Supporting Information

Synthesis of Putative Uniflorine A

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(6E)-5-(Allylamino)-5,6,7-trideoxy-7-phenyl-D-glucO-hept-6-enitol (4).

MS (CI+ve) *m/z* 294 (M+H⁺, 100%), 172 (M-(CHOH)₃CH₂OH, 13%), 120 ((CHOH)₃CH₂OH-H⁺, 21 %). ¹H NMR (300 MHz, CD₃OD) δ 7.44-7.29 (m, 5H, Ar), 6.56 (d, 1H, *J* 16.2 Hz, H7), 6.17 (dd, 1H, *J* 9.2, 16.1 Hz, H6), 5.29 (dddd, 1H, *J* 5.7, 6.6, 9.9, 17.0 Hz, H2'), 5.20 (dq, 1H, *J* 1.5, 17.1 Hz, H3'), 5.12 (dq, 1H, *J* 1.4, 9.9 Hz, H3'), 3.85 (t, 1H, *J* 4.8 Hz, H4), 3.76 (ddd, 1H, *J* 3.0, 5.1, 6.3 Hz, H2), 3.69 (dd, 1H, *J* 3.2, 5.1 Hz, H3), 3.62 (d, 1H, *J* 5.1 Hz, H1), 3.61 (d, 1H, *J* 6.2 Hz, H1), 3.50 (dd, 1H, *J* 4.8, 9.0 Hz, H5), 3.34 (ddt, 1H, *J* 1.5, 5.6, 13.8 Hz, H1'), 3.17 (ddt, 1H, *J* 1.5, 6.6, 13.5 Hz, H1'). ¹³C NMR (75 MHz, CD₃OD) δ 137.9 (ArC), 136.3 (CH), 135.8 (CH), 129.5 (2 x ArCH), 128.7 (Ar CH), 127.4 (2 x ArCH), 117.9 (CH), 74.4 (CH), 73.1 (CH), 72.8 (CH), 64.4 (CH₂), 63.4 (CHN), 50.0 (CH₂).

(6E)-5-[Allyl(*tert*-butylcarbonyl)amino]-5,6,7-trideoxy-7-phenyl-D-glucO-hept-6-enitol (5).

MS (CI+ve) *m/z* 394 (M+H⁺, 30 %), 320 (M-O^tBu, 26 %), 102 (Boc+H⁺, 100 %). ¹H NMR (300 MHz, CDCl₃) δ 7.37 - 7.17 (m, 5H, Ar), 6.56 (d, 1H, *J* 15.9 Hz, H7), 6.40 (dd, 1H, *J* 6.6, 15.9 Hz, H6), 5.76 (m, 1H, H2'), 5.13-5.05 (m, 2H, H3'), 4.42 (m, 1H, H5), 4.38 (m, 1H, OH), 4.31 (m, 1H, OH), 4.14 (m, 1H, OH), 4.00 (m, 1H, H4), 3.87 (m, 1H, H2), 3.78-3.69 (m, 4H, H1α, H1β, H1'), 3.57 (m, 1H, H3), 1.44 (s, 9H, *t*Bu). ¹³C NMR (75 MHz, CDCl₃) δ 156.4 (CO), 136.6 (ArC), 134.7 (C2'), 134.4 (C7), 128.4 (2 x ArCH), 127.6 (ArCH), 126.4 (ArCH), 125.1 (C6), 116.9 (C3'), 80.8 (q C Boc), 73.0 (CH, C2), 72.4 (CH, C4), 70.2 (CH, C3), 63.8 (CH₂), 60.2 (CH, C5), 48.9 (CH₂), 28.3 (CH₃).

(6E)-5-[Allyl(*tert*-butylcarbonyl)amino]-1-*O*-triphenylmethyl-5,6,7-trideoxy-7-phenyl-D-glucO-hept-6-enitol (6).

MS (ES+ve) *m/z* 658 (M + Na⁺, 43 %), 243 (Tr, 100 %). ¹H NMR (300 MHz, CDCl₃) δ 7.46 - 7.19 (m, 20H, Ar), 6.57 (d, 1H, *J* 15.9 Hz, H7), 6.36 (dd, 1H, *J* 6.9, 15.9 Hz, H6), 5.75 (m, 1H, H2'), 5.10 - 5.01 (m, 2H, H3'), 4.48 (m, 1H, H5), 3.93 (m, 1H, H2), 3.91 - 3.79 (m, 2H, H4, H3), 3.76 (m, 2H, H1'), 3.37 (dd, 1H, *J* 2.7, 9.3 Hz, H1), 3.19 (m, 1H,

