Supporting Information

MPC1001 and its Analogs, New Antitumor Agents from the Fungus *Cladorrhinum* Species

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Culture

The MPC1001 and its analogs producing fungal strain KY4922 was isolated from an Indonesian soil sample and identified as *Cladorrhinum* sp. KY4922 was cultured in the first seed medium consisting of glucose 10%, dried mashed potato 3%, and yeast extract 0.5% (pH6.5) for 120 hr at 28°C on a rotary shaker. The first seed culture was added to Erlenmeyer flasks containing 50 ml of the same medium. After incubation on a ratary shaker at 28°C for 10 hr, 1.5 ml of the sencond seed culture was innoculated into each of 100 Erlenmeyer flasks containing 50 ml of a production medium composed of soluble starch 5%, dried yeast 1.5%, KH_2PO_4 0.05%, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ 0.05%, and CaCO_3 0.5% (pH 7.0) and cultured on a rotary shaker (220 rpm) for 168 hr at 25°C.

Extraction and Purification

The cultivated mycelium was extracted with 1.7 L of MeOH. The extract was diluted with 2.3 L of water and then subjected to a Diaion HP-20 (250 ml, wet, Mitsubishi Chemical Corp.) column chromatography. The column was washed with 800 ml of 70% aqueous MeOH and the active principles were eluted with 1 L of MeOH–aceton (70:30) yielded 3.84 g of yellow oil. Further purification steps were summarized in Figure 1S and 2S.

Scheme 1

Culture Broth 5 L (300 mL Erlenmeyer flasks x 100)

Figure 1S. Purification of MPC1001 and its analogs (Scheme 1).

Scheme 2

Figure 2S. Purification of MPC1001 and its analogs (Scheme 2).

Chemicals

General Methods. ^1H and ^{13}C NMR spectra were recorded on Bruker DMX-500 or JEOL JNM- α 400 spectrometer. Chemical shifts were reported in ppm using the residual solvent as an internal standard (chloroform, 7.26 and 77.05 ppm for ^1H and ^{13}C NMR, respectively). NMR data are reported as follows: chemical shifts, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant, and position. FAB-MS spectra were obtained with JEOL JMS-HX/HX110A spectrometer using *m*-nitrobenzyl alcohol (NBA) as a matrix. IR spectra were recorded on JEOL JIR-RFX3001 or JASCO IR-870 spectrometer. UV spectra were measured in MeOH on Shimadzu UV-1600PC or UV-2200 spectrometer. Optical rotations were measured in MeOH or CHCl_3 at 20 or 28°C on a JASCO DIP-370 polarimeter. Melting points were determined using Yanagimoto micro melting point apparatus and are uncorrected. HPLC analysis was performed on a Develosil ODS-HG-3 column (4.6 i.d. $\times$ 50 mm, Nomura Chemical Co., LTD, Seto, Japan) with aqueous 20-100% MeCN gradient elution. Peaks were monitored with a Waters996 photodiode array detector.

