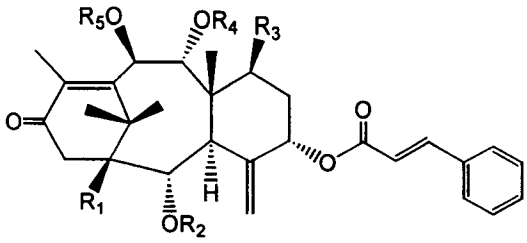
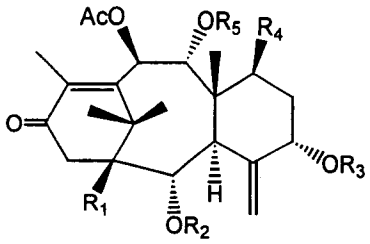
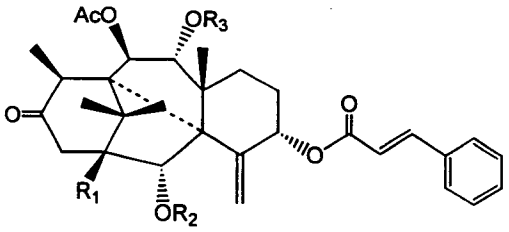
Supporting Information



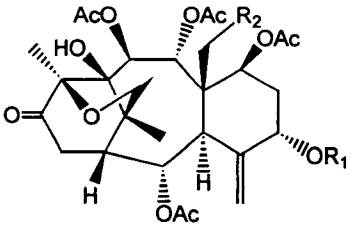
6 R_1 = OH R_2 = Ac R_3 = H R_4 = H R_5 = Ac
7 R_1 = OH R_2 = Ac R_3 = H R_4 = Ac R_5 = H
8 R_1 = H R_2 = H R_3 = H R_4 = H R_5 = Ac
9 R_1 = OH R_2 = H R_3 = H R_4 = H R_5 = Ac
10 R_1 = OH R_2 = H R_3 = H R_4 = Ac R_5 = H
11 R_1 = H R_2 = Ac R_3 = H R_4 = Ac R_5 = Ac
12 R_1 = OH R_2 = Ac R_3 = H R_4 = Ac R_5 = Ac
13 R_1 = H R_2 = Ac R_3 = H R_4 = H R_5 = Ac
14 R_1 = H R_2 = Ac R_3 = OAc R_4 = Ac R_5 = Ac



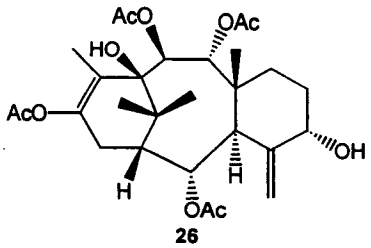
15 R_1 = H R_2 = Ac R_3 = H R_4 = OAc R_5 = Ac
16 R_1 = H R_2 = H R_3 = Ac R_4 = H R_5 = Ac
17 R_1 = H R_2 = H R_3 = H R_4 = H R_5 = H
18 R_1 = OH R_2 = Ac R_3 = OH R_4 = H R_5 = Ac



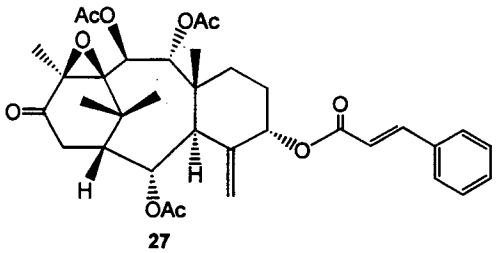
19 R_1 = H R_2 = H R_3 = H
20 R_1 = OH R_2 = Ac R_3 = Ac
21 R_1 = H R_2 = Ac R_3 = Ac



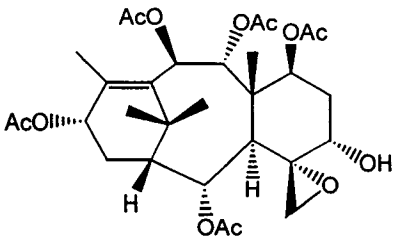
22 R_1 = H R_2 = OBz
23 R_1 = H R_2 = H
24 R_1 = Cinn R_2 = H
25 R_1 = Cinn R_2 = OBz



