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# 多荚草中的新三萜皂甙

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摘要: 从石竹科植物多荚草(*Polycarpon prostratum* (Forssk.) Aschers. et Schwein. ex Aschers)中分离得到3个新的柴胡皂甙类化合物: prostratoside A~ C (**1~ 3**)。它们的结构通过波谱方法分别鉴定为: 3_O_{β_D_xylopyranosyl_(1→2)_β_D_glucopyranosyl_(1→4)_[β_D_glucopyranosyl_(1→2)]_α_L_arabinopyranoside}_22α_acetoxy_saikogenin G, 3_O_{β_D_xylopyranosyl_(1→2)_β_D_glucopyranosyl_(1→4)_[β_D_glucopyranosyl_(1→2)]_α_L_arabinopyranoside}_16α_hydroxy_22α_acetoxy_saikogenin E 和 3_O_{β_D_xylopyranosyl_(1→2)_β_D_glucopyranosyl_(1→4)_[β_D_glucopyranosyl_(1→2)]_α_L_arabinopyranoside}_21β_acetoxy_saikogenin G.

关键词: 多荚草; 石竹科; 三萜皂甙
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# New Triterpenoid Saponins from *Polycarpon prostratum* (Caryophyllaceae)

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**Abstract:** Three new triterpenoid saponins, namely prostratosides A- C (**1- 3**), were isolated from the whole plant of *Polycarpon prostratum* (Forssk.) Aschers. et Schwein. ex Aschers. By spectroscopic methods, their structures were determined as 3_O_{β_D_xylopyranosyl_(1→2)_β_D_glucopyranosyl_(1→4)_[β_D_glucopyranosyl_(1→2)]_α_L_arabinopyranoside}_22α_acetoxy_saikogenin G, 3_O_{β_D_xylopyranosyl_(1→2)_β_D_glucopyranosyl_(1→4)_[β_D_glucopyranosyl_(1→2)]_α_L_arabinopyranoside}_16α_hydroxy_22α_acetoxy_saikogenin E and 3_O_{β_D_xylopyranosyl_(1→2)_β_D_glucopyranosyl_(1→4)_[β_D_glucopyranosyl_(1→2)]_α_L_arabinopyranoside}_21β_acetoxy_saikogenin G, respectively.

**Key words:** *Polycarpon prostratum*; Caryophyllaceae; triterpenoid saponin

*Polycarpon* is a genus of Caryophyllaceae consisting of 16 species. Some phytochemical researches on this genus have been published[1- 2]. *Polycarpon prostratum* (Forssk.) Aschers. et Schwein. ex Aschers is a small annual herb growing at the river side and road sides in damp soil. It is said to be toxic and has anti_inflammatory and anodyne activities[3]. Our investigation on the n_BuOH soluble fraction of this whole plant led to the isolation of three new saikosaponin_like compounds, namely prostratosides A- C (**1- 3**). We report herein the isolation and structure elucidation of these three compounds.

## 1 Results and Discussion

The HRFABMS of prostratoside A (**1**) gave a $[M-1]^-$ ion at m/z 1 117.550 5, in agreement with the molecular formula $C_{54}H_{86}O_{24}$ (calcd for $C_{54}H_{86}O_{24}$ m/z 1 117.543 1). The IR spectrum showed absorption bands at 3 371, 1 717, 1 646 and 1 046 $cm^{-1}$. The $^1$H-NMR spectrum exhibited the presence of four anomeric protons at δ 4.92 (d, $J$= 7.2 Hz), 4.98 (d, $J$= 8.0 Hz), 5.02 (d, $J$= 6.0 Hz) and 5.49 (d, $J$= 8.0 Hz). The $^{13}$C-NMR spectrum showed four anomeric carbon resonances at δ 103.9, 104.2, 105.1 and 107.6. Correlations between anomeric carbon resonances and anomeric proton signals were also observed in HMQC spectrum. This information suggested that compound **1** is a tetraglycoside.

