Supporting information

New Cyclic Peptides from the Seeds of *Annona squamosa* L. and Their Anti-inflammatory Activities

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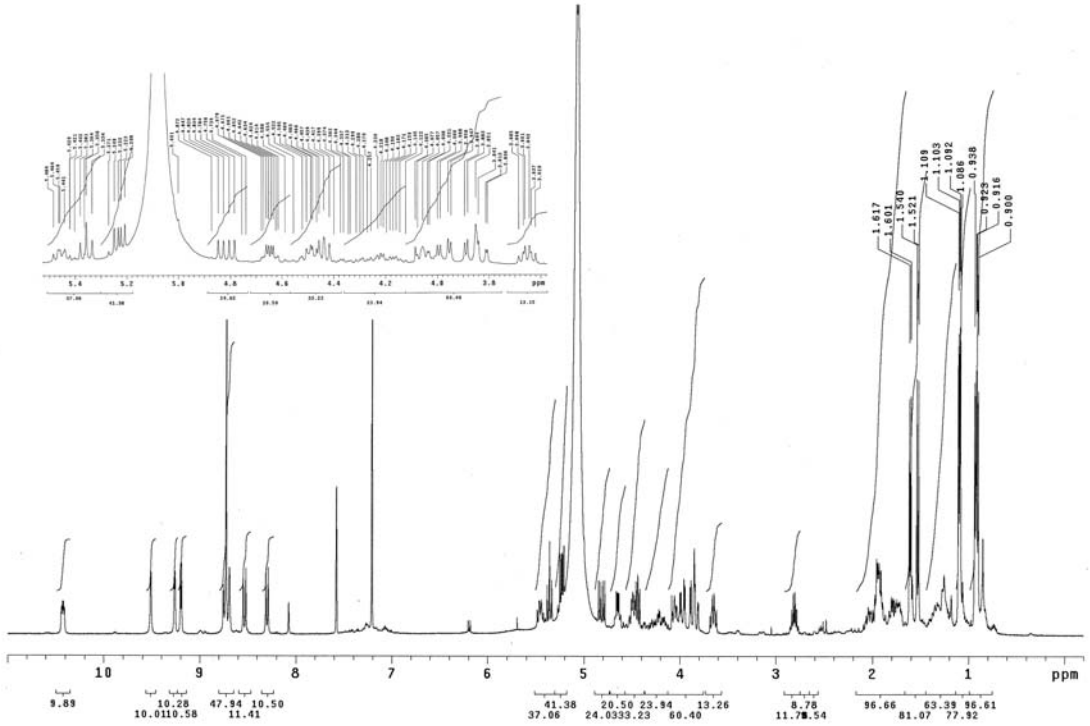


