

• 化学成分 •

Two new monoglycosides from *Polycarpon prostratum*

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Abstract: Object To study the chemical constituents from the whole plants of *Polycarpon prostratum* (Forssk.) Aschers. et Schwein. ex Aschers. **Methods** The compounds were isolated and purified on silica gel column chromatography, their structures were identified by spectroscopic methods. **Results** Two new monoglycosides, named prostratosides I and J were isolated from the ethyl acetate extract, their structures were determined to be 3-*O*- α -*L*-arabinopyranosyl-16 α -hydroxy-22 α -acetoxy-saikogenin E (I) and 3-*O*- α -*L*-arabinopyranosyl saikogenin F (II), respectively. **Conclusion** Compound I and II are two new triterpenoid saponins.

Key words: *Polycarpon prostratum* (Forssk.) Aschers. et Schwein. ex Aschers.; Caryophyllaceae; triterpenoid saponin; prostratosides I and J

多莢草中的两个新单糖苷

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摘要:目的 对石竹科植物多莢草 *Polycarpon prostratum* 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, 通过波谱分析进行结构鉴定。结果 从其乙酸乙酯萃取部分分离得到了两个新的柴胡皂苷类化合物: prostratosides I 和 J。通过波谱方法分别鉴定其结构为 3-*O*- α -*L*-arabinopyranosyl-16 α -hydroxy-22 α -acetoxy-saikogenin E (I) 和 3-*O*- α -*L*-arabinopyranosyl saikogenin F (II)。结论 化合物 I 和 II 均为新化合物。

关键词: 多莢草; 石竹科; 三萜皂苷; 多莢草皂苷 I 和 J

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We previously reported the isolation and structural elucidation of eight new triterpenoid saponins (named prostratosides A-H)^[1-3] and three new cyclic peptides (named polycarponin A-H)^[4,5] from the whole plants of *Polycarpon prostratum* (Forssk.) Aschers. et Schwein. ex Aschers. Our further investigation on the EtOAc soluble fraction of this plant led to the isolation of two new monoglycosides, named prostratosides I and J (I, II). In this paper, we report the isolation and structural elucidation of these two compounds.

1 Results and discussion

Prostratoside I (I) was obtained as white powder. Its FAB-MS gave a [M-H]⁻ ion at *m/z* 645.

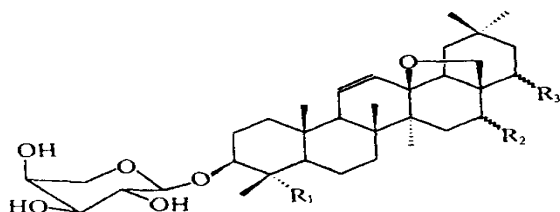
On acid hydrolysis, only *L*-arabinose was detected as the sugar component. The ¹H NMR spectrum exhibited the presence of eight methyl groups at δ 0.92, 0.96, 1.00, 1.05, 1.08, 1.29, 1.70, 1.99 (3H each, s), two olefinic methine signals at δ 5.99 (d, *J* = 10.5 Hz, H-11) and 5.67 (dd, *J* = 10.5, 2.8 Hz, H-12), and an anomeric proton at δ 4.77 (d, *J* = 7.2 Hz, H-1'). The ¹³C NMR spectral data of I was shown in table 1. The ¹³C NMR and DEPT spectra showed the anomeric carbon resonances at δ 107.4. And the presence of a carbonyl signal at δ 170.5, two olefinic methane carbons at δ 132.3 (G-11) and 131.5 (G-12), two oxy-methane carbons at δ 70.8 (G-16) and 77.0 (G-22), an oxymethylene

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carbon at δ 76.7 (G-28), a quaternary carbon at δ 84.8 (G-13), and eight methyl carbons at δ 16.3, 18.2, 18.3, 19.6, 21.0, 25.1, 27.9 and 33.3 indicated that compound I had the same aglycone as prostratoside B, a tetraglycoside isolated from the same plant^[1]. The signals at G-16 and G-28 are in relative low field, indicating the presence of an α -OH at G-16^[6]. The ¹H NMR signal of H-22 (δ 5.28, dd, J = 12.4, 5.6 Hz), suggested H-22 to be an axial H. Therefore, the structure of prostratoside I (I) was determined to be 3-*O*- α -*L*-arabiopyranosyl-16 α -hydroxy-22 α -acetoxy-saikogenin E.



	R ₁	R ₂	R ₃
I	CH ₃	α -OH	α -OAc
II	CH ₂ OH	β -OH	H

Fig 1 Structures of prostratosides I (I) and J (II)

Prostratoside J (II) was obtained as white powder and revealed the $[M-H]^-$ ion peak at m/z 603 in the negative FAB-MS. A ¹³C NMR spectral comparison with I showed that II also had the same linked sugar moiety, different structurally from I only in its aglycone. The ¹H NMR spectrum of II showed six angular methyl groups at δ 0.91, 0.96, 0.98, 1.00, 1.13 and 1.41, two olefinic proton signals at δ 6.00 (1H, d, J = 10.6 Hz, H-11) and 5.66 (1H, dd, J = 10.6, 2.5 Hz, H-12), and an anomeric proton at δ 4.74 (1H, d, J = 8.0 Hz, H-1'). The ¹³C NMR spectral data of II was shown in Table 1. The ¹³C NMR and DEPT spectra showed an anomeric carbon resonance at δ 107.6, two olefinic signals at δ 132.1 and 131.2 corresponding to two methine carbons (G-11 and G-12), two methylene carbon signals at δ 73.1 (G-28) and 64.6 (G-23), a quaternary carbon signal at δ 84.2 (G-13). The signals at G-16 (δ 64.0) and G-28 are in relative high field, indicating the presence of a β -OH at G-16^[6]. The above data revealed that the aglycone of II was saikogenin F^[7]. Therefore, the structure of II was characterized as 3-

O- α -*L*-arabinopyranosyl-saikogenin F.

