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Synthesis of two piperidine alkaloids, (−)-deoxoprosopinine and (−)-deoxoprosophylline, from 6-hydroxylated dihydrosphingosine derivatives☆

Ken-ichi Fuhshuku† and Kenji Mori*

Glycosphingolipid Synthesis Group, Laboratory for Immune Regulation, RIKEN Research Center for Allergy and Immunology, Hirosawa 2-1, Wako-shi, Saitama 351-0198, Japan

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Abstract—(−)-Deoxoprosopinine **1** [(2*S*,3*R*,6*S*)-6-dodecyl-2-hydroxymethylpiperidin-3-ol] and (−)-deoxoprosophylline **3** [(2*S*,3*R*,6*R*)-6-dodecyl-2-hydroxymethylpiperidin-3-ol] were synthesized from (6*R*)- and (6*S*)-6-mesyloxydihydrosphingosine derivatives **7** and **7′**, respectively, by intramolecular cyclization to generate a piperidine ring.

1. Introduction

An African plant *Prosopis africana* produces several 2,6-disubstituted piperidin-3-ols as *Prosopis* alkaloids.[2] Their unique structures together with antibiotic and anaesthetic properties rendered the alkaloids **1**–**4** (Scheme 1) popular synthetic targets. Indeed, there have been at least 17 different syntheses reported of the enantiomers of deoxoprosopinine **1** and deoxoprosophylline **3**.[3–19] These syntheses start from the chiral building blocks of natural (amino acids,[3,7,8,12,16] malic acid,[6] vitamin C[10] and carbohydrates[5,15,18,19]) or synthetic origins.[4,9,11,13,14,17]

In continuation of our recent work on (+)-carpamic acid **5**, we became interested in synthesizing **1** and **3** by cyclization of the derivatives of sphingosine **6**. Our retrosynthetic analysis of (−)-**1** and (−)-**3** is shown in Scheme 1. The piperidine alkaloid **1** or **3** could be obtained by cyclization of **7** or **7′** to generate a new C–N bond. The 6-mesyloxylated and protected dihydrosphingosine **7** or **7′** would be prepared from the known compound **8** or **8′**, which served as the key intermediates for the synthesis of ceramides B, 4, 7 and 8, the 6-hydroxylated new ceramides in human skin.[20] The same C_{18} carbon skeleton of **1**, **3** and **8** would make the present approach especially favourable. The intermediates **8** and **8′** were previously prepared from (*S*)-Garner's aldehyde **9**[21] while the enantiomers **10** and **10′** were secured by a lipase-catalyzed asymmetric process.[20]

2. Results and discussion

Scheme 2 summarizes our synthesis of (−)-deoxoprosopinine **1** and (−)-deoxoprosophylline **3**. Coupling of (*S*)-Garner's aldehyde **9** with (*R*)-3-*tert*-butyldimethylsilyl(TBS)oxy-1-pentadecyne **10** was executed as reported previously to give (4*S*,1′*R*,4′*R*)-**8**.[20] After removal of the TBS protecting group of **8**, the resulting alkynediol **11** was hydrogenated over a palladium catalyst to give 6-hydroxylated dihydrosphingosine derivative (4*S*,1′*R*,4′*R*)-**12**. Treatment of **12** with aqueous acetic acid afforded triol (2*S*,3*R*,6*R*)-**13**. Protection of the 1,3-diol system of **13** as benzylidene acetal yielded (2*S*,4*R*,5*S*,3′*R*)-**14**, which was mesylated to furnish **7**, the precursor for cyclization.

Treatment of mesylate **7** with sodium hydride in THF smoothly effected cyclization to give crystalline (1*S*,2*S*,4*R*,6*S*)-**15** in 89% yield based on **14**. Finally, removal of the benzylidene protective group with methanolic hydrogen chloride was followed by treatment with sodium hydroxide to give (−)-deoxoprosopinine **1**, mp 87–88 °C, $[\alpha]_D^{24} = -14.3$ (*c* 0.54, $CHCl_3$). The overall yield of (−)-**1**

☆ Synthesis of sphingosine relatives, Part 29. For Part 28, see: Ref. 1.

