Supporting Information:

Synthetic studies of the tridentatols

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Experimental:

General: All solvents were distilled from glass. NMR spectral analyses were performed on an 8.46-T NMR instrument operating at 360 MHz for ^{1}H and 90 MHz for ^{13}C; chemical shifts are reported in ppm with the chemical shift of residual solvent nuclides used as internal standards. A Waters 401 HPLC system with a Waters 490E UV detector and YMC ODS-Aq (10x250 mm, 5μ) column were used for HPLC.

Methyl *N*-dithiocarbamato-2-amino-1-phenylethanol (**4**): 2-amino-1-phenylethanol (**3**, 2.74 g, 20 mmol) and CS_2 (1.6 g, 21 mmol) were stirred in 20 mL chloroform while 2.12 g Et_3N were introduced. After 1 hr at RT, MeI (3.31 g, 23 mmol) were added. The reaction was refluxed for 1 hr in the dark, then quenched by addition of 20 mL water. The organic layer was separated, dried ($MgSO_4$) and concentrated in vacuo. After purification on SiO_2 in 50% hexane/ethyl acetate, 2.27 g of the intermediate amide were obtained (50 %). ^{1}H NMR ($CDCl_3$): 2.65 (s, SCH_3), 3.6, 4.3 (m, H_2-8), 5.0 (m, H-7), 7.3-7.5 (m, H_5-Ar); ^{13}C NMR ($CDCl_3$): 18.47 (SCH_3), 53.87 (C-8), 72.59 (C-7), 125.97 (C_2-2,6), 128.55 (C-4), 128.97 (C_2-3,5), 141.8 (C-1), 214.05 (C=S); EIMS M^+ 227. The amide from the prior reaction was dissolved in 30 mL acetone and treated with K_2CO_3 (1.93 g, 14 mmol) and MeI (1.7 g, 12 mmol) and refluxed in the dark for 2.5 hr. The mixture was cooled, filtered and washed with water. The organic phase was dried ($MgSO_4$) and evaporated to give an oily residue which was purified by column chromatography on silica gel using 20% ethyl acetate in hexane to yield **4** (1.8g, 75%). ^{1}H NMR ($CDCl_3$): 2.41 (s, SCH_3), 2.54 (s, SCH_3), 3.45, 3.62 (m, H_2-8), 4.98 (m, H-7), 7.31-7.59 (m, H_5-Ar); ^{13}C NMR ($CDCl_3$): 14.74 (SCH_3), 60.42 (C-8), 73.47 (C-7), 126.30 (C_2-2,6), 127.60 (C-4), 128.36 (C-3,5), 142.13 (C-1), 161.62 (C=S); EIMS M^+ 241.

Deoxytridentatol A (**5**): Compound **4** (0.12 g, 0.5 mmol) in pyridine (0.4 mL) and CH_2Cl_2 (2 mL) was added to a mixture of diethylaminosulfur trifluoride (DAST, 0.06 mL, 0.5 mmol) in CH_2CL_2 (2 mL) at 0°C. The mixture was stirred for 1 hr at 0°C, washed with 5% $NaHCO_3$, then the organic phase dried ($MgSO_4$) and concentrated in vacuo. Initial purification on silica gel (5% EtOAc/Hexane) yielded a mixture of 2:1 *trans*/*cis* product (22 mg, 20%) which could be separated by HPLC. ^{1}H NMR ($CDCl_3$): 2.6 (s, 2 X SCH_3), 6.70 (d, J = 13.3 Hz, H-7) and 7.66 (d, J = 13.3 Hz, H-8), 7.2-7.4 (m, H_5-Ar); EIMS M^+ 223.

Dihydrotridentatol C (**7**): DL-octopamine hydrochloride (1.3 g, 6.8 mmol) in 20 mL chloroform and TEA (1.5 g, 15 mmol) was added CS_2 (0.56 g, 7.4 mmol) and MeI (1.2 g, 8.3 mmol) The reaction mixture was refluxed for 3 hr in the dark, then quenched by addition of 15 mL water. The organic layer was separated, dried ($MgSO_4$) and concentrated *in vacuo*. After purification on SiO_2 in 50% hexane/ethyl acetate, compound **7** was obtained (0.86 g, 52% yield). ^{1}H NMR ($CDCl_3$): 2.58 (s, H_3-10), 4.31, 4.49 (m, H_2-8),

5.04 (m, H-4), 6.76 (d, J = 9.3 Hz, H_2-2/6), 7.16 (d, J = 9.3 Hz, H_2-3/5); ^{13}C NMR ($CDCl_3$): 15.56 (C-10), 56.38 (C-7), 72.02 (C-8), 115.9 (C_2-2/6), 128.52 (C_2-3/5), 132.66 (C-4), 155.95 (C-1), 167.75 (C-9); EIMS M^+ 225.

