Asymmetric Synthesis via Heterocyclic Intermediates, XLVIII[1]

Asymmetric Synthesis of Diastereomerically and Enantiomerically Pure, 3-Substituted (2*S*,3*R*)-*N*-Methylserine Esters

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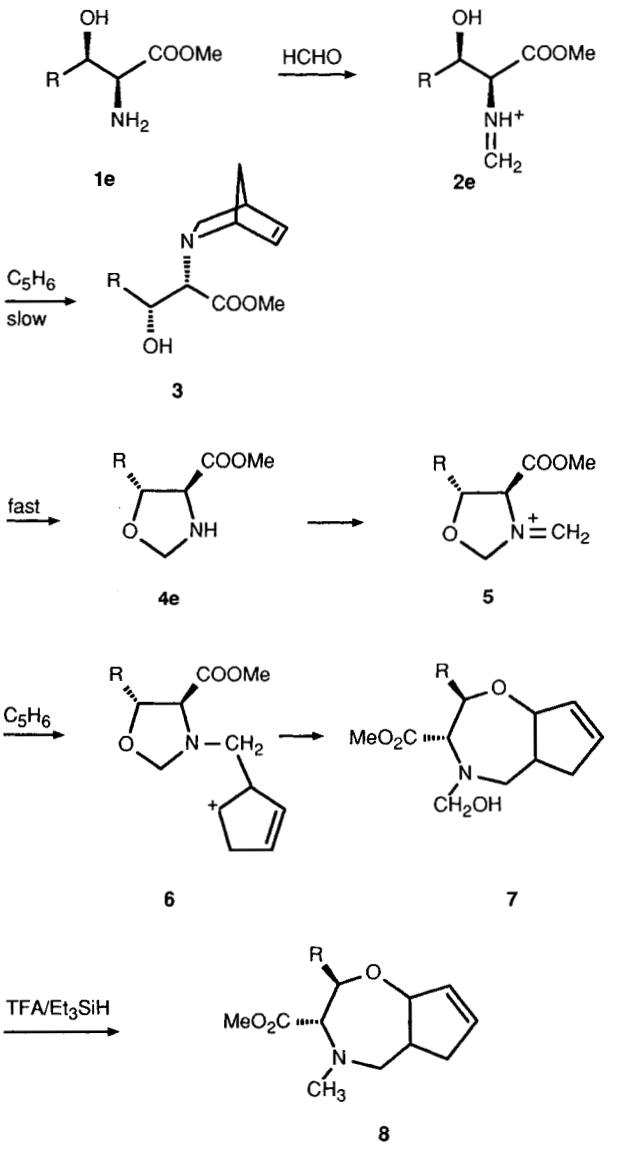
A novel method for the synthesis of *N*-methylserines has been developed. The oxazolidines **4** are formed by condensation of the serine methyl esters **1** with formaldehyde. These intermediates are subsequently reduced to the *N*-methylserine methyl esters **9** by an acid-catalyzed ring opening via their iminium ions **2** with triethylsilane/trifluoroacetic acid.

N-Methyl amino acids deserve special attention as biologically active species[2] and for the preparation of peptide analogues[3]. These peptide analogues are of increasing interest for obtaining information about the backbone conformation of peptides[4]. Only a few satisfactory methods are currently available for the *N*-methylation of amides[5], *N*-acyl amino acids[6] and their imine-type derivatives[7], but no general method has been reported for the *N*-methylation of serine esters until now. In 1976 Weinreb and co-workers[5] showed that simple amides can be *N*-methylated by reduction of their methylol derivatives with triethylsilane/trifluoroacetic acid. In 1983 this method was employed by Freidinger and co-workers[6b] for the *N*-alkylation of Fmoc-protected amino acids via their oxazolidinone derivatives. In 1987 Grieco and Bahsas[8] reported on a two-step sequence for the *N*-methylation of amino acids and peptides compatible with unprotected phenols and hydroxy compounds. The iminium ion generated in situ from the amino acid and aqueous formaldehyde solution undergoes an aza Diels-Alder reaction with cyclopentadiene to give the corresponding 2-azanorbornene derivative. The iminium-ion species, generated during an acid-catalyzed retro aza Diels-Alder reaction, can be reduced with triethylsilane to provide the *N*-methyl amino acid in a total yield of 54–86%.

