Triterpenoids from the Edible Leaves of *Photinia serrulata*

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Five new triterpenoids, serrulatins A–E (**1**–**5**), including two new artifacts, together with ten known serrulatins, were isolated from the edible leaves of *Photinia serrulata* after extraction and purification. Their structures were identified on the basis of spectroscopic methods including 2D NMR experiments. Compounds **1** and **3** are unusual ursolic triterpenoids characterized by the occurrence of a C(13)=C(18) bond.

Introduction. – The genus *Photinia* (Rosaceae) consists of about 60 species, most of which are distributed in the east and south of Asia [1]. *P. serrulata*, known as 'Shi-Nan', is indigenous to China; its leaves are edible and have been used as invigorator and diuretic to treat nephropathy, rheumatism, and spermatorrhea [2]. However, few chemical investigations were carried out on the leaves of this plant, and this promoted us to conduct this project which led to the isolation, after extraction and purification, of five new triterpenoids, named serrulatins A–E (**1**–**5**), along with ten known ones. In this paper, we describe the isolation and structure elucidation of these triterpenoids.

Results and Discussion. – Compound **1** was obtained as a white powder. Its molecular formula was deduced as $C_{33}H_{50}O_4$ on the basis of the HR-ESI-MS (*m*/*z* 533.3594 ($[M+Na]^+$)). The ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*), ^{1}H,^{1}H-COSY, HMQC, and HMBC (*Figure*) data suggested that **1** possesses an ursane-type triterpene skeleton.

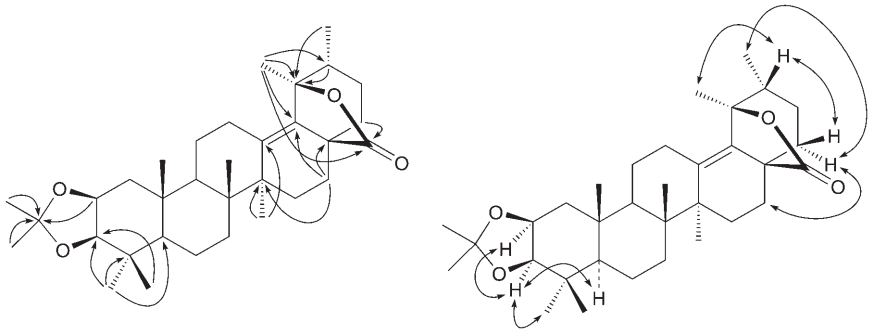

Figure. *Significant HMBC* (H → C; left) *and ROESY* (H → H; right) *correlations for* **1**

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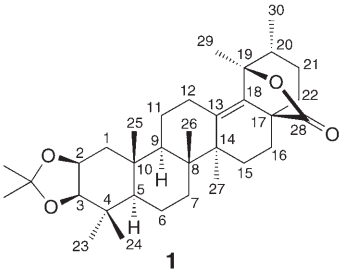
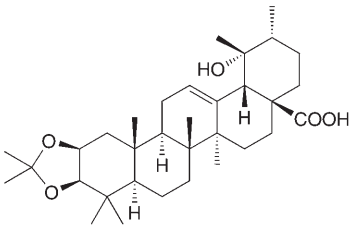


1



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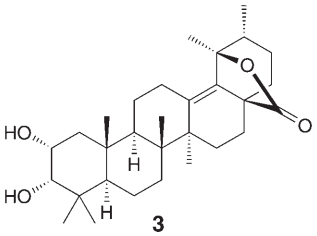

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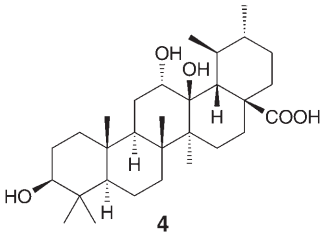

