CYCLODIPEPTIDES FROM THE ROOTS OF *PANAX NOTOGINSENG*

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Abstract From the roots of *Panax notoginseng* fourteen cyclodipeptides 1 ~ 14 were isolated including one new compound(1), seven new natural compounds(4 ~ 10) and six known compounds(2 ~ 3, 11 ~ 14). Their structures were elucidated as following based on spectral methods: cyclo-(Leu-Thr)(1), cyclo-(Leu-Ile)(2), cyclo-(Leu-Val)(3), cyclo-(Ile-Val)(4), cyclo-(Leu-Ser)(5), cyclo-(Leu-Tyr)(6), cyclo-(Val-Pro)(7), cyclo-(Ala-Pro)(8), cyclo-(Phe-Tyr)(9), cyclo-(Phe-Ala)(10), cyclo-(Phe-Val)(11), cyclo-(Leu-Ala)(12), cyclo-(Ile-Ala)(13), cyclo-(Val-Ala)(14). Among them Compounds 2 and 11, 3 and 4, 12 and 13 are mixtures with 2 : 1, 1 : 1, 2 : 1 ratios, respectively.

Key words *Panax notoginseng*; Araliaceae; cyclodipeptides

三七环二肽成分

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摘 要 从三七(*Panax notoginseng*)的根中分离得到14个环二肽成分,通过波谱解析其结构分别鉴定为环-(亮氨酸-苏氨酸)(1)、环-(亮氨酸-异亮氨酸)(2)、环-(亮氨酸-缬氨酸)(3)、环-(异亮氨酸-缬氨酸)(4)、环-(亮氨酸-丝氨酸)(5)、环-(亮氨酸-酪氨酸)(6)、环-(缬氨酸-脯氨酸)(7)、环-(丙氨酸-脯氨酸)(8)、环-(苯丙氨酸-酪氨酸)(9)、环-(苯丙氨酸-丙氨酸)(10)、环-(苯丙氨酸-缬氨酸)(11)、环-(亮氨酸-丙氨酸)(12)、环-(异亮氨酸-丙氨酸)(13)、环-(缬氨酸-丙氨酸)(14)。其中化合物1为新化合物,化合物4 ~ 10为新天然化合物,化合物2 ~ 3、11 ~ 14为已知化合物;化合物2和11、3和4、12和13分别为一对混合物,比例分别为2:1、1:1和2:1。

关键词 三七;五加科;环二肽

Introduction

Panax notoginseng (Bur.) F. H. Chen (Araliaceae) is one of famous Traditional Chinese Medicines. There are a lot of chemical studies on it, especially saponins. In the previous communication[1] we isolated fourteen cyclodipeptides 1 ~ 14 from the roots of *P. notoginseng*, in which compound 1 is one new compound, compounds 4 ~ 10 are new natural compounds, compounds 2 ~ 3 and 11 ~ 14 are known compounds, and compounds 2 and 11, 3 and 4, 12 and 13 are mixtures with 2 : 1, 1 : 1, 2 : 1 ratios, respectively. In this full paper we report the structure elucidation of compounds 1 ~ 14.

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Results and Discussion

Cyclodipeptides 1 ~ 14 were isolated from the EtOAc fractions of the H_2O extracts of the roots of *P. notoginseng* by column chromatography as described in the experimental.

Compound 1 Colorless needles (CH_3OH), gave a negative ninhydrin reaction but positive after

hydrolysis with 6 mol/L HCl[2]. Its molecular formular was determined as $C_{10}H_{18}O_3N_2$ by means of DEPT spectrum and FAB$^+$-MS in which its quasimolecular ion peak at *m/z* 215[(M + 1)$^+$]. The 100 MHz ^{13}C NMR spectrum clearly showed the presence of two amides CO at 166.8, 168.6, four mehtines CH at δ66.9, 60.5, 52.8, 23.3, one methene CH_2 at δ45.0, three methyls CH_3 at δ23.1, 21.5, 20.1, respectively. The 400 MHz ^{1}H NMR spectrum clearly showed the presence of two amides NH at δ8.02, 8.21, three mehtines CH at δ4.00～5.02, one methine CH and one methene CH_2 at δ 1.55～1.80, three methyls CH_3 at δ0.82～1.06, respectively. These facts indicated that 1 is a cyclodipeptide and composed of Leu (1eq) and Thr (1eq). Therefore, the structure of 1, a new cyclodipeptide, was elucidated as cyclo-(Leu-Thr).