Figure 1. ^{1}H NMR spectrum of **1**

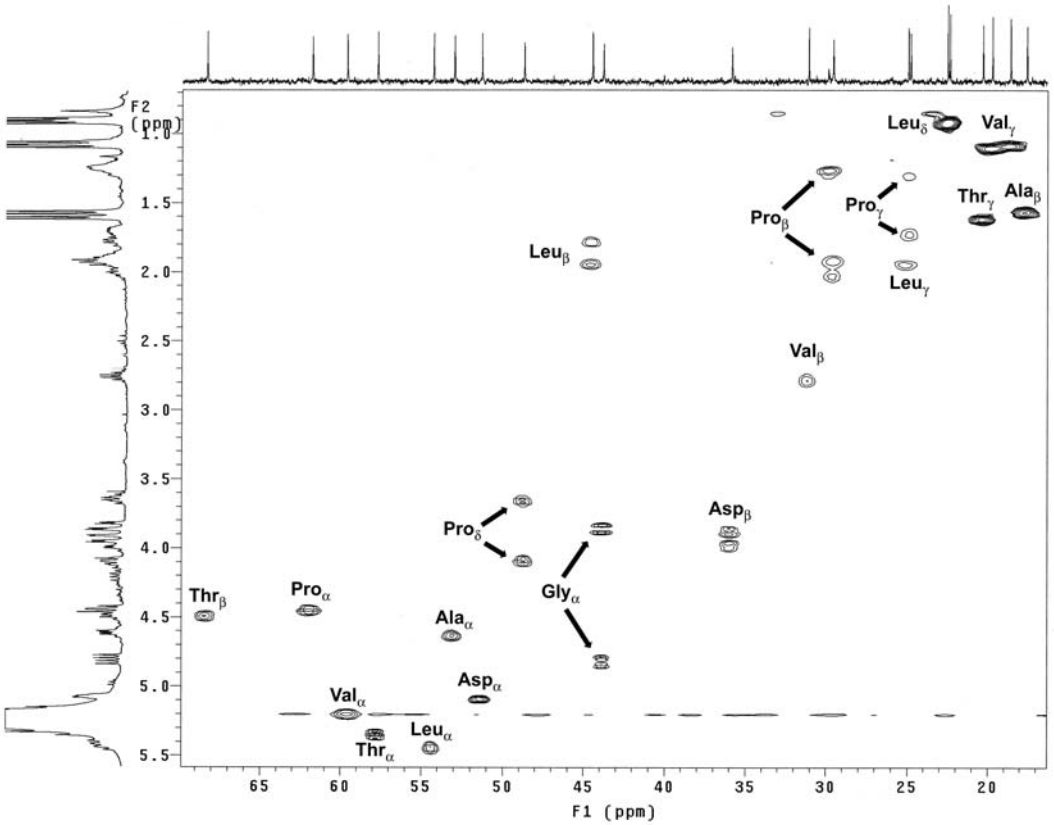


Figure 2. HSQC spectrum of **1**

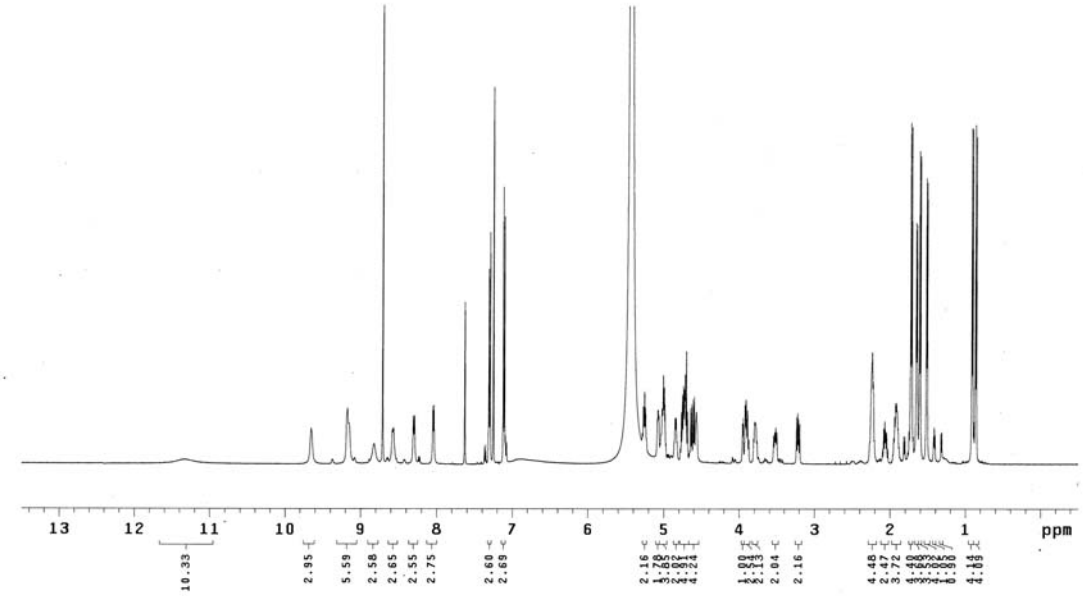


Figure 3. ^{1}H NMR spectrum of **2**

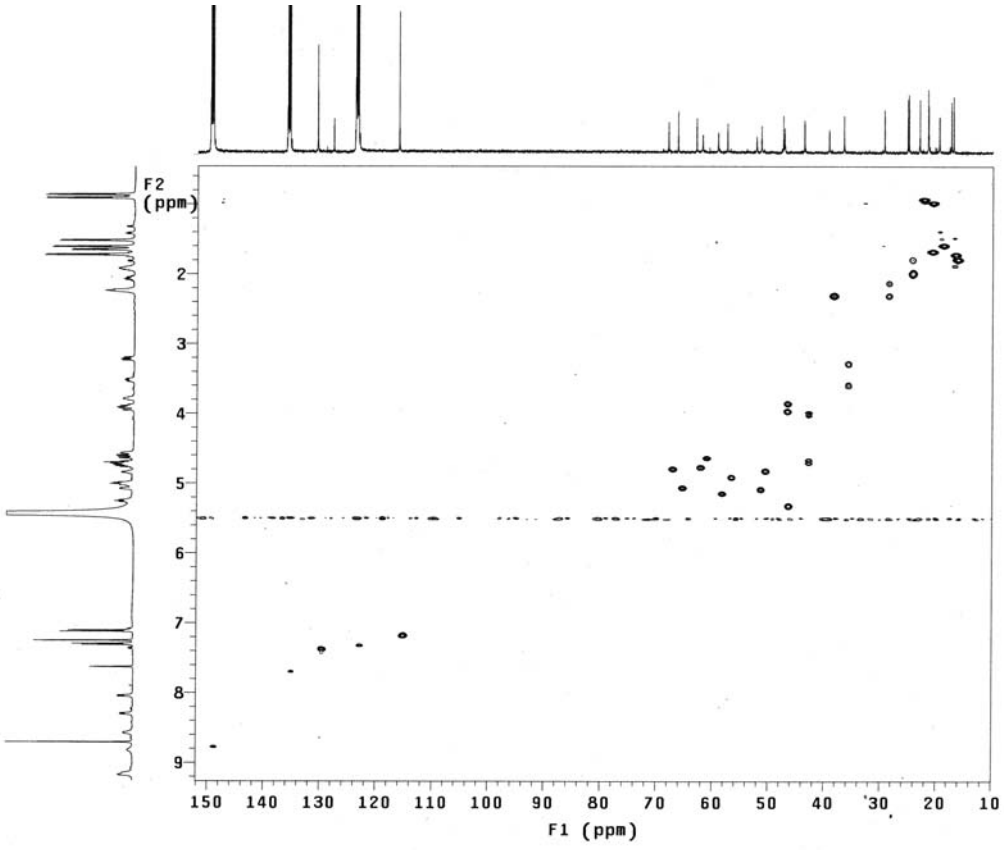


Figure 3. HSQC spectrum of **2**

Table 1. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) Data of **3** in Pyridine-d_5

Position		δ_H (*J* in Hz)		δ_C	Position		δ_H (*J* in Hz)		δ_C
Pro	α	5.29,	t (8.4)	63.9	**Thr**	α	5.61,	dd (9.8, 2.8)	56.7
	β	1.91,	m	30.1		β	4.95,	qd (6.0, 2.8)	70.6
		2.32,	m			γ	1.38,	d (6.0)	19.4
	γ	1.83,	m	25.3		**NH**	8.04,	d (9.8)	
		2.16,	m			**C=O**			172.3
	δ	4.07,	m	48.0	**Val**	α	4.16,	dd (6.4, 3.4)	63.0
	C=O			176.7		β	2.30,	m	29.6
OMet	α	4.61,	dt (7.2, 4.0)	55.7		γ	1.11,	d (7.2)	19.5