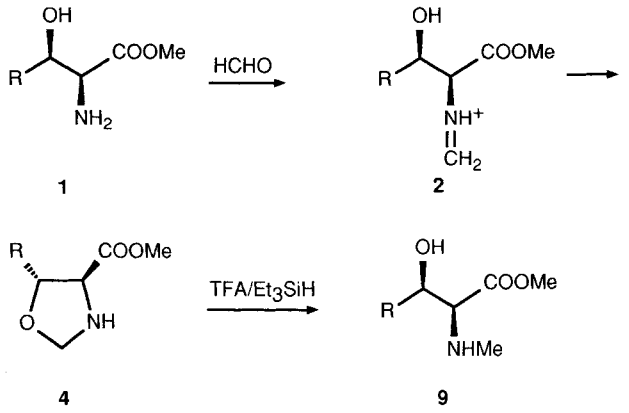
In the course of an asymmetric synthesis of MeBmt[9], the unusual amino acid of cyclosporine A, we were interested in the monomethylation of the serine ester **1e**. According to Grieco's protocol, the *syn*-serine ester **1e** was treated with formaldehyde and cyclopentadiene in order to give the expected 2-azanorbornene derivative **3**. To our surprise, the reduction of the obtained intermediate yielded in 63% the tetrahydrooxazepine **8**.

This result is in agreement with the following proposed mechanism: After addition of one equivalent of formaldehyde and subsequent dehydration, the iminium ion **2** cyclizes substantially faster to the *trans*-oxazolidine **4e** then it undergoes an aza Diels-Alder reaction towards **3**. The oxa-



zolidine **4e** adds a second equivalent of formaldehyde yielding the iminium ion **5**. Since this cannot undergo an aza Diels-Alder reaction, it adds cyclopentadiene in an electrophilic addition. The rearrangement of **6** to the more stable iminium ion and addition of water leads to the methylol **7**. This intermediate is reduced in the second step to the tetrahydrooxazepine **8**. This compound was obtained as a single diastereomer; the stereochemistry at C-5a and C-8a was not determined.

However, the isolation of the fairly stable oxazolidine **4** should open up a simple and efficient method for the *N*-methylation of serine esters by an acid-catalyzed ring opening of **4** and in situ reduction of the generated iminium-ion species.



1,2,4,9	R	yield of **9** (%)
a	H	42
b	CH_3	57
c	$CH_3(CH_2)_2$	73
d	(E)-CH_3-CH=CH-$(CH_2)_2$	53
e	(4R,6E)-CH_3-CH=CH-$CH_2CH(CH_3)$	64

Consequently, the serine methyl esters **1** were treated with 0.1 N trifluoroacetic acid and 1.0 equivalents of a 37% aqueous formaldehyde solution to afford the oxazolidines **4**. Exposure of **4** to trifluoroacetic acid and triethylsilane provides the *N*-methyl serine esters **9** in 42–73% yield.

Upon reaction according to the conditions described above the *anti*-serine ester **10** afforded the corresponding *N*-methyl derivative **13** in only 25% yield. This result is in agreement with the proposed mechanism, because the cyclization of the iminium ion **11** to the sterically crowed *cis*-substituted oxazolidine **12** only proceeds sluggishly.

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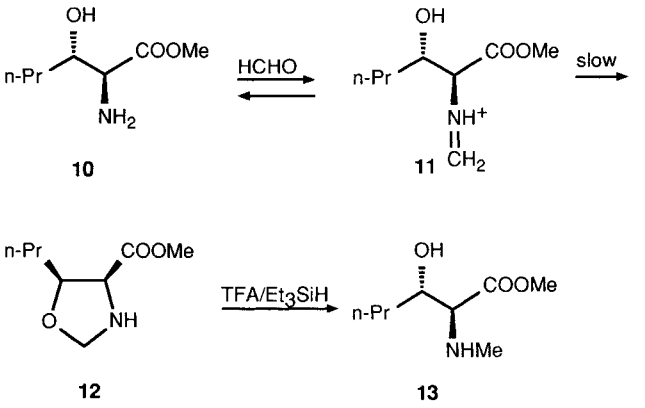

