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Asymmetric Synthesis of Furo[3,2-*i*]indolizines from L-Malic Acid

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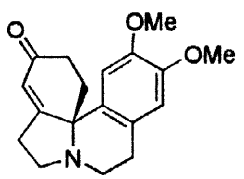
Abstracts: A chiral enamide **6**, derived from L-malic acid, was converted to furo-indolizine **2** via *N*-acyliminium ion cyclization. Furo-indolizine **2** was transformed to indolizine derivatives **8** and **9** which have a substituent at angular position.

INTRODUCTION

Indolizine ring system containing a substituent in ring juncture is a common skeleton of naturally occurring erythrina alkaloids such as 3-demethoxyerythratidinone and β-erythrolidine.[1] Recently, indolizine derivative **1** was considered as a useful intermediate for the synthesis of conformationally constrained polypeptide mimics of the type VI β-turn for analysis of peptide conformation-activity relationships.[2] Owing to their unique structure and interesting biological activities, a number of synthetic methods of indolizines and pyrrolizines having an angular substituent have been reported.[3]



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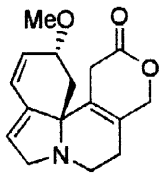
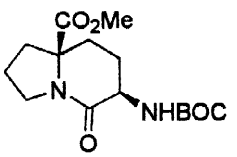
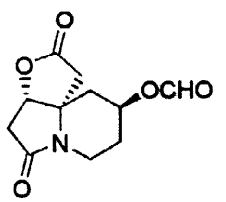


β-erythrolidine



1



2

We have previously shown that the angular substituents in indolizine ring could be introduced stereoselectively by the *N*-acyliminium ion cyclization of a chiral enamides derived from L-malic acid or L-tartaric acid.[4] While several syntheses of indolizine nucleus having an angular substituent by the capture of *N*-acyliminium ion or iminium ion by aromatic ring have been reported,[5] the reaction of a chiral *N*-acyliminium ion with double bond as a π-nucleophile were scarce. In connection with our efforts to develop new heterocyclic ring systems,[4,6] we herein report the asymmetric synthesis of furo-indolizine ring system (**2**) from L-malic acid through *N*-acyliminium ion cyclization involving a double bond as a π-nucleophile. Furthermore, we wish to show that furo-indolizine **2** can be a potential intermediate in synthesizing several angular-substituted indolizine derivatives.

RESULTS AND DISCUSSION

The synthesis of **2** was carried out following the procedure summarized in Scheme 1. *N*-(3-Butenyl)imide derivative **3** could be obtained using (3*S*)-3-acetoxysuccinimide and 3-buten-1-ol by Mitsunobu

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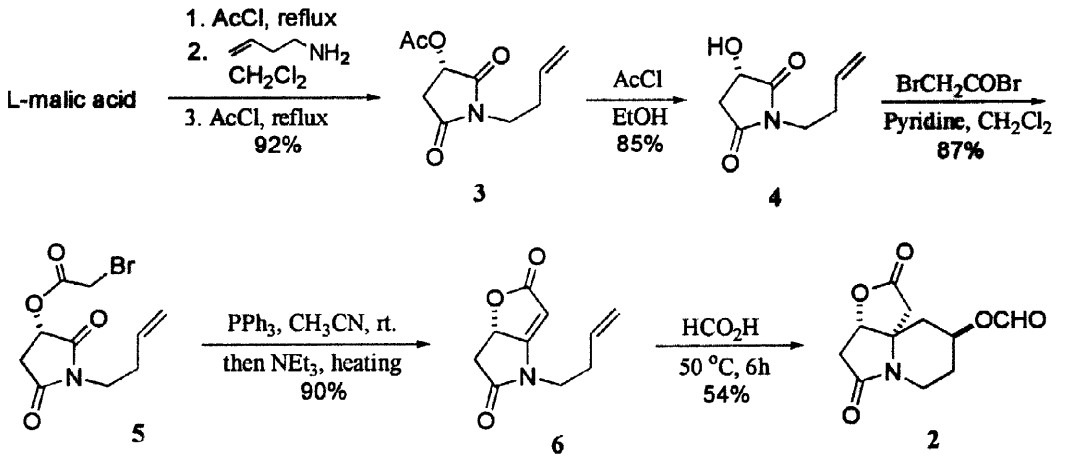
coupling in 86% yield. In the Mitsunobu conditions, the removal of side products such as triphenylphosphine oxide and *N,N*-diethoxycarbonylhydrazine was not easy by silica gel column chromatography due to their similar polarity with **3**. However, using Chamberlin's protocol, imide **3** could be obtained in 92% yield from L-malic acid without any difficulty in chromatographic separation.[7] Acetyl group in **3** was removed by treatment with acetyl chloride in ethanol and then bromoacetylated to provide **5**. Compound **5** was converted to chiral enamide **6** through intramolecular Wittig reaction following the known procedure in 90% yield.[4,8]



Scheme 1.

