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Synthesis of an analogue of the naturally occuring Aristotelia indole alkaloid, fruticosoline

Md. Abul Hashem*, Israt Sultana & Md. Abdul Hai
Department of Chemistry, Jahangirnagar University, Savar, Dhaka-1342, Bangladesh

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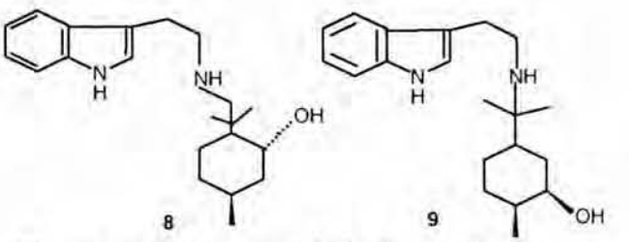
A synthesis of an analogue of the rare Aristotelia indole alkaloids is reported. The monoterpene, Pulegone, **1** on nitromethylation give nitromethylpulegone, **2**, which on reduction with $LiAlH_4$ and as well as with $NaBH_4$ yield the compounds **3**, **4** and **5**. The amino-alcohol **5** is condensed with indolyloxalyl chloride **6** to furnish the α-ketoamide **7**, which is converted to the corresponding monoterpenoid indole alkaloid **8**, an analogue of fruticosoline **9**.

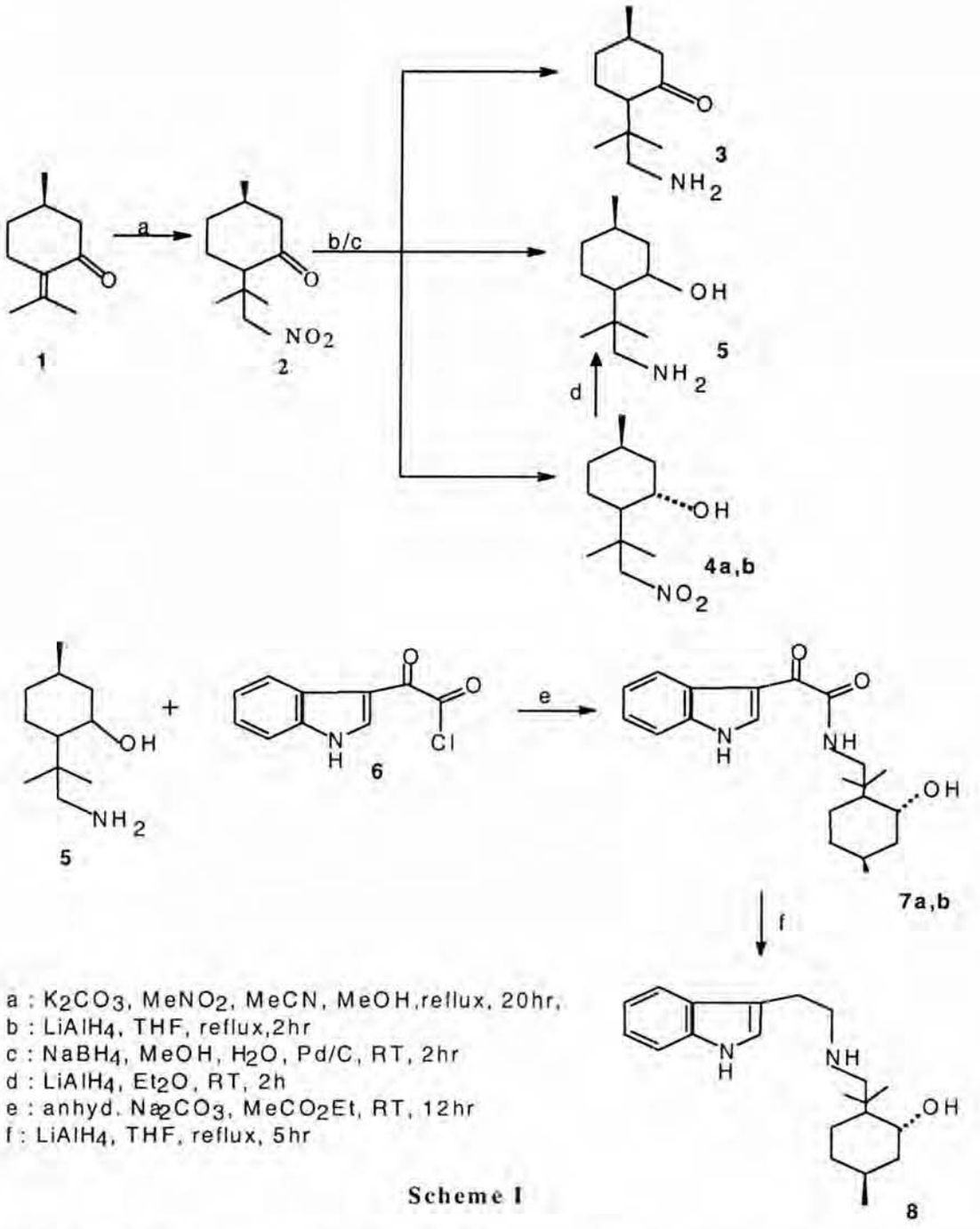
A number of Aristotelia alkaloids[1-4] have been discovered recently in Australia, New Zealand, Chile, Peru, France and Argentina. Synthesis[4-7] of only a few of these alkaloids isolated in minor amounts from the plants of genus, Aristotelia have been reported. No pharmacological studies have yet been carried out with these alkaloids owing to their occurrence in the plants in minute amount. The simplest indole alkaloid in Aristoteline family is fruticosoline, **9**[8,9], which was isolated from *Aristotelia fruticosa*. Our aim was to synthesize some analogues of the monoterpenoid , fruticosoline in higher yield. The basic skeleton of monoterpenoid Aristotelia alkaloids consists of an indole nucleus and a monoterpene unit.A joining of the two parts forms the alkaloid. For this purpose we have selected pulegone **1** as a source of the monoterpenoid unit, which, after a few conversions, was condensed with the indole nucleus. The condensed product was then reduced to **8,** the analogue of fruticosoline **9**.