Compound 2 and compound 11 A mixture with a 2:1 ratio, gave a negative ninhydrin reaction but positive after hydrolysis with 6 mol/L HCl[2]. The positive FAB-MS showed two different quasimolecular ion peaks at *m/z* 453[(2M+1)$^+$], 227[(M+1)$^+$] for 2 and 493[(2M + 1)$^+$], 247[(M + 1)$^+$] for 11. Their moleclular formulars were determined as $C_{12}H_{22}O_2N_2$ for 2 and $C_{14}H_{18}O_2N_2$ for 11 by means of DEPT spectrum and FAB$^+$-MS. The 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR spectra clearly showed the presence of four amides NH at δ8.17, 8.12, 8.04, 7.92 and two groups of amides CO at δ166.8, 168.3, respectively. Using 2D NMR including COSY, HMQC and HMBC we found that 2 was composed of Leu (leq) and Ile (leq), and 11 was composed of Phe (leq) and Val (leq). Thus, the structures of 2, a new cyclodipeptide, and 11, a known cyclodipeptide, were determined as cyclo-(Leu-Ile) and cyclo-(Phe-Val), respectively.

With the same method as compound 1, compound 7, compound 8, compound 9, compound 12, compound 13 and compound 14 were determined as cyclo-(Val-Pro), cyclo-(Ala-Pro), cyclo-(Phe-Tyr), cyclo-(Leu-Ala), cyclo-(Ile-Ala), cyclo-(Val-Ala), respectively.

With the same method as compound 2 and compound 11, compound 3, compound 4, compound 5, compound 6 and compound 10 were elucidated as cyclo-(Leu-Val), cyclo-(Ile-Val), cyclo-(Leu-Ser), cyclo-(Leu-Tyr), cyclo-(Phe-Ala), respectively.

