Enantioselective Synthesis of (−)-Dendroprimine and Isomers

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An enantioselective and diastereoselective synthesis of six 5,7-dimethylindolizidine isomers is described via an intramolecular cyclization that involves an allylsilyl nucleophilic group and an acyliminium ion. The first total synthesis of naturally occurring (−)-dendroprimine has been achieved in five steps.

(−)-Dendroprimine (**10a**) is an alkaloid isolated from *Dendrobium primulinum* Lindl (*Orchidaceae*) and shown to be a 5,7-dimethylindolizidine.[1] Its relative configuration was determined after the synthesis of the four racemic diastereomers of this indolizidine, and a conformational analysis of these diastereomers has been discussed.[2] Its identification as (5*R*,7*S*,9*R*)-5,7-dimethylindolizidine has been firmly established.[3] Its asymmetric synthesis has never been reported; only (−)-(5*R*,7*S*,9*S*)-9-*epi*-dendroprimine has been synthesized.[4]

In a previous publication we have described the enantioselective synthesis of indolizidine alkaloid (−)-167B.[5] The key step in the synthesis was an intramolecular cyclization of acyliminium ion substituted by an allylsilyl side chain as an internal π-nucleophile. This reaction has proved to be a very powerful method for elaboration of the indolizidine ring system. We describe here application of this methodology to the enantioselective synthesis of (−)-dendroprimine and its isomers.

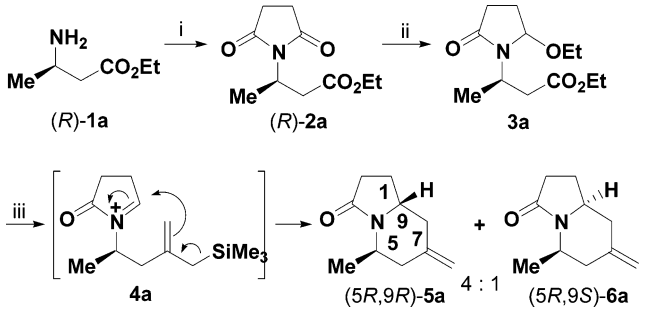
Results and Discussion

The first steps of our synthesis were carried out as shown in Scheme 1. The starting material was ethyl-2-aminopropanoate (**1**). Chirality was introduced with isomers (*R*)-**1a** and (*S*)**-1b**, which were prepared by a Michael reaction according to Davies' procedure from ethyl crotonate and respectively (*R*)- and (*S*)-*N*-benzyl-α-methylbenzylamine.[6]

Reaction of **1a** with succinic anhydride and then with acetyl chloride in refluxing toluene gave imide **2a** in quantitative yield. Imide **2a** was reduced into ethoxylactam **3a** in 65% isolated yield. Ethoxylactam **3b**, the enantiomer of **3a**, was synthesized in the same way from (*S*)-**1b**. These compounds were isolated as a mixture of two diastereomers, which were not separated.

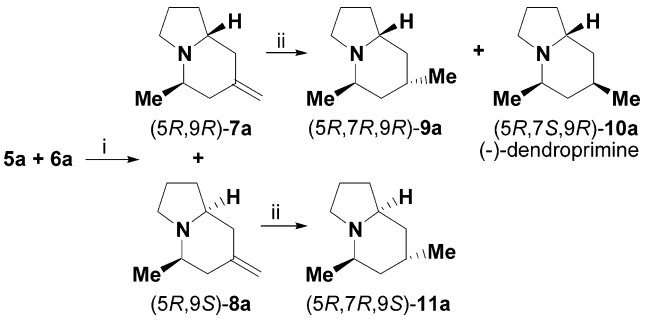
The intramolecular cyclization reaction was performed in the next step. Ethoxylactam **3a** was treated with the cerium reagent derived from trimethylsilylmethylmagnesium chloride and cerium chloride. The mixture was then hydrolyzed with 1 N HCl to give methyleneindolizidinones **5a** and **6a** in a 4:1 ratio and 90% yield. These diastereoisomers could not be separated. Their relative configuration was deduced from their NMR spectra, by comparison with 5-propyl analogues.[5] This reaction involved formation of allylsilyl-substituted acyliminium ion **4a**, which cyclized spontaneously. In the same way, ethoxylactam **3b** was also reacted with trimethylsilylmethylmagnesium chloride and $CeCl_3$ to give a mixture of cyclization products (5*S*,9*S*)-**5b** and (5*S*,9*R*)-**6b**.

