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多荚草皂甙 D 和 E 的结构*

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摘要: 从石竹科植物多荚草 (*Polycarpon prostratum* (Forssk.) Aschers. et Schwein. ex Aschers) 的全草中分离得到了 2 个新的柴胡皂甙类化合物: prostratoside D 和 E。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}－saikogenin D 和 3－O－{β－D－xylopyranosyl－(1→2)－β－D－glucopyranosyl－(1→4)－[β－D－glucopyranosyl－(1→2)]－α－L－arabinopyranoside}－saikogenin G。

关键词 多荚草; 石竹科; 三萜皂甙; 多荚草皂甙 D 和 E
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Structures of Prostratoside D and E*

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Abstract: Two new triterpenoid saponins, namely prostratoside D and E, were isolated from the whole plants 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}－saikogenin D and 3－O－{β－D－xylopyranosyl－(1→2)－β－D－glucopyranosyl－(1→4)－[β－D－glucopyranosyl－(1→2)]－α－L－arabinopyranoside}－saikogenin G, respectively.

Key words: *Polycarpon prostratum*; Caryophyllaceae; Triterpenoid Saponin; Prostratoside D and E

We previously reported the isolation and structure elucidation of three new triterpenoid saponins, namely prostratosides A, B and C from the whole plants of *Polycarpon prostratum* (Forssk.) Aschers. et Schwein. ex Aschers (Ding et al, 1999; 2000). Our Further investigation on this plant led to the isolation of two new saikosaponin－like compounds, namely prostratoside D and E (1, 2). In this paper, we report the structure elucidation of these two compounds.

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Results and Discussion

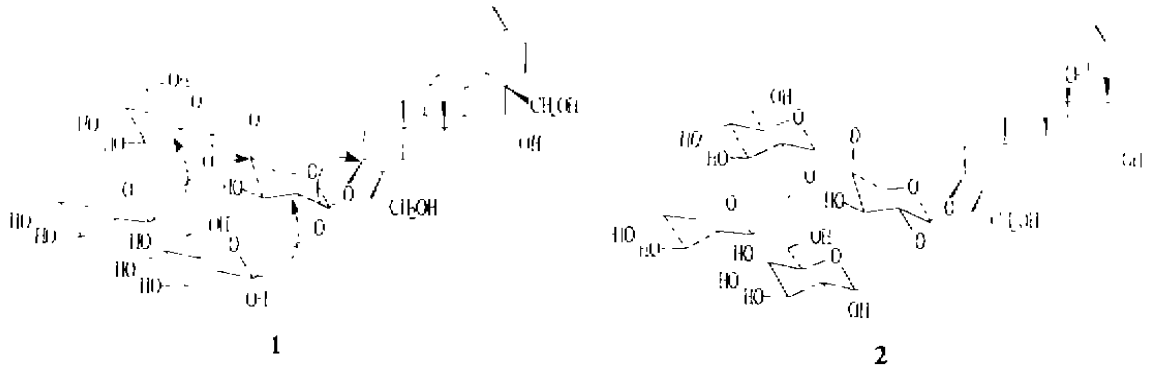
Prostratoside D (1) was obtained as white powder. Its HRFAB－MS gave a [M－H]⁻ ion at *m/z* 1059.5425, in agreement with the molecular formula $C_{52}H_{84}O_{22}$ (calcd. m/z 1059.5376). The IR spectrum showed absorption bands at 3368, 1642 and 1079cm－1, and it UV absorption maxima at 253 nm suggested the existence of a heteroannular diene moiety. The ^{1}H NMR spectrum exhibited the presence of six angular methyl groups at δ 0.86, 0.96, 0.98, 1.03, 1.05 and 1.63, two olefinic methine signals at δ 6.68 (d, J＝10.5Hz) and 5.68 (d, J＝10.5Hz). Its ^{13}C NMR and DEPT spectra showed olefinic resonances at δ126.3 corresponding to two methine carbons and at δ 136.2 and 133.1 corresponding to two olefinic quaternary carbons, revealed the presence of a conjugated diene system at the C－11 and C－13 (18) positions in an oleanane skeleton. The ^{13}C, ^{1}H NMR spectral data of 1 were very similar to those of polycarponoside A (3), a triterpenoid saponin isolated from Polycarpon loeflingiae (Bhandari *et al*, 1990), indicating both of them have the same aglycone as olean－11－13 (18) －diene －3β,16α, 23 28－tetraol (saikogenin D). This also reflected the absence of glycosidation at C－16 and C－28 due to close similarity in chemical shifts for ring B－E resonances of 1 and saikogenin D.