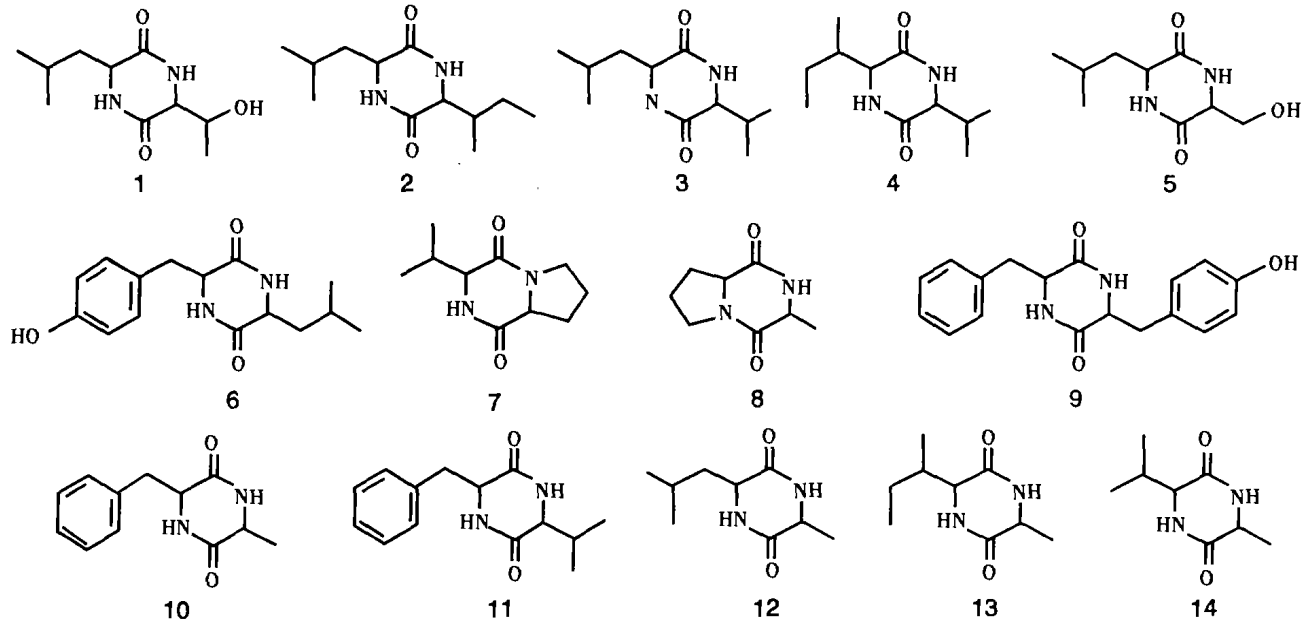

Fig.1 Structures of cyclodipeptides 1～14 from *Panax notoginseng*

Experimental

General Mps were recorded on XRC-1(uncorr.). IR spectra were taken on Bio-Rad FTS-135 infrared spectrometer with KBr disc. UV spectra were obtained on UV 210A spectrophotometer. NMR spectra were measured on Bruker AM-400 NMR spectrometer using TMS as the internal standard. MS spectra were carried out on VG Autospec-3000 mass spectrometer.

Extraction and isolation The H_2O syrup (160 kg) was dissolved in H_2O and extracted with petroleum ether, EtOAc and n-BuOH, respectively. Then the EtOAc solution was evaporated and the residues (6 kg) was defatted with petroleum ether and then subjected to D-101 resin column eluting with H_2O and CH_3OH for removing a

lot of water-soluble principles. The CH_3OH fraction(800 g) was chromatoghrophied on Al_2O_3 column eluting with CH_3OH, detected with the TLC chemical method for cyclopeptides[2], and collected the cyclopeptide fraction (130 g). Then by the combination of silica gel and Rp-18 column, from the cyclopeptide fraction we obtained 1(3 mg),2 and 11(25 mg),3 and 4(24 mg),5(3 mg),6(25 mg),7(2 mg),8(7 mg),9(20 mg),10,12(7 mg),13 (50 mg,including 12)and 14(15 mg),respectively.

Cyclo-(Leu-Thr) (1) $C_{10}H_{18}O_3N_2$, needles(CH_3OH), mp.280~282 ℃. ^{1}H NMR(DMSO): δ 8.21(1H,s, Leu_{NH})[a],8.02(1H,s,Thr_{NH})[a],5.02(1H,d,J = 5.4Hz, Thr_α)[b],4.00(2H,m,Thr_β and Leu_α[b]),1.80(1H,m, Leu_γ),1.68(1H,m,$Leu_{\beta1}$),1.55(1H,m,$Leu_{\beta2}$),1.06 (3H,d,J = 6.5 Hz,Thr_γ),0.84(3H,d,J = 6.6 Hz, $Leu_{\delta1}$),0.82(3H,d,J = 6.5 Hz,$Leu_{\delta2}$). ^{13}C NMR (DMSO): δ 168.6(Leu_{CO})[c],166.8(Thr_{CO})[c],66.9 (Thr_β),60.5(Thr_α)[d],52.8(Leu_α)[d],45.0(Leu_β),23.3 (Leu_γ),23.1($Leu_{\delta1}$),21.5($Leu_{\delta2}$),20.1(Thr_γ). Assignments[a-d] may be reversed. FAB^+-MS m/z:215($M+1)^+$,115.