Scheme 1[a]



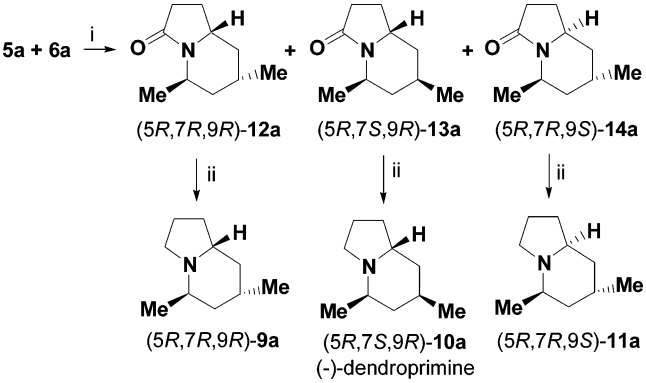
[a] (i) Succinic anhydride, AcCl, toluene, reflux; (ii) $NaBH_4$, H_2SO_4/EtOH, −30 °C; (iii) Me_3SiCH_2MgCl, $CeCl_3$, HCl.

Scheme 2[a]



[a] (i) $LiAlH_4$, THF; (ii) H_2, Pd/C or PtO_2.

Scheme 3[a]



[a] (i) H_2, Pd/C or PTO_2; (ii) $LiAlH_4$, THF.

Two ways were then studied to prepare dendroprimine and isomers. They are summarized in Schemes 2 and 3.

According to Scheme 2, in a first step, reduction of the lactam functional group of cyclization products **5a** and **6a** with lithium aluminum hydride afforded a 4:1 mixture of methyleneindolizidines **7a** and **8a** in quantitative yield.

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These isomers were separated by flash column chromatography to give **7a** and **8a** in 50 and 18% yields, respectively. Enantiomers (5*S*,9*S*)-**7b** and (5*S*,9*R*)-**8b** were also prepared from a crude mixture of methyleneindolizidinones (5*S*,9*S*)-**5b** and (5*S*,9*R*)-**6b**.

Catalytic hydrogenation of the olefinic bond of these isomers was subsequently studied.

Palladium-catalyzed hydrogenation of **7a** was found to be stereoselective, giving a mixture of **9a** and **10a** in a 3:1 ratio. A similar stereoselectivity was observed (**9a**/**10a** = 2:1) when hydrogenation was catalyzed over platinum oxide. The major isomer was attributed a configuration that corresponds to a *trans* orientation of the methyl groups. Flash column chromatography afforded **9a** in 70% yield. Catalytic hydrogenation of **8a** over either palladium on carbon or platinum oxide gave one isomer in quantitative yield. We have assigned to this isomer the structure of compound **11a**, in which the methyl groups have a *trans* orientation. The reaction proceeded with excellent diastereoselectivity (>90%), as the C-7 diastereomer of **11a** was only detected as a minor component in the crude reaction mixture. Synthesis of enantiomers (5*S*,7*S*,9*S*)-**9b** and (5*S*,7*S*,9*R*)-**11b** was achieved in 50 and 15% isolated yields, respectively, from the product of catalytic hydrogenation over palladium on carbon of a crude mixture of diastereomers **7b** and **8b** (**7b**/**8b** = 4:1).