* Corresponding author. Fax: +81 48 467 9381; e-mail: kjk-mori@arion.ocn.ne.jp

† Present address: Department of Biotechnology, Toyama Prefectural University, Toyama 939-0398, Japan.

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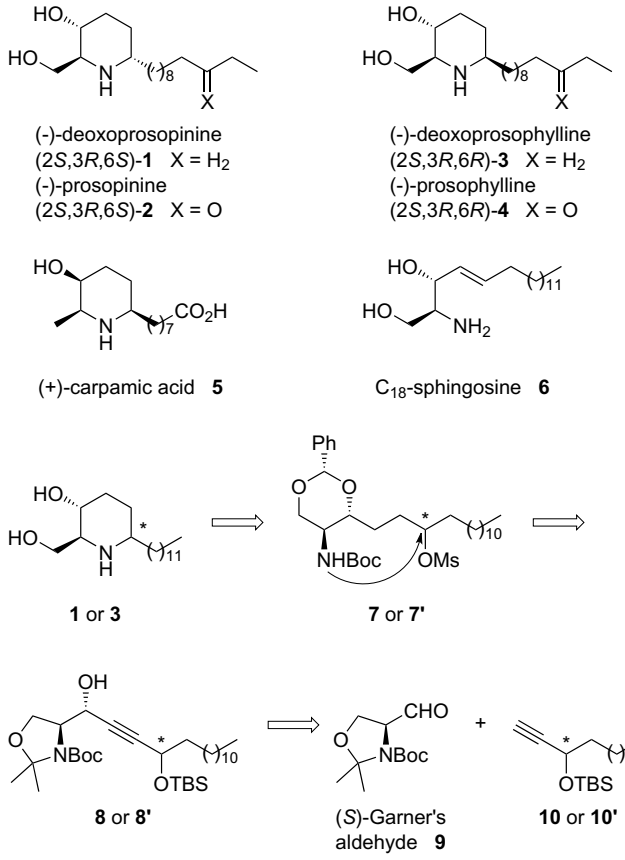
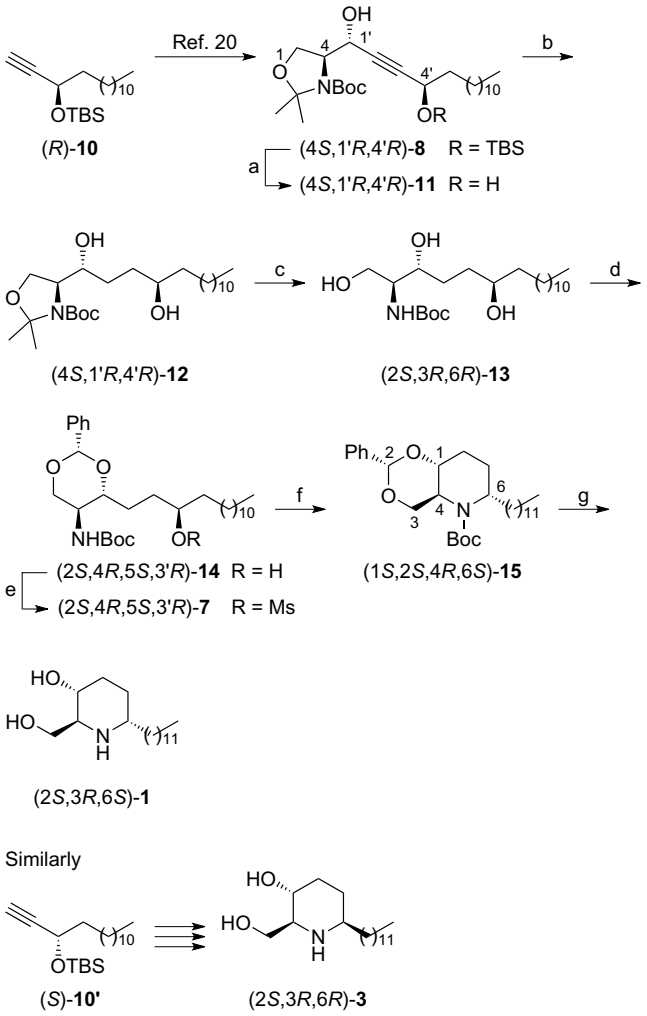


Scheme 1. Retrosynthetic analysis of (−)-deoxoprosopinine **1** and (−)-deoxoprosophylline **3**.