Cyclo-(Leu-Ile)(2)and Cyclo-(Phe-Val)(11) 2:$C_{12}H_{22}O_2N_2$; 11:$C_{14}H_{18}O_2N_2$. ^{1}H NMR(DMSO): δ 2:8.17 (1H,s,Leu_{NH}),8.04(1H,s,Ile_{NH}),3.77(1H,br., Leu_α),3.70(1H,br.,Ile_α),1.83(2H,m,Leu_r and Ile_β), 1.63(1H,m,$Leu_{\beta1}$),1.44(2H,m,$Leu_{\beta2}$ and $Ile_{\gamma1}$),1.19 (1H,m,$Ile_{\gamma2}$),0.89(12H,m,$Leu_{\delta1}$,$Leu_{\delta2}$,$Ile_{\gamma3}$ and Ile_δ); 11:8.12(1H,s,Val_{NH})[a],7.92(1H,s,Phe_{NH})[a], 7.19(5H,m,Phe_ϕ),4.21(1H,br.,Phe_α)[b],3.53(1H, br.,Val_α)[b],3.14(1H,dd,$Phe_{\beta1}$),2.90(1H,dd,$Phe_{\beta2}$), 1.63(1H,m,Val_β),0.65(3H,d,J = 6.9 Hz,$Val_{\gamma1}$), 0.26(3H,d,J = 6.9 Hz,$Val_{\gamma2}$). ^{13}C NMR(DMSO): δ 2:168.3(Leu_{CO})[c],166.8(Ile_{CO})[c],58.8(Ile_α),52.3 (Leu_α),43.6(Leu_β),38.3(Ile_β),24.3($Ile_{\gamma1}$),23.5 (Leu_γ),23.0($Leu_{\delta1}$),21.7($Leu_{\delta2}$),15.1($Ile_{\gamma2}$),11.6 (Ile_δ); 11:168.3(Val_{CO})[d],166.8(Phe_{CO})[d],136.0 ($Phe_{\phi1'}$),130.2($Phe_{\phi3',5'}$),127.9($Phe_{\phi2',6'}$),126.4 ($Phe_{\phi4'}$),59.2(Val_γ Val_α)[e],55.0(Phe_α)[e],37.9(Phe_β), 31.0(Val_β),18.2($Val_{\gamma1}$),16.3($Val_{\gamma2}$). Assignments [a-e] may be reversed. FAB^+-MS m/z:2:453($2M+1)^+$,227 $(M+1)^+$;11:493($2M+1)^+$,247($M+1)^+$. The ratio of 2 and 11 is 2:1.

Cyclo-(Leu-Val)(3)and Cyclo-(Ile-Val)(4) 3 and 4: $C_{11}H_{20}O_2N_2$. ^{1}H NMR(DMSO): δ 3:8.20(1H,s, Leu_{NH}),8.06(1H,s,Val_{NH}),3.74(1H,br.,Leu_α),3.60 (1H,m,Val_α),2.08(1H,m,Val_β),1.83(1H,m,Leu_γ), 1.58(1H,m,$Leu_{\beta1}$),1.42(1H,m,$Leu_{\beta2}$),0.80~0.94 (12H,m,$Leu_{\delta1}$,$Leu_{\delta2}$,$Val_{\gamma1}$ and $Val_{\gamma2}$); 4:7.95(1H,s, Ile_{NH}),7.93(1H,s,Val_{NH}),3.74(1H,br.,Ileα),3.67 (1H,br.,Valα),2.17(1H,m,Val_β),1.83(1H,m,Ile_β), 1.42(1H,m,$Ile_{\gamma1}$),1.18(1H,m,$Ile_{\gamma2}$),0.80~0.94 (12H,m,$Leu_{\delta1}$,$Leu_{\delta2}$,$Val_{\gamma1}$ and $Val_{\gamma2}$). ^{13}C NMR (DMSO): δ 3:168.6(Leu_{CO}),167.0(Val_{CO}),59.6 (Val_α),52.5(Leu_α),44.0(Leu_β),31.6(Val_β),23.6 (Leu_γ),23.1($Leu_{\delta1}$),21.6($Leu_{\delta2}$),18.8($Val_{\gamma1}$)[a],17.4 ($Val_{\gamma2}$); 4:167.6(Ile_{CO}),167.5(Val_{CO}),59.2(Val_α), 58.6(Ile_α),38.0(Ile_β),31.0(Val_β),24.4($Ile_{\gamma1}$),18.7 ($Val_{\gamma1}$)[a],17.4($Val_{\gamma2}$),15.1($Ile_{\gamma2}$),11.9(Ile_δ). Assignments [a] may be reversed. FAB^+-MS m/z:425($2M+1)^+$,213($M+1)^+$,113,86,72,59. The ratio of 3 and 4 is 1:1.