Another way was studied to prepare these compounds. Hydrogenation of the double bond of methylene lactam isomers was first studied, then the lactam functional group was reduced. This procedure is summarized in Scheme 3.

Hydrogenation of a crude mixture of cyclization prducts **5a** and **6a** (**5a**/**6a** = 4:1) over palladium on carbon provided a mixture of lactams **12a**, **13a**, and **14a** in which isomer **12a** was preponderant (**12a**/**13a**/**14a** = 50:30:20), whereas in hydrogenation over platinum oxide lactam **13a** was formed as the major isomer (**12a**/**13a**/**14a** = 15:65:20). Flash column chromatography gave pure **14a** in 18% yield, but **12a** and **13a** could not be separated (50% yield). A mixture of the three isomers was used without purification for the next step.

The last step was reduction of the lactam functional group with lithium aluminum hydride. A crude mixture of lactam isomers (**12a**/**13a**/**14a** = 15:65:20) was quantitatively converted to the corresponding indolizidines (**9a**/**10a**/**11a** = 15:65:20), which were separated by flash column chromatography. Pure **10a** was obtained in 30% yield. The specific rotation found for **10a** ($[\alpha]^{25}_D$ −37.5 (*c* 1.3, $CHCl_3$)) was in agreement with the literature value[1] for (−)-dendroprimine ($[\alpha]_D$ −38 (*c* 1.00, $CHCl_3$)), thus confirming the stereochemistry attributed to hydrogenation products.

Enantiomer (5*S*,7*R*,9*S*)-**10b** was prepared from a crude mixture of (5*S*,9*S*)-**5b** and (5*S*,9*R*)-**6b** (**5b**/**6b** = 4:1) after catalytic hydrogenation over platinum oxide, reduction of the lactam functional group, and purification by flash column chromatography.

In conclusion, we have developed a concise method for the enantioselective synthesis of six enantiomers of 5,7-dimethylindolizidine, starting from readily available materials. The key step in the synthesis is a stereoselective intramolecular cyclization that involves an allylsilyl nucleophilic group and an acyliminium ion. The other steps are functional group transformations. By proper choice of reactions and hydrogenation conditions either (−)-dendroprimine **10a** or its 7-*epi*-isomer **9a** could be obtained. These isomers and their enantiomers **10b** and **9b** were prepared in five steps with overall yields of 17 and 20%, respectively. Synthesis of diastereomer **11a** and enantiomer **11b** was also achieved in five steps, with 10% overall yield. These results constitute the first total synthesis of naturally occurring (−)-dendroprimine.

Experimental Section

General Experimental Procedures. Optical rotations were recorded on a Jasco model DIP-370 polarimeter. ^1H (400.13 MHz) and ^{13}C (100.61 MHz) NMR spectra were recorded on a Bruker AC 400 spectrometer. Chemical shifts are measured as δ values (ppm). TLC analyses were performed on Merck 60 F_{254} silica gel plates and were visualized using iodine. Flash column chromatography was carried out using Merck silica gel (grade 60, 230−400 mesh).

***N*-(1-Methyl-2-ethoxycarbonylethyl)succinimide (2a).** A solution of **1a** (13.1 g, 0.1 mol) and succinic anhydride (11 g, 0.11 mol) in toluene (300 mL) was refluxed for 24 h. Then acetyl chloride (29 mL, 0.4 mol) was added, and the solution was refluxed for 5 h. The solvent was removed in vacuo, and the resulting mixture was taken up with 100 mL of methylene chloride and washed with 10% HCl (50 mL), 10% NaOH (50 mL), and then with water (50 mL). The organic layer was dried and concentrated in vacuo. Imide **2a** was isolated with a quantitative yield and was used in the next step without purification: $[\alpha]^{25}_D$ −1.0 (*c* 1.9, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 4.56 (1H, m), 4.08 (2H, m), 3.05 (1H, dd, *J* = 16.1, 9.7 Hz), 2.59 (1H, dd, *J* = 16.1, 5.6 Hz), 2.57 (4H, s), 1.32 (3H, d, *J* = 7.0 Hz), 1.16 (3H, t, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 177.1 (C), 170.7 (C), 60.5 (CH_2), 44.0 (CH), 36.8 (CH_2), 27.9 (CH_2), 17.7 (CH_3), 14.0 (CH_3); *anal.* C 56.50%, H 7.26%, N 6.79%, calcd for $C_{10}H_{15}NO_4$, C 56.34%, H 7.04%, N 6.57%.

