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A New Stereoselective Synthesis of Ladybug Defence Alkaloid Precoccinelline [1]

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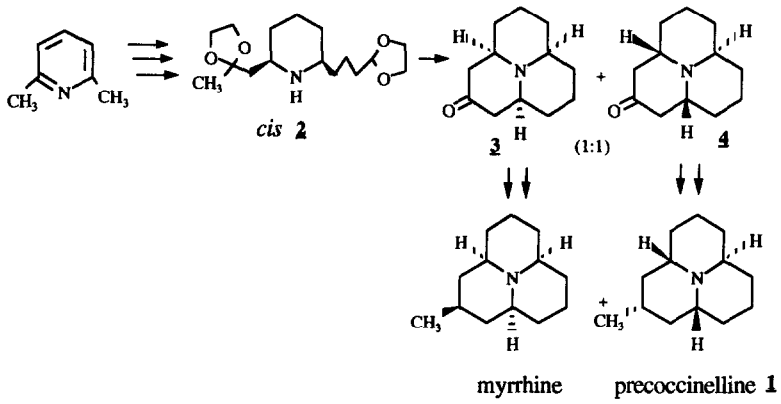
Abstract: We have accomplished a new stereoselective synthesis of precoccinelline **1** in six steps from the chiral synthon **6** with a overall yield of 31 %. The main feature of this synthesis is the asymmetric synthesis of the *trans* 2,6-keto-acetal piperidine **14** which assures a stereospecific cyclisation in the construction of key intermediate ketone **4**.

Introduction

Ladybugs are known to play a beneficial ecological role in controlling the population of harmful agricultural pests such as aphids and scale insects.

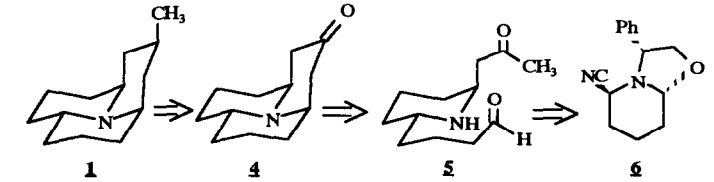
Interestingly, ladybugs have few natural enemies; when threatened, they secrete from their joints droplets of a fluid which repulses ants, quails and other would-be predators. This phenomenon, known as "reflex bleeding", serves as an efficient means of protection. From this fluid, precoccinelline **1**, (along with its N-oxide coccinelline) a methyl derivative of perhydropyrido [2,1,6-de] quinolizine, has been isolated, precoccinelline and coccinelline have been also found in several other ladybug species. [2]

To date only three syntheses of precoccinelline have been reported.[3,4,5] In the synthesis from Ayer's group, double cyclisation of the *cis*-piperidine derivative **2** gave exclusively an all-*cis* tricyclic ketone **3** (Scheme 1) which possesses the configuration of myrrhine. Tricyclic ketone **4** (a precursor of precoccinelline **1**) was obtained together with the all-*cis* ketone **3** (1:1 mixture) by epimerisation. It thus appeared that a stereoselective synthesis of precoccinelline **1** necessitated the preparation of a *trans*-piperidine derivative, the epimer of **2**.



Scheme 1

On the basis of our previously reported CN(*R,S*) strategy [6] for stereoselective syntheses of either *cis* or *trans* -2,6-dialkylpiperidines from **6**, we anticipated a stereoselective synthesis of precoccinelline **1** *via* the *trans*-piperidine derivative **5** (Scheme 2). It is noteworthy that the target molecule precoccinelline is symmetric; nevertheless we undertook its synthesis starting from the (2S,6R)-2-cyano-6-oxazolo-piperidine **6** due to its high potential for the stereoselective construction of piperidines and the ease of its preparation.



