

A NEW ROUTE TO THE INDOLOPYRIDONAPHTHYRIDINE RING SYSTEM:
 SYNTHESIS OF *N*-BENZYL-13b,14-DIHYDRONAUCLÉFINE AND
N-BENZYL-13b,14-DIHYDROANGUSTINE^a

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^aA preliminary account of a part of this work has appeared¹.

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ABSTRACT - The indolo[2:3,3':4']pyrido[1,2-*b*]naphthyridine ring system, which is present in several alkaloids, has been prepared in a single reaction between the lithio derivative of a 3-cyano-4-methylpyridine and *N*-benzyl-3,4-dihydro- β -carboline in the presence of trimethylsilyl trifluoromethanesulfonate. Using appropriately substituted starting materials, *N*-benzyl-13b,14-dihydronaucléfine and *N*-benzyl-13b,14-dihydroangustine have been made in this way. A new preparation of the synthetic intermediate 9-benzyl-3,4-dihydro- β -carboline is also described.

In recent years a relatively large number of alkaloids containing the indolopyridonaphthyridine ring system have been isolated and characterized. The alkaloids of this group are considered to be derived from secologanin 1 and tryptamine 2 as shown in Figure 1 and often occur together with the structurally related glycoalkaloids, 3-6². The structures of the alkaloids are shown in Figure 2 and references to their isolation are collated in Table 1. The majority of the alkaloids retain the 10 carbon framework of secologanin but in others this structural feature has been modified.

