and Discussion.** – The crude extract of *C. asiatica* was repeatedly subjected to column chromatography (silica gel) and preparative HPLC to afford seven compounds. Compounds **1–3** were new, and their structures were elucidated on the basis of 1D- and 2D-NMR data in combination with MS studies. The other four compounds were identified as asiaticoside B (**4**) [6], madecassoside (**5**) [7], scheffoleoside A (**6**) [8], and centellasaponin A (**7**) [9] by comparison of their spectroscopic data with those reported in the literature.

Compound **1** was isolated as white amorphous powder. The HR mass spectrum exhibited a *quasi*-molecular-ion peak at  $m/z$  1159.5516 ( $[M + Na]^+$ ; calc. 1159.5512) consistent with the molecular formula C<sub>54</sub>H<sub>88</sub>O<sub>25</sub>. The IR spectrum displayed characteristic absorptions for OH (3442 cm<sup>-1</sup>), C=O (1735 cm<sup>-1</sup>), and olefin moieties (1637 cm<sup>-1</sup>). The <sup>13</sup>C-NMR data (Table) of **1** showed two olefinic signals at  $\delta(C)$  126.3 and 138.0. The HMBCs CH<sub>2</sub>(11) ( $\delta(H)$  2.08–2.15, 2.23–2.27)/ $\delta(C)$  126.3, CH<sub>2</sub>(11)/C(13) ( $\delta(C)$  138.0); H–C(18) ( $\delta(H)$  2.50)/C(12) ( $\delta(C)$  126.3); H–C(18)/C(13) ( $\delta(C)$  138.0), and Me(27) ( $\delta(H)$  1.11)/C(13) established the presence of the C(12)=C(13)

