# Stereochemically Reliable Syntheses of Pachastrissamine and Its 2-*epi*-Congener via Oxazolidinone Precursors from an Established Starting Material *N*-*tert*-Butoxycarbonyl-Protected Phytosphingosine

Hoon Bae,[a] Hongjun Jeon,[a] Dong Jae Baek,[a] Dongjoo Lee,*[b] Sanghee Kim*[a]

[a] College of Pharmacy, Seoul National University, San 56-1, Shilim, Kwanak, Seoul 151-742, Republic of Korea
Fax +82(2)8880649; E-mail: pennkim@snu.ac.kr

[b] Department of Pharmacology, College of Medicine, Dankook University, San 29, Anseo-dong, Dongnam-gu, Cheonan-si, Chungnam 330-714, Republic of Korea
Fax +82(41)5597899; E-mail: drlee21@dankook.ac.kr

*Received: 04.08.2012; Accepted after revision: 06.10.2012*

**Abstract:** Efficient, stereochemically unambiguous, total syntheses of pachastrissamine and its 2-*epi*-congener from the readily available common precursor (1*R*)-1-{(4*S*,5*S*)-2-oxo-4-[(trityloxy)methyl]-1,3-oxazolidin-5-yl}pentadecyl methanesulfonate are reported. Syntheses of (3a*S*,6*R*,6a*R*)- and (3a*S*,6*S*,6a*R*)-6-tetradecylhexahydro-2*H*-cyclopenta[*d*][1,3]oxazol-2-one by this route have unambiguously resolved a dispute over the structures of these products.

**Key words:** natural products, stereoselective synthesis, heterocycles

In 2005, Datta and co-workers reported a total synthesis of pachastrissamine (also known as jaspine B; **1**) (Figure 1) through construction of the oxazolidinone intermediate **3** from an L-serine-derived chiral bicyclic lactone as an advanced intermediate.[1]

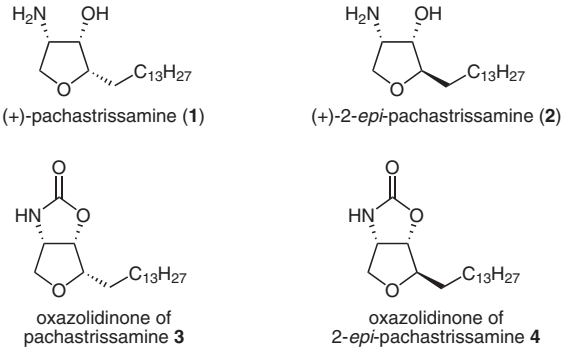
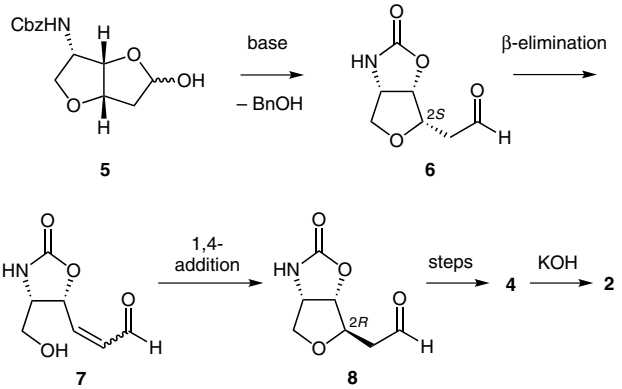



