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PII: S0040-4020(16)31128-0

DOI: 10.1016/j.tet.2016.10.069

Reference: TET 28210

To appear in: *Tetrahedron*

Received Date: 5 July 2016

Revised Date: 24 October 2016

Accepted Date: 31 October 2016

Please cite this article as: Meesala R, Arshad ASM, Mordi MN, Mansor SM, Iodine-catalyzed one-pot decarboxylative aromatization of tetrahydro-β-carbolines, *Tetrahedron* (2016), doi: 10.1016/j.tet.2016.10.069.

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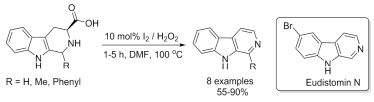

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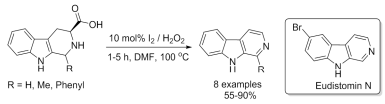

Tetrahedron
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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
β-Carboline
Decarboxylative aromatization
Iodine
Hydrogen peroxide
Tetrahydro-β-Carboline

ABSTRACT

A synthetic strategy was developed for the preparation of β-carbolines by one-pot decarboxylation and aromatization of tetrahydro-β-carboline-3-carboxylic acids by employing 10 mol% of iodine in presence of oxidant aqueous H_2O_2. The method was also successfully extended for the aromatization of tetrahydro-β-carboline-3-methyl esters. The utility of the method was demonstrated in the synthesis of β-carboline alakaloids norharmane, harmane and eudistomin N.

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1. Introduction

β-Carbolines,[1] are of great importance in the field of pharmaceuticals and are also versatile building blocks for bioactive compounds, natural products and drugs.[2] Compounds bearing aromatic β-carboline skeleton have been found to exhibit a wide variety of biological properties, such as, antitumor,[3] antimalarial,[4] anti-HIV[5] and antibacterial[6] activities. Moreover, certain β-carboline derivatives have also exhibited excellent binding affinities towards benzodiazepine receptors,[7] 5-hydroxyserotonin receptors,[8] and monoamine oxidase[9] in the central nervous system. Compounds bearing a β-carboline moiety are playing an important role as versatile synthetic intermediates in the synthesis of pharmaceutically important molecules.[10]

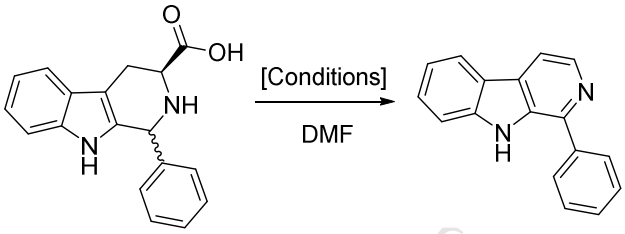
Their importance has attracted organic chemists to develop new synthetic strategies to construct the β-carboline moiety. Dehydrogenation of a suitable tetrahydro-β-carboline unit is a general method for its synthesis. This transformation involves heating the substrate with palladium on carbon,[11] sulfur,[12] SeO_2,[13] and $K_2Cr_2O_7$[14] with excess usage of the reagents and extended reaction times. DDQ[15] and chloranil[16] were also found useful reagents for aromatization, but the yields are not always satisfactory. IBX-mediated aromatization of tetrahydro-β-carbolines is known to produce β-carbolines at room temperature.[17] We have also developed a $CuCl_2$ catalyzed protodecarboxylation and aromatization of tetrahydro-β-carbolines.[18] Recently, NCS[19] and iodobenzene diacetate[20] were also found to perform the decarboxylative aromatization of tetrahydro-β-carbolines. However, these methods require 2 equivalents of the reagents which are expensive. Hence, the development of easy, economical and conventional methods for the aromatization of tetrahydro-β-carbolines is desirable.

