Triterpenoid Saponins from *Luculia pincia* Hook

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Two new triterpenoid saponins, cincholic acid-3-*O*-*β*-*D*-xylopyranoside, 28-*O*-*β*-*D*-glucopyranosyl ester (1), quinovic acid-28-*O*-*β*-*D*-glucopyranosyl ester (4), and a new phenolic glucoside, 4-[4′-*O*-(2′, 3′, 5′, 6′-tetrahydroxy phenyl)-*β*-*D*-glucoside]-1-butene (2), along with five known triterpenoid saponins and one phenolic glucoside were isolated from the *n*-butanol fraction of the stems of *Luculia pinciana* Hook. Their structures were established by means of spectroscopic methods.

Keywords *Luculia pinciana*, triterpenoid saponins, phenolic glucosides

Introduction

Luculia pinciana Hook (Rubiaceae) is a kind of medicinal plant widely distributed in Yunnan and Guangxi provinces of China.[1] As a frequently used drug against tracheitis, tuberculosis and rheumatic diseases in traditional Chinese medicine, it can relieve pain, dredge all the channels and vessels, promote blood circulation.[2,3] The first investigated components of the plant material were paenol[3] and volatile oil,[4] and the pharmacological experiments proved that the ethanol extract had anti-tumor and anti-biotic activities.[5] From the *n*-butanol fraction, two new triterpenoid saponins, cincholic acid-3-*O*-*β*-*D*-xylopyranoside, 28-*O*-*β*-*D*-glucopyranoid ester (**1**),[6,7] quinovic acid-28-*O*-*β*-*D*-glucopyranosyl ester (**4**),[8] a new phenolic glucoside 4-[4′-*O*-(2′, 3′, 5′, 6′-tetrahydroxy phenyl)-*β*-*D*-glucoside]-1-butene (**2**),[9] as shown in Fig. 1, six known compounds, quinovic acid-3-*O*-*β*-*D*-glucopyranoside (**3**),[10] quinovic acid-3-*O*-6-deoxy-*β*-*D*-glucopyraside, 28-*O*-*β*-*D*-glucopyranosyl ester (**5**),[8-10] quinovic acid-3-*O*-*α*-*L*-rhamnopyranoside, 28-*O*-*β*-*D*-glucopyranosyl ester (**6**),[8-10] quinovic acid-3-*O*-*β*-*D*-glucopyraside, 28-*O*-*β*-*D*-glucopyranosyl ester (**7**),[10] cincholic acid-3-*O*-*β*-*D*-glucopyranoside, 28-*O*-*β*-*D*-glucopyranosyl ester (**8**),[8,11] glucose-1-[3-(3′-methoxy-4′-hydroxy phenyl)-2-*cis*-propenoate (**9**)[7] were isolated. Among the above-mentioned compounds, compound **6** was richly found in the *n*-butanol fraction, compounds **3**, **5**—**9** were isolated from this plant and genus for the first time. All structures were elucidated by spectroscopic methods. The assignments of the NMR data of compounds **1**, **2**, **4** were established by 2D NMR experiments.

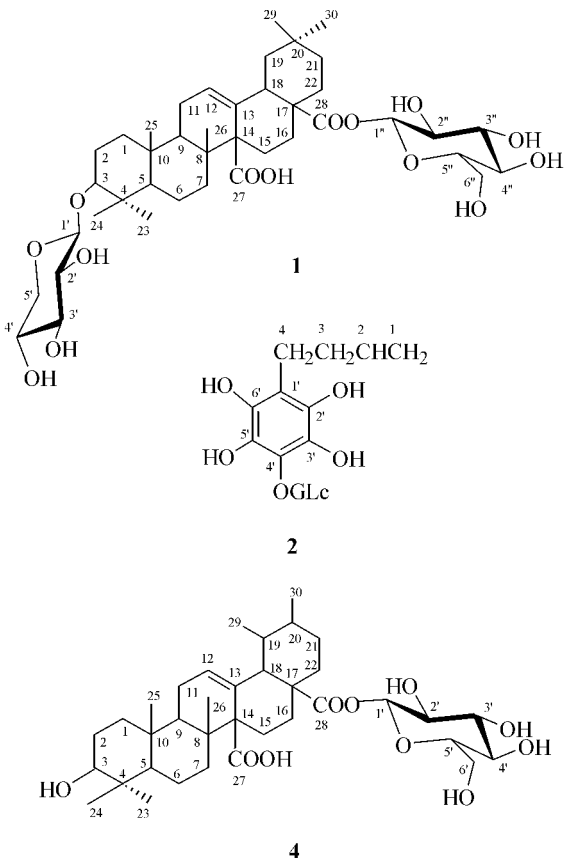

Fig. 1 Chemical structrues of **1**, **2** and **4**.

