Aryl Radical Cyclizations of 1-(2'-Bromobenzyl)isoquinolines with AIBN-Bu_3SnH: Formation of Aporphines and Indolo[2,1-*a*]isoquinolines

Supporting Information

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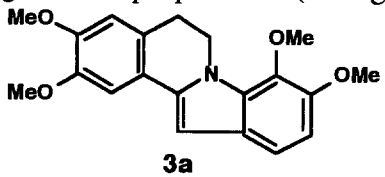
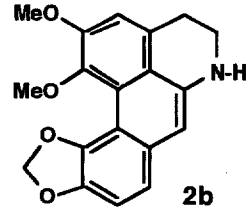
Experimental Procedure for Radical Cyclizations and
Spectral Data for Aporphines and Indolo[2,1-*a*]isoquinolines

General Procedure for Radical Cyclization of 1-(2'-Bromobenzyl)-3,4-dihydroisoquinolines (1a~i, 9, 11a~c, and 13c) and 1-(2'-Bromobenzoyl)-3,4-dihydroisoquinolines (4, 8).[1] A solution of AIBN (66 mg, 0.4 mmol), Bu_3SnH (233 mg, 0.8 mmol) in dry toluene (15 mL) was added in four portions at every 30 min during 1.5 h to a boiling solution of **1b**[1] (162 mg, 0.5 mmol) in dry toluene (15 mL) with stirring under nitrogen in an oil bath at 130°C. After the mixture was heated for an additional 2.5 h, the solvent was evaporated under reduced presure. ^1H NMR analysis revealded that the residue comprised **2b** and **3b** in 55:45. It was dissolved in CH_3CN (10 mL), and washed with hexane (30 mL × 5). One half of this CH_3CN fraction was subjected to preparative TLC on a Merck silica gel 60 PF_{254} developed with CH_2Cl_2 containing 1% MeOH, followed by crystallization from MeOH-Et_2O, gave indolo[2,1-*a*]isoquinoline **3b** (19 mg, 30%, R_f 0.37), mp 195-198 °C. Another one half was dissolved in MeOH (10mL) containing 3 drops of 2N-NaOH solution, and stirred at rt overnight. The mixture was concentrated, treated with CH_2Cl_2 (10 mL × 2) and water (10 mL). The CH_2Cl_2 layers were washed with saturated brine (10 mL), dried (Na_2SO_4), and concentrated. Separation of the residue in the same manner as the above gave oxoaporphine **2b** (27 mg, 42%, R_f 0.89), mp > 300 °C (MeOH-Et_2O).

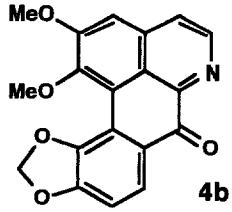


3a

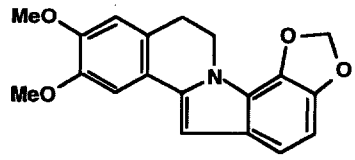
2,3,8,9-Tetramethoxy-5,6-dihydroindolo[2,1-*a*]isoquinoline (3a): 68%; dark green crystals; mp 193-195 °C (MeOH-Et_2O) (lit.[1] mp 193-195 °C); ^1H NMR (270 MHz, $CDCl_3$) δ 3. 09, 4.63 (each t, J = 6.6 Hz, each 2H), 3.92, 3.93, 3.95, 3.97 (each s, each 3H), 6.67, 6.75 (each s, each 1H), 6.81, 7.24 (AB type, J = 8.6 Hz, each 1H), 7.18 (s, 1H).



2b



4b



3b

4*H*-1,2-Dimethoxy-10,11-(methylenedioxy)-5,6-dihydrodibenzo[*de*, *g*]quinoline (2b):* ^1H NMR (270 MHz, $CDCl_3$) δ 3.21 (t, J = 5.9 Hz, 2H), 3.40 (t, J = 5.9 Hz, 2H), 3.72, 3.99 (s, each 3H), 6.07 (s, 2H), 6.54 (s, 1H), 7.05 (s, 1H), 7.09, 7.10 (each s, each 1H).

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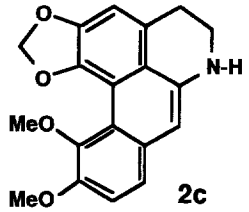
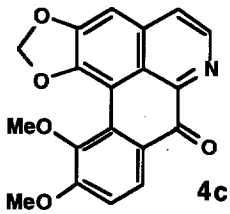
* The word of "methylenedioxy" is conveniently used for "benzodioxolo" or "dioxolo" through this manuscript.