Molecular iodine has been utilized in pharmaceutical and organic syntheses due to its inexpensive, non-toxic, environmental friendly nature and operational simplicity.[21] Usually, I_2 has been extensively used in combination with TBHP in many oxidative transformations to overcome the drawbacks of the metal catalysed reactions.[22] For any iodine catalyzed reactions, the reduced iodide species have to be reoxidised to iodine to maintain the catalytic cycle. This oxidation can be attained with an external oxidant like TBHP. If this process can be accomplished with the help of an environmental friendly and cheap oxidant such as aqueous hydrogen peroxide, the method would be very impressive. Hence, we aspired to report a novel and an efficient protocol for the aromatization of tetrahydro-β-carbolines employing a catalytic amount of iodine in presence of hydrogen peroxide.

2. Results and Discussion

Our initial investigations focused on identifying conditions that would best attain the one-pot decarboxylation and aromatization of 1-phenyl-tetrahydro-β-carboline-3-carboxylic acid **1a** to aromatic β-carboline **2a** (Table 1). When 10 mol% of iodine was used in DMF at room temperature, the yield of the product was only 12% after 24 h (Table 1, entry 1). Increasing the amount of catalyst to 20 mol% and 50 mol% did not affect the yield of the product (entry 2-3, Table 1). Encouragingly, the product **2a** was formed in 64% yield using 10 mol% of I_2 in DMF at 100 °C (Table 1, entry 4). By increasing or decreasing the mol% of I_2, there was not much variation of yield (entry 5–6). Adding 1 mmol of external oxidant, hydrogen peroxide, delivered the product **2a** in 86% yield in 1 h (entry 7, Table 1). Changing the amount of iodine catalyst in the presence of oxidant has no effect on the yield (entry 8-9, Table 1).

Table 1. Screening of the reaction conditions



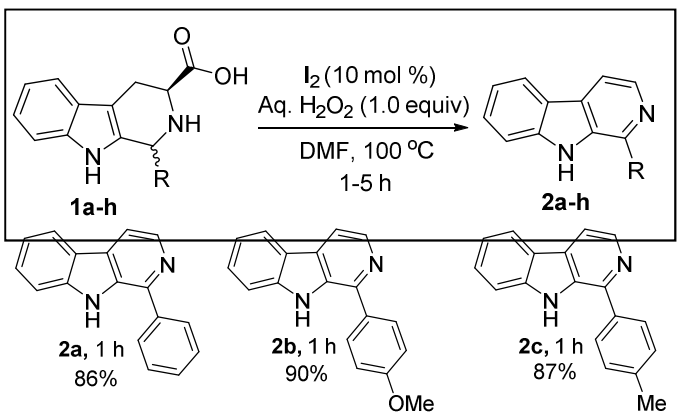
Entry	I_2 (mol %)	Temp (°C)	Time (h)	Yield (%)[a]
1	10	RT	24	12
2	20	RT	24	10
3	50	RT	24	10
4	10	100	3	64
5	20	100	3	60
6	5	100	3	61
7[b]	10	100	1	86
8[b]	5	100	1	77
9[b]	20	100	1	81

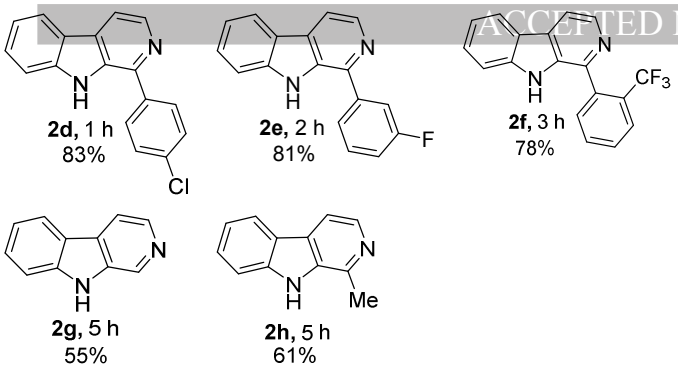
[a] Isolated yields.

[b] 1 mmol of aq H_2O_2 was added.