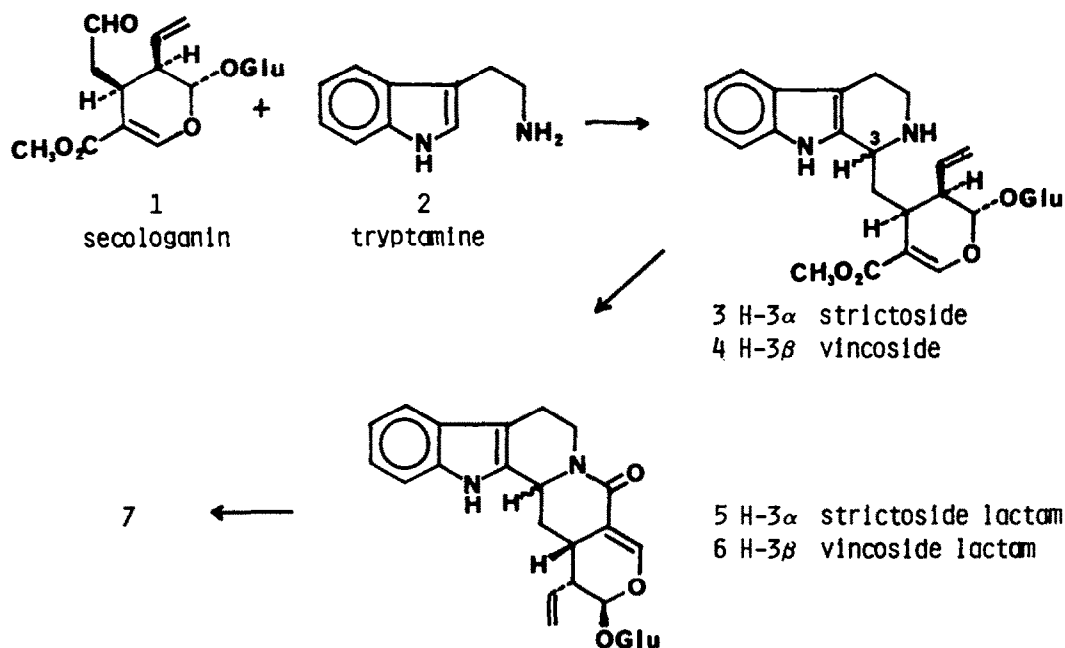


FIGURE 1

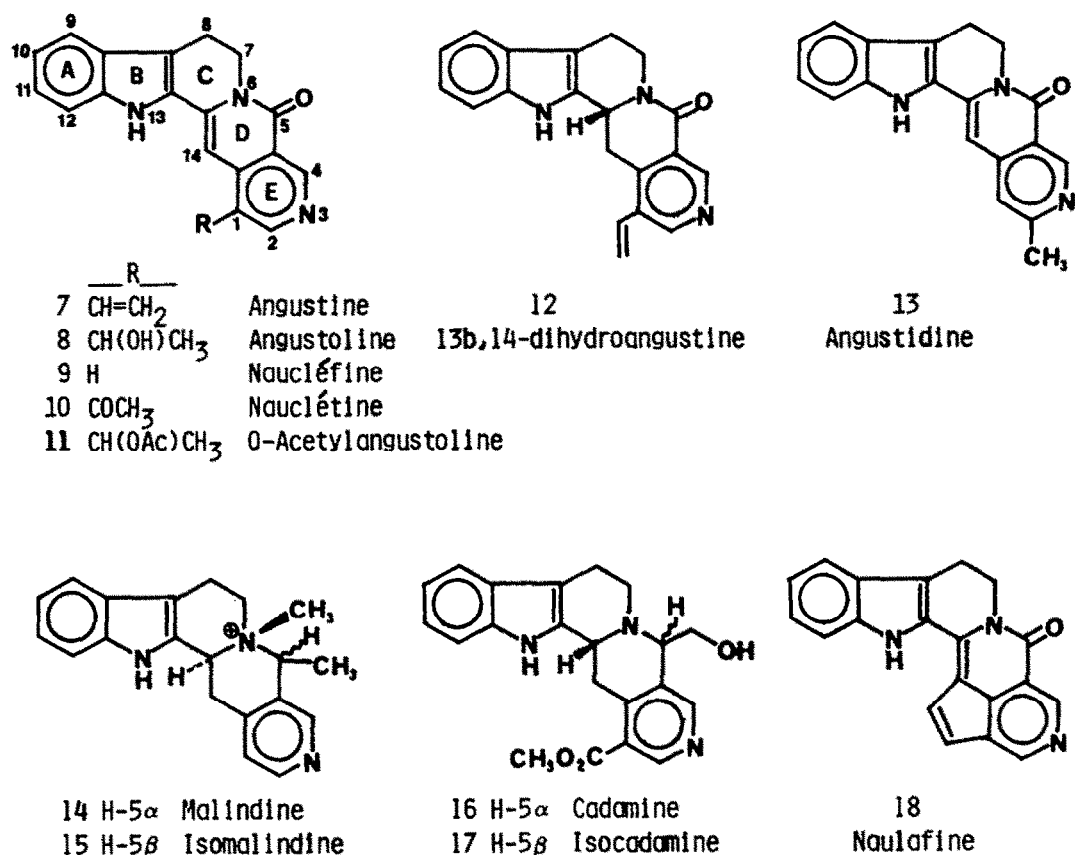


FIGURE 2

Table 1

Indolo[2:3,3':4']pyridol[1,2-b]naphthyridine alkaloids

<u>Name</u>	<u>Structure</u>	<u>Reference</u>	<u>Source</u>
O-Acetylanguistoline	11	3	<i>Nauclea pobequinii</i>
Angustidine	13	4	<i>Strychnos angustifolia</i>
Angustine	7	4,5,6,7	<i>S. angustifolia</i>
Angustoline	8	4,5	<i>S. angustifolia</i>
Cadamine	16	8	<i>Anthocephalus cadamba</i>
13b,14-Dihydroanguistine	12	3	<i>N. pobequinii</i>
Isocadamine	17	8	<i>A. cadamba</i>
Isomalindine	15	9	<i>S. usambarensis</i>
Malindine	14	10	<i>S. decussata</i>
Naulafine	18	6	<i>N. latifolia</i>
Nauclefine	9	4,6,7	<i>N. latifolia</i>
Nauclefine	10	4	<i>N. latifolia</i>

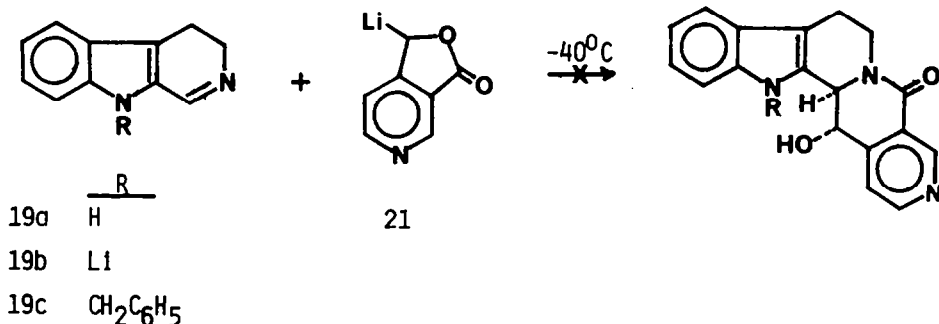
A variety of strategies have been employed in the synthesis of alkaloids of this series². These can most easily be compared by considering which of the five rings is closed in the final steps of the sequence. The approach of Kametani et al.^{11,12} ultimately involved the closure of ring C in a single C-C bond forming process under acidic conditions to form augustine 7 and nauclefine 9, respectively. Pandit and co-workers¹³ have also synthesized nauclefine 9 in a sequence which ends with the formation of a single C-C bond to give ring C. In contrast, in the synthesis of augustidine 13, Shafiee and Winterfeldt¹⁴ added rings sequentially, essentially in alphabetical order, finishing with the cyclization of ring E in which two C-N bonds were formed. In several syntheses of alkaloids of this series (e.g., nauclefine 9) ring D is formed in the final step of the sequence through cyclization of an enamide.^{4,7,15-20}