Enamide **6** was subjected to *N*-acyliminium ion cyclization condition to form furo-indolizine ring system. It was found that the cyclization of **6** in formic acid under reflux temperature afforded cyclization product **2** in low yield (ca. 20% yield) accompanying several by-products.[9] The problem could be solved by lowering the reaction temperature to 50 °C to obtain furo-indolizine **2** selectively in 54% reproducible yield. The structure of **2** was supported by the 600 MHz ^{1}H-NMR and 2D ^{1}H-^{1}H COSY spectra as well as NOE experiments. The configuration of angular position (C-7a) in **2** was assigned to *S* since the double bond would attack the less hindered side opposite to acyloxy group.[5] The configuration of C-6 was also assigned to *S* by the analogy with the previous reports[9] and further confirmed unambiguously by 2D ^{1}H-^{1}H COSY and NOE experiments. When the signal of H-6 proton at 5.06 ppm was irradiated, the enhancements of protons of H-4a at 2.80 ppm, H-5a at 2.09 ppm, H-7a at 2.25 ppm, H-8a and H-8b at 2.69 and 2.89 ppm were observed indicating *S*-configuration of C-6 in **2** as shown in Figure 1.

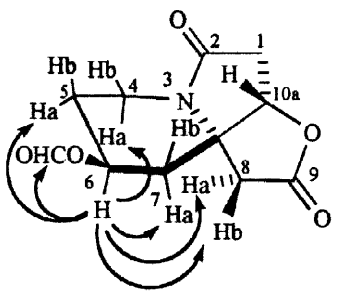
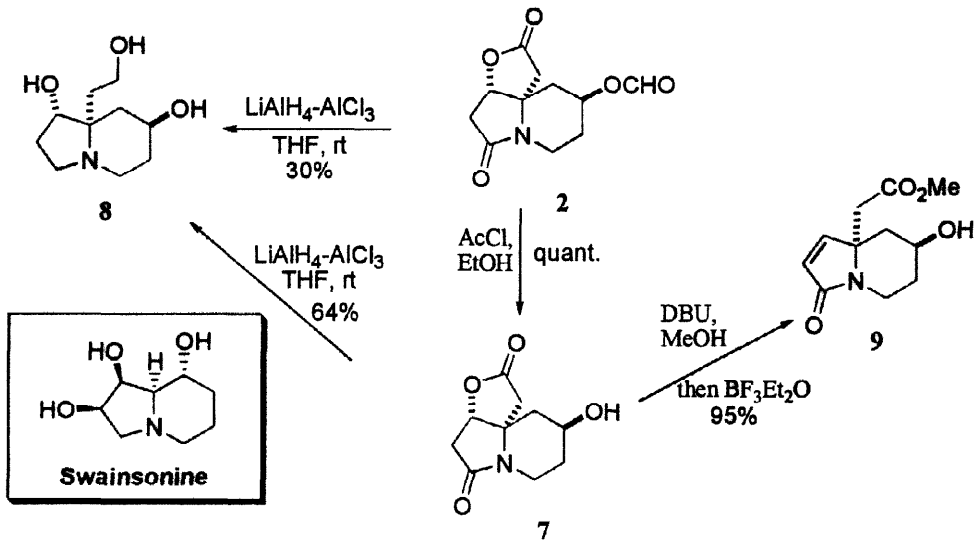


Figure 1. Observed NOE's of **2**

To explore the synthetic utility of furo-indolizine **2**, some chemical transformations were examined (Scheme 2). The furo-indolizine **2** was treated with $LiAlH_4$ in the presence of $AlCl_3$[10] to afford trihydroxyindolizine **8** in modest yield (30%). However, the reduction of 6-hydroxy furo-indolizine **7**, which was obtained in quantitative yield by treatment of acetyl chloride in ethanol, with the same reducing agents provided trihydroxyindolizine **8** in improved 64% yield. Since the structure of **8** resembles naturally occurring glycosidase inhibitors such as swainsonine and castanospermine,[11] compound **8** can be considered as a potential glycosidase inhibitory polyhydroxy indolizines which has a 2-hydroxyethyl substituent at angular

position. When compound 7 was treated with DBU and then BF_3•Et_2O in methanol in one-pot procedure, β-elimination and esterification reactions occurred consecutively to afford product 9 in high yield. Compound 9 could also serve as a valuable intermediate for the synthesis of indolizines having an angular substituent by the chemical modification of conjugated lactam, ester, and hydroxy groups.[12]



Scheme 2.