**Figure 1** Structures of pachastrissamine (**1**), 2-*epi*-pachastrissamine **2**, and their oxazolidinone derivatives

In 2008, Davies and co-workers[2] claimed, in a review, that the original stereochemical assignment of both Datta's synthetic pachastrissamine (**1**) and its oxazolidinone intermediate **3** were incorrect and that the actual structures should be revised to those of the corresponding 2-epimers **2** and **4**, respectively, both of which possess a (2*R*,3*S*,4*S*) configuration. This claim was based on the observation that Datta's spectroscopic results for pachastrissamine (**1**) were inconsistent with those reported by other groups,[3] and that they resembled those of its 2-*epi*-congener **2**.[3b,f,l,q,r,w,z,aa,4] To rationalize the unexpected formation of **4** and **2** from lactol **5**, Davies and co-workers suggested an epimerization pathway (Scheme 1) in which aldehyde **6**, generated in situ from lactol **5**, readily undergoes C(2)-epimerization through a β-elimination/1,4-addition sequence during the Wittig olefination step, leading, via the enal **7**, to the more sterically favored *trans*-tetrahydrofuran intermediate **8**.[2] When Davies and co-workers raised the problem of the stereochemical assignment of Datta's oxazolidinone structure, spectroscopic data for both **1** and **2** had been published by several research groups, so that Davies's claim regarding the structural assignment of Datta's pachastrissamine was highly relevant. However, the lack of available spectroscopic data for **3**[5] and **4**[6] at the time precluded any firm conclusion with respect to Davies's proposal for a revision of the structure of Datta's oxazolidinone.




**Scheme 1** A plausible mechanism for the C(2)-epimerization of Datta's lactol **5** during the Wittig reaction, as suggested by Davies and co-workers (ref. 2)

This situation prompted us to develop an efficient synthesis of both pachastrissamine (**1**) and its 2-*epi*-congener **2** via the corresponding oxazolidinone intermediates **3** and **4**, respectively, to resolve the dispute regarding the struc-

**SYNTHESIS** 2012, 44, 3609–3612
Advanced online publication: 05.11.2012
DOI: 10.1055/s-0032-1317506; Art ID: SS-2012-F0644-OP

tures of the oxazolidinones. We developed concise and efficient syntheses of both pachastrissamine (**1**) and its 2-*epi*-congener **2** from the common precursor **10** through a stereoselective intramolecular etherification, with a minimal manipulation of protecting groups.

We recently reported a two-step preparation of **10** (90%) from *N*-*tert*-butoxycarbonyl-protected phytosphingosine **9**.[7] Oxazolidinone **3** was synthesized in two steps from the common precursor **10** via mesylate **11** (Scheme 2). The secondary hydroxy group of **10** reacted with mesyl chloride in pyridine to give the mesylate **11** in 95% yield. Fortunately, treatment of the resulting intermediate **11** with boron trifluoride etherate at ambient temperature gave the oxazolidinone **3** in 90% yield through removal of the trityl group of **11** and concomitant spontaneous internal etherification.

Having successfully achieved the conversion of **10** into oxazolidinone **3**, we then examined the transformation of the same precursor **10** into the 2-epimeric oxazolidinone **4**. The trityl group on **10** was initially removed with boron trifluoride etherate to give the diol **12** in 90% yield. The primary hydroxy group of **12** was then selectively protected by treatment with tosyl chloride in pyridine. Subsequent etherification at high temperature gave the oxazolidinone **4** in excellent yield. The spectral data for this product were identical in all respects to those previously reported by our group,[7] confirming that the stereochemistry was completely controlled in the desired manner during the reaction sequences. Finally, the oxazolidinones **3** and **4** were converted into pachastrissamine (**1**) and its 2-*epi*-congener **2**, respectively, by base-induced cleavage of the cyclic carbamate under standard hydrolytic conditions (potassium hydroxide in refluxing ethanol). Pachastrissamine (**1**) and its 2-*epi*-congener **2** were generated in good yields, and their spectral data were in excellent agreement with those reported in the literature.[3b,f,r,z,aa]

Having achieved an efficient synthesis of the naturally occurring pachastrissamine (**1**) and its 2-*epi*-congener **2**, and armed with a full set of spectroscopic data for all the synthetic intermediates, we turned our attention to an investigation of the stereochemical assignment of the disputed oxazolidinone structure proposed by Davies and co-workers.