Scheme 2. Synthesis of (−)-deoxoprosopinine **1** and (−)-deoxoprosophylline **3**. Reagents and conditions: (a) TBAF, THF, 99%; (b) H_2, $Pd(OH)_2$/C, EtOAc, 86%; (c) AcOH–H_2O (8:2), 94%; (d) $PhCH(OMe)_2$, PPTS, CH_2Cl_2, 89%; (e) MsCl, C_5H_5N, 0 °C; (f) NaH, THF, reflux, 89% (2 steps); (g) (i) HCl in MeOH; (ii) NaOH, H_2O, 72%.

was 46% based on **8** (7 steps). In the same manner, (*S*)-**10**′ was converted to (−)-deoxoprosophylline **3**, mp 88–89 °C, $[\alpha]_D^{24} = -14.2$ (*c* 0.58, $CHCl_3$). The overall yield of (−)-**3** was 34% based on **8**′ (7 steps). The IR, ^1H and ^{13}C NMR spectra of our synthetic (−)-**1** and (−)-**3** were identical to those reported previously.[5,9,18]

3. Conclusion

A new and efficient synthesis of (−)-deoxoprosopinine **1** and (−)-deoxoprosophylline **3** was accomplished by employing the cyclization of 6-mesyloxydihydrosphingosine derivatives **7** and **7**′ as the key step. Sphingosine derivatives have proven to be versatile starting materials for the synthesis of piperidine alkaloids.

4. Experimental

4.1. General

All melting points (mp) are uncorrected. Refractive indices (n_D) were measured on an Atago 1T refractometer. Optical rotation values were measured on a Jasco DIP-1010 instrument. IR spectra were recorded on Jasco FT/IR-460 plus spectrometer. ^1H and ^{13}C NMR spectra were recorded on Jeol AL-270 (270 MHz) and AL-400 (400 MHz) ($CHCl_3$ at $\delta_H = 7.26$ and $\delta_C = 77.00$ as an internal standard). Mass spectra were recorded on JMS-SX102A. Column chromatography was carried out with Silica Gel 60 (spherical; 100–210 μm, 37558-79) purchased from Kanto Chemical Co., and thin-layer chromatography was carried out with Merck Silica Gel 60 F_{254} thin-layer plates (1.05715).

4.2. *tert*-Butyl 4-(1′,4′-dihydroxyhexadecyl)-2,2-dimethyl-3-oxazolidinecarboxylate 12 and 12′

4.2.1. (4*S*,1′*R*,4′*R*)-Isomer 12. To an ice-cooled solution of (4*S*,1′*R*,4′*R*)-**8** (3.98 g, 7.01 mmol) in dry THF (56.0 mL), a solution of TBAF (1.0 M in THF, 14.0 mL, 14.0 mmol) was added. The reaction mixture was stirred for 2 h at room temperature, and diluted with water. The mixture was extracted with EtOAc. The organic extract was washed with brine, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by silica

