Synthesis of Carbalexin B, Clausine A, Clauszoline M, and 2,8-Dihydroxy-3-methylcarbazole

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Abstract: Using a palladium(II)-catalyzed oxidative cyclization of an *N*,*N*-diarylamine, we have achieved the total synthesis of the 2,8-dioxygenated carbazole alkaloids carbalexin B, clausine A, clauszoline M, and 2,8-dihydroxy-3-methylcarbazole.

Key words: alkaloids, catalysis, cyclization, natural products, palladium

A broad structural variety has been found in carbazole natural products.[1,2] The simple tricyclic carbazole alkaloids have been classified based on their oxygenation pattern.[2] A minor group are the 2,8-dioxygenated carbazole alkaloids (Figure 1). Greger et al. observed the stress-induced formation of the phytoalexin carbalexin B (**1**) in the leaves of *Glycosmis parviflora*.[3] Carbalexin B (**1**) exhibits strong antifungal activity. Clausine A (**2**) was isolated by Wu et al. from the stem bark of *Clausena excavata*.[4] Clauszoline M (**3**) was described by Ito et al. and extracted from the leaves of *Clausena excavata*.[5] 2,8-Dihydroxy-3-methylcarbazole (**4**) represents the parent compound for this group, but so far it has not been found in nature.[6]

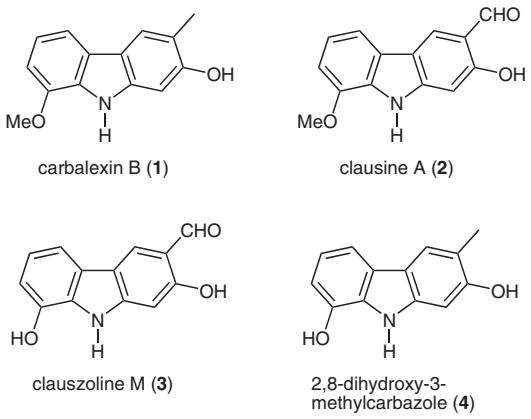
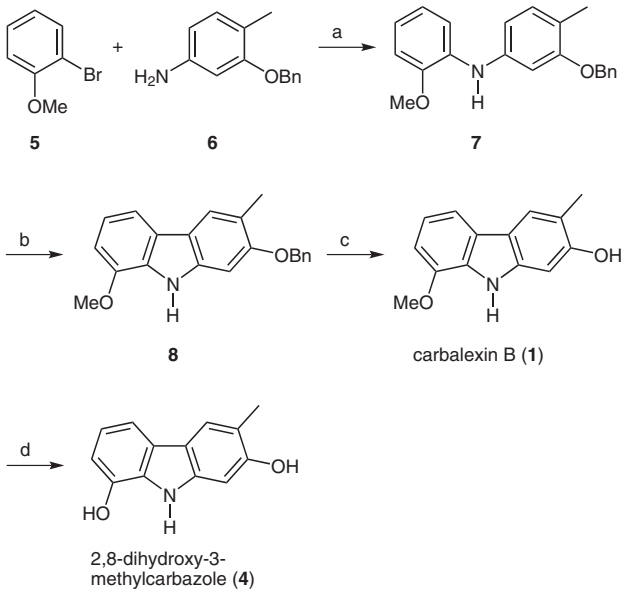


Figure 1 2,8-Dioxygenated carbazole alkaloids

The useful biological activities of carbazoles and their pharmacological potential have induced intense research activity.[7] We have developed an efficient two-step palladium-catalyzed synthetic route to carbazoles that is very flexible with respect to the substitution pattern.[8] Using this palladium-catalyzed approach, we have previously constructed 2,8-dioxygenated carbazoles that have been applied in the total synthesis of murrafoline A,[9] 8-oxygenated pyrano[3,2-*a*]carbazole alkaloids,[10] and 7-oxygenated pyrano[2,3-*a*]carbazole alkaloids.[10] Herein,[11] we describe in full detail the application of our method to the synthesis of the 2,8-dioxygenated tricyclic carbazole alkaloids carbalexin B (**1**), clausine A (**2**), clauszoline M (**3**), and 2,8-dihydroxy-3-methylcarbazole (**4**).