When we carefully compared the spectroscopic data for the penultimate oxazolidinone reported by Datta and co-workers[1] with those reported by other groups[3k,p] and with ours for compound **3**,[3ad] we realized that there was good agreement in both the $^1$H- and $^{13}$C NMR data, whereas our spectroscopic data for oxazolidinone **4** were significantly different from those of Datta and co-workers (Figure 2). The most striking difference between the spectra of oxazolidinones **3** and **4** is that **3** has a peak at $\delta = 3.50$ ppm for two protons at C(5), whereas **4** has a corresponding reso-

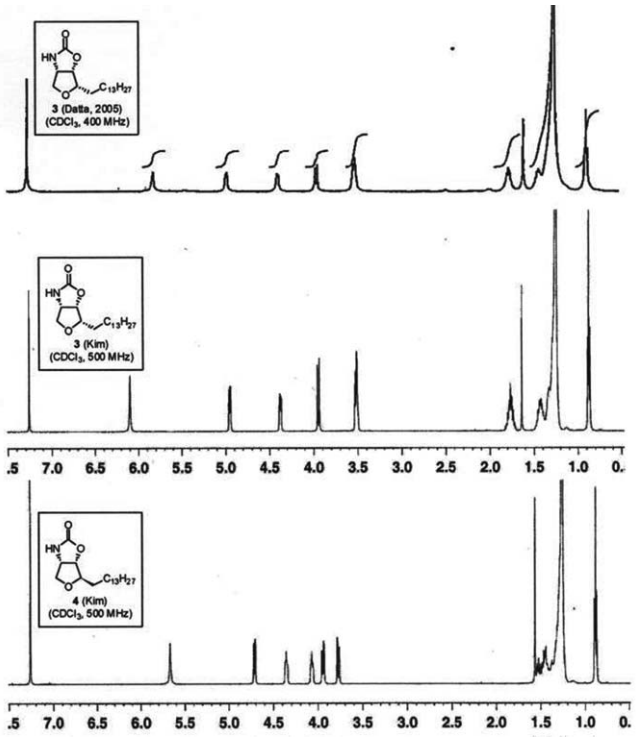
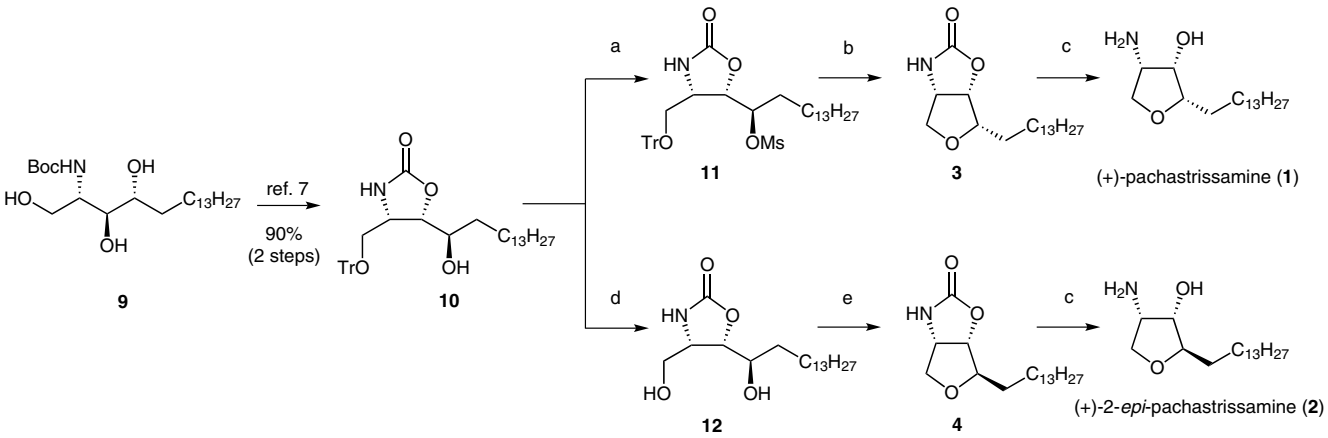



**Figure 2** Comparisons of $^1$H NMR spectra of the Datta's oxazolidinone with those of our oxazolidinones **3** and **4**




**Scheme 2** *Reagents and conditions*: (a) MsCl, py, r.t., 12 h, 95%; (b) $BF_3{\cdot}OEt_2$, toluene–MeOH, r.t., 12 h, 90%; (c) aq KOH, EtOH, reflux, 12 h, 72%; (d) $BF_3{\cdot}OEt_2$, toluene–MeOH, r.t., 12 h, 90%; (e) TsCl, DMAP, py, reflux, 12 h, 94%.

nance at δ = 3.76–3.96 ppm with a splitting pattern. From this evident difference in the spectral data, we can firmly conclude that the structure of the penultimate oxazolidinone originally reported by Datta and co-workers was correctly assigned as **3**, and that this is the oxazolidinone form of **1**. However, Datta's reported spectroscopic data for pachastrissamine are actually those of its 2-*epi*-congener **2**.