H1), 1.43 (s, 9H, *t*Bu). ^{13}C NMR (75 MHz, CDCl_3) δ 156.4 (CO), 143.7 (ArC), 136.5 (ArC), 134.8 (C2'), 134.5 (C7), 128.6 (3 x ArCH), 128.5 (2 x ArCH), 127.8 (3 x ArCH), 127.7 (2 x ArCH), 127.0 (ArCH), 126.5 (ArCH), 124.9 (C6), 116.9 (C3'), 86.9 (q C Tr), 80.9 (q C Boc), 73.2 (C4), 72.2 (C2), 69.3 (C3), 64.0 (C1), 60.4 (C5), 48.8 (C1'), 28.3 (CH_3).

***tert*-Butyl(2*R*)-2-[(2*S*,3*S*)-4-(triphenylmethyloxy)-1,2,3-trihydroxybutyl]-2,5-dihydro-1*H*-pyrrole-1-carboxylate (7).**

MS (ES +ve) m/z 554 ($\text{M} + \text{Na}^+$, 60 %), 243 (Tr, 100 %). ^1H NMR (300 MHz, CDCl_3) δ 7.44 - 7.20 (m, 15H, Ar), 5.87 (dd, 1H, *J* 1.8, 6.4 Hz, H4), 5.81 (d, 1H, *J* 6.6 Hz, H3), 4.67 (m, 1H, H2), 4.22 (dd, 1H, *J* 1.5, 15.9 Hz, H5), 3.98 (dd, 1H, *J* 3.0, 15.6 Hz, H5), 3.83 (m, 1H, H3'), 3.80 (m, 1H, H2'), 3.53 (m, 1H, H1'), 3.33 (dd, 1H, *J* 4.8, 9.6 Hz, H4'), 3.15 (dd, 1H, *J* 4.8, 9.6 Hz, H4'), 1.47 (s, 9H, *t*Bu). ^{13}C NMR (75 MHz, CDCl_3) δ 157.0 (CO), 143.8 (ArC), 128.6 (ArCH), 128.5 (ArCH), 127.8 (ArCH), 127.0 (ArCH), 126.4 (C3), 86.6 (q C Tr), 80.8 (q C Boc), 75.3 (C1'), 72.5 (C3'), 69.5 (C2'), 67.2 (C2), 64.3 (C4'), 54.3 (C5), 28.4 (CH_3).

***tert*-Butyl(2*R*,3*S*,4*R*)-3,4-dihydroxy-2-[(2*S*,3*S*)-1,2,3-trihydroxy-4-triphenylmethyloxybutyl] pyrrolidine-1-carboxylate (8).**

MS (ES+ve) m/z 588 ($\text{M} + \text{Na}^+$, 26 %), 243 (Tr, 100 %). ^1H NMR (300 MHz, CDCl_3) δ 7.40 - 7.38 (m, 15H, Ar), 4.24 (m, 1H, H4), 4.11 (m, 1H, H3), 3.85 (m, 1H, H2'), 3.78 (m, 1H, H3'), 3.74 (m, 1H, H1'), 3.37 (m, 1H, H2), 3.35 (m, 2H, H4'), 3.30 (m, 1H, H5), 3.08 (m, 1H, H5), 1.39 (s, 9H, *t*Bu). ^{13}C NMR (75 MHz, CDCl_3) δ 157.3 (CO), 143.7 (q Ar), 128.6 (2 x ArCH), 127.8 (2 x ArCH), 127.0 (ArCH), 86.5 (q C Tr), 81.0 (q C Boc), 73.3 (C2), 72.6 (C4), 72.5 (C2'), 69.9 (C3), 69.0 (C3'), 65.1 (C1'), 63.9 (C5), 51.2 (C4'), 28.3 (CH_3).

***tert*-Butyl (2*S*, 3*S*, 4*R*)-3,4-bis(benzyloxy)-2-[(2*R*,3*R*)-1,2,3-tris(benzyloxy)-4-triphenylmethyloxybutyl] pyrrolidine-1-carboxylate (9).**