Buchwald–Hartwig coupling of *o*-bromoanisole (**5**) and arylamine **6** in the presence of XPhos as ligand[12] afforded the *N*,*N*-diarylamine **7** (Scheme 1). The palladium(II)-catalyzed oxidative cyclization[13] of **7** led to the orthogonally diprotected 2,8-dioxygenated carbazole **8** in 60% yield. Using stoichiometric amounts of palladium(II) acetate,[14] compound **8** was obtained in 68% yield (see experimental section, Method A). Removal of the benzyl protecting group by hydrogenolysis led to carbalexin B (**1**).[15] Cleavage of the methyl ether by treatment of **1** with boron tribromide at low temperature provided 2,8-dihydroxy-3-methylcarbazole (**4**).[6]



Scheme 1 Synthesis of carbalexin B (**1**) and 2,8-dihydroxy-3-methylcarbazole (**4**). *Reagents and conditions*: (a) $Pd(OAc)_2$ (10 mol%), XPhos (20 mol%), Cs_2CO_3 (1.5 equiv), toluene, reflux, 24 h (98%); (b) $Pd(OAc)_2$ (10 mol%), K_2CO_3 (10 mol%), PivOH, air, 85 °C, 24 h (60%); (c) 10% Pd/C, H_2 (1 atm), MeOH–CH_2Cl_2 (2:1), r.t., 5 d (64%); (d) BBr_3 (2 equiv), CH_2Cl_2, –78 °C to 0 °C, 19 h (63%).

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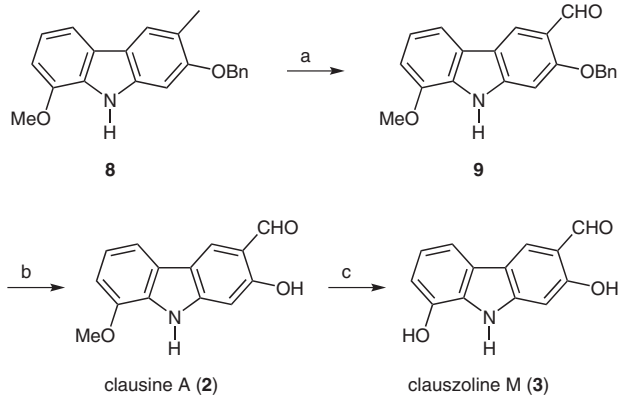
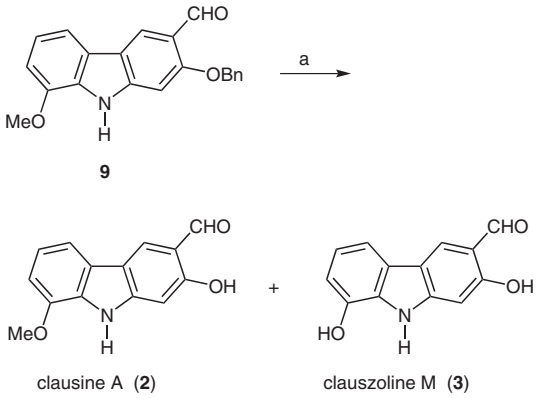
Oxidation of the orthogonally diprotected carbazole **8** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) afforded the corresponding carbazole-3-carbaldehyde **9** (Scheme 2). Cleavage of the benzyl ether by treatment with an excess of aluminum trichloride in 1,4-dioxane at reflux provided clausine A (**2**) in 71% yield.[16] Using hydrogenolytic conditions [10% Pd/C, 1 atm H_2, MeOH–CH_2Cl_2 (2:1), r.t., 18 h], the best result for this transformation was a yield of 57% for clausine A (**2**). The moderate yield of clausine A (**2**) by palladium-catalyzed hydrogenation of **9** is ascribed to the transformation of **2** into carbalexin B (**1**) under these reaction conditions, as previously reported.[6b] Cleavage of the methyl ether by treatment of clausine A (**2**) with boron tribromide at low temperature led largely to decomposition and afforded clauszoline M (**3**) in only 18% yield.