Experimental

The serine esters **1a** and **b** were purchased from Fluka[10] and used directly as their commercially available hydrochloride. The serine esters **1c** and **d** were prepared according to ref.[11] starting from the bislactim ether of cyclo(-D-Val-Gly-)[12]. The serine ester **1e** was prepared as described in ref.[9]. – Infrared (IR) spectra were obtained using a Perkin-Elmer 298 spectrometer. – NMR spectra were obtained using a Varian XL 200, a VXR 200 or a VXR 500 S spectrometer for ^1H and ^{13}C NMR. Chemical shifts are given in δ values, tetramethylsilane as internal standard for ^1H- and ^{13}C NMR. – Optical rotations were measured on a Perkin-Elmer Mod. 141 polarimeter. – TLC analyses were performed on Polygram Sil G/UV_{254} silica gel plates. Silica gel (30–60 μm) from Baker was used for flash chromatography. – Combustion analyses were carried out by the microanalytical laboratory at the University of Göttingen. – All reagents were purified and dried if necessary prior to use.

(1R)-1-[(2'S,5'R)-2',5'-Dihydro-5'isopropyl-3',6'-dimethoxy-2'-pyrazinyl]-1-butanol and (1S)-1-[(2'S,5'R)-2',5'-Dihydro-5'-isopropyl-3',6'-dimethoxy-2'-pyrazinyl]-1-butanol: A solution of *n*-butyllithium in hexane (1.7 N, 15.9 ml, 27 mmol) was added slowly to a solution of the bislactim ether of cyclo(-D-Val-Gly-) (4.60 g, 25 mmol) in THF (200 ml) at −78°C. After 15 min a solution of butanal (2.16 g, 30 mmol) in THF (15 ml) was added dropwise and stirring was continued at −78°C for 10 h. – Phosphate buffer (100 ml, pH = 7) was added and the solution was allowed to warm up to room temp. within 10 min. Volatile components were removed in vacuo (30°C/12 Torr), and the residue was extracted three times with diethyl ether (50 ml each). The combined organic layers were dried with $MgSO_4$, and the solvent was removed in vacuo (20°C/12 Torr). Flash chromatography on silica gel with diethyl ether/petroleum ether (1:2) afforded 4.30 g (67%) of the (1*R*,2'*S*,5'*R*) adduct and 1.20 g (19%) of the (1*S*,2'*S*,5'*R*) adduct.

(1R)-1-[(2'S,5'R)-2',5'-Dihydro-5'isopropyl-3',6'-dimethoxy-2'-pyrazinyl]-1-butanol: R_f = 0.16. For the spectroscopic data of the (1*S*,2'*R*,5'*S*) enantiomer see ref.[11]

(1S)-1-[(2'S,5'R)-2',5'-Dihydro-5'isopropyl-3',6'-dimethoxy-2'-pyrazinyl]-1-butanol: R_f = 0.25. – IR (film): $\tilde{\nu}$ = 3100–3600 (O–H), 1685 cm^{-1} (C=N). – ^1H NMR ($CDCl_3$): δ = 0.71 and 1.03 [2 d, *J* = 7 Hz; 3H each, $CH(CH_3)_2$], 0.90 (t, *J* = 7 Hz; 3H, 3-CH_3), 1.10–1.68 [m; 4H, $(CH_2)_2$], 2.25 [dsept, J_1 = 7 Hz, J_2 = 3.5 Hz; 1H, $CH(CH_3)_2$], 2.71 (br.; 1H, OH), 3.70 and 3.72 (2s; 3H each, OCH_3), 3.99 (m; 2H, 1-H and 5'-H), 4.18 (dd, J_1 = J_2 = 4 Hz; 1H, 2'-H). – ^{13}C NMR ($CDCl_3$): δ = 14.10 and 16.72 [$CH(CH_3)_2$], 18.98 (C-3), 19.01 (C-4), 32.17 [$CH(CH_3)_2$], 34.32 (C-2), 52.42 and

52.62 (2 OCH_3), 59.90 and 61.23 (C-2′ and C-5′), 71.48 (C-1), 161.84 and 164.77 (C-3′ and C-6′).