Results and discussion

Compound **1**, yellow amorphous powder, showed ion peak at *m*/*z* 780, and a base peak at *m*/*z* 573 in the negative FAB-MS spectrum. The high-resolution negative

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FAB-MS exhibited the molecular ion peak at *m/z* 779.4171 (Calcd 779.4218) corresponding to the molecular formula of $C_{41}H_{64}O_{14}$ which was also confirmed by the ^{13}C NMR and DEPT spectral data. The IR spectrum of **1** indicated the presence of hydroxyl (ν_{max} 3477, 1073 cm^{-1}) and carboxyl (ν_{max} 1701 cm^{-1}) groups. The ^{13}C NMR spectrum showed signals for six methyl groups, twelve methylene groups, fourteen methane groups and nine quaternary carbons together with two carboxyl groups at δ 178.8 and δ 176.8 (Table 1). The chemical shifts

Table 1 ^{13}C NMR data of compound **1**, **4** (pyridine-d_5, 125 MHz)

Position	**1**	Position	**4**
Carbon		Carbon	
1	39.0 (t)	1	39.3 (t)
2	25.6 (t)	2	28.2 (t)
3	88.5 (d)	3	79.3 (d)
4	39.5 (s)	4	40.2 (s)
5	55.9 (d)	5	55.8 (d)
6	18.6 (t)	6	18.9 (t)
7	37.4 (t)	7	37.6 (t)
8	40.1 (d)	8	40.8 (d)
9	47.6 (d)	9	47.4 (d)
10	37.2 (s)	10	37.4 (s)
11	23.8 (t)	11	23.5 (t)
12	126.6 (d)	12	129 .6 (d)
13	137.4 (s)	13	133.3 (s)
14	56.7 (d)	14	56.0 (d)
15	26.9 (t)	15	26.2 (t)
16	25.4 (t)	16	25.2 (t)
17	48.1 (s)	17	49.0 (s)
18	44.1 (d)	18	54.7 (d)
19	43.8 (t)	19	39.1 (d)
20	30.8 (s)	20	37.5 (d)
21	33.9 (t)	21	30.3 (t)
22	37.6 (t)	22	36.5 (t)
23	28.0 (q)	23	28.6 (q)
24	17.1 (q)	24	19.3 (q)
25	16.6 (q)	25	16.7 (q)
26	19.1 (q)	26	18.2 (q)
27	178.8 (s)	27	178.1 (s)
28	176.8 (s)	28	176.6 (s)
29	32.2 (q)	29	16.6 (q)
30	23.6 (q)	30	21.2 (q)
3-*O*-xyl		28-*O*-glc	
1′	107.6 (d)	1′	95.7 (d)
2′	75.5 (d)	2′	74.2 (d)
3′	78.6 (d)	3′	78.0 (d)
4′	71.3 (d)	4′	71.2 (d)
5′	67.1 (t)	5′	78.9 (d)
6′	28-*O*-glc	6′	62.5 (t)
28-*O*-glc			
1″	95.8 (d)		
2″	74.2 (d)		
3″	78.9 (d)		
4″	71.3 (d)		
5″	79.5 (d)		
6″	62.3 (t)		