We report here a new synthetic route to the ring system present in this class of alkaloids. In this sequence, ring D is created by the formation of a C-C and a C-N bond in the final step by the condensation of lithio derivatives of 3-cyano-4-methylpyridines (ring E) with 9-benzyl-3,4-dihydro- β -carboline 19c (ring C), previously complexed with trimethylsilyl trifluoromethanesulfonate (TMSOTf). The procedure used is similar to that employed by us in the synthesis of *Alangium* alkaloids containing the isoquino[2,1-*b*][2,7]naphthyridine ring system.^{1,21-23} We also report a convenient preparation of 1-benzyltryptamine 20 which was converted to 9-benzyl-3,4-dihydro- β -carboline 19c, a key intermediate in this investigation.

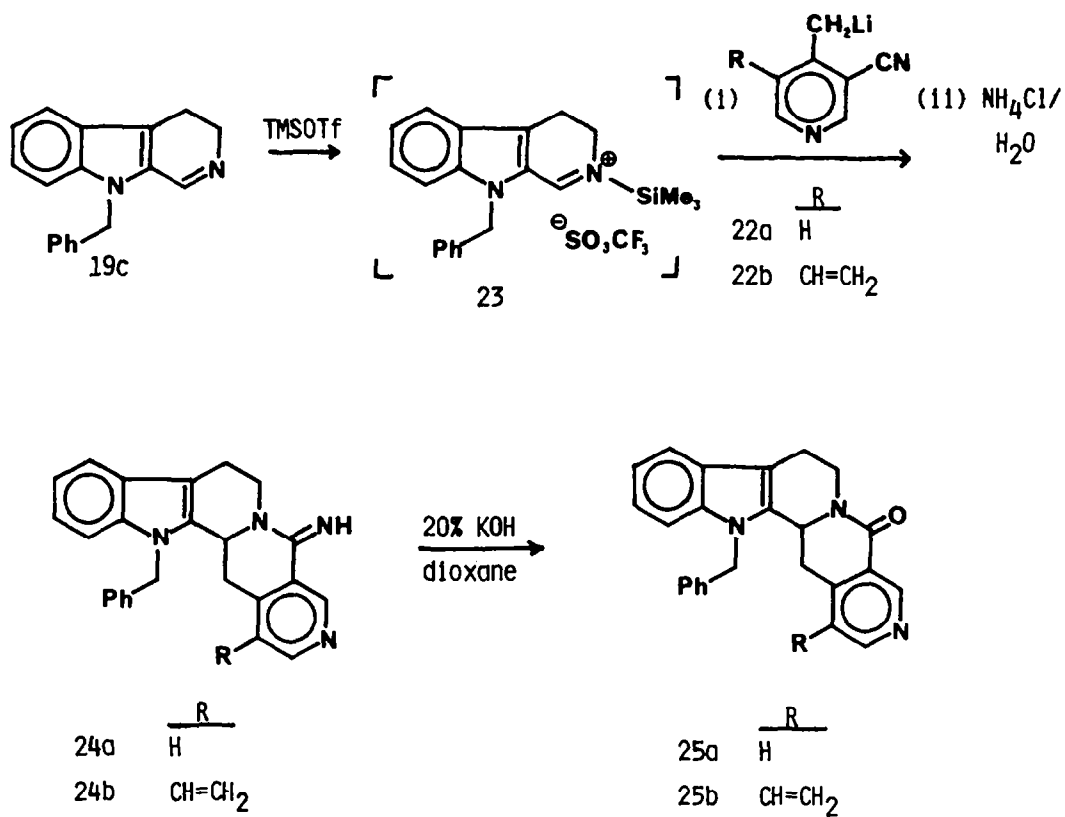
RESULTS AND DISCUSSION

It has been previously demonstrated by us^{1,21} that 3,4-dihydroisoquinolines react readily with the lithio derivative of furo[3,4-*c*]pyridine-3[1*H*]-one 21 forming isoquino[2,1-*b*][2,7]-naphthyridines. Our attempts to prepare indolo[2',3',3,4]-pyrido-[1,2-*b*][2,7]-naphthyridines by carrying out a related condensation on 3,4-dihydro- β -carboline 19a, its 9-lithio derivative 19b or its 9-benzyl derivative 19c were unsuccessful (Scheme 1); only starting materials were recovered.²⁴ The lithio derivatives of 3-cyano-4-methylpyridine 22a and 3-cyano-4-methyl-5-vinylpyridine 22b were similarly unreactive toward the same carbolines. We found, however, that the complex 23 formed between 9-benzyl-3,4-dihydro- β -carboline and trimethylsilyl trifluoromethanesulfonate reacted readily with the lithio derivatives of 22a and 22b¹ affording in one step the pentacyclic amidines, 24a and 24b (Scheme 2). Hydrolysis of the amidines was effected with boiling alkali; the corresponding lactams, 25a and 25b, were isolated in high yield. Lactam 25a is the *N*-benzyl derivative of 13b,14-dihydronauclefine and lactam 25b is the *N*-benzyl derivative of 13b,14-dihydroangustine. The spectroscopic properties (¹H and ¹³C nmr, ir and mass) of 24a, 24b, 25a, and 25b agree with the structural assignments.