MS (ES+ve) m/z 1038 ($\text{M} + \text{Na}^+$, 85 %), 1016 ($\text{M} + \text{H}^+$, 33 %), 106 (OBn - H^+ , 100 %). ^1H NMR (500 MHz, CDCl_3) δ 7.44 - 6.69 (m, 40H, Ar), 4.80 - 4.40 (m, 10H, CH_2Ph), 4.40 - 3.26 (m, 10H, H2 - H5, H1' - H4'), 1.43 (s, 9H, *t*Bu). ^{13}C NMR (125 MHz, CDCl_3) δ (Major rotamer) 154.3 (CO), 143.9 (ArC), 138.7 (ArC), 138.6 (ArC), 138.3 (ArC), 138.0 (ArC), 137.8 (ArC), 128.8 (ArCH), 128.7 (ArCH), 128.2 (ArCH), 128.14 (ArCH), 128.10 (ArCH), 128.0 (ArCH), 127.9 (ArCH), 127.8 (ArCH), 127.4 (ArCH), 127.3 (ArCH), 127.2 (ArCH), 126.8 (ArCH), 86.9 (q C Tr), 80.0 (q C Boc), 79.9 (CH), 79.1 (CH), 78.0 (CH), 77.4 (CH), 76.9 (CH), 75.7 (CH), 75.1 (CH), 74.6 (CH_2), 73.7 (CH_2), 72.5 (CH_2), 71.7 (CH_2), 64.0 (C2), 63.8 (C4'), 48.7 (C5).

(2*S*,3*S*)-4-[(2*R*,3*S*,4*R*)-3,4-Dibenzyloxypyrrolidin-2-yl]-2,3,4-tribenzyloxybutan-1-ol (10) and (1*S*,2*R*,6*S*,7*R*,8*R*,8*aR*)-1,2,6,7,8-pentabenzyloxyoctahydroindolizine (11).

10: MS (CI +ve) m/z 674 (M + H⁺, 2 %), 566 (M - OBn, 3 %), 91 (Bn, 100 %). ¹H NMR (300 MHz, CDCl₃) δ 7.33 - 7.21 (m, 25H, Ar), 4.82 (d, 1H, J 11.4 Hz, CH₂Ph), 4.72 (d, 1H, J 11.4 Hz, CH₂Ph), 4.68 (d, 1H, J 11.1 Hz, CH₂Ph), 4.64 (d, 1H, J 11.7 Hz, CH₂Ph), 4.60 (d, 1H, J 11.1 Hz, CH₂Ph), 4.57 (d, 1H, J 11.4 Hz, CH₂Ph), 4.54 (d, 2H, J 12.0 Hz, CH₂Ph), 4.46 (d, 1H, J 12.0, CH₂Ph), 4.41 (d, 1H, J 11.4 Hz, CH₂Ph), 4.02 (dd, 1H, J 5.1, 5.7 Hz, H3), 3.87 (m, 1H, H4), 3.81 (m, 1H, H1'), 3.78 (m, 1H, H3'), 3.72 (m, 1H, H4'), 3.68 (m, 1H, H2'), 3.66 (m, 1H, H2'), 3.66 (m, 1H, H4'), 3.39 (dd, 1H, J 4.8, 5.4 Hz, H2), 2.98 (dd, 1H, J 4.5, 12.0 Hz, H5), 2.90 (dd, 1H, J 4.5, 12.0 Hz, H5). ¹³C NMR (75 MHz, CDCl₃) δ 138.6 (ArC), 138.2 (ArC), 138.11 (ArC), 138.06 (ArC), 138.0 (ArC), 128.3 (ArCH), 128.25 (ArCH), 128.23 (ArCH), 128.0 (ArCH), 127.9 (ArCH), 127.8 (ArCH), 127.7 (ArCH), 127.64 (ArCH), 127.60 (ArCH), 127.4 (ArCH), 80.6 (C3'), 80.2 (C1'), 79.7 (C3), 78.6 (C2'), 77.6 (C4), 74.8 (CH₂Ph), 74.3 (CH₂Ph), 72.1 (CH₂Ph), 71.9 (CH₂Ph), 71.4 (CH₂Ph), 62.1 (C2), 61.2 (C4'), 48.9 (C5).