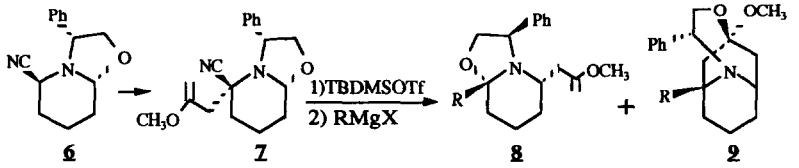
Scheme 2

Results and Discussion

Preparation of trans-*2-acetonyl-6-alkylpiperidine derivatives*

It was well established that *trans*-2,6-dialkylpiperidines could be formed stereoselectively by reduction of 2,6-dialkyl-1,2,3,4-tetrahydropyridines [7] and thus we planned the stereoselective preparation of *trans*-piperidine derivative **5** and, more generally *trans*-2-acetonyl-6-alkylpiperidine compounds from **6** (Scheme 2). In our recently reported asymmetric synthesis of (-)-euphococcinine and (-)-adaline [8] (other ladybug alkaloids) it was shown that sequential treatment of alkylated aminonitrile **7** by TBDMSOTf followed by a Grignard reagent gave rise to the formation of two products **8** and **9** (Scheme 3). It was also shown that when R was larger than methyl group, the oxazolidine **8**, resulting from a tandem

alkylation/aza-Cope rearrangement, was formed as the major product (R=*n*-C_5H_{11}; **8b** : **9b** 78:22). These results have been rationalised as the effect of a steric interaction between the phenyl group and the incoming alkyl chain. Consequently it was anticipated that the oxazolidine **8c** (R = 1, 3-dioxolano-2-propyl) would be a major product from the alkylation of the enol ether **7** with 1,3-dioxolano-2-propyl magnesium chloride as alkylating reagent.



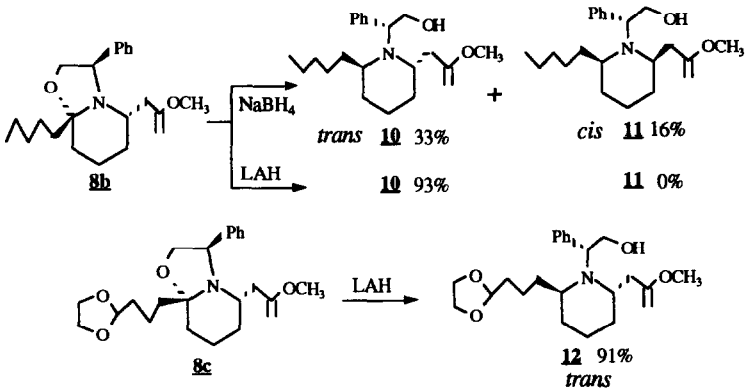
a: R = CH_3
b: R = n-C_5H_{11}
c: R = $(CH_2)_3$-(1,3-dioxolan-2-yl)

Scheme 3

Indeed, the sequential treatment of enol ether **7** with TBDMSOTf in CH_2Cl_2 followed by 1,3-dioxolano-2-propylmagnesium chloride in ether at -78°C led to the oxazolidine **8c** in 74 % yield, accompanied only by 12 % of the ketal **9c** in this tandem reaction.

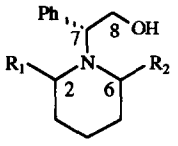
Having the *trans* 2,6-disubstituted oxazolidine **8c** in hand, we undertook the stereoselective reduction of oxazolidine ring to obtain the requisite *trans* 2,6-disubstituted piperidine.

At first, a trial experiment on the model pentyl derivative **8b**[8] was carried out. Thus, **8b** was treated with $NaBH_4$ in refluxing ethanol for 48 h (no reaction was observed at room temperature) to give a seperable 2:1 mixture of the *trans* product **10** and its *cis*-isomer **11** in moderate yield (Scheme 4).



Scheme 4

The moderate *trans* stereoselectivity together with the apparent low reactivity of $NaBH_4$ for this reduction led us to examine the LAH reduction. By the use of LAH in ether at