Scheme 2 Synthesis of clausine A (**2**). *Reagents and conditions*: (a) DDQ (2.2 equiv), THF–MeOH–H_2O (1:5:1), r.t., 90 min (64%); (b) $AlCl_3$ (5 equiv), 1,4-dioxane, reflux, 2 h (71%); (c) BBr_3 (3 equiv), CH_2Cl_2, –78 °C to 0 °C, 4 h (18%).

In an alternative route to clauszoline M (**3**) we have tried to remove both protecting groups of the orthogonally diprotected carbazole **9** in a one-pot process (Scheme 3). Slow addition of boron tribromide to a solution of compound **9** at –78 °C provided, after an increase of the temperature to 0 °C, clausine A (**2**) in 50% yield and clauszoline M (**3**) in 45% yield.



Scheme 3 Synthesis of clauszoline M (**3**). *Reagents and conditions*: (a) BBr_3 (3 equiv), CH_2Cl_2, –78 °C to 0 °C, 16 h (50% **2** and 45% **3**).

In conclusion, we have developed an efficient route to the 2,8-dioxygenated carbazole alkaloids carbalexin B (**1**), clausine A (**2**), clauszoline M (**3**), and 2,8-dihydroxy-3-methylcarbazole (**4**). A total synthesis of clauszoline M (**3**) has been described for the first time [4 steps and 19% overall yield, based on *o*-bromoanisole (**5**) and 68% yield for the cyclization step]. The key steps of our approach are a palladium(0)-catalyzed C–N bond formation followed by a palladium(II)-catalyzed oxidative cyclization of the intermediate *N*,*N*-diarylamine **7**. The spectroscopic data of the products are in full agreement with those reported in the literature.[3–6]

All reactions were carried out in oven-dried glassware using dry solvents under an argon atmosphere unless stated otherwise. CH_2Cl_2, THF, and toluene were dried using a solvent purification system (MBraun-SPS). $Pd(OAc)_2$ was recrystallized from glacial AcOH. All other chemicals were used as received from commercial sources. Flash chromatography was performed on a Büchi Sepacore system equipped with an UV monitor using silica gel (Acros Organics, 0.035–0.070 mm). TLC was performed with TLC plates from Merck (60 F_{254}) using UV light for visualization. Melting points were measured on a Gallenkamp MPD 350 melting point apparatus. UV spectra were recorded on a Perkin Elmer 25 UV/VIS spectrophotometer. IR spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrophotometer using the ATR method. NMR spectra were recorded on a Bruker DRX 500 spectrometer with non-deuterated solvent as internal standard. Mass spectra were recorded on a Finnigan MAT-95 spectrometer (electron impact, 70 eV) or by GC/MS-coupling using an Agilent Technologies 6890 N GC System equipped with a 5973 Mass Selective Detector (electron impact, 70 eV). ESI-MS spectra were recorded on an Esquire LC with an ion trap detector from Bruker. Positive and negative ions were detected. Elemental analyses were measured on an EuroVector EuroEA3000 elemental analyzer.

3-Benzyloxy-*N*-(2-methoxyphenyl)-4-methylaniline (7)

A solution of *o*-bromoanisole (**5**) (0.789 g, 4.22 mmol) in toluene (20 mL) was added dropwise over a period of 3 h to a solution of 3-benzyloxy-4-methylaniline[8g] (**6**) (1.08 g, 5.06 mmol), Cs_2CO_3 (2.08 g, 6.38 mmol), $Pd(OAc)_2$ (95 mg, 0.42 mmol), and XPhos (402 mg, 0.84 mmol) in toluene (50 mL) at reflux. After heating at reflux for 24 h, the mixture was allowed to cool to r.t. Removal of the solvent and flash chromatography of the crude product (silica gel, petroleum ether–EtOAc, 9:1) afforded **7** as a light brown solid; yield: 1.32 g (98%); mp 74 °C.