of olefinic carbons at δ 137.4 and δ 126.6 indicated that the aglycone of compound **1** possessed an olean-12-ene triterpenoid skeleton,[12] and the ^1H NMR spectrum showed six methyl groups at δ 0.70, 0.84, 0.88, 0.93, 1.13, 1.19 (s, $6 \times CH_3$), an olefinic proton at δ 6.00 (br,s, 1H) and a signal at δ 3.12 (dd, J = 11.6, 4.3 Hz, 1H). Thus, the aglycone of compound **1** was identified as cincholic acid. The location of the sugar units at the triterpenoid skeleton of **1** was determined by using HMQC and HMBC. The connectivities of the anomeric carbons and protons of the sugar units δ 107.6 and 4.64 (d, J = 7.8 Hz, H-1′), δ 95.8 and 6.38 (d, J = 8.2 Hz, H-1″) respectively were established from the HMQC spectrum. In the HMBC spectrum, the correlation peaks between the anomeric carbon C-1′ (δ 107.6) and H-3 (δ 3.12, dd, J = 11.6, 4.3 Hz), C-28 (δ 176.8) and the anomeric proton H-1″ (δ 6.38, d, J = 7.8 Hz) were observed. The type of the sugar moiety was determined by using the anomeric proton as the starting point by ^1H-^1H COSY and HMQC-TOCSY experiments, and the β-configuration at the anomeric carbon was suggested by the coupling constants of the anomeric proton respectively. The sugar moieties were determined as xylose and glucose. With respect to the stereochemistry of the sugar, NOESY correlation was observed between H-1′ and H-3, H-3′, H-5a′, and H-1″ and H-3″, H-5″, indicating that the sugars were *D*-xylose and *D*-glucose respectively. Accordingly, the structure of **1** was concluded to be cincholic acid-3-*O*-β-*D*-xylopyranoside, 28-*O*-β-*D*-glucopyranoid ester.

Compound **4** was a white amorphous powder. The molecular formula was established as $C_{36}H_{56}O_{10}$ by negative high-resolution FAB-MS. Its FAB-MS displayed fragment ions at *m/z* 647 $[M^+ - H]^-$, and 441 $[M^+ - H - 162 - 44]^-$. The IR spectrum showed the presence of hydroxyl (ν_{max} 3438, 1068 cm^{-1}) and carboxyl (ν_{max} 1717 cm^{-1}) groups. The ^1H NMR (Table 2) and ^{13}C NMR (Table 1) spectra of **4** showed six methyl groups together with two doublet signals at δ 1.15 (d, J = 6.0 Hz, 3H, H-29), 0.72 (d, J = 6.3 Hz, 3H, H-30), indicating that **4** possesses a urs-12ene triterpenoid skeleton. This was further confirmed by the chemical shifts of the olefinic carbons at δ 133.3, 129.6. The location of the sugar unit at the triterpenoid skeleton of **4** was C-28 which was determined by the HMQC and HMBC experiments, which was further confirmed by the glycosidation shift value at δ 4.00 of the C-28. In the HMBC spectrum, the long-range connectivity of the correlation peaks of the anomeric proton at δ 6.36 (d, J = 8.1 Hz 1H, H-1′) and C-28 was observed. The coupling constant of the anomeric proton of the sugar indicated the β-configuration at C-28. Comparing the ^{13}C NMR data of the sugar with literature data,[8] the structure of **4** was found to be quinovic acid-28-*O*-β-*D*-glucopyranosyl ester.

Compound **2** was obtained as a white powder. In the high-resolution negative FAB-MS, it afforded a peak at *m/z* 373.1199 (calcd. 373.1135) which suggested a

Table 2 ^{1}H NMR data of compounds **1** and **4** (pyridine-d_5, 500 MHz)