Substituents	*Trans*-isomers			*Cis*-isomers		
	δC7	δC8	Δ(δC7-δC8)	δC7	δC8	Δ(δC7-δC8)
R^1= pentyl R^2= CH_2–C(=CH_2)–OCH_3	58.7	59.8	-1.1	69.8	62.3	7.5
R^1= CH_2–(1,3-dioxolan-2-yl) R^2= CH_2–C(=CH_2)–OCH_3	58.6	59.7	-1.1			
R^1= CH_2–(1,3-dioxolan-2-yl) R^2= CH_2–C(OCH_3)(OCH_3)–CH_3	60.7	61.8	-1.1			
R^1= CH_2–C(2-CH_3-1,3-dioxolan-2-yl)–CH_3 R^2= CH_3 (Ref 11)	59.4	60.8	-1.4	65.5	62.3	3.3
R^1= propyl R^2= CH_3	59.3	60.6	-1.3	65.6	62	3.6
R^1= CH_3 R^2= n-$C_{11}H_{23}$ (Ref 6c)	59.5	60.7	-1.2	66.3	62.3	4.0
R^1= CH_2–(2-CH_3-1,3-dioxolan-2-yl) R^2= CH_2–C(CH_3)(1,3-dioxolan-2-yl) (Ref 12)	59.7	61.4	-1.7	68.2	62.7	5.5
R^1= CH_2–C(CH_3)(1,3-dioxolan-2-yl) R^2= CH_2-CH=CH_2 (Ref 12)				68.4	62.3	6.1
R^1= CH_2–C(CH_3)(1,3-dioxolan-2-yl) R^2= CH_2–C≡CH				69.3	62.0	7.3
R^1= CH_2–(1,3-dioxolan-2-yl) R^2= CH_2–CH(CH_3)–C(=O)– (Ref 12)				68.2	63.3	4.9

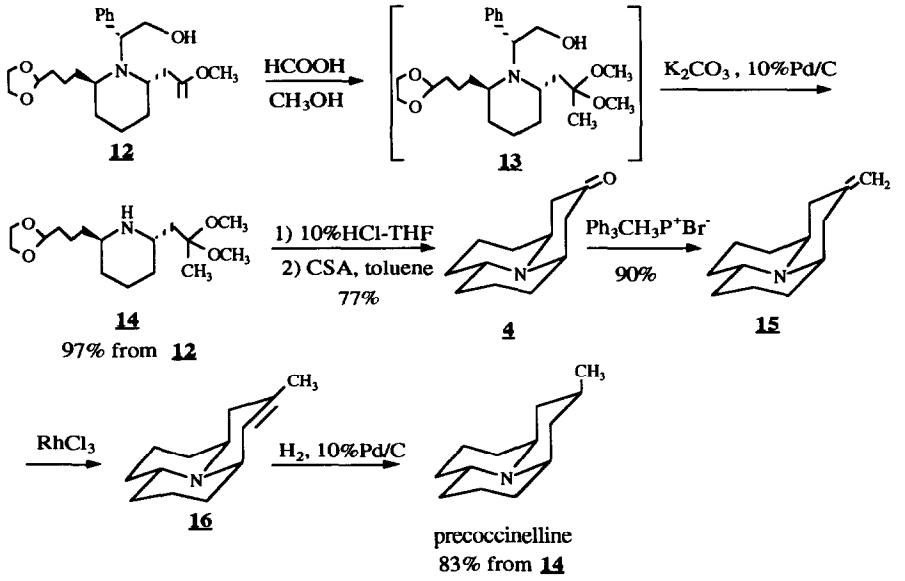
room temperature, the oxazolidine **8b** was cleaved cleanly to give a single *trans* -isomer **10** in 93 % yield .

Encouraged by the remarkable result with the model reaction, we used the same LAH reduction on the oxazolidine **8c** and obtained exclusively the *trans*-isomer **12** in 91 % yield (Scheme 4). In spite of the difficulties in the verification of the *trans* structure by ^1H NMR, because of the complicate couplings, unambiguous confirmation of the *trans* stereochemical assignment to compounds **10** and **12** was achieved by comparing directly with the ^{13}C NMR data obtained in our laboratory on a number of *cis* and *trans* -2, 6-piperidines.

It was noticed that without exception the *cis*-isomers have a significant difference of chemical shifts in ^{13}C NMR between C-7 and C-8 with a positive ppm value of $\Delta(\delta C_7\text{-}\delta C_8)$ ranging from 3.3 to 7.3 ppm; in contrast, the corresponding *trans*-isomers show a slight negative value of $\Delta(\delta C_7\text{-}\delta C_8)$ from -1.1 to -1.7 ppm (see Table).