IR (ATR): 3414, 3058, 3031, 2934, 2849, 1596, 1507, 1481, 1460, 1435, 1409, 1381, 1339, 1296, 1242, 1215, 1173, 1124, 1024, 909, 829, 734, 695, 627 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.25 (s, 3 H), 3.88 (s, 3 H), 5.06 (s, 2 H), 6.09 (br s, 1 H), 6.67 (dd, *J* = 2.1, 7.9 Hz, 1 H), 6.74 (d, *J* = 2.1 Hz, 1 H), 6.80–6.83 (m, 2 H), 6.85–6.88 (m, 1 H), 7.06 (d, *J* = 8.0 Hz, 1 H), 7.09–7.11 (m, 1 H), 7.33 (m, 1 H), 7.39 (m, 2 H), 7.43 (m, 2 H).

^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 15.79 (CH_3), 55.54 (CH_3), 69.68 (CH_2), 103.79 (CH), 110.32 (CH), 111.49 (CH), 113.79 (CH), 119.19 (CH), 120.16 (C), 120.85 (CH), 127.01 (2 CH), 127.67 (CH), 128.50 (2 CH), 130.96 (CH), 133.56 (C), 137.37 (C), 141.26 (C), 147.80 (C), 157.23 (C).

MS (EI): *m*/*z* (%) = 319 (100) [M^+], 200 (23), 196 (19), 91 (81).

Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39. Found: C, 78.98; H, 6.71; N, 4.31.

2-Benzyloxy-8-methoxy-3-methyl-9*H*-carbazole (8)

Method A: A mixture of 3-benzyloxy-*N*-(2-methoxyphenyl)-4-methylaniline (**7**) (382 mg, 1.19 mmol), $Pd(OAc)_2$ (322 mg, 1.43 mmol), and AcOH (20 mL) was heated at 85 °C for 48 h. After cooling to r.t., EtOAc was added and the mixture was washed several times with sat. aq K_2CO_3 solution; the organic layer was dried ($MgSO_4$). Removal of the solvent and flash chromatography of the crude product (silica gel, petroleum ether–EtOAc, 7:1) afforded **8**; yield: 257 mg (68%).

Method B: A mixture of 3-benzyloxy-*N*-(2-methoxyphenyl)-4-methylaniline (**7**) (3.18 g, 9.95 mmol), $Pd(OAc)_2$ (223.3 mg, 0.995 mmol), K_2CO_3 (137.5 mg, 0.995 mmol), and pivalic acid (8.95 g) was heated at 85 °C for 24 h in the presence of air. After cooling to r.t., EtOAc was added and the mixture was washed several times with sat. aq K_2CO_3 solution; the organic layer was dried ($MgSO_4$). Removal of the solvent and flash chromatography of the crude product (silica gel, petroleum ether–EtOAc, 7:1) afforded **8**; yield: 1.88 g (60%).

Brownish solid; mp 114–117 °C.

IR (ATR): 3420, 3367, 3009, 2919, 2849, 1632, 1579, 1509, 1450, 1428, 1390, 1333, 1302, 1264, 1251, 1222, 1174, 1152, 1093, 1040, 1027, 993, 883, 824, 779, 738, 723, 692 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 3.98 (s, 3 H), 5.15 (s, 2 H), 6.80 (d, *J* = 7.8 Hz, 1 H), 6.92 (s, 1 H), 7.10 (t, *J* = 7.8 Hz, 1 H), 7.32 (m, 1 H), 7.39 (m, 2 H), 7.48 (m, 2 H), 7.54 (d, *J* = 7.8 Hz, 1 H), 7.78 (s, 1 H), 8.07 (br s, 1 H).

^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 16.92 (CH_3), 55.46 (CH_3), 70.07 (CH_2), 94.11 (CH), 104.66 (CH), 112.10 (CH), 116.85 (C), 119.60 (CH), 119.68 (C), 121.72 (CH), 124.45 (C), 127.08 (2 CH), 127.73 (CH), 128.52 (2 CH), 129.35 (C), 137.45 (C), 138.66 (C), 145.44 (C), 156.33 (C).

MS (EI): *m*/*z* (%) = 317 (100) [M^+], 302 (15).

HRMS: *m*/*z* [M^+] calcd for $C_{21}H_{19}NO_2$: 317.1416; found: 317.1410.

UV (MeOH): λ = 253 (sh), 263 (sh), 298, 317, 330 nm.