Oxoaporphine derived from 2b, 1,2-dimethoxy-10,11-(methylenedioxy)-7-oxodibenzo[*de, g*]quinoline (4b): 42%; yellow crystals; mp > 300 °C (MeOH-Et_2O); IR (Nujol) 1652, 1606, 1576 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.93, 4.08 (s, each 3), 6.20 (s, 2H), 7.06, 8.23 (AB type, J = 8.3 Hz, each 1H), 7.19 (s, 1H), 7.75, 8.85 (ABtype, J = 5.3 Hz, each 1H); EIMS *m/z* (rel. int.) 336 [$(M + H)^+$, 4.3], 335 (M^+, 100), 320 [(M - CH_3), 28.8], 292 (29.2). Anal. Calcd for $C_{19}H_{13}NO_5$: C, 68.10; H, 3.91; N, 4.18. Found; C, 67.97; H, 4.08; N, 3.95.

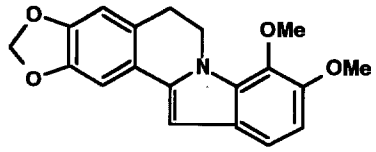
2,3-Dimethoxy-8,9-(methylenedioxy)-5,6-dihydroindolo[2,1-*a*]isoquinoline (3b): 30%; dark green crystals, mp 195-198 °C (MeOH-Et_2O) (lit.[1] 198-200 °C); ^1H NMR (270 MHz, $CDCl_3$) δ 3. 11, 4.39 (each t, J = 6.6 Hz, each 2H), 3.91, 3.95 (each s, each 3H), 6.00 (s, 2H), 6.68, 6.74 (each s, each 1H), 6.74, 7.06 (AB type, J = 8.6 Hz, each 1H), 7.18 (s, 1H).



2c



4c

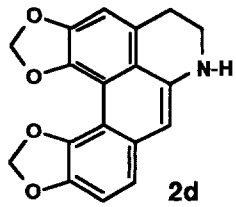


3c

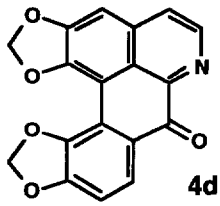
4*H*-10,11-Dimethoxy-1,2-(methylenedioxy)-5,6-dihydrodibenzo[*de, g*]quinoline (2c): ^1H NMR (270 MHz, $CDCl_3$) δ 3.20 (t, J = 5.6 Hz, 2H), 3.44 (t, J = 5.9 Hz, 2H), 3.75, 3.93 (s, each 3H), 6.11 (s, 2H), 6.48 (s, 1H), 6.99 (s, 1H), 7.21 (s, 2H).

Oxoaporphine derived from 2c, 10,11-dimethoxy-1,2-(methylenedioxy)-7-oxodibenzo[*de, g*]quinoline (4c): 18%; yellow crystals; mp > 300 °C (MeOH-Et_2O (lit.[2] mp 240-241 °C); IR 1663, 1638, 1575, 1510 cm^{-1}; ^1HNMR (270 MHz, $CDCl_3$) δ 3.81, 4.03 (s, each 3H), 6.26 (s, 2H), 7.17, 8.37 (ABtype, J = 8.9 Hz, each 1H), 7.18 (s, 1H), 7.72, 8.82 (AB type, J = 5.3 Hz, each 1H). EIMS *m/z* (rel. int.) 336 [$(M + H)^+$, 25.7], 335 (M^+, 100), 320 [$(M - CH_3)^+$, 48.9], 292 (21.2), 364 (27.7), 221 (24.9). Anal. Calcd for $C_{19}H_{13}NO_5$: C, 68.10; H, 3.91; N, 4.18. Found; C, 67.85; H, 3.93; N, 4.36.

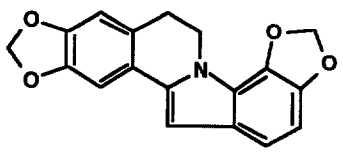
8,9-Dimethoxy-2,3-(methylenedioxy)-5,6-dihydroindolo[2,1-*a*]isoquinoline (3c): 52%; gray crystals; mp 180.5-182 (MeOH-Et_2O) (lit.[1] 177-180 °C); ^1H NMR (270 MHz, $CDCl_3$) δ 3. 06, 4.58 (each t, J = 6.3 Hz, each 2H), 3.93, 3.96 (each s, each 3H), 6.97 (s, 2H), 6.62, 6.72 (each s, each 1H), 6.80, 7.20 (AB type, J = 8.6 Hz, each 1H), 7.19 (s, 1H).



2d



4d



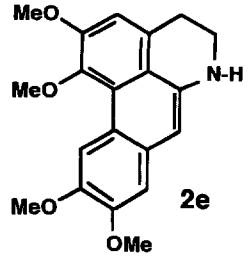
3d

4*H*-1,2:10,11-Bis(methylenedioxy)-5,6-dihydrodibenzo[*de, g*]quinoline (2d): ^1H NMR (270 MHz, $CDCl_3$) δ 3.19, 3.43 (t, J = 5.9 Hz, each 2H), 6.07, 6.12 (s, each 2H), 6.53 (s, 1H), 6.97 (s, 1H), 7.06, 7.08 (s, each 1H).