$C_{13}H_{24}N_2O_3$ (256.3) Calcd. C 60.91 H 9.44
Found C 61.00 H 9.55

Serine Methyl Esters **1c** *and* **10**. — *General Procedure:* A 0.2 N solution of the above described bislactim ether adducts (6 mmol) in acetonitrile (50 ml) was added to aqueous TFA (0.1 N, 180 ml, 18 mmol), and stirring was continued for 20 h at ambient temp. The mixture was concentrated to dryness, the residue was diluted with methylene chloride (50 ml), and conc. aqueous ammonia solution was added until pH = 8–10. The solvent was removed in vacuo and the residue purified by chromatography [silica gel, 10 g, diethyl ether/acetonitrile/conc. aqueous ammonia solution (10:1:0.1)].

Methyl (2S,3R)-2-Amino-3-hydroxyhexanoate (**1c**): 1.54 g (6 mmol) of the (1*R*,2′*S*,5′*R*) bislactim ether adduct was used; yield 0.62 g (64%) of **1c**, R_f = 0.15, $[\alpha]_D^{23}$ = +23.5 (*c* = 0.9, methanol). For the spectroscopic data of the (2*R*,3*S*) enantiomer see ref.[11]

Methyl (2S,3S)-2-Amino-3-hydroxyhexanoate (**10**): 0.87 g (3.3 mmol) of the (1*S*,2′*S*,5′*R*) adduct was used; yield 0.29 g (53%) of **10**, R_f = 0.12, $[\alpha]_D^{20}$ = +15.8 (*c* = 1.0, methanol). — IR (film): $\tilde{\nu}$ = 3040–3620 (O–H, NH_2), 1720 (O–C=O), 1575 cm^{-1} (C–NH_2). — ^{1}H NMR ($CDCl_3$): δ = 0.93 (t, *J* = 7 Hz; 3H, 5-H_3), 1.22–1.62 [m; 4H, $(CH_2)_2$], 2.20 (br. s; 3H, NH_2 and OH), 3.58 (d, *J* = 4 Hz; 1H, 2-H), 3.76 (s; 3H, OCH_3), 3.80 (m; 1H, 3-H). — ^{13}C NMR ($CDCl_3$): δ = 13.98 (C-6), 19.08 (C-5), 34.59 (C-4), 52.04 (OCH_3), 58.87 (C-2), 72.25 (C-3), 174.45 (C-1).