MPC1001 (1). ^1H NMR (CDCl_3 , 400 MHz) δ 7.76 (1H, dd, 8.5, 2.1, H-6'), 7.66 (1H, d, 2.2, H-6''), 7.63 (1H, d, 2.1, H-2'), 7.10 (1H, dd, 8.4, 2.2, H-4''), 7.05 (1H, d, 8.5, H-5'), 6.92 (1H, d, 8.4, H-3''), 6.91 (1H, d, 2.7, H-10), 6.32 (1H, dd, 8.4, 2.4, H-8), 5.91 (1H, dd, 7.7, 2.7, H-5a), 5.43 (1H, br.d, 12.3, H-7''), 5.21 (1H, br.s, 11-OH), 4.95 (1H, dd, 8.4, 2.4, H-7), 4.92 (1H, s, H-11), 4.79 (1H, ddd, 7.7, 2.4, 2.4, H-6), 4.75 (1H, br.d, 12.3, 7''-OH), 3.99 (3H, s, 4'-OCH₃), 3.94 (3H, s, 2''-OCH₃), 3.41 (3H, s, 2-CH₃); ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.7 (C-1), 165.1 (C-7'), 163.4 (C-4), 154.6 (C-4'), 151.8 (C-2''), 147.0 (C-1''), 145.1 (C-3'), 143.3 (C-10), 137.7 (C-8), 126.8 (C-5''), 125.6 (C-6'), 124.2 (C-4''), 122.3 (C-1'), 122.2 (C-2'), 119.8 (C-6''), 112.2 (C-5'), 111.4 (C-10a), 111.0 (C-3''), 107.3 (C-7), 78.8 (C-3), 76.6 (C-11), 75.3 (C-6), 74.8 (C-7''), 73.8 (C-11a), 61.1 (C-5a), 56.2 (4'-OCH₃), 56.0 (2''-OCH₃), 27.9 (2-CH₃); white powder; mp 181-184 °C; $[\alpha]_D^{20} +117^\circ$ (c 0.3, MeOH); HRFAB-MS found m/z 611.0802 $[\text{M-H}]^+$, calcd m/z 611.0794 for $\text{C}_{28}\text{H}_{23}\text{N}_2\text{O}_{10}\text{S}_2$; FAB-MS m/z 635 $[\text{M+Na}]^+$, m/z 613 $[\text{M+H}]^+$, m/z 548 $[\text{M-S}_2]^+$, m/z 531 $[\text{M-S}_2\text{-H}_2\text{O+H}]^+$, m/z 611 $[\text{M-H}]^-$; UV $\lambda_{\text{max}}^{\text{MeOH}}$ (ϵ) 205 (38,000), 263 (14,000), 283 (8,000) nm; IR $\nu_{\text{max}}^{\text{KBr}}$ 3442, 1716, 1684, 1668, 1614, 1515, 1346, 1271, 1200, 1174, 1136, 1122, 1051, 1024, 891, 822, 762 cm^{-1} ; R_f value on TLC (*n*-hexane-acetone, 1:1) =0.45; Soluble in methanol, acetonitrile, acetone, ethyl acetate, chloroform, dimethyl sulfoxide.

MPC1001B (2). ^1H NMR (CDCl_3 , 400 MHz) δ 8.04 (1H, d, 2.2, H-6''), 7.66 (1H, dd, 8.5, 2.0, H-6'), 7.63 (1H, d, 2.0, H-2'), 7.15 (1H, dd, 8.4, 2.2, H-4''), 7.01 (1H, d, 8.5, H-5'), 6.88 (1H, d,

8.4, H-3''), 6.63 (1H, ddd, 2.2, 2.2, 2.2, H-10), 6.32 (1H, dd, 8.3, 2.2, H-8), 5.44 (1H, d, 12.3, H-7''), 5.40 (1H, dddd, 8.8, 2.2, 2.0, 1.1, H-5a), 5.12 (1H, d, 12.3, 7''-OH), 4.99 (1H, ddd, 8.8, 2.2, 1.7, H-6), 4.93 (1H, dd, 8.3, 1.7, H-7), 4.16 (1H, ddd, 18.1, 2.2, 1.1, H-11 β), 4.01 (3H, s, 4'-OCH₃), 3.86 (3H, s, 2''-OCH₃), 3.48 (3H, s, 2-CH₃), 3.02 (1H, ddd, 18.1, 2.2, 2.0, H-11 α); ¹³C NMR (CDCl₃, 100 MHz) δ 166.4 (C-7'), 166.2 (C-1), 164.4 (C-4), 154.3 (C-4'), 152.6 (C-2''), 146.2 (C-1'), 146.0 (C-3'), 140.6 (C-8), 139.4 (C-10), 127.1 (C-5''), 125.6 (C-4''), 125.4 (C-6'), 122.8 (C-6''), 122.8 (C-1'), 119.3 (C-2'), 112.8 (C-10a), 112.2 (C-5'), 111.0 (C-3''), 105.6 (C-7), 78.4 (C-3), 75.3 (C-7''), 73.0 (C-6), 72.5 (C-11a), 62.3 (C-5a), 56.4 (4'-OCH₃), 56.0 (2''-OCH₃), 34.9 (C-11), 28.3 (2-CH₃); white powder; mp 171-172 °C; [α]_D²⁸ +242.6° (c 0.23, CHCl₃); HRFAB-MS found m/z 595.0850 [M-H]⁺, calcd m/z 595.0845 for C₂₈H₂₃N₂O₉S₂; FAB-MS m/z 597 [M+H]⁺, m/z 532 [M-S₂]⁺, m/z 595 [M-H]⁻, m/z 531 [M-S₂-H]⁻, m/z 513 [M-S₂-H₂O-H]⁻; UV $\lambda_{\max}^{\text{MeOH}}$ (ε) 257 (19,700), 284 (8,900) nm; IR $\nu_{\max}^{\text{KBr}}$ 3474, 2940, 1686, 1611, 1577, 1513, 1457, 1440, 1412, 1350, 1268, 1195, 1172, 1135, 1122, 1055, 1024, 990, 965, 907, 818, 762 cm⁻¹; Soluble in chloroform, dimethyl sulfoxide.

