

## A New Cyclopeptide from *Polycarpon prostratum*

Zhong Tao DING<sup>2</sup>, Jun ZHOU<sup>1\*</sup>, Yong Xian CHENG<sup>1</sup>, Ning Hua TAN<sup>1</sup>

<sup>1</sup>Laboratory of Phytochemistry, Kunming Institute of Botany, Academia Sinica, Kunming 650204

<sup>2</sup>Department of Chemistry, Yunnan University, Kunming 650091

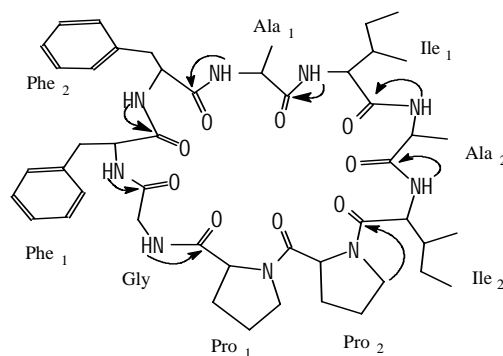
**Abstract:** A new cyclic peptide named polycarponin A, was isolated from the whole plants of *Polycarpon prostratum*. Its structure was determined by detailed spectroscopic analysis.

**Keywords:** *Polycarpon prostratum*, Caryophyllaceae, cyclopeptide, polycarponin A.

In our previous paper, we have reported a new triterpenoid saponin from *Polycarpon prostratum* (Forssk.) Aschers. *et* Schwein. *ex* Aschers<sup>1</sup>. As a series of our investigation on Caryophyllaceae cyclopeptides<sup>2-4</sup>, a continuing study of this plant led to the isolation of a new cyclopeptide named polycarponin A.

Polycarponin A (**1**), colorless needles, showed negative reaction to ninhydrin reagent, but positive after hydrolysis with 6 mol/L HCl. Its FABMS gave an  $[M+2H]^+$  ion at  $m/z$  915 and the molecular formula  $C_{48}H_{67}N_9O_9$  derived from the HR-FABMS ( $[M+H]^+$  at  $m/z$  914.5043, calcd  $m/z$  914.5140). IR spectrum showed absorption bands at 3300 (NH) and 1650 (C=O)  $cm^{-1}$ . The <sup>13</sup>C and <sup>1</sup>H NMR spectra (**Table 1**) showed the presence of nine amide carbonyl signals and seven amide NH signals respectively, suggesting that **1** was a cyclopeptide. By analysis of the <sup>1</sup>H-<sup>1</sup>H COSY, HMQC and HMBC spectra, these amino acid units were determined to be two phenylalanine, two proline, two isoleucine, two alanine and one glycine. These amino acid residues

**Figure 1.** Structure of Polycarponin A (**1**); Arrows show selected HMBC correlations



accounted for the mol wt. observed in FABMS. From the HMBC correlations among each H $_{\alpha}$ , NH (H $_{\delta}$  for proline) and C=O (**Figure 1**), the sequence was identified as cyclo(-Pro $_1$ -Gly-Phe $_1$ -Phe $_2$ -Ala $_1$ -Ile $_1$ -Ala $_2$ -Ile $_2$ -Pro $_2$ -).

**Table 1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectral Data of Polycarponin A (**1**) in Pyridine- $d_5$  (400MHz for  $^1\text{H}$  NMR, 100MHz for  $^{13}\text{C}$  NMR)

	CO	C $_{\alpha}$	C $_{\beta}$	C $_{\gamma}$	C $_{\delta}$	H $_N$	H $_{\alpha}$	H $_{\beta}$	H $_{\gamma}$	H $_{\delta}$
Gly	170.2	43.9				10.16 (br.s)	4.62(d) J=17.2 3.68(d) J=16.8			
Phe $_1$	173.2	56.1	39.8	138.9	130.0 <sup>a</sup> 129.2 <sup>b</sup> 127.0 <sup>c</sup>	8.41(d) J=8.8	5.48(m)	3.84(d) J=13.6 3.51(ca.)	7.16-7 .59	
Phe $_2$	171.3	54.9	39.0	136.8	129.8 <sup>a</sup> 128.9 <sup>b</sup> 127.7 <sup>c</sup>	8.70 (br.s)	5.35(m)	3.32(dd) J=8.0,4.0 3.07(t) J=8.6	7.16-7 .59	
Ala $_1$	174.2	48.9	19.3			8.64 (br.s)	5.25(m)	1.57(d) J=6.8		
Ala $_2$	172.1	47.8	17.8			7.97(d) J=6.4	4.87(m)	1.46(d) J=6.4		
Ile $_1$	170.5	58.5	34.1	25.1 16.6	10.8	9.51 (br.s)	4.60(m)	2.26(m)	1.54(m) 1.23(m) 1.03(d) J=7.6 J=6.8	0.740 (t)
Ile $_2$	172.3	60.3	35.5	26.2 16.2	10.7	8.96 (br.s)	4.67(m)	2.42(m)	1.70(m) 1.42(m) 1.06(d) J=7.2 J=6.8	0.827 (t)
Pro $_1$	173.4	61.9	29.5	25.6	47.9		4.54(t) J=7.2	2.11(m)	2.00(m) 1.63(m)	3.49 (m)
Pro $_2$	171.7	61.6	31.6	22.5	47.0		3.91(d) J=8.0	2.23(m) 1.26(m)	1.60(m)	3.63 (m)

<sup>a,b,c</sup> Assignments with the same superscripts may be interchanged.

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