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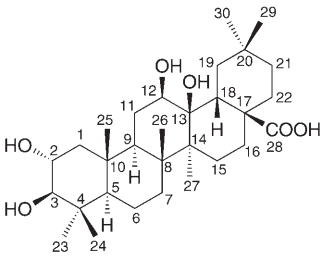

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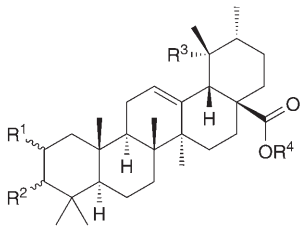
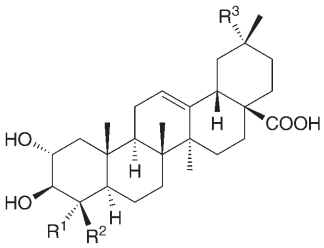


6 $R^1 = R^3 = R^4 = H$, $R^2 = \beta$-OH
7 $R^1 = R^2 = R^3 = \alpha$-OH, $R^4 = H$
8 $R^1 = R^3 = \alpha$-OH, $R^2 = \beta$-OH, $R^4 = H$
9 $R^1 = \alpha$-OH, $R^2 = \beta$-OH, $R^3 = R^4 = H$
10 $R^1 = R^2 = R^3 = \alpha$-OH, R^4 = Glc
11 $R^1 = R^3 = \alpha$-OH, $R^2 = \beta$-OH, R^4 = Glc



12 $R^1 = R^2 = R^3$ = Me
13 $R^1 = R^3$ = Me, $R^2 = CH_2OH$
14 $R^1 = CH_2OH$, $R^2 = R^3$ = Me
15 $R^1 = R^3 = CH_2OH$, R^2 = Me

Further data established the structure of **1** as (2β,3β, 19α)-19-hydroxy-2,3-(isopropylidenedioxy)urs-13(18)-en-28-oic acid γ-lactone, with the trivial name serrulatin A. Note that **1** is an artifact formed during the purification procedure, and is not present in the crude extract (HPLC evidence). However, the parent (2β,3β,19α)-2,3,19-trihydroxyurs-13(18)-en-28-oic acid γ-lactone represents a new metabolite. Of the 33 C-signals displayed in the ^{13}C-NMR spectrum of **1**, three were assigned to an isopropylidenedioxy moiety (Me_2CO_2); the other thirty signals were ascribable to seven Me, nine