In conclusion, we have developed efficient and highly regio- and stereocontrolled syntheses of pachastrissamine (**1**) and its 2-*epi*-congener **2** from the readily available common intermediate oxazolidinone **10**. The stereochemical inconsistency between the Datta and co-workers' penultimate oxazolidinone and their final product cannot be accounted for by any logical mechanism, because the stereogenic centers of **3** and **4** remain intact under the hydrolytic conditions that are present during the final step. Biological assays of the synthetic samples will be reported later.

Except as otherwise indicated, all reactions were carried out under argon in flame- or oven-dried glassware. In aqueous workup, all organic solns were dried over $Na_2SO_4$ or $MgSO_4$ and filtered before to rotary evaporation at water-aspirator pressure. Reactions were monitored by TLC on 0.25-mm precoated silica gel plates (Kieselgel $60F_{254}$; Merck). Spots were detected by viewing under UV radiation or by colorization through charring after dipping in a soln of anisaldehyde, HOAc, and $H_2SO_4$ in MeOH, in $KMnO_4$ soln containing $H_2SO_4$ and EtOH, or in ceric ammonium molybdate soln containing $H_2SO_4$ and EtOH. Flash chromatography was performed on silica gel (particle size 0.040–0.063 mm; Merck). Yields refer to chromatographically and spectroscopically pure compounds unless otherwise noted. Commercial reagents and solvents were used as received, except that all solvents were freshly purified and dried by standard techniques immediately before use. $^1$H and $^{13}$C spectra were recorded on Bruker AMX-500 (500 MHz), Bruker Avance 400 (400 MHz), or JEOL JNM-LA 300 (300 MHz) spectrometers. Chemical shifts are reported relative to $CHCl_3$ as an internal standard (δ = 7.26 for $^1$H and δ = 77.0 for $^{13}$C). IR spectra were recorded on a PerkinElmer 1600 FT-IR spectrometer, referenced to a polystyrene standard. Low- and high-resolution mass spectra were recorded at the Seoul National University national center for inter-university research facilities using JEOL JMS-700 (FAB or Cl).

**(1*R*)-1-{(4*S*,5*S*)-2-Oxo-4-[(trityloxy)methyl]-1,3-oxazolidin-5-yl}pentadecyl Mesylate (11)**

MsCl (27 μL, 0.34 mmol) was added to a soln of oxazolidinone **10** (100 mg, 0.17 mmol) in pyridine (3 mL) at r.t. and the mixture was stirred for 12 h at r.t. The reaction was quenched by slow addition of $H_2O$, and the aqueous layer was extracted with EtOAc. The organic phases were combined, washed with brine, dried ($Na_2SO_4$), filtered, and concentrated in vacuo. The residue was purified by flash chromatography [silica gel, hexanes–EtOAc (2:1)] to give a yellowish oil; yield: 106 mg (95%); $[\alpha]_D^{24}$ –13.1 (*c* 1.0, $CHCl_3$).

IR ($CHCl_3$): 3267, 2925, 2853, 1763, 1598, 1491, 1448, 1358, 1220, 1176 cm$^{-1}$.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.3 Hz, 3 H), 1.12–1.47 (m, 24 H), 1.48–1.76 (m, 2 H), 2.76 (s, 3 H), 3.28 (dd, *J* = 7.8, 9.9 Hz, 1 H), 3.38 (dd, *J* = 3.9, 9.9 Hz, 1 H), 4.06 (dt, *J* = 4.1, 7.6 Hz, 1 H), 4.72 (dd, *J* = 5.0, 8.0 Hz, 1 H), 4.78–4.86 (m, 1 H), 5.72–5.90 (m, 1 H, NH), 7.19–7.33 (m, 9 H), 7.34–7.42 (m, 6 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.6, 24.4, 29.1, 29.27, 29.30, 29.47, 29.53, 29.60, 29.62, 30.6, 31.9, 38.6, 54.6, 62.2, 77.7, 79.0, 87.6, 127.4, 128.0, 128.2, 128.5, 143.0, 157.9.

