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A New Cyclopeptide from *Brachystemma calycinum*

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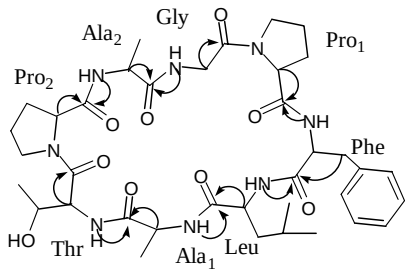
Abstract: A new cyclopeptide, brachystemin A, has been isolated from the roots of *Brachystemma calycinum*. The structure was elucidated by spectral methods.

Keywords: *Brachystemma calycinum*, Caryophyllaceae, cyclopeptide, brachystemin A.

Brachystemma calycinum D. Don is a folk medicine used for rheumatism. We investigat--ed it and isolated a new minor cyclopeptide brachystemin A **1,** together with three known heterocycles L-pyroglutamic acid **2**, 2-minaline **3** and 3′-furfuryl-pyrrole-2-carboxylate **4**[1]. The structure elucidation of **1**was made by 1D and 2D NMR techniques.

Brachystemin A **1**, was negative to ninhydrin reagent but positive after hydrolysis with 6 mol/L HCl[2]. The molecular formula $C_{37}H_{54}O_9N_8$ was derived from the HR-FABMS ($[M+H]^+$ at *m/z* 755.4073, Calc. for *m/z* 755.4092). IR bands at 3413, 3309, 3279 and 1681, 1653, 1621 cm^{-1} were characteristics of amino and amide carbonyl groups respectively. The ^{13}C NMR and ^1H NMR spectra (**Table 1**) exhibited the presence of eig-

Figure 1. The key HMBC correlations of Brachystemin A (H→C)



-ht amide carbonyl signals, seven methines signals and six amide NH signals respecti-vely. The above facts suggested **1** was a cyclopeptide. Using ^1H-^1H COSY,TOCSY, HMQC and HMBC spectra, the amino acid residues were identified as

one phenylalanine, one leucine, one threonine, one glycine, two alanines and two prolines. The sequence of these amino acid residues was achieved by HMBC as summarized in **(Figure 1)**. By analysis of HMBC correlations between each amide proton (NH) and carbonyl carbon, two peptide residues are found to be -N-Pro_1-Phe-Leu-Ala_1-Thr-CO - and -N-Pro_2-Ala_2-Gly-CO-. Only one linkage is reasonable. Hence the structure of **1** was established as cyclo(Pro_1-Phe-Leu-Ala_1-Thr-Pro_2-Ala_2-Gly).

Table 1. ^{1}H and ^{13}C NMR Spectral Data of Brachystemin A in Pyridine-d_5

	C=O	C_α	C_β	C_γ	C_δ	H_N	H_α	H_β	H_γ	H_δ
Pro_1	172.4	66.6	28.2	25.1	47.6		4.94 d (4.4)	2.31 m 1.80 m	2.05 m 1.96 m	4.01 m 3.40 m
Phe	169.8	55.7	36.1	138.9	130.1 129.0 127.2	7.73 d (5.6)	5.01 m	3.45 m 3.34m		7.18-7.53
Leu	177.2	49.7	29.1	24.8	21.3 23.8	7.10 (br.s)	5.43 m	1.31 m 1.25 m	2.03 m	0.89 d (6.8) 0.99 d (6.0)
Ala_1	174.2	53.6	16.8			10.61 d (2.0)	4.30 m	1.55 d (5.6)		
Thr	172.2	59.8	68.0	21.8		7.50 d (7.6)	4.79 d (8.0)	5.03 m	1.40 d (6.4)	
Pro_2	172.0	64.0	30.0	26.4	47.2		4.61 m	2.02 m	1.55 m 1.32 m	3.16 m 3.38 m
Ala_2	173.7	48.8	18.8			7.96 d (9.6)	5.20 m	1.84 d (7.6)		
Gly	169.6	44.1				8.96 t (6.4)	4.54 dd (16.8, 5.6) 3.87 dd (16.8, 5.6)			

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