Table 1 ¹³C NMR data for prostratosides I (I) and J (II) in C₅D₅N (125 MHz)

Position	I	II	Position	I	II
1	38.6	38.7	20	33.3	31.5
2	26.6	26.0	21	42.1	34.7
3	88.6	82.0	22	77.0	25.9
4	40.2	43.7	23	27.9	64.6
5	55.4	47.6	24	16.3	13.1
6	18.0	17.7	25	18.3	18.7
7	31.9	31.7	26	19.6	20.1
8	42.1	42.4	27	18.2	21.1
9	52.9	53.2	28	76.7	73.1
10	36.4	36.3	29	33.3	33.6
11	132.3	132.1	30	25.1	23.9
12	131.5	131.2	OAC	170.5	
13	84.8	84.2		21.0	
14	44.2	45.8	1'	107.4	107.6
15	35.2	36.3	2'	72.9	73.1
16	70.8	64.0	3'	74.6	74.7
17	49.5	47.1	4'	69.5	69.5
18	51.0	52.3	5'	66.7	66.9
19	37.6	37.8			

2 Experiment

2.1 General experimental procedures. NMR spectra were obtained on Bruker DRX-500 MHz spectrometers. A VG Auto Spec-3000 spectrometer was used to record FAB-MS spectrum 200–300 meshes and 300–400 meshes silica gel and Diaion HP-20 were used for column chromatography.

2.2 Plant material. The whole plants of *P. prostratum* (Forssk.) Aschers et Schwein ex Aschers. were collected in Xishuangbanna, Yunnan Province, China, in July 1997. The botanical identification was made by senior engineer Wang Hong, from Xishuangbanna Tropical Botanical Garden, the Chinese Academy of Sciences.

2.3 Extraction and isolation. The plant material (17.8 kg) was extracted with hot ethanol four times to afford an EtOH extract that was suspended in water, and extracted with ethyl acetate and *n*-butanol, respectively. The EtOAc residue (168.0 g) was chromatographed on Diaion HP-20 with a H₂O-MeOH gradient system (1:0 \rightarrow 0:1). The fraction eluted with 70% MeOH was further subjected to silica gel (CHCl₃-MeOH = 9:1) column chromatography to afford prostratosides I (I, 18 mg) and J (II, 12 mg), respectively.

2.4 Identification. Prostratoside I (I):

$C_{37}H_{58}O_9$, white powder. FAB-MS $[M - H]^- m/z$: 645; 1H NMR (C_5D_5N , 500 MHz); δ 0.92, 0.96, 1.00, 1.05, 1.08, 1.29, 1.70, 1.99 (3H each, s), 4.77 (1H, d, $J = 7.2$ Hz, H-1_{ara}), 5.99 (1H, d, $J = 10.5$ Hz, H-11), 5.67 (1H, dd, $J = 10.5, 2.8$ Hz, H-12), 5.28 (1H, dd, $J = 12.4, 5.6$ Hz, H-22).

Prostratoside J (II): $C_{35}H_{56}O_8$, white powder. FAB-MS $[M - H]^- m/z$: 603; 1H NMR (C_5D_5N , 500 MHz); δ 0.91, 0.96, 0.98, 1.00, 1.13, 1.41 (3H each, s), 4.74 (1H, d, $J = 8.0$ Hz, H-1_{ara}), 6.00 (1H, d, $J = 10.6$ Hz, H-11), 5.66 (1H, dd, $J = 10.6, 2.5$ Hz, H-12).

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水甘草化学成分的研究

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摘要: 目的 研究水甘草甲醇提总生物碱的化学成分。方法 利用离子交换树脂、大孔吸附树脂、硅胶柱层析分离纯化, 根据化合物的光谱数据鉴定其结构。结果 从水甘草甲醇提总碱中分得 3 个化合物, 分别鉴定为 rhazidigenine, I, 水甘草酸(amsonic acid, II), 反式芥子酸甲酯(trans-sinapic acid methylester, III)。结论 化合物 II 为新化合物, I 和 III 为首次从该植物中得到。

关键词: 水甘草; 吲哚生物碱; 水甘草酸

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Studies on chemical constituents of *Amsonia sinensis*

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Abstract: **Object** To study the chemical constituents of alkaloids of *Amsonia sinensis* Tsiang extracted with methanol. **Methods** Compounds were separated by exchange resin, macroporous resin and silica gel column chromatography. Their structures were elucidated by spectroscopic analysis. **Results** Three compounds were isolated from total alkaloids of *A. sinensis* extracted with methanol. They were identified as: rhazidigenine (I), amsonic acid (II), trans-sinapic acid methylester (III). **Conclusion** Compound II is a new one, and compound I and III are obtained from this plant for the first time.

Key words: *Amsonia sinensis* Tsiang; indole alkaloid; amsonic acid

水甘草 *Amsonia sinensis* Tsiang 是我国特有的 夹竹桃科水甘草属植物, 分布于长江流域, 民间用作

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