HRMS-FAB: *m/z* $[M + H]^+$ calcd for $C_{39}H_{54}NO_6S$: 664.3672; found: 664.3636.

**(4*S*,5*S*)-4-(Hydroxymethyl)-5-[(1*R*)-1-hydroxypentadecyl]-1,3-oxazolidin-2-one (12)**

$BF_3{\cdot}OEt_2$ (43 μL, 0.34 mmol) was added to a soln of oxazolidinone **10** (100 mg, 0.17 mmol) in toluene (3 mL) and MeOH (1 mL) at r.t. and the mixture was stirred for 12 h at r.t. The reaction was quenched by slow addition of sat. aq $NaHCO_3$, and the aqueous layer was extracted with EtOAc. The organic phases were combined, washed with brine, dried ($Na_2SO_4$), filtered, and concentrated in vacuo. The residue was purified by flash chromatography [silica gel, hexanes–EtOAc (1:1)] to give a white solid; yield: 53 mg (90%); $[\alpha]_D^{24}$ –39.9 (*c* 0.5, $CHCl_3$).

IR ($CHCl_3$): 3340, 2917, 2850, 1717, 1691, 1054, 941, 705 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.2 Hz, 3 H), 1.26–1.48 (m, 24 H), 1.49–1.62 (m, 1 H), 1.65–1.78 (m, 1 H), 3.66 (dd, *J* = 5.1, 11.4 Hz, 1 H), 3.77 (dd, *J* = 5.6, 11.4 Hz, 1 H), 3.83–3.92 (m, 2 H), 4.32–4.40 (m, 1 H).

$^{13}$C NMR [75 MHz, $CDCl_3$–$CD_3OD$ (1:3)]: δ = 15.2, 24.3, 26.5, 31.0, 31.29, 31.32, 31.34, 33.6, 35.9, 58.0, 62.0, 69.9, 82.9, 162.1.

HRMS-FAB: *m/z* $[M + H]^+$ calcd for $C_{19}H_{38}NO_4$: 344.2801; found: 344.2815.

**(3a*S*,6*S*,6a*S*)-6-Tetradecyltetrahydrofuro[3,4-*d*][1,3]oxazol-2(3*H*)-one (3)**

$BF_3{\cdot}OEt_2$ (30 μL, 0.24 mmol) was added to a soln of mesylate **11** (80 mg, 0.12 mmol) in toluene (3 mL) and MeOH (1 mL) at r.t., and the mixture was stirred for 12 h at r.t. The reaction was quenched by slow addition of sat. aq $NaHCO_3$, and the aqueous layer was extracted with EtOAc. The organic phases were combined, washed with brine, dried ($Na_2SO_4$), and concentrated in vacuo. The residue was purified by flash column chromatography [silica gel, $CH_2Cl_2$–MeOH (15:1)] to give a white solid; yield: 35 mg (90%); $[\alpha]_D^{24}$ +57.5 (*c* 0.5, $CHCl_3$).

IR ($CHCl_3$): 3330, 3240, 2952, 2925, 2847, 1759, 1720, 1463, 1406, 1321 cm$^{-1}$.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.8 Hz, 3 H), 1.18–1.48 (m, 24 H), 1.67–1.82 (m, 2 H), 3.45–3.54 (m, 2 H), 3.93 (d, *J* = 10.5 Hz, 1 H), 4.35 (dd, *J* = 4.1, 7.7 Hz, 1 H), 4.93 (dd, *J* = 3.8, 7.4 Hz, 1 H), 6.09 (br s, 1 H, NH).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.7, 26.0, 28.1, 29.3, 29.47, 29.54, 29.61, 29.63, 29.65, 31.9, 57.1, 63.9, 73.3, 77.2, 159.3.