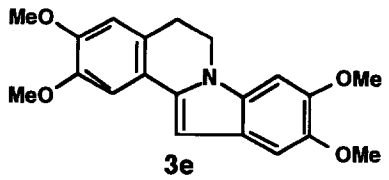
Oxoaporphine derived from 2d, hernandinine (4d): 29%; yellow crystals; mp > 300 °C (MeOH-$CHCl_3$) (lit.[3] mp >280 °C; [4,5] 298-300 °C); ^1HNMR (270 MHz, $CDCl_3$) δ 6.17, 6.25 (s, each each 2H), 7.04, 8.27 (ABtype, J = 8.6 Hz, each 1H), 7.16 (s, 1H), 7.72, 8.83 (ABtype, J = 5.3 Hz, each 1H); EI-MS *m/z* (rel. int.) 320 [$(M + 1)^+$, 23.2], 319 (M^+, 100), 175 (12.3).

2,3:8,9-Bis(methylenedioxy)-5,6-dihydroindolo[2,1-*a*]isoquinoline (3d): 29%; gray crystals; mp 205-206°C (EtOH) (lit.[1] mp 205-206 °C); ^1H NMR (270 MHz, $CDCl_3$) δ

3.08, 4.37 (each t, J = 6.6 Hz, each 2H), 5.97, 5.99 (each s, each 2H), 6.64, 6.72 (each s, each 1H), 6.75, 7.06 (AB type, J = 8.3 Hz, each 1H), 7.16 (s, 1H).



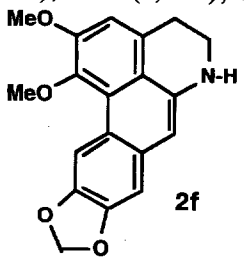
2e



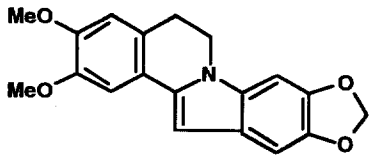
3e

4*H*-1,2,9,10-Tetramethoxy-5,6-dihydrodibenzo[*de, g*]quinoline (2e): 62 %; yellow crystals ; mp 179.5-182 °C (MeOH-ether); IR (Nujol) 3224, 1635, 1597, 1504 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.23 (t, J = 5.6 Hz, 2H), 3.47 (t, J = 5.6 Hz, 2H), 3.91, 3.99, 4.01, 4.02 (each s, each 3H), 6.60 (s, 1H), 6.94 (s, 1H), 6.99 (s, 1H), 9.09 (s, 1H). EIMS *m/z* (rel. int.) 340 [$(M + H)^+$, 25.8], 339 (M^+, 100), 324 [$(M - CH_3)^+$, 55.6], 266 (17.1), 170 (19.7). Anal.Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13. Found; C, 70.95; H, 6.36; N, 3.88.

2,3,9,10-Tetramethoxy-5,6-dihydroindolo[2,1-*a*]isoquinoline (3e): 3%; deep green crystals; mp 207-208°C (MeOH-Et_2O) (lit.[6] mp 199°C; [7] lit. 201-203°C; [8] 202-203°C; [9] 202-204°C; [1] 207-208°C; [10,11] 209-210°C): ^1H NMR (270 MHz, $CDCl_3$) δ 3.12 (t, J = 6.6 Hz, 2H), 3.91, 2.93, 3.96, 3.96 (each s, each 3H), 4.17 (t, J = 6.6 Hz, 2H), 6.64 (s, 1H), 6.75 (s, 1H), 6.80 (s, 1H), 7.07 (s, 1H) , 7.17 (s, 1H).



2f

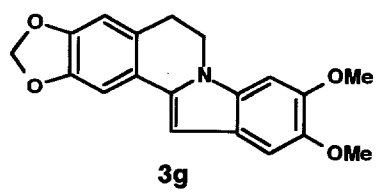


3f

4*H*-1,2-Dimethoxy-9,10-(methylenedioxy)-5,6-dihydrodibenzo[*de, g*]quinoline (2f): 79%; yellow crystals; mp 185.5-188 °C (MeOH-Et_2O); IR (Nujol) 3346, 1633, 1593, 1492 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.23 (t, J = 5.9 Hz, 2H), 3.48 (t, J = 5.9 Hz, 2H), 3.89, 4.01 (s, each 3H), 6.03 (s, 2H), 6.61 (s, 1H), 6.95 (s, 1H), 7.00 (s, 1H), 8.99 (s, 1H); EIMS *m/z* (rel. int.) 324 [$(M + H)^+$, 21.1], 323 (M^+, 100), 308 [$(M - CH_3)^+$, 31.4], 162 (18.5). Anal.Calcd for $C_{19}H_{17}NO_4$: C, 70.57; H, 5.30; N, 4.33. Found; C, 70.53; H, 5.40; N, 4.13.