Under the optimal conditions, our attention shifted to explore the scope of the aromatic process with a variety of tetrahydro-β-carboline-3-carboxylic acids (Scheme 1). A variety of aliphatic and aromatic substituents at position-1 of tetrahydro-β-carboline acids[23] are well tolerated under the optimized reaction conditions. The substrates containing aromatic substituents delivered better yields compared to those with aliphatic substituents. The electronic nature of the substituents plays an important role on outcome of the reactions. The substrates carrying electron-rich groups (**2b**, **2c**) furnished products in higher yields than those bearing electron deficient groups (**2d**-**2f**). Naturally occurring β-carbolines, norharmane (**2g**) and harmane (**2h**), were also synthesized in good yields.

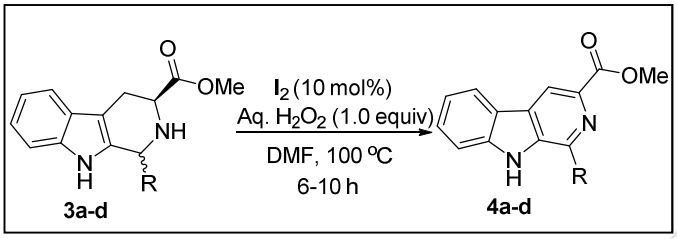
Scheme 1. Synthesis of β-carbolines

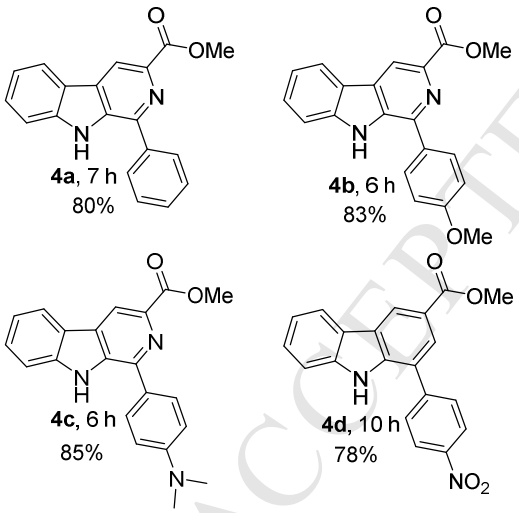




The same method was also successfully extended to tetrahydro-β-carboline methyl esters. These esters were subjected to aromatization to provide the corresponding products **4a–d** in good yield without losing the ester group as shown in Scheme 2. A variety of substituents were found to be well tolerated. β-Carboline esters with electron donating groups provided better yields than the ones with electron withdrawing groups.

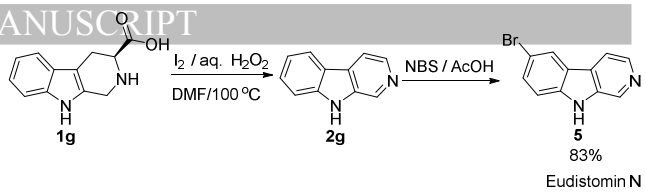
Scheme 2. Aromatization of tetrahydro-β-carboline-3-carboxylic esters





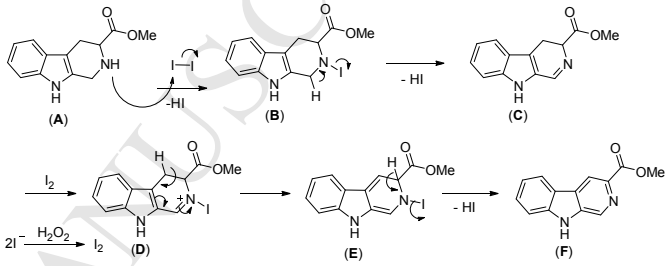
Finally, the synthesis of eudistomin N (**5**) was accomplished using the current protocol as shown in Scheme 3. Norharmane (**2g**) was synthesized by one-pot decarboxylative aromatization with I_2 and H_2O_2 in DMF. The bromination of **2g** with NBS in acetic acid furnished eudistomin N (**5**) in 83% yield.