The $^1$H-NMR spectrum exhibited the presence of six angular methyl groups at δ 0.95, 0.98, 1.01, 1.09, 1.30 and 1.61, and two olefinic methines at δ 6.00 (d, $J$= 10.2 Hz), 5.65 (dd, $J$= 10.4, 2.8 Hz). In the

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$^{13}$C-NMR and DEPT spectra, two olefinic signals were observed at δ 132.6 and 131.5 corresponding to two methine carbons C_11 and C_12. One methylene carbon (δ 76.8, C_28) and one quaternary carbon (δ 84.9, C_13) were also seen. This information suggested that the aglycone of compound **1** is a saikogenin_like compound. A correlation in HMQC spectrum between a $^{13}$C_NMR signal at δ 21.1 and a $^{1}$H-NMR resonance at δ 2.01(s) and a correlation in the HMBC spectrum between signals at $\delta_H$ 2.01 and $\delta_C$ 170.7 confirmed the presence of one acetoxy group in the molecule. A comparison of compound **1** with 22α_hydroxy_saikogenin G[4] showed that the $^{13}$C_NMR data of the aglycones of these two compounds are very similar, except for C_22 (δ 77.1), C_21 (δ 42.2) and C_17 (δ 49.6) which showed shifts + 2.8, − 3.5 and + 2.1, respectively, indicating that acetoxy group was attached to C_22. The HMBC correlation between the C═O of the acetoxy group and H_22 gave further confirmation. The $^{1}$H_NMR signal of H_22 (δ 5.29, dd, $J$ = 12.0, 5.5 Hz) suggested H_22 to be an axial H. The NOE were observed between H_22 and H_30 (δ 0.98), and H_22 and H_28 (δ 3.68, 3.78), that also showed the orientation of H_22 to be in β_position. C_16 (δ 71.0) and C_28 were at relative low field, indicating the presence of an α_OH was at C_16[5]. Therefore, the structure of the aglycone was determined as 22α_acetoxy_saikogenin G.

The sugar units of compound **1** were established as arabinose, xylose, glucose by TLC comparing with authentic samples. The common D configuration for xylose and glucose, and L configuration for arabinose were assumed according to those most often encountered among the plant glycosides. The sequence of monosaccharide units, interglycosidic linkages and anomeric configurations were determined by spectral analysis, including FABMS, $^{1}$H-NMR, $^{13}$C_NMR, HMQC, HMBC and HMQC_TOCSY. The FABMS (negative_ion mode) gave four fragments (m/z 986 [M− pentose]$^-$, 956 [M− glc]$^-$, 823 [M− pentose− glc− H]$^-$, 661[M− pentose− glc− glc − H]$^-$), indicating that a pentose and a glucose were terminal sugars. By analysis of HMQC_TOCSY and HMBC spectra, the $^{1}$H and $^{13}$C_NMR signals of the sugar moieties could be assigned. The HMBC correlations were observed between C_3 (δ 82.4) of the aglycone and H_1 (δ 5.02) of arabinose, C_2 (δ 80.4) of arabinose and H_1 (δ 5.49) of glucose$_1$, C_4 (δ 78.2) of arabinose and H_1 (δ 4.98) of glucose$_2$, and C_2 (δ 85.3) of glucose$_2$ and H_1 (δ 4.92) of xylose (Fig. 1). Therefore, the sequence of these sugars could be determined. All the carbon signals due to these sugar moieties were in good agreement with the published data for similarly linked sugar moieties[6,7]. β_Configuration at the anomeric positions may be inferred from the values of the coupling constants for both glucopyranosyl units ($J$ = 8.0 Hz) and xylopyranosyl unit ($J$ = 7.2 Hz). The configuration and ring size of the arabinosyl unit were less clear. The value of its coupling constant ($J$ = 6.0 Hz) is midway between that observed for methyl β_L_arabinofuranoside ($J$ = 4.0 Hz) and methyl α_L_arabinopyraoside ($J$ = 8.0 Hz). According to the references[7,8], the coupling constant observed in compound **1** is consistent with an α_L_arabinopyranoside moiety in a conformational equilibrium ($^{4}C_1$ and $^{1}C_4$).

On the basis of the above results and the assumption that xylose and glucose are members of the commonly found D series and arabinose of the L series, prostratoside A (**1**) was identified as 3_O_{β_D_xylopyranosyl_(1→2)_β_D_glucopyranosyl_(1→4)_[β_D_glucopyranosyl_(1→2)]_α_L_arabinopyranoside}_22α_acetoxy_saikogenin G.

Prostratoside B (**2**) exhibited four fragments at 1 101 [M− 1]$^-$, 969 [M_pentose− H]$^-$, 939 [M− glc− H]$^-$, and 807 [M− pentose− glc− H]$^-$ in the negative FABMS. The information obtained from FAB_MS, $^{13}$C,