HRMS-FAB: *m/z* $[M + H]^+$ calcd for $C_{19}H_{36}NO_3$: 326.2695; found: 326.2706.

**(3a*S*,6*R*,6a*S*)-6-Tetradecyltetrahydrofuro[3,4-*d*][1,3]oxazol-2(3*H*)-one (4)**

DMAP (5 mg, 0.05 mmol) and TosCl (335 mg, 1.75 mmol) were added to a soln of diol **12** (200 mg, 0.60 mmol) in pyridine (10 mL) at r.t. The mixture was refluxed for 12 h then cooled to r.t. The reaction was quenched by slow addition of $H_2O$, and the aqueous layer was extracted with EtOAc. The organic phases were combined, washed with brine, dried over $Na_2SO_4$, filtered, and concentrated in vacuo. The residue was purified by flash chromatography [silica gel, $CH_2Cl_2$–MeOH (10:1)] to give a white solid; yield: 36 mg (94%); $[\alpha]_D^{24}$ +8.2 (*c* 0.5, $CHCl_3$).

IR ($CHCl_3$): 3249, 2954, 2920, 2850, 1758, 1728, 1703, 1469, 1408, 1250 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.8 Hz, 3 H), 1.19–1.55 (m, 26 H), 3.75 (dd, *J* = 2.5, 10.2 Hz, 1 H), 3.92 (dd, *J* = 4.9, 10.2 Hz, 1 H), 4.01–4.06 (m, 1 H), 4.30–4.34 (m, 1 H), 4.69 (dd, *J* = 2.3, 8.1 Hz, 1 H), 5.63 (br s, 1 H, NH).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.7, 25.4, 29.27, 29.35, 29.45, 29.51, 29.61, 29.64, 29.7, 30.6, 31.9, 56.3, 63.0, 72.6, 77.2, 84.0, 84.2, 158.7.

HRMS-FAB: *m/z* $[M + H]^+$ calcd for $C_{19}H_{36}NO_3$: 326.2695; found: 326.2674.

**(2*S*,3*S*,4*S*)-4-Amino-2-tetradecyltetrahydrofuran-3-ol [(+)-Pachastrissamine] (1)**

1.0 M aq KOH (1 mL) was added to a soln of oxazolone **3** (20 mg, 0.06 mmol) in EtOH (1 mL) at r.t. The mixture was refluxed for 12 h, cooled to r.t., concentrated, and azeotropically dried with MeOH (3 × 5 mL) and toluene (3 × 5 mL). The residue was purified by flash column chromatography [silica gel, $CH_2Cl_2$–MeOH–$NH_4OH$ (100:10:1)] to give a white solid; yield: 13.3 mg (72%); $[\alpha]_D^{24}$ +23.2 (*c* 1.0, MeOH).

IR ($CHCl_3$): 3420, 2917, 2851, 1474 $cm^{-1}$.

$^1H$ NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.6 Hz, 3 H), 1.24–1.60 (m, 26 H), 2.13 (br s, 3 H), 3.39 (dd, *J* = 6.9, 8.4 Hz, 1 H), 3.45 (m, 1 H), 3.60 (dd, *J* = 5.1, 10.8 Hz, 1 H), 3.62 (m, 1 H), 4.11 (dd, *J* = 6.0, 8.4 Hz, 1 H).

$^{13}C$ NMR (75 MHz, CDCl3): δ = 14.1, 22.7, 26.3, 29.3, 29.4, 29.57, 29.59, 29.7, 29.8, 31.9, 54.3, 71.8, 72.3, 83.2.

HRMS-FAB: *m/z* $[M + H]^+$ calcd for $C_{18}H_{38}NO_2$: 300.2903; found: 300.2923.

**(2*R*,3*S*,4*S*)-4-Amino-2-tetradecyltetrahydrofuran-3-ol (2-*epi*-Pachastrissamine) (2)**

1.0 M aq KOH (1 mL) was added to a soln of oxazolone **4** (20 mg, 0.06 mmol) in EtOH (1 mL) at r.t. The mixture was refluxed for 12 h, cooled to r.t., concentrated, and azeotropically dried with MeOH (3 × 5 mL) and toluene (3 × 5 mL). The residue was purified by flash column chromatography [silica gel, $CH_2Cl_2$–MeOH–$NH_4OH$ (100:10:1)] to give a white solid; yield: 13.3 mg (72%); $[\alpha]_D^{24}$ +38.4 (*c* 1.0, $CHCl_3$).