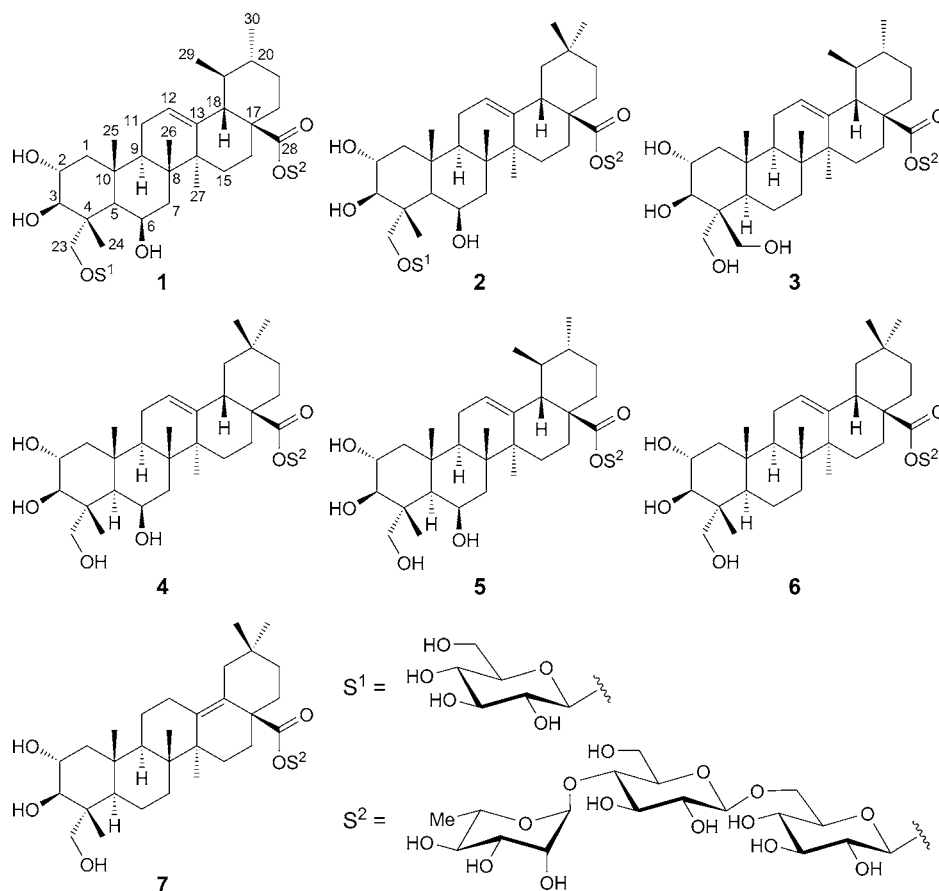


Fig. 1. Compounds **1**–**7**, isolated from *Centella asiatica*

bond (Fig. 2). The long-range correlations Me(29) ( $\delta(\text{H})$  0.90)/C(18) ( $\delta(\text{C})$  53.4), Me(29) ( $\delta(\text{H})$  0.90)/C(20) ( $\delta(\text{C})$  39.1); Me(30) ( $\delta(\text{H})$  0.86)/C(21) ( $\delta(\text{C})$  30.0); and Me(30) ( $\delta(\text{H})$  0.86)/C(22) ( $\delta(\text{C})$  35.8) showed that compound **1** possessed an ursane-type skeleton. The long-range correlations H–C(1'') ( $\delta(\text{H})$  6.13)/C(28) ( $\delta(\text{C})$  176.3); H–C(1''') ( $\delta(\text{H})$  4.92–4.94)/C(6'') ( $\delta(\text{C})$  69.5), and H–C(1''''') ( $\delta(\text{H})$  5.84)/C(4''') ( $\delta(\text{C})$  77.9) revealed the linkage sequence of the sugar units. The *quasi*-molecular-ion peak established that compound **1** had 162 mass units more than madecassoside (**5**). Moreover, the signals of a sugar unit were observed in the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of **1** (Table), which were absent in the spectra of madecassoside (**5**). In the HMBC experiment, the long-range correlation H–C(1') ( $\delta(\text{H})$  5.29)/C(23) ( $\delta(\text{C})$  73.3) was observed, revealing that the single sugar unit was linked to C(23) of the skeleton. From the above evidences, the structure of compound **1**, named centellasaponin G, was elucidated as depicted in Fig. 1.

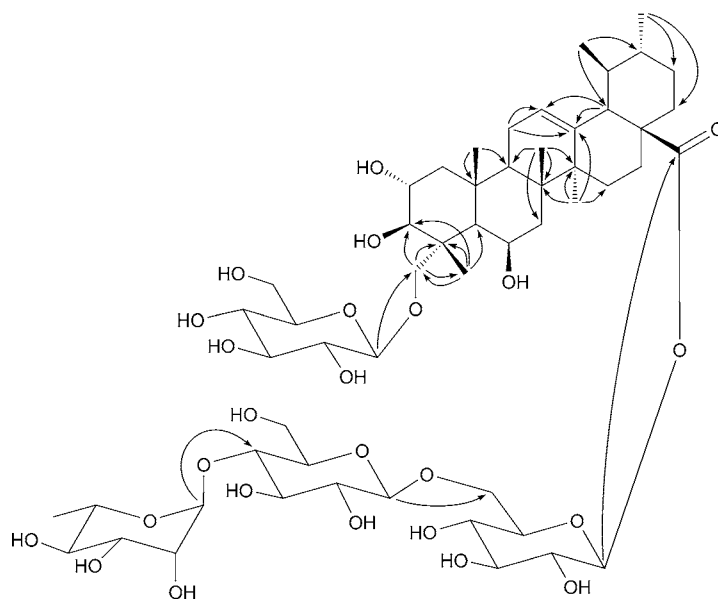
Compound **2** was isolated as white amorphous powder. The HR-ESI mass spectrum exhibited a *quasi*-molecular-ion peak at  $m/z$  1159.5519 ( $[M + \text{Na}]^+$ ; calc. 1159.5512)

Table.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR Data of **1**, **2**, and **3** (in  $\text{D}_2\text{O}$ /pyridine, at 600 and 150 MHz, resp.).  $\delta$  in ppm,  $J$  in Hz.

