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# THREE CYCLOPEPTIDES FROM *STELLARIA DELAVAYI*

YU-RUI ZHAO,* JUN ZHOU,†‡ XIANG-KAI WANG, HOU-MING WU,§ XIAO-LIN HUANG§ and CHENG ZOU†

Department of Medicinal Chemistry of Natural Products, School of Pharmacy, West China University of Medical Sciences, Chengdu 610041, P. R. China; †Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, P. R. China; §State Key Laboratory of Bio-organic Chemistry & Natural Products, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China

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**Key Word Index**—*Stellaria delavayi*; Caryophyllaceae; roots; cyclopeptides; stelladelins A–C.

**Abstract**—From the fresh roots of *Stellaria delavayi*, three new cyclopeptides, stelladelins A–C, were obtained. Their structures were established on the basis of spectral analyses, chemical methods and enzymatic degradation. © 1997 Elsevier Science Ltd

## INTRODUCTION

Recently cyclopeptides have received considerable attention as a result of their unique structures and bioactivities. As part of our programme of searching for bioactive cyclopeptides from higher plant resources, we have investigated the constituents of fresh roots of *Stellaria delavayi*, which is indigenous to Yunnan, China, and is used as a tonic [1]. We obtained three new cyclopetides named stelladelins A–C and their structural elucidation is reported in the present paper.

## RESULTS AND DISCUSSION

A methanolic extract of *S. delavayi* was suspended in $H_2O$ and extracted with petrol, EtOAc and *n*-BuOH, successively. The EtOAc extract was subjected to extensive column chromatography to give three new cyclopeptides namely stelladelins A–C.

Stelladelin A (**1**), gave a negative reaction with ninhydrin but a positive one when hydrolyzed with 6 N HCl. The IR spectrum exhibited intense N—H, C=O absorptions at 3300 and 1625 $cm^{-1}$, respectively. The $^{13}C$ NMR spectrum showed the presence of 22 amide carbonyls in the range $\delta$ 167.7–173.6 and overlapping methines in the range $\delta$ 45–65 [2]. These data indicated that results mentioned above, stelladelin A is a cyclopeptide (Fig. 1).

The 600 MHz $^1H$ NMR spectrum clearly showed the presence of 12 amide protons. Utilization of TOCSY and DQF–COSY spectra indicated that these protons consisted of 12 independent spin systems ($4\times$AB(NH), $4\times$ABX(NH) and $4\times A_3B_3$MPT (NH)). By following these spin systems using HMQC and HMBC spectra, these amino acid residues were revealed to be four glycine, four leucine and four tyrosine units. Further extensive analyses of 2D-NMR spectra (TOCSY, DQF–COSY, HMQC and HMBC) indicated that the remaining signals were composed of ten independent spin systems of the type (X—CH—$CH_2$—$CH_2$—$CH_2$—X) typical of proline. Amino acid analysis of the hydrolysate prepared from **1** with 6 N HCl at 110° for 24 hr indicated the presence of Gly (2 eq.), Leu (2 eq.), Tyr (2 eq.) and Pro (5 eq.). However, these amino acid residues accounted for $2\times M_r$ observed in the mass spectrum FAB ($[M+1]^+$ at *m/z* 1152). This implied that **1** may exist as two conformational isomers in the same proportion at equilibrium (Aa : Ab = 1 : 1), suggesting that the compound is a cyclic undecapeptide. It contained some interesting features, especially the high content of aliphatic amino acid residues, giving rise to strong overlap of signals in the high field region of the spectrum and the high content of proline residues. These factors complicated the sequence assignment by NMR techniques (combination of NOE and HMBC) [3].

For sequence assignment of the amino acid residues in **1**, HMBC and NOESY experiments were run in $C_5D_5N$ at 600 MHz and 300 K. (Fig. 2). The HMBC ($Gly_1$—$H_N$/$Tyr_2$—CO, $Tyr_2$—$H_N$/$Tyr_1$—CO, $Tyr_1$—$H_N$/Pro—CO, $Leu_1$—$H_N$/$Leu_2$—CO, $Leu_2$—$H_N$/Pro—CO) and NOESY ($Gly_1$—$H_N$/$Tyr_2$—$H_\alpha$, $Tyr_2$—$H_N$/$Tyr_1$—$H_\alpha$, $Tyr_1$—$H_N$/Pro—$H_\alpha$, $Leu_1$—$H_N$/$Leu_2$—$H_\alpha$ and $Leu_2$—$H_N$/Pro—$H_\alpha$) correlations indicated the presence of two peptide fragment (—Pro—$Tyr_1$—$Tyr_2$—$Gly_1$— and —Pro-

* Present address: Department of Chemistry, University of Lanzhou, Lanzhou 730000, P. R. China.