(*S*)-2b: $[\alpha]^{25}_D$ +1.1 (*c* 1.6, $CHCl_3$).

5-Ethoxy-*N*-(1-methyl-2-ethoxycarbonylethyl)pyrrolidin-2-one (3a). $NaBH_4$ (1.9 g, 0.05 mol) was slowly added to a solution of **2a** (2.13 g, 0.01 mol) in anhydrous ethanol (100 mL) at −10 °C under argon. After stirring for 15 min, 10 drops of a 2 N solution of HCl in ethanol were added every 15 min during 2 h. The $NaBH_4$ excess was destroyed by adding a 2 N solution of HCl in ethanol until pH = 3. Then, the solvent was removed and the residue, taken up with methylene chloride, was washed with 100 mL of saturated aqueous $NaHCO_3$. The organic layer was dried and concentrated in vacuo. The resulting oil (2.1 g) was purified by column chromatography on silica gel (ethyl ether/pentane, 8:2) to give **3a** (1.6 g, 65% yield), which was isolated as a mixture of two diastereomers in a 3:2 ratio: ^1H NMR ($CDCl_3$) δ 4.99 (0.4H, d, *J* = 5.5 Hz), 4.95 (0.6H, d, *J* = 5.5 Hz), 4.40 (0.4H, m), 4.20 (0.6H, m,), 4.08 (0.8H, q, *J* = 7.1 Hz), 4.05 (1.2H, q, *J* = 7.1 Hz), 3.40 (2H, m), 2.92 (0.6H, dd, *J* = 16.2, 7.4 Hz), 2.30−2.15 (1H, m), 2.65−2.35 (2.4H, m), 2.05−1.85 (2H, m), 1.28 (1.8H, d, *J* = 6.9 Hz), 1.25 (1.2H, d, *J* = 6.9 Hz), 1.19 (1.8H, t, *J* = 7.2 Hz), 1.18 (1.2H, t, *J* = 7.2 Hz), 1.17 (1.8H, t, *J* = 7.1 Hz), 1.16 (1.2H, t, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 174.9 (C), 174.7 (C), 171.5 (C), 170.9 (C), 89.4 (CH), 88.2 (CH), 61.4 (CH_2), 61.0 (CH_2), 60.4 (CH_2), 60.2 (CH_2), 45.7 (CH), 45.3 (CH), 39.3 (CH_2), 38.8 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 24.9 (CH_2), 24.8 (CH_2), 19.3 (CH_3), 17.7 (CH_3), 15.2 (CH_3), 14.0 (CH_3).

5-Methyl-7-methyleneindolizidin-3-ones (5a and 6a). $CeCl_3 \cdot 7H_2O$ (16.4 g, 0.044 mol) was dried by stirring under 0.01 mbar for 48 h at 120 °C. The flask was flushed with argon, then dry THF (75 mL) was added and the white suspension was stirred at room temperature for 2 h. This slurry was cooled to −78 °C under argon, and trimethylsilylmethylmagnesium chloride in THF [prepared from chloromethyltrimethylsilane (6.15 mL, 0.044 mol) and magnesium pellets (1.1 g, 0.045 mol) in dry THF (25 mL)] was added dropwise over a period of 60 min. The cold mixture was stirred for 2 h, and a solution of **3a** (2.4 g, 0.01 mol) in 10 mL of dry THF was added. The resulting mixture was allowed to warm to room temperature and stirred for 3 days. The reaction mixture was then cooled to 0 °C, and a 1 N HCl solution (160 mL) was added. After stirring for 1 h the aqueous layer was extracted with ether (3 × 150 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The resulting crude oil (1.5 g, 90% yield) was shown by ^1H and ^{13}C NMR spectroscopy to be a