MPC1001C (3). ¹H NMR (CDCl₃, 500 MHz) δ 7.73 (1H, dd, 8.5, 2.0, H-6'), 7.63 (1H, d, 2.1, H-6''), 7.60 (1H, d, 2.0, H-2'), 7.10 (1H, dd, 8.3, 2.1, H-4''), 7.03 (1H, d, 8.5, H-5'), 6.91 (1H, d, 8.3, H-3''), 6.90 (1H, d, 2.4, H-10), 6.31 (1H, dd, 8.4, 2.5, H-8), 5.87 (1H, dd, 7.7, 2.4, H-5a), 5.21 (1H, br.s, 11-OH), 4.94 (1H, dd, 8.4, 2.1, H-7), 4.93 (1H, s, H-11), 4.81 (1H, ddd, 7.7, 2.5, 2.1, H-6), 3.98 (3H, s, 4'-OCH₃), 3.91 (3H, s, 2''-OCH₃), 3.83 (1H, d, 13.3, H-7'' β), 3.45 (1H, d, 13.3, H-7'' α), 3.21 (3H, s, 2-CH₃); ¹³C NMR (CDCl₃, 125 MHz) δ 166.8 (C-1), 165.3 (C-7'), 162.5 (C-4), 154.3 (C-4'), 151.0 (C-2''), 146.0 (C-1'), 145.2 (C-3'), 143.2 (C-10), 137.7 (C-8), 126.4 (C-4''), 125.4 (C-6'), 124.7 (C-6''), 123.4 (C-5''), 122.5 (C-1'), 121.8 (C-2'), 112.0 (C-5'), 111.8 (C-10a), 111.5 (C-3''), 107.6 (C-7), 79.2 (C-3), 76.8 (C-11), 75.4 (C-6), 74.0 (C-11a), 61.0 (C-5a), 56.1 (4'-OCH₃), 55.9 (2''-OCH₃), 36.2 (C-7''), 27.9 (2-CH₃); white powder; mp 167-168 °C; [α]_D²⁸ +188.7° (c 0.13, CHCl₃); HRFAB-MS found m/z 595.0858 [M-H]⁺, calcd m/z 595.0845 for C₂₈H₂₃N₂O₉S₂; FAB-MS m/z 597 [M+H]⁺, m/z 532 [M-S₂]⁺, m/z 515 [M-S₂-H₂O+H]⁺, m/z 596 [M]⁻; UV $\lambda_{\max}^{\text{MeOH}}$ (ε) 262 (13,400), 284 (6,700) nm; IR $\nu_{\max}^{\text{KBr}}$ 3470, 1712, 1688, 1611, 1577, 1513, 1459, 1440, 1413, 1351, 1268, 1219, 1195, 1172, 1135, 1122, 1108, 1091, 1055, 1024, 990, 969, 904, 818, 761 cm⁻¹; Soluble in chloroform, dimethyl sulfoxide.