‡ Author to whom correspondence should be addressed.

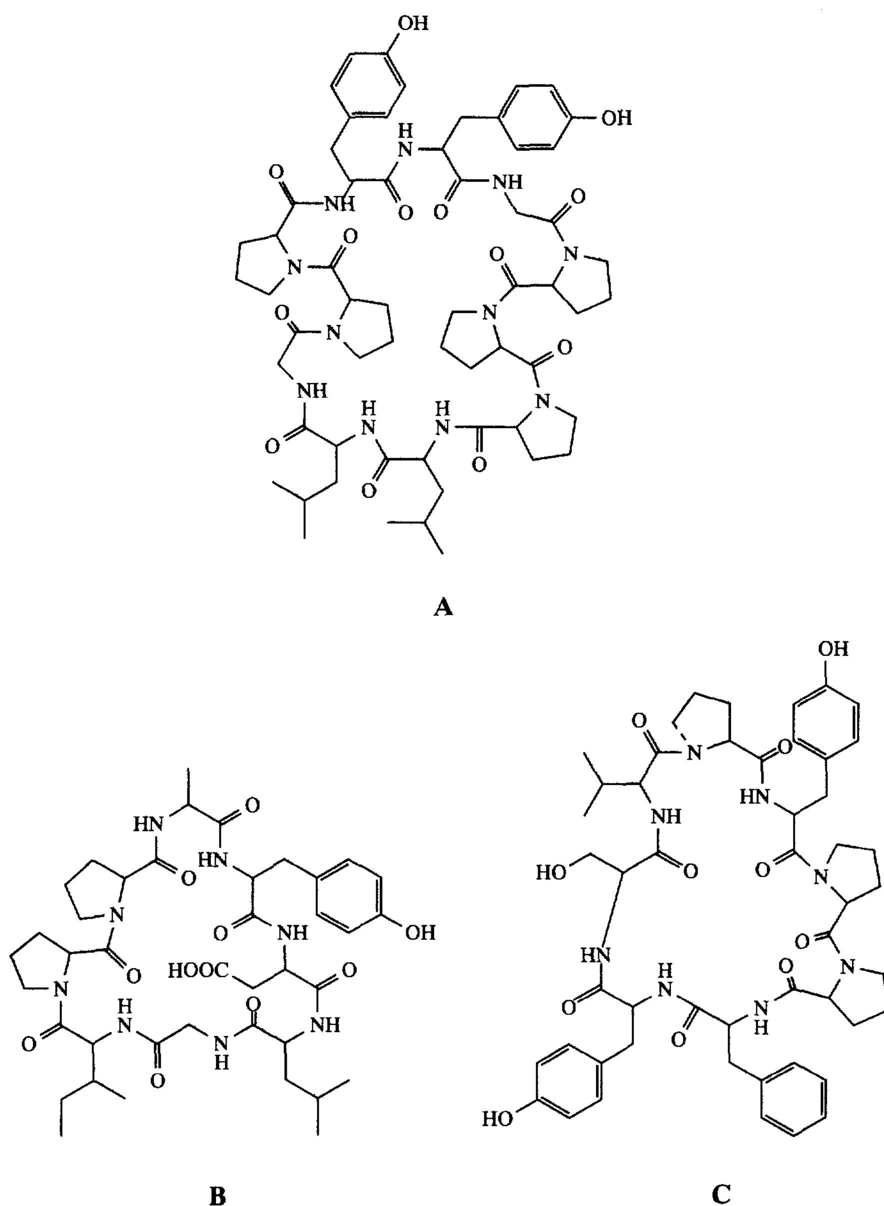



Fig. 1. Structures of stelladelins A, B and C.