Fluorescence (MeOH): λ_{ex} = 330 nm, λ_{em} = 373 nm.

Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 78.99; H, 6.69; N, 4.01.

Carbalexin B (1)

A mixture of 2-benzyloxy-8-methoxy-3-methyl-9*H*-carbazole (**8**) (145 mg, 0.457 mmol) and 10% Pd on activated carbon (29 mg) in MeOH–CH_2Cl_2 (2:1, 15 mL) was stirred at r.t. for 5 d under a H_2 atmosphere at normal pressure. The mixture was filtered over Celite and the Celite was subsequently washed with Et_2O. Removal of the solvent from the combined filtrates and flash chromatography of the crude product (silica gel, petroleum ether–EtOAc, 2:1) afforded **1** as a colorless solid; yield: 67.6 mg (64%); mp 193–195 °C (Lit.[3] 196–198 °C, Lit.[6b] 195–196 °C).

IR (ATR): 3448, 3049, 2918, 2847, 1718, 1638, 1621, 1578, 1504, 1468, 1446, 1426, 1387, 1303, 1263, 1244, 1218, 1164, 1134, 1085, 1057, 991, 887, 858, 835, 780, 737, 727 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 3.99 (s, 3 H), 4.79 (br s, 1 H), 6.82 (d, *J* = 7.8 Hz, 1 H), 6.85 (s, 1 H), 7.10 (t, *J* = 7.8 Hz, 1 H), 7.54 (d, *J* = 7.8 Hz, 1 H), 7.75 (s, 1 H), 8.04 (br s, 1 H).

^1H NMR (500 MHz, acetone-d_6): δ = 2.38 (s, 3 H), 3.99 (s, 3 H), 6.87 (d, *J* = 7.8 Hz, 1 H), 7.06 (t, *J* = 7.8 Hz, 1 H), 7.07 (s, 1 H), 7.57 (d, *J* = 7.8 Hz, 1 H), 7.78 (s, 1 H), 8.32 (s, 1 H), 9.98 (br s, 1 H).

^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 16.17 (CH_3), 55.46 (CH_3), 96.66 (CH), 104.89 (CH), 112.07 (CH), 116.32 (C), 117.68 (C), 119.65 (CH), 121.93 (CH), 124.40 (C), 129.51 (C), 138.95 (C), 145.43 (C), 153.01 (C).

^{13}C NMR and DEPT (125 MHz, acetone-d_6): δ = 16.72 (CH_3), 55.66 (CH_3), 97.30 (CH), 105.32 (CH), 112.48 (CH), 117.25 (C), 117.74 (C), 119.80 (CH), 122.12 (CH), 125.44 (C), 130.42 (C), 140.66 (C), 146.53 (C), 155.48 (C).

MS (EI): *m*/*z* (%) = 227 (100) [M^+], 212 (41), 184 (64).

HRMS: *m*/*z* [M^+] calcd for $C_{14}H_{13}NO_2$: 227.0946; found: 227.0934.

UV (MeOH): λ = 252, 262 (sh), 300, 317, 331 nm.

Fluorescence (MeOH): λ_{ex} = 300 nm, λ_{em} = 356 nm.

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.38; H, 6.51; N, 5.68.

2,8-Dihydroxy-3-methyl-9*H*-carbazole (4)

A 1 M solution of BBr_3 in CH_2Cl_2 (309 μL, 0.309 mmol) was added slowly to a solution of carbalexin B (**1**) (35.1 mg, 0.154 mmol) in CH_2Cl_2 (5 mL) at –78 °C. The mixture was stirred for an additional 30 min at –78 °C, warmed to 0 °C, and stirred overnight. After the addition of H_2O at 0 °C, the mixture was extracted with Et_2O (3 ×), and the combined organic layers were dried ($MgSO_4$). Removal of the solvent and flash chromatography of the crude product (silica gel, petroleum ether–EtOAc, 1:1) afforded **4** as a colorless solid; yield: 20.8 mg (63%); mp 250 °C dec. (Lit.[6b] 272 °C dec.).