gel column chromatography (100 g). Elution with hexane–EtOAc (10:1 to 2:1) afforded (4*S*,1′*R*,4′*R*)-**11** (3.16 g, 99%). This compound was immediately employed for the next step without further purification. To a suspension of $Pd(OH)_2$ (0.275 g, 20% on carbon) in EtOAc (20.0 mL), **11** (2.72 g, 6.00 mmol) was added. The reaction mixture was vigorously stirred for 7 days at room temperature under a H_2 atmosphere, and filtered through a Celite pad. The filter cake was washed with EtOAc and concentrated in vacuo. The residue was purified by silica gel column chromatography (150 g). Elution with hexane–EtOAc (10:1 to 2:1) afforded **12** (2.37 g, 86%), mp 62.0–63.0 °C (colourless powder from hexane–EtOAc); $[\alpha]_D^{26} = -16.8$ (*c* 1.02, $CHCl_3$); IR (KBr) ν_{max} 3400, 1697, 1676; δ_H (270 MHz, $CDCl_3$): 0.88 (3H, t, *J* 6.6), 1.25–1.75 (41H, m), 2.80–2.97 (2H, m), 3.52–4.42 (5H, m); Anal. Calcd for $C_{26}H_{51}NO_5$: C, 68.23; H, 11.23; N, 3.06. Found: C, 68.05; H, 11.41; N, 3.05.

4.2.2. (4*S*,1′*R*,4′*S*)-Isomer 12′. In the same manner, (4*S*,1′*R*,4′*S*)-**8′** (3.12 g, 5.49 mmol) yielded 1.93 g (78%) of **12′**, mp 106.5–107.5 °C (colourless powder from hexane–EtOAc); $[\alpha]_D^{26} = -15.1$ (*c* 1.03, $CHCl_3$); IR (KBr) ν_{max} 3302, 1694; δ_H (270 MHz, $CDCl_3$): 0.88 (3H, t, *J* 6.6), 1.25–1.72 (41H, m), 3.24 (2H, m), 3.57 (2H, m) 3.73–4.43 (3H, m); Anal. Calcd for $C_{26}H_{51}NO_5$: C, 68.23; H, 11.23; N, 3.06. Found: C, 68.00; H, 11.39; N, 3.00.

4.3. 2-*tert*-Butoxycarbamidooctadecane-1,3,6-triol 13 and 13′

4.3.1. (2*S*,3*R*,6*R*)-Isomer 13. A mixture of (4*S*,1′*R*,4′*R*)-**12** (602 mg, 1.32 mmol) and AcOH (80% in water, 26.0 mL) was stirred for 24 h at room temperature and neutralized with a saturated aqueous $NaHCO_3$ solution. The mixture was extracted with $CHCl_3$. The organic extract was washed with a saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography (30 g). Elution with $CHCl_3$–MeOH (60:1 to 20:1) afforded **13** (514 mg, 94%), mp 105.0–106.0 °C (colourless powder from $CHCl_3$); $[\alpha]_D^{26} = +3.3$ (*c* 0.53, $CHCl_3$); IR (KBr) ν_{max} 3353, 1669, 1529; δ_H (270 MHz, $CDCl_3$): 0.88 (3H, t, *J* 6.6), 1.26 (20H, m), 1.45 (9H, s), 1.39–1.74 (6H, m), 3.10 (3H, br s), 3.53 (1H, br s), 3.69–3.80 (3H, m), 3.99 (1H, m), 5.37 (1H, br s); δ_C (67.5 MHz, $CDCl_3$): 14.2, 22.8, 25.9, 28.5, 29.4, 29.7, 30.1, 32.0, 33.2, 37.2, 55.0, 62.7, 71.9, 73.9, 79.8, 155.9; Anal. Calcd for $C_{23}H_{47}NO_5$: C, 66.15; H, 11.34; N, 3.35. Found: C, 65.91; H, 11.52; N, 3.33.

4.3.2. (2*S*,3*R*,6*R*)-Isomer 13′. In the same manner, (4*S*,1′*R*,4′*S*)-**12′** (298 mg, 0.651 mmol) yielded 252 mg (93%) of **13′**, mp 98.0–99.0 °C (colourless powder from $CHCl_3$); $[\alpha]_D^{26} = +5.8$ (*c* 0.53, $CHCl_3$); IR (KBr) ν_{max} 3364, 1694, 1567; δ_H (270 MHz, $CDCl_3$): 0.87 (3H, t, *J* 6.6), 1.25 (20H, m), 1.44 (9H, s), 1.38–1.75 (6H, m), 3.50 (1H, br s), 3.59–3.80 (6H, m), 3.96 (1H, m), 5.45 (1H, br s); δ_C (67.5 MHz, $CDCl_3$): 14.2, 22.8, 25.8, 28.5, 29.4, 29.7, 29.8, 31.6, 32.0, 34.4, 37.9, 55.3, 62.5, 72.6, 74.3, 79.7, 156.0; Anal. Calcd for $C_{23}H_{47}NO_5$: C, 66.15; H, 11.34; N, 3.35. Found: C, 66.04; H, 11.54; N, 3.31.