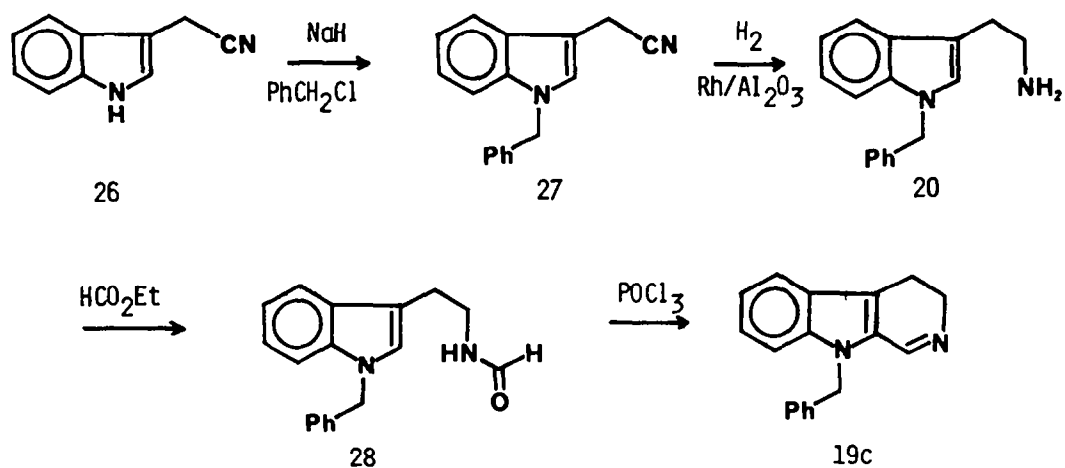
The 9-benzyl-3,4-dihydro- β -carboline used in this investigation was prepared from 3-indolylacetonitrile by the route outlined in Scheme 3. 3-Indolylacetonitrile 26 was converted to its *N*-benzyl derivative 27 in 78% yield by treatment of 26 with sodium hydride followed by



SCHEME 1



SCHEME 2



SCHEME 3

benzylation with benzyl bromide. *N*-Benzyltryptamine 20 was prepared by the reduction of 27 in ethanolic ammonia with hydrogen (2.5 atm.) over rhodium on alumina at room temperature.²⁵ *N*-formyltryptamine, prepared by treatment of 20 with ethyl formate at 120°C in a sealed tube, was cyclized to 19c with neat POCl₃. This procedure compares favourably with a previously reported method for the synthesis of 19c.²⁶

The synthetic method described in this investigation should be applicable to the synthesis of many of the alkaloids depicted in Figure 2. The introduction of a double bond into the 13b,14 position of 25a or 25b by oxidation with I₂ in MeOH should proceed without complication as it does in the related isoquinonaphthyridines²¹ thereby providing access to alkaloids such as angustine 7 and nauclefine 9. Modification of the vinyl side chain should provide entry into compounds such as 8, 10 and 11. The alkaloids, malindine 14 and isomalindine 15, should also be accessible using the procedure reported for synthesis of alamaridine²³, an isoquinonaphthyridine analogue. The application of this reaction to the synthesis of the alkaloids themselves is currently under investigation.

EXPERIMENTAL

The experimental methods used in this investigation have been reported previously (21-23).