Results and discussion

The Michael addition of nitromethane to pulegone **1** yielded a colourless crystal of compound **2** (**Scheme I**). Strong absorptions of IR peaks at 1550 and 1380 cm^{-1} clearly indicate the presence of nitro group in **2**. In the ^1H NMR spectra two methylene (**Table I**) protons attached to NO_2 group appear as two doublets (J=10Hz) at δ 5.02 and 4.27, which indicates that two methylene protons are not equivalent. In ^{13}C NMR spectra the peaks at δ 211 and 83 clearly indicates the carbon of C=O and CH_2-NO_2 respectively.



The reduction of nitromethylpulegone **2** gave compounds **3,4** and **5** with $LiAlH_4$ as well as with $NaBH_4$ (**Table II**). $LiAlH_4$ reduction gave almost exclusively the aminomethylpulegone **3** whereas the $NaBH_4$ reduction in MeOH gave nitromethylpulegol **4** and $NaBH_4$ in combination with Pd/C in MeOH/H_2O gave the aminomethylpulegol **5**. IR spectrum of compound **3** gave a medium broad band for -NH stretching at 3300 cm^{-1} and a sharp peak at 1735 cm^{-1} due to C=O stretching. Broad ^1H NMR peak at δ 7.64 for NH_2 confirmed the reduction of nitro group. The two methylene protons attached to the carbon containing NH_2 showed absorption peaks at δ 2.37 and 2.32. Compound **4** is found to be a mixture of two isomers (2:3) on GC which could not be separated. IR absorption at δ 3612 cm^{-1} indicate the reduction of keto group to alcoholic group. The 500 MHz ^1H NMR spectra clearly indicates two sets of absorption for the isomers of **4**. The ^{13}C NMR spectrum also showed two sets of carbon signals of eleven carbon each with different intensity ratio. IR spectrum of compound **5** showed the two broad bands at 3300 and 3200 cm^{-1} which are for -OH and -NH_2 groups respectively. Compound **5** showed two broad absorptions as singlets at δ 3.5 and at δ 2.22 in the ^1H NMR spectra.



Scheme I

These confirmed the presence of $-NH_2$ and -OH groups in the compound (**Table II**). The methylene protons attached to the carbon atom containing the NH_2 absorbs at δ 2.84 and 2.75 whereas the methine proton (CHOH) attached to hydroxyl group absorbs at δ 4.1. The ^{13}CNMR values also confirm the structure of **5**. The stereochemistry of the compound **5** could not be determined.