	β	2.30,	m	24.3			1.13,	d (7.6)	19.6
		2.48,	m			**NH**	9.14,	d (3.4)	
	γ	2.75,	dt (13.4, 7.2)	48.8		**C=O**			172.1
		2.99,	dt (13.4, 5.2)		**Ala**	α	4.82,	dd (7.6, 6.8)	51.8
	SOMe	2.35,	s	36.6		β	1.57,	d (7.6)	18.1
	NH	9.61,	d (4.0)			**NH**	7.70,	d (6.8)	
	C=O			172.1		**C=O**			173.8
Tyr	α	5.68,	ddd (12.4, 10.0, 2.6)	53.0	**Ile**	α	4.85,	t (9.4)	55.9
	β	3.30,	dd (15.6, 12.4)	36.8		β	2.24,	m	36.5
		4.27,	dd (15.6, 2.6)			γ	1.26,	m	23.8
	γ			129.2			1.55,	m	
	δ	7.39,	d (8.6)	129.8		γ	0.98,	d (6.4)	18.0
		7.17,	d (8.6)	116.0		δ	0.61,	t (7.2)	11.1
	ε			157.3		**NH**	7.66,	d (9.4)	
	OH	10.4,	br s			**C=O**			172.2
	NH	8.69,	d (10.0)						
	C=O			172.9					
Gly	α	3.98,	dd (17.2, 5.6)	44.5					
		4.70,	dd (17.2, 6.8)						
	NH	8.72,	dd (6.8, 5.6)						
	C=O			170.4					