The sugar units of 1 were established as arabinose, xylose and glucose by TLC comparing with authentic samples. The negative FAB－MS gave the main fragment ion peaks at m/z 927 [M－pentose－H]⁻, 897 [M－glc－H]⁻, 765 [M－pentose－glc－H]⁻, 603 [M－pentose－glc－glc－H]⁻, indicating a pentose and a glucose were terminal sugars. The ^{1}H NMR spectrum showed four anomeric protons at δ 4.92 (d, J＝7.0Hz), 4.98 (d, J＝8.0Hz), 5.03 (d, J＝6.0Hz) and 5.48 (d, J＝7.5Hz) respectively. The ^{13}C NMR spectrum showed four anomeric carbon resonances at δ 103.9, 104.2, 105.1 and 107.7. Correlations between anomeric carbon resonance and anomeric proton signals were also observed in HMQC spectrum. This information suggested 1 being a tetraglycoside. The ^{1}H, ^{13}C NMR spectral data for sugar units of 1 were very similar to those of prostratoside A－C and anagallosaponin II (4) (Shoji *et al*, 1994), indicating all of them had the same linked sugar moiety, and the sugar units were also affixed to C－3 position of aglycone. These conclusions were further confirmed by HMBC spectrium (Fig. 1).

On the basis of the foregoing evidences, the structure of prostratoside D (1) is proposed to be 3－O－{β－D－xylopyranosyl－(1→2)－β－D－glucopyranosyl－(1→4)－[β－D－glucopyranosyl－(1→2)]－α－L－arabinopyranoside}－saikogenin D (Fig. 1). Its ^{13}C NMR data were summarized in Table 1.

Prostratoside E (2) was obtained as white power and revealed the main ion peaks at m/z 1059 [M－H]⁻, 92 [M－pentose－H]⁻, 897 [M－hexose－H]⁻, 765 [M－pentose－hexose－H]⁻ and 603 [M－pentose－hexose－hexose－H]⁻ as 1 in the negative FAB－MS. The IR spectrum showed peaks at 3400, 1646 and 1045 cm－1. A ^{13}C NMR spectral comparison with 1 showed that 2 also had the same linked sugar moiety, varying structurally from 1 only in its aglycone.

Its ^{1}H NMR spectrum exhibited the presence of six angular methyl groups at δ 0.94, 0.96, 1.01, 1.05, 1.34 and 1.57, two olefinic methine signals at δ 6.00 (d, J＝10.4Hz) and 5.65



1　　2

Fig 1　Structure of Prostratoside D (1) and E (2). Arrows Show Selected HMBC Correlations

(dd, J = 10.4, 2.4Hz) respectively. The ^{13}C NMR and DEPT spectra showed two olefinic signals at δ 132.2 and 132.1 corresponding to two methine carbons (C－11 and C－12), two methylene carbon signals at δ 77.9 (C－28) and 64.8 (C－23), a quaternary carbon signal at δ 85.1 (C－13). C－16 (δ77.3) and C－28 signals were at relative low field, indicating the presence of an α－OH was at C－16 (*Jia et al*, 1989). Compared with saikosaponin D (5) (Gong, 1986), the ^{13}C NMR spectral data of 2 were very similar to those of saikosaponin D, except the sugar moiety, indicating both of them had the same aglycone as saikogenin G.

Therefore, the structure of 2 is proposed to be 3－O－[β－D－xylopyranosyl－(1→2)－β－D－glucopyranosyl－(1→4)－[β－D－glucopyranosyl－(1→2)]－α－L－arabinopyranoside－saikogenin G (Fig. 1).

From the Ploycarpon prostratum, five tetraglycosides (saikosaponin－like compounds) were obtained. It is noteworthy that saikosaponin－like compounds were isolated from the plants of Caryophyllaceae.

Table 1　^{13}C NMR Data for Prostratosides D (1) and E (2) in C_5D_5N (100 MHz)

Position	1	3*	2	5*	Position	1	2	4*
Aglycone moiety					Sugar moiety			
1	38.4	38.4	38.7	38.8	Ara			
2	25.9	25.8	25.9	25.8	1	103.9	103.9	104.1
3	82.4	82.4	82.5	82.5	2	80.4	80.3	80.3
4	43.9	43.8	43.8	43.8	3	73.5	73.5	73.5
5	47.9	47.8	47.9	48.1	4	78.2	78.2	78.1
6	18.4	18.3	17.8	17.8	5	64.4	64.4	64.3
7	32.0	31.9	31.7	31.8	Glc_1			
8	41.2	41.1	42.0	42.1	1	105.1	105.1	105.1
9	54.1	54.0	53.1	53.2	2	76.3	76.3	76.2
10	36.6	36.6	36.5	36.6	3	78.5	78.5	78.4
11	126.3	126.4	132.2	131.9	4	71.7	71.7	71.5
12	126.3	126.4	132.1	131.9	5	78.4	78.4	78.3
13	136.2	136.3	85.1	85.0	6	62.9	63.0	62.8
14	42.0	41.9	43.9	43.7	Glc_2			