The reaction of indole with oxalyl chloride in anhyd. ether for 1 hr at 0°C yielded the compound **6** as yellow powder in high yield. The reaction of compound **5** with compound **6** in presence of anhyd. Na_2CO_3 in dry ethyl acetate at room temperature yielded two isomeric condensation products **7a** and **7b**, the later being the major product. The IR spectrum of both the compounds showed a medium sharp

Table I — IR, ^{1}H and ^{13}C NMR, and MS of the isolated compounds

Compd	IR	^{1}H NMR(δ)	^{13}C NMR(δ)	MS: m/z
2	2960,2940 m(sh,CH), 1705 s(sh,C=O), 1380 s(sh,C-NO_2)	5.02 (d, 1H, *J*=10Hz, 8-H), 4.27 (d, 1H, *J*=10 Hz, 8-H), 2.43 (dd, 1H, *J*=5, 13Hz, 4-H), 2.33 (ddd, 1H, *J*=2, 4, 13 Hz, 2-H), 2.13 (m, 1H, 2-H), 2.09 (dt, 1H, *J*=1, 13Hz, 5-H), 1.94 (m, 1H, 6-H), 1.90 (m, 1H, 5-H), 1.49 (ddd, 1H, *J*=3.13, 16 Hz, 6-H), 1.37 (ddq, 1H, *J*=3,6,14 Hz, 1-H), 1.12 (s, 3H, 7-CH_3), 1.09 (s, 3H, 7-CH_3), 1.02 (d, 3H, *J*=6Hz, 1-CH_3).	211.2 (C=O), 83.6 (8-C), 54.5 (4-C), 51.7(2-C), 36.2 (7-C), 36.0 (1-C), 34.3 (5-C), 28.0 (6-C), 24.6(7-C(Me)), 22.1 (7-C (Me)), 21.5 (1-C(Me))	198(M^{+}-CH_3, 1), 183(M^{+}-NO, 12), 167(M^{+}-NO_2, 22), 151 (M^{+}-H-NO_2–CH_3 ,26), 137(M^{+}-NO_2-2×CH_3, 24), 123 (M^{+}–H–NO_2–CH_3–CO, 46), 112 (58), 109 (50), 83 (58), 69 (100)
3	3300m (br, NH), 2970, 2935m (sh,C.H), 1735 s(sh, C=O)	7.64 (br, 2H, NH_2), 2.37(d, 1H, *J*=10Hz, 8-H), 2.32 (d, 1H, *J*=10Hz,8-H), 1.97-2.02 (m, 2H, 1, 4-H), 1.84, 1.90 (m, 2H, 2, 2-H), 1.72-1.79 (m, 1H, 6-H), 1.25-1.33 (m, 3H, 5, 5, 6-H), 1.23 (s, 6H, 2x7-Me), 1.03 (d, 3H, *J*=6, 5 Hz,1-Me),	184 (C=O), 65.6 (8-C), 58.6 (4-C), 52.3 (7-C), 42.2 (2-C), 36.6 (1.C), 24.4(5-C), 25.9(6-C), 24.4(7-Me), 22.3(7-Me), 21.0(1-Me)	183(M^{+}, 4), 182 (M^{+}–H, 17), 167(M^{+}–H–CH_3,11), 154 (M^{+}–H–CO,1), 138 (M^{+}–CH_2 NH_2–CH_3, 14), 111 (M^{+}–$C_4H_{26}N$, 8), 100 (47), 87 (100).
4a	3612, 3565 m(s,-OH), 2960,2910 (s, CH), 1550 s(s, C-NO_2, assym. str.), 1378 s(sh, C-NO_2, symm. sr.)	5.07 (d,1H, *J*=10.5 Hz,8-H), 4.46 (d,1H, *J*=10.5 Hz,8-H), 3.49-3.58 (m,1H. 3-H), 2.04(s, 1H, OH), 1.80-1.84 (m,1H,1-H), 1.71-1.74 (m, 2H, 2-H), 1.61-1.65 (m,2H,5-H), 1.40-1.46 (m, 1H, 4-H), 1.30-1.40 (m,2H,6-H), 1.08 (m, 3H, 7-Me), 1.07 (s,3H, 7-Me), 0.91 (d, 3H, *J*=6 Hz, 1-Me)	83.8 (8-C), 67.2(CH-OH), 54.5 (4-C), 41.6(2-C), 39.0 (7-C), 34.0(1-C), 32.6 (5-C),31.3(6-C), 27.0 (7-C(Me)), 24.0 (7-C(Me)), 20.5 (1-C(Me))	No mole peak 197 (M^{+}–H_2O,1), 182 (M^{+}–H_2O-CH_2,1), 167 (M^{+}–H_2O–NO, 9), 151 (M^{+}–H_2O–NO_2, 9), 137 (M^{+}–HP–NO_2, CH_3, 9), 121 (M^{+}–H_2O–NO_2–2, CH_3, 12), 109 (20), 81 (60), 69 (70), 55 (100)
4b	3612, 3565 m(s,-OH), 2960,2910 (s, CH), 1550 s(s, C-NO_2, assym. str.), 1378 s(sh, C-NO_2, symm. str.)	4.67 (d,1H, *J*=10Hz,8-H), 4.31 (d,1H, *J*=10Hz, 8-H), 4.12 (dd,1H, *J*=7,14Hz, 3-H), 1.91-1.98 (m,1H, 1-H), 1.75-1.80 (dt, 2H, *J*=3,13 Hz, 2-H), 1.65-1.69 (m, 2H, 5-H), 1.59 (s,1H, OH), 1.47-1.56 (m,2H, 6-H), 1.17-1.26 (m,1H, 4-H), 1.16 (s, 3H, 7-Me), 1.14 (s,3H, 7-Me), 0.88(d,3H, *J*=6Hz, 1-Me).	83.9 (8-C), 67.3(CH-OH), 51.0 (4-C), 43.5(2-C), 38.8 (7-C), 36.0(1-C), 26.5 (7-C(Me)), 26.0 (6-C), 25.5(5-C), 22.5 (7-C(Me)), 22.0 (1-C(Me)),	—