Condensation of 9-benzyl-3,4-dihydro- β -carboline 19c activated by reaction with trimethylsilyl trifluoromethanesulfonate with lithium salts of 3-cyano-4-methylpyridines:

(a) 13-Benzyl-8,13,13b,14-tetrahydroindolo[2',3':3,4]pyrido[1,2-b][2,7]-naphthyridin-6[7H]-imine 24a

A solution of 9-benzyl-3,4-dihydro- β -carboline 19c (0.54 g, 2.0 mmol) in dry THF (8 mL) was treated dropwise with TMSOTf (0.45 mL, 2.2 mmol), at -78°C under an argon atmosphere. The resulting cloudy suspension was stirred first at -78°C for 1 h then at 0°C for an additional 2 h. Meanwhile a solution of *n*-BuLi (1.42 mL, 1.55 M in hexane, 2.2 mmol) was added dropwise to a stirred solution of 1,1,1,3,3,3-hexamethyldisilazane (0.46 mL, 2.2 mmol) in THF (3 mL) at -78°C. The lithium hexamethyldisilazide (LHS) solution so generated was stirred for an additional 10 min at -20°C and then cooled to -78°C. A solution of 3-cyano-4-methylpyridine 22a (0.248 g, 2.0 mmol) in THF (2 mL) was added dropwise to the above LHS solution at -78°C, and the red solution so generated was stirred for a further 20 min at -78°C. The red anion solution was then added dropwise at -78°C to the imine-TMSOTf complex and when the addition was complete the mixture was stirred at -40°C for 4 h. The mixture was allowed to warm to room temperature and stirred for ca. 12 h. The reaction mixture was quenched with saturated NH₄Cl solution (1 mL aq.) and the resulting mixture was evaporated, water added, and the contents extracted with CHCl₃; the CHCl₃ extract was dried (Na₂SO₄ anhyd.) and evaporated to dryness *in vacuo*. The crude product was purified by column chromatography on neutral alumina, eluting first with CHCl₃ then with increasing concentrations of MeOH (5-25%) in CHCl₃. The product 24a, after the removal of the solvent, was crystallized from ethyl acetate (0.669 g, 89%); mp 190-192°C; ir (CHCl₃, film), ν_{max} : 1615 cm⁻¹; ¹H nmr (500 MHz) CDCl₃, δ : 2.84-3.08 (5H, complex m, C-7 H_{ax}, C-8, and C-14 H's), 4.71 (1H, apparent d, J=11.6 Hz, C-13b H), 5.08 (1H, m, C-7 H_{eq}), 5.11 (1H, br s, -NH), 5.32 (2H, s, -NCH₂Ar), 6.91 (1H, d, J=4.9 Hz, C-1 H), 6.99 (2H, m, aromatic H's), 7.18 - 7.32 (6H, complex m, aromatic H's), 7.62 - 7.64 (1H, apparent d, J=7.1 Hz, aromatic H), 8.54 (1H, d, J=4.9 Hz, C-2 H), and 9.11 (1H, s, C-4 H); ¹³C nmr (125.76 MHz), δ : 21.5 (C-8), 37.2 (C-14), 40.5 (C-7), 47.4 (-NCH₂Ar), 51.4 (C-13b), 110.0, 118.7, 120.1, 122.2, 122.5, 125.9, 125.9, 127.8, 129.1, 129.1, 147.9, and 150.8 (12 x ArCH's), 110.9, 125.3, 126.5, 132.6, 137.3, 138.2 and 144.0 (7 x ArC's), and 159.7 (>C=NH); ms(EI), m/z(%): 378 (57)M⁺, 377 (25), 361 (23), 287 (100), 286 (5), 285 (10), 261 (5), 260 (7), 259 (7), 170 (10), 169 (23), 168 (9), 118 (7), and 91 (67); Exact mass (hrms): calcd. for C₂₅H₂₂N₄: 378.184; found: 378.181; calcd. for fragment ion C₁₈H₁₅N₄ (M-CH₂C₆H₅): 287.130; found: 287.128.

(b) 13-Benzyl-1-ethenyl-8,13,13b,14-tetrahydroindolo[2',3':3,4]pyrido[2,1-b][2,7]naphthyridin-5[7H]-imine 24b