Position	Centellasaponin G ( <b>1</b> )		Centellasaponin H ( <b>2</b> )		Centellasaponin F ( <b>3</b> )	
	$\delta(\text{H})$	$\delta(\text{C})$	$\delta(\text{H})$	$\delta(\text{C})$	$\delta(\text{H})$	$\delta(\text{C})$
1	1.38–1.42 ( <i>m</i> ), 2.30–2.34 ( <i>m</i> )	50.3 ( <i>t</i> )	1.38–1.43 ( <i>m</i> ), 2.28–2.34 ( <i>m</i> )	50.0 ( <i>t</i> )	1.34–1.41 ( <i>m</i> )	48.2 ( <i>t</i> )
2	4.29–4.33 ( <i>m</i> )	68.8 ( <i>d</i> )	4.22–4.26 ( <i>m</i> )	68.8 ( <i>d</i> )	4.04–4.08 ( <i>m</i> )	69.9 ( <i>d</i> )
3	4.01–4.06 ( <i>m</i> )	79.0 ( <i>d</i> )	3.99–4.03 ( <i>m</i> )	79.1 ( <i>d</i> )	3.43–3.47 ( <i>m</i> )	79.6 ( <i>d</i> )
4		44.3 ( <i>s</i> )		44.4 ( <i>s</i> )		47.9 ( <i>s</i> )
5	1.88–1.94 ( <i>m</i> )	48.8 ( <i>d</i> )	1.84–1.89 ( <i>m</i> )	50.0 ( <i>d</i> )	1.58–1.64 ( <i>m</i> )	48.6 ( <i>d</i> )
6	4.86–4.92 ( <i>m</i> )	67.9 ( <i>d</i> )	4.92 ( <i>br. s</i> )	68.0 ( <i>d</i> )	0.94–0.98 ( <i>m</i> )	19.6 ( <i>t</i> )
7	1.83–1.88 ( <i>m</i> ), 2.18–2.22 ( <i>m</i> )	41.1 ( <i>t</i> )	1.82–1.89 ( <i>m</i> ), 2.10–2.17 ( <i>m</i> )	41.0 ( <i>t</i> )		34.0 ( <i>t</i> )
8		39.5 ( <i>s</i> )		39.4 ( <i>s</i> )		43.4 ( <i>s</i> )
9	1.88–1.92 ( <i>m</i> )	49.5 ( <i>d</i> )	1.84–1.89 ( <i>m</i> )	48.8 ( <i>d</i> )	1.58–1.64 ( <i>m</i> )	48.3 ( <i>d</i> )
10		38.0 ( <i>s</i> )		38.0 ( <i>s</i> )		38.8 ( <i>s</i> )
11	2.08–2.15 ( <i>m</i> ), 2.23–2.27 ( <i>m</i> )	23.9 ( <i>t</i> )	1.97–2.02 ( <i>m</i> )	23.5 ( <i>t</i> )	1.93–1.98 ( <i>m</i> )	24.7 ( <i>t</i> )
12	5.49 ( <i>br. s</i> )	126.3 ( <i>d</i> )	5.45 ( <i>br. s</i> )	123.8 ( <i>d</i> )	5.24 ( <i>br. s</i> )	126.9 ( <i>d</i> )
13		138.0 ( <i>s</i> )		143.7 ( <i>s</i> )		139.4 ( <i>s</i> )
14		43.2 ( <i>s</i> )		42.8 ( <i>s</i> )		41.0 ( <i>s</i> )
15	1.11–1.15 ( <i>m</i> ), 1.18–1.22 ( <i>m</i> )	28.6 ( <i>t</i> )	1.20–1.26 ( <i>m</i> ), 1.28–1.32 ( <i>m</i> )	28.1 ( <i>t</i> )	1.34–1.41 ( <i>m</i> )	29.3 ( <i>t</i> )
16	1.88–1.94 ( <i>m</i> )	24.7 ( <i>t</i> )	1.97–2.02 ( <i>m</i> )	24.0 ( <i>t</i> )	1.93–1.98 ( <i>m</i> )	25.3 ( <i>t</i> )
17		48.5 ( <i>s</i> )		47.1 ( <i>s</i> )		49.2 ( <i>s</i> )
18	2.50 ( <i>d</i> , $J=12$ )	53.4 ( <i>d</i> )	3.15 ( <i>dd</i> , $J=12,6$ )	41.7 ( <i>d</i> )	2.23 ( <i>d</i> , $J=5.4$ )	54.1 ( <i>d</i> )
19	1.28–1.35 ( <i>m</i> )	39.4 ( <i>d</i> )	1.63–1.67 ( <i>m</i> )	46.3 ( <i>d</i> )	0.95–0.98 ( <i>m</i> )	40.4 ( <i>d</i> )
20	0.84–0.87 ( <i>m</i> )	39.1 ( <i>d</i> )	1.28–1.32 ( <i>m</i> )	30.7 ( <i>d</i> )	0.95–0.98 ( <i>m</i> )	40.2 ( <i>d</i> )
21	1.28–1.33 ( <i>m</i> )	30.0 ( <i>t</i> )	1.20–1.26 ( <i>m</i> )	34.1 ( <i>t</i> )	1.28–1.33 ( <i>m</i> )	31.7 ( <i>t</i> )
22	1.63–1.66 ( <i>m</i> )	35.8 ( <i>t</i> )	1.66–1.72 ( <i>m</i> )	32.5 ( <i>t</i> )	1.70–1.76 ( <i>m</i> )	37.6 ( <i>t</i> )
23	3.64–3.68 ( <i>m</i> )	73.3 ( <i>t</i> )	3.69 ( <i>d</i> , $J=6$ ), 4.25–4.28 ( <i>m</i> )	73.7 ( <i>t</i> )	3.48–3.52 ( <i>m</i> ), 4.02–4.05 ( <i>m</i> )	64.6 ( <i>t</i> )
24	1.72 ( <i>s</i> )	15.9 ( <i>q</i> )	1.72 ( <i>s</i> )	15.9 ( <i>q</i> )	3.59–3.67 ( <i>m</i> ), 3.77–3.84 ( <i>m</i> )	61.9 ( <i>t</i> )
25	1.76 ( <i>s</i> )	19.3 ( <i>q</i> )	1.74 ( <i>s</i> )	19.1 ( <i>q</i> )	1.04 ( <i>s</i> )	17.9 ( <i>q</i> )
26	1.69 ( <i>s</i> )	19.4 ( <i>q</i> )	1.66 ( <i>s</i> )	18.9 ( <i>q</i> )	0.81 ( <i>s</i> )	17.9 ( <i>q</i> )
27	1.11 ( <i>s</i> )	23.8 ( <i>q</i> )	1.16 ( <i>s</i> )	26.1 ( <i>q</i> )	1.11 ( <i>s</i> )	24.0 ( <i>q</i> )
28		176.3 ( <i>s</i> )		176.5 ( <i>s</i> )		178.0 ( <i>s</i> )
29	0.90 ( <i>s</i> )	17.3 ( <i>q</i> )	0.83 ( <i>s</i> )	33.1 ( <i>q</i> )	0.89 ( <i>s</i> )	17.7 ( <i>q</i> )
30	0.86 ( <i>s</i> )	21.3 ( <i>q</i> )	0.84 ( <i>s</i> )	23.6 ( <i>q</i> )	0.95 ( <i>s</i> )	21.6 ( <i>q</i> )