Contd –

Table I — IR, ^{1}H and ^{13}C NMR, and MS of the isolated compounds — *Contd*

Compd	IR	^{1}H NMR(δ)	^{13}C NMR(δ)	MS (m/z)
5	3300 m (br, –OH), 3200 m(br, NH), 2955, 2852 m(s,CH)	4.10 (br,s,1H,3-H), 3.50 (s, br, 2H, NH_2), 2.84 (d, 1H, *J*=12.63 Hz, CHa-NH_2), 2.75(d,1H, *J*=12.63 Hz, CHb-NH_2), 2.20 (s, 1H, OH), 1.7-2.0 (m, 2H, 2, 2-H), 1.61 (m, 1H, 4H), 1.50 (dt, 1H, 6-H), 1.0-1.3 (m, 4H, 1, 5, 5, 6-H), 1.07 (s, 3H, 7-Me), 0.95 (s, 3H, 7-Me), 0.87 (d, 3H, *J*=6.4 Hz, 1-Me)	65.1 (3-C), 52.6(8-C), 46.3 (7-C), 42.8(1-C), 37.1 (4-C), 36.2(2-C), 29.1 (5-C), 25.1(6-C), 23.5 (7-Me), 22.4 (7-Me), 21.2 (1-Me),	185(M$^+$, 5), 170 (M$^+$–CH_3, 2), 157 (M$^+$–CO, 9), 152 (M$^+$–CH_3–H_2O, 5), 140 (M$^+$–$CH_3CH_2NH_2$, 18), 95 (M$^+$–$C_4H_{10}N$–H_2O, 100), 81(98), 69(62).
7a	3590 m(sh, –OH), 3450m (sh-NH), 3050 s (sh, =C–H),2990 s (sh, C–H), 1715 m (sh, C=O), 1635 s(C=C)	9.4 (s, 1H, NH), 8.40 (d, 1H, 4-H), 8.12 (m, 1H, NH amide), 7.4 (d, 1H, 7-H), 7.3 (m, 2H, 2, 6-H), 7.1 (dd, 1H, 5-H), 4.2 (dt, 1H, 14-H), 3.98 (s, 1H, OH), 2.4 (s, 2H, 11, 11-H), 2.30 (m, 1H, 13-H), 1.7 (m, 3H, 10, 18, 18-H), 1.2-1.45 (m, 4H, 15, 17-H), 1.27 (d, 3H,16-Me), 1.20 (s, 6H, 12, 12-Me),	—	—
7b	3590 m(sh,OH), 3450 m(sh,NH), 3050 s(sh, C,H),2990 s(sh,CH), 1715 m(sh,C=O),1635 s(sh,C=C)	10.15 (s,1H, NH), 9.7 (s, 1H, NH, ami-de), 8.48 (d, 1H, 4-H), 8.3 (m, 1H, 7-H), 7.1-7.5 (m, 3H, 2, 5, 6-H), 5.1 (dt, 1H,14-H), 3.8 (d, 1H, 11-H), 3.52 (d, 1H, 11-H), 2..02-2.30 (m, 3H, 13, 15, 15-H), 2.02 (s, 1H, OH), 1.6-1.8 (m, 3H, 16, 18, 18-H), 1.05-1.2 (m, 2H, 17-H), 1.25 (d, 3H, 16-Me), 1.12 (s, 3H, 12-Me), 0.98 (s, 3H, 12-Me)	—	—