Cyclo-(Leu-Ser) (5) $C_9H_{16}O_3N_2$, needles(CH_3OH), mp.240~242 ℃. IR υ_{max} cm^{-1}:3443,3197,3057,2959, 2927,2856,1669,1468,1333. ^{1}H NMR(DMSO): δ 8.23(1H,s,Leu_{NH}),7.93(1H,s,Ser_{NH}),5.14(1H,m, $Ser_{\beta1}$),3.79(2H,m,Leu_α and Ser_α),3.42(1H,m,$Ser_{\beta2}$), 1.79(1H,m,Leu_γ),1.59(2H,m,Leu_β),0.84(6H,m, $Leu_{\delta1}$ and $Leu_{\delta2}$). ^{13}C NMR(DMSO): δ 168.2(Leu_{CO}), 166.3(Ser_{CO}),62.3(Ser_β),57.2(Ser_α),52.7(Leu_α), 44.6(Leu_β),23.3(Leu_γ),23.1($Leu_{\delta1}$),21.5($Leu_{\delta2}$). FAB^+-MS m/z:401($2M+1)^+$,201($M+1)^+$,115, 86.

Cyclo-(Leu-Tyr) (6) $C_{15}H_{20}O_3N_2$, needles(CH_3OH), mp.260~262 ℃. UV $\lambda_{max}^{CH_3OH}$ nm:202.5,225.5,277.5. IR υ_{max} cm^{-1}:3439,3321,3215,2959,2932,1673,1616, 1598,1515,1469,1384,1335,1244,842,818. ^{1}H NMR (DMSO): δ 9.27(1H,s,$Tyr_{\phi4'\text{-}OH}$),8.07(2H,m,Leu_{NH} and Tyr_{NH}),6.88(2H,d,J = 8.2 Hz,$Tyr_{\phi2',6'}$),6.63 (2H,d,J = 8.1 Hz,$Tyr_{\phi3',5'}$),4.05(1H,br.,Tyr_α), 3.44(1H,br.,Leu_α),3.00(1H,dd,J = 13.5,3.3 Hz, $Tyr_{\beta1}$),2.67(1H,dd,J = 13.6,4.6 Hz,$Tyr_{\beta2}$),1.40 (1H,m,Leu_γ),0.72(1H,m,$Leu_{\beta1}$),0.62(6H,m,$Leu_{\delta1}$ and $Leu_{\delta2}$),0.08(1H,m,$Leu_{\beta2}$). ^{13}C NMR(DMSO): δ 167.5(Leu_{CO}),166.3(Tyr_{CO}),156.4($Tyr_{\phi4'}$),131.2 ($Tyr_{\phi2',6'}$),125.9($Tyr_{\phi1'}$),114.9($Tyr_{\phi3',5'}$),55.7 (Tyr_α),52.3(Leu_α),43.7(Leu_β),37.7(Tyr_β),23.0 (Leu_γ),22.7($Leu_{\delta1}$),21.4($Leu_{\delta2}$). FAB^+-MS m/z: 279($M+3)^+$,113.

Cyclo-(Val-Pro) (7) $C_{10}H_{16}O_2N_2$, needles(CH_3OH), mp,145~147 ℃. IR υ_{max} cm^{-1}:3247,2959,2927,2856, 1650,1454,1289,1275. ^{1}H NMR(DMSO): δ 8.38(1H, d,J = 3.8 Hz,Val_{NH}),4.13(1H,m,Val_α),3.34(3H,m, Pro_α and Pro_δ),2.14(1H,m,Val_β),1.70~2.02(4H,m, Pro_β and Pro_γ),0.90(3H,d,J = 11.8 Hz,$Val_{\gamma1}$),0.86 (3H,d,J = 10.2 Hz,$Val_{\gamma2}$). ^{13}C NMR(DMSO): δ 168.9(Pro_{CO})[a],165.2(Val_{CO})[a],62.7(Pro_α)[b],57.8 (Val_α)[b],45.2(Pro($_\delta$),32.5(Val_β),29.0(Pro_β),21.6 (Pro_γ),19.0($Val_{\gamma1}$),18.3($Val_{\gamma2}$). Assignments [a-b] may

be reversed. FAB$^+$-MS m/z:197($M+1$)$^+$,115,98,70.