Scheme 3. Synthesis of Eudistomin N



The following mechanism has been proposed based on the literature report[19] for synthesis of β-carboline esters. Initially 'N' of (**A**) attacks on I_2 to give the N-iodo-tetrahydro-β-carboline (**B**). Subsequent elimination of HI from (**B**) produce the partially aromatized product (C) which attacks on I_2 to provide iminium intermediate (D). Elemination of proton to give the intermediate (E) and subsequent release of HI giving the desired product (F) as shown in the Scheme 4.

Scheme 4. Proposed Mechanism for the aromatization of Tetrahydro-β-carboline esters.



3. Conclusions

In summary, we have developed a facile metal-free method for one-pot decarboxylative aromatization of tetrahydro-β-carbolin-3-carboxylic acids and the aromatization of tetrahydro-β-carbolin-3-methyl esters employing a catalytic amount of I_2 in presence of aq. H_2O_2. The current protocol has been successfully utilized in the synthesis of β-carboline alkaloids such as, norharmane, harmane and eudistomin N. Overall, an economical and environmental friendly catalyst and compatibility with a wide range of substrates make this protocol useful for the synthesis of attractive pharmaceutical intermediates of β-carboline analogues.

4. Experimental Section

General Information:

Tetrahydro-β-carbolines **1a-h** and **3a-d** were prepared according to literature protocols by Pictet-Spengler reaction of L-tryptophan and L-tryptophan methyl ester hydrochloride respectively with the appropriate aldehyde.[14a,24] The procedure does not require an inert atmosphere. All the products obtained were purified by column chromatography using silica gel (100-200 mesh). Hexane was used as a co-eluent. ^{1}H and ^{13}C NMR were recorded in Brucker 500 and 125 MHz spectrometer respectively. The chemical shifts are reported in ppm downfield to TMS (δ = 0) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0) for ^{13}C NMR. GC-MS was used for the mass spectral analysis. IR spectra were recorded on a FT-IR spectrometer. Elemental analysis was carried out in CHN analyzer EA 1112, Thermo Finnigan.

General procedure for the synthesis of 1-Phenyl-9*H*-pyrido[3,4-*b*]indole (2a): To a mixture of 1-phenyl-tetrahydro-β-carboline-3-carboxylic acid **1a** (1 mmol, 292 mg), and I_2 (10

mol%, 25.4 mg) in DMF (5 mL) was added 30% aqueous solution of H_2O_2 (0.113 mL, 1 mmol). The reaction was stirred at 100 °C for 1 h. After completion of the reaction (TLC), the reaction mixture was treated with a 5% hypo solution (5 mL). The reaction mixture was then extracted with ethyl acetate (2 x 20 mL) and the combined ethyl acetate layer was washed with water (2 x 5 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified over column chromatography to afford 1-phenyl-β-carboline **2a** (210 mg, 86% yield).[19] mp 242-244 °C; IR (neat) 3213, 3064, 2956, 2879, 1624, 1496, 1467, 1234, 736 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ: 11.52 (s, 1H), 8.48 (d, J = 5.0 Hz, 1H), 8.28 (d, J = 7.5 Hz, 1H), 8.13 (d, J = 5.5 Hz, 1H), 8.05 (d, J = 7.2 Hz, 2H), 7.68-7.61 (m, 3H), 7.58-7.52 (m, 2H), 7.28 (t, J = 7.9 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 142.2, 141.1, 138.4, 138.3, 133.0, 129.1, 128.7, 128.5, 128.4, 128.1, 121.5, 120.8, 119.5, 113.8, 112.4; GC-MS (EI): m/z = 244; Anal. Calcd. for molecular formula $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47%. Found: C, 83.61; H, 4.89; N, 11.50%.