Table 2. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) Data of **4** in Pyridine-d_5

Position		δ_H (*J* in Hz)	δ_C	Position		δ_H (*J* in Hz)	δ_C
Pro	α	5.30, t (8.4)	63.0	**Thr**	α	5.61, dd (9.8, 3.2)	56.0
	β	1.90, m	30.0		β	4.94, qd (6.0, 3.2)	70.0
		2.36, m			γ	1.38, d (6.0)	19.4
	γ	1.80, m	25.4		**NH**	8.07, d (9.8)	
		2.20, m			**C=O**		172.3
	δ	4.00, m	47.0	**Val**	α	4.18, dd (6.4, 3.4)	62.0
	C=O		176.7		β	2.30, dq (6.4, 5.2)	29.0
OMet	α	4.58, dt (8.4, 3.8)	55.7		γ	1.11, d (5.2)	19.6
	β	2.30, m	24.7			1.12, d (5.2)	19.6
		2.63, m			**NH**	9.13, d (3.4)	
	γ	2.70, ddd (14.8, 8.0, 3.2)	48.0		**C=O**		172.0
		2.90, ddd (14.8, 9.2, 3.2)		**Ala**	α	4.83, qd (7.6, 7.2)	51.0
	SOMe	2.52, s	37.0		β	1.56, d (7.6)	18.0
	NH	9.71, d (3.8)			**NH**	7.71, d (7.2)	
	C=O		172.0		**C=O**		173.7
Tyr	α	5.69, ddd (12.6, 8.8, 2.6)	52.0	**Ile**	α	4.87, t (9.6)	55.8
	β	3.30, dd (15.6, 8.8)	36.9		β	2.24, m	36.5
		4.30, dd (15.6, 2.6)			γ	1.30, m	24.4
	γ		129.2			1.60, m	
	δ	7.40, d (8.4)	129.7		γ	0.98, d (6.4)	17.0
		7.18, d (8.4)	116.1		δ	0.63, t (7.2)	11.0
	ε		157.3		**NH**	7.65, d (9.6)	
	OH	10.4, br s			**C=O**		172.2
	NH	8.70, d (12.6)					
	C=O		172.9				
Gly	α	3.90, m	44.0				
		4.71, dd (17.2, 6.8)					
	NH	8.78, m					
	C=O		170.5				

