HETEROCYCLES, Vol. 65, No. 2, 2005, pp. 395 - 402
Received, 5th November, 2004, Accepted, 8th December, 2004, Published online, 10th December, 2004

SYNTHESIS OF LUPININE

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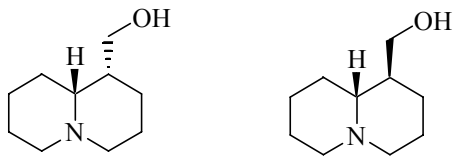
Abstract — A synthesis of lupinine (**1a**) is performed from 5-amino-1-pentanol in ten steps. The glutarimide (**3**) was obtained from 1-(5-hydroxypentyl)-2-(4-methylphenylsulfonyl)acetamide (**5**) and acrylate (**4**) *via* a formal [3+3] annulation. This formation of quinolizidine skeleton was established *via* a key acid-catalyzed cyclization method.

1. INTRODUCTION

The quinolizidine skeleton is frequently encountered in nature, particularly among the *lupin* alkaloids.[1-5] In structural complexity, the natural products luipinine (**1a**) and epilupinine (**1b**) are relatively simple in the members of this class range. These compounds have a wide and varied distribution in nature and display a broad range of interesting biological activity.[6-8] Due to their an importance, the construction of fused nitrogen heterocycles has attracted an attention and a number of interesting and new strategies for the synthesis of quinolizidines skeleton have been proposed.[9-36]

Figure 1.



lupinine (**1a**) epilupinine (**1b**)

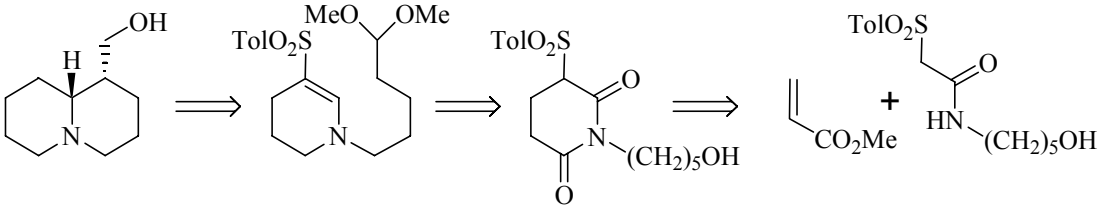
Recently, we reported a facile [3+3] cyclization reaction between different α-sulfonylacetamide derivatives and a series of the α- or β-, aryl- and alkyl-substituted acyclic α,β-unsaturated esters that lead to corresponding glutarimides (piperidine-2,6-diones) in good yields.[37-40] We have already proposed a mechanism of reaction and presented some successful methodologies for the syntheses of natural products and potential drugs *via* this cyclization. In continuing the previous investigations and building upon these observations on the chemistry of α-sulfonyl piperidine-2,6-dione, we envisaged that a facile entry into

quinolizidine skeleton could be achieved based on a formal [3+3] annulation reaction between α-sulfonylacetamide and methyl acrylate.

2. RESULTS AND DISCUSSION

Retrosynthetic route of lupinine (**1a**) was shown in Scheme 1. We envisioned that the quinolizidine skeleton could be achieved *via* the facile [3+3] annulation to glutarimide skeleton followed by acid-catalyzed cyclization.