*1-(4-methoxyphenyl)-9H-pyrido[3,4-b]indole (**2b**)*[20]*:* White solid: mp 158-159 °C; IR (neat) 3123, 3055, 2928, 2851, 1625, 1513, 1251, 1236, 1173, 751 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ: 11.46 (s, 1H), 8.43 (d, J = 5.0 Hz, 1H), 8.26 (d, J = 7.5 Hz, 1H), 8.07 (d, J = 5.5 Hz, 1H), 8.01 (d, J = 9.0 Hz, 2H), 7.66 (d, J = 8.5 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.27 (t, J = 8.0 Hz, 1H), 7.18 (d, J = 8.5 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 159.6, 142.1, 141.0, 138.2, 132.7, 130.9, 129.6, 129.0, 128.0, 121.5, 120.9, 119.4, 114.1, 113.2, 112.4, 55.3; GC-MS (EI): *m/z* 274; Anal. Calcd. for molecular formula $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21%. Found: C, 78.79; H, 5.21; N, 10.26%.

*1-(p-tolyl)-9H-pyrido[3,4-b]indole (**2c**)*[19]*:* White solid: mp 190-193 °C; IR (neat) 3645, 3128, 3060, 2923, 1626, 1470, 1237, 739 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ: 11.46 (s, 1H), 8.45 (d, J = 5.0 Hz, 1H), 8.26 (d, J = 7.5 Hz, 1H), 8.10 (d, J = 5.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.5 Hz, 1H), 7.56 (t, J = 8.0 Hz, 1H), 7.43 (d, J = 7.5 Hz, 2H),7.27 (t, J = 8.0 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 142.3, 141.0, 138.3, 137.9, 135.6, 132.9, 129.3, 129.0, 128.2, 128.0, 121.5, 120.8, 119.4, 113.6, 112.4, 20.9; GC-MS (EI): *m/z* 258; Anal. Calcd. for molecular formula $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84%. Found: C, 83.63; H, 5.43; N, 10.94%.

*1-(4-chlorophenyl)-9H-pyrido[3,4-b]indole (**2d**)*[19]*:* Light yellow solid: mp 197-198 °C; IR (neat) 3136, 3064, 2922, 2851, 1623, 1423, 1234, 1090, 1013, 819, 746 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ: 11.56 (s, 1H), 8.48 (d, J = 5.0 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 5.5 Hz, 1H), 8.07 (d, J = 9.0 Hz, 2H), 7.68-7.65 (m, 3H), 7.58 (t, J = 8.0 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 141.1, 140.8, 138.4, 137.2, 133.2, 133.0, 130.1, 129.4, 128.7, 128.3, 121.6, 120.8, 119.6, 114.2, 112.4; GC-MS (EI): *m/z* 278; Anal. Calcd. for molecular formula $C_{17}H_{11}ClN_2$: C, 73.25; H, 3.98; N, 10.05%. Found: C, 73.31; H, 4.08; N, 9.94%.

1-(3-fluorophenyl)-9*H*-pyrido[3,4-*b*]indole (**2e**)[20]: White solid: mp 181-182 °C; IR (neat) 3135, 3069, 1625, 1589, 1472, 1234. 1201, 796, 738 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ: 11.59 (s, 1H), 8.49 (d, J = 5.5 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 6.0 Hz, 1H), 7.91 (d, J = 7.5 Hz, 1H), 7.82 (d, J = 10.0 Hz, 1H), 7.69-7.65 (m, 2H), 7.58 (t, J = 8.0 Hz, 1H), 7.37 (t, J = 9.0 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 141.2, 138.4, 133.0, 130.7, 130.6, 129.5, 128.3, 124.5, 121.6, 120.8, 119.6, 115.4, 115.2, 115.1, 114.9, 114.4, 112.4; GC-MS (EI): *m/z* 262; Anal. Calcd. for molecular formula $C_{17}H_{11}FN_2$: C, 77.85; H, 4.23; N, 10.68%. Found: C, 77.81; H, 4.28; N, 10.74%.