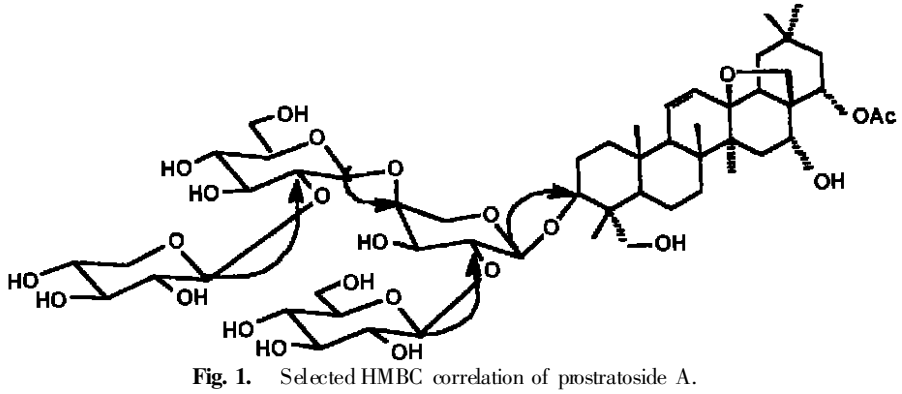
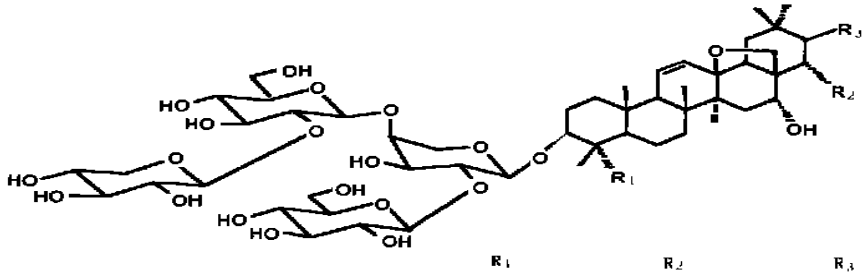



**Fig. 1.** Selected HMBC correlation of prostratoside A.

$^1$H NMR and DEPT spectra implied a $C_{54}H_{86}O_{23}$ molecular formula. A comparison with compound **1** showed that compound **2** had the same sugar moiety at C_3 as compound **1** and structural similarity in the aglycone moiety. The main difference was at C_23, which was a methyl carbon signal of δ 28.0 in compound **2**, but a methylene in compound **1**. And the signals at δ 16.4, 39.1, 26.6, 89.2, 40.2, 55.6, 18.1 and 32.0 were assigned to C_24 and C_1 through C_7 respectively, which were also different from that of compound **1**. These facts indicated the aglycone of compound **2** to be 16α_hydroxy_22α_acetoxy_saikogenin E. Therefore, the structure of prostratoside B (**2**) was assigned as 3_O_{β_D_xylopyranosyl_(1→2)_β_D_glucopyranosyl_(1→4)_[β_D_glucopyranosyl_(1→2)]_α_L_arabinopyranoside}_16α_hydroxy_22α_acetoxy_saikogenin E.

Prostratoside C (**3**) revealed the same ion peaks at m/z 1 118 [M]$^-$, 986 [M − pentose]$^-$, 956 [M − glc]$^-$, 823 [M − pentose − glc − H]$^-$ as compound **1** in the negative FABMS. A $^{13}$C_NMR spectral comparison of compound **3** with compound **1** showed that compound **3** had the same sugar moiety as compound **1**, and was similar structurally to compound **1** in rings A − D of the aglycone, varying only in the E ring of the aglycone. The two methyl carbon signals assigned to C_29 (δ 30.0) and C_30 (δ 19.5) were shifted upfield by 3.42 and 5.75, respectively, when compared with compound **1**, which suggested the presence of an acetoxy function at C_19 or C_21[9]. Comparing compound **3** with saikosponin D[4] showed that C_22 (δ 36.5), C_17 (δ 48.0) and C_20 (δ 36.0) of compound **3** changed shifts (+ 5.3, + 2.5 and + 4.2, respectively) and the C_18 (δ 50.6) only changed by − 0.92, suggesting the acetoxy function to be at C_21 (δ 77.9). The HMBC spectrum exhibited the correlations between H_21 and C═O (OAc, δ 171.0), H_21 and C_30, which gave further confirmation. The $^1$H_NMR signal of H_21 (δ 6.10, dd, $J$ = 11.2, 5.2 Hz) showed the presence of an axial proton at C_21. Consequently, the structure of prostratoside C (**3**) represented as 3_O_{β_D_xylopyranosyl_(1→2)_β_D_glucopyranosyl_(1→4)_[β_D_glucopyranosyl_(1→2)]_α_L_arabinopyranoside}_21β_acetoxy_saikogenin G.