11: MS (CI +ve) m/z 656 (M + H⁺, 5 %), 548 (M - OBn, 4 %), 107 (OBn, 100 %). ¹H NMR (300 MHz, CDCl₃) δ 7.33 - 7.20 (m, 25H, Ar), 4.93 (d, 1H, J 10.8 Hz, CH₂Ph), 4.89 (d, 1H, J 11.7 Hz, CH₂Ph), 4.81 (d, 1H, J 10.8 Hz, CH₂Ph), 4.72 (d, 1H, J 11.1 Hz, CH₂Ph), 4.66 - 4.51 (m, 6H, CH₂Ph), 3.99 (appar. q, 1H, J 7.2 Hz, H2), 3.80 (dd, 1H, J 5.7, 6.9 Hz, H1), 3.63 (m, 1H, H6), 3.57 (m, 1H, H7), 3.35 (dd, 1H, J 8.4, 9.3 Hz, H8), 3.19 (m, 1H, H3), 3.15 (m, 1H, H5), 2.56 (m, 1H, H8a), 2.51 (m, 1H, H3), 2.20 (t, 1H, J 10.2 Hz, H5). ¹³C NMR (75 MHz, CDCl₃) δ 138.7 (ArC), 138.5 (ArC), 138.3 (ArC), 138.2 (ArC), 138.0 (ArC), 128.4 (ArCH), 128.3 (2 x ArCH), 128.2 (ArCH), 128.1 (ArCH), 128.0 (ArCH), 127.8 (3 x ArCH), 127.7 (ArCH), 127.6 (ArCH), 127.5 (ArCH), 127.4 (ArCH), 127.3 (ArCH), 87.1 (C7), 81.6 (C8), 80.2 (C1), 79.0 (C6), 76.0 (C2), 75.7 (CH₂Ph), 74.3 (CH₂Ph), 72.8 (CH₂Ph), 72.2 (CH₂Ph), 72.0 (CH₂Ph), 70.3 (C8a), 57.1 (C3), 53.5 (C5).

(1S,2R,6S,7R,8R,8aR)-Octahydroindolizine-1,2,6,7,8-pentyl pentaacetate (12).

MS (CI+ve) m/z 416 (M + H⁺, 87 %), 356 (M - OAc, 100 %). ¹H NMR (500 MHz, CDCl₃) δ 5.25 (q, 1H, $J_{1,2} = J_{2,3\alpha} = J_{2,3\beta} = 6.3$ Hz, H2), 5.11 (t, 1H, $J_{6,7} = J_{7,8} = 9.3$ Hz, H7), 5.02 (t, 1H, $J_{1,2} = J_{1,8a} = 7.3$ Hz, H1), 4.97 (dd, 1H, $J_{5\beta,6} = 5.8$ Hz, $J_{5\alpha,6} = 9.8$ Hz, H6), 4.96 (t, 1H, $J_{7,8} = J_{8,8a} = 9.3$ Hz, H8), 3.57 (dd, 1H, $J_{2,3\beta} = 6.8$ Hz, $J_{3\alpha,3\beta} = 10.3$ Hz, H3 β), 3.28 (dd, 1H, $J_{5\beta,6} = 5.5$ Hz, $J_{5\alpha,5\beta} = 10.5$ Hz, H5 β), 2.60 (t, 1H, $J_{1,8a} = J_{8,8a} = 8.5$ Hz, H8a), 2.42 (dd, 1H, $J_{2,3\alpha} = 5.0$ Hz, $J_{3\alpha,3\beta} = 10.0$ Hz, H3 α), 2.27 (t, 1H, $J_{5\alpha,5\beta} = J_{5\alpha,6} = 10.3$ Hz, H5 α), 2.04 (s, 3H, Ac), 2.028 (s, 3H, Ac), 2.025 (s, 3H, Ac), 2.02 (s, 3H, Ac), 2.01 (s, 3H, Ac). ¹³C NMR (75 MHz, CDCl₃) δ 170.3 (CO), 169.9 (CO), 169.8 (CO), 169.6 (CO), 168.9 (CO), 73.9 (C7), 73.7 (C1), 72.0 (C8), 69.9 (C6), 69.3 (C2), 65.7 (C8a), 57.3 (C3), 52.0 (C5), 20.74 (CH₃), 20.67 (CH₃), 20.60 (2 x CH₃), 20.2 (CH₃).

^1H NMR (300 MHz, CD_3OD)

^{13}C NMR (75 MHz, CD_3OD)

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (125 MHz, CDCl_3)

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^1H NMR (500 MHz, D_2O)

^{13}C NMR (75 MHz, D_2O)

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

Molecular projection of **12** showing 50% probability amplitude displacement ellipsoids, for C, N, O atoms, H atoms having arbitrary radii of 0.1 Å.

$\text{C}_{18}\text{H}_{25}\text{NO}_{10}$, $M = 415.4$ Orthorhombic, $P2_12_12_1$, $a = 7.667(1)$, $b = 11.555(2)$, $c = 22.671(4)$ Å, $V = 2073$ Å³ at 150 K. 2412 ($F > 4\sigma(F)$) CCD diffractometer reflections refined to $R = 0.045$, the chirality being assumed from the chemistry.
CCDC deposition # 226165