8	3590 m(sh,-OH), 3440 m (sh, –NH), 3040 m (sh, –CH), 2990 s(sh, –CH), 3590 s (m, C=C)	8.07 (s, br, 2H, NH, indolic and amine), 7.62 (d, 1H, *J*=7.8 Hz, 4-H), 7.37 (d, 1H, *J*=8.1 Hz, 7-H), 7.21 (dt, 1H, *J*=1, 7.1 Hz, 6-H), 7.13 (dt, 1H, *J*=1, 7.9 Hz, 5-H), 7.09 (d, 1H, *J*=2.1 Hz, 2-H), 4.27 (ddd, 14-H), 3.91 (t, 2H, *J*=6.3 Hz, 9-H), 3.05 (t, 2H, *J*=6.3, 8-H), 2.35 (s,1H, OH), 2.1 (m, 2H, 11-H), 1.5-1.8 (m, 8H, 13, 15, 10, 17, 18-H), 1.33 (s, 3H, 12-Me), 1.28 (s, 3H, 12-Me), 1.23 (d, 3H, 16-Me)	—	328(M$^+$, 2), 254 (M$^+$,100), 144 (M$^+$–$C_{11}H_{22}NO$, 38), 130 (M$^+$–$C_{12}H_{24}$ NO, 79).

band at 3600 and at 3450 cm^{-1} which were assigned to -OH stretching and NH stretching respectively. A strong sharp band at 1710 cm^{-1} was assigned to C=O stretching. The ^{1}H NMR spectrum of compound **7a** showed a broad peak at δ 9.40 for indolic -NH proton. Absorption at δ 8.12 was for amide -NH. The peak at δ 3.98 corresponds to -OH proton. On the otherhand the ^{1}H NMR spectrum of **7b** showed a peak at δ 10.15 for indolic -NH proton and another broad singlet at δ 9.70 for the amide -NH. The singlet at δ 2.02 was assigned to the hydroxyl proton.

Finally the reduction of compound **7b** with $LiAlH_4$

Table II — Reduction of nitromethylpulegone **2** with $LiAlH_4$ and $NaBH_4$ to give compounds **3, 4** and **5**

Reagents and conditions	Percentage of products		
	3	**4**	**5**
$LiAlH_4$, CH_2Cl_2 R.T. 3 hr	44	5	2
$LiAlH_4$, THF Reflux, 2 hr	48	21	5
$NaBH_4$, MeOH/H_2O Reflux, 12 hr	8	74	2
(i) $NaBH_4$,dry ethanol (ii) Pd/C, R.T. 4 hr	24	41	30
(i) $NaBH_4$, MeOH/H_2O (ii) Pd/C, 2 hr, RT.	5	2	65

in THF gave the reduced product **8**. IR of **8** showed no absorptions for the C = O groups. Moreover, the compound **8** showed two triplets on ^1H NMR spectra at δ 3.91 and 3.05 which clearly indicate two methylene groups at position C-9 and C-8, thus confirming that reduction of the keto as well as amide group has taken place. The synthesis of **8,** the analogue of fruticosoline **9** has been achieved in only 5 steps from pulegone **1**.