$C_7H_{15}NO_3$ (161.2) Calcd. C 52.16 H 9.38
Found C 52.01 H 9.27

Methyl (2R,3S)-3,4,5,5a,6,8a-Hexahydro-4-methyl-2-[(1′R,3′E)-1′-methyl-3′-pentenyl]-2H-cyclopent[f]-1,4-oxazepine-3-carboxylate (**8**): To a solution of the serine ester **1c** (0.6 g, 3 mmol) in 1.5 N hydrochloric acid (2.3 ml) cyclopentadiene (1.4 ml, 15 mmol) and aqueous formaldehyde solution (0.8 ml, 37%) were added, and stirring was continued at ambient temp. for 2 h. The reaction mixture was neutralized with sodium hydrogen carbonate solution, and the product was isolated by extraction of the reaction mixture with ethyl acetate (four times, 50 ml each). The combined organic layers were dried with magnesium sulfate, and the solvent was removed in vacuo (30°C/12 Torr). The residue was diluted with chloroform and trifluoroacetic acid (17 ml each), and triethylsilane (1.7 ml, 3 equiv.) was added and stirring continued under argon at ambient temp. for 20 h. The mixture was concentrated to dryness, the residue was dissolved in 10% hydrochloric acid (10 ml) and washed with hexane (20 ml). Methylene chloride (100 ml) was added, and to the aqueous layer was added conc. aqueous ammonia solution until pH = 10. The layers were separated, and the aqueous layer was reextracted with methylene chloride (three times, 50 ml each). The combined organic layers were dried with magnesium sulfate, the solvent was removed under reduced pressure (20°C, 12 Torr) and the product purified by chromatography with diethyl ether: 0.55 g (63%) of **8** were obtained; R_f = 0.33, $[\alpha]_D^{20}$ = +22.0 (*c* = 1.06, methanol). — IR (Film): $\tilde{\nu}$ = 1730 (O–C=O), 1660 and 960 cm^{-1} (C=C). — ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.94 (d, *J* = 6.8 Hz; 3H, 1′-CH_3), 1.34 (dddq, J_1 = 14 Hz, J_2 = 3 Hz, J_3 = 2 Hz, J_4 = 6.8 Hz; 1H, 1′-H), 1.64 (dddd, $^3J_1$ = 6.8 Hz, $^4J_2$ = 1.4 Hz, $^5J_3$ = $^5J_4$ < 1 Hz; 3H 5′-H_3), 1.83 (ddddq, $^2J_1$ = 14.5 Hz, $^3J_2$ = 14 Hz, $^3J_3$ = 7.8 Hz, $^4J_4$ = 1 Hz, $^5J_5$ = 1 Hz, 1H, 2′-H), 2.03 (m; 1H, 6-H), 2.26 (ddddq, $^2J_1$ = 14.5 Hz, $^3J_2$ = 6 Hz, $^3J_3$ = 3 Hz, $^4J_4$ = 1.5 Hz, $^5J_5$ = 1 Hz; 1H, 2′-H), 2.35 (s; 3H, NCH_3), 2.51 (m; 1H, 6-H), 2.68 (m; 2H, 2 × 5-H), 2.84 (m; 1H, 5a-H), 3.22 (d, *J* = 9.2 Hz; 1H, 3-H), 3.58 (dd, J_1 = 9.2 Hz, J_2 = 2 Hz; 1H, 2-H), 3.74 (s; 3H, OCH_3), 4.65 (ddddd, $^3J_1$ = 7.5 Hz, $^3J_2$ = 2.2 Hz, $^4J_3$ = 1.4 Hz, $^5J_4$ = $^5J_5$ = 1.8 Hz; 1H, 8a-H), 5.32 (dddq, $^3J_1$ = 15 Hz, $^3J_2$ = 7.8 Hz, $^3J_3$ = 6 Hz, $^4J_4$ = 1,4 Hz; 1H, 3′-H), 5.40 (dddq, $^3J_1$ = 15 Hz, $^4J_2$ = $^4J_3$ = 1 Hz, $^3J_4$ = 6.2 Hz; 1H, 4′-H), 5.68 (dddd, $^3J_1$ = 5.6 Hz, $^3J_2$ = 2.2 Hz, $^4J_3$ = $^4J_4$ = 2 Hz, 1H, 8-H), 5.90 (ddt, $^3J_1$ = 5.6 Hz, $^4J_2$ = 1.4 Hz, $^3J_3$ = 2.4 Hz; 1H, 7-H). — ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 16.86 (1′-CH_3), 17.93 (C-5′), 32.78 (C-2′), 36.40 (C-1′), 37.17 (C-6), 42.25 (C-5a), 45.16 (NCH_3), 51.89 (OCH_3), 59.09 (C-5), 74.04 (C-3), 85.22 (C-2), 89.13 (C-8a), 126.07 (C-4′), 130.03 (C-3′), 130.15 (C-8), 134.27 (C-7), 172.09 (C=O).

$C_{17}H_{27}NO_3$ (293.3) Calcd. C 69.57 H 9.28
Found C 69.42 H 9.35

N-Methylation of the Serine Esters **1**. — *Compounds* **9**. — *General Procedure:* To a solution of the serine ester **1** (2 mmol) in methylene chloride (20 ml) 0.1 N aqueous TFA (20 ml) was added and the resulting mixture cooled down to 0°C. With vigorous stirring a 37% aqueous solution of formaldehyde (0.15 ml, 2 mmol) was added dropwise and stirring continued at ambient temp. for 3–8 h. The reaction mixture was neutralized with sodium hydrogen carbonate solution, and the product was isolated by extraction with methylene chloride (four times, 20 ml each). The combined organic extracts were dried with magnesium sulfate and concentrated in vacuo. The crude product **4** was used directly in the next reaction. A solution of the oxazolidine **4** in methylene chloride (20 ml) was cooled down to 0°C, and TFA (20 ml) and triethylsilane (2 ml) were added. The resulting mixture was stirred at ambient temp. under argon for 12 h. Volatile components were removed in vacuo, and the residue was stirred with 1 N hydrochloric acid (5 ml) for 30 min. The mixture was diluted with methylene chloride (50 ml) and conc. aqueous ammonia solution was added u.ntil pH = 10. The layers were separated, the aqueous layer was saturated with sodium chloride and extracted four times with methylene chloride (20 ml each). The solvent of the combined extracts was removed in vacuo, and the serine esters **9** were purified by chromatography [silica gel, 20 g, diethyl ether/acetonitrile/conc. aqueous ammonia solution (10:1:0.1)].