Table 1. *^{1}H-NMR Data of Compounds* **1**–**5**

	1[a])	**2**[a])	**3**[b])	**4**[c])	**5**[d])
CH_2(1)	1.89–1.91, 1.06–1.07 (2*m*)	1.75–1.78, 1.02–1.04 (2*m*)	2.04–2.07, 1.73–1.76 (2*m*)	1.85–1.88, 1.05–1.08 (2*m*)	2.08–2.12, 1.03–1.04 (2*m*)
H–C(2) or CH_2(2)	4.19–4.23 (*m*)	4.16–4.21 (*m*)	4.34–4.37 (*m*)	1.76–1.80 (2*m*)	3.70–3.73 (*m*)
H–C(3)	3.70 (*d*, *J* = 4.3)	3.70 (*d*, *J* = 4.3)	3.79 (*d*, *J* = 2.6)	3.29 (*dd*, *J* = 9.2, 4.0)	3.04 (*d*, *J* = 9.6)
H–C(5)	1.26–1.27 (*m*)	1.19–1.21 (*m*)	1.61–1.63 (*m*)	0.75–0.79 (*m*)	0.88–0.90 (*m*)
CH_2(6)	1.55–1.56, 1.46–1.50 (2*m*)	1.48–1.52 (2*m*)	1.22–1.24, 0.80–0.81 (2*m*)	1.63–1.65 (2*m*)	1.61–1.63, 1.49–1.51 (2*m*)
CH_2(7)	1.62–1.66, 1.48–1.51 (2*m*)	1.53–1.56, 1.32–1.34 (2*m*)	1.40–1.46 (2*m*)	1.53–1.56, 1.36–1.40 (2*m*)	1.64–1.66, 1.36–1.40 (2*m*)
H–C(9)	1.54–1.56 (*m*)	1.67–1.69 (*m*)	1.61–1.63 (*m*)	1.43–1.47 (*m*)	1.81–1.84 (*m*)
CH_2(11)	2.73–2.77 (2*m*)	1.94–1.99 (2*m*)	1.98–2.03, 1.52–1.54 (2*m*)	2.15–2.19, 2.12–2.14 (2*m*)	2.31–2.34, 1.81–1.84 (2*m*)
CH_2(12) or H–C(12)	1.27–1.28 (2*m*)	5.29 (*t*, *J* = 3.4)	1.99–2.01, 1.54–1.55 (2*m*)	4.56 (*dd*, *J* = 9.2, 4.4)	4.18 (br. *s*)
CH_2(15)	2.73–2.77 (2*m*)	1.83–1.85 (2*m*)	1.16–1.18 (2*m*)	2.05–2.08, 1.31–1.35 (2*m*)	1.97–1.99, 1.24–1.27 (2*m*)
CH_2(16)	1.28–1.31 (2*m*)	2.54–2.61, 1.50–1.54 (2*m*)	1.63–1.65, 1.27–1.29 (2*m*)	1.63–1.65, 1.26–1.29 (2*m*)	2.21–2.24, 1.32–1.35 (2*m*)
H–C(18)		2.54 (*s*)		2.40 (*d*, *J* = 9.2)	2.06–2.08 (*m*)
H–C(19) or CH_2(19)				1.86–1.90 (*m*)	2.21–2.24, 2.08–2.14 (2*m*)
H–C(20)	2.04–2.08 (*m*)	1.50–1.52 (*m*)	2.01–2.02 (*m*)	1.02–1.05 (*m*)	
CH_2(21)	1.78–1.84, 1.45–1.48 (2*m*)	1.54–1.56 (2*m*)	0.95–0.99 (2*m*)	1.90–1.92 (2*m*)	1.40–1.42, 1.33–1.36 (2*m*)
CH_2(22)	1.80–1.83, 1.45–1.48 (2*m*)	1.71–1.73, 1.64–1.66 (2*m*)	1.51–1.53 (2*m*)	1.66–1.68 (2*m*)	1.69 (*dd*, *J* = 8.8, 3.2)
Me(23)	1.06 (*s*)	1.06 (*s*)	1.23 (*s*)	1.06 (*s*)	1.04 (*s*)
Me(24)	0.91 (*s*)	0.91 (*s*)	0.86 (*s*)	0.84 (*s*)	0.82 (*s*)
Me(25)	0.91 (*s*)	0.91 (*s*)	0.88 (*s*)	0.98 (*s*)	0.98 (*s*)
Me(26)	0.87 (*s*)	0.77 (*s*)	0.74 (*s*)	1.29 (*s*)	1.25 (*s*)
Me(27)	1.22 (*s*)	1.34 (*s*)	0.93 (*s*)	1.31 (*s*)	1.45 (*s*)
Me(29)	1.66 (*s*)	1.21 (*s*)	1.63 (*s*)	1.14 (*d*, *J* = 6.4)	0.90 (*s*)
Me(30)	0.97 (*d*, *J* = 7.0)	0.93 (*d*, *J* = 5.6)	0.75 (*d*, *J* = 7.0)	1.04 (*d*, *J* = 6.4)	0.99 (*s*)
Me_2C	1.40, 1.24 (2*s*)	1.38, 1.24 (2*s*)			

[a]) In CD_3COCD_3. [b]) In C_5D_5N. [c]) In $CDCl_3$. [d]) In $CDCl_3/CD_3OD$ 4 : 1.