IR (ATR): 3433, 2921, 2856, 2547, 1697, 1624, 1581, 1540, 1505, 1463, 1449, 1384, 1327, 1291, 1273, 1242, 1197, 1167, 1136, 1056, 1003, 957, 883, 820, 783, 741, 631, 597, 556 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 2.38 (s, 3 H), 6.79 (d, *J* = 7.7 Hz, 1 H), 6.94 (t, *J* = 7.7 Hz, 1 H), 7.05 (s, 1 H), 7.48 (d, *J* = 7.7 Hz, 1 H), 7.76 (s, 1 H), 8.24 (s, 1 H), 8.52 (s, 1 H), 9.81 (br s, 1 H).

^{13}C NMR and DEPT (125 MHz, acetone-d_6): δ = 16.71 (CH_3), 97.27 (CH), 109.60 (CH), 111.42 (CH), 117.46 (C), 117.51 (C), 119.86 (CH), 122.12 (CH), 126.07 (C), 130.07 (C), 140.76 (C), 143.51 (C), 155.44 (C).

MS (EI): *m*/*z* (%) = 213 (100) [M^+], 184 (24).

UV (MeOH): λ = 235, 254 (sh), 300, 320, 333 nm.

Fluorescence (MeOH): λ_{ex} = 333 nm, λ_{em} = 363 nm.

2-Benzyloxy-3-formyl-8-methoxy-9*H*-carbazole (9)

DDQ (233 mg, 1.028 mmol) was added portionwise to a solution of 2-benzyloxy-8-methoxy-3-methyl-9*H*-carbazole (**8**) (148 mg, 0.467 mmol) in THF–MeOH–H_2O (1:5:1, 105 mL). The mixture was stirred at r.t. for 90 min, then diluted with Et_2O, washed with 2 M NaOH (3 ×) and with sat. aq NaCl solution; the organic layer was dried ($MgSO_4$). Removal of the solvent and flash chromatography of the crude product (silica gel, petroleum ether–EtOAc, 2:1) afforded **9** as an orange powder; yield: 100 mg (64%); mp 236 °C.

IR (ATR): 3151, 2923, 2849, 1656, 1626, 1604, 1574, 1507, 1456, 1437, 1392, 1316, 1244, 1213, 1172, 1155, 1091, 1019, 995, 911, 863, 817, 780, 731, 696 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 3.97 (s, 3 H), 5.33 (s, 2 H), 6.99 (d, *J* = 7.8 Hz, 1 H), 7.126 (s, 1 H), 7.130 (t, *J* = 7.8 Hz, 1 H), 7.36 (m, 1 H), 7.43 (m, 2 H), 7.56 (m, 2 H), 7.72 (d, *J* = 7.8 Hz, 1 H), 8.48 (s, 1 H), 10.43 (s, 1 H), 11.76 (s, 1 H).

^{13}C NMR and DEPT (125 MHz, DMSO-d_6): δ = 55.44 (CH_3), 69.94 (CH_2), 94.58 (CH), 106.73 (CH), 112.62 (CH), 117.06 (C), 118.19 (C), 120.61 (CH), 121.27 (CH), 124.06 (C), 127.53 (2 CH), 127.93 (CH), 128.53 (2 CH), 130.07 (C), 136.66 (C), 144.96 (C), 145.52 (C), 159.67 (C), 188.17 (CHO).

MS (ESI, +10 V): *m*/*z* = 332 [(M + $H)^+$].

UV (MeOH): λ = 241, 272, 294, 356 nm.

Fluorescence (MeOH): λ_{ex} = 350 nm, λ_{em} = 363 nm.

Anal. Calcd for $C_{21}H_{17}NO_3$: C, 76.12; H, 5.12; N, 4.23. Found: C, 76.22; H, 5.31; N, 4.25.

Clausine A (2)

$AlCl_3$ (85.7 mg, 0.643 mmol) was added to a solution of 2-benzyloxy-3-formyl-8-methoxy-9*H*-carbazole (**9**) (42.6 mg, 0.129 mmol) in 1,4-dioxane (4 mL) and the mixture was heated at reflux for 2 h. After addition of H_2O, the mixture was extracted with Et_2O (3 ×), and the combined organic layers were dried (Na_2SO_4). Removal of the solvent and flash chromatography of the crude product (silica gel, petroleum ether–EtOAc, 2:1) afforded clausine A (**2**) as light yellow crystals; yield: 22.0 mg (71%); mp 179–181 °C (Lit.[4] 184–186 °C).