Triterpenoid saponins isolated from the plants belonging to Caryophyllaceae are mainly glycosides of gypsogenin, gyposgenic acid, quillaic acid, hederagenin or medicagenic acid having different sugar moieties. Saikosaponins, with different combinations of glucose, rhamnose and fucose as sugar moieties, are prominent in *Bupleurum* species (Umbelliferae)[5], and are also found in plants of the genus *Clinopodium* (Labiatae)[9]. Some of them were reported to have antiviral, anti_inflammatory, haemolytic and plasma_cholesterol lowering activities. It is noteworthy that saikosaponin_like compounds with an 11_ene and a five_membered ether ring in the aglycone moiety, and arabinose, glucose and xylose as sugar moiety, were isolated from Caryophyllaceae for the first time.




## 2 Experimental

### 2.1 General experimental procedures

Melting points were determined on Kofler block and uncorrected. Optical rotations were measured with a SEPA_300 polarimeter. IR spectra were measured on a Bio_Rad FTS_135 spectrometer. NMR spectra were obtained on Bruker AM_400 MHz and DRX_500 MHz spectrometers. A VG Auto Spec_3000 spectrometer was used to record FABMS spectrum. 200 − 300 mesh and 300 − 400 mesh silica gel, D_101 resin and RP_18 were used for column chromatography.

### 2.2 Plant material

The whole plants of *Polycarpon 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 Hong Wang, Xishuangbanna Tropical Botanical Garden, the Chinese Academy of Sciences.

### 2.3 Extraction and isolation

The plant material (6.0 kg) was extracted with hot ethanol four times to afford an EtOH extract that was sus-

**Table 1** $^{13}$C-NMR data for prostratosides A-C in $C_5D_5N$ (100 MHz)

| Position | A | B | C | Position | A | B | C |
|---|---|---|---|---|---|---|---|
| Aglycone moiety | | | | Sugar moiety | | | |
| 1 | 38.7 | 39.1 | 38.7 | Ara | | | |
| 2 | 25.9 | 26.6 | 26.0 | 1 | 103.9 | 104.3 | 104.0 |
| 3 | 82.4 | 89.2 | 82.5 | 2 | 80.4 | 80.0 | 80.3 |
| 4 | 43.9 | 40.3 | 43.7 | 3 | 73.5 | 73.5 | 73.5 |
| 5 | 47.9 | 55.6 | 47.9 | 4 | 78.2 | 78.1 | 78.1 |
| 6 | 17.7 | 18.1 | 17.8 | 5 | 64.4 | 64.6 | 64.8 |
| 7 | 31.7 | 32.0 | 31.8 | $Glc_1$ | | | |
| 8 | 42.2 | 42.3 | 42.1 | 1 | 105.1 | 105.0 | 105.0 |
| 9 | 53.1 | 53.0 | 53.1 | 2 | 76.3 | 76.3 | 76.3 |
| 10 | 36.4 | 36.5 | 36.5 | 3 | 78.5 | 78.8 | 78.6 |
| 11 | 132.6 | 132.6 | 132.6 | 4 | 71.7 | 72.1 | 71.8 |
| 12 | 131.5 | 131.6 | 131.6 | 5 | 78.4 | 78.3 | 78.4 |
| 13 | 84.9 | 85.0 | 84.9 | 6 | 62.9 | 63.2 | 63.0 |
| 14 | 44.2 | 44.3 | 44.0 | $Glc_2$ | | | |
| 15 | 35.3 | 35.3 | 35.2 | 1 | 104.2 | 104.9 | 104.2 |
| 16 | 71.0 | 70.9 | 70.9 | 2 | 85.3 | 85.3 | 85.3 |
| 17 | 49.6 | 49.7 | 48.0 | 3 | 77.7 | 77.6 | 77.7 |
| 18 | 51.1 | 51.1 | 50.6 | 4 | 71.2 | 71.3 | 71.3 |
| 19 | 37.6 | 38.3 | 38.4 | 5 | 78.4 | 78.3 | 78.4 |
| 20 | 33.3 | 33.4 | 36.0 | 6 | 62.5 | 62.5 | 62.5 |
| 21 | 42.2 | 42.3 | 77.9 | Xyl | | | |
| 22 | 77.1 | 77.4 | 36.5 | 1 | 107.6 | 107.6 | 107.6 |
| 23 | 64.8 | 28.0 | 64.8 | 2 | 76.1 | 76.1 | 76.1 |
| 24 | 13.0 | 16.4 | 13.0 | 3 | 77.9 | 77.9 | 77.9 |
| 25 | 18.9 | 18.6 | 18.8 | 4 | 70.9 | 70.9 | 70.9 |
| 26 | 19.7 | 19.7 | 19.7 | 5 | 67.6 | 67.6 | 67.6 |
| 27 | 18.2 | 18.4 | 18.2 | | | | |
| 28 | 76.8 | 77.1 | 76.9 | | | | |
| 29 | 33.4 | 33.5 | 30.0 | | | | |
| 30 | 25.2 | 25.3 | 19.5 | | | | |
| OAc | 170.7 | 170.9 | 171.0 | | | | |
| | 21.1 | 21.1 | 21.4 | | | | |