Position	**1**	**4**
Proton		
H-3	3.12 (dd, J = 11.6, 4.3 Hz, 1H)	3.29 (dd, J = 11.4, 4.6 Hz, 1H)
H-12	6.00 (br,s, 1H)	6.00 (br,s, 1H)
H-18	2.59—2.64 (m, 1H)	2.68 (d, J = 10.6 Hz, 1H)
Me-23	1.13 (s, 3H)	0.82 (s, 3H)
Me-24	0.93 (s, 3H)	1.20 (s, 3H)
Me-25	0.88 (s, 3H)	0.96 (s, 3H)
Me-26	1.19 (s, 3H)	0.87 (s, 3H)
Me-29	0.70 (s, 3H)	1.15 (d, J = 6.0 Hz, 3H)
Me-30	0.84 (s, 3H)	0.72 (d, J = 6.3 Hz, 3H)
28-*O*-glc		28-*O*-glc
1′	6.38 (d, J = 7.8 Hz,1H)	6.36 (d, J = 8.1 Hz, 1H)
2′	4.23 (m, 1H)	4.39 (t, J = 7.8 Hz, 1H)
3′	4.36 (m, 1H)	4.23 (t, J = 8.4 Hz, 1H)
4′	4.36 (m, 1H)	4.31 (t, J = 8.8 Hz, 1H)
5′	4.05 (m, 1H)	4.05 (m, 1H)
6′	4.47 (d, J = 12.2 Hz, 1H)	4.46 (d, J = 11.9 Hz, 1H)
	4.42 (dd, J = 10.1, 4.9 Hz, 1H)	4.42 (dd, J = 10.3, 1.5 Hz, 1H)
3-*O*-xyl		
1″	4.64 (d, J = 8.2 Hz, 1H)	
2″	3.96 (t, J = 8.0 Hz, 1H)	
3″	4.12 (t, J = 8.2 Hz, 1H)	
4″	4.36 (m, 1H)	
5″	4.32, 3.71 (tt, J = 8.8, 10.0 Hz, 2H)	

molecular formula of $C_{16}H_{22}O_{10}$ and was confirmed by its ^{13}C NMR spectral data. The IR spectrum showed a strong broad absorption band for the hydroxyl groups (ν_{max} 3419 cm^{-1}), and aromatic rings (ν_{max} 1620, 1405, 1269 and 1202 cm^{-1}). The ^{13}C NMR data (Table 2) revealed that compound **2** was a phenolic glycoside. This was further confirmed by HMQC and HMBC analysis. The signals at δ_H 5.35 (d, J = 7.8 Hz, 1H) and δ_C 100.6 correlated to each other in the HMQC spectrum and were assignable to the anomeric proton and the carbon of the sugar moiety. The β-configuration at the anomeric carbon was suggested by the coupling constants. The location of the sugar unit at C-4 on the phenol of **2** was easily determined by the symmetry of the chemical shifts of the aromatic carbon.

In the ^{1}H NMR spectra, no signals appeared in the aromatic region, showing that the aromatic ring was completely substituted. A pair of olefinic protons at δ 5.80 (br,s, 1H), δ 5.03 (dd, J = 8.0, 3.2 Hz, 1H) and two methylene groups at δ 1.29 (br,s, 2H) and δ 1.24 (br,s, 2H) indicated the presence of 1-butene, which was confirmed by ^{1}H-^{1}H COSY and HMQC. Therefore, the structure of **2** was 4-[4′-*O*-(2′,3′,5′,6′-tetrahydroxyphenyl)-β-*D*-glucoside]-1-butene.

Experimental

Optical rotations were measured on a HORIBA SEPA-300 high sensitive spectropolarimeter. IR spectra were recorded on a BIO-RAD FTS-135 spectrometer with KBr pellets. MS and HRMS were taken on a VG AUTO SPCE-3000 spectrometer. 1D and 2D NMR experiments were performed on a BRUKER AM-400 or a DRX-500 spectrometer with TMS as internal standard. Column chromatography was performed either on silica gel (200—300 mesh, Qingdao Marine Chemical Inc, China), silica gel H (60u ; Qingdao Marine Chemical Inc, China), Lichroprep RP_{18} gel (40—63 μm, Merck, Darmstadt, Germany), sephadex-LH-20 (25—100 μm). Spots on TLC-plates were detected by spraying with 5% ethanolic H_2SO_4 followed by heating.

Plant material

Dried stems of *L. pinciana* Hook were collected at Dali, Yunnan, P.R. China, in May 2000. A voucher specimen (No. 0358685) was deposited in the Herbarium of the Department of Taxonomy, Kunming Institute of Botany, Chinese Academy of Sciences. The plant was identified by Prof. Hua Peng.

