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Triterpenoids from the roots of *Rubus parvifolius*

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[ABSTRACT] Two new oleanane-type triterpenoids, parvifolactone A (**1**) and rubuside P (**2**), together with 11 known triterpenoids, fupenzic acid (**3**), 18,19-seco,2*α*,3*α*-dihydroxyl-19-oxo-urs-11,13(18)-dien-28-oic acid (**4**), euscaphic acid (**5**), maslinic acid (**6**), 1*β*-hydroxyeuscaphic acid (**7**), 2*α*,3*α*,19*α*,23-tetrahydroxyolean-12-en-28-oic acid (**8**), 2*α*,3*β*,19*α*,23-tetrahydroxyurs-12-en-28-oic acid (**9**), glucosyl pinfaensate (**10**), rubuside J (**11**), 2*α*,3*α*,19*α*,23-tetrahydroxyurs-12-en-24,28-dioic acid (**12**), and 2*α*,3*β*,19*α*-trihydroxyurs-12-en-23,28-dioic acid (**13**), were isolated from the roots of *Rubus parvifolius*.

[KEY WORDS] Triterpenoid; Parvifolactone A; Rubuside P; *Rubus parvifolius*

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Introduction

Rubus parvifolius belonging to the family Rosaceae is a small shrub widely distributed in China. The roots of *R. parvifolius* are widely used for the treatment of rheumatism, hepatitis, and abdominal pain caused by postpartum stasis [1]. Previous investigations on the chemical constituents of the roots of *R. parvifolius* led to the isolation and identification of triterpenoids and flavonoids [2-10]. As part of ongoing effort to search for bioactive compounds from natural plants, the chemical constituents of *R. parvifolius* were investigated in the present study. Herein, we report the isolation and structural elucidation of two new triterpenoids, parvifolactone A (**1**) and rubuside P (**2**), together with 11 known triterpenoids, from the roots of *R. parvifolius*. All compounds but **5** and **13** were firstly isolated from the roots of *R. parvifolius*.

Results and Discussion

Compound **1** was obtained as an amorphous powder. The positive HR-ESI-MS gave a $[M + H]^+$ ion peak at *m/z* 469.337 6, in accordance with an empirical molecular formula $C_{30}H_{44}O_4$, which was supported by the ^{13}C NMR spectroscopic data (Table. 1). The IR absorptions at 3 440 cm^{-1} and 1 774 cm^{-1} indicated the presence of hydroxyl group and carbonyl group, respectively. The ^1H NMR spectrum of **1** indicated the presence of seven methyl singlets at δ_H 0.77, 0.87, 0.93, 0.94, 1.04, 1.07, and 1.29, three oxymethine protons at 4.42 (1H, m), 3.82 (1H, d, J = 2.5 Hz), and 4.93 (1H, s), and two olefinic protons at δ_H 5.96 (1H, dd, J = 10.0, 2.0 Hz) and 6.26 (1H, d, J = 10.0 Hz). The ^{13}C NMR spectrum of **1** showed the presence of 30 carbons, including two tertiary olefinic carbons at δ_C 123.3 and 130.3, two quaternary olefinic carbons at δ_C 133.4 and 135.3, two oxymethine carbons at δ_C 66.1 and 79.6, one oxygen-bearing tertiary carbon at δ_C 85.1, and one carbonyl carbon at δ_C 178.0. The assignment of protons and carbons of **1** was achieved by HSQC, HMBC, and NOESY experiments (Table 1).

In the HMBC spectrum of **1** (Fig. 1), the observation of the long-range correlations between H-19 (δ_H 4.93) and C-28 (δ_C 178.0) indicated the occurrence of a five-membered lactone ring in **1**. The four unsaturated carbons (δ_C 123.3, 130.3, 133.4, and 135.3) contributed to two conjugated double bonds were unambiguously assigned by the HMBC correlations from H-11 (δ_H 5.96, dd, J = 10.0, 2.0 Hz) to C-8 (δ_C 41.7) and C-13 (δ_C 135.3), from H-12 (δ_H 6.26, d, J = 10.0 Hz)