In conclusion, we have accomplished the synthesis of furo-indolizine derivative **2** through *N*-acyliminium ion cyclization involving a double bond as a π-nucleophile. Additionally, we have shown that furo-indolizine **2** could be a potential intermediate in synthesizing fully functionalized indolizines having a substituent at angular position. The use of L-tartaric acid as a chiral source would also open up the possibility of the synthesis of antipode of **2**.[4,6c]

EXPERIMENTAL

Melting points (mp) were determined on a Thomas-Hoover capillary melting apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Gemini Varian-300 (300 MHz) spectrometer or on a Varian Unity 600 (600 MHz) spectrometer. ^{1}H-^{1}H COSY and NOE spectra were recorded on a Varian Unity 600 (600 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Gemini Varian-300 (75 MHz) spectrometer. Infrared (IR) spectra were recorded on Perkin Elmer 16F-PC FT-IR and MIDAC 101025 using a potassium bromide pellet. Optical rotations were determined on a Autopol III automatic polarimeter (Rudolph Research Co.) using the sodium D line (λ = 589nm). Low (EI) resolution mass spectra were determined on HP GC 5972 and HP MS 5988A system at 70eV and High (EI) resolution mass spectra were determined on VG70-VSEQ (VG ANALITICAL, UK) at 70eV. Elemental analysis was performed by Elementar Analysensysteme GmbH Vario EL. Analytical thin layer chromatographies (TLC) were carried out by precoated silica gel (E. Merck Kiesegel $60F_{254}$ layer thickness 0.25 mm). Flash column chromatographies were performed with Merck Kiesegel 60 Art 9385 (230 - 400mesh). All solvents used were purified according to standard procedures.

(3*S*)-3-Acetoxy-1-(3-buten-1-yl)pyrrolidine-2,5-dione (3). A solution of L-malic acid (4 g, 29.8 mmol) in

acetyl chloride (50 ml) was heated at reflux for 12 h. After evaporation of acetyl chloride, the residue was dissolved in CH_2Cl_2 (50 ml) and treated dropwise with a solution of 4-amino-1-butene[13] (5.43 g, 76 mmol) at 0 °C and stirred at room temperature for 6 h. After evaporation of solvent, the residue was treated with acetyl chloride (50 ml) and heated at reflux for 12 h. The mixture was concentrated and purified by flash column chromatography (EtOAc/*n*-hexane = 2:5) to afford **3** (5.81 g, 92%) as a white solid: mp 53-55 °C; $[\alpha]_D^{23}$ -19.4 (*c* 1.0, $CHCl_3$); IR (KBr) 1750, 1704 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.64 (1H, m, $\underline{CH}=CH_2$), 5.36 (1H, dd, *J*=8.7, 4.5 Hz, $\underline{CH}OAc$), 4.97-5.03 (2H, m, $CH=\underline{CH_2}$), 3.55 (2H, t, *J*=7.2 Hz, $N\underline{CH_2}$), 3.08 (1H, dd, *J*=18.3, 8.7 Hz, $\underline{CH_2}CHOAc$), 2.58 (1H, dd, *J*=18.3, 4.5 Hz, $\underline{CH_2}CHOAc$), 2.30 (2H, td, *J*=7.2, 6.7 Hz, $NCH_2\underline{CH_2}$), 2.09 (3H, s, OAc); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.00, 173.40, 168.77, 134.01, 117.69, 67.38, 38.16, 35.60, 31.66, 20.47; MS (EI), m/z (relative intensity, %) 211 (M^+, 3), 170 (15), 151 (100), 110 (56), 100 (50), 71 (23), 54 (71); *Anal.* Calcd for $C_{10}H_{13}NO_4$: C, 56.86; H, 6.20; N, 6.63. Found: C, 56.69; H, 6.21; N, 6.57.