CH_2, and five CH groups (two oxygenated ones), and nine quaternary C-atoms (a C=O, an oxygenated one, and two olefinic ones). The ^{1}H-NMR spectrum exhibited nine Me signals, two of which were *s* attributed to an acetonide moiety; the others accounted for a secondary Me and six tertiary Me groups. These data were compatible with an ursane-type skeleton.

The ^{1}H,^{1}H-COSY interactions of H–C(2) with H–C(3), and the HMBC cross-peaks of Me(23) and Me(24) both with C(3) and C(4), and of Me(23) with C(5), suggested that C(2) and C(3) are both oxygenated. Additional HMBC interactions (*Figure*) of all proton signals at δ 4.19–4.23, 1.40, and 1.24 with a quaternary C-atom at δ 107.5 were observed, which implied the presence of a 1,3-dioxolane structure formed by C(2) and C(3), and a ketal group. The observed HMBC cross-peaks of Me(29) with C(18), C(19), and C(20), of Me(27) with C(14) and C(13), and of CH_2(16) with C(14), C(17), and C(18)

Table 2. *^{13}C-NMR Data of Compounds* **1**–**5**

	1[a])	**2**[a])	**3**[b])	**4**[c])	**5**[d])
C(1)	43.8	43.3	43.5	39.0	46.4
C(2)	72.5	72.3	66.3	27.2	69.0
C(3)	83.4	83.4	79.3	78.7	83.7
C(4)	36.2	36.1	38.9	38.9	39.4
C(5)	50.7	50.6	48.8	55.1	55.3
C(6)	19.1	19.2	18.5	17.6	17.7
C(7)	35.1	33.5	35.0	33.9	34.3
C(8)	43.0	40.7	43.2	42.7	42.6
C(9)	51.9	47.5	51.9	51.2	44.8
C(10)	39.2	38.7	39.1	37.2	37.8
C(11)	26.8	24.2	26.6	31.0	29.5
C(12)	28.4	128.8	26.2	62.7	64.8
C(13)	137.3	139.5	136.8	92.0	91.5
C(14)	43.0	42.3	42.6	45.1	43.2
C(15)	26.8	29.2	27.9	27.8	29.0
C(16)	22.6	26.4	22.1	22.5	21.3
C(17)	48.9	48.3	48.8	45.3	45.7
C(18)	134.0	54.4	133.1	54.2	51.9
C(19)	91.3	73.2	91.1	38.6	39.8
C(20)	40.3	42.6	39.8	39.6	31.8
C(21)	27.5	26.9	27.0	31.4	33.9
C(22)	32.7	38.4	32.1	30.7	27.5
C(23)	28.7	28.8	29.4	27.9	28.4
C(24)	23.8	24.1	22.1	15.3	16.5
C(25)	19.2	15.7	18.0	16.4	18.0
C(26)	17.0	17.2	18.9	18.4	18.9
C(27)	24.6	24.4	24.6	17.3	20.2
C(28)	177.8	179.3	178.2	178.0	179.1
C(29)	23.1	27.3	22.9	15.9	23.6
C(30)	15.7	16.5	15.4	19.4	33.2
Me_2C	107.5	107.3			
	29.2	29.2			
	26.9	26.8			

[a]) In CD_3COCD_3. [b]) In C_5D_5N. [c]) In $CDCl_3$. [d]) In $CDCl_3/CD_3OD$ 4 : 1.

suggested the presence of a C=C bond between C(13) and C(18). Me(29), Me(30), and H–C(20) all correlated with a quaternary C-atom resonating at δ 91.3 in the HMBC plot indicating that C(19) is oxygenated. A carbonyl group was assigned as C(28)=O due to the HMBC cross-peak CH_2(22)/C(28). The molecular mass together with the downfield shift of C(19) required that C(17) and C(19) are linked *via* an ester group, which was further confirmed by a weak ^4J HMBC interaction Me(29)/C(28). The orientations of H–C(2) and H–C(3) were both assigned as α on the basis of the small coupling constant of H–C(3) (δ 3.70 (d, J = 4.3)) [3–5] and ROESY correlation peaks (*Figure*) of H–C(3) with H–C(2), Me(23), and H–C(5). The additional ROESY correlations Me(29)/H_β–C(20), H_β–C(20)/Me(30) and H_β–C(22) (δ 1.45–1.48), and H_α–C(22) (δ 1.80–1.83)/Me(30) and CH_2(16) were also observed.