—$Leu_2$—$Leu_1$—$Gly_2$—). A series of fragments at *m/z* 675, 575, 519 and 405 were also observed in the FAB-mass spectrum, suggesting the presence of the peptide fragments (—Leu—Leu—Gly—Pro—). In addition, the fragment at *m/z* 464 implied the presence of the peptide fragment (—Gly—Pro—Pro—Pro—Leu—). Combination of all these results let to the assignment of stelladelin A (**1**) as cyclo (Gly—Pro—Pro—Pro—Leu—Leu—Gly—Pro—Pro—Tyr—Tyr).

To corroborate the structure of **1**, it was hydrolyzed with α-chymotrypsin (Scheme 1) [4] to give a peptide(SDE) ($[M+2]^+$ at *m/z* 1171). This peptide showed a positive reaction with ninhydrin. In the manual DABITC/PITC double-coupling method [5] SDE was shown to be Gly—Pro—Pro—Pro—Leu—Leu—Gly—Pro—Pro—Tyr—Tyr. These results confirm the structure assigned to **1** by spectroscopic methods. The assignments of NMR signals for **1** (Tables 1 and 2) were carried out by 2D-NMR techniques.

Stelladelin B (**2**), also gave a negative reaction to ninhydrin but a positive one when hydrolyzed with 6 N HCl. Its molecular formula was determined as $C_{40}H_{58}O_{11}N_8$ by combination of NMR data (Tables 3 and 4) and FAB mass spectrometry ($[M+Li]^+$ at *m/z* 833), indicating 16 degrees of unsaturation. Absorptions at 3300 and 1650 $cm^{-1}$ in the IR spectrum indicated the presence of N—H and C=O groups. The $^{13}C$ NMR spectrum exhibited the presence of eight carbonyls (δ 169.4, 170.1, 170.2, 171.9, 172.5, 173.6, 174.8 and 175.4) and seven methines (δ 48.1, 52.1, 53.7, 54.7, 59.6, 61.0 and 61.6). From these results, **2** is deduced to be a peptide.

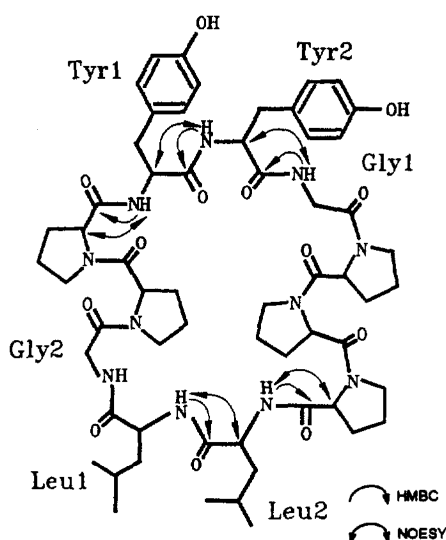


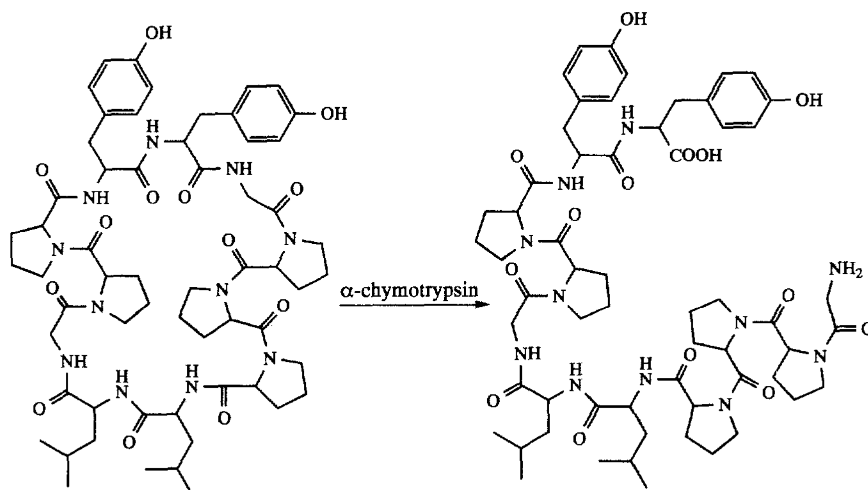

Fig. 2. Selected HMBC and NOESYs for compound **1** in $C_5D_5N$.