The excellent stereochemical outcome observed in the reduction of oxazolidine ring with LAH was tentatively rationalised by a stereochemically preferred axial attack of hydride on the favorable iminium ion [9] which contains the enol ether group in the axial orientation due to $A^{(1,2)}$ strain.[10]

A "one-pot" methanolysis and hydrogen transfer debenzylation of **12** furnished the ketoacetal piperidine **14** in 97 % yield. In this transformation formic acid acts as catalyst for the methanolysis and hydrogen donner for the debenzylation (Scheme 5).



Scheme 5

Up to this point, we had achieved an efficient asymmetric synthesis of *trans*-2,6-disubstituted piperidine derivative from the chiral synthon **6**. Application of this method was

expected to lead to the stereoselective synthesis of *trans*-2-alkyl-6-acetonylpiperidine analogues by varying the Grignard reagent in the alkylation of the enol ether **7**.

Synthesis of precoccinelline

The key intermediate, tricyclic ketone **4**, was obtained as a single product in 77 % yield upon hydrolysis of the ketoacetal group followed by an intramolecular Mannich reaction promoted by 3 eq of CSA in refluxing toluene.

This novel synthesis of the tricyclic ketone **4** is superior to all those previously reported, having fewer steps and higher overall yield.

Conversion of **4** into the *exo*-cyclic olefin **15** was accomplished in 90 % yield *via* a Wittig reaction. Direct hydrogenation of the *exo*-olefin **15** gave a 3.5:1 mixture of precoccinelline and its axial methyl isomer, which compares with the result obtained by Mueller group.[5]

To improve the stereoselectivity of the hydrogenation, the *exo*-olefin **15** was first isomerized to its *endo*-isomer **16** by treatment with $RhCl_3$ in boiling ethanol.[13] Subsequent hydrogenation of the resulting *endo*-olefin **16** gave the final product precoccinelline **1** in 83 % yield in two steps with a stereoselectivity greater than 90 %, as has been reported by Ayer and Mueller groups. [3,5]

Experimental section

Alkylation of 7: To a solution of **7** [8] (2.544 g, 8.54 mmol) in CH_2Cl_2 (20 mL), TBDMSOTf (4 mL, 17.4 mmol) was added at room temperature. The reaction mixture was stirred for 40 min then was diluted with Et_2O (40 mL) and cooled to -78°C while 1,3-dioxolano-2-propylmagnesium chloride [prepd. from 2.5 mL (18.9 mmol) 2-chloropropyl-1,3-dioxolane, 1.34 g (55 mmol) magnesium and 200 mL dibromoethane in 15 mL THF, and used as such], was added. After 3 h at -78°C, the reaction was quenched by a saturated solution of NH_4Cl and extracted with CH_2Cl_2. The combined extracts were dried (Na_2SO_4), and evaporated to dryness. The crude product was purified by flash chromatography (heptane-Et_2O, 2:1 then 1:1 respectively) to afford **8c** (2.446 g, 74 %) and **9c** (402 mg, 12 %) as colorless oils. Starting material **7** (200 mg, 8 %) was also recovered.

8c : IR (neat) : 2937, 2874, 1667, 1280 cm^{-1}; MS (EI) m/z : 387 (M^+, 2), 372 (19), 316 (29), 273 (18), 272 (93), 198 (68), 154 (100). ^1H NMR (200 MHz, CD_3CN) δ 7.1-7.45 (m, 5H), 4.80 (brs, 1H), 4.26 (m, 2H), 3.80 (m, 4H), 3.62 (d, J = 2.9 Hz, 1H), 3.58 (d, J = 2.0 Hz, 1H) 3.40 (dd, J = 8.0, 6.0 Hz, 1H), 3.30 (s, 3H), 3.05 (m, 1H), 1.2-1.94 (m, 14); ^{13}C NMR (50 MHz, CD_3CN) δ 18.6, 22.0, 23.1, 29.6, 34.9, 35.9, 42.7, 54.5, 55.1, 60.1, 65.4, 73.5, 82.4, 97.9, 105.3, 127.6, 127.9, 129.0, 147.7, 162.5; HRMS calcd for $C_{23}H_{33}NO_4$: 387.2410; found: 387.2405.