Compound **2** was isolated as a white powder, having the molecular formula $C_{33}H_{52}O_5$, as deduced from its HR-ESI-MS (m/z 527.3739 ($[M-H]^-$)). The

resemblance of the ^{13}C-NMR spectra of **1** and **2** suggested that they are close analogues. The main differences were a C(12)=C(13) bond and a free OH group at C(19) in **2** *vs.* a C(13)=C(18) bond and a 19(28)-lactone with (19α) configuration of the ursane skeleton in **1**. According to the ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*), HMBC, and ROESY data, compound **2** was assigned as (2β,3β)-19-hydroxy-2,3-(isopropylidenedioxy)urs-12-en-28-oic acid, with the trivial name serrulatin B. Note that **2** is also a new artifact formed during the purification process, and does not exist in the crude extract (HPLC evidence). The parent (2β,3β)-2,3,19-trihydroxyurs-12-en-28-oic acid was previously isolated from *Sabia parviflora* [6], *Cowainea mexicana* [7], and *Cunila lythrifolia* [8].

The structure of **2** was supported by the observed HMBC interactions of H–C(12) with C(9), C(13), C(14), C(18), and C(19), and of H–C(18) with C(13), C(16), C(17), C(19), C(20), and a carbonyl group at δ 179.3 (C(28)), by the molecular-mass increase of 18 mass units compared with **1**, and by a distinct upfield shift of C(19) from δ 91.3 in **1** to δ 73.2 in **2**. Likewise, the configurations of H–C(2) and H–C(3) were determined to be α by means of the small coupling constant of H–C(3) (δ 3.70 (*d*, *J* = 4.3)) [3–5] and ROESY correlations of H–C(3) with H–C(2), Me(23), and H–C(5).

Compound **3** was obtained as a white powder. The HR-ESI-MS of **3** showed a quasimolecular-ion peak at *m*/*z* 493.3284 ($[M+Na]^+$), corresponding to a molecular formula $C_{30}H_{46}O_4$, requiring eight degrees of unsaturation. The similarities between the ^{13}C-NMR (*Table 2*) and DEPT spectra of **3** and **1** suggested that they are closely related. Compared to **1**, two Me groups and a quaternary C-atom (δ 107.5) in **1** disappeared in **3**, indicating that **3** possesses two free OH groups at C(2) and C(3), respectively. The OH groups at C(2) and C(3) were both α oriented, as suggested by the coupling constant of H–C(3) (δ 3.79 (*d*, *J* = 2.6)) [3] (*Table 1*), and the ROESY correlation H_β–C(3)/Me(25). Accordingly, the structure of **3** was assigned as (2α,3α,19α)-2,3,19-trihydroxyurs-13(18)-en-28-oic acid γ-lactone, with the trivial name serrulatin C. Similarly to **1**, **3** is also an unusual ursolic acid lactone derivative with a C=C bond between C(13) and C(18).

Compound **4** was obtained as a white powder. The molecular formula of $C_{30}H_{50}O_5$ was derived from its HR-ESI-MS (*m*/*z* 525.3342 ($[M+Cl]^-$)). The ^{13}C-NMR and DEPT spectra of **4** were reminiscent of ursolic acid (**6**) [3]. According to the ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*), ^{1}H,^{1}H-COSY, HMBC, and ROESY data the structure of **4** was assigned as (3β,12α,13β)-3,12,13-trihydroxyursan-28-oic acid, with the trivial name serrulatin D.