4.4. 5-*tert*-Butoxycarbamido-4-(3′-hydroxypentadecyl)-2-phenyl-1,3-dioxacyclohexane 14 and 14′

4.4.1. (2*S*,4*R*,5*S*,3′*R*)-Isomer 14. A mixture of (2*S*,3*R*,6*R*)-**13** (512 mg, 1.23 mmol), $PhCH(OMe)_2$ (368 μL, 2.45 mmol), PPTS (340 mg, 1.35 mmol) and CH_2Cl_2 (12.0 mL) was stirred for 24 h at room temperature and neutralized with a saturated aqueous $NaHCO_3$ solution. The mixture was extracted with Et_2O. The organic extract was successively washed with a saturated aqueous $NaHCO_3$ solution, water and brine, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography (25 g). Elution with hexane–EtOAc (10:1 to 3:1) afforded **14** (552 mg, 89%), mp 120.5–121.0 °C (colourless powder from hexane–EtOAc); $[\alpha]_D^{26} = +25.0$ (*c* 0.54, $CHCl_3$); IR (KBr) ν_{max} 3346, 1683, 1531; δ_H (270 MHz, $CDCl_3$): 0.88 (3H, t, *J* 6.6), 1.25 (22H, m), 1.46 (9H, s), 1.55–2.00 (5H, m), 3.46–3.73 (4H, m), 4.30 (2H, m), 5.45 (1H, s), 7.30–7.40 (3H, m), 7.46–7.49 (2H, m); δ_C (67.5 MHz, $CDCl_3$): 14.2, 22.8, 25.8, 28.0, 28.4, 28.5, 29.4, 29.71, 29.74, 32.0, 32.9, 37.5, 47.4, 69.9, 71.8, 80.0, 81.3, 101.0, 126.0, 128.2, 128.8, 137.6, 155.0; Anal. Calcd for $C_{30}H_{51}NO_5$: C, 71.25; H, 10.16; N, 2.77. Found: C, 71.02; H, 10.16; N, 2.72.

4.4.2. (2*S*,4*R*,5*S*,3′*S*)-Isomer 14′. In the same manner, (2*S*,3*R*,6*S*)-**13′** (612 mg, 1.47 mmol) yielded 646 mg (87%) of **14′**, mp 92.0–93.0 °C (colourless powder from hexane–EtOAc); $[\alpha]_D^{26} = +19.7$ (*c* 0.54, $CHCl_3$); IR (KBr) ν_{max} 3355, 1685, 1525; δ_H (270 MHz, $CDCl_3$): 0.88 (3H, t, *J* 6.6), 1.25 (22H, m), 1.45 (9H, s), 1.59–1.91 (5H, m), 3.47–3.76 (4H, m), 4.30 (2H, m), 5.45 (1H, s), 7.29–7.40 (3H, m), 7.45–7.49 (2H, m); δ_C (67.5 MHz, $CDCl_3$): 14.2, 22.8, 25.8, 27.8, 28.4, 28.5, 29.4, 29.72, 29.74, 29.8, 32.0, 32.6, 37.8, 46.9, 69.9, 71.5, 80.1, 80.9, 101.1, 126.0, 128.2, 128.9, 137.6, 155.1; Anal. Calcd for $C_{30}H_{51}NO_5$: C, 71.25; H, 10.16; N, 2.77. Found: C, 71.23; H, 10.21; N, 2.67.