MPC1001D (4). ¹H NMR (CDCl₃, 500 MHz) δ 8.35 (1H, d, 2.3, H-6''), 7.98 (1H, d, 2.0, H-2'), 7.73 (1H, dd, 8.5, 2.0, H-6'), 7.03 (1H, dd, 8.4, 2.3, H-4''), 7.02 (1H, d, 8.5, H-5'), 6.83 (1H, d, 2.4, H-10), 6.83 (1H, d, 8.4, H-3''), 6.35 (1H, dd, 8.0, 2.3, H-8), 5.39 (1H, dd, 8.2, 2.4, H-5a), 5.28 (1H,

d, 12.5, H-7''), 5.26 (1H, ddd, 8.2, 2.6, 2.3, H-6), 5.02 (1H, dd, 8.0, 2.6, H-7), 4.79 (1H, d, 2.0, H-11), 4.30 (1H, d, 12.5, 7''-OH), 4.03 (3H, s, 4'-OCH₃), 3.86 (3H, s, 2''-OCH₃), 3.56 (3H, s, 2-CH₃), 3.52 (1H, d, 2.0, 11-OH); ¹³C NMR (CDCl₃, 125 MHz) δ 168.2 (C-1), 166.4 (C-7'), 165.3 (C-4), 154.7 (C-4'), 152.3 (C-2''), 146.3 (C-3'), 145.7 (C-1''), 143.0 (C-10), 138.6 (C-8), 128.7 (C-4''), 127.1 (C-5''), 125.9 (C-6'), 125.6 (C-6''), 122.4 (C-1'), 119.6 (C-2'), 112.2 (C-5'), 110.8 (C-3''), 110.0 (C-7), 108.0 (C-10a), 83.4 (C-11a), 79.8 (C-11), 78.1 (C-3), 76.6 (C-7''), 74.9 (C-6), 59.0 (C-5a), 56.4 (4'-OCH₃), 56.1 (2''-OCH₃), 28.9 (2-CH₃); white powder; mp 188-190 °C; [α]_D²⁸ +174.2° (c 0.66, CHCl₃); HRFAB-MS found *m/z* 643.0516 [M-H]⁺, calcd *m/z* 643.0514 for C₂₈H₂₃N₂O₁₀S₃; FAB-MS *m/z* 644 [M]⁺, *m/z* 627 [M-H₂O+H]⁺, *m/z* 548 [M-S₃]⁺, *m/z* 531 [M-S₃-H₂O+H]⁺, *m/z* 643 [M-H]⁻, *m/z* 611 [M-S-H]⁻, *m/z* 579 [M-S₂-H]⁻; UV λ_{max}^{MeOH} (ε) 258 (19,700), 284 (7,900) nm; IR ν_{max}^{KBr} 3484, 2958, 1681, 1610, 1577, 1513, 1462, 1441, 1409, 1358, 1268, 1195, 1172, 1135, 1122, 1102, 1056, 1026, 900, 820, 800, 762 cm⁻¹; Soluble in methanol, chloroform, ethyl acetate, dimethyl sulfoxide.