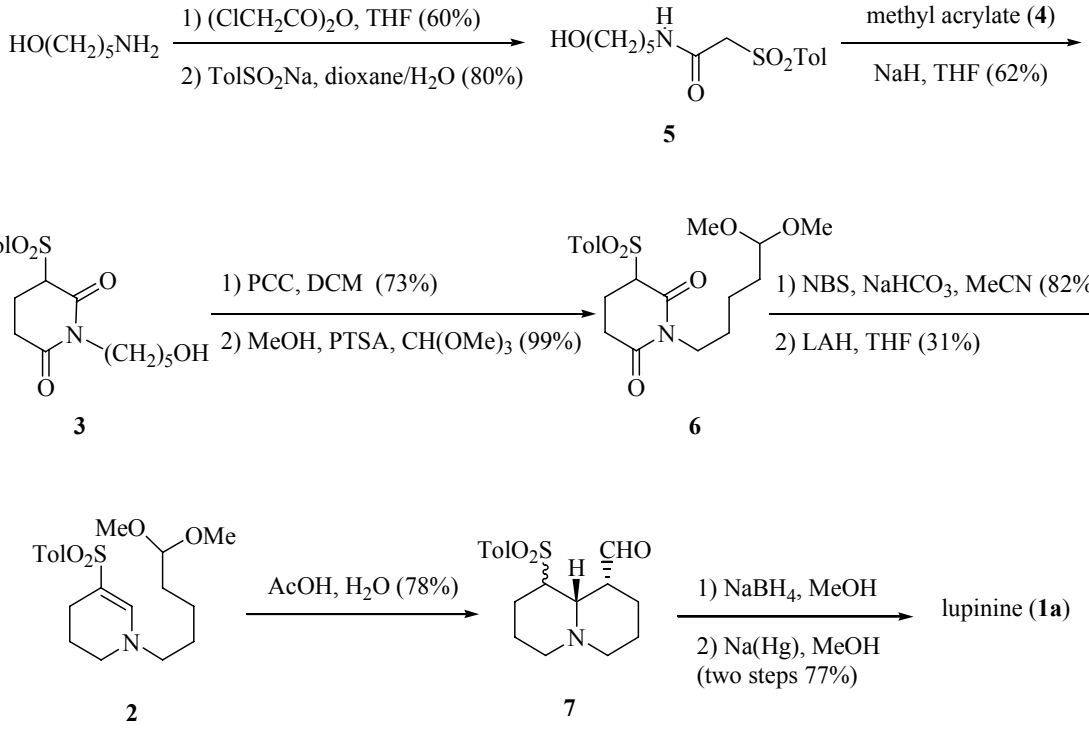
Scheme 1.



lupinine (**1a**) **2** **3** **4** **5**

5-Amino-1-pentanol was treated with chloroacetic anhydride and triethylamine to produce α-chloroacetamide, which was then treated with *p*-toluenesulfinic acid sodium salt; the two-step reaction gave α-sulfonylacetamide (**5**) in 48% yield of two steps. Compound (**5**) and methyl acrylate (**4**) were chosen as the reasonable starting materials for the synthesis of glutarimide skeleton. The stepwise [3+3] annulation reaction of amide (**5**) with acrylate (**4**) (NaH/THF) proceeded smoothly, the cyclized glutarimide (**3**) was obtained as a single isomer in 62% yield (Scheme 2).[38]

***Scheme* 2.**



Preparation of compound (**6**) was achieved by oxidation of alcohol (**3**) by pyridinium chlorochromate followed by protection of the resulting aldehyde with trimethyl orthoformate in acidic condition. With the requisite compound (**6**) in hand, we then examined the bromination reaction. The NBS/$NaHCO_3$/MeCN system is an efficient method for the bromination reaction of compound (**6**).[39] In next step, the resulting bromide was treated by with lithium aluminum hydride to vinyl sulfone (**2**). To build up the quinolizidine skeleton, compound (**2**) was subjected to acid-catalyzed cyclization to yield compound (**7**) in 78% yield under aqueous acetic acid solution condition. Compound (**7**) was isolated as a mixture of the inseparable isomer. The relative stereochemical relationship of three contiguous chiral centers for the major product of compound (**7**) can be assumed as the *trans* orientation to each other under reflux condition. Finally, lupinine (**1a**) was obtained in sole compound by reduction of **7** by sodium borohydride followed by desulfonation of the resulting alcohol with 6% sodium amalgam (Na/Hg) in 77% yield of two steps. Thus we could achieve a synthesis of lupinine (**1a**) *via* a formal [3+3] annulation and acid-catalyzed cyclization as key reactions.

3. CONCLUSION

A synthesis of quinolizidine skeleton is explored. A synthesis of lupinine (**1a**) was accomplished.

EXPERIMENTAL

General. Tetrahydrofuran (THF) was distilled prior to use from a deep-blue solution of sodium-benzophenone ketyl. All other reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. Extract was dried with anhydrous magnesium sulfate before concentration *in vacuo*. Crude products were purified using preparative TLC or column chromatography on silica gel. All reported temperatures were uncorrected.