1-(2-(trifluoromethyl)phenyl)-9*H*-pyrido[3,4-*b*]indole (**2f**): White solid: mp 114-116 °C; IR (neat) 3623, 3066, 2923, 2853, 1627, 1500, 1311, 1170, 1114, 1062, 1033, 753 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ: 11.26 (s, 1H), 8.40 (d, J = 5.5 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 5.5 Hz, 1H), 7.98 (d, J = 7.5 Hz, 1H), 7.86 (t, J = 7.5 Hz, 1H), 7.79 (t, J = 8.0 Hz, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.54-7.53 (m, 2H),7.29-7.25 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 141.7, 140.9, 137.4, 137.0, 134.0, 132.4, 131.6, 129.0, 128.2, 127.8, 126.6, 126.5, 121.7, 120.6, 119.4, 114.3, 112.1; GC-MS (EI): *m/z* 312; Anal. Calcd. for molecular formula $C_{18}H_{11}F_3N_2$: C, 69.23; H, 3.55; N, 8.97%. Found: C, 69.19; H, 3.56; N, 8.93%.

*9H-pyrido[3,4-b]indole (**2g**)*[19]*:* White solid: mp 196-197 °C; IR (neat) 3122, 3051, 2841, 1642, 1461, 1228, 1126, 1011, 818, 745 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ: 11.63 (s, 1H), 8.89 (d, J = 0.5 Hz, 1H), 8.31 (d, J = 5.5 Hz, 1H), 8.2 (d, J = 7.0 Hz, 1H), 8.09 (dd, J_1 = 0.5 Hz, J_2 = 1.0 Hz, 1H), 7.60 (d, J = 10.0 Hz, 1H), 7.55-7.53 (m, 1H), 7.24-7.21 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 140.5, 137.9, 135.9, 133.7, 128.5, 127.6, 121.7, 120.4, 119.4; 114.7, 112.1, GC-MS (EI): *m/z* 168; Anal. Calcd. for molecular formula $C_{11}H_8N_2$: C, 78.55; H, 4.79; N, 16.66%. Found: C, 78.63; H, 4.73; N, 16.64%.

*1-Methyl-9H-pyrido[3,4-b]indole (**2h**)*[19]*:* White solid: mp 235-236 °C; IR (neat) 3126, 3046, 2912, 2841, 1645, 1423, 1252, 1112, 1017, 827, 737 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ: 11.68 (s, 1H), 8.17-8.15 (m, 2H), 7.90 (d, J = 5.5 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.54-7.51 (m, 1H), 7.21 (t, J = 10.0 Hz, 1H), 2.75 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 141.9, 140.4, 137.0, 134.4, 128.0, 127.1, 120.8, 119.5, 112.8, 111.9; GC-MS (EI): *m/z* 182; Anal. Calcd. for molecular formula $C_{12}H_{10}N_2$: C, 79.10; H, 5.53; N, 15.37%. Found: C, 79.19; H, 5.56; N, 15.25%.

*Methyl 1-phenyl-9H-pyrido[3,4-b]indole-3-carboxylate (**4a**)*[17]*:* White solid: mp 257-258 °C; IR (neat) 3317, 3002, 2951, 1720, 1351, 1290, 1253, 756, 740 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ: 11.96 (s, 1H), 8.94 (s, 1H), 8.44 (d, J = 7.5 Hz, 1H), 8.04 (d, J = 7.0 Hz, 2H), 7.72 (d, J = 8.5 Hz, 1H), 7.66-7.58 (m, 4H), 7.34 (t, J = 7.5 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 166.1, 142.1, 141.5, 137.5, 136.7, 134.6, 129.2, 129.0, 128.8, 128.7, 128.6, 122.0, 121.1, 120.4, 116.6, 112.8, 52.00; GC-MS (EI): *m/z* 302; Anal. Calcd. for molecular formula $C_{19}H_{14}N_2O_2$: C, 75.48; H, 4.67; N, 9.27%. Found: C, 75.50; H, 4.62; N, 9.31%.