(3*S*)-1-(3-Buten-1-yl)-3-hydroxypyrrolidine-2,5-dione (4). To a solution of **3** (5.67 g, 26.9 mmol) in EtOH (150 ml) was added dropwise acetyl chloride (5.84 ml, 82 mmol) at 0 °C and stirred at room temperature overnight. The mixture was evaporated and purified by flash column chromatography (EtOAc/*n*-hexane = 1:1) to afford **4** (3.86 g, 85%) as an oil: $[\alpha]_D^{23}$ -85.0 (*c* 1.6, $CHCl_3$); IR (KBr) 3448, 1702 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.57 (1H, m, $\underline{CH}=CH_2$), 4.88-4.94 (2H, m, $CH=\underline{CH_2}$), 4.55 (1H, dd, *J*=8.6, 4.5 Hz, $\underline{CH}OH$), 3.43 (2H, t, *J*=6.9 Hz, $N\underline{CH_2}$), 2.94 (1H, dd, *J*=18.2, 8.6 Hz, $\underline{CH_2}CHOH$), 2.53 (1H, dd, *J*=18.2, 4.5 Hz, $\underline{CH_2}CHOH$), 2.19 (2H, td, *J*=6.9, 6.6 Hz, $NCH_2\underline{CH_2}$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 178.70, 174.62, 134.01, 117.58, 66.72, 37.85, 37.24, 31.64; MS (EI), m/z (relative intensity, %) 169 (M^+, 9), 151 (M^+-H_2O), 85), 110 (18), 100 (37), 71 (4), 54 (100); HRMS (EI) Calcd for $C_8H_{11}NO_3$: (M^+) m/z 169.0739. Found: 169.0737.

(3*S*)-3-Bromoacetoxy-1-(3-buten-1-yl)pyrrolidine-2,5-dione (5). Bromoacetyl bromide (2.8 ml, 31.8 mmol) was added to a stirred solution of **4** (5.38 g, 31.8 mmol) and pyridine (2.5 g, 31.8 mmol) in CH_2Cl_2 (50 ml) at 0 °C under nitrogen. The reaction mixture was stirred at room temperature for 30 min and diluted with ice-cold water (30 ml). The organic layer was washed successively with 10% $CuSO_4$ (20 ml), water (30 ml), and saturated $NaHCO_3$ (30 ml), dried ($MgSO_4$), and concentrated. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:1) to afford **5** (8.02 g, 87%) as a white solid: mp 72-74 °C; $[\alpha]_D^{23}$ -21.8 (*c* 0.1, $CHCl_3$); IR (KBr) 1738, 1714 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.65 (1H, m, $\underline{CH}=CH_2$), 5.48 (1H, dd, *J*=8.7, 4.7 Hz, $\underline{CH}OCO$), 5.01-5.06 (2H, m, $CH=\underline{CH_2}$), 3.90 (2H, s, $BrCH_2$), 3.60 (2H, t, *J*=7.2 Hz, $N\underline{CH_2}$), 3.16 (1H, dd, *J*=18.4, 8.7 Hz, $\underline{CH_2}CHOAc$), 2.66 (1H, dd, *J*=18.4, 4.7 Hz, $\underline{CH_2}CHOAc$), 2.34 (2H, td, *J*=7.2, 6.7 Hz, $NCH_2\underline{CH_2}$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 177.01, 172.61, 166.40, 133.87, 117.92, 68.66, 38.35, 35.24; MS (EI), m/z (relative intensity, %) 290 (M^+, 3), 150 (100), 122 (34), 110 (47), 71 (30), 54 (49); *Anal.* Calcd for $C_{10}H_{12}BrNO_4$: C, 41.40; H, 4.17; N, 4.83. Found: C, 41.71; H, 4.17; N, 4.84.

(6a*S*)-6,6a-Dihydro-4-(3-buten-1-yl)-2*H*-furo[3,2-*b*]pyrrole-2,5(4*H*)-dione (6). Triphenylphosphine (8.08 g, 30.8 mmol) was added to a stirred solution of **5** (7.45 g, 25.7 mmol) in 60 ml of CH_3CN under nitrogen and stirred at 50 °C for 2 h. After cooling to room temperature the mixture was treated with triethylamine (2.86 g, 28.24 mmol) and further stirred at 50 °C for 16 h. The mixture was concentrated and purified by flash column chromatography (EtOAc/*n*-hexane = 1:3 - 2:1) to afford **6** (4.46 g, 90 %) as an oil: $[\alpha]_D^{23}$ -15.5 (*c* 0.3, $CHCl_3$); IR (KBr) 1762, 1652 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.70 (1H, m, $\underline{CH}=CH_2$), 5.27 (1H, s, C=*CH*CO),