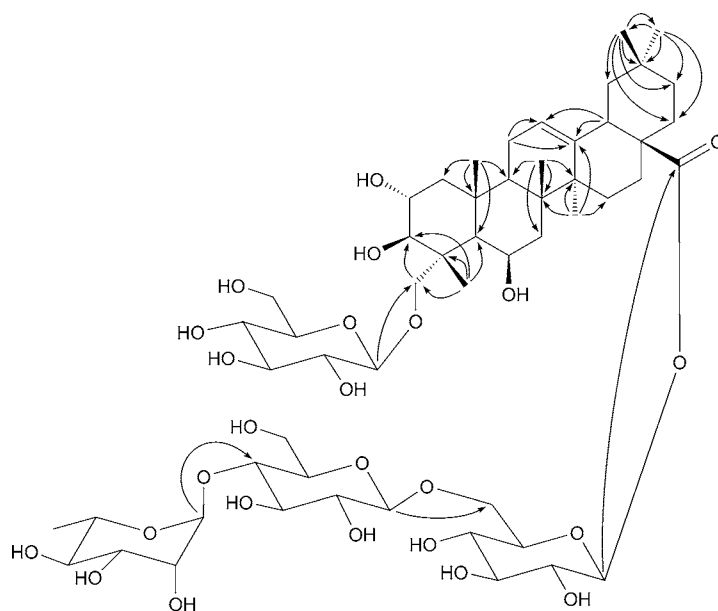
Table (cont.)