Experimental Section

Fisher-John's electrothermal melting point apparatus was used for recording the melting points and are uncorrected. IR spectra were recorded either as KBr or as solution in $CHCl_3$ or CCl_4 or as nujol mull in perkin-Elmer 257 spectrometer, ^1H NMR spectra in $CDCl_3$ on a Bruker WM400 spectrometer with TMS as internal standard,^{13}C NMR spectra on a Bruker WH270 instrument with DEPT Programme in $CDCl_3$ using TMS as internal standard and mass spectra on a varian MAT-711 (70ev) and varian MAT 445 with GC combination. Column chromatography was performed on kiesel gel 60GF 254 (E merck). A varian 3700 type, GC and TLC were used for reaction monitering. All reactions were carried out in dry nitrogen atmosphere. All organic solutions after work-up were dried over anhyd. Na_2SO_4. Pet. ether refer to fraction of b.p. 40-60°. For test of alkaloids Dragendorff and Mayer's reagents were used[10].

Preparation of 8-nitromethylparamenthan-3-one 2. Pulegone **1** (7.6 g ; 0.05 mole), nitromethane (9.15 g ; 150 mL, 0.15 mole) and K_2CO_3 (10 g) in the mixture of acetonitrile (45 mL) and methanol (15 mL) was refluxed with continuous stirring at 120°C. TLC examination of the reaction showed the increase of the product with time. After 20 hr reaction the solids were filtered off and the filtrate was evaporated *in vacuo*. It was extracted with benzene to remove K_2CO_3 and the extract was concentrated to brown coloured liquid (12.97 g). The crude product was chromatographed over a column of kiesel gel using pet. ether : ethyl acetate (24:1) as solvent system to give pure **2** as colourless crystals (9.0226 g ;85%), m.p. 57-58°C.

Reduction of 2 with lithium aluminium hydride. A solution of **2** (1.5 g; 10 mmole) was added dropwise to the suspended $LiA1H_4$ (3 g) in 30 ml THF and was refluxed for 2 hr with continuous stirring under nitrogen atmosphere. After 2 hr the reaction was worked up by adding dropwise to ice water. THF was then distilled *in vacuo*. The concentrate was then treated with few drops of dil. H_2SO_4 and stirred for 30 min. The mixture was extracted with dichloromethane (4×30 mL). The organic layer was washed with water, dried and evaporated *in vacuo* to yield the crude liquid product (1.20 g). The crude on TLC examination gave four spots, one of them was reactant **2**. The liquid was chromatographed over a column of kiesel gel using initially with pet. ether : ethyl acetate (7:1) solvent system and afterwards with continuous increase of ethyl acetate. From the column chromatography, three pure fractions were collected. Fractions (6-10) yielded the compound **4** (0.390 g; 21%), fractions (15-25) was found to be the compound **3** (0.620 g ; 48%) and fractions (30-38) gave the compound **5** (0.063 g ; 5%).

The compound **4** was light yellow liquid; its GC analysis showed it to be a mixture of two isomers **4a**, **4b**, ratio 2:3 respectively. Compound **5** was obtained as colourless crystals m.p. 53-54°C and compound **3** was also obtained as colourless crystals m.p. 156-157°C. The compounds **3**, **4** and **5** were characterized by spectral analysis (**Table I**).

Reduction of 2 with sodium borohydride. In a 2-necked flask a suspension of 125 mg sodium borohydride in 10 mL of water was quickly added to 1.7 g of Pd/C in 10 mL water. The nitro compound **2** (0.5 g, 2.34 mmole) in 20 mL of methanol was then added over a period of 5 min. The reaction was continued for 2 hr. Then the solution was filtered off and the filtrate was extracted with dichloromethane (3×25 mL). The combined organic portion was dried and evaporated *in vacuo*. A pale yellow coloured crystaline product was

obtained (0.49 g). The crude crystal was then recrystallized from *n*-hexane : dichloromethane (10 : 1) and a pure colourless crystals of the compound **5** (0.28 g ; 65%) were obtained.

Reduction of 4 to 5 with lithium aluminium hydride. To a stirred solution of 4.7 g $LiAlH_4$ in 10 mL of dry ether was added dropwise a solution of **4** (0.7 g; 4.7 mmole) in 5 mL of ether at room temperature. Stirring was continued for 2 hr. After completion of the reaction it was added dropwise to ice. The mixture was treated with a few drops of dilute H_2SO_4 and then the whole solution was extracted with dichloromethane (4×30 mL). The extracts were washed with water, dried and evaporated *in vacuo* to yield the crude product (0.86 g). The crude product was then recrystallised with the solvent systems *n*-hexane : dichloromethane (10:1) and pure crystals (0.67 g; 77 %) of **5** were isolated.