9c : IR (neat) : 2940, 2880, 1126 cm^{-1} ; MS (EI) m/z : 387 (M^+, 33), 372 (17), 356 (58), 342 (100), 326 (75), 316 (79), 299 (88); ^1H NMR (200 MHz, $CDCl_3$) δ 7.1-7.45 (m, 5H), 4.50 (m, 2H), 4.33 (t, *J* = 12.0 Hz, 1H), 4.0 (dd, *J* = 12.0, 5.0 Hz, 1H), 3.80 (m, 4H), 3.45 (m, 1H), 3.38 (s, 3H), 0.85-2.40 (m, 19 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.6, 18.4, 33.4, 34.2, 39.0, 39.2, 42.4, 48.3, 56.4, 57.6, 64.4, 64.7, 76.5, 101.4, 104.4, 126.2, 127.9, 143.5; HRMS calcd for $C_{23}H_{33}NO_4$: 387.2410; found : 387.2431.

Reduction of 8b [8]

With $NaBH_4$: To a solution of $NaBH_4$ (400 mg, 10.6 mmol) in ethanol (20 mL) was added a solution of **8b** (300 mg, 0.88 mmol) at room temperature. The reaction mixture was heated at reflux for 48 h then H_2O (20 mL) was added, and the mixture was extracted with CH_2Cl_2. The combined extracts were concentrated after being dried over Na_2SO_4 and the residue was purified by flash chromatography to give *trans*-isomer **10** (98 mg, 33 %, heptane-Et_2O 3:1) and *cis*-isomer **11** (50 mg, 16 %) as colorless oils and the starting material (40 mg, 13 %).

Trans-Isomer **10**: IR (neat) : 3428, 2930, 1650 cm^{-1}; MS (EI) m/z : 345 (M^+), 314, 275, 274 (100), 202, 154; ^1H NMR (200 MHz, $CDCl_3$) δ 7.2-7.4 (m, 5H), 4.37 (dd, *J* = 10.0, 4.5 Hz, 1H), 4.03 (t, *J* = 1.5 Hz, 1H), 3.62 (dd, *J* = 10.0, 4.5 Hz, 1H), 3.45 (s, 3H), 3.33 (m, 1H), 3.0 (m, 1H), 2.10 (dd, *J* = 13.5, 10.0 Hz , 1H), 1.92 (dd, *J* = 13.5, 4.5,Hz 1H), 1.0 -1.7 (m, 14H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 19.5, 22.9, 26.3, 30.6, 31.2, 31.6, 32.3, 36.3, 50.0, 52.2, 54.7, 58.7, 59.8, 82.0, 127.4, 128.4, 128.5, 140.7, 162.6.

Cis-Isomer **11** : IR (neat) 3438, 2930, 1650 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.2-7.4 (m, 5H), 4.38 (dd, *J* = 10.0, 4.5 Hz, 1H), 3.9 (m, 3H), 3.58 (dd, *J* = 10.0, 4.5 Hz, 1H), 3.54 (s, 3H), 3.29 (m, 1H), 2.85 (m, 1H), 2.54 (dd, *J* = 14.0, 8.0 Hz, 1H), 2.08 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.1-1.7 (m, 14H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 14.9, 22.7, 25.9, 28.1, 28.2, 31.6, 35.4, 41.3, 54.1, 54.8, 55.9, 62.3, 69.8, 82.6, 127.7, 128.4, 140.7, 163.1.

With $LiAlH_4$: To a suspension of $LiAlH_4$ (70 mg, 1.8 mmol) in Et_2O (5 mL) was added a solution of **8b** (120 mg, 0.35 mmol) at room temperature. After 5 h, water (7 mL) was added and the mixture was filtered through celite. The filtrate was concentrated to dryness and the residue was purified by flash chromatography (heptane-Et_2O 3:1) to afford the *trans*-isomer **10** (112 mg, 93 %).

Synthesis of *trans*-isomer 12: The same procedure as that described with $LiAlH_4$ for **8b** was used to reduce **8c** (3.4 g, 8.88 mmol) to afford the *trans*-isomer **12** (3.15 g, 91 %) as a colorless oil.