Addition of the red anion of 3-cyano-4-methyl-5-vinylpyridine 22b (288 mg, 2.0 mmol), prepared in the same manner as the anion of 3-cyano-4-methylpyridine, to the complex of 9-benzyl-3,4-dihydro-*p*-carboline 23 (542 mg, 2.0 mmol) with TMSOTf (0.45 mL, 2.2 mmol), and work-up as described for the preparation of 24a, gave a residue which furnished amidine 24b (458 mg) on crystallization from MeOH. The mother liquor was chromatographed on neutral alumina, first eluting with CHCl_3 , then with increasing concentrations of MeOH in CHCl_3 . In this way another 234 mg of 24b was obtained, [combined yield (86%)]; mp 276-278°C (MeOH); ir (nujol), ν_{max} 1620 cm^{-1} ; ^1H nmr (500 MHz), $\text{CDCl}_3 + \text{CD}_3\text{OD}$, δ : 2.69 (1H, dd, $J=17.0$ and 13.4 Hz, C-7 H_{ax}), 3.13-3.54 (4H, complex m, C-8, C-14 H's), 4.65 (1H, dd, $J=13.0$ and 3.5 Hz, C-13b H), 5.06 (1H, m, C-7 H_{eq}), 5.28 (1H, d, $J=17.9$ Hz, $-\text{NCH}_2\text{Ar}$), 5.32 (1H, d, $J=11.2$ Hz, $-\text{CH}=\text{CH}_2$), 5.46 (1H, d, $J=17.9$ Hz, $-\text{NCH}_2\text{Ar}$), 5.62 (1H, d, $J=17.5$ Hz, $-\text{CH}=\text{CH}_2$), 5.99 (1H, dd, $J=17.5$ and 11.2 Hz, $-\text{CH}=\text{CH}_2$), 7.03-7.04 (2H, m, aromatic H's), 7.24-7.41 (6H, complex m, aromatic H's), 7.66-7.67 (1H, m, aromatic H), 8.80 (1H, s, C-2 H), and 9.03 (1H, s, C-4 H); ^{13}C nmr (125.76 MHz), $\text{CDCl}_3 + \text{CD}_3\text{OD}$, δ : 20.9 (C-8), 32.6 (C-14), 44.5 (C-7), 47.0 ($-\text{NCH}_2\text{Ar}$), 52.5 (C-13b), 110.0, 119.2, 120.7, 123.5, 125.8, 125.8, 127.9, 128.4, 129.4, 146.7 and 151.7 (11 \times $\text{ArCH}'\text{s} + -\text{CH}=\text{CH}_2$), 109.5, 120.1, 121.8, 125.7, 130.3, 131.8, 137.0, 138.5 and 143.2 (8 \times $\text{ArC}'\text{s} + -\text{CH}=\text{CH}_2$), and 158.9 ($>\text{C}=\text{NH}$); ms (EI), m/z (%): 404 (15) M^+ , 403 (6), 313 (30), 287 (17), 286 (3), 260 (6), 259 (3), 169 (18), 168 (7), 144 (5), 143 (12), 117 (4) and 91 (100); Exact mass (hrms): calcd. for $\text{C}_{27}\text{H}_{24}\text{N}_4$: 404.200; found: 404.192; calcd. for fragment ion $\text{C}_{20}\text{H}_{17}\text{N}_4$ ($\text{M}-\text{CH}_2\text{C}_6\text{H}_5$): 313.145, found: 313.142; calcd. for fragment ion $\text{C}_{18}\text{H}_{16}\text{N}_2$: 260.131, found: 260.129.

Hydrolysis of amidines 24a and 24b to lactams 25a and 25b

(a) 13-Benzyl-13b,14-dihydroangustifine [14-Benzyl-8,13,13b,14-tetrahydroindolo[2',3':3,4]pyrido[1,2-b][2,7]naphthyridin-5[7H]one] 25a