Preparation of 3-indolyloxalyl chloride 6. To a stirred solution of indole (2g ; 17 mmole) in 50 ml anhyd. ether at 0-5°C oxalyl chloride (2.25 g ; 17.71 mmole) was added dropwise during 30 min, stirring and cooling were continued for 1 hr more. The resulting yellow powder was collected, washed with anhyd. ether and dried *in vacuo* to give the compound **6**, a yellow coloured powder (2.4 g ; 72.7%), m.p. 134-35°C (decom) (Lit. m.p. 135°C)[11].

Reaction of compound 5 with 6 to give 7. To a mixture of anhyd. Na_2CO_3 (500 mg ; 4.71 mmole) and compound **5** (225 mg ; 1.22 mmole) in 10 mL freshly distilled dry ethyl acetate, compound **6** (337 mg ; 1.62 mmole) in 20 mL of dry ethyl acetate was added with vigorous stirring at room temperature. The reaction was continued for 12 hr. Then the reaction mixture was filtered off and the filtrate was dried and evaporated *in vacuo*. Finally a brown coloured gummy product (0.53 g) was obtained. On TLC examination two spots were found. The crude product was chromatographed over a column of kiesel gel using dichloromethane: ethyl acetate (10:1), when two pure isomeric products were isolated in addition to the mixture. The compound **7a** (34 mg; 8%) was a light violet coloured gummy product and compound **7b** (260 mg; 60 %) was a light green coloured solid m.p. 130-32°C.

Reduction of 7b with lithium aluminium hydride. To a stirred solution of excess $LiAlH_4$ (141 mg; 3.70 mmole) in 20 mL of dry THF was added dropwise a solution of compound **7b** (100 mg; 0.28 mmole) in 5 mL of THF at room temperature. It was refluxed for 5 hr. Then the reaction mixture was added dropwise with stirring to ice-water. The THF was evaporated *in vacuo*. The concentrate was treated with a few drops of dilute HCl and was extracted with CH_2Cl_2 (4×30 mL). The extracts were washed with water, dried and evaporated *in vacuo* to yield the crude gummy product (83 mg). The crude product was chromatographed over a column of kiesel gel using pet. ether : ethyl acetate (8:1) and successively eluted with solvent of increasing polarity. First fractions gave the starting material **7b** and then compound **8** (45 mg; 49%) as brown coloured gummy product.

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References

1 Darbre T, Nussbaumer C & Borschberg H-J, *Helv Chim Acta*, 67, **1984**, 1040.

2 Bick I R C, Bremner J B & Calder I C, *J Chem Soc, Chem Commun*, **1971**, 115.

3 Bick I R C & Hai M A, *The Alkaloids* edited by A Brossi (Academic press , Orlando) 24 , **1985** , p113.

4 Borschberg H J, *The Alkaloids* edited by A Cordell (Academic press , New York) 48, **1996** , p191.

5 (i) Chaichit N, Gate House B M, Bick I R C , Hai M A & Preston N W , *J Chem Soc Chem Commun*, **1979**, 874.

(ii) Hai A, PhD Thesis, University of Tasmania, Hobart, **1981.**

6 (i) Mirand C, Massiot G & Levy J, *J Org Chem*, 47, **1982**, 4169.

(ii) Stevens R V & Kenney P M, *J Chem Soc, Chem Commun*, **1983**, 384.

7 Gibble G W & Barden T C, *J Org Chem*, 50, **1985** , 5900.

8 Hai M A & Bick I R C, *Indian J Chem*, 29B, **1990** , 586.

9 Borschberg H J, *The Chemistry of Heterocyclic Compounds* edited by J E Saxton (Wiley, Chichester) 25, 1994, p. 15.

10 Agarwala S K & Agarwala R C, *Advanced Organic Analysis, part 1* (Pragati Prakashani, India), pp. 495-96.

11 Shaw K N F, McMillian A, Gudmundson A G & Armstrong M D, *J Org Chem*, 23, **1985**, 1171.