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A new triterpenoid saponin from *Lysimachia candida*

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Abstract **Object** To investigate the chemical constituents from the whole plant of *Lysimachia candida* Ldl.. **Methods** The constituents were isolated and purified on silica gel column chromatography. Their structures were elucidated by chemical and spectroscopic evidence. **Results** A triterpenoid saponin, named candidoside A (Ⅰ), was isolated from the extract of *n*-BuOH. Its structure was shown to be 3β, 16α-dihydroxy-olean-12-en-28-al-3-*O*-β-*D*-glucopyranosyl-23-*O*-α-*D*-ribofuranoside. **Conclusion** Candidoside A was a new triterpenoid saponin.

Key words *Lysimachia candida* Ldl.; triterpenoid saponin; candidoside A

从单条草中分得一个新的三萜皂苷

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摘 要:目的 对报春花科珍珠菜属药用植物单条草 *Lysimachia candida* 的化学成分进行研究。方法 采用硅胶柱层析进行分离和纯化,通过波谱和化学方法进行结构鉴定。结果 从正丁醇萃取部分分离出 1个三萜皂苷类化合物,结构鉴定为:3β,16α-二羟基齐墩果-12烯-28醛-3-*O*-β-*D*-吡喃葡萄糖基-23-*O*-α-*D*-呋喃核糖苷,命名为单条草苷甲(Ⅰ)。结论 单条草苷甲是新结构的三萜皂苷。

关键词:单条草;三萜皂苷;单条草苷甲
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The plant of *Lysimachia candida* Ldl. (Primulaceae), a Chinese folk medicine, has long been used to treat detoxication and promote blood circulation. We reported one new triterpenoid saponin and 12 known compounds from the methanolic extracts[1]. This paper deals with the separation and structure elucidation of another new triterpenoid saponin, named as candidoside A (Ⅰ).

1 Results and Discussion

Candidoside A (Ⅰ) was obtained as amorphous powder. Its formula was determined as $C_{41}H_{66}O_{13}$ by HR-FAB-MS at m/z 767.455 7 ([M+H]$^+$, calcd. 767.458 2). The IR spectrum exhibited absorptions at 3 432 (OH) and 1 710 cm^{-1} (C=O). Acid hydrolysis of Ⅰ yielded glucose and ribose on TLC. In the positive FAB-MS of Ⅰ, besides the quasi-molecular ion peak, fragment ion peaks at m/z 605 [M-glc+H]$^+$ and 455 [M-glc-rib-H_2O+H]$^+$ were observed. The EI-MS of acetylated Ⅰ showed fragment ion peaks at m/z 259 [rib(OAc)$_3$]$^+$ and 331 [glc(OAc)$_4$]$^+$, suggesting that glucose and ribose moieties should be terminal monosaccharide. In the ^{1}HNMR and ^{13}CNMR spectra, the presence of seven quaternary carbon atoms and the chemical shifts of C-12 at δ 123.6 and C-13 at δ 143.6 were characteristics of a Δ^{12}-oleanene skeleton. Acid hydrolysis of Ⅰ gave aglycone Ⅰa, whose ^{13}CNMR spectrum disclosed the presence of three hydroxylated carbons (δ 78.1, 73.0, 73.5). The signal of C-3 (δ 78.1) suggested an equatorial position for the 3-OH.