A solution of amidine 24a (250 mg) in dioxane (30 mL) and 20% KOH solution (aq., 10 mL) was gently heated under reflux for 48 h and the progress of the reaction was monitored by tlc. When the reaction was complete the mixture was evaporated *in vacuo*, the residue treated with water (50 mL) and the solution thoroughly extracted with CH_2Cl_2 . The combined CH_2Cl_2 extracts were washed with brine, dried (MgSO_4 anhyd.) and solvent removed *in vacuo* affording lactam 25a (223 mg, 89%); mp 125-127°C (EtOAc); R_f 0.52 (alumina, EtOAc); ir (CHCl_3 , film), ν_{max} : 1655 cm^{-1} ; ^1H nmr (500 MHz), CDCl_3 δ : 2.86-3.07 (5H, complex m, C-7 H_{ax} , C-8, and C-14 H's), 4.97 (1H, apparent d, $J=12.6$ Hz, C-13b H), 5.21-5.23 (1H, m, C-7 H_{eq}), 5.35 (2H, s, $-\text{NCH}_2\text{Ar}$), 6.94 (1H, d, $J=4.9$ Hz, C-1 H), 7.00-7.02 (2H, d, $J=6.9$ Hz, aromatic H's), 7.18-7.33 (6H, complex m, aromatic H's), 7.62 (1H, m, aromatic H), 8.60 (1H, d, $J=4.9$ Hz, C-2 H), and 9.26 (1H, s, C-4 H); ^{13}C nmr (125.76 MHz), δ : 21.6 (C-8), 36.0 (C-14), 39.6 (C-7), 47.6 ($-\text{NCH}_2\text{Ar}$), 51.8 (C-13b), 111.3, 118.9, 120.3, 121.5, 122.8, 126.0, 126.0, 128.0, 129.3, 150.4 and 152.3 (12 \times $\text{ArCH}'\text{s}$), 110.1, 124.9, 126.9, 133.1, 137.2, 138.2 and 145.1 (7 \times $\text{ArC}'\text{s}$), and 163.6 ($>\text{C}=\text{O}$); ms (EI), m/z (%): 379 (63), 378 (10), 288 (35), 287 (9), 260 (7), 259 (13), 169 (5), 168 (5), 119 (14), and 91 (100); Exact mass (hrms): calcd. for $\text{C}_{25}\text{H}_{21}\text{N}_3\text{O}$: 379.168, found: 379.165; calcd. for fragment ion $\text{C}_{18}\text{H}_{14}\text{N}_3\text{O}$ ($\text{M}-\text{CH}_2\text{C}_6\text{H}_5$): 288.114; found 288.112.

(b) 13-Benzyl-13b,14-dihydroangustifine [13-Benzyl-1-ethenyl-8,13,13b,14-tetrahydroindolo[2',3':3,4]pyrido[2,1-b][2,7]naphthyridin-5[7H]-one] 25b

The hydrolysis of amidine 24b (300 mg) was carried out in a similar manner to that described above for amidine 24a yielding lactam 25b (283 mg, 94%); mp 226-230°C (EtOH); R_f 0.35 (alumina, EtOAc); ir (CHCl_3 , film), ν_{max} : 1650 cm^{-1} ; ^1H nmr (500 MHz), CDCl_3 , δ : 2.60 (1H, dd,

J=16.6 and 13.0 Hz, C-7 H_{ax}), 2.93-3.06 (3H, complex m, C-8 and C-14 H's), 3.25 (1H, dd, J=16.6 and 3.4 Hz, C-14 H), 4.96 (1H, d, J=11.8 Hz, C-13b H), 5.19 (1H, d, partially overlapped by C-7 H_{eq} signal, J=11.2 Hz, $-CH=CH_2$), 5.27 (1H, m, C-7 H_{eq}), 5.27 (1H, d, J=17.6 Hz, $-CH=CH_2$), 5.46-5.52 (2H, m, four lines, $-NCH_2Ar$), 6.02 (1H, dd, J=17.6 and 11.2 Hz, $-CH=CH_2$), 7.04 (2H, d, J=6.6 Hz, aromatic H's), 7.06-7.35 (6H, complex m, aromatic H's), 7.63-7.65 (1H, m, aromatic H), 8.67 (1H, s, C-2 H), and 9.17 (1H, s, C-4 H); ^{13}C nmr (125.76 MHz), δ : 21.6 (C-8), 32.9 (C-14), 39.6 (C-7), 47.5 ($-NCH_2Ar$), 51.4 (C-13b), 109.9, 118.9, 120.4, 123.0, 125.9, 125.9, 127.8, 129.3, 129.3, 129.8, 149.4, and 150.1 (11 \times ArCH's and $-CH=CH_2$), 111.1, 119.7, 124.5, 126.4, 130.4, 133.1, 137.4, 138.5, and 142.0 (8 \times ArC's and $-CH=CH_2$), and 163.8 ($>C=O$); ms (EI), m/z (%): 405 (61) M^+ , 404 (9), 314 (32), 313 (7), 261 (4), 260 (11), 259 (8), 169 (6), 168 (5), 145 (3), 117 (13), and 91 (100); Exact mass (hrms): calcd. for $C_{27}H_{23}N_3O$: 405.184, found: 405.183; calcd. for fragment ion $C_{20}H_{16}N_3O$ ($M-CH_2C_6H_5$): 314.129, found: 314.123.