Extraction and isolation

The air-dried stems of *L. piniana* Hook (20 kg) were extracted repeatedly (three times) with 95% ethanol. After evaporation of the solvent *in vacuo*, the concentrated extract was suspended in water and extracted with petroleum ether, EtOAC and *n*-BuOH. The *n*-BuOH partition (150 g) was chromatographed on a silica gel column (1500 g, 200—300 mesh) using gradient elution (1000 mL each solvent system) MeOH (0—50%) in $CHCl_3$

(0%, 2%, 5%, 10%, 20%, 50% each). Fractions were pooled based on TLC analysis (7 combined fractions). Fraction 2 (16 g) was further separated on a silica gel H (800 g) column with $CHCl_3$-MeOH-H_2O (9:1:0.1 to 8:2:0.2, $V:V:V$) to give three fractions A, B and C. Fraction A was chromatographed on sephadex-LH-20 (methanol), and developed with $CHCl_3$-MeOH-H_2O (9:1:0.1) to give compounds **2** (7 mg), **9** (56 mg) and **8** (118 mg). Fraction C was repeatedly chromatographed over a silica gel H column with $CHCl_3$-MeOH-H_2O (9:1:0.1), and purified by an RP-18 silica gel column using MeOH-H_2O (6:4 to 7:3) to yield compounds **1** (16 mg) and **7** (56 mg). Compounds **3** (1.4 g), **4** (860 mg) and **5** (18 mg) were isolated from fraction B using silica gel H and RP-18 columns. Fraction **3** was developed with $CHCl_3$-MeOH-H_2O (8:2:0.2) on a silica gel H column, and yielded the enriched compound **6** (4.8 g).

1 m.p. 250—251 ℃; $[\alpha]_D^{16.5}$ + 27.8 (*c* 0.0045, MeOH); IR (KBr) ν: 3447, 1701, 1629, 1073 cm^{-1}; negative FAB-MS *m/z* (%): 780 $[M^+]$, 573 $[M^+ - 162 - 45]^-$, 441 $[M^+ - 207 - 132]^-$; HRFABMS (negative): cacld for $C_{41}H_{64}O_{14}$ 779.4218, found 779.4171. ^1H NMR data see Table 2 and ^{13}C NMR data see Table 1.

2 m.p. 220—222 ℃; $[\alpha]_D^{20.6}$ – 92.3 (*c* 0.002, MeOH); IR (KBr) ν: 3419, 2925, 1620, 1405, 1269, 1202, 1151, 1072 cm^{-1}; UV (MeOH) λ_{max}: 327, 255, 249, 238, 201 nm; negative FAB-MS *m/z* (%): 373 $[M^+ - H]^-$, 356 $[M^+ - H - 17]^-$, 337 $[M^+ - H - 34]^-$, 167 $[M^+ - H - 162 - 44]^-$; HRFABMS (negative): cacld for $C_{16}H_{22}O_{10}$ 373.1135, found 373.1199. ^1H NMR and ^{13}C NMR data see Table 3.

Table 3 ^1H NMR and ^{13}C NMR data of compound **2** (pyridine-d_5, 500 MHz)

Position	Proton	Carbon
1	5.03 (dd, *J* = 3.2, 8.0 Hz, 2H)	119.8 (t)
2	5.80 (br,s, 1H)	96.9 (d)
3	1.24 (br,s, 2H)	30.0 (t)
4	1.29 (br,s, 2H)	29.6 (t)
1′		120.3 (s)
2′		132.6 (s)
3′		123.3 (s)
4′		135.1 (s)
5′		123.3 (s)
6′		132.6 (s)
Glc		
1″	5.35 (d, *J* = 7.8 Hz, 1H)	100.6 (d)
2″	4.07—4.08 (m, 1H)	74.7 (d)
3″	4.28—4.31 (m, 1H)	78.5 (d)
4″	4.28—4.31 (m, 1H)	71.4 (d)
5″	3.96—4.01 (m, 1H)	79.0 (d)
6″	4.52 (d, *J* = 10.8 Hz, 1H)	62.6 (t)
	4.42 (dd, *J* = 6.9, 11.8 Hz, 1H)	

3 m.p. 247—250 ℃; $[\alpha]_D^{20}$ + 62.0 (*c* 1.0, MeOH); ^1H NMR (C_5D_5N, 400 MHz) δ: 6.00 (br,s, 1H, H-12), 4.77 (d, *J* = 7.7 Hz, 1H, H-1′), 4.56 (d, *J* = 11.6 Hz, 1H, H-6′), 4.41 (dd, *J* = 11.6, 5.1 Hz, 1H, H-6′), 4.18—4.22 (m, 2H, H-3′, H-4′), 3.87—3.93 (m, 2H, H-2′, H-5′), 3.19 (dd, *J* = 11.3, 4.2 Hz, 1H, H-3), 2.62 (d, *J* = 11.4 Hz, 1H, H-18), 1.22 (d, *J* = 5.6 Hz, 3H, H-30), 1.12, 1.07, 0.93, 0.83 (s, 4 × CH_3), 0.78 (d, *J* = 6.0 Hz, 3H, H-29); EI-MS *m/z* (%): 604 (27), 442 (26), 425 (56), 287 (28), 227 (35), 189 (48).