2,3-Dimethoxy-9,10-(methylenedioxy)-5,6-dihydroindolo[2,1-*a*]isoquinoline (3f): 7%; dark green crystals; mp 241-242.5 °C (MeOH-Et_2O); IR (Nujol) 1610, 1549, 1502, 1490 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.10 (t, J = 6.6 Hz, 2H), 4.12 (t, J = 6.6 Hz, 2H), 3.91, 3.95 (s, each 3H), 5.93 (s, 2H), 6.63 (s, 1H), 6.74 (s, 1H), 6.78 (s, 1H), 6.99 (s, 1H , 7.15 (s, 1H); EIMS *m/z* (rel. int.) 324 [$(M + H)^+$, 23.1], 323 (M^+, 100), 308 [$(M - CH_3)^+$, 43.2], 279 (24.0), 162 (22.4). Anal.Calcd for $C_{19}H_{17}NO_4$: C, 70.57; H, 5.30; N, 4.33. Found; C, 70.35; H, 5.41; N, 4.23.

2g

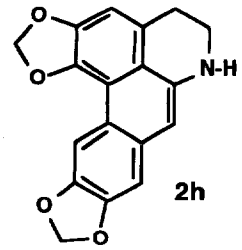


3g

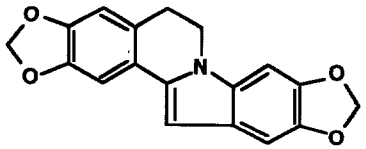
4*H*-9,10-Dimethoxy-1,2-(methylenedioxy)-5,6-dihydrodibenzo[*de, g*]quinoline (2g): 55%; yellow crystals; mp 182-186 °C (MeOH-Et_2O); IR (Nujol) 1633, 1604, 1487 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.20 (t, J = 5.6 Hz, 2H), 3.47 (t, J = 5.9 Hz, 2H), 3.99,

4.02 (s, each 3H), 6.20 (s, 2H), 6.57 (s, 1H), 6.92 (s, 1H), 6.95 (s, 1H), 8.41 (s, 1H); EIMS *m/z* (rel. int.) 324 [(M + H)$^+$, 24.62], 323 (M$^+$, 100), 308 [(M - CH_3), 74.7], 279 (13.0), 162 (20.7). Anal.Calcd for $C_{19}H_{17}NO_4$: C, 70.57; H, 5.30; N, 4.33. Found; C, 70.66; H, 5.34; N, 4.15.

9,10-Dimethoxy-2,3-(methylenedioxy)-5,6-dihydroindolo[2,1-*a*]isoquinoline (3g): 7%; dark green crystals; mp 212-216 °C (MeOH-Et_2O); IR (Nujol) 1599, 1550, 1503, 1475 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.09 (t, *J* = 6.3 Hz, 2H), 4.14 (t, *J* = 6.3 Hz, 2H), 3.93, 3.96 (s, each 3H), 5.96 (s, 2H), 6.60 (s, 1H), 6.72 (s, 1H), 6.79 (s, 1H), 7.06 (s, 1H), 7.15 (s, 1H) ; EIMS *m/z* (rel. int.) : 324 [(M + 1)$^+$, 24.09], 323 (M$^+$, 100), 308 [(M - CH_3)$^+$, 64.7], 280 (16.0), 162 (27.4). Anal.Calcd for $C_{19}H_{17}NO_4$: C, 70.57; H, 5.30; N, 4.33. Found; C, 70.66; H, 5.38; N, 4.38.



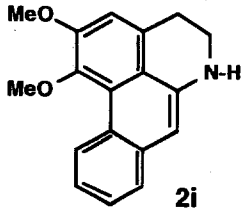
2h



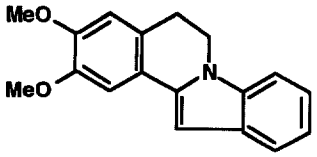
3h

4*H*-1,2:9,10-Bis(methylenedioxy)-5,6-dihydrodibenzo[*de*, *g*]quinoline (2h): 45%; yellow crystals: mp 204-207°C (MeOH-Et_2O); IR (Nujol) 3368, 1632, 1599, 1510 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.20 (t, *J* = 5.9 Hz, 2H), 3.47 (t, *J* = 5.9Hz, 2H), 6.02, 6.19 (s, each 2H), 6.56 (s, 1H), 6.92 (s, 1H), 6.95 (s, 1H), 8.40 (s, 1H); EIMS *m/z* (rel. int.) 308 [(M + H)$^+$, 23.5], 307 (M$^+$, 100), 249 (12.3), 154 (15.1). Anal.Calcd for $C_{18}H_{13}NO_4$: C, 70.35; H, 4.26; N, 4.56. Found; C, 70.49; H, 4.41; N, 4.49.