Preparation of 9-benzyl-3,4-dihydro- β -carboline 19c

(a) 1-Benzyl-3-indolylacetonitrile 27

To a stirred solution of 3-indolylacetonitrile 26 (25 g, 0.16 mol) in dry benzene (300 mL) was added NaH (9.2 g, 50% suspension in oil, 1.2 equiv.) and the reaction mixture was heated under reflux for 15 min. Benzyl chloride (20 mL) was then added dropwise at room temperature with stirring, the mixture heated under reflux for 20 min, and then left at room temperature for ca. 12 h. The mixture was poured into ice-water (200 mL), the benzene layer was separated and the aqueous phase extracted with CH_2Cl_2 . The combined organic extract was dried (Na_2SO_4 anhyd.) and evaporated yielding the crude product 27 which crystallized from EtOH. (30.5 g, 78%); mp 95-96°C (lit.²⁷ mp 95-96°C). 1H nmr (90 MHz), $CDCl_3$, δ : 3.38 (2H, s, $-CH_2-CN$), 5.28 (2H, s, $-NCH_2-Ar$), 7.05-7.43 (9H, m, aromatic H's), 7.54-7.70 (1H, m, aromatic H); ms(EI), m/z(%): 246 (35) M^+ , 156 (14), 155 (19), 130 (10), and 91 (100).

(b) 1-Benzyltryptamine 20

A mixture containing 1-benzyl-3-indolylacetonitrile 27 (10 g, 40.65 mmol), THF (50 mL), 10% ethanolic-ammonia (150 mL) and 5% Rh- Al_2O_3 (2 g) was treated with H_2 at 40 psi for 2 days. The catalyst was removed by filtration and the evaporation of the filtrate *in vacuo* afforded the desired 1-benzyltryptamine 20 (9.7 g, 95%), bp 193-198°C/0.1 Torr (lit.²⁸, bp 148-200°C/0.5 Torr); 1H nmr (90 MHz), $CDCl_3$, δ : 1.15 (2H, br s, $-NH_2$ exchanges with D_2O), 2.75-3.20 (4H, m, $-CH_2-CH_2$), 5.23 (2H, s, $-NCH_2Ar$), 6.96 (1H, s, C-2 H), 7.03-7.50 (7H, m, aromatic H's), 7.55-7.85 (2H, m, aromatic H's); ms(EI), m/z(%): 250(9) M^+ , 221(25), 220(42), and 91(100).

(c) 1-Benzyl-N-formyltryptamine 28

A mixture of 1-benzyltryptamine 20 (15 g) and ethyl formate (100 mL) was heated in a sealed tube at 120°C for 2 h. The removal of excess ethyl formate and EtOH *in vacuo* gave 1-benzyl-N-formyltryptamine 28 (16.05 g, 96%) as an oil; 1H nmr (90 MHz), $CDCl_3$, δ : 2.85-3.05 (2H, m, $-CH_2CH_2-N-$), 3.37-3.75 (2H, m, $-CH_2CH_2-N-$), 5.02 (2H, s, $-NCH_2Ar$), 5.70 (1H, br s, $-NH$), 6.96 (1H, s, C-2 H), 7.00-7.30 (8H, m, aromatic H's), 7.60-7.80 (1H, m, aromatic H), and 8.05 (1H, br, s, $-CHO$); ms(EI), m/z(%): 278(15) M^+ , 233 (27), 220 (71), 129 (9), and 91 (100).

(d) 9-Benzyl-3,4-dihydro- β -carboline 19c

This compound was prepared from 1-benzyl-N-formyltryptamine 28 (5 g) by treatment with freshly distilled $POCl_3$ (30 mL) at ice bath temperature in a flask protected with a $CaCl_2$ tube. When the vigorous initial reaction subsided, the mixture was warmed to room temperature over a period of 10-20 min, then heated to 40°C for 5 min, and finally kept at room temperature for 2h.

The excess POCl_3 was destroyed carefully by addition of the reaction mixture to crushed ice and the resulting solution made basic with conc. aqueous NH_3 . The mixture was extracted with CHCl_3 , the CHCl_3 extract dried (Na_2SO_4 anhyd.) and evaporated, and the residue purified by bulb to bulb distillation.

The product 19c crystallized from ethanol or ethyl acetate (3.58 g, 77%); mp 148-149°C (EtOAc), and 140-141°C (EtOH) (lit.²⁶ mp 138°C (EtOH)); R_f 0.76 (alumina, EtOAc); ^1H nmr (90 MHz), CDCl_3 , δ : 2.95 (2H, t, $J=8.0$ Hz, C-4 H's), 3.94 (2H, d of t, $J=8.0$ and 2.0 Hz, C-3 H's), 5.42 (2H, s, benzylic H's), 6.95-7.45 (8H, m, aromatic H's), 7.55-7.73 (1H, m, aromatic H), and 8.50 (1H, m, C-1 H); ms(EI), $m/z(\%)$: 260(100) M^+ , 169(36), 156(16), 142(34), 140(15), 116(21), 115(41), 91(87), and 65(26).

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