MPC1001E (5). ¹H NMR (CDCl₃, 500 MHz) δ 9.81 (1H, s, H-7''), 8.03 (1H, dd, 8.6, 2.1, H-6'), 7.71 (1H, d, 2.1, H-2'), 7.64 (1H, dd, 8.4, 1.9, H-4''), 7.40 (1H, d, 1.9, H-6''), 7.11 (1H, d, 8.4, H-3''), 7.08 (1H, d, 8.6, H-5'), 6.84 (1H, d, 2.4, H-10), 6.29 (1H, dd, 8.1, 2.3, H-8), 5.43 (1H, dd, 8.4, 2.4, H-5a), 5.28 (1H, ddd, 8.4, 2.3, 2.1, H-6), 4.97 (1H, s, H-3), 4.87 (1H, dd, 8.1, 2.1, H-7), 4.87 (1H, s, H-11), 3.98 (3H, s, 2''-OCH₃), 3.93 (3H, s, 4'-OCH₃), 3.21 (3H, br.s, 11-OH), 3.03 (1H, s, 2-CH₃); ¹³C NMR (CDCl₃, 125 MHz) δ 190.8 (C-7''), 167.2 (C-1), 165.6 (C-7'), 163.3 (C-4), 156.0 (C-2''), 155.0 (C-4'), 146.5 (C-1''), 144.9 (C-3'), 143.0 (C-10), 139.1 (C-8), 130.2 (C-5''), 128.5 (C-4''), 128.0 (C-6'), 122.6 (C-1'), 121.0 (C-2'), 118.4 (C-6''), 112.0 (C-3''), 111.8 (C-5'), 110.3 (C-10a), 107.8 (C-7), 80.0 (C-11a), 78.2 (C-11), 71.8 (C-6), 67.5 (C-3), 60.0 (C-5a), 56.4 (2''-OCH₃), 56.2 (4'-OCH₃), 32.5 (2-CH₃); white powder; mp 166-167 °C; [α]_D²⁸ -128.4° (c 0.76, CHCl₃); HRFAB-MS found *m/z* 676.0339 [M]⁻, calcd *m/z* 676.0313 for C₂₈H₂₄N₂O₁₀S₄; FAB-MS *m/z* 677 [M+H]⁺, *m/z* 548 [M-S₄]⁺, *m/z* 676 [M]⁻; UV λ_{max}^{MeOH} (ε) 228 (35,800), 263.5 (22,000) nm; IR ν_{max}^{KBr} 3428, 2936, 1686, 1603, 1573, 1509, 1451, 1431, 1411, 1390, 1334, 1268, 1221, 1195, 1176, 1130, 1116, 1060, 1020, 907, 812, 761 cm⁻¹; Soluble in chloroform, dimethyl sulfoxide.

MPC1001F (6). ¹H NMR (CDCl₃, 400 MHz) δ 9.81 (1H, s, H-7''), 8.02 (1H, dd, 8.6, 2.2, H-6'), 7.64 (1H, dd, 8.5, 2.0, H-4''), 7.61 (1H, d, 2.2, H-2'), 7.33 (1H, d, 2.0, H-6''), 7.10 (1H, d, 8.5, H-3''), 7.09 (1H, d, 8.6, H-5'), 6.89 (1H, d, 2.4, H-10), 6.35 (1H, dd, 8.2, 2.4, H-8), 5.85 (1H, ddd, 8.1, 2.4, 2.2, H-6), 5.39 (1H, dd, 8.1, 2.4, H-5a), 4.91 (1H, dd, 8.2, 2.2, H-7), 4.89 (1H, s, H-11),

3.98 (3H, s, 2''-OCH₃), 3.91 (3H, s, 4'-OCH₃), 3.30 (3H, s, 2-CH₃), 2.75 (1H, br.s, 11-OH), 2.06 (3H, s, 11a-SCH₃) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 190.7 (C-7''), 166.3 (C-1), 165.2 (C-7'), 156.6 (C-3), 155.7 (C-2''), 155.1 (C-4'), 152.5 (C-4), 146.5 (C-1''), 144.8 (C-3'), 142.3 (C-10), 139.3 (C-8), 130.2 (C-5''), 128.1 (C-6'), 127.8 (C-4''), 122.1 (C-1'), 121.1 (C-2'), 118.2 (C-6''), 112.3 (C-5'), 112.1 (C-3''), 111.0 (C-10a), 107.7 (C-7), 78.1 (C-11), 76.3 (C-11a), 72.3 (C-6), 60.3 (C-5a), 56.4 (2''-OCH₃), 56.2 (4'-OCH₃), 27.7 (2-CH₃), 13.0 (11a-SCH₃); white powder; mp 138-139 °C; [α]_D²⁸ +19.7° (c 0.12, CHCl₃); HRFAB-MS found *m/z* 611.1334 [M+H]⁺, calcd *m/z* 611.1335 for C₂₉H₂₇N₂O₁₁S; FAB-MS *m/z* 611 [M+H]⁺, *m/z* 633 [M+Na]⁺, *m/z* 563 [M-SCH₃-H]⁻; UV λ_{max}^{MeOH} (ε) 262.5 (21,600) nm; IR ν_{max}^{KBr} 3452, 1708, 1692, 1604, 1511, 1431, 1406, 1336, 1316, 1271, 1240, 1223, 1195, 1175, 1130, 1119, 1020, 762 cm⁻¹; Soluble in chloroform, dimethyl sulfoxide.