IR (ATR): 3367, 2921, 2849, 1727, 1631, 1580, 1508, 1462, 1436, 1392, 1367, 1315, 1272, 1227, 1198, 1161, 1090, 1008, 895, 842, 832, 783, 744, 717 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 4.03 (s, 3 H), 6.98 (s, 1 H), 7.03 (d, *J* = 7.9 Hz, 1 H), 7.20 (t, *J* = 7.9 Hz, 1 H), 7.70 (d, *J* = 7.9 Hz, 1 H), 8.45 (s, 1 H), 10.02 (s, 1 H), 10.80 (br s, 1 H), 11.46 (s, 1 H).

^{13}C NMR and DEPT (125 MHz, acetone-d_6): δ = 55.92 (CH_3), 97.57 (CH), 107.60 (CH), 113.06 (CH), 116.33 (C), 118.80 (C), 121.98 (CH), 125.24 (C), 128.83 (CH), 131.47 (C), 146.65 (C), 146.74 (C), 161.61 (C), 196.66 (CHO).

MS (EI): *m*/*z* (%) = 241 (100) [M^+], 226 (32), 198 (52).

HRMS: *m*/*z* [M^+] calcd for $C_{14}H_{11}NO_3$: 241.0739; found: 241.0740.

UV (MeOH): λ = 216, 241, 274, 289, 351.

Fluorescence (MeOH): λ_{ex} = 351 nm, λ_{em} = 422 nm.

Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81. Found: C, 69.71; H, 5.45; N, 5.27.

Clauszoline M (3)

A 1 M solution of BBr_3 in CH_2Cl_2 (337 µL, 0.337 mmol) was added slowly to a solution of 2-benzyloxy-3-formyl-8-methoxy-9*H*-carbazole (**9**) (37.2 mg, 0.112 mmol) in CH_2Cl_2 (7 mL) at –78 °C. The mixture was stirred for 3 h at –78 °C, warmed to 0 °C, and stirred overnight. After the addition of H_2O at 0 °C, the mixture was extracted with Et_2O (3 ×), and the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent and flash chromatography of the crude product (silica gel, petroleum ether–EtOAc, 2:1) afforded clausine A (**2**) (13.4 mg, 50%), and clauszoline M (**3**) as a light yellow solid; yield: 11.4 mg (45%); mp >240 °C.

IR (ATR): 3325, 2923, 2851, 2472, 1698, 1624, 1581, 1501, 1472, 1456, 1399, 1356, 1317, 1286, 1225, 1193, 1162, 1092, 1061, 921, 870, 837, 776, 721, 702, 684 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 6.95 (d, *J* = 7.8 Hz, 1 H), 6.98 (s, 1 H), 7.10 (t, *J* = 7.8 Hz, 1 H), 7.63 (d, *J* = 7.8 Hz, 1 H), 8.46 (s, 1 H), 8.95 (s, 1 H), 10.03 (s, 1 H), 10.72 (br s, 1 H), 11.48 (s, 1 H).

^{13}C NMR and DEPT (125 MHz, acetone-d_6): δ = 97.34 (CH), 111.76 (CH), 112.07 (CH), 116.14 (C), 118.97 (C), 121.99 (CH), 125.80 (C), 128.77 (CH), 130.84 (C), 143.77 (C), 146.63 (C), 161.43 (C), 196.56 (CHO).

MS (EI): *m*/*z* (%) = 227 (100) [M^+].

HRMS: *m*/*z* [M^+] calcd for $C_{13}H_9NO_3$: 227.0582; found: 227.0568.

UV (MeOH): λ = 242, 267 (sh), 275, 295, 356 nm.

Fluorescence (MeOH): λ_{ex} = 356 nm, λ_{em} = 400 nm.

Supporting Information for this article is available online at http://www.thieme-connect.com/products/ejournals/journal/10.1055/s-00000084.

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