4 $[\alpha]_D^{15.9}$ + 65.7 (*c* 0.035, MeOH); IR (KBr) ν: 3438, 1697, 1445, 1386, 1068 cm^{-1}; negative FAB-MS *m/z* (%): 647 $[M^+ - H]^-$, 485 $[M^+ - H - 162]^-$, 441 $[M^+ - H - 162 - 44]^-$; HRFABMS (negative): cacld for $C_{36}H_{56}O_{10}$ 647.2399, found 647.2384. ^1H NMR data see Table 2 and ^{13}C NMR data see Table 1.

5 m.p. 247—250 ℃; $[\alpha]_D^{20}$ + 62.0 (*c* 1.0, MeOH); ^1H NMR (C_5D_5N, 400 MHz) δ: 6.36 (d, *J* = 8.2 Hz, 1H, H-1″), 5.98 (br,s, 1H, H-12), 4.67 (d, *J* = 7.8 Hz, 1H, H-1′), 4.58 (d, *J* = 11.6, 1H, H-6″), 4.45 (dd, *J* = 11.6, 5.3 Hz, 1H, H-6″), 4.38 (t, *J* = 8.3 Hz, 1H, H-4″), 4.31 (t, *J* = 7.8, 1H, H-2″), 4.23 (t, *J* = 7.8 Hz, 1H, H-3″), 4.10 (t, *J* = 7.8 Hz, 1H, H-3′), 4.02—4.06 (m, 1H, H-5″), 3.78—3.80 (m, 1H, H-5′), 3.70 (t, *J* = 7.8 Hz, 1H, H-4′), 3.16 (dd, *J* = 11.3, 4.6 Hz, 1H, H-3), 2.68 (d, *J* = 11.8 Hz, 1H, H-18), 1.66 (d, *J* = 6.0 Hz, 3H, H-6′), 1.16 (d, *J* = 5.8 Hz, 3H, H-29), 0.73 (d, *J* = 6.0 Hz, 3H, H-30), 1.20, 1.11, 0.92, 0.88 (s, 4 × CH_3); EI-MS *m/z* (%): 588 (67), 442 (62), 425 (98), 287 (24), 189 (46), 135 (40).

6 $[\alpha]_D^{20}$ + 60 (*c* 0.05, MeOH); Negative FAB-MS *m/z* (%): 809 $[M^+ - H]^-$, 647 $[M^+ - H - 162]^-$, 603 $[M^+ - H - 162 - 44]^-$.

7 $[\alpha]_D^{20}$ + 31.6 (*c* 1.13, MeOH); negative FAB-MS *m/z* (%): 793 $[M^+ - H]^-$, 587 $[M^+ - H - 162 - 44]^-$.

8 $[\alpha]_D^{16}$ + 53.3 (*c* 0.12, MeOH); EI-MS *m/z* (%): 604 (51), 442 (13), 425 (64), 287 (22), 135 (51).

9 m.p. 123—126 ℃; $[\alpha]_D^{20}$ – 13.9; ^1H NMR (C_5D_5N, 400 MHz) δ: 7.52 (d, *J* = 7.8 Hz, 1H, H-7), 7.21 (s, 1H, H-2), 7.10 (d, *J* = 8.3 Hz, 1H, H-6), 6.80 (d, *J* = 8.3 Hz, 1H, H-5), 6.42 (d, *J* = 11.0 Hz, 1H, H-8), 5.01 (d, *J* = 7.3 Hz, 1H, H-1′); negative FAB-MS *m/z* (%): 577 $[M^+ - H]^-$, 415 $[M^+ - H - 162]^-$.

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