mixture of **5a** and **6a** in a 4:1 ratio. These isomers could not be separated by flash column chromatography. The mixture was purified by flash column chromatography on silica gel (ethyl acetate): *anal*. C 72.97%, H 9.20%, N 8.00%, calcd for $C_{10}H_{15}NO$, C 72.73%, H 9.09%, N 8.48%.

5a: ^{1}H NMR ($CDCl_3$) δ 4.83 (1H, s), 4.72 (1H, s), 4.40 (1H, m), 3.60−3.45 (1H, m), 2.45−1.40 (8H, m), 1.00 (3H, d, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 174.1 (C), 141.9 (C), 113.3 (CH_2), 54.8 (CH), 45.0 (CH), 43.0 (CH_2), 39.6 (CH_2), 31.3 (CH_2), 25.9 (CH_2), 19.3 (CH_3).

6a: ^{1}H NMR ($CDCl_3$) δ 4.80 (1H, s), 4.73 (1H, s), 3.60−3.45 (2H, m), 2.50 (1H, dd, J = 15.4, 3.0 Hz), 2.45−1.40 (7H, m), 1.38 (3H, d, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 175.6 (C), 142.5 (C), 112.2 (CH_2), 58.4 (CH), 50.4 (CH), 40.5 (CH_2), 40.4 (CH_2), 32.6 (CH_2), 26.9 (CH_2), 20.7 (CH_3).

Reduction of the Lactam Functional Group. A mixture of lactam (0.2 g, 0.0012 mol) and $LiAlH_4$ (0.16 g, 0.0042 mol) in dry THF (10 mL) was refluxed for 12 h. Ether was added, followed by water (0.16 mL), 10% NaOH (0.16 mL), and water (0.48 mL). After filtration, the organic layer was dried and concentrated to give the crude reduction product in quantitative yield. It was purified by flash chromatography (ethyl ether).

Catalytic Hydrogenation of the Olefinic Bond. Methyleneindolizidine (0.2 g) was dissolved in methanol (10 mL), and catalyst (0.2 g Pd/C or 0.05 g PtO_2) was added. The resultant mixture was stirred under 1 atm of hydrogen at room temperature for 5 h in a Parr apparatus. The catalyst was removed by filtration through a Celite pad, and the solvent was evaporated. The crude product was purified by flash chromatography (ethyl ether).

5-Methyl-7-methyleneindolizidines. (5*R*,9*R*)-7a: 50% yield; $[\alpha]^{25}_D$ +8.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.77 (1H, q, J = 1.8 Hz, C=CH_2), 4.69 (1H, q, J = 1.8 Hz, C=CH_2), 3.30 (1H, d quin, J = 1.9, 6.0 Hz, H-5), 2.85 (1H, dt, J = 3.2, 8.8 Hz, H-3a), 2.60−2.46 (3H, m, H-3b, H-6a, H-9), 2.35 (1H, ddd, J = 1.9, 3.3, 12.8 Hz, H-8a), 2.05 (1H, dt, J = 1.9, 13.0 Hz, H-6b), 1.94−1.77 (3H, m, H-1a, H-2a, H-8b), 1.67 (1H, m, H-2b), 1.36 (1H, m, H-1b), 0.91 (3H, d, J = 6.0 Hz, NCHCH_3); ^{13}C NMR ($CDCl_3$) δ 144.1 (C, C-7), 110.0 (CH_2, C=*C*H_2), 55.4 (CH, C-9), 50.4 (CH, C-5), 48.5 (CH_2, C-3), 40.2 (CH_2, C-6), 40.1 (CH_2, C-8), 30.4 (CH_2, C-1), 21.2 (CH_2, C-2), 10.3 (CH_3, NCH*C*H_3); *anal*. C 79.25%, H 11.41%, N 8.97%, calcd for $C_{10}H_{17}N$, C 79.47%, H 11.26%, N 9.27%.