1-(5-Hydroxypentyl)-2-(4-methylphenylsulfonyl)acetamide (5)

A solution of 5-amino-1-pentanol (1.75 g, 10.23 mmol) and triethylamine (2.88 g, 28.46 mmol) in THF (40 mL) was added to chloroacetic anhydride (1.03 g, 10.0 mmol) in THF (10 mL) at ice bath for 1 h. After the reaction mixture was stirred at rt for 36 h, the mixture was concentrated under reduced pressure. Water (30 mL) was added to the crude product, and the mixture was extracted with ethyl acetate (3 x 100 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to yield crude chloro compound. The crude product (1.00 g) was refluxed with *p*-toluenesulfinic acid sodium salt ($TolSO_2Na$-$2H_2O$, 1.44 g, 6.72 mmol) in the co-solvent of dioxane (20 mL) and water (20 mL) for 16 h. The reaction mixture was concentrated under reduced pressure. The resulting residue was extracted with ethyl acetate (3 x 150 mL). The combined organic layers were washed with brine, dried, filtered and evaporated. Recrystallization of the residue from ethyl acetate yielded the product (**5**) (1.34 g, 80%) as a

white solid. mp = 61-63 °C; EI-MS: $C_{14}H_{21}NO_4S$ m/z (%) = 91 (100), 300 (M^++1, 4); HRMS (EI, M^+) calcd for $C_{14}H_{21}NO_4S$ 299.1191, found 299.1196; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* = 5.1 Hz, 1H), 4.03 (s, 2H), 3.60 (t, *J* = 6.3 Hz, 2H), 3.32-3.20 (m, 2H), 2.85 (br s, 1H), 2.44 (s, 3H), 1.60-1.46 (m, 4H), 1.46-1.33 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.07, 160.72, 145.33, 135.17, 129.80 (2C), 128.02 (2C), 62.08, 39.79, 31.91, 28.67, 22.80, 21.57; Anal. Calcd for $C_{14}H_{21}NO_4S$ C, 56.16; H, 7.07; N, 4.68. Found C, 56.42; H, 7.16; N, 4.42.

1-(5-Hydroxypentyl)-3-(4-methylphenylsulfonyl)-2,6-azinanedione (3)

A solution of compound (**5**) (6.40 g, 21.40 mmol) in THF (150 mL) was added to a rapidly stirred suspension of sodium hydride (60%, 2.60 g, 65.00 mmol) in THF (200 mL). After the reaction mixture was stirred at rt for 20 min, a solution of methyl acrylate (1.84 g, 21.40 mmol) in THF (200 mL) was added. The resulting mixture was stirred at rt for 10 h, quenched with 20% $NH_4Cl_{(aq)}$ and concentrated under reduced pressure. The resulting residue was extracted with ethyl acetate (3 x 100 mL), and the combined organic layers were washed with brine, dried, filtered and evaporated. Purification on silica gel (hexane/ethyl acetate = 1/2) yielded product (**3**) (4.70 g, 62%) as a viscous oil. EI-MS: $C_{17}H_{23}NO_5S$ m/z (%) = 91 (100), 353 (M^+, 1); HRMS (EI, M^+) calcd for $C_{17}H_{23}NO_5S$ 353.1297, found 353.1303; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 4.11 (t, *J* = 4.8 Hz, 1H), 3.77 (t, *J* = 7.2 Hz, 2H), 3.61 (t, *J* = 6.6 Hz, 2H), 3.19 (ddd, *J* = 5.4, 13.5, 18.9 Hz, 1H), 2.80-2.67 (m, 2H), 2.47 (s, 3H), 2.41-2.25 (m, 1H), 1.87 (br s, 1H), 1.62-1.48 (m, 4H), 1.41-1.32 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.69, 164.76, 145.68, 134.79, 129.79 (2C), 128.86 (2C), 65.56, 62.41, 40.15, 32.16, 29.18, 27.28, 22.85, 21.70, 17.76; Anal. Calcd for $C_{17}H_{23}NO_5S$ C, 57.77; H, 6.56; N, 3.96. Found C, 57.96; H, 6.88; N, 3.63.