Cyclo-(Ala-Pro) (8) $C_8H_{12}O_2N_2$, needles (CH_3OH), mp. 170~172 ℃. IR υ_{max} cm^{-1}:3290,2925,2854,1658, 1420. ^{1}H NMR(DMSO): δ 8.17(1H, s, Ala_{NH}), 4.15 (1H, t, J = 7.6 Hz, Pro_α), 4.07(1H, dd, J = 13.6, 6.8 Hz, Ala_α), 3.34(2H, m, Pro_δ), 1.74~2.12(4H, m, Pro_β and Pro_γ), 1.19(3H, d, J = 6.8 Hz, Ala_β). ^{13}C NMR (DMSO): δ 170.0 (Pro_{CO})^a, 166.6 (Ala_{CO})^a, 58.7 (Pro_α)^b, 50.2 (Ala_α)^b, 44.9 (Pro_δ), 27.7 (Pro_β), 22.4 (Pro_γ), 15.3 (Ala_β). Assignments $^{a\text{-}b}$ may be reversed. FAB$^+$-MS m/z:337($2M+1$)$^+$, 169($M+1$)$^+$, 115, 98, 86, 70.

Cyclo-(Phe-Tyr) (9) $C_{18}H_{18}O_3N_2$, needles (CH_3OH), mp. 291~293 ℃. UV $\lambda_{max}^{CH_3OH}$ nm: 202.5, 223, 278. IR υ_{max} cm^{-1}: 3541, 3223, 3032, 2924, 2855, 1678, 1657, 1616, 1518, 1496, 1466. ^{1}H NMR(DMSO): δ 9.27(1H, s, $Tyr_{\phi 4'\text{-}OH}$), 7.89(2H, m, Phe_{NH} and Tyr_{NH}), 7.26(2H, t, J = 7.4 Hz, $Phe_{\phi 3',5'}$), 7.20(1H, d, J = 7.3 Hz, $Phe_{\phi 4'}$), 7.01(2H, d, J = 7.3 Hz, $Phe_{\phi 2',6'}$), 6.81(2H, d, J = 8.3 Hz, $Tyr_{\phi 2',6'}$), 6.66(2H, d, J = 8.2 Hz, $Tyr_{\phi 3',5'}$), 3.92(1H, br., Tyr_α)^a, 3.87(1H, br., Phe_α)^a, 2.50(2H, m, Phe_β)^b, 2.14(2H, m, Tyr_β)^b. ^{13}C NMR (DMSO): δ 166.3 (Tyr_{CO})^c, 166.2 (Phe_{CO})^c, 156.1 ($Tyr_{\phi 4'}$), 136.6 ($Phe_{\phi 1'}$), 130.8 ($Tyr_{\phi 2',6'}$), 129.7 ($Phe_{\phi 3',5'}$), 128.1 ($Phe_{\phi 2',6'}$), 126.4 ($Phe_{\phi 4'}$ and $Tyr_{\phi 1'}$), 115.0 ($Tyr_{\phi 3',5'}$), 55.7 (Tyr_α)^d, 55.4 (Phe_α)^d, 39.1 (Tyr_β)^e, 38.9 (Phe_β)^e. Assignments $^{a\text{-}e}$ may be reversed. FAB$^+$-MS m/z:310(M^+), 282, 85.

Cyclo-(Phe-Ala) (10) $C_{12}H_{14}O_2N_2$. ^{1}H NMR(DMSO): δ 8.16(1H, s, Phe_{NH}), 8.06(1H, s, Ala_{NH}), 7.29(2H, t, J = 7.2 Hz, $Phe_{\phi 3',5'}$), 7.23(1H, d, J = 6.8 Hz, $Phe_{\phi 4'}$), 7.15(2H, d, J = 7.1 Hz, $Phe_{\phi 2',6'}$), 4.18(1H, br., Phe_α), 3.61(1H, m, Ala_α), 3.13(1H, dd, J = 3.4, 13.4 Hz, $Phe_{\beta 1}$), 2.85(1H, dd, J = 4.9, 13.4 Hz, $Phe_{\beta 2}$), 0.44 (3H, d, J = 6.9 Hz, Ala_β). ^{13}C NMR(DMSO): δ 167.6 (Ala_{CO}), 165.8 (Phe_{CO}), 136.0 ($Phe_{\phi 1'}$), 130.3 ($Phe_{\phi 3',5'}$), 127.9 ($Phe_{\phi 2',6'}$), 126.5 ($Phe_{\phi 4'}$), 55.3 (Phe_α), 49.7 (Ala_α), 38.3 (Phe_β), 19.6 (Ala_β). FAB$^+$-MS m/z:218 M^+.