(5*R*,9*S*)-8a: 18% yield; $[\alpha]^{25}_D$ −12.0 (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.65 (2H, s, C=CH_2), 3.24 (1H, dt, J = 2.3, 8.8 Hz, H-3a), 2.38 (1H, ddd, J = 1.6, 1.8, 12.2 Hz, H-8a), 2.18 (1H, dd, J = 1.6, 10.4 Hz, H-6a), 2.00−1.60 (8H, m), 1.53−1.40 (1H, m, H-1a), 1.13 (3H, d, J = 5.8 Hz, NCHCH_3); ^{13}C NMR ($CDCl_3$) δ 146.2 (C, C-7), 108.2 (CH_2, C=*C*H_2), 65.4 (CH, C-9), 58.9 (CH, C-5), 51.0 (CH_2, C-3), 42.7 (CH_2, C-6), 40.0 (CH_2, C-8), 30.3 (CH_2, C-1), 20.9 (CH_3, NCH*C*H_3) 20.8 (CH_2, C-2).

(5*S*,9*S*)-7b: $[\alpha]^{25}_D$ −9.2 (*c* 1.9, $CHCl_3$).

(5*S*,9*R*)-8b: $[\alpha]^{25}_D$ +12.9 (*c* 1.3, $CHCl_3$).

5,7-Dimethylindolizidines. (5*R*,7*R*,9*R*)-9a: $[\alpha]^{25}_D$ +7.0 (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 3.28 (1H, m, H-5); 2.75 (1H, dt, J = 2.7, 8.6 Hz, H-3a), 2.50 (1H, q, J = 8.6 Hz, H-3b), 2.40 (1H, m, H-9), 1.80−1.65 (3H, m, H-2a, H-1a, H-8a), 1.65−1.50 (2H, m, H-7, H-2b), 1.50−1.35 (2H, m, H-6a, H-6b), 1.35−1.20 (1H, m, H-8b), 0.92 (3H, d, J = 6.7 Hz, NCHCH_3), 0.85 (3H, d, J = 6.4 Hz, CHCH_3), 0.75 (1H, m, H-1b); ^{13}C NMR ($CDCl_3$) δ 54.2 (CH, C-5), 49.9 (CH, C-9), 48.6 (CH_2, C-3), 40.6 (CH_2, C-1), 40.0 (CH_2, C-6), 30.8 (CH_2, C-8), 25.6 (CH, C-7), 22.4 (CH_3, CH*C*H_3), 21.1 (CH_2, C-2), 9.7 (CH_3, NCH*C*H_3).

(5*R*,7*S*,9*R*)-10a: $[\alpha]^{25}_D$ −37.5 (*c* 1.3, $CHCl_3$) [lit.[1] $[\alpha]_D$ −38 (*c* 1.00, $CHCl_3$)]; ^{1}H NMR ($CDCl_3$) δ 3.18 (1H, m, H-9), 3.10 (1H, m, H-3a), 2.80 (1H, m, H-3b), 2.38 (1H, m, H-5), 1.9−1.5 (8H, m), 1.00 (3H, d, J = 6.0 Hz, NCHCH_3), 0.95−0.90 (1H, m, H-8), 0.88 (3H, d, J = 6.3 Hz, CHCH_3); ^{13}C NMR ($CDCl_3$) δ 60.8 (CH, C-9), 51.7 (CH_2, C-3), 50.6 (CH, C-5), 43.7 (CH_2, C-8), 35.9 (CH_2, C-1), 27.4 (CH_2, C-6), 26.1 (CH, C-7), 22.9 (CH_3, CH*C*H_3), 22.7 (CH_2, C-2), 22.6 (CH_3, NCH*C*H_3).