Table 3. ^{1}H (500 MHz) and ^{13}C NMR (125 MHz) Data of **5** in Pyridine-d_5

Position		δ_H (*J* in Hz)	δ_C	Position		δ_H (*J* in Hz)	δ_C
Pro	α	5.28, dd (7.2, 3.22)	65.2	**Thr**	α	5.57, dd (9.6, 3.1)	57.4
	β	1.96, m	30.8		β	4.92, qd (6.3, 3.1)	71.7
		2.37, m			γ	1.37, d (6.3)	20.5
	γ	1.73, m	25.9		**NH**	7.95, d (9.6)	
		2.20, m			**C=O**		173.4
	δ	3.99, m	48.8	**Val**	α	4.16, dd (6.4, 3.3)	63.9
	C=O		177.3		β	2.32, dq (7.4, 6.4)	30.5
Met	α	4.75, m	57.2		γ	1.11, d (7.4)	20.4
	β	2.13, m	31.5			1.12, d (7.4)	20.4
		2.23, m			**NH**	9.17, d (3.3)	
	γ	2.54, m	31.3		**C=O**		172.9
		2.61, m		**Ala**	α	4.76, qd (8.8, 7.3)	52.9
	SMe	1.86, s	15.8		β	1.56, d (7.3)	19.0
	NH	8.91, d (3.8)			**NH**	7.63, d (8.8)	
	C=O		173.0		**C=O**		174.7
Tyr	α	5.67, ddd (12.5, 10.0, 2.4)	54.1	**Ile**	α	4.72, m	57.0
	β	3.28, dd (15.5, 12.5)	37.8		β	2.27, m	37.5
		4.25, dd (15.5, 2.4)			γ	1.28, m	25.3
	γ		130.1			1.55, m	
	δ	7.37, d (8.5)	130.6		γ	1.00, d (6.6)	18.4
		7.16, d (8.5)	117.0		δ	0.62, t (7.4)	12.1
	ε		158.3		**NH**	7.63, d (8.7)	
	NH	8.62, d (10.0)			**C=O**		173.5
	C=O		173.9				
Gly	α	3.98, m	45.5				
		4.71, m					
	NH	8.73, m					
	C=O		171.3				

Table 4. ESI-MS/MS Data for **3** and **4**

$[M]^+$ *m/z* 849			$[M+H-CO]^+$ *m/z* 821		
Mass loss	Mass *m/z*	Residue	Mass loss	Mass *m/z*	Residue
113	736	Ile	113	708	Ile
71	665	Ala	384	437	Ala-Val-Thr
99	566	Val	57	380	Gly
101	465	Thr	163	217	Tyr
57	408	Gly	147	70	OMet
163	245	Tyr			

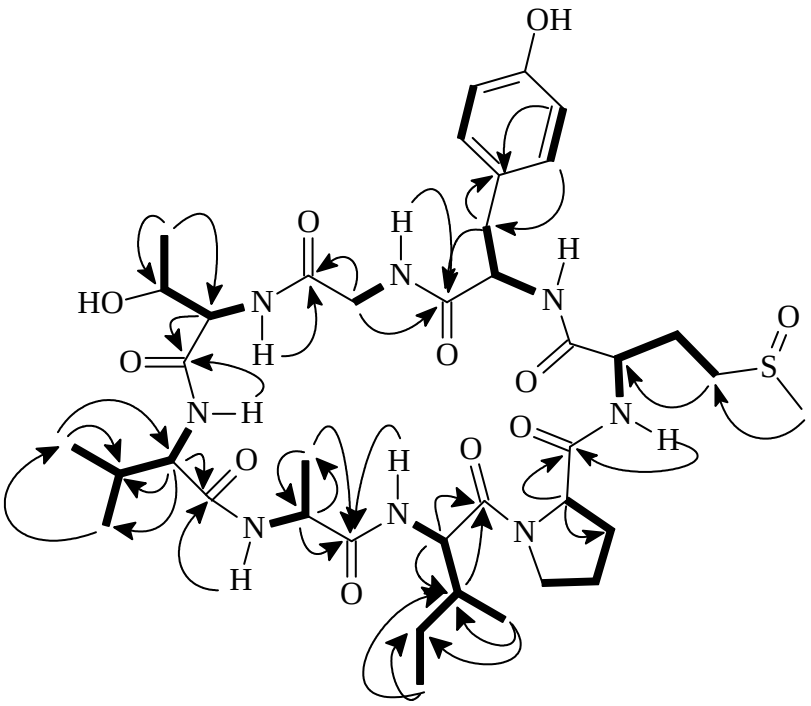


Figure 1. ^{1}H-^{1}H COSY and HMBC correlations of **3** and **4**