Cyclo-(Leu-Ala) (12) $C_9H_{16}O_2N_2$, needles (CH_3OH), mp. 145~147 ℃. IR υ_{max} cm^{-1}:3424, 3192, 3051, 2959, 2888, 1678, 1469, 1327. ^{1}H NMR(DMSO): δ 8.22(1H, s, Leu_{NH})^a, 8.12(1H, s, Ala_{NH})^a, 3.94(1H, dd, J = 6.9, 13.7 Hz, Leu_α)^b, 3.64(1H, m, Ala_α)^b, 1.73(1H, m, Leu_γ), 1.49(2H, m, Leu_β), 1.21(3H, d, J = 6.8 Hz, Ala_β), 0.87(3H, d, J = 6.6 Hz, $Leu_{\delta 1}$), 0.85(3H, d, J = 6.6 Hz, $Leu_{\delta 2}$). ^{13}C NMR(DMSO): δ 168.8 (Leu_{CO})^c, 168.4 (Ala_{CO})^c, 53.4 (Leu_α)^d, 49.0 (Ala_α)^d, 42.1 (Leu_β), 23.6 (Leu_γ), 22.8 ($Leu_{\delta 1}$), 21.8 ($Leu_{\delta 2}$), 17.8 (Ala_β). Assignments $^{a\text{-}d}$ may be reversed. FAB$^+$-MS m/z: 184 (M^+), 145, 113, 97, 87, 69.

Cyclo-(Ile-Ala) (13) $C_9H_{16}O_2N_2$. ^{13}C NMR(DMSO): δ 168.4 (Ala_{CO})^a, 166.6 (Ile_{CO})^a, 58.8 (Ile_α)^b, 49.6 (Ala_α)^b, 38.0 (Ile_β), 24.2 ($Ile_{\gamma 1}$), 19.9 (Ala_β), 15.0 ($Ile_{\gamma 2}$), 11.8 (Ile_δ). Assignments $^{a\text{-}b}$ may be reversed. FAB$^+$-MS m/z: 370($2M+2$)$^+$, 184 M^+, 169, 157, 141, 128, 115, 98, 86, 70. The ratio of 12 and 13 is 2:1.

Cyclo-(Val-Ala) (14) $C_8H_{14}O_2N_2$, needles (CH_3OH), mp. 265~267 ℃. IR υ_{max} cm^{-1}:3326, 3193, 3052, 2968, 2934, 2896, 1681, 1669, 1457, 1343, 1332, 1140, 861, 832. ^{1}H NMR(DMSO): δ 8.15(1H, s, Ala_{NH})^a, 8.01 (1H, s, Val_{NH})^a, 3.87(1H, dd, J = 6.7, 13.5 Hz, Ala_α), 3.67(1H, s, Val_α), 2.13(1H, m, Val_β), 1.25(3H, d, J = 7.0 Hz, Ala_β), 0.93(3H, d, J = 7.0 Hz, $Val_{\gamma 1}$), 0.81 (3H, d, J = 6.8 Hz, $Val_{\gamma 2}$). ^{13}C NMR(DMSO): δ 168.6 (Ala_{CO})^c, 166.5 (Val_{CO})^c, 59.4 (Val_α)^d, 49.6 (Ala_α)^d, 31.0 (Val_β), 20.0 (Ala_β)^e, 18.4 ($Val_{\gamma 1}1$)^e, 16.6 ($Val_{\gamma 2}$)^e. Assignments $^{a\text{-}e}$ may be reversed. FAB$^+$-MS m/z:171($M+1$)$^+$, 98, 72.

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