Position	Centellasaponin G (1)		Centellasaponin H (2)		Centellasaponin F (3)	
	$\delta$ (H)	$\delta$ (C)	$\delta$ (H)	$\delta$ (C)	$\delta$ (H)	$\delta$ (C)
<b>Glc I</b>						
1'	5.29 (br. s)	101.2 (d)	5.29 (d, $J=6$ )	101.2 (d)		
2'	4.57–4.62 (m)	70.5 (d)	4.56–4.59 (m)	70.5 (d)		
3'	3.61–3.66 (m)	77.2 (d)	3.62 (br. d, $J=12$ )	77.1 (d)		
4'	4.20–4.26 (m)	71.0 (d)	4.20–4.25 (m)	71.0 (d)		
5'	4.34–4.40 (m)	71.8 (d)	4.34–4.38 (m)	71.8 (d)		
6'	4.33–4.39 (m)	62.6 (t)	4.34–4.38 (m)	62.6 (t)		
<b>Glc II</b>						
1''	6.13 (d, $J=6$ )	95.8 (d)	6.16 (d, $J=6$ )	95.8 (d)	5.28 (d, $J=7.8$ )	95.9 (d)
2''	4.04–4.11 (m)	73.8 (d)	4.02–4.07 (m)	73.8 (d)	3.29–3.34 (m)	73.8 (d)
3''	4.13–4.17 (m)	78.6 (d)	4.02–4.07 (m)	78.6 (d)	3.36–3.40 (m)	78.2 (d)
4''	4.21–4.26 (m)	71.1 (d)	4.42–4.44 (m)	71.0 (d)	3.83–3.88 (m)	71.0 (d)
5''	4.00–4.08 (m)	78.2 (d)	4.11–4.17 (m)	78.3 (d)	3.36–3.40 (m)	77.9 (d)
6''	4.23–4.28 (m), 4.60–4.66 (m)	69.5 (t)	4.58–4.63 (m)	69.3 (t)	3.74–3.78 (m), 4.03–4.08 (m)	69.6 (t)
<b>Glc III</b>						
1'''	4.92–4.94 (m)	105.0 (d)	4.92–4.95 (m)	104.8 (d)	4.36 (d, $J=7.8$ )	104.5 (d)
2'''	3.91 (t, $J=6$ )	75.4 (d)	3.89 (t, $J=6$ )	75.3 (d)	3.21–3.25 (m)	75.3 (d)
3'''	4.08–4.15 (m)	76.5 (d)	4.07–4.12 (m)	76.5 (d)	3.44–3.48 (m)	76.9 (d)
4'''	4.36–4.43 (m)	77.9 (d)	4.34–4.38 (m)	78.0 (d)	3.50–3.56 (m)	79.5 (d)
5'''	4.62–4.68 (m)	72.6 (d)	4.61–4.65 (m)	72.5 (d)	3.44–3.48 (m)	76.7 (d)
6'''	4.02–4.08 (m), 4.14–4.21 (m)	61.3 (t)	4.02–4.07 (m), 4.11–4.17 (m)	61.3 (t)	3.60–3.64 (m), 4.01–4.05 (m)	62.7 (t)
<b>Rha IV</b>						
1''''	5.84 (br. s)	102.7 (d)	5.81 (br. s)	102.7 (d)	4.84 (br. s)	102.9 (d)
2''''	4.45–4.54 (m)	72.7 (d)	4.47–4.53 (m)	72.7 (d)	3.38–3.42 (m)	72.5 (d)
3''''	4.45–4.54 (m)	72.8 (d)	4.47–4.53 (m)	72.7 (d)	3.60–3.64 (m)	72.3 (d)
4''''	4.26–4.33 (m)	74.0 (d)	4.07–4.12 (m)	74.0 (d)	3.28–3.34 (m)	73.8 (d)
5''''	4.91–4.98 (m)	70.3 (d)	4.56–4.60 (m)	70.3 (d)	3.92–3.97 (m)	70.7 (d)
6''''	1.68 (s)	18.5 (q)	1.67 (s)	18.5 (q)	1.26 (s)	18.0 (q)

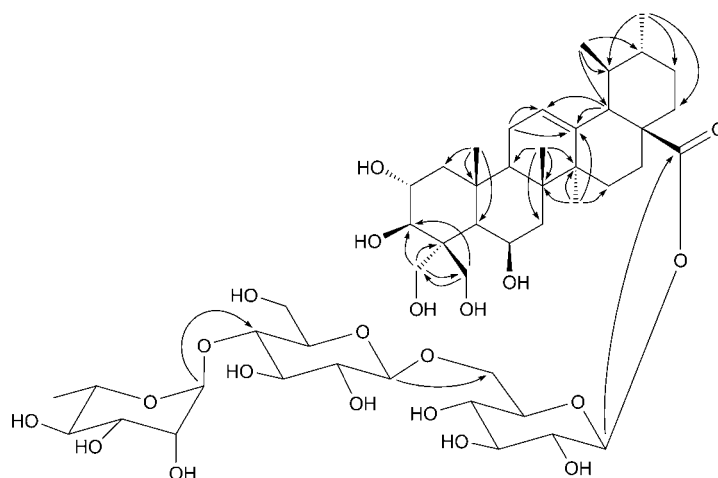
Fig. 2. Key HMBC (H → C) features for **1**