The C(12)=C(13) bond of ursolic acid (**6**) was replaced by a CH moiety at δ 62.7 and a quaternary C-atom at δ 92.0 in **4**; this was evident from the ^{1}H,^{1}H-COSY cross-peaks H–C(9)/CH_2(11) and CH_2(11)/H–C(12), and the HMBC cross-peaks of CH_2(11), H–C(12), Me(27), and H–C(18), all with C(13). The configuration of H_α–C(3) was deduced by comparison of its ^{13}C-NMR data with literature [9], the typical vicinal coupling constants of H–C(3) (*J* = 9.2, 4.0) also indicated a β-oriented OH–C(3), and this was further confirmed by the ROESY interactions of H–C(3) with H–C(5) and Me(23). The coupling constant of H_{ax}–C(18) (δ 2.40 (*d*, *J* = 9.2)) indicated a *cis*-fusion of rings D and E and the β orientation of Me(29), which was further confirmed by ROESY correlations of H–C(18) with H–C(12), H–C(20), H–C(22), and Me(29), these ROESY interactions also established that the OH groups at C(12) and C(13) are α and β oriented, resp.

Compound **5** was obtained as a white powder. Its molecular formula was determined to be $C_{30}H_{50}O_6$ by means of the HR-ESI-MS (*m/z* 541.3288 ($[M+Cl]^-$)). According to the ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*), ^{1}H,^{1}H-COSY, HMBC, and ROESY data, the structure of **5** was determined to be (2α,3β,12β,13β)-2,3,12,13-tetrahydroxyoleanan-28-oic acid, with the trivial name serrulatin E. While compound **5** has been reported before by partial synthesis [16], this report represents the first isolation of **5** from natural sources. In addition, the ^{13}C-NMR spectrum is fully interpreted for the first time and the relative configuration at C(12) was firstly established.

The ^{13}C-NMR spectrum of **5** displayed thirty signals, *i.e.*, for seven Me, nine CH_2 and six CH groups (three oxygenated ones), and eight quaternary C-atoms (an oxygenated one and a C=O). The ^{1}H-NMR showed seven Me *s*. These data, together with the analysis of the ^{1}H,^{1}H-COSY and HMBC plots, suggested that **5** possesses an oleanane-type skeleton. Comparison of the NMR data of **5** with those of **12** disclosed that the two olefinic C-atoms of **12** were replaced by two oxygenated C-atoms in **5** (δ 64.8 and 91.5). This was further supported by ^{1}H,^{1}H-COSY cross-peaks of CH_2(11) with H–C(12), and HMBC interactions of CH_2(11), H–C(12), Me(27), H–C(18), and CH_2(15) all with C(13). The H–C(2) and H–C(3) were assigned as β- and α-orientated, resp., by a large coupling constant of H–C(3) (δ 3.04 (*d*, $J = 9.6$)), which was further supported by the ROESY correlations H–C(2)/Me(24), and H–C(3)/H–C(5) and Me(23). The additional ROESY correlation H–C(12)/H–C(9) implied that OH–C(12) was β-oriented.

The ten known compounds were identified as ursolic acid (**6**) [3], euscaphic acid (**7**) [4], tormentic acid (**8**) [3], corosolic acid (**9**) [10], kajiichigoside F1 (**10**) [11], tormentic acid glucosyl ester (**11**) [12], masilinic acid (**12**) [3], hyptatic acid A (**13**) [13], urjinolic acid (**14**) [14], and stachlic acid A (**15**) [15] by measurement of their spectroscopic data and comparison with literature values.

This work was financially supported by a *Talent Scholarship for the Youth of Yunnan* (No. 2007PY01-48), the *Xi-Bu-Zhi-Guang Project* from the Chinese Academy of Sciences (2005–2008), and the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences. We thank Mr. *Renqiang Mei* for determining the melting points.