Tridentatol C (**2**): Dihydrotridentatol C **7** (0.1 g, 0.44 mmol) in chloroform (5 mL) was refluxed with DDQ (0.11 g, 0.48 mmol) for 3 hr. Spectroscopic analysis of the reaction mixture indicated the presence of tridentatol C (50% conversion). ^{1}H NMR ($CDCl_3$): 2.77 (s, SCH_3), 6.86 (d, J = 9.6 Hz, H_2-2/6), 7.36 (d, J = 9.5 Hz, H_2-3/5); 7.68 (s, H-8).

2-(*p*-Methoxyphenyl)-2-methoxyethylamine (**8**): 4-methoxynitrostyrene (1.87 g, 10.5 mmol) was prepared in 60% yield from 4-methoxybenzaldehyde (2.3 g, 16 mmol) by treatment with nitromethane (2.4 ml, 40 mmol) in acetic acid/ammonium acetate (8.0 mL/1.3 g). Treatment of the nitrostyrene with freshly prepared sodium methoxide (1.24 g, 23 mmol) in methanol (15 mL) yielded, after work-up with HOAc, the addition product (2 g, 90%). Reduction of the addition product with excess lithium aluminum hydride yielded 1.3 g (76 %) of **8**. ^{1}H NMR ($CDCl_3$): 2.8-2.95 (m, H_2-8), 3.26 (s, CH_3), 3.82 (s, Ar-OCH_3), 4.1 (m, H-7) and 6.92 (d, J = 9.6 Hz, H_2-2/6), 7.23 (d, J = 9.6 Hz, H_2-3/5).

2-(*p*-Methoxyphenyl)-2-methoxyethyldithiocarbamate (**9**): Compound **8** (1.3 g, 7.2 mmol) was stirred for 2 hr in the dark with CS_2 (0.45 mL), Et_3N (1.05 mL) and MeI (0.52 mL) in 25 mL of chloroform, and the crude amide was subsequently refluxed with K_2CO_3 (0.4 g) and MeI (0.5 g) in acetone (20 mL) for 1 hr in the dark. Compound **9** (1.1 g) in 61% yield was isolated after purification. ^{1}H NMR ($CDCl_3$): 2.35 (s, SCH_3), 2.49 (s, SCH_3), 3.31 (s, OCH_3), 3.80 (s, Ar-OCH_3), 3.51, 3.74 (m, H_2-8), 4.47 (m, H-7), 6.90 (d, J = 9.4 Hz, H_2-2/6), 7.31 (d, J = 9.4 Hz, H_2-3/5); ^{13}C NMR ($CDCl_3$): 14.72 (SCH_3), 14.83 (SCH_3), 55.35 (Ar-OCH_3), 57.08 (OCH_3), 59.45 (C-8), 83.71 (C-7), 113.74 (C_2-2,6), 128.06 (C-4), 128.39 (C_2-3,5), 132.97 (C-1), 159.28 (C-9); EIMS M^+ 285.

Methoxytridentatol A (**10**): Compound **9** (0.12 g, 0.43 mmol) in chloroform (10 mL) was added P_2O_5 (0.49 g, mmol) and the mixture stirred at RT for 1 hr. The organic layer separated, dried (MgSO4) and evaporated to yield (77.5 mg, 70%) of methoxytridentatol A (**10**) after purification on silica gel using 10% ethyl acetate in hexane. UV (MeOH) λ_{max} (ε): 334 (31,500); ^{1}H NMR ($CDCl_3$): 2.5 (s, SCH_3), 2.6 (s, SCH_3), 3.82 (s, OCH_3), 6.64 (d, J = 13.2 Hz, H-7) 7.57 (d, J = 13.2 Hz, H-8), 6.86 (d, J = 8.7 Hz, H_2-2/6), 7.37 (d, J = 8.7 Hz, H_2-3/5); ^{13}C NMR ($CDCl_3$): 15.24 (SCH_3), 15.35 (SCH_3), 55.47 (OCH_3), 114.31 (C_2-2,6), 126.61 (C-7), 127.76 (C_2-3,5), 132.43 (C-8), 159.20 (C-1), 161.34 (C-9); EIMS M^+ 253.