

### Three New Saikosaponin-like Compounds from *Polycarpon prostratum*

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**Abstract:** Three new saikosaponin-like compounds (named prostratoside F-H) were isolated from the whole plants of *Polycarpon prostratum* (Forssk.) Aschers. et Schwein. ex Aschers. By detailed spectroscopic analysis, their structures were determined as 13 $\beta$ , 28-epoxy-16-keto-22 $\alpha$ , 23-dihydroxyolean-11-en-3 $\beta$ -yl- $\alpha$ -L-arabinopyranoside, 13 $\beta$ , 28-epoxy-16-keto-23-hydroxy-olean-11-en-3 $\beta$ -yl- $\alpha$ -L-arabinopyranoside and 13 $\beta$ , 28-epoxy-16-keto-22 $\alpha$ -hydroxyolean-11-en-3 $\beta$ -yl- $\alpha$ -L-arabinopyranoside, respectively.

**Keywords:** *Polycarpon prostratum*, Caryophyllaceae, saikosaponin-like compound.

In our previous paper<sup>1-4</sup>, we have reported five new tetraglycosides (named prostratoside A-E) and a new cyclic peptide (named polycarponin A) from this plant. Our continuing study on the EtOAc soluble fraction of this plant led to the isolation of three new saikosaponin-like compounds: prostratoside F-H (1-3). This paper describes the structure elucidation of these three new compounds.

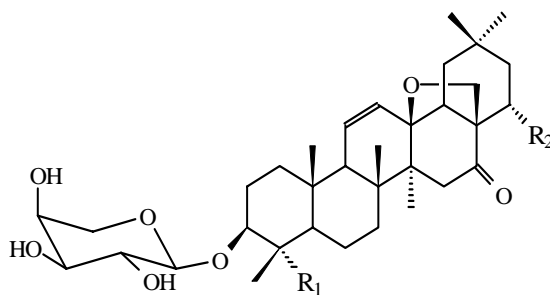
Prostratosid F (**1**): white powder, mp. 186-188°C,  $[\alpha]_D^{24} +22.0$  (c 0.27, MeOH). Its HRFAB-MS gave a [M-H] ion at  $m/z$  617.3785 (calcd.  $m/z$  617.3842), in agreement with the molecular formula C<sub>35</sub>H<sub>54</sub>O<sub>9</sub>. The IR(KBr) spectrum showed peaks at 3400 (OH), 1720 (C=O) cm<sup>-1</sup>. On acid hydrolysis, only L-arabinose was detected as the sugar component. The <sup>1</sup>H NMR spectrum of **1** ( $\delta$  ppm, pyridin-*d*<sub>5</sub>) showed six angular methyl proton signals ( $\delta$  0.85, 0.89, 0.91, 0.97, 1.02, 1.35), two olefinic proton signals due to H-11 ( $\delta$  6.03, 1H, d, J=10.5Hz) and H-12 ( $\delta$  5.68, 1H, dd, J=10.5, 2.8 Hz). In the <sup>13</sup>C NMR spectrum, the presence of one carbonyl signal ( $\delta$  213.9), two methine carbons ( $\delta$  133.3, 129.2), one methylene carbon ( $\delta$  75.3) and one quaternary carbon ( $\delta$  84.6) indicated that the aglycone might be a keto-saikogenin, with an 11-ene and a five-membered ether ring.

A comparison of compound **1** with 22 $\alpha$ -hydroxy-saikogenin G<sup>5</sup> showed that the aglycone of **1** was structurally similar to 22 $\alpha$ -hydroxy-saikogenin G in rings A-C and E, but varying in the D ring. In HMBC spectrum, the ketonic carbonyl carbon was correlated to H-15 ( $\delta$  2.91, 1H, d, J=14.0Hz;  $\delta$  1.84, 1H, d, J=14.0Hz), H-28 ( $\delta$  4.45, 1H;  $\delta$  3.92, 1H, d, J=7.2 Hz) and H-18 ( $\delta$  2.32, 1H, dd, J=14.0, 3.2Hz) and assigned to C-16. At the low field, one methine carbon ( $\delta$  72.8) and one methylene carbon ( $\delta$  64.2) might be with oxygen function respectively, the former carbon signal was correlated to

H-21 ( $\delta$  2.19, 1H, t,  $J=12.0\text{Hz}$ ;  $\delta$  1.71, 1H) and assigned to C-22, and the latter carbon signal was correlated to H-24 ( $\delta$  0.91, 3H, s) and assigned to C-23. H-22 ( $\delta$  3.87, 1H, dd,  $J=12.0, 4.4\text{Hz}$ ) indicated the presence of a OH group with equatorial configuration at C-22. These above facts suggested that the aglycone is  $13\beta$ , 28-epoxy-16-keto- $22\alpha$ , 23-dihydroxy-11-en-oleanane.