IR (CHCl3): 3336, 3277, 3096, 2952, 2916, 2849, 1739, 1596, 1469, 1370 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.8 Hz, 3 H), 1.15–1.34 (m, 22 H), 1.35–1.47 (m, 2 H), 1.48–1.62 (m, 2 H), 3.35–3.41 (m, 1 H), 3.41–3.50 (m, 1 H), 3.55–3.62 (m, 2 H), 4.11 (dd, *J* = 6.4, 8.8 Hz, 1 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 25.9, 29.4, 29.56, 29.59, 29.66, 29.67, 31.9, 33.7, 52.6, 73.2, 74.8, 77.2, 85.2.

HRMS-FAB: *m/z* $[M + H]^+$ calcd for $C_{18}H_{38}NO_2$ 300.2903; found: 300.2892.

## Acknowledgment

This work was supported by the SRC/ERC program (R-11-2007-107-02001-0) and the Basic Science Research Program (2011-0014370) through the National Research Foundation of Korea (NRF) funded by the Korean government (MEST). We are grateful to the Research Institute of Pharmaceutical Sciences at Seoul National University for providing some experimental equipment.

**Supporting Information** for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

## References

(1) Bhaket, P.; Morris, K.; Stauffer, C. S.; Datta, A. *Org. Lett.* **2005**, *7*, 875.
(2) Abraham, E.; Davies, S. G.; Roberts, P. M.; Russell, A. J.; Thomson, J. E. *Tetrahedron: Asymmetry* **2008**, *19*, 1027.
(3) (a) Sudhakar, N.; Kumar, A. R.; Prabhakar, A.; Jagadeesh, B.; Rao, B. V. *Tetrahedron Lett.* **2005**, *46*, 325. (b) van den Berg, R.; Boltje, T.; Verhagen, C.; Litjens, R.; van der Marel, G.; Overkleeft, H. *J. Org. Chem.* **2006**, *71*, 836. (c) Du, Y.; Liu, J.; Linhardt, R. J. *J. Org. Chem.* **2006**, *71*, 1251. (d) Liu, J.; Du, Y.; Dong, X.; Meng, S.; Xiao, J.; Cheng, L. *Carbohydr. Res.* **2006**, *341*, 2653. (e) Ribes, C.; Falomir, E.; Carda, M.; Marco, J. A. *Tetrahedron* **2006**, *62*, 5421. (f) Lee, T.; Lee, S.; Kwak, Y. S.; Kim, D.; Kim, S. *Org. Lett.* **2007**, *9*, 429. (g) Reddy, L. V. R.; Reddy, P. V.; Shaw, A. K. *Tetrahedron: Asymmetry* **2007**, *18*, 542. (h) Ramana, C. V.; Giri, A. G.; Suryawanshi, S. B.; Gonnade, R. G. *Tetrahedron Lett.* **2007**, *48*, 265. (i) Prasad, K. R.; Chandrakumar, A. *J. Org. Chem.* **2007**, *72*, 6312. (j) Abraham, E.; Candela-Lena, J. I.; Davies, S. G.; Georgiou, M.; Nicholson, R. L.; Roberts, P. M.; Russell, A. J.; Sánchez-Fernández, E. M.; Smith, A. D.; Thomson, J. E. *Tetrahedron: Asymmetry* **2007**, *18*, 2510. (k) Yakura, T.; Sato, S.; Yoshimoto, Y. *Chem. Pharm. Bull.* **2007**, *55*, 1284. (l) Abraham, E.; Brock, E. A.; Candela-Lena, J. I.; Davies, S. G.; Georgiou, M.; Nicholson, R. L.; Perkins, J. H.; Roberts, P. M.; Russell, A. J.; Sánchez-Fernández, E. M.; Scott, P. M.; Smith, A. D.; Thomson, J. E. *Org. Biomol. Chem.