5.07-5.18 (3H, m, $CH_2\underline{CH}O$, $CH{=}\underline{CH_2}$), 3.86 (1H, m, $N\underline{CH_2}CH_2$), 3.50 (1H, m, $N\underline{CH_2}CH_2$), 3.06 (1H, dd, *J*=15.7, 7.7 Hz, $\underline{CH_2}CHO$), 2.66 (1H, dd, *J*=15.7, 8.8 Hz, $\underline{CH_2}CHO$), 2.38-2.45 (2H, m, $NCH_2\underline{CH_2}$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.79, 172.37, 170.82, 133.77, 118.00, 89.26, 75.23, 41.43, 38.29, 31.59; MS (EI), m/z (relative intensity, %) 193 (M^+, 26), 152 (34), 121 (80), 110 (100), 82 (93), 55 (88); HRMS (EI) Calcd for $C_{10}H_{11}NO_3$: (M^+) m/z 193.0739. Found: 193.0738.

(6*S*,7a*S*,10a*S*)-1,4,5,6,7,10a-Hexahydro-6-formyloxy-2*H*-furo[3,2-*i*]indolizine-2,9(8*H*)-dione (2). A solution of **6** (0.2 g, 0.10 mmol) in formic acid (10 ml) was stirred at 50 °C for 6 h. The mixture was concentrated and purified by flash column chromatography (EtOAc/*n*-hexane = 2:3 - 1:1) to afford **2** (0.14 g, 54 %) as a white solid: mp 164-165 °C; $[\alpha]_D^{23}$ -38.3 (*c* 1.5, $CHCl_3$); IR (KBr) 1782, 1714, 1695 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 8.00 (1H, s, $O\underline{CH}O$), 5.06 (1H, tt, *J*=11.7, 4.4 Hz, H_6), 4.78 (1H, dd, *J*=5.5, 2.8 Hz, H_{10a}), 4.32 (1H, ddd, *J*=14.3, 5.6, 1.6 Hz, H_4), 2.76-2.83 (3H, m, 2 x H_1 and H_4), 2.69 & 2.89 (2H, ABq, *J*=18.3 Hz, 2 x H_8), 2.25 (1H, ddd, *J*=12.3, 6.0, 1.6 Hz, H_7), 2.09 (1H, m, H_5), 1.46-1.59 (2H, m, H_5 and H_7); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.83, 169.79, 159.92, 79.32, 67.86, 65.84, 39.08, 37.63, 36.21, 35.26, 30.36; MS (m/z) 241 [$(M+1)^+$, 10], 195 (24), 180 (100), 150 (8), 134 (31); *Anal.* Calcd for $C_{11}H_{13}NO_5$: C, 55.23; H, 5.48; N, 5.86. Found: C, 55.34; H, 5.47; N, 5.85.

(6*S*,7a*S*,10a*S*)-1,4,5,6,7,10a-Hexahydro-6-hydroxy-2*H*-furo[3,2-*i*]indolizine-2,9(8*H*)-dione (7). To a solution of formate **2** (340 mg, 1.42 mmol) in MeOH (10 ml) was added acetyl chloride (1.1 mL, 82.1 mmol) at 0 °C and stirred at room temperature for 14 h. The reaction mixture was concentrated and purified by flash column chromatography (MeOH/EtOAc = 1:10) to afford 7 (300 mg, quantitative) as a foam: $[\alpha]_D^{23}$ -0.3 (*c* 1.0, $CHCl_3$); IR (KBr) 3416, 1788, 1680 cm^{-1}; ^1H NMR (CD_3OD, 300 MHz) δ 4.89 (1H, m, H_{10a}), 4.09 (1H, m, H_4), 3.83 (1H, m, H_6), 2.90-2.98 (2H, m, H_1 and H_4), 2.81 & 2.98 (2H, ABq, *J*=18.3 Hz, 2 x H_8), 2.62 (1H, d, *J*=18.5 Hz, H_1), 2.17 (1H, m, H_7), 1.94 (1H, *br* d, *J*=12.5 Hz, H_5), 1.44 (1H, t, *J*=11.8 Hz, H_7), 1.23 (1H, m, H_5); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.83, 169.79, 159.92, 79.32, 67.86, 65.84, 39.08, 37.63, 36.21, 35.26, 30.36; MS (m/z) 211 (M^+, 54), 193 [$(M-H_2O)^+$, 11), 169 (100), 151 (34), 124 (18), 108 (16); HRMS (EI) Calcd for $C_{10}H_{13}NO_4$: (M^+) m/z 211.0845. Found: 211.0843.