Methyl (2S)-3-Hydroxy-2-(methylamino)propanoate (**9a**): 0.31 g (2 mmol) L-serine methyl ester hydrochloride **1a** was used; yield 0.11 g (42%) of **9a**, R_f = 0.07, $[\alpha]_D^{20}$ = +7.8 (*c* = 1.02, methanol). — IR (film): $\tilde{\nu}$ = 3100–3600 (O–H, N–H), 1720 cm^{-1} (O–C=O). — ^{1}H NMR ($CDCl_3$): δ = 2.44 (s; 3H, NCH_3), 2.73 (br. s; 2H, NH and OH), 3.31 (X part of ABX, J_{AX} = 5.6 Hz, J_{BX} = 4.8 Hz; 1H, 2-H), 3.68 (*A*BX, J_{AB} = 11.2 Hz, J_{AX} = 5.6 Hz; 1H, 3-H), 3.77 (s; 3H, OCH_3), 3.84 (A*B*X, J_{AB} = 11.2 Hz, J_{BX} = 4.8 Hz; 1H, 3-H). — ^{13}C NMR ($CDCl_3$): δ = 34.77 (NCH_3), 52.11 (OCH_3), 62.37 (C-3), 64.68 (C-2), 173.39 (C-1).

$C_5H_{11}NO_3$ (133.1) Calcd. C 45.10 H 8.33
Found C 44.97 H 8.46

Methyl (2S,3R)-3-Hydroxy-2-(methylamino)butanoate (**9b**): 0.34 g (2 mmol) L-threonine methyl ester hydrochloride **1b** was used; yield 0.17 g (57%) of **9b**, R_f = 0.21, $[\alpha]_D^{20}$ = –18.02 (*c* = 1.01, methanol). — IR (film): $\tilde{\nu}$ = 3100–3600 (O–H, N–H), 1720 cm^{-1}), 1720 cm^{-1} (O–C=O). — ^{1}H NMR ($CDCl_3$): δ = 1.21 (d, *J* = 7 Hz; 3H, 3-CH_3), 2.42 (s; 3H, NCH_3), 2.45 (br. s; 2H, NH and OH), 2.91 (d, *J* = 8 Hz; 1H, 2-H), 3.66 (dq, J_1 = 8 Hz, J_2 = 7 Hz; 1H, 3-H), 3.77 (s; 3H, OCH_3). — ^{13}C NMR ($CDCl_3$): δ = 19.48 (C-4), 35.25 (NCH_3), 51.92 (OCH_3), 67.85 (C-3), 69.93 (C-2), 174.15 (C-1).

$C_6H_{13}NO_3$ (147.2) Calcd. C 48.97 H 8.90
Found C 49.29 H 9.26

Methyl (2S,3R)-3-Hydroxy-2-(methylamino)hexanoate (**9c**): 0.32 g (2 mmol) of **1c** was used; yield 0.25 g (73%) of **9c**, R_f = 0.39, $[\alpha]_D^{20}$ = +6.42 (*c* = 1.01, methanol). – IR (film): $\tilde{\nu}$ = 3100–3600 (N–H, O–H), 1720 cm^{-1} (O–C=O). – ^1H NMR ($CDCl_3$): δ = 0.99 (t, *J* = 7 Hz; 3H, 5-CH_3), 1.43 [m; 4H, $(CH_2)_2$], 2.40 (s; 3H, NCH_3), 2.44 (br. s; 2H, NH and OH), 2.96 (d, *J* = 7 Hz; 1H, 2-H), 3.54 (m; 1H, 3-H), 3.75 (s; 3H, OCH_3). – ^{13}C NMR ($CDCl_3$): δ = 14.05 (C-6), 18.84 (C-5), 35.32 (NCH_3), 35.98 (C-4), 51.93 (OCH_3), 68.42 (C-2), 71.46 (C-3), 174.35 (C-1).