Comparing the ^{13}CNMR signals of Ⅰ a with

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those of oleanolic acid[2], C-5 of Ⅰa was shifted upfield to δ 49.8. According to the rule of steric effect, a hydroxyl must be linked to C-23 (δ 73.5). The signal of δ 205.7 (d) and 73.1 (d) indicated an aldehyde and a tertiary hydroxyl group. Except for C-17, C-22 and C-28, the ^{13}CNMR signals of Ⅰa were almost identical with those of 3β, 16α, 23, 28-tetrahydroxy-olean-12-ene[3], which revealed that α-OH and -CHO were linked to C-16 and C-17, respectively. This conclusion was further supported by the HMBC spectrum of Ⅰ. The aldehyde proton at δ 9.49 (-CHO) correlated with the carbons at δ 73.1 (C-16), 51.5 (C-17), and 40.8 (C-18). In the ^{13}CNMR spectrum of Ⅰ, the signals of C-3 and C-23 were shifted downfield to δ 85.6 and 78.3 respectively as compared to signals of its aglycone Ⅰa. According to the rule of glycosylation shift, C-3 and C-23 of Ⅰ must link with a monosaccharide, respectively. The ^{1}HNMR spectrum of Ⅰ had two anomeric proton signals at δ 5.27 (d, J= 6.8 Hz) and 5.17 (d, J= 7.8 Hz) and its ^{13}CNMR spectral data indicated the presence of terminal β-*D*-glucopyranosyl unit and α-*D*-ribofuranosyl unit[4]. Based on the HMBC spectrum of Ⅰ, the proton at δ 4.01 (H-3) had correlation with C-1 (δ 105.4) of glucose and the hydroxymethyl proton at δ 3.87 (H-23) had a cross-peak with C-1 (δ 103.7) of ribose. It was confirmed that glucose was attached to the C-3 position and ribose to C-23. Thus, the structure of Ⅰ was elucidated to be 3β, 16α-dihydroxy-olean-12-en-28-al-3-*O*-β-*D*-glucopyranosyl-23-*O*-α-*D*-ribofuranoside. The key HMBC correlations for Ⅰ (see Fig. 1), chemical shifts of Ⅰ and Ⅰa (see Table 1).

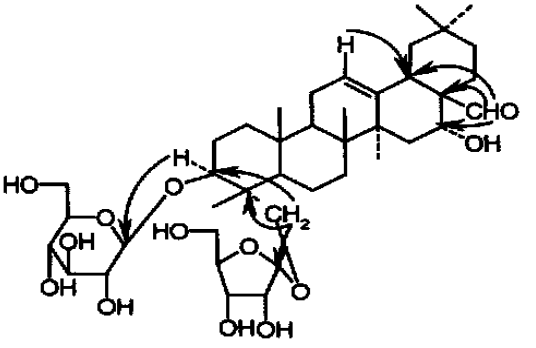

Fig. 1 The key HMBC correlations for Ⅰ

Table 1 Chemical shifts of compounds Ⅰ (in C_5D_5N, 500 MHz for ^{1}H and 125 MHz for ^{13}C) and Ⅰa (in C_5D_5N, 75 MHz) (J Hz)

C, H atom	^{13}CNMR of Ⅰ *	^{13}CNMR of Ⅰa	^{1}HNMR of Ⅰ	HMBC (H to C)
1	38.9 (t)	38.2		
2	27.3 (t)	26.2		
3	85.6 (d)	78.1	4.01, dd	C: 1, 5, Glc-1
4	37.2 (s)	41.8		
5	51.6 (d)	49.8		
6	17.7 (t)	18.4		
7	32.7 (t)	32.7		
8	40.0 (s)	39.7		
9	47.0 (d)	46.6		
10	37.1 (s)	36.8		
11	23.6 (t)	23.1		
12	123.6 (d)	123.7	5.45, brs	C: 18
13	143.6 (s)	142.1		
14	40.9 (s)	41.4		
15	35.5 (t)	34.6		
16	73.1 (d)	73.0		
17	51.5 (s)	50.7		
18	40.8 (d)	40.3		
19	46.9 (t)	46.2		
20	30.8 (s)	30.4		
21	34.9 (t)	35.4		
22	23.6 (t)	23.3		
23	78.3 (t)	73.5	3.88, d, J= 10.3 3.86, d, J= 10.3	C: 3, 4, Rib-1
24	13.8 (q)	11.4	1.06, s	C: 3, 4, 5, 23
25	16.6 (q)	17.1	0.797, s	C: 1, 5, 9, 10
26	17.4 (q)	17.6	0.739, s	C: 7, 8, 9, 14
27	27.1 (q)	26.9	1.65, s	C: 8, 13, 14, 15
28	205.7 (d)	204.7	9.49, s	C: 16, 17, 18
29	33.3 (q)	32.9	0.977, s	C: 19, 20, 21
30	24.2 (q)	23.9	1.00, s	C: 19, 20, 21

* Sugar moieties of Ⅰ: Glc: 105.4 (d), 75.2 (d), 78.5 (d), 70.5 (d), 78.4 (d), 62.7 (t); Rib: 103.7 (d), 71.2 (d), 71.7 (d), 83.8 (d), 64.4 (t)

2 Experimental

2.1 General experimental procedures: IR spectrum was measured on a Nicolet MX-1 spectrometer as a pressed KBr disk. NMR spectra were recorded on Bruker AP-300 and DRX-500 MHz spectrum was TMS as the internal standard. MS spectra were measured on a VG AutoSpec-3000 mass spectrometer. Silica gel with 200-300 mesh was used for column chromatography.