1-(5,5-Dimethoxypentyl)-3-(4-methylphenylsulfonyl)-2,6-azinanedione (6)

A solution of compound (**3**) (1.30 g, 3.68 mmol) in dichloromethane (70 mL) was added to a mixture suspension of pyridinium chlorochromate (1.30 g, 6.03 mmol) and Celite (4 g) in dichloromethane (15 mL). After being stirred at rt for 18 h, the mixture was filtered through a short silica gel column. The filtrate was dried, filtered and evaporated. Purification on silica gel (hexane/ethyl acetate = 1/1) yielded aldehyde (944 mg, 73%) as a gum. EI-MS: $C_{17}H_{21}NO_5S$ m/z (%) = 91 (100), 351 (M^+, 1); HRMS (EI, M^+) calcd for $C_{17}H_{21}NO_5S$ 351.1140, found 351.1142; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.73 (t, *J* = 1.5 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 4.15 (t, *J* = 4.8 Hz, 1H), 3.76 (t, *J* = 7.2 Hz, 2H), 3.24-3.08 (m, 1H), 2.77-2.71 (m, 1H), 2.70-2.65 (m, 1H), 2.46 (s, 3H), 2.44-2.29 (m, 3H), 1.67-1.46 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.85, 170.55, 164.64, 145.51, 134.62, 129.63 (2C), 128.68 (2C), 65.31, 43.06, 39.49, 28.98, 26.81, 21.52, 18.89, 17.57.

A solution of the resulting aldehyde compound (1.00 g, 2.85 mmol) in methanol (10 mL) was added to a mixture solution of *p*-toluenesulfonic acid (0.2 g) and trimethyl orthoformate (2 mL, 18.2 mmol) in

methanol (40 mL). After being stirred at rt for 2 h, the mixture was quenched with saturated sodium bicarbonate solution (5 mL) and concentrated under reduced pressure. The resulting residue was extracted with ethyl acetate (3 x 30 mL), and the combined organic layers were washed with brine, dried, filtered and evaporated. Purification on silica gel (hexane/ethyl acetate = 4/1) yielded product (**6**) as a viscous gum (1.13 g, 99%). EI-MS: $C_{19}H_{27}NO_6S$ m/z (%) = 75 (100), 366 (M^+-31, 10), 396 (M^+-1, 1); HRMS (EI, M^+) calcd for $C_{19}H_{27}NO_6S$ 397.1559, found 397.1566; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 4.34 (t, *J* = 5.7 Hz, 1H), 4.11 (t, *J* = 3.9 Hz, 1H), 3.75 (t, *J* = 7.8 Hz, 2H), 3.30 (s, 6H), 3.28-3.12 (m, 1H), 2.80-2.67 (m, 2H), 2.47 (s, 3H), 2.42-2.30 (m, 1H), 1.65-1.45 (m, 4H), 1.40-1.30 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.51, 164.65, 145.56 , 134.79, 129.70 (2C), 128.83 (2C), 104.13, 65.46, 52.70 (2C), 40.06, 31.99, 29.11, 27.32, 21.72, 21.64, 17.68; Anal. Calcd for $C_{19}H_{27}NO_6S$ C, 57.41; H, 6.85; N, 3.52. Found C, 57.73; H, 6.93; N, 3.93.

1-(5,5-Dimethoxypentyl)-5-(4-methylphenylsulfonyl)-1,2,3,4-tetrahydropyridine (2)