*Methyl1-(4-methoxyphenyl)-9H-pyrido[3,4-b]indole-3-carboxylate (**4b**)*[17]*:* White solid: mp 228-230 °C; IR (neat) 3267, 3012, 2952, 2838, 1716, 1624, 1610, 1514, 1302, 1282, 1252, 1175, 839, 749 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ: 11.94 (s, 1H), 8.94 (s, 1H), 8.47 (d, J = 7.5 Hz, 1H), 8.05 (d, J = 9.0 Hz, 2H), 7.76 (d, J = 8.5 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 7.39 (t, J = 7.0 Hz, 1H), 7.26 (d, J = 8.5 Hz, 2H), 3.99 (s, 3H), 3.95 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 166.1, 159.9, 142.0, 141.4, 136.6, 134.3, 130.0, 129.9, 129.0, 128.5, 121.9, 121.2, 120.3, 116.2, 114.2, 112.8, 55.4, 51.2; GC-MS (EI): *m/z* 332; Anal. Calcd. for molecular formula $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.43%. Found: C, 72.23; H, 4.79; N, 8.39%.

*Methyl 1-(4-dimethylamino)-9H-pyrido[3,4-b]indole-3-carboxylate (**4c**):* White solid: mp 208-210 °C; IR (neat) 3647, 3275, 2944, 1709, 1612, 1561, 1354, 1257, 1103, 746 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ: 11.82 (s, 1H), 8.82 (s, 1H), 8.40 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 9.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 9.0 Hz, 2H), 3.94 (s, 3H), 3.05 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 166.2, 150.8, 142.7, 141.3, 136.6, 134.1,

129.4, 128.6, 128.3, 125.1, 121.8, 121.2, 120.2, 115.4, 112.8, 112.1, 51.9, 40.0; GC-MS (EI): *m/z* 345; Anal. Calcd. for molecular formula $C_{21}H_{19}N_3O_2$: C, 73.03; H, 5.54; N, 12.17%. Found: C, 72.95; H, 5.62; N, 12.21%.

*Methyl 1-(4-nitrophenyl)-9H-pyrido[3,4-b]indole-3-carboxylate (**4d**)*[17]*:* Yellow solid: mp 264-266 °C; IR (neat) 3513, 3399, 3204, 2965, 1703, 1524, 1245, 1122, 744 cm^{-1} ; ^1H NMR (500 MHz, DMSO-d_6) δ: 12.18 (s, 1H), 9.07 (s, 1H), 8.55-8.52 (m, 3H), 8.37 (d, *J* = 9.0 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 165.8, 147.5, 143.7, 141.6, 139.5, 136.9, 134.8, 129.9, 129.1, 123.9, 122.2, 121.0, 120.7, 117.6, 112.7, 52.1; GC-MS (EI): *m/z* 347; ; Anal. Calcd. for molecular formula $C_{19}H_{13}N_3O_4$: C, 65.70; H, 3.77; N, 12.10%. Found: C, 65.75; H, 3.71; N, 12.06%.

*6-Bromo-9H-pyrido[3,4-b]indole or Eudistomin N (**5**)*[19]*:* Creamish solid: mp 266-268 °C; IR (neat) 3211, 3117, 3047, 2935, 2830, 2740, 2660, 1628, 1562, 1495, 1475, 1452, 1432, 1272, 1244, 798 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ: 11.79 (s, 1H), 8.95 (s, 1H), 8.52 (d, *J* = 1.5 Hz, 1H), 8.37 (d, *J* = 5.5 Hz, 1H), 8.17 (d, *J* = 5.5 Hz, 1H), 7.67 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 139.2, 138.4, 136.3, 134.4, 130.5, 126.5, 124.4, 122.5, 115.0, 114.0, 111.2; GC-MS (EI): *m/z* 246; Anal. Calcd. for molecular formula $C_{11}H_7N_2$: C, 53.47; H, 2.86; N, 11.34%. Found: C, 53.53; H, 2.83; N, 11.29%.

Acknowledgements

This work was supported by the Research University (RUT) Grant Scheme (1001/CDADAH/855005) and Research University (RUI) Grant Scheme (1001/CDADAH/811257), Universiti Sains Malaysia, Malaysia. Ramu Meesala is gratefully acknowledged International Medical University (IMU), Malaysia for providing the lab space.

Supplementary Material

^1H and ^{13}C spectra of all compounds have been provided in a separate electronic file as a supplementary data.

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