* **2008**, *6*, 1665. (m) Passiniemi, M.; Koskinen, A. M. P. *Tetrahedron Lett.* **2008**, *49*, 980. (n) Venkatesan, K.; Srinivasan, K. V. *Tetrahedron: Asymmetry* **2008**, *19*, 209. (o) Enders, D.; Terteryan, V.; Paleček, J. *Synthesis* **2008**, 2278. (p) Ichikawa, Y.; Matsunaga, K.; Masuda, T.; Kotsuki, H.; Nakano, K. *Tetrahedron* **2008**, *64*, 11313. (q) Canals, D.; Mormeneo, D.; Fabriàs, G.; Llebaria, A.; Casas, J.; Delgado, A. *Bioorg. Med. Chem.* **2009**, *17*, 235. (r) Reddipalli, G. S.; Venkataiah, M.; Mishra, M. K.; Fadnavis, N. W. *Tetrahedron: Asymmetry* **2009**, *20*, 1802. (s) Inuki, S.; Yoshimitsu, Y.; Oishi, S.; Fujii, N.; Ohno, H. *Org. Lett.* **2009**, *11*, 4478. (t) Jayachitra, G.; Sudhakar, N.; Anchoori, R. K.; Rao, B. V.; Roy, S.; Banerjee, R. *Synthesis* **2010**, 115. (u) Vichare, P.; Chattopadhyay, A. *Tetrahedron: Asymmetry* **2010**, *21*, 1983. (v) Inuki, S.; Yoshimitsu, Y.; Oishi, S.; Fujii, N.; Ohno, H. *J. Org. Chem.* **2010**, *75*, 3831. (w) Yoshimitsu, Y.; Inuki, S.; Oishi, S.; Fujii, N.; Ohno, H. *J. Org. Chem.* **2010**, *75*, 3843. (x) Urano, H.; Enomoto, M.; Kuwahara, S. *Biosci., Biotechnol., Biochem.* **2010**, *74*, 152. (y) Salma, Y.; Ballereau, S.; Maaliki, C.; Ladeira, S.; Andrieu-Abadie, N.; Génnison, Y. *Org. Biomol. Chem.* **2010**, *8*, 3227. (z) Passiniemi, M.; Koskinen, A. M. P. *Org. Biomol. Chem.* **2011**, *9*, 1774. (aa) Llaveria, J.; Díaz, Y.; Matheu, M. I.; Castillón, S. *Eur. J. Org. Chem.* **2011**, 1514. (ab) Sriniavas Rao, G.; Venkateswara Rao, B. *Tetrahedron Lett.* **2011**, *52*, 6076. (ac) Prasad, K. R.; Penchalaiah, K. *Tetrahedron: Asymmetry* **2011**, *22*, 1400. (ad) Lee, H.-J.; Lim, C.-M.; Hwang, S.-H.; Jeong, B.-S.; Kim, S. *Chem.–Asian J.* **2011**, *6*, 1943. (ae) Cruz-Gregorio, S.; Espinoza-Rojas, C.; Quintero, L.; Sartillo-Piscil, F. *Tetrahedron Lett.* **2011**, *52*, 6370. (af) Zhao, M.-L.; Zhang, E.; Gao, J.; Zhang, Z.; Zhao, Y.-T.; Qu, W.; Liu, H.-M. *Carbohydr. Res.* **2012**, *351*, 126.
(4) Sánchez-Eleuterio, A.; Quintero, L.; Sartillo-Piscil, F. *J. Org. Chem.* **2011**, *76*, 5466.
(5) Because syntheses of oxazolidinone **3** were reported independently by Yakura (2007), Ichikawa (2008), and our group (2011), spectroscopic data for the oxazolidinone structure **3** of pachastrissamine were not available until 2007; see references 3k, 3p, and 3ad.
(6) The first synthesis of oxazolidinone **4** was reported by our group in 2011. See ref. 7.
(7) Jeon, H.; Bae, H.; Baek, D. J.; Kwak, Y. S.; Kim, D.; Kim, S. *Org. Biomol. Chem.* **2011**, *9*, 7234.