MPC1001G (7). ¹H NMR (CDCl₃, 500 MHz) δ 9.80 (1H, s, H-7''), 8.01 (1H, dd, 8.6, 2.1, H-6'), 7.62 (1H, dd, 8.4, 1.9, H-4''), 7.61 (1H, d, 2.1, H-2'), 7.28 (1H, d, 1.9, H-6''), 7.09 (1H, d, 8.4, H-3''), 7.07 (1H, d, 8.6, H-5'), 7.04 (1H, d, 2.4, H-10), 6.83 (1H, s, H-11), 6.41 (1H, dd, 8.4, 2.2, H-8), 5.61 (1H, dd, 8.2, 2.4, H-5a), 5.43 (1H, ddd, 8.2, 2.2, 2.0, H-6), 5.03 (1H, dd, 8.4, 2.0, H-7), 3.98 (3H, s, 2''-OCH₃), 3.91 (3H, s, 4'-OCH₃), 3.65 (3H, s, 2-CH₃); ¹³C NMR (CDCl₃, 125 MHz) δ 190.7 (C-7''), 186.9 (C-3), 165.6 (C-7'), 155.5 (C-2''), 155.3 (C-4'), 154.2 (C-1), 148.1 (C-4), 146.8 (C-1''), 144.4 (C-3'), 141.3 (C-10), 140.1 (C-8), 131.5 (C-11a), 130.1 (C-5''), 128.4 (C-6'), 127.5 (C-4''), 122.1 (C-1'), 122.0 (C-11), 121.7 (C-2'), 119.3 (C-10a), 117.6 (C-6''), 112.1 (C-5'), 112.0 (C-3''), 108.0 (C-7), 69.4 (C-6), 64.4 (C-5a), 56.4 (2''-OCH₃), 56.2 (4'-OCH₃), 34.7 (2-CH₃); dark orange powder; mp 117-119 °C; [α]_D²⁸ -578.8° (c 0.17, CHCl₃); HRFAB-MS found *m/z* 563.1126 [M+H]⁺, calcd *m/z* 563.1124 for C₂₈H₂₃N₂O₉S; FAB-MS *m/z* 563 [M+H]⁺, *m/z* 531 [M-S]⁺, *m/z* 562 [M]⁻; UV λ_{max}^{MeOH} (ε) 263.5 (23,300), 341 sh (7,100), 415.5 (6,400) nm; IR ν_{max}^{KBr} 3452, 2936, 1704, 1689, 1634, 1596, 1509, 1429, 1398, 1300, 1267, 1224, 1177, 1140, 1116, 1019, 815, 760, 750, 737 cm⁻¹; Soluble in chloroform, dimethyl sulfoxide.

MPC1001H (8). ¹H NMR (CDCl₃, 400 MHz) δ 9.81 (1H, s, H-7''), 8.02 (1H, dd, 8.6, 2.2, H-6'), 7.63 (1H, dd, 8.5, 1.9, H-4''), 7.60 (1H, d, 1.9, H-2'), 7.31 (1H, d, 1.9, H-6''), 7.10 (1H, d, 8.5, H-3''), 7.07 (1H, d, 8.6, H-5'), 6.99 (1H, d, 2.4, H-10), 6.85 (1H, s, H-11), 6.39 (1H, dd, 8.4, 2.2, H-8), 5.54 (1H, dd, 8.2, 2.4, H-5a), 5.42 (1H, ddd, 8.2, 2.2, 1.7, H-6), 4.98 (1H, dd, 8.4, 1.7, H-7), 3.97 (3H, s, 2''-OCH₃), 3.91 (3H, s, 4'-OCH₃), 3.30 (3H, s, 2-CH₃); ¹³C NMR (CDCl₃, 100 MHz) δ 190.7 (C-7''), 165.5 (C-7'), 157.0 (C-3), 156.0 (C-1), 155.6 (C-2''), 155.2 (C-4'), 149.2 (C-4), 146.5 (C-1''), 144.7 (C-3'), 141.1 (C-10), 140.1 (C-8), 131.1 (C-11a), 130.1 (C-5''), 128.2