The  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra exhibited anomeric proton and carbon signals at  $\delta$  4.99 (d,  $J=7.2\text{Hz}$ ) and  $\delta$  106.62 respectively, indicating the presence of an  $\alpha$ -linkage for L-arabinose. The HMBC spectrum showed the correlation between the anomeric proton and the carbon signal ( $\delta$  81.5) which was assigned to C-3 of the aglycone, indicating the binding site for sugar unit at C-3 of the aglycone. Therefore, the structure of **1** was determined to be  $13\beta$ , 28-epoxy-16-keto- $22\alpha$ , 23-dihydroxyolean-11-en- $3\beta$ -yl- $\alpha$ -L-arabino-pyranoside.

**Figure 1** Structure of prostratoside F-H (**1-3**)



	R <sub>1</sub>	R <sub>2</sub>
Prostratosid F ( <b>1</b> )	CH <sub>2</sub> OH	OH
Prostratosid G ( <b>2</b> )	CH <sub>2</sub> OH	H
Prostratosid H ( <b>3</b> )	CH <sub>3</sub>	OH

Prostratosid G (**2**): white powder, mp. 271-273°C;  $[\alpha]_D^{24} +40.9$  (c 0.47, MeOH). The HRFAB-MS of compound **2** gave an [M-H] ion at  $m/z$  601.3822 (calcd.  $m/z$  601.3740), in agreement with the molecular formula C<sub>35</sub>H<sub>54</sub>O<sub>8</sub>. A detailed comparison of MS and  $^{13}\text{C}$  NMR spectra of **2** with those of **1** showed that **2** had the same sugar moiety at C-3 of the aglycone as **1**, and differed from **1** only in a lack of 22-OH in the aglycone moiety. And the  $^{13}\text{C}$  NMR spectral data of **2** was very similar to that of clinoposaponin XVIII<sup>6</sup>, except for the sugar moiety. Therefore, the structure of **2** was determined to be  $13\beta$ , 28-epoxy-16-keto-23-hydroxyolean-11-en- $3\beta$ -yl- $\alpha$ -L-arabino-pyranoside.

Prostratosid H (**3**): white powder, mp 188-190°C;  $[\alpha]_D^{24} 16.5$  (c 0.39, MeOH). The HRFAB-MS of compound **3** gave an [M-H] ion at  $m/z$  601.3830 (calcd.  $m/z$  601.3740), in agreement with the molecular formula C<sub>35</sub>H<sub>54</sub>O<sub>8</sub> as compound **2**. A comparison of  $^{13}\text{C}$  NMR spectra of **3** with that of **1** showed that **3** had the same sugar moiety and rings B-E of the aglycone as **1**, and differed from **1** only in ring A of the aglycone moiety. The main difference was at C-23, which was a methyl carbon signal of  $\delta$  27.9 in compound **3**, but a methylene in compound **1**. And the signals at  $\delta$  16.3,

**Table 1**  $^{13}\text{C}$  NMR data of compound **1**, **2** and **3** (100MHz, in pyridin- $d_5$ )

Carbon	1	2	Ref. 6	3
1	38.6	38.6	38.5	38.5
2	26.0	26.0	26.0	26.5
3	81.5	81.5	82.4	88.5
4	43.7	43.8	43.8	39.7
5	47.4	47.3	47.8	55.2
6	17.5	17.4	17.5	17.8
7	31.5	31.4	31.4	31.7
8	42.4	42.1	42.1	42.3
9	52.9	52.8	52.8	52.7
10	36.3	36.3	36.2	36.4
11	133.3	133.3	133.2	133.2
12	129.2	129.5	129.4	129.2
13	84.6	84.3	84.3	84.6
14	50.5	49.8	49.8	50.5
15	45.6	44.8	44.8	45.6
16	213.9	212.2	212.2	213.8
17	61.5	56.4	56.4	61.5
18	55.6	55.1	55.1	55.6
19	38.2	39.0	39.0	38.2
20	33.6	31.6	31.6	33.3
21	46.0	35.9	35.9	45.9
22	72.8	24.5	24.5	72.7
23	64.2	64.1	64.6	27.9
24	13.0	13.0	12.7	16.3
25	18.6	18.6	18.5	18.1
26	19.9	19.8	19.8	19.8
27	20.0	20.2	20.2	20.1
28	75.3	75.5	75.5	75.3
29	33.2	33.3	33.3	33.6
30	24.2	23.2	23.1	24.2
Ara				
1	106.6	106.7		107.4
2	73.1	73.1		72.9
3	74.7	74.7		74.6
4	69.5	69.6		69.4
5	66.7	66.9		66.7

39.7 and 55.2 were assigned to C-24, C-3, C-4 and C-5 respectively, which were also different from those of **1**. These above facts suggested that the aglycone is  $13\beta$ , 28-epoxy-16-keto-22 $\alpha$ -hydroxy-11-en-oleanane. Therefore, the structure of **3** was determined to be  $13\beta$ , 28-epoxy-16-keto-22 $\alpha$ -hydroxyolean-11-en-3 $\beta$ -yl- $\alpha$ -L-arabinopyranosid.

Saikosaponin homologues having a 16- keto function have been rarely found in the plants, and this is the first report of 16-ketosaikosaponins isolated from Caryophyllaceae.

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