(5*R*,7*R*,9*S*)-11a: $[\alpha]^{25}_D$ −32.8 (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 3.30 (1H, td, J = 2.8, 8.6 Hz, H-9), 2.30−1.40 (11H, m), 1.10 (3H, d, J = 6.4 Hz), 1.05−0.95 (1H, m), 0.90 (3H, d, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 64.7 (CH), 58.1 (CH), 51.4 (CH_2), 43.1 (CH_2), 39.5 (CH_2), 31.3 (CH), 30.3 (CH_2), 21.9 (CH_3), 21.6 (CH_3), 21.0 (CH_2).

(5*S*,7*S*,9*S*)-9b: $[\alpha]^{25}_D$ −6.9 (*c* 1.0, $CHCl_3$).

(5*S*,7*R*,9*S*)-10b: $[\alpha]^{25}_D$ +36.8 (*c* 1.2, $CHCl_3$).

(5*S*,7*S*,9*R*)-11b: $[\alpha]^{25}_D$ +33.7 (*c* 2.0, $CHCl_3$).

5,7-Dimethylindolizidin-3-ones. 12: ^{1}H NMR ($CDCl_3$) δ 4.30 (1H, m, H-5), 3.52 (1H, m, H-9), 2.23 (2H, m), 2.10 (1H, m), 1.75 (2H, m), 1.45 (3H, m), 1.05 (3H, d, J = 7.0 Hz, NCHCH_3), 0.86 (3H, d, J = 6.4 Hz, CHCH_3), 0.72 (1H, m, H-8a); ^{13}C NMR ($CDCl_3$) δ 173.2 (C, *C*O), 53.0 (CH, C-9), 43.4 (CH, C-5), 42.2 (CH_2, C-8), 38.1 (CH_2), 30.6 (CH_2), 25.4 (CH_2), 25.1 (CH), 21.9 (CH_3, CH*C*H_3), 16.6 (CH_3, NCH*C*H_3).

13: ^{1}H NMR ($CDCl_3$) δ 4.05 (1H, m, H-5), 3.72 (1H, m, H-9), 2.3−1.3 (8H, m), 1.10−0.90 (1H, m), 1.12 (3H, d, J = 6.9 Hz, NCHCH_3), 1.01 (3H, d, J = 7.1 Hz, CHCH_3); ^{13}C NMR ($CDCl_3$) δ 173.8 (C, *C*O), 48.9 (CH, C-9), 44.5 (CH, C-5), 38.9 (CH_2), 36.0 (CH_2), 30.4 (CH_2), 25.9 (CH), 25.8 (CH_2), 20.9 (CH_3, CH*C*H_3), 19.8 (CH_3, NCH*C*H_3).

14: 18% yield; ^{1}H NMR ($CDCl_3$) δ 3.20 (1H, m, H-9). 3.10 (1H, m, H-5), 2.22 (2H, m, H-2a, H-2b), 2.00 (1H, m, H-1a), 1.72 (1H, d, J = 12.8 Hz, H-8a), 1.60 (3H, d, J = 6.5 Hz, NCHCH_3), 1.60−1.40 (3H, m, H-1b, H-6a, H-7), 0.85 (3H, d, J = 5.8 Hz, CHCH_3), 0.85 (1H, m, H-6b), 0.80 (1H, m, H-8b); ^{13}C NMR ($CDCl_3$) δ 175.6 (C, *C*O), 59.8 (CH, C-9), 52.7 (CH, C-5), 43.6 (CH_2, C-6), 41.5 (CH_2, C-8), 32.2 (CH_2, C-2), 30.6 (CH, C-7), 25.1 (CH_2, C-1), 21.7 (CH_3, CH*C*H_3), 19.7 (CH_3, NCH*C*H_3).

References and Notes

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