2,3:9,10-Bis(methylenedioxy)-5,6-dihydroindolo[2,1-*a*]isoquinoline (3h): 7%; deep green crystals; mp 219.5-222.5 °C (MeOH-Et_2O) (lit.[1] mp 214.5-217.5 °C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.07 (t, *J* = 6.6 Hz, 2H), 4.09 (t, *J* = 6.6 Hz, 2H), 5.93, 5.96 (s, each 2H), 6.59 (s, 1H), 6.71 (s, 1H), 6.77 (s, 1H), 6.98 (s, 1H) , 7.12 (s, 1H).



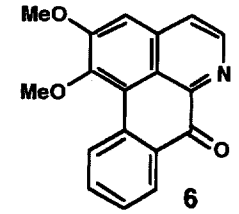
2i



3i

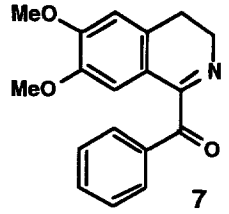
4*H*-1,2-Dimethoxy-5,6-dihydrodibenzo[*de*, *g*]quinoline (2i): 48%; yellow crystals; mp 144-146 °C (MeOH-CH_2Cl_2); IR (Nujol) 3370, 1625, 1595, 1527, 1508 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.27 (t, *J* = 5.9 Hz, 2H), 3.51 (t, *J* = 5.9 Hz, 2H), 3.91, 4.02 (s, each 3H), 6.76 (s, 1H), 7.06 (s, 1H), 7.38 (dt, J = 6.9, 6.9, 1.3 Hz, 1H), 7.45 (dt, *J* = 7.9, 7.9, 1.3 Hz, 1H), 7.57 (dd, *J* = 7.9, 1.3 Hz, 1H), 9.48 (d, *J* = 8.3 Hz, 1H); EIMS *m/z* (rel. int.) 279 (M$^+$, 100), 264 [(M - CH_3)$^+$, 39.7). Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found; C, 77.38; H, 6.13; N, 4.86.

9,10-Dimethoxy-5,6-dihydroindolo[2,1-*a*]isoquinoline (3i): 3%; deep green crystals; mp 177.5-179.5 °C (MeOH-CH_2Cl_2); IR (Nujol) 1607, 1505 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.12 (t, *J* = 6.6 Hz, 2H), 4.22 (t, *J* = 6.6 Hz, 2H), 3.91, 3.96 (each s, each 3H), 6.75 (s, 1H), 6.76 (s, 1H), 7.06-7.21 (m, 2H), 7.24 (s, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H); EI-MS *m/z* (rel. int.) 280 [(M + H)$^+$, 23.45], 279 (M$^+$, 100), 264 [(M - CH_3)$^+$, 22.8], 236 (23.7), 221 (10.5), 204 (8.4), 192 (12.0), 140 (14.3). Anal. Calcd for $C_{18}H_{17}NO_2$; C, 77.40; H, 6.13; N, 5.01. Found; C, 77.49; H, 6.14; N, 4.99.



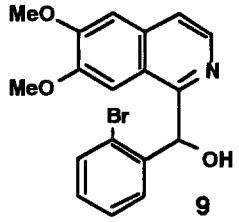
6

Lysicamine (6): mp 203-205 °C dec (MeOH-hexane) (lit.[12] mp 210-211 °C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.02 (s, 3H), 4.11 (s, 3H), 7.23 (s, 1H), 7.58 (ddd, J = 8.3, 7.9, 1.0 Hz, 1H), 7.74-7.81 (m, 2H), 8.59 (dd, J = 7.9, 1.7 Hz, 1H), 8.9 (d, J = 5.3 Hz, 1H), 9.20 (d, J = 8.3 Hz, 1H).



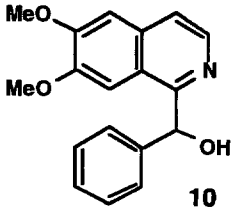
7

1-(Benzoyl)-6,7-dimethoxy-2,3-dihydroisoquinoline (7): a colorless oil;[13] ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.82 (t, J = 7.6 Hz, 2H), 3.78 (s, 3H), 3.92 (t, J = 7.6 Hz, 2H), 3.93 (s, 3H), 6.76 (s, 1H), 7.44-7.50 (m, 2H), 8.02-8.06 (m, 2H).