2.2 Plant material: The whole plant of *L. candida* was collected in Mianyang, Sichuan Province, China and identified by Professor Xiao Shunchang, Chengdu Institute of Biology, Chinese Academy of Sciences.

2.3 Extraction and isolation: The dried powder (7.25 kg) was extracted three times with MeOH for ten days each time at room temperature. After removal of the solvent. the residue was suspended in H_2O and successively extracted with petroleum ether (bp 60 ℃~ 90 ℃), EtOAc and *n*-BuOH. The *n*-BuOH extracts (108 g) were subjected to silica gel ($CHCl_3$-MeOH= 35∶ 1) column chromatography to obtain six fractions. Fraction sixth was chromatographed over silica gel eluted with $CHCl_3$-MeOH (20∶ 1) to afford compound Ⅰ (30 mg).

2.4 Identification: Compound Ⅰ white powder, IR ν_{max}^{KBr} (cm^{-1}): 3 432, 2 946, 2 936, 1 710, 1 112, 1 075, 1 040. HR-FAB-MS [M + H]$^+$ m/z 767.455 8 ($C_{41}H_{67}O_{15}$, calcd. 767.458 2). FAB-MS (-) m/z 765 [M- H]$^-$, 603 [M- glc]$^-$. FABMS (+) m/z 767 [M+ H]$^+$, 605 [M- glc+ H]$^+$, 455 [M- glc- rib- H_2O+ H]$^+$.

Hydrolysis of Ⅰ: Compound Ⅰ (8 mg) hydrolyzed with 0.5 mol/L H_2SO_4 (5 mL, EtOH-H_2O = 1∶ 1) in boiling water bath for 4 h. After removal of EtOH under reduced pressure, the mixture was extracted with chloroform three times. The organic layer was evaporated to dryness to give Ⅰa (5 mg).

Acetylation of Ⅰ: Compound Ⅰ (2 mg) was acetylated with Ac_2O-pyridine (1∶ 2, 0.75 mL) at room temperature for 48 hours to yield acetate of Ⅰ. EI-MS (m/z): 331, 259.

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山楂化学成分研究

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摘 要: 目的 从山里红 *Crataegus pinnatifida* var. *major* 的成熟干燥果实寻找中药山楂中的专属性成分和降血脂的活性成分。方法 利用多种柱色谱技术进行分离和纯化,根据 UV、IR、EI-MS、FAB-MS、^{1}HNMR、^{13}CNMR、HMBC、HMQC和^{13}CGATE等波谱数据分析鉴定结构。结果 从山里红成熟果实中分离鉴定了 6个化合物,分别为: 5,7,4′-三羟基黄酮-8-*C*-α-*L*-吡喃鼠李糖基-(1→2)-β-*D*-吡喃葡萄糖苷(Ⅰ),即牡荆素鼠李糖苷(vitexin rhamnoside),金丝桃苷(hyperoside,Ⅱ),枸橼酸(citric acid,Ⅲ),牡荆素(vitexin,Ⅳ),槲皮素(quercetin,Ⅴ),熊果酸(ursolic acid,Ⅵ)。结论 化合物Ⅰ为中药山楂中的专属性成分,首次由山里红果实中分得,化合物Ⅱ为山楂中的降血脂主要黄酮成分。

关键词: 山里红;牡荆素鼠李糖苷;金丝桃苷

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Studies on chemical constituents from fruit of *Crataegus pinnatifida*

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Abstract Object To look for the proprietary constituent and the constituents with blood lipid regulating effect from the dried fruit of *Crataegus pinnatifida* Bge. var. *major* N. E. Br. **Methods** Various column chromatographic techniques were employed for isolation and purification of the constituents. UV,

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