$C_8H_{17}NO_3$ (175.2) Calcd. C 54.84 H 9.76
Found C 54.87 H 9.97

Methyl (2S,3R,6E)-3-Hydroxy-2-(methylamino)-6-octenoate (**9d**): 0.15 g (0.8 mmol) of **1d** was used; yield 85 mg (53%) of **9d**, R_f = 0.40, $[\alpha]_D^{20}$ = +11.2 (*c* = 1.01, methanol). – IR (film): $\tilde{\nu}$ = 3100–3600 (N–H, O–H), 1720 cm^{-1} (O–C=O). – ^1H NMR ($CDCl_3$): δ = 1.52 (dt, J_1 = 6 Hz; J_2 = 7.5 Hz; 2H, 3-CH_2), 1.64 (ddt, $^3J_1$ = 4.5 Hz, $^4J_2$ = $^5J_3$ = 1 Hz; 3H, 7-CH_3), 2.13 (m; 2H, 4-CH_2), 2.42 (s; 3H, NCH_3), 2.63 (br. s; 2H, NH and OH), 3.00 (d, *J* = 7 Hz; 1H, 2-H), 3.58 (dt, J_1 = 7 Hz, J_2 = 6 Hz; 1H, 3-H), 3.77 (s; 3H, OCH_3), 5.45 (m; 2H, 6-H and 7-H). – ^{13}C NMR ($CDCl_3$): δ = 17.93 (C-8), 28.63 and 33.75 (C-4 and C-5), 35.31 (NCH_3), 51.99 (OCH_3), 68.32 and 71.13 (C-2 and C-3), 125.45 and 130.59 (C-6 and C-7), 174.13 (C-1).

$C_{10}H_{19}NO_3$ (201.3) Calcd. C 59.68 H 9.51
Found C 59.65 H 9.57

Methyl (2S,3R,4R,6E)-3-Hydroxy-2-(methylamino)-4-methyl-6-octenoate (**9e**): 0.40 g (2 mmol) of **1e** was used; yield 0.28 g (64%) of **9e**, R_f = 0.46, $[\alpha]_D^{20}$ = +13.5 (*c* = 1.1, methanol). For the spectroscopic data see ref.[9].

$C_{11}H_{21}NO_3$ (215.3) Calcd. C 61.37 H 9.83
Found C 61.41 H 9.81

Methyl (2S,3S)-3-Hydroxy-2-(methylamino)hexanoate (**13**): 0.28 g (1.7 mmol) of serine ester **10** was used; yield 75 mg (25%) of **13**, R_f = 0.21, $[\alpha]_D^{20}$ = –3.9 (*c* = 1.2, methanol). – IR (film): $\tilde{\nu}$ = 3100–3600 (N–H, O–H), 1720 (O–C=O). – ^1H NMR ($CDCl_3$): δ = 0.92 (t, *J* = 7 Hz; 3H, 5-CH_3), 1.22–1.64 [m; 4H, $(CH_2)_2$], 2.23 (br. s; 2H, NH and OH), 2.42 (s; 3H, NCH_3), 3.25 (d, *J* = 4.5 Hz; 1H, 2-H), 3.76 (s; 3H, OCH_3), 3.79 (m; 1H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 13.96 (C-6), 19.14 (C-5), 35.31 (NCH_3), 35.40 (C-4), 51.81 (OCH_3), 67.79 (C-2), 71.25 (C-3), 173.69 (C-1).

$C_8H_{17}NO_3$ (175.2) Calcd. C 54.84 H 9.76
Found C 55.08 H 9.65

CAS Registry Numbers

1a · HCl: 5680-80-8 / **1b** · HCl: 39994-75-7 / **1c**: 139564-70-8 / **1d**: 139629-07-5 / **1e**: 139564-71-9 / **8**: 139564-73-1 / **9a**: 111934-24-8 / **9b**: 95599-23-8 / **9c**: 139564-75-3 / **9d**: 139564-76-4 / **9e**: 139564-77-5 / **10**: 139564-72-0 / **13**: 139564-74-2 / C_5H_6: 542-92-7 / butanal: 123-72-8 / cyclo(-D-Val-Gly-) bislactim ether: 109838-85-9 / (1*R*)-1-[(2′*S*,5′*R*)-2′,5′-dihydro-5′-isopropyl-3′,6′-dimethoxy-2′-pyrazinyl]-1-butanol: 139629-06-4 / (1*S*)-1-[(2′*S*,5′*R*)-2′,5′-dihydro-5′-isopropyl-3′,6′-dimethoxy-2′-pyrazinyl]-1-butanol: 135514-16-8

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