Compound (**6**) (0.90 g, 2.27 mmol) was added to a suspension of *N*-bromosuccinimide (0.58 g, 3.26 mmol) and sodium bicarbonate (0.42 g, 5.00 mmol) in dry acetonitrile (20 mL). The mixture was stirred under nitrogen atmosphere at rt for 90 min, and the reaction was quenched with water (1 mL). Evaporation of solvent followed by purification of the crude product by column chromatography on silica gel (hexane/ethyl acetate = 1/1) yielded crude bromo compound (883 mg). Without further purification, a solution of bromo compound (883 mg) in THF (20 mL) *via* syringe was added to a suspension of lithium aluminum hydride (141 mg, 3.72 mmol) in THF (20 mL) in an ice bath for 30 min. The mixture was refluxed for 2 h, quenched with saturated aqueous ammonium chloride solution (5 mL) under cooling, and concentrated. Water (15 mL) was added to the residue and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with brine (2 x 20 mL), dried, filtered and evaporated. Purification on silica gel (hexane/ethyl acetate = 1/1) yielded product (**2**) (211 mg, 31%) as a viscous oil. EI-MS: $C_{19}H_{29}NO_4S$ m/z (%) = 75 (100), 367 (M^+, 1); HRMS (EI, M^+) calcd for $C_{19}H_{29}NO_4S$ 367.1817, found 367.1815; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.28 (s, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 4.35 (t, *J* = 5.7 Hz, 1H), 3.32 (s, 6H), 3.13 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 5.4 Hz, 2H), 2.40 (s, 3H), 2.14 (t, *J* = 6.3 Hz, 2H), 1.83-1.75 (m, 2H), 1.66-1.51 (m, 4H), 1.39-1.25 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.83, 142.03, 139.82, 129.26 (2C), 126.68 (2C), 104.21, 99.44, 55.73, 52.2 (2C), 45.20, 32.14, 28.25, 21.60, 21.42, 21.04, 19.64.

9-(4-Methylphenylsulfonyl)perhydroazino[1,2-*a*]azin-1-ylcarbaldehyde (7)

A co-solvent solution of acetic acid and water (3/1, 8 mL) was added to compound (**2**) (100 mg, 0.27 mmol). The mixture was stirred at reflux for 4 h. Evaporation of solvent followed by purification of the crude product by column chromatography on silica gel (hexane/ethyl acetate = 1/1) yielded product (**7**) (68 mg, 78%) as an oil. EI-MS: $C_{17}H_{23}NO_3S$ m/z (%) = 137 (100), 321 (M^+, 1); HRMS (EI, M^+) calcd for

$C_{17}H_{23}NO_3S$ 321.1399, found 321.1398; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (d, *J* = 0.9 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.36 (s, 1H), 3.93-3.81 (m, 1H), 3.77-3.61 (m, 1H), 2.98-2.91 (m, 1H), 2.67-2.61 (m, 1H), 2.46 (s, 3H), 2.32-2.24 (m, 1H), 2.19-2.07 (m, 1H), 2.00-1.90 (m, 1H), 1.66-1.40 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.30, 147.75, 135.01, 129.73 (2C), 128.57 (2C), 61.69, 61.63, 57.43, 56.11, 47.26, 27.19, 25.25, 23.62, 21.87, 21.64.

Lupinine (1a)

Sodium borohydride (38 mg, 1.0 mmol) was added to a solution of compound (**7**) (50 mg, 0.16 mmol) in methanol (15 mL) at rt. The mixture was stirred for 2 h at rt. Saturated $NaHCO_{3(aq)}$ (1 mL) was added to the mixture and the mixture was concentrated under reduced pressure. Water (5 mL) was added to the residue, and the mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine (2 x 10 mL), dried, filtered and evaporated. Without purification, a suspension of crude compound (45 mg) and sodium phosphate (36 mg, 0.25 mmol) in methanol (10 mL) was stirred, and 6% sodium amalgam (Na/Hg, 0.5 g) was added. The mixture was vigorously stirred for 2 h at rt. The residue was filtered and washed with methanol (2 x 10 mL). The combined organic layers were concentrated to leave the crude compound. Purification on silica gel (hexane/ethyl acetate = 1/1) and then recrystallization from ethyl acetate yielded lupinine (**1a**) (19 mg, 77%) as a white solid. mp = 166-168 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.41 (br s, 1H), 4.16 (dd, *J* = 4.5, 10.5 Hz, 1H), 3.69 (d, *J* = 10.5 Hz, 1H), 2.85-2.81 (m, 2H), 2.20-212 (m, 2H), 2.05-2.00 (m, 1H), 1.87-1.83 (m, 2H), 1.82-1.72 (m, 2H), 1.61-1.50 (m, 6H), 1.31-1.21 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 66.01, 65.07, 57.11, 57.03, 38.08, 31.43, 29.66, 25.56, 24.59, 22.92. The ^{1}H NMR spectral data were in accordance with the reported in the literature.

ACKNOWLEDGEMENTS

The authors would like to thank the National Science Council (NSC 93-2113-M-390-004) of the Republic of China for financial support.

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