consistent with the molecular formula  $C_{54}H_{88}O_{25}$ . The IR spectrum displayed characteristic absorptions for OH ( $3441\text{ cm}^{-1}$ ), C=O ( $1736\text{ cm}^{-1}$ ), and olefin moieties ( $1637\text{ cm}^{-1}$ ). The NMR data (Table) were similar to those of **1** for rings A–D and the sugar moieties. Comparison of the differing data for ring E and of the olefinic signals between **1** and **2** indicated that they exactly correspond to the typical spectral features of an ursane- and oleanane-type aglycon, respectively. The  $^{13}\text{C}$ -NMR data of compound **2** exhibited two olefinic signals at  $\delta(\text{C})$  123.8 and 143.7. The long-range correlations Me(29) ( $\delta(\text{H})$  0.83)/C(19) ( $\delta(\text{C})$  46.3); Me(29)/C(20) ( $\delta(\text{C})$  30.7); Me(29)/C(21) ( $\delta(\text{C})$  34.1); Me(29)/C(22) ( $\delta(\text{C})$  32.5); Me(29)/C(30) ( $\delta(\text{C})$  23.6); Me(30) ( $\delta(\text{H})$  0.84)/C(20); Me(30)/C(21); Me(30)/C(22); and Me(30)/C(29) ( $\delta(\text{C})$  33.1) evidenced that compound **2** possessed an oleanane-type skeleton (Fig. 3). The long-range correlations H–C(1'') ( $\delta(\text{H})$  6.16)/C(28) ( $\delta(\text{C})$  176.5); H–C(1''') ( $\delta(\text{H})$  4.92–4.95)/C(6'') ( $\delta(\text{C})$  69.3); and H–C(1''''') ( $\delta(\text{H})$  5.81)/C(4''') ( $\delta(\text{C})$  78.0) revealed the linkage sequence of the sugar units. The long-range correlations H–C(1') ( $\delta(\text{H})$  5.29)/C(23) ( $\delta(\text{C})$  73.7) was also observed, indicating that the single sugar unit is linked to C(23) of the aglycon. From the above evidences, the structure of compound **2**, named centellasaponin H, was elucidated as depicted in Fig. 1.

Compound **3** was isolated as white amorphous powder. The HR-ESI mass spectrum exhibited a quasi-molecular-ion peak at  $m/z$  997.4990 ( $[M + \text{Na}]^+$ ; calc. 997.4984), consistent with the molecular formula  $C_{48}H_{78}O_{20}$ . The IR spectrum displayed characteristic absorptions for OH ( $3423\text{ cm}^{-1}$ ), C=O ( $1735\text{ cm}^{-1}$ ), and olefin moieties ( $1637\text{ cm}^{-1}$ ). The  $^{13}\text{C}$ -NMR spectrum data of compound **3** displayed two olefinic signals at  $\delta(\text{C})$  126.9 and 139.4. The correlations  $\text{CH}_2(11)$  ( $\delta(\text{H})$  1.93–1.98)/C(12) ( $\delta(\text{C})$  126.9);  $\text{CH}_2(11)$ /C(13) ( $\delta(\text{C})$  139.4); H–C(18) ( $\delta(\text{H})$  2.23)/C(12); H–C(18)/C(13); and

Fig. 3. Key HMBC (H → C) features for **2**

Me(27) ( $\delta(\text{H})$  1.11)/C(13) established the presence of the C(12)=C(13) bond as shown in Fig. 4. The long-range correlations Me(29) ( $\delta(\text{H})$  0.89)/C(18) ( $\delta(\text{C})$  54.1); Me(29)/C(19) ( $\delta(\text{C})$  40.4); Me(29)/C(20) ( $\delta(\text{C})$  40.2); Me(30) ( $\delta(\text{H})$  0.95)/C(19); Me(30)/C(20); and Me(30)/C(21) ( $\delta(\text{C})$  31.7) indicated that compound **3** possessed an ursane-type skeleton. The NMR data (Table) were different from those of madecassoside (**5**) concerning rings A and B. Compound **3** is lacking a Me signal and displays an additional