Structural elucidation of **2** was begun with the identification of the different amino acid units. The $^1$H NMR spectrum exhibited the presence of six amide protons ($\delta$ 9.41, 9.19, 8.30, 8.18 and 7.39). By following the spin systems of these amide protons using TOCSY and DQF–COSY, these amino acid residues were proved to be glycine, alanine, leucine, isoleucine and tyrosine units. Another amide proton exhibited an AMXY spin system in the DQF–COSY spectrum and correlations between the XY protons and a carbonyl signal ($\delta$ 171.90) was observed in the HMBC spectrum. This indicated that this residue may be an aspartic acid unit. Utilization of DQF–COSY, HMQC and HMBC revealed that the remaining signals consist of two independent spin systems of the type (X—CH—$CH_2$—$CH_2$—$CH_2$—X), typical of proline. These amino acid residues accounted for the $M_r$ observed in the FAB mass spectrum. Amino acid analysis of the hydrolysate prepared from **1** with 6 N HCl also supported the presence of these amino acid units established by spectroscopic methods. Since only 15 degrees of unsaturation could be accounted for by the functionality present in the eight amino acid residues, it was apparent that **2** was also a cyclopeptide.

Amino acid sequences in **2** were determined by HMBC, NOESY and FAB mass spectrometry. The HMBC (Tyr—$H_N$/Ala—CO, Ala—$H_N$/$Pro_1$—CO, Gly—$H_N$/Leu—CO) and NOESY (Ile—$H_N$/Gly—$H_{\alpha 1}$, Gly—$H_N$/Leu—$H_\alpha$, Asp—$H_N$/Tyr—$H_\alpha$, Tyr—$H_N$/Ala—$H_\alpha$ and Ala—$H_N$/$Pro_1$—$H_\alpha$) correlations (Fig. 3) indicated the presence of the peptide fragments (—Leu—Gly—Ile—, —$Pro_1$—Ala—Tyr—Asp—). The fragments at $m/z$ 229, 265, 305 observed in FAB mass spectrum implied the presence of the peptide fragments —Asp—Leu—, —Pro—Pro—Ala— and —Ile—Pro—Pro—, respectively. Combination of these results led to the assignment of the structure for stelladelin B (**2**) as cyclo (Gly—Ile—$Pro_2$—$Pro_1$—Ala—Tyr—Asp—Leu).

Stelladelin C (**3**) showed a negative reaction to ninhydrin. Its molecular formula was determined as $C_{50}H_{62}O_{11}N_8$ by combination of NMR data (Tables 3 and 4) and FAB-mass spectrometry ($[M+Na]^+$ at $m/z$ 973, base peak), indicating 24 degrees of unsaturation. The IR spectrum showed intense N—H and C=O absorptions at 3300 and 1650cm$^{-1}$, respectively. The $^{13}$C NMR spectrum exhibited the presence of eight amide carbonyls ($\delta$ 167.8, 169.0, 169.9, 171.2, 171.4, 171.7, 171.8 and 172.3) and eight methine groups ($\delta$ 57.0, 58.2, 58.2, 58.2, 59.2, 59.7 and 61.0). From these data, **3** was deduced to be a peptide.

Extensive analysis of 2D-NMR spectra of **3** including DQF–COSY, TOCSY, HMQC and HMBC, led to the conclusion that the peptide was composed of valine, serine, phenylalanine, two tyrosine and three proline units, being consistent with the results of amino acid analysis. These amino acid residues




Scheme. 1. Enzymatic hydrolysis of compound **1** with α-chymotrypsin.