4.5. *tert*-Butyl 6-dodecyl-2-phenylhexahydro[1,3]dioxino-[5,4-*b*]pyridine-5-carboxylate 15 and 15′

4.5.1. (1*S*,2*S*,4*R*,6*S*)-Isomer 15. To an ice-cooled solution of (2*S*,4*R*,5*S*,3′*R*)-**14** (552 mg, 1.09 mmol) in dry pyridine (9.0 mL), MsCl (340 μL, 4.39 mmol) was added in one portion. The reaction mixture was stirred for 48 h at 4 °C and diluted with water. The mixture was extracted with Et_2O. The organic extract was washed with a saturated aqueous $CuSO_4$ solution, water, a saturated aqueous $NaHCO_3$ solution and brine, dried over anhydrous $MgSO_4$ concentrated in vacuo. The residual **7** was dissolved in dry THF (10.0 mL), cooled to 0 °C, and NaH added (60% in mineral oil, 135 mg, 3.38 mmol). The reaction mixture was stirred at reflux for 48 h and diluted with water. The mixture was extracted with Et_2O. The organic extract was washed with brine, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography (30 g). Elution with hexane–EtOAc (30:1 to 10:1) afforded **15** (474 mg, 89%, 2 steps), mp 81.0–82.0 °C (colourless needles from hexane–EtOAc); $[\alpha]_D^{26} = -24.3$ (*c* 0.54, $CHCl_3$); IR (KBr) ν_{max} 1699; δ_H

(270 MHz, $CDCl_3$): 0.89 (3H, t, *J* 6.6), 1.27 (22H, m), 1.46 (9H, s), 1.41–1.98 (4H, m), 3.33 (1H, ddd, *J* 4.6, 9.9, 9.9), 3.67 (1H, ddd, *J* 4.9, 9.6, 9.6), 4.32 (1H, br s), 4.45 (1H, dd, *J* 10.9, 10.9), 4.83 (1H, dd, *J* 4.0, 11.2), 5.57 (1H, s), 7.29–7.40 (3H, m), 7.47–7.52 (2H, m); δ_C (67.5 MHz, $CDCl_3$): 14.2, 22.8, 26.0, 26.4, 26.5, 28.5, 29.4, 29.6, 29.7, 32.0, 52.3, 52.7, 70.7, 78.3, 80.1, 101.1, 126.0, 128.2, 128.8, 137.9, 154.6; HRMS (FAB): $[M+H]^+$ calcd for $C_{30}H_{49}NO_4{}^+$, 487.3662; found, 487.3660.

4.5.2. (1*S*,2*S*,4*R*,6*R*)-Isomer 15′. In the same manner, (2*S*,4*R*,5*S*,3′*S*)-**14** (304 mg, 0.601 mmol) yielded 201 mg (69%, 2 steps) of **15′** as a colourless oil, $n_D^{26} = 1.4960$; $[\alpha]_D^{26} = -24.3$ (*c* 0.54, $CHCl_3$); IR (KBr) ν_{max} 1696; δ_H (270 MHz, $CDCl_3$): 0.89 (3H, t, *J* 6.6), 1.27 (20H, m), 1.48 (9H, s), 1.44–1.79 (4H, m), 2.01–2.15 (2H, m), 3.51–3.65 (2H, m), 4.01 (1H, m), 4.16 (1H, ddd, *J* 5.6, 10.2, 10.2), 4.92 (1H, m), 5.57 (1H, s), 7.30–7.41 (3H, m), 7.48–7.52 (2H, m); δ_C (67.5 MHz, $CDCl_3$): 14.7, 23.2, 24.3, 24.6, 27.7, 29.0, 29.9, 30.13, 30.17, 30.21, 32.4, 39.0, 52.3, 54.3, 72.2, 76.5, 80.6, 102.4, 126.6, 128.7, 129.3, 138.2, 156.3; HRMS (FAB): $[M+H]^+$ calcd for $C_{30}H_{49}NO_4{}^+$, 487.3662; found, 487.3665.