Fig. 4. Key HMBC (H → C) features for **3**

HO–CH<sub>2</sub> group signal (CH<sub>2</sub> ( $\delta$ (C) 61.9/ $\delta$ (H) 3.59–3.67, 3.77–3.84)). In the HMBC experiment, the long-range correlations CH<sub>2</sub>(23) ( $\delta$ (H) 3.48–3.52, 4.02–4.05)/C(24) ( $\delta$ (C) 61.9); CH<sub>2</sub>(23)/C(3) ( $\delta$ (C) 79.6); CH<sub>2</sub>(23)/C(4) ( $\delta$ (C) 47.9); and CH<sub>2</sub>(24) ( $\delta$ (H) 3.59–3.67)/C(23) ( $\delta$ (C) 64.6) were observed (Fig. 4). The <sup>1</sup>H,<sup>1</sup>H-COSY and NOESY plots showed the correlations CH<sub>2</sub>(23) ( $\delta$ (H) 4.02–4.05) and CH<sub>2</sub>(24) ( $\delta$ (H) 3.77–3.84), which suggested that the HO–CH<sub>2</sub> group ( $\delta$ (C) 61.9) was positioned at C(4) as OH–CH<sub>2</sub>(23). The long-range correlations H–C(1') ( $\delta$ (H) 5.28)/C(28) ( $\delta$ (C) 178.0); H–C(1'') ( $\delta$ (H) 4.36)/C(6') ( $\delta$ (C) 69.6); and H–C(1''') ( $\delta$ (H) 4.84)/C(4'') ( $\delta$ (C) 79.5) revealed the linkage sequence of the sugar units. From the above evidence, the structure of compound **3**, named centellasaponin F, was elucidated as depicted in Fig. 1.

### Experimental Part

**General.** TLC: Silica gel HSGF<sub>254</sub> (Yantai Jiangyou Guijiao Kaifa Co., Ltd., P. R. China); detection by spraying with 10% H<sub>2</sub>SO<sub>4</sub> in EtOH, followed by heating. Column chromatography (CC): silica gel (SiO<sub>2</sub>, 200–300 mesh; Shanghai Sanpout Co., Ltd., P. R. China). Prep. HPLC: CXTH LC3000 HPLC system (P3000 pump, UV 3000 scanning spectrophotometer, P. R. China); column: YMC-Pack ODS-AQ, 5  $\mu$ m, i.d. 20  $\times$  250 mm; Waters  $\mu$ Bondapak C18, 10  $\mu$ m, i.d. 7.8  $\times$  300 mm; Inertsil ODS-3, 5  $\mu$ m, i.d. 7.6  $\times$  250 mm. Optical rotations: Perkin-Elmer-341 polarimeter. IR Spectra: Nicolet-NEXUS-670-FT-IR spectrophotometer, KBr pellets; in cm<sup>-1</sup>. NMR Spectra: Varian INOVA-400/500 instrument at 400/500 MHz (<sup>1</sup>H) and 100/125 MHz (<sup>13</sup>C) in (D<sub>5</sub>)pyridine; Bruker 600 instrument at 600 (<sup>1</sup>H) and 150 MHz (<sup>13</sup>C) in (D<sub>5</sub>)pyridine;  $\delta$  in ppm rel. to Me<sub>4</sub>Si;  $J$  in Hz. MS: Waters Q-ToFmicro YA019 mass spectrometer; in  $m/z$ .

**Plant Material.** The whole-plant material of *Centella asiatica* (L.) URBAN was collected in the Guangxi Zhuang Autonomous Region, P. R. China, in July 2008, and identified by Dr. Tong Wu at the Shanghai Institute of Pharmaceutical Industry. A voucher specimen (SIPITCM-080711) has been deposited with the institute.

**Extraction and Isolation.** The air-dried whole plants of *C. asiatica* (10 kg) were extracted two times with H<sub>2</sub>O (100 l for 1.5 h; 80 l for 1 h). The extracts were combined and concentrated to 3 l, and then 95% EtOH (15 l) was added, and the mixture was kept for 24 h. The precipitate was removed by filtration. After solvent removal from the filtrate to reach a volume of 3 l, the crude extract was suspended in H<sub>2</sub>O and extracted two times with BuOH (6 and 4.8 l, resp.). The BuOH extract (165 g) was subjected to CC (SiO<sub>2</sub>; CHCl<sub>3</sub>/MeOH/H<sub>2</sub>O 10:2:0.2, 10:4:0.4, 10:5:0.6, and 10:6:1, finally EtOH, each 6 l); Frs. 1–12. Fr. 11 (1.8 g) was purified by prep. HPLC (MeCN/H<sub>2</sub>O 15:85, 2 ml/min; 204 nm) to afford Frs. A<sub>11</sub>–G<sub>11</sub>. Fr. D<sub>11</sub> (85 mg) was further separated by prep. HPLC (MeCN/H<sub>2</sub>O 18:82; 2 mmol/L- $\beta$ -cyclodextrin; 1 ml/min; 204 nm): **1** ( $t_R$  27 min; 6 mg) and **2** ( $t_R$  19 min; 5 mg). Fr. 6 (3.4 g) was purified by prep. HPLC (MeCN/H<sub>2</sub>O 22:53; 6 ml/min; 204 nm) to afford Frs. A<sub>6</sub>–F<sub>6</sub>. Fr. D<sub>6</sub> (273 mg) was further separated by prep. HPLC (MeCN/H<sub>2</sub>O 24:76; 2 mmol/L- $\beta$ -cyclodextrin; 6 ml/min; 204 nm): **3** ( $t_R$  66 min; 3 mg), **6** ( $t_R$  57 min; 9 mg), and **7** ( $t_R$  68 min; 14 mg). Similarly, **4** ( $t_R$  28 min; 23 mg) and **5** ( $t_R$  34 min; 14 mg) were isolated from Fr. C<sub>6</sub> (140 mg) by prep. HPLC (MeCN/H<sub>2</sub>O 22:78; 2 mmol/L- $\beta$ -cyclodextrin; 2 ml/min; 204 nm).