Experimental Part

General. Column chromatography (CC) and vacuum liquid chromatography (VLC): silica gel (200–300 mesh, 10–40 μm) from *Qingdao Marine Chemical Factory*, Qingdao, P. R. China, *Sephadex LH-20* from *Amersham Pharmacia Biotech*, Sweden, and *RP-C_{18}* silica gel (40–63 μm) from *Daiso Co.*, Japan. TLC: silica gel *GF254* from *Qingdao Marine Chemical Factory*. M.p.: *XRC-1* micromelting apparatus; uncorrected. Optical rotations: *Jasco-20C* digital polarimeter. IR Spectra: *Bruker-Tensor-27-FT-IR* spectrophotometer; KBr pellets. ^{1}H- (400 MHz) and ^{13}C-NMR (100 MHz) Spectra: *Bruker-AM-400* spectrometer; $SiMe_4$ as internal reference. 2D-NMR Spectra: *DRX-500* spectrometer. MS: *VG-Auto-Spec-3000* spectrometer for EI (70 eV) and FAB; *API-QSTAR-Pulsar-1* spectrometer for ESI and HR-ESI; in *m/z* (rel %).

Plant Material. The dried leaves of *P. serrulata* were purchased from *Nanjing Pharmaceutical Ltd. Corporation*, Jiangsu Province, P. R. China, in March 2006, and identified by Mrs. *Xuedong Geng*, *Nanjing Pharmaceutical Ltd. Corporation*. A voucher specimen (CHYX0392) was deposited at the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, P. R. China.

Extraction and Isolation. The dried and powdered leaves of *P. serrulata* (15 kg) were extracted with 80% EtOH under reflux (3×). After evaporation of the solvent, the residue was suspended in H_2O and

extracted with petroleum ether, AcOEt, and BuOH, resp. The AcOEt extract (866 g) was subjected to CC (SiO_2, $CHCl_3$/MeOH 15:1): *Fractions 1–3*. *Fr. 2* (160 g) was submitted to CC (SiO_2, $CHCl_3$/MeOH/AcOEt 6:1:1): *Fr. 2.1* and *2.2*. *Fr. 2.1* (9 g) was subjected to VLC (SiO_2, gradient $CHCl_3$/Me_2CO): **6** (80 mg) and **7** (252 mg). *Fr. 2.2* (145 g) was subjected to CC (SiO_2, $CHCl_3$/MeOH 98:2, 96:4, and 95:5): *Fr. 2.2.1–2.2.5*. *Fr. 2.2.1* (16 g) was fractionated by CC (SiO_2, $CHCl_3$/Me_2CO 50:1, 40:1, 30:1, and 15:1): *Fr. 2.2.1.1–2.2.1.4*. *Fr. 2.2.1.1* (4 g) was repeatedly submitted to CC (1. SiO_2, gradient $CHCl_3$/^{i}PrOH; 2. *Sephadex LH-20*, $CHCl_3$/MeOH 6:4): **2** (127 mg), **4** (22.8 mg), and **5** (15.8 mg). *Fr. 2.2.1.2* (6 g) was purified by VLC (SiO_2, gradient $CHCl_3$/Me_2CO) followed by prep. TLC (SiO_2, petroleum ether/Me_2CO 2:1): **1** (34.2 mg), **3** (2.5 mg), and **12** (139.5 mg). *Fr. 2.2.2* (12 g) was submitted to CC (SiO_2, gradient $CHCl_3$/Me_2CO): *Fr. 2.2.2.1* and *2.2.2.2*. *Fr. 2.2.2.1* was purified by repeated CC (1. SiO_2, $CHCl_3$/^{i}PrOH 5:1; 2. *Sephadex LH-20*, MeOH; 3. *RP-C*$_{18}$, MeOH/H_2O 70:30, 80:20, and 90:10): **8** (192 mg), **9** (165 mg), **13** (30 mg), and **14** (53 mg). *Fr. 2.2.3* (10 g) was purified by repeated CC (1. SiO_2, gradient $CHCl_3$/Me_2CO; 2. *RP-C*$_{18}$, MeOH/H_2O 70:30): **15** (12 mg). Similarly, *Fr. 2.2.4* (10 g) and *2.2.5* (15 g) were purified by VLC (SiO_2, gradient $CHCl_3$/MeOH) and CC (*RP-C*$_{18}$, MeOH/H_2O 70:30 and 80:20): **10** (47 mg), and **11** (5 mg), resp.