pended in water, and extracted with ethyl acetate and n-butanol, respectively. The n-BuOH residue (40.0 g) was chromatographed on D-101 resin with a $H_2O$-EtOH gradient system (1∶0 → 0∶1). The fraction eluted with 70% MeOH was further subjected to silica gel ($CHCl_3$∶MeOH=7∶3) and RP-18 (MeOH∶$H_2O$ = 7∶3) column chromatography to afford prostratosides A (**1**, 120 mg, 0.001 8%), B (**2**, 40 mg, 0.000 6%) and C (**3**, 60 mg, 0.001 5%), respectively.

## 2.4 Identification

**Prostratoside A (1)** White powder. mp 250-252 ℃. $[\alpha]_D^{24}$ + 4.3° (c = 0.88, MeOH). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3 371, 1 717, 1 642, 1 046. FABMS m/z: 1 118 $[M]^-$ (100), 986(22), 956(7), 823(12), 661(2); HRFABMS: $[M-1]^-$ at m/z 1 117.550 5 (calcd for $C_{54}H_{86}O_{24}$, 1 117.543 1). $^1$H-NMR ($C_5D_5N$, 400 MHz): δ 0.98 (3H, s, H-30), 1.01 (3H, s, H-29), 1.09 (3H, s, H-24), 0.95 (3H, s, H-25), 1.61 (3H, s, H-27), 1.30 (3H, s, H-26), 2.01 (3H, s, H-OAc), 6.00 (1H, d, *J* = 10.2 Hz, H-11), 5.65 (1H, dd, *J* = 10.4, 2.8 Hz, H-12), 5.29 (1H, dd, *J* = 12.0, 5.5 Hz, H-22), 5.02 (1H, d, *J* = 6.0 Hz, $H\_1_{ara}$), 5.49 (1H, d, *J* = 8.0 Hz, $H\_1_{glc1}$), 4.98 (1H, d, *J* = 8.0 Hz, $H\_1_{glc2}$), 4.92 (1H, d, *J* = 7.2 Hz, $H\_1_{xyl}$). $^{13}$C-NMR data, see Table 1.

**Prostratoside B (2)** White powder. $C_{54}H_{86}O_{23}$. mp 235-238 ℃. $[\alpha]_D^{25}$ + 4.9° (c = 0.46, MeOH). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3 420, 1 721, 1 646, 1 082. FABMS m/z: 1 101 $[M-1]^-$ (100), 969(23), 939(4), 807(12). $^1$H-NMR ($C_5D_5N$, 400 MHz): δ 5.97 (1H, d, *J* = 10.8 Hz, H-11), 5.65 (1H, dd, *J* = 10.4, 2.8 Hz, H-12), 5.24 (1H, dd, *J* = 11.2, 5.2 Hz, H-22), 4.97 (2H, d, *J* = 7.6 Hz, $H\_1_{ara}$, $H\_1_{glc2}$), 5.48 (1H, d, *J* = 7.6 Hz, $H\_1_{glc1}$), 4.94 (1H, d, *J* = 7.2

Hz, H_1$_{xyl}$). $^{13}$C-NMR data, see Table 1.

**Prostratoside C (3)** White powder. $C_{54}H_{86}O_{24}$. mp 240–242 ℃; $[\alpha]_D^{25}$ + 6.7° (c = 0.67, MeOH); IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3 404, 1 716, 1 647, 1 047. FABMS m/z: 1 118 [M]$^-$ (100), 986 (9), 956 (3), 823 (3). $^1$H-NMR ($C_5D_5N$, 400 MHz): 6.00 (1H, d, *J* = 10.4 Hz, H_11), 5.67 (1H, d, *J* = 10.0 Hz, H_12), 6.10 (1H, dd, *J* = 11.2, 5.2 Hz, H_21), 5.00 (1H, d, *J* = 5.8 Hz, H_1$_{ara}$), 5.48 (1H, d, *J* = 8.0 Hz, H_1$_{glc1}$), 4.95 (1H, d, *J* = 7.6 Hz, H_1$_{glc2}$), 4.91 (1H, d, *J* = 7.2 Hz, H_1$_{xyl}$). $^{13}$C-NMR data, see Table 1.

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