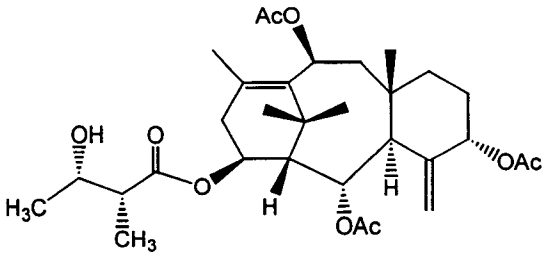
26



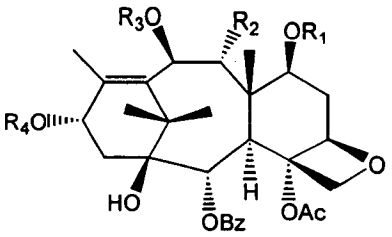
27



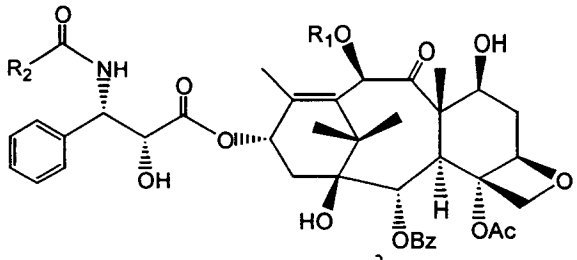
28



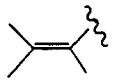
29



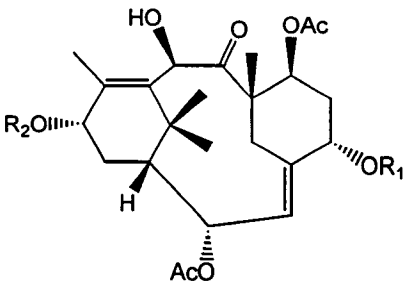
30 R_1 = H R_2 = O R_3 = H R_4 = H
31 R_1 = OH R_2 = OAc R_3 = Ac R_4 = Ac



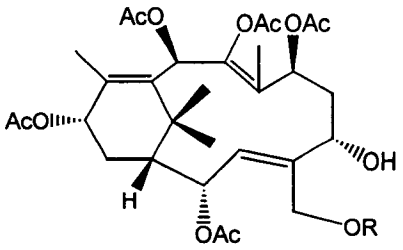
32 R_1 = Ac R_2 =



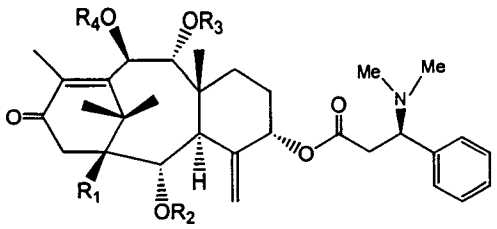
33 R_1 = Ac R_2 = Ph
34 R_1 = H R_2 = Ph

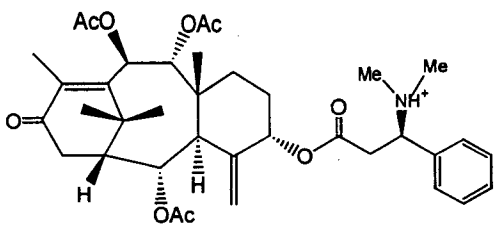


35 R_1 = H R_2 = Ac
36 R_1 = H R_2 = H
37 R_1 = H R_2 = Cinn



38 R = H **39** R = Ac





40 R_1 = OH R_2 = H R_3 = H R_4 = Ac
41 R_1 = OH R_2 = H R_3 = Ac R_4 = H
42 R_1 = H R_2 = Ac R_3 = Ac R_4 = Ac
43 R_1 = H R_2 = H R_3 = H R_4 = Ac
44 R_1 = H R_2 = H R_3 = Ac R_4 = H

45

2α,10β-Diacetoxy-1β,9α-dihydroxy-5α-cinnamoyloxytaxa-4(20),11-dien-13-one (6).