$[\alpha]^{20}_D$ -46° ($CHCl_3$, c 0.1); IR (neat) : 3480, 2935, 1650 cm^{-1}. MS (EI) m/z : 389 (M^+), 358 (17), 319 (22), 318 (100), 202 (21), 198 (24); ^1H NMR (250 MHz, $CDCl_3$) δ 7.3 (brs, 5H), 4.73 (t, *J* = 4.5 Hz, 1H), 4.35 (dd, *J* = 10.0, 5.0 Hz, 1H), 4.02 (t, *J* = 10.0 Hz, 1H), 3,7-3.95

(m, 6H), 3.63 (dd, J = 10.0, 5.5 Hz, 1H), 3.5 (s, 3H), 3.35 (m, 1H), 3.2 (brs, 1H), 3.0 (brs, 1H), 2.05 (m, 1H), 0.8-1.8 (m, 12 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 19.3, 21.0, 30.5, 30.7, 31.0, 33.9, 36.5, 49.8, 51.9, 54.6, 58.6, 59.7, 64.8, 82.0, 104.4, 127.2, 128.2, 140., 162.3; HRMS calcd for $C_{23}H_{35}NO_4$: 389.2566; found : 389.2564.

Synthesis of 14: To a solution of **12** (1.74 g, 4.47 mmol) in methanol (50 mL) was added 88% formic acid (2 mL, 46 mmol) at room temperature. After 30 min, the methanolysis was complete [ketal **13** can be isolated at this stage as a colorless oil after neutralisation with K_2CO_3 powder, filtration and flash chromatography (heptane-Et_2O, 3:1)]. K_2CO_3 powder (2.5 g) and 400 mg of 10 % Pd/C were added successively . After stirring for 30 min, the reaction mixture was neutralised by the addition of excess of K_2CO_3 powder, then filtered. The filtrate was distilled to dryness *in vacuo* and the residue was purified by flash chromatography (CH_2Cl_2-CH_3OH, 20:1) to give **14** (1.31 g, 97 %) as a colorless oil.

13 : IR (neat) 3430, 2940, 1379, 1171 cm^{-1}; MS (FAB) = 422 (M^{+1}), 390, 358, 318, 274, 198; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.35-7.70 (m, 5H), 4.90 (t, J = 4.5 Hz , 1H), 4.46 (brs, 1H), 4.16 (d, J = 6.0, 5.0 Hz, 2H), 4.0 (m, 4H), 3.50 (m, 1H), 3.30 (m, 1H), 3.20 (s, 3H), 3.18 (s, 3H), 2.04 (dd, J = 14.0, 8.0 Hz, 1H), 1.40-1.95 (m, 14H), 1.26 (s, 3H); ^{13}C NMR (50 MHz $CDCl_3$) δ 20.1, 21.1, 29.7, 32.8, 33.9, 37.8, 47.7, 49.0, 53.3, 60.0, 61.8, 64.8, 101.6, 104.4, 127.0, 128.2, 128.5, 141.8.

14: $[\alpha]^{20}_D$ -10° ($CHCl_3$, c 0.1); IR (neat) 3350, 2945, 1140 cm^{-1}; MS (EI) m/z 301 (M^+, 2), 270 (4) , 254 (8), 199 (17), 198 (99), 196 (24), 154 (100); ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.78 (t, J = 4.5, 1H), 3.83 (m, 4 H), 3.14 (s, 6H), 3.05 (m, 1H), 2.86 (brs, 1H), 2.03 (dd, J = 14.0 9.5 Hz, 1H), 1.30-1.75 (m, 13H), 1.27 (s , 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 19.9, 20.7, 21.6, 29.9, 32.3, 33.1, 33.1, 33.8, 47.3, 48.1, 48.3, 50.9, 64.8, 101.9, 104.4; HRMS calcd for $C_{16}H_{31}NO_4$: 301.2253; found: 301.2258.