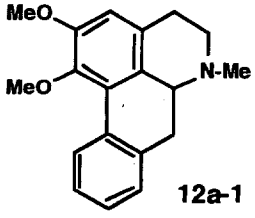
9

1-[(2'-Bromophenyl)hydroxymethyl]-6,7-dimethoxyisoquinoline (9): prepared by treatment of the compound **8** with $NaBH_4$; colorless crystals (98 %); mp 143-145 °C (benzene-hexane); IR (Nujol) 3744-3370, 1510 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.88, 3.99 (each s, each 3H), 6.71 (s, 1H), 6.88-6.93 (m, 1H), 7.05-7.13 (m, 4H), 7.54 (d, J = 5.6 Hz, 1H), 7.61-7.64 (m, 1H), 8.41 (d, J = 5.6 Hz, 1H). EI-MS *m/z* (rel. int.) 373 (M^+, 14), 294 [$(M - Br)^+$, 100), 278 (12), 262 (5). Anal. Calcd for $C_{18}H_{20}NO_3Br$; C, 57.77; H, 4.31; N, 3.74; Br, 21.35. Found; C, 57.65; H, 4.23; N, 3.87; Br, 21.27.



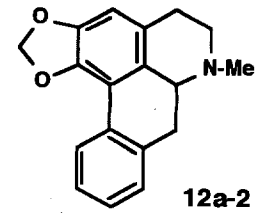
10

1-[(phenyl)hydroxymethyl]-6,7-dimethoxyisoquinoline (10): colorless crystals; mp 130-131 °C (MeOH-Et_2O) (lit.[13] mp 140 °C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.78, 3.98, (each s, each 3H), 6.18, 7.06, 7.07 (each s, each 1H), 7.22-7.36 (m, 5H), 7.50, 8.40 (each d, J = 6.6 Hz, each 1H).



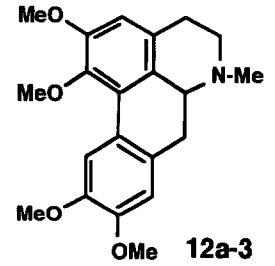
12a-1

(±)-Nuciferine (12a-5): 27%; colorless crystals; mp 135-136 °C (hexane) (lit.[14] mp 134.5-135.5 °C; [15] 136-137 °C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.44-2.72 (m, 3H), 2.55 (s, 3H), 3.00-3.21 (m, 4H), 3.65 (m, 3H), 3.88 (s, 3H), 6.63 (s, 1H), 7.22-7.36 (m, 2H), 8.53 (d, J = 8.0 Hz, 1H).



12a-2

(±)-Roemerine (12a-2): a colorless oil (35%); IR (neat) 1503 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.44-2.74 (m, 3H), 2.56 (s, 3H), 3.02-3.20 (m, 4H), 5.93, 6.08 (each d, *J* = 1.7 Hz, each 1H), 6.56 (s, 1H), 7.22-7.34 (m, 2H), 8.08 (d, *J* = 8.0 Hz, 1H); EIMS *m/z* (rel. int.) 279 (M+, 100), 236 (62), 190 (93); HRMS Calcd for $C_{18}H_{17}NO_2$: 279.1253. Found; 279.1259.

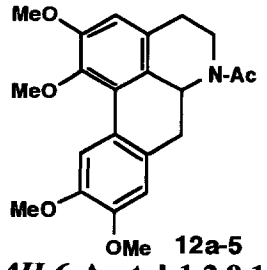


12a-3

(±)-Glaucine (12a-3): 24%; light yellow crystals; mp 132-133°C (MeOH-Et_2O) (lit.[16] mp 118-120 °C); ^1H NMR (270MHz, $CDCl_3$) δ 2.46~2.71 (m, 4H), 2.55 (s, 3H), 2.99-3.17 (m, 3H), 3.65, 3.89, 3.90, 3.93 (each s, each 3H), 6.59, 6.78, 8.09 (each s, each 1H).

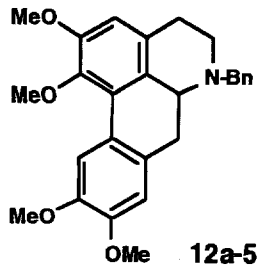
12a-4

(±)-Neolitsine (12a-4): 22%; colorless crystals; mp 137-8°C (Et_2O-hexane) (lit.[17] mp 193-195 °C); ^1H NMR (270MHz, $CDCl_3$) δ 2.45-2.66 (m, 3H), 2.53 (s, 3H), 3.00-3.16 (m, 3H), 3.00-3.16 (m, 4H), 5.92, 6.05 (AB type, *J* = 1.3 Hz, each 1H), 5.95, 5.97 (AB type, *J* = 1.3 Hz, each 1H), 6.52, 6.75, 7.61 (s, 1H).