Table 1. $^1$H NMR data of stelladelins $A_a$ and $A_b$

| | | $H_N$ | α | β | γ | δ |
|---|---|---|---|---|---|---|
| $A_a$ | $Gly_1$ | 9.30 *brs* | 3.75 *ca* (over) | | | |
| | | | 4.65 *m* | | | |
| | $Gly_2$ | 8.90 *t* (5.6) | 4.45 *d* (7.8) | | | |
| | | | 3.96 *ca* (over) | | | |
| | $Leu_1$ | 8.97 *d* (8.5) | 4.75 *ca* (over) | 2.05 *m* | 1.65 *ca* (over) | 0.55 *d* (6.6) |
| | | | | | | 0.65 *d* (6.6) |
| | $Leu_2$ | 8.05 *d* (8.5) | 5.10 *ca* (over) | 1.85 *m* | 1.25 *m* | 0.85 *d* (6.6) |
| | | | | | | 1.05 *d* (6.6) |
| | $Tyr_1$ | 9.38 *brs* | 4.95 *ca* (over) | 3.73 *ca* (over) | | |
| | | | | 3.50 *m* | | |
| | $Tyr_2$ | 8.80 *d* (8.9) | 4.80 *ca* (over) | 3.65 *ca* (over) | | |
| | | | | 3.45 *m* | | |
| $A_b$ | $Gly_1$ | 8.33 *dd* (12.3, 4.8) | 4.80 *ca* (over) | | | |
| | | | 3.65 *ca* (over) | | | |
| | $Gly_2$ | 7.90 *d* (7.8) | 4.95 *ca* (over) | | | |
| | | | 4.05 *d* (8.9) | | | |
| | $Leu_1$ | 8.25 *d* (8.5) | 5.10 *ca* (over) | 1.95 *m* | 1.95 *m* | 0.65 *d* (6.6) |
| | | | | | | 0.75 *d* (6.6) |
| | $Leu_2$ | 7.59 *ca* (over) | 5.25 *dd* (12.8, 4.9) | 1.75 *m* | 1.30 *m* | 0.90 *d* (6.6) |
| | | | | | | 1.05 *d* (6.6) |
| | $Tyr_1$ | 7.93 *d* (4.8) | 5.10 *ca* (over) | 3.55 *m* | | |
| | $Tyr_2$ | 8.30 *d* (8.7) | 5.30 *ca* (over) | 3.55 *m* | | |
| | | | | 4.05 *d* (14.0) | | |

δ from internal TMS at 600 MHz in $C_5D_5N$.
Coupling constants (Hz) are given in parentheses.

Table 2. $^{13}$C NMR data of stelladelins $A_a$ and $A_b$

| | | C=O | α | β | γ | δ |
|---|---|---|---|---|---|---|
| $A_a$ | $Gly_1$ | 168.2 | 42.0 | | | |
| | $Gly_2$ | 168.7 | 42.5 | | | |
| | $Leu_1$ | 172.9 | 52.1 | 37.6 | 25.2 | 20.7 |
| | | | | | | 21.3 |
| | $Leu_2$ | 172.9 | 52.1 | 38.0 | 25.6 | 21.8 |
| | | | | | | 21.9 |
| | $Tyr_1$ | 171.3 | 56.7 | 35.0 | | |
| | $Tyr_2$ | 173.5 | 57.3 | 35.3 | | |
| $A_b$ | $Gly_1$ | 167.7 | 42.0 | | | |
| | $Gly_2$ | 167.7 | 42.7 | | | |
| | $Leu_1$ | 171.6 | 53.0 | 38.2 | 25.3 | 21.9 |
| | | | | | | 22.3 |
| | $Leu_2$ | 173.6 | 53.8 | 39.0 | 25.8 | 22.6 |
| | | | | | | 22.4 |
| | $Tyr_1$ | 172.6 | 57.2 | 34.3 | | |
| | $Tyr_2$ | 172.7 | 57.7 | 35.3 | | |
| | Proline | 170.7 | 59.6 | 31.0 | 23.1 | 46.3 |
| | units | 170.7 | 59.7 | 30.5 | 23.1 | 46.7 |
| | | 170.7 | 59.8 | 28.7 | 23.1 | 46.9 |
| | | 171.0 | 59.6 | 28.5 | 23.4 | 46.9 |
| | | 171.1 | 61.5 | 28.4 | 23.7 | 47.2 |
| | | 171.2 | 61.5 | 28.4 | 24.9 | 47.4 |
| | | 171.3 | 61.5 | 28.4 | 23.5 | 47.0 |
| | | 171.6 | 61.7 | 28.4 | 24.9 | 47.5 |
| | | 173.2 | 61.5 | 27.6 | 25.1 | 47.6 |
| | | 173.0 | 61.4 | 27.6 | 25.2 | 47.0 |

δ from internal TMS at 150 MHz in $C_5D_5N$.

required 23 degrees of unsaturation; therefore, another degree of unsaturation for **2** indicated the cyclic nature of the peptide.