Synthesis of tricyclic ketone 4: A mixture of **14** (1.31 g, 4.35 mmol) in THF (2.5 mL) and 5% HCl (25 mL) was stirred at room temperature for 1 h then the reaction mixture was adjusted to pH = 8 with 10% NaOH, and extracted with CH_2Cl_2. The extracts dried over Na_2SO_4 and CH_2Cl_2 was distilled. The residue was dissolved in toluene (250 mL) and camphorsulfonic acid (3 g, 13 mmol) was then added. The mixture was heated at reflux for 2 h, then cooled to room temperature and a saturated solution of $NaHCO_3$ was added. After extraction with CH_2Cl_2, the combined organic extracts were dried (Na_2SO_4) and concentrated. The crude product was purified by flash chromatography (CH_2Cl_2-CH_3OH 10:1) to give the tricyclic ketone **4** (647 mg, 77 %) as a white powder.

m.p. 81-83°C; IR(KBr) 2870, 2820, 1705 cm^{-1}; MS (EI) m/z 193 (M^+, 69), 192 (30), 178 (19), 150 (100), 136 (65); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.24 (brd J = 13.0 Hz, 2H), 2.78 (t,

J = 13.0 Hz, 3H). 1.2-2.1 (m, 14H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 19.0, 21.9, 33.9, 40.5, 48.3, 58.8, 210.9; HRMS calcd for $C_{12}H_{19}NO$: 193.1467; found: 193.1450.

Synthesis of *exo*-olefin 15: To a suspension of $Ph_3CH_3P^+Br^-$ (940 mg, 2.63 mmol) in THF (10 mL) was added 1.6 M *n*-BuLi in hexane (1.4 mL) at -78°C. The reaction mixture was stirred at room temperature for 1 h followed by the addition of a solution of tricyclic ketone **4** (200 mg, 1.04 mmol) in THF (5 mL). After stirring for 5 h at room temperature, the reaction was quenched with water (3 mL) and extracted with CH_2Cl_2. The combined extracts were evaporated to dryness then purified by flash chromatography (Al_2O_3, heptane-Et_2O, 5:1) to afford *exo*-olefin **15** (179 mg, 90 %) as an oil.
IR (neat) : 3060, 2930, 2870, 1605 cm^{-1}; MS (EI) m/z : 191 (M^+, 100), 190 (79), 176 (75), 162 (25), 148 (42), 136 (63); ^1H NMR (250 MHz, $CDCl_3$) δ 4.60 (s, 2H), 2.93 (brd, J = 13.0 Hz, 2H), 2.82 (t, J = 11.0 Hz, 1H), 2.58 (t, J = 13.0 Hz, 2H), 1.10-1.98 (m, 14H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 19.6, 30.7, 32.5, 34.5, 48.1, 59.5, 106.5, 149.0; HRMS calcd. for $C_{13}H_{21}N$: 191.1674; found : 191.1692.

Synthesis of precoccinelline 1: A mixture of *exo*-olefin **15** (50 mg, 0.26 mmol) and $RhCl_3 \cdot H_2O$ (20 mg, 0.1 mmol) in ethanol (2 mL) was heated at reflux for 2 h, then filtered to give an ethanolic solution of crude *endo*-olefin **16**, which was hydrogenated in the presence of 10 % Pd-C. The catalyst was filtered off, and the solvent removed *in vacuo*. The residue was purified by flash chromatography (Al_2O_3, Et_2O) to give precoccinelline as a colorless oil (42 mg, 83 %).

***Endo*-Olefin 15:** IR (neat): 3000, 2930, 2860, 1680 cm^{-1}; MS (EI) m/z : 191 (M^+, 99), 190 (100), 177 (35), 162 (35), 148 (30); ^1H NMR (250 MHz, $CDCl_3$) δ 5,15 (s, 1H), 3.60 (brs, 1H), 3.15 (m, 1H), 2.20-2.55 (m, 3H), 1.0-2.0 (m, 12H), 1,68 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 19.4, 20.0, 23.0, 27.7, 29.6, 31.5, 34.0, 34.3, 48.9, 54.8, 123.4.

Precoccinelline IR (neat): 2930, 2870 cm^{-1}; MS (EI): m/z 193 (M^+ 73) , 192 (100), 178 (50), 164 (51), 151 (77), 150 (75), 137 (61). ^1H NMR (250 MHz, $CDCl_3$) δ 3.00 (dd J = 10.5, 4.8 Hz, 2H), 2.78 (brt J = 11.0 Hz, 1H), 9.85 (m, 2H), 1.00-1.60 (m, 15H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 19.9, 22.8, 31.8, 31.4, 32.8, 34.8, 48.3, 58.2; HRMS calcd. for $C_{13}H_{23}N$: 193.1831; found : 193.1804.

References and notes

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