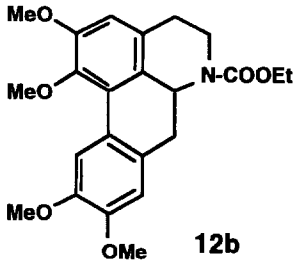
12a-5

4*H*-6-Acetyl-1,2,9,10-tetramethoxy-5,6,6a,7-tetrahydrodibenzo[*de*, *g*]quinoline (12a-5): 25%; a colorless oil; IR (neat) 1641, 1515 cm^{-1}; ^1H NMR (270MHz, $CDCl_3$) δ 2.19, 2.23 (each s, 2:3, 3 H), 2.63-3.12 (m, 5H), 3.26-3.32 (m, 0.6H), 3.67 (s, 3H, s), 3.90-3.94 (m, 9H), 4.54-4.60 (m, 0.4 H), 4.40-4.99 (m, 0.4 H), 5.05-5.12 (m, 0.6 H), 6.65 (s, 0.6H), 6.67 (s, 0.4 H), 6.79 (br, s, 1H), 8.15 (s, 0.6 H), 8.18 (s, 0.4 H); EIMS *m/z* (rel. int.) 383 (M^+, 80), 311 [(M - $CH_2NAc)^+$, 100]. HRMS calcd for $C_{22}H_{26}NO_5$ 383.1730, found 389.1733.



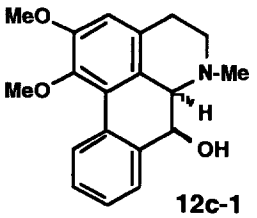
12a-5

4*H*-6-Benzyl-1,2,9,10-tetramethoxy-5,6,6a,7-tetrahydrodibenzo[*de*, *g*]quinoline (12a-6): 33%; colorless crystals; mp 161-163°C (MeOH-Et_2O); IR (Nujol) 1515 cm^{-1}: ^1H NMR (270MHz, $CDCl_3$) δ 2.30-2.56 (m, 1H), 2.63-2.65 (m, 2H), 2.73 (d, J = 13.5 Hz, 1H), 2.94-3.17 (m, 3H), 3.30-3.38 (m, 2H), 2.88, 3.65, 3.91, 3.94 (each s, each 3H), 4.54-4.60 (m, 0.4 H), 4.37 (d, J = 13.5 Hz, 1H), 6.59. 6.79 (each s, each 1H), 7.28-7.65 (m, 5H), 8.09 (s, 1H); EIMS *m/z* (rel. int.) 431 (M^+, 71.0), 416 [$(M - CH_3)^+$, 52.0], 352 [$(M - C_6H_5CH_2)^+$, 18.0], 91 (100). HRMS calcd for $C_{27}H_{29}NO_4$ 431.2081, found 431.2096. Anal. Calcd for $C_{27}H_{29}NO_4$: C, 75.15; H, 6.77; 3.25. Found: C, 75.31; H, 6.87; N, 3.29.



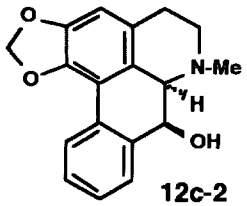
12b

4*H*-6-Carbethoxy-1,2,9,10-tetramethoxy-5,6,6a,7-tetrahydrodibenzo[*de*, *g*]quinoline (12b): 50%; colorless crystals; mp 166-168 °C (MeOH) (lit. [18] mp 124-125 °C; [19] 143-144 °C); ^1H NMR (270MHz, $CDCl_3$) δ 1.29 (t, J = 6.9 Hz, 3H), 2.61-3.05 (m, 5 H), 3.66, 3.90, 3.91, 3.93 (each s, each 3H), 4.22 (q, J = 6.9 Hz, 2H), 4.45 (br, d, J = 10.5 Hz, 1H), 4.74 (dd, J = 13.2, 4.6 Hz, 1H), 6.64, 6.78, 8.16 (each s, each 1H).



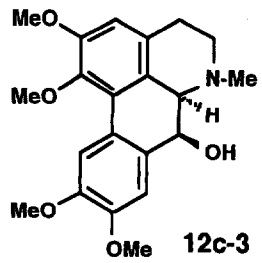
12c-1

(±)-*trans*-7-Hydroxynuciferine (12c-1): 67%; colorless crystals; mp 140-142°C (Et_2O-MeOH); IR (Nujol) 3612-3004, 1599, 1499 cm^{-1}; ^1H NMR (270MHz, $CDCl_3$) δ 2.59 (m, 3H), 2.67-2.73 (m, 2H), 3.05-3.16 (d, J = 2.0 Hz, 1H), 3.67, 3.89 (each s, each 3H), 4.81 (d, J = 2.6 Hz, 1H), 6.64 (s, 1H), 7.30-7.33 (m, 1H), 7.40-7.89 (s, 2H), 8.48 (d, J = 8.9 Hz, 1H); EIMS *m/z* (rel. int.) 311 (M^+, 70), 293 [$(M - H_2O)^+$, 85], 280 [$(M - MeOH)^+$, 85], 91 (00). HRMS calcd for $C_{19}H_{21}NO_3$ 311.1531, found 311.1521.