续表 1

Position	1	3*	2	5*	Position	1	2	4*
15	32.4	32.4	35.6	35.7	1	104.2	104.1	103.7
16	67.9	67.9	77.4	77.5	2	85.4	85.3	85.5
17	45.4	45.3	45.5	45.5	3	77.7	77.7	77.7
18	133.1	133.2	51.5	51.5	4	71.2	71.3	71.1
19	39.1	39.1	38.7	38.7	5	78.4	78.4	78.4
20	32.7	32.6	32.0	31.8	6	62.4	62.5	62.4
21	35.2	35.1	37.0	37.0	Xyl			
22	24.6	24.5	31.4	31.2	1	107.7	107.8	107.7
23	64.8	64.7	64.8	65.2	2	76.2	76.1	76.2
24	13.0	12.9	13.0	12.8	3	77.9	77.9	77.9
25	18.9	18.8	18.7	18.7	4	70.8	70.8	70.7
26	17.4	17.3	19.7	19.4	5	67.6	67.5	67.5
27	22.0	21.9	18.3	18.1				
28	64.9	64.9	77.9	77.5				
29	25.2	25.2	33.9	33.7				
30	32.7	32.6	24.6	24.5				

* ref. data

Experimental

General 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. UV spectrum was obtained in MeOH with UV – 3400 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.

Plant material The plant of *Polycarpon prostratum* was collected in Xishuangbanna, Yunnan, China, in July 1997. The botanical identification was made by senior engineer Hong Wang, Xishuangbanna Tropical Botanical Garden, the Chinese Academy of Sciences.

Extraction and isolation The plant material (6.0kg) 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 *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% EtOH was further subjected to silica gel ($CHCl_3$: MeOH = 7: 3) and RP – 18 (MeOH : H_2O = 7: 3) column chromatography to afford prostratosides D (1, 1.0g, 0.015%) and E (2, 50mg, 0.0009%), respectively.

Prostratoside D (1) white powder, mp 246 – 248℃. $[\alpha]_D^{25}$ – 21.0° (c, 0.58, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3368, 1642, 1079. UV λ_{max}^{MeOH} 253nm. FABMS m/z (%): 1059 $[M-H]^-$ (100), 927 (13), 897 (5), 765 (8), 603 (2); HRFABMS: $[M-H]^-$ at m/z 1059.5425 (calcd for $C_{52}H_{84}O_{22}$, 1059.5376). ^1H NMR (C_5D_5N, 400 MHz): (0.98 (3H, s, H – 30), 1.03 (3H, s,

H－29），1.05（3H，s，H－24），0.96（3H，s，H－25），1.63（3H，s，H－27），0.86（3H，s，H－26），6.68（1H，d，J＝10.5Hz，H－11），5.68（1H，d，J＝10.5Hz，H－12），5.03（1H，d，J＝6.0Hz，H－1ara），5.48（1H，d，J＝7.5Hz，H－1glc1），4.98（1H，d，J＝8.0Hz，H－1glc2），4.92（1H，d，J＝7.0Hz，H－1xyl）。^{13}C NMR spectral data，see Table 1.

Acid Hydrolysis on TLC of Prostratoside D. Prostratoside D（1）was applied on silica gel G TLC and left in an HCl atmosphere at 100℃ for 1 hour. HCl vapours were eliminated and then authentic sugars were applied to the plate. The chromatoplate was developed（$CHCl_3$：MeOH：H_2O＝6：4：0.8）and spots were detected by spraying with 10% H_2SO_4 soln followed by heating. The sugar units were identified as arabinose，xylose and glucose.

Prostratoside E（2）white powder. $C_{52}H_{84}O_{22}$. mp 223－226℃. $[\alpha]_D^{25}$ ＋14.7°（c，0.51，MeOH）. IR ν_{max}^{KBr} cm^{-1}：3403，1646，1045. FABMS m/z（%）：1060［M］$^+$（100），928（23），898（15），765（11），603（3）. ^{1}H NMR（C_5D_5N，400 MHz）：（0.94，0.96，1.01，1.05，1.34，1.57（3H each，s），6.00（1H，d，J＝10.4Hz，H－11），5.65（1H，dd，J＝10.4，2.4Hz，H－12），5.02（1H，d，J＝5.8Hz，H－1ara），5.48（1H，d，J＝7.6Hz，H－1glc1），4.97（1H，d，J＝8.0Hz，H－1glc2），4.92（1H，d，J＝7.2Hz，H－1xyl）. ^{13}C NMR spectral data，see Table 1.

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