Evidence for the amino acid units in **3** was provided by HMBC, ROESY and FAB mass spectrometry experiments. The HMBC ($Tyr_2$—$H_N$/$Pro_3$—CO, Val—$H_N$/Ser—CO and Ser—$H_N$/$Tyr_1$—CO) and ROESY (Val—$H_N$/Ser—$H_\alpha$, Ser—$H_N$/$Tyr_1$—$H_\alpha$, $Tyr_1$—$H_N$/Phe—$H_\alpha$ and Phe—$H_N$/$Pro_1$—$H_\alpha$) correlations (Fig. 4) suggested the presence of the peptide fragments —$Pro_1$—$Tyr_1$—Ser—Val— and —$Pro_3$—$Tyr_2$. The fragments at *m/z* 359 and 552 present in the FAB-mass spectrum implied the presence of the peptide fragments —Val—Pro—Tyr— and —Val—Pro—Tyr—Pro—Pro—). The structure of stelladelin C (**3**) was thus established as cyclo (Val—$Pro_3$—$Tyr_2$—$Pro_2$—Pro—Phe—$Tyr_1$—Ser).

## EXPERIMENTAL

$^1$H, $^{13}$C and 2D-NMR spectra were recorded with a Bruker AMX-600 spectrometer, using TMS as int. standard.

*Plant material.* Fresh roots of *S. delavayi* were collected in Kunming, Yunnan Province, in October 1992. A specimen is deposited in the Herbarium of the Kunming Institute of Botany.

*Extraction and isolation.* Fresh roots (38 kg) were extracted 3× with MeOH under reflux for 4 hr.

Table 3. ^{1}H NMR data of stelladelins B and C

| | | $H_N$ | α | β | γ | δ |
|---|---|---|---|---|---|---|
| B | Asp | 9.41 *brs* | 5.09 *ca* (over) | 3.33 *t* (13.2) | | |
| | Ala | 9.19 *d* (8.5) | 4.95 *brs* | 1.58 *d* (7.2) | | |
| | Gly | 8.30 *brs* | 4.47 *dd* (6.8, 17.2) | | | |
| | | | 3.96 *dd* (9.8, 14.2) | | | |
| | Leu | 8.23 *ca* (over) | 5.09 (over) | 2.24 *m* | 1.91 *m* | 0.82 *d* (6.3) |
| | | | | 2.11 *m* | | 0.88 *d* (7.3) |
| | Ile | 7.39 *ca* (over) | 5.02 *t* (6.5) | 2.11 *m* | 1.33 *m* | 0.91 *t* (5.4) |
| | | | | | 1.10 *d* (6.6) | |
| | Tyr | 8.18 *brs* | 4.15 *d* (10.2) | 3.13 *t* (12.1) | ArH (7.30, 8.2) | |
| | | | | 3.33 *t* (13.2) | 7.16 *d* (8.2) | |
| | $Pro_1$ | | 4.26 *d* (8.2) | 2.46 *d* (11.6) | 1.58 *m* | 3.36 *m* |
| | | | | 2.01 *m* | | 3.50 *m* |
| | $Pro_2$ | | 3.66 *m* | 1.83 *m* | 1.64 *m* | 3.91 *t* (7.8) |
| | | | | 1.89 *m* | 1.91 *m* | 3.67 *ca* (over) |
| C | Val | 7.96 *d* (10.3) | 4.89 *d* (9.6) | 2.70 *m* | 1.14 *d* (6.4) | |
| | | | | | 1.38 *d* (6.4) | |
| | Phe | 8.71 (over) | 4.68 *brs* | 3.68 *t* (11.7) | | |
| | | | | 3.37 *ca* (over) | | |
| | Ser | 8.60 *d* (6.3) | 4.42 *m* | 4.44 *ca* (over) | | |
| | | | | 4.74 *m* | | |
| | $Tyr_1$ | 9.81 *brs* | 4.78 *brs* | 3.15 *dd* (7.4, 14.2) | | |
| | | | | 3.38 *ca* (over) | | |
| | $Tyr_2$ | 9.26 *d* (6.8) | 4.36 *m* | 4.03 *t* (3.8, 9.7) | | |
| | $Pro_1$ | | 5.01 *m* | 1.65 *m* | 2.09 *m* | 3.61 *m* |
| | | | | 1.96 *m* | 1.87 *m* | 4.10 *m* |
| | $Pro_2$ | | 4.44 *ca* (over) | 2.15 *m* | 1.31 *m* | 3.07 *t* (8.0) |
| | | | | 1.33 *ca* (over) | 0.92 *m* | 3.49 *dd* (7.8, 11.3) |
| | $Pro_3$ | | 5.26 *d* (7.2) | 2.57 *brs* | 2.18 *m* | 3.94 *t* (6.0) |
| | | | | 2.15 *m* | 1.89 *m* | 3.80 *m* |

δ in $C_5D_5N$ from internal TMS at 600 MHz.
Coupling constants (Hz) are given in parentheses.