(1*S*,7*S*,8a*S*)-1,7-Dihydroxy-8a-(2-hydroxyethyl)indolizidine (8). To a stirred suspension of $LiAlH_4$ (54 mg, 1.41 mmol) in THF (6 ml) was added dropwise an ice-cold solution of $AlCl_3$ (32 mg, 0.24 mmol) in THF (3 ml) at –78 °C under argon atmosphere. The mixture was allowed to warm to room temperature and further stirred for 20 min. The resulting alane solution was cooled to –78 °C and treated with a solution of **7** (50 mg, 0.21 mmol) in THF (4 ml). After stirring for 1 h the mixture was allowed to warm to room temperature and further stirred for 12 h. The reaction mixture was quenched by addition of $Na_2SO_4{\cdot}10H_2O$ (ca. 0.3 g) at 0 °C and filtered through Celite. The filtrate was concentrated and purified by flash column chromatography (CH_2Cl_2/MeOH/NH_4OH = 4:8:1) to afford **8** (30 mg, 64%) as an oil: $[\alpha]_D^{24}$ +19.5 (*c* 1.3, CH_3OH); IR (KBr) 3400, 2950 cm^{-1}; ^1H NMR (CD_3OD, 300 MHz) δ 4.21 (1H, m, H_1), 4.00 (1H, m, H_7), 3.78 (2H, m, $CH_2\underline{CH_2}OH$), 3.54-3.63 (2H, m, H_3 and H_5), 3.30-3.89 (2H, m, H_3 and H_5), 2.60 (1H, m, H_2), 2.04-2.18 (5H, m, H_2, H_6, H_8 and $\underline{CH_2}CH_2OH$), 1.82 (1H, m, H_6), 1.29 (1H, m, H_8); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 63.29, 62.04, 49.98, 44.58, 35.53, 31.39, 21.13, 18.10, 17.68, 14.90; MS (m/z) 201 (M^+, 0.01), 184 (0.02), 156 (100), 140 (0.2), 112 (0.2); HRMS (EI) Calcd for $C_{10}H_{19}NO_3$: 201.1365. Found 201.1361.

Methyl 2-[(7*S*,8a*S*)-1,2-dehydro-7-hydroxy-3-oxo-indolizidin-8a-yl]acetate (9). To a solution of 6-hydroxy furo-indolizine **7** (86 mg, 0.41 mmol) in MeOH (25 ml) was added DBU (0.10 g, 0.66 mmol) and stirred for 12 h to complete disappearance of starting material. The reaction mixture was cooled to 0 °C and treated with BF_3·Et_2O (0.15 ml, 1.22 mmol). After stirring at room temperature for 12 h, the reaction mixture was neutralized by addition of $NaHCO_3$ (0.2 g). The mixture was filtered and the filtrate was concentrated, and purified by flash column chromatography (MeOH/EtOAc = 1:10) to afford **9** (91 mg, 95%) as an oil: $[\alpha]_D^{23}$ +72.1 (*c* 0.4, $CHCl_3$); IR (KBr) 3404, 1734, 1670 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.33 (1H, d, *J*=6.0 Hz, H_1), 6.07 (1H, d, *J*=6.0 Hz, H_2), 4.23 (1H, dd, *J*=14.0, 4.4 Hz, H_5), 4.00 (1H, m, H_7), 3.62 (3H, s, OCH_3), 2.83 (1H, m, H_5), 2.42 & 2.85 (2H, ABq, *J*=14.6 Hz, $C\underline{CH_2}CO$), 2.35 (1H, dd, *J*=12.8, 2.4 Hz, H_8), 1.97 (1H, *br* d, *J*=12.5 Hz, H_6), 1.78 (1H, m, H_6), 1.04 (1H, t, *J*=12.1 Hz, H_8); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.55, 169.07, 152.33, 125.60, 65.31, 64.75, 52.01, 41.23, 38.45, 34.58, 34.40; MS (m/z) 225 (M^+, 14), 152 (100), 108 (92), 96 (37); HRMS (EI) Calcd for $C_{11}H_{15}NO_4$: (M^+) m/z 225.1001. Found: 225.1002.

ACKNOWLEDGEMENTS

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