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Table 1 NMR data of Compounds 1 and 2 (500 MHz for ^{1}H , 125 MHz for ^{13}C, in pyridine-d_5)

position	1		2	
	δ_H (*J* in Hz) *	δ_C	δ_H (*J* in Hz) *	δ_C
1	1.83, m; 2.25, dd (11.5, 4.0)	43.1 (CH_2)	1.38, m; 2.29, dd (13.0, 4.0)	47.7 (CH_2)
2	4.42, m	66.1 (CH)	4.24, m	68.3 (CH)
3	3.82, d (2.5)	79.6 (CH)	4.04, m	77.3 (CH)
4	—	39.2 (C)	—	56.9 (C)
5	1.75, m	48.5 (CH)	2.09, m	48.6 (CH)
6	1.59, m	18.4 (CH_3)	1.05, m; 1.55, m	21.2 (CH_2)
7	1.48, m; 1.54, m	33.6 (CH_2)	1.36, m; 1.56, m	32.8 (CH_2)
8	—	41.7 (C)	—	40.6 (C)
9	2.37, brs	53.4 (CH)	1.66, m	48.5 (CH)
10	—	38.5 (C)	—	38.8 (C)
11	5.96, dd (10.0, 2.0)	130.3 (CH)	2.09, m	24.5 (CH_2)
12	6.26, d (10.0)	123.3 (CH)	5.51, brs	123.7 (CH)
13	—	135.3 (C)	—	144.7 (C)
14	—	41.1 (C)	—	42.4 (C)
15	1.15, m; 1.40, m	26.1 (CH_2)	1.05, m; 1.22, m	29.2 (CH_2)
16	2.46, m	24.9 (CH_2)	2.13, m	28.2 (CH_2)
17	—	44.5 (C)	—	46.7 (C)
18	—	133.4 (CH)	3.54, br.s	44.9 (CH)
19	4.93, s	85.1 (CH)	3.59, m	81.2 (CH)
20	—	36.1 (C)	—	35.8 (C)
21	1.28, m; 1.40, m	33.1 (CH_2)	1.05, m; 1.22, m	29.2 (CH_2)
22	1.51, m; 1.75, m	35.0 (CH_2)	1.96, m; 2.06, m	33.3 (CH_2)
23	1.29, s	29.5 (CH_3)	9.66, s	206.7 (C)
24	0.94, s	22.0 (CH_3)	1.45, s	10.9 (CH_3)
25	1.04, s	19.7 (CH_3)	1.08, s	17.3 (CH_3)
26	0.77, s	17.4 (CH_3)	1.15, s	17.8 (CH_3)
27	0.93, s	19.4 (CH_3)	1.62, s	25.2 (CH_3)
28	—	178.0 (C)	—	177.5 (C)
29	1.07, s	28.0 (CH_3)	0.99, s	24.9 (CH_3)
30	0.87, s	23.3 (CH_3)	1.15, s	29.0 (CH_3)
Glc1			6.40, d (8.0)	96.1 (CH)
2			4.24, m	74.4 (CH)
3			4.04, m	79.6 (CH)
4			4.38, m	71.3 (CH)
5			4.30, m	79.2 (CH)
6			4.44, m	62.4 (CH_2)

to C-9 (δ_C 53.4), from H-27 (δ_C 0.93, s) to C-13 (δ_C 135.3), and from H-19 (δ_H 4.93, s) to C-13 (δ_C 135.3) and C-18 (δ_C 133.4), respectively. The two oxymethine carbons at δ_C 66.1 (C-2) and 79.6 (C-3) were assigned by the HMBC correlations of H-2/C-1, H-2/C-3, and H-23/C-3. Comparison of the NMR data of **1** with those of the known compound 2*α*, 3*β*-dihydroxyolean-11, 13(18)-dien-19*β*, 28-olide suggested that these two compounds shared a similar skeleton [11]. However, the notable difference of the coupling constants between H-2 and H-3 of these two compounds ($J_{2,3}$ = 2.5 Hz and 9.6 Hz, respectively) suggested that the configuration of the hydroxy groups of these two compounds might be different. In the NOESY spectrum of **1**, the cross-peaks of H-2/H-25, H-2/H-24, H-2/H-3, and H-19/H-29 allowed the assignment of *β*-orientation of H-2 and H-3, and the *α*-orientation of H-19. Therefore, the structure of **1** was