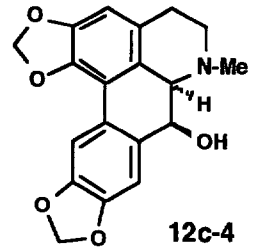
12c-2

(±)-Ushinsunine (12c-2): 60 %; colorless crystals; mp 143-145 °C (Et_2O) (lit.[19,20] mp 144-145°C); ^1H NMR (270MHz, $CDCl_3$) δ 2.60 (m, 3H), 2.62-2.75 (m, 2H), 3.06-3.16 (m, 2H), 3.72, 4.88 (each d, J = 2.3 Hz, each 1H), 5.93, 6.09 (d, J = 1.3 Hz, 1H), 7.27-7.33 (m, 1H), 7.40-7.46 (m, 2H), 8.15 (d, J = 8.9 Hz, 1H).



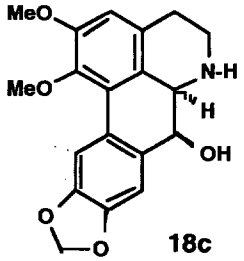
12c-3

(±)-*trans*-7-Hydroxyglaucine (12c-3): 57%; a colorless oil: IR (neat) 1638, 1598, 1519, 1519 cm^{-1}; ^1H NMR (270MHz, $CDCl_3$) δ 2.60 (s, 3H), 2.67-2.74 (m, 2H), 3.06-3.13 (m, 2H), 3.15 (d, J = 2.6 Hz, 1H), 3.68, 3.89, 3.93, 3.95 (s, each 3H), 4.76 (d, J = 2.6 Hz, 1H), 6.60 (s, 1H), 6.95 (s, 1H), 8.22 (s, 1H); EIMS *m/z* (rel. int.) 371 (M^+, 43), 293 [$(M - H_2O)^+$, 100], 338 [$(M - H_2O - CH_3)^+$, 66], 91 (100). HRMS Calcd for $C_{21}H_{25}NO_5$: 371.1762, found; 371.1732.



12c-4

***t*(±)-*trans*-7-Hydroxyneolitsine (12c-4)**: 68 %; colorless crystals; mp 150-152°C; IR (neat) 1662, 1629, 1585, 1559, 1525, 1510 cm^{-1}; ^1H NMR (270MHz, $CDCl_3$) δ 2.58 (s, 3H), 2.63-2.73 (m, 2H), 3.03-3.16 (m, 2H), 3.21 (d, J = 2.7 Hz, 1H), 4.75 (d, J = 2.7 Hz, 1H), 5.92, 6.60 (AB type, J = 1.7 Hz, each 1H), 5.98, 6.00 (AB type, J = 1.7 Hz, each 1H), 6.52 (s, 1H), 6.91 (s, 1H), 7.70 (s, 1H); EIMS *m/z* (rel. int.) 339 (M^+, 100), 321 [$(M - H_2O)^+$, 63.4], 310 (17.8), 296 (50.2), 280 (24), 190 (76.9). Anal. Calcd for $C_{19}H_{17}NO_5$: C, 67.25; H, 5.05: N, 4.13. Found: C, 67.37; H, 5.20: N, 4.06.



18c

(±)-*trans*-4*H*-1,2-Dimethoxy-7-hydroxy-9,10-(methylenedioxy)-5,6,6a,7-tetrahydrodibenzo[*de*, *g*]quinoline (18c): 14 %; a colorless oil; IR (Nujol) 3710-3072, 1609, 1509 cm^{-1}; ^1H NMR (270MHz, $CDCl_3$) δ 2.61-2.72 (m, 2H), 2.88-3.18 (m, 2H), 3.37-3.48 (m, 1H), 3.70 (s, 3H), 3.88 (s, 3H), 4.42 (d, J = 3.0 Hz, 1H), 6.00 (d, J = 1.0 Hz, 2H), 6.63, 6.87, 8.07 (each s, each 1H); EIMS *m/z* (rel. int.) 341 (M^+, 38), 323 [$(M - H_2O)^+$, 100], 310 (47), (17), 296 (50), 280 (17), 190 (76). HRMS calcd for $C_{19}H_{19}NO_5$ 341.1251, found 341.1263.

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