**Centellasaponin G** (=  $\alpha$ -L-Rhamnopyranosyl-(1  $\rightarrow$  4)- $\beta$ -D-glucopyranosyl-(1  $\rightarrow$  6)-I-O-[(2 $\alpha$ ,3 $\beta$ ,6 $\beta$ )-23-( $\beta$ -D-glucopyranosyloxy)-2,3,6-trihydroxy-28-oxours-12-en-28-yl]- $\beta$ -D-glucopyranose; **1**). White amorphous powder.  $[\alpha]_D^{20} = 5.304$  ( $c = 0.198$ , MeOH). IR (KBr): 3442, 2925, 1735, 1637, 1458, 1380, 1234, 1062, 801, 558. <sup>1</sup>H- and <sup>13</sup>C-NMR: see the Table. ESI-MS (pos.): 1159.36 ([ $M + Na$ ]<sup>+</sup>). ESI-MS (neg.): 1135.08 ([ $M - H$ ]<sup>-</sup>). HR-ESI-MS: 1159.5516 ([ $M + Na$ ]<sup>+</sup>, C<sub>54</sub>H<sub>88</sub>NaO<sub>25</sub><sup>+</sup>; calc. 1159.5512).

**Centellasaponin H** (=  $\alpha$ -L-Rhamnopyranosyl-(1  $\rightarrow$  4)- $\beta$ -D-glucopyranosyl-(1  $\rightarrow$  6)-I-O-[(2 $\alpha$ ,3 $\beta$ ,6 $\beta$ )-23-( $\beta$ -D-glucopyranosyl)oxy]-2,3,6-trihydroxy-28-oxolean-12-en-28-yl]- $\beta$ -D-glucopyranose; **2**). White amorphous powder.  $[\alpha]_D^{20} = 12.069$  ( $c = 0.174$ , MeOH). IR (KBr): 3441, 2924, 2855, 1736, 1637, 1459, 1377, 1261, 1061, 804, 582. <sup>1</sup>H- and <sup>13</sup>C-NMR: see the Table. ESI-MS (pos.): 1159.39 ([ $M + Na$ ]<sup>+</sup>). ESI-MS (neg.): 1135.24 ([ $M - H$ ]<sup>-</sup>). HR-ESI-MS: 1159.5519 ([ $M + Na$ ]<sup>+</sup>, C<sub>54</sub>H<sub>88</sub>NaO<sub>25</sub><sup>+</sup>; calc. 1159.5512).

*Centellasaponin F* (=  $\alpha$ -L-Rhamnopyranosyl-(1  $\rightarrow$  4)- $\beta$ -D-glucopyranosyl-(1  $\rightarrow$  6)-1-O-[(2 $\alpha$ ,3 $\beta$ )-2,3,23,24-tetrahydroxy-28-oxours-12-en-28-yl]- $\beta$ -D-glucopyranose; **3**). White amorphous powder.  $[\alpha]_D^{20} = -11.628$  ( $c = 0.043$ , MeOH). IR (KBr): 3423, 2924, 2855, 1735, 1637, 1458, 1382, 1261, 1063, 802, 577.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR: see the Table. ESI-MS (pos.): 997.36 ( $[M + \text{Na}]^+$ ). ESI-MS (neg.): 973.39 ( $[M - \text{H}]^-$ ). HR-ESI-MS: 997.4990 ( $[M + \text{Na}]^+$ ,  $\text{C}_{48}\text{H}_{78}\text{NaO}_{20}^+$ ; calc. 997.4984).

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