(2β,3β,19α)-19-Hydroxy-2,3-[(1-methylethylidene)bis(oxy)]urs-13(18)-en-28-oic Acid γ-Lactone (**1**): White powder. M.p. 229–230°. $[\alpha]_D^{28.0} = +54.55$ ($c = 0.06$, Me_2CO). IR (KBr): 2952, 2938, 2894, 2875, 1767, 1629, 1460, 1376, 1239, 1218, 1167, 1047, 875. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 510 (6, M^+). HR-ESI-MS (pos.): 533.3594 ($[M+Na]^+$, $C_{33}H_{50}NaO_4^+$; calc. 533.3606).

(2β,3β)-19-Hydroxy-2,3-[(1-methylethylidene)bis(oxy)]urs-12-en-28-oic Acid (**2**): White powder. M.p. 193–194°. $[\alpha]_D^{28.0} = +34.78$ ($c = 0.12$, Me_2CO). IR (KBr): 3440, 2980, 2937, 1795, 1697, 1640, 1629, 1459, 1379, 1368, 1238, 1218, 1167, 1050, 862. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. FAB-MS (neg.): 527 ($[M-H]^-$, 100). HR-ESI-MS (neg.): 527.3739 ($[M-H]^-$, $C_{33}H_{51}O_5^-$; calc. 527.3736).

(2α,3α,19α)-2,3,19-Trihydroxyurs-13(18)-en-28-oic Acid γ-Lactone (**3**): White powder. M.p. 232–233°. $[\alpha]_D^{26.6} = -3.64$ ($c = 0.32$, Me_2CO). IR (KBr): 3423, 2940, 2874, 1768, 1631, 1460, 1385, 1031. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. ESI-MS (pos.): 509 ($[M+K]^+$), 493 ($[M+Na]^+$), 491 ($[M+K-H_2O]^+$). ESI-MS (neg.): 505 ($[M+Cl]^-$). HR-ESI-MS (pos.): 493.3284 ($[M+Na]^+$, $C_{30}H_{46}NaO_4^+$; calc. 493.3293).

(3β,12α,13β)-3,12,13-Trihydroxyursan-28-oic Acid (**4**): White powder. M.p. 269–270°. $[\alpha]_D^{26.9} = +11.11$ ($c = 0.24$, $CHCl_3$). IR (KBr): 3440, 2925, 2871, 2854, 1771, 1639, 1630, 1462, 1392, 1361, 1104, 1029, 998, 939, 764. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. FAB-MS (pos.): 491 (0.5, $[M+H]^+$). ESI-MS (neg.): 525 ($[M+Cl]^-$). HR-ESI-MS (neg.): 525.3342 ($[M+Cl]^-$, $C_{30}H_{50}ClO_5^-$; calc. 525.3346).

(2α,3β,12β,13β)-2,3,12,13-Tetrahydroxyoleanan-28-oic Acid (**5**): White powder. M.p. 288–289°. $[\alpha]_D^{27.9} = +3.92$ ($c = 0.09$, $CHCl_3$). IR (KBr): 3428, 2950, 2936, 2868, 1768, 1631, 1456, 1392, 1363, 1133, 1050. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. ESI-MS (neg.): 541 ($[M+Cl]^-$), 505 ($[M-H]^-$). HR-ESI-MS (neg.): 541.3288 ($[M+Cl]^-$, $C_{30}H_{50}ClO_6^-$; calc. 541.3295).

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Received November 19, 2008