Table 4. ^{13}C NMR data of stelladelins B and C

| | | C═O | α | β | γ | δ |
|---|---|---|---|---|---|---|
| B | Asp | * | 53.7 | 35.0 | 171.9 | |
| | Ala | 175.4 | 48.1 | 14.9 | | |
| | Gly | 169.4 | 43.7 | | | |
| | Leu | 173.6 | 52.1 | 41.2 | 24.9 | 23.5 |
| | | | | | | 21.0 |
| | Ile | 170.1 | 54.7 | 38.3 | 24.7 | 11.5 |
| | | | | | 15.6 | |
| | Tyr | 174.8 | 61.0 | 36.5 | 131.3 | 127.4 |
| | | | | | | 116.6 |
| | | | | | | 158.1 |
| | $Pro_1$ | 172.5 | 61.6 | 31.5 | 22.4 | 47.2 |
| | $Pro_2$ | 170.2 | 59.6 | 29.2 | 25.8 | 48.1 |
| C | Val | 169.9 | 57.0 | 30.6 | 21.0 | |
| | | | | | 20.2 | |
| | Phe | 171.8 | 58.2 | 37.2 | 139.0 | |
| | $Tyr_1$ | 172.3 | 58.2 | 36.2 | 153.8 | |
| | $Tyr_2$ | 167.8 | 56.9 | 34.6 | 157.4 | |
| | Ser | 171.2 | 58.2 | 62.4 | | |
| | $Pro_1$ | 169.0 | 59.7 | 30.7 | 25.7 | 47.7 |
| | $Pro_2$ | 171.7 | 61.0 | 30.0 | 23.0 | 46.2 |
| | $Pro_3$ | 171.4 | 59.2 | 29.6 | 21.7 | 47.1 |

δ in $C_5D_5N$ from internal TMS at 150 MHz.
* Missing, observed in HMBC δ 171.90.

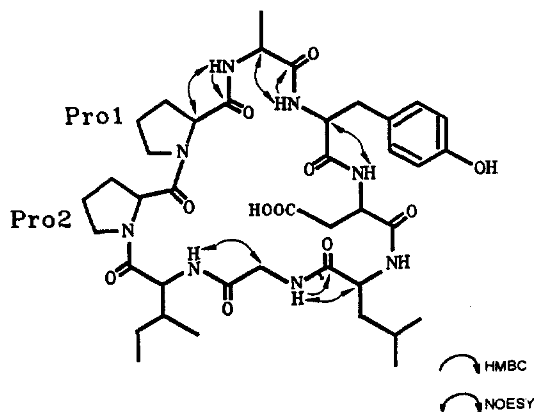



Fig. 3. Selected HMBC and NOESYs for compound **2** in $C_5D_5N$.

Removal of solvents by evaporation *in vacuo* yielded a syrup. This was suspended in $H_2O$ and extracted with petrol, EtOAc and *n*-BuOH, successively. The EtOAc extracts were concd to afford a residue (45 g), which was submitted to CC on silica gel eluted with $CHCl_3$–MeOH (5–35%) successively to give frs A–D. Fr A was subjected to CC over silica gel eluting with $CHCl_3$–EtOAc–MeOH(7 : 2 : 1) to give stelladelin A

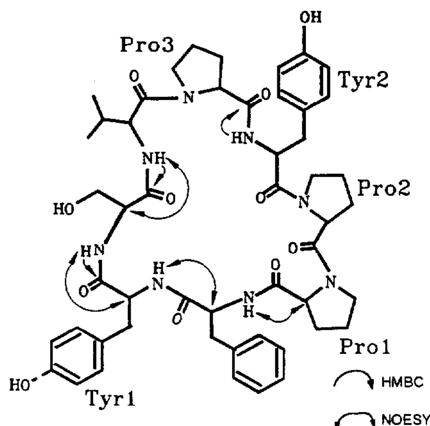



Fig. 4. Selected HMBC and NOESYs for compound **3** in $C_5D_5N$.