(C-6'), 127.5 (C-4''), 122.1 (C-11), 122.0 (C-1'), 121.2 (C-2'), 118.9 (C-10a), 118.1 (C-6''), 112.2 (C-5'), 112.1 (C-3''), 107.8 (C-7), 69.2 (C-6), 63.8 (C-5a), 56.3 (2''-OCH₃), 56.2 (4'-OCH₃), 27.4 (2-CH₃); pale yellow powder; mp 127-128 °C; $[\alpha]_D^{28} -306.7^\circ$ (*c* 0.21, CHCl₃); HRFAB-MS found *m/z* 547.1337 [M+H]⁺, calcd *m/z* 547.1352 for C₂₈H₂₃N₂O₁₀; FAB-MS *m/z* 547 [M+H]⁺, *m/z* 546 [M]⁻; UV $\lambda_{\max}^{\text{MeOH}}$ (ϵ) 261.5 (26,200), 364.5 (8,800) nm; IR $\nu_{\max}^{\text{KBr}}$ 3468, 1712, 1681, 1637, 1602, 1508, 1429, 1399, 1338, 1278, 1223, 1178, 1117, 1019, 819, 760, 741 cm⁻¹; Soluble in chloroform, dimethyl sulfoxide.

Figure 3S. ^1H NMR spectrum of MPC1001 (**1**, CDCl_3 , 400 MHz).

Figure 4S. ^{13}C NMR spectrum of MPC1001 (**1**, CDCl_3 , 100 MHz).

MPC1001

$$[\theta]_{235.7} - 5.59 \times 10^4$$

$$[\theta]_{267.6} + 4.14 \times 10^4$$

$$[\theta]_{301.0} + 7.01 \times 10^4$$

$$[\theta]_{340.6} - 3.69 \times 10^3$$

Emestrin

$$[\theta]_{233} - 9.50 \times 10^4$$

$$[\theta]_{266} + 6.24 \times 10^4$$

$$[\theta]_{301} + 9.32 \times 10^4$$

$$[\theta]_{338} - 0.38 \times 10^4$$

Measurement parameters

Blank : MeOH

Cell : 1 cm (1 mL)

Sense : 2 m degree/cm

Scan : 20 nm/min

Acquisition : 2

Figure 5S. Comparison of CD spectral data of MPC1001 (**1**) to those of emestrin.

Figure 6S. ^1H NMR spectrum of MPC1001B (**2**, CDCl_3 , 400 MHz).

Figure 7S. ^{13}C NMR spectrum of MPC1001B (**2**, CDCl_3 , 100 MHz).

Figure 8S. ^1H NMR spectrum of MPC1001C (**3**, CDCl_3 , 500 MHz).

Figure 9S. ^{13}C NMR spectrum of MPC1001C (**3**, CDCl_3 , 125 MHz).

Figure 10S. ^1H NMR spectrum of MPC1001D (**4**, CDCl₃, 500 MHz).

Figure 11S. ^{13}C NMR spectrum of MPC1001D (**4**, CDCl₃, 125 MHz).

Figure 13S. ^{13}C NMR spectrum of MPC1001E (5, CDCl_3 , 125 MHz).

Figure 14S. ^1H NMR spectrum of MPC1001F (**6**, CDCl_3 , 400 MHz).

Figure 15S. ^{13}C NMR spectrum of MPC1001F (**6**, CDCl_3 , 100 MHz).

Figure 16S. ^1H NMR spectrum of MPC1001G (7, CDCl_3 , 500 MHz).

Figure 17S. ^{13}C NMR spectrum of MPC1001G (7, CDCl_3 , 125 MHz).

Figure 18S. ^1H NMR spectrum of MPC1001H (**8**, CDCl_3 , 400 MHz).

Figure 19S. ^{13}C NMR spectrum of MPC1001H (**8**, CDCl_3 , 100 MHz).