4.6. 6-Dodecyl-2-hydroxymethylpiperidin-3-ol 1 and 3

4.6.1. (2*S*,3*R*,6*S*)-Isomer, (−)-deoxoprosopinine 1. A mixture of (1*S*,2*S*,4*R*,6*S*)-**15** (77.4 mg, 0.159 mmol) and dry HCl (10% in MeOH, 3.2 mL) was stirred for 48 h at room temperature and concentrated in vacuo. The residue was mixed with a solution of NaOH (15% in water, 3.2 mL) and stirred for 3 h at room temperature. The mixture was extracted with CH_2Cl_2, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography (2 g). Elution with toluene–EtOH (1:0 to 6:1) afforded (−)-deoxoprosopinine **1** (34.0 mg, 72%), mp 87.0–88.0 °C (colourless needles from $CHCl_3$) (Ref. 5: mp 89.0–89.5 °C); $[\alpha]_D^{24} = -14.3$ (*c* 0.54, $CHCl_3$) {Ref. 5: $[\alpha]_D^{21.5} = -15.9$ (*c* 0.28, $CHCl_3$)}; IR (KBr) ν_{max} 3372, 3114, 2920, 2849, 1451, 1055; δ_H (400 MHz, $CDCl_3$): 0.88 (3H, t, *J* 6.5, Me), 1.26 (22H, m, 1′, 2′, 3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′, 11′-H_2), 1.45–1.79 (4H, m, 4, 5-H_2), 2.08 (3H, br s, OH × 2, NH), 2.77 (1H, m, 6-H), 2.88 (1H, m, 2-H), 3.54 (1H, m, 3-H), 3.61 (1H, dd, *J* 5.6, 10.6, 2-CHH–OH), 3.66 (1H, dd, *J* 8.0, 10.4, 2-CHH–OH); δ_C (100 MHz, $CDCl_3$): 14.2, 22.8, 26.5, 27.4, 28.7, 29.4, 29.7, 29.8, 32.0, 34.0, 49.8, 58.0, 62.3, 68.1; HRMS (FAB): $[M+H]^+$ calcd for $C_{18}H_{37}NO_2{}^+$, 299.2824; found, 299.2826.

4.6.2. (2*S*,3*R*,6*R*)-Isomer, (−)-deoxoprosophylline 3. In the same manner, (1*S*,2*S*,4*R*,6*R*)-**15′** (80.4 mg, 0.165 mmol) yielded 38.6 mg (78%) of **3**, mp 88.0–89.0 °C (colourless needles from $CHCl_3$) (Ref. 5: mp 90.5 °C); $[\alpha]_D^{24} = -14.2$ (*c* 0.58, $CHCl_3$) {Ref. 5: $[\alpha]_D^{21} = -13.9$ (*c* 0.25, $CHCl_3$)}; IR (KBr) ν_{max} 3267, 2922, 2850, 1468, 1059; δ_H (400 MHz, $CDCl_3$): 0.88 (3H, t, *J* 6.5, Me), 1.12 (1H, dddd, *J* 3.4, 13.3, 13.3, 13.3, 5-H), 1.25–1.43 (23H, m, 4-H, 1′, 2′, 3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′, 11′-H_2), 1.74 (1H, m, 5-H), 2.04 (1H, dd, *J* 3.6, 12.3, 4-H), 2.19 (3H, br s, OH × 2, NH), 2.52–2.59 (2H, m, 2, 6-H), 3.46 (1H, ddd, *J* 4.6, 9.1, 10.6, 3-H), 3.70 (1H, dd, *J* 5.3, 10.9, 2-C*H*H–OH), 3.83 (1H, dd, *J* 4.8, 10.6, 2-CH*H*–OH); δ_C (100 MHz, $CDCl_3$): 14.2, 22.8, 26.3, 29.4, 29.69, 29.74, 29.9, 31.3, 32.0, 34.0, 36.7, 56.0, 63.2, 64.8, 70.8; HRMS (FAB): $[M+H]^+$ calcd for $C_{18}H_{37}NO_2{}^+$, 299.2824; found, 299.2824.

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