(89 mg, 0.00090%). Fr B was submitted to CC over silica gel eluting with EtOAc–MeOH(4 : 1) to give frs F and G. Fr F was then subjected to chromatography on reverse-phase silica gel (RP-8) eluting with MeOH–$H_2O$ (3 : 2) to afford stelladelin B (48 mg, 0.00050%). Fr. G was subjected to CC an reversed-phase silica gel (RP-8) eluting with MeOH–$H_2O$ (4 : 1) to give stelladelin C (47 mg, 0.00050%).

*Stelladelin A* (**1**). $C_{59}H_{81}O_{13}N_{11}$. Amorphous powder. Ninhydrin reaction (−). $[\alpha]_D^{17} -15.9$ (*c* 0.561, MeOH). UV $\lambda_{Max}^{EtOH}$ nm (logε): 222(4.41), 276(3.75). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3300, 1625, 1525, 1450. FABMS *m/z*: 1152 ($[M+1]^+$, base peak), 1174$[M+Na]^+$, 1136, 997, 898, 851, 784, 743, 675, 574, 519, 405, 307. $^1$H NMR: Table 1. $^{13}$C NMR: Table 2.

*Amino acid analysis of* **1**. Analysis of the hydrolysate prepd from **1** with 6 N HCl by heating at 110° for 24 hr in a sealed tube suggested the presence of Gly (2 eq.), Leu (2 eq.), Tyr (2 eq.), and Pro (5 eq.).

*Enzymatic hydrolysis of* **1**. α-Chymotrypsin (0.21 mg) was suspended in 1 ml of 3.6 mg of **1** in 0.2 M *N*-methylmorpholine acetate buffer (pH 8.1). After mixing, the mixt. was incubated at 37° until the reaction mixt. showed a positive reaction to ninhydrin on TLC. The reaction mixt. was purified by HPLC (ODS, 1/25 cm, Ultrasphere), eluted with MeOH–$H_2O$ (3 : 2) to give a peptide (SDE) (1.5 mg, $[M+2]^+$ at *m/z* 1171). Using the manual DABITC–PITC double-coupling method, it was determined to be Gly—Pro—Pro—Pro—Leu—Leu—Gly—Pro—Pro—Tyr—Tyr.

*Stelladelin B* (**2**). $C_{40}H_{58}O_{11}N_8$. Amorphous powder. Ninhydrin reaction (−). $[\alpha]_D^{19} -81.4$ (*c* 0.842, MeOH). UV $\lambda_{max}^{EtOH}$ (logε): 220(3.17), 264(2.41). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3325, 2950, 1650, 1510, 1480. FABMS *m/z*: 833 ($[M+Li]^+$, base peak), 849$[M+Na]^+$, 827$[M+1]^+$, 443, 329, 313, 305, 285, 267, 229. $^1$H NMR: Table 3. $^{13}$C NMR: Table 4.

*Amino acid analysis of* **2**. Amino acid analysis of the hydrolysate prepared as described for **1** indicated the presence of Asp (1 eq.), Leu (1 eq.), Ile (1 eq.), Pro (2 eq.), Tyr (1 eq.), Ala (1 eq.) and Gly (1 eq.).

*Stelladelin C* (**3**). $C_{50}H_{62}O_{11}N_8$. Amorphous powder. Ninhydrin reaction (−). $\alpha]_D^{21} -65.1$ (*c*, 0.515, $C_5H_5N$). UV $\lambda_{max}^{EtOH}$ nm (logε): 222(4.18). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3300, 2900, 1625, 1510, 1480, 1250. FABMS *m/z*: 990$[M+K+1]^+$, 973$[M+Na]^+$, 951$[M+1]^+$, 867, 816, 595, 552, 373, 359, 357, 331, 283 (base peak), 257. $^1$H NMR: Table 3. $^{13}$C NMR: Table 4.

*Amino acid analysis of* **3**. Amino acid analysis of the hydrolysate prepared as described for **1** indicated the presence of Tyr (2 eq.), Pro (3 eq.), Phe (1 eq.), Ser (1 eq.) and Val (1 eq.).

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