Gum; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.56 (1H, d, *J* = 6.2 Hz, H-2), 3.52 (1H, d, *J* = 6.2 Hz, H-3), 5.33 (1H, m, H-5), 1.99 (1H, m, H-6a), 1.75 (1H, m, H-6b), 1.87 (1H, m, H-7a), 1.52 (1H, m, H-7b), 4.36 (1H, d, *J* = 9.8 Hz, H-9), 5.88 (1H, d, *J* = 9.8 Hz, H-10), 2.88 (1H, d, *J* = 19.6 Hz, H-14a), 2.65 (1H, d, *J* = 19.6 Hz, H-14b), 1.22 (3H, s, Me-16), 1.57 (3H, s, Me-17), 2.28 (3H, s, Me-18), 1.15 (3H, s, Me-19), 5.33 (1H, br.s, H-20a), 5.76 (1H, br.s, H-20b), 2.16 (3H, s, *CH*$_3$CO-), 2.13 (3H, s, *CH*$_3$CO-), 6.43 (1H, d, *J* = 15.9 Hz, H-2′), 7.65 (1H, d, *J* = 15.9 Hz, H-3′), 7.75 (2H, br.d, *J* = 7.5 Hz, Ph-*o*), 7.45 (2H, m, Ph-*m*), 7.40 (1H, m, Ph-*p*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 78.2 (C-1), 71.8 (C-2), 45.7 (C-3), 141.9 (C-4), 78.6 (C-5), 28.5 (C-6), 26.2 (C-7), 45.4 (C-8), 75.2 (C-9), 76.4 (C-10), 152.8 (C-11), 139.6 (C-12), 199.3 (C-13), 44.0(C-14), 42.7 (C-15), 33.9 (C-16), 19.8 (C-17), 13.7 (C-18), 17.4 (C-19), 116.5 (C-20), 166.2 (C-1′), 117.8 (C-2′), 145.5 (C-3′), 134.6 (C-4′), 128.4 (C-5′), 128.9 (C-6′), 130.2 (C-7′), 20.0, 20.0 (2 × *CH*$_3$CO-), 169.8, 171.3 (2 × CH$_3$*C*O-); HMBC correlations: H/C 2/171.3 10/9, 10/11, 10/12, 10/15, 110/169.8, 14a/1, 14a/2, 14a/13, 14a/15, 14b/1,

14b/2, 16/1, 16/11, 16/15, 16/17, 17/1, 17/11, 17/15, 17/16, 18/11, 18/12, 18/13, 19/3, 19/7, 19/8, 19/9, 20a/4; HRFABMS *m/z* 619.2309 $[M + K]^+$ (calcd for $C_{33}H_{40}O_9K$, 619.2309).

2α,9α-Diacetoxy-1β,10β-dihydroxy-5α-cinnamoyloxytaxa-4(20),11-dien-13-one (7). Amorphous powder; ^1H NMR (500 MHz, $CDCl_3$) δ 5.60 (1H, d, *J* = 6.2 Hz, H-2), 3.52 (1H, d, *J* = 6.2 Hz, H-3), 5.33 (1H, m, H-5), 1.99 (1H, m, H-6a), 1.75 (1H, m, H-6b), 1.87 (1H, m, H-7a), 1.60 (1H, m, H-7b), 5.81 (1H, d, *J* = 10.1 Hz, H-9), 5.08 (1H, d, *J* = 10.1 Hz, H-10), 2.89 (1H, d, *J* = 19.7 Hz, H-14a), 2.65 (1H, d, *J* = 19.7 Hz), 1.32 (3H, s, Me-16), 1.75 (3H, s, Me-17), 2.12 (3H, s, Me-18), 0.95 (3H, s, Me-19), 5.33 (1H, br.s, H-20a), 4.70 (1H, br.s, H-20b), 6.43 (1H, d, *J* = 15.9 Hz, H-2′), 7.65 (1H, d, *J* = 15.9 Hz, H-3′), 7.75 (2H, br.d, *J* = 7.5 Hz, Ph-*o*), 7.45 (2H, m, Ph-*m*), 7.40 (1H, m, Ph-*p*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 78.0 (C-1), 71.8 (C-2), 45.7 (C-3), 141.9 (C-4), 78.6 (C-5), 28.5 (C-6), 26.9 (C-7), 44.4 (C-8), 78.4 (C-9), 71.6 (C-10), 156.1 (C-11), 137.4 (C-12), 199.3 (C-13), 44.0 (C-14), 42.5 (C-15), 34.4 (C-16), 19.4 (C-17), 13.7 (C-18), 17.4 (C-19), 116.7 (C-20), 166.2 (C-1′), 117.8 (C-2′), 145.5 (C-3′), 134.6 (C-4′), 128.4 (C-5′), 128.9 (C-6′), 130.2 (C-7′), 20.5, 21.0 (2 × *CH*$_3$CO-), 168.1, 170.8 (2 × CH$_3$*C*O-); HRFABMS *m/z* 619.2309 $[M + K]^+$ (calcd for $C_{33}H_{40}O_9K$, 619.2309).

1-Hydroxyltaxuspine C (20): ^1H NMR (500 MHz, Acetone-D_6) δ 6.13 (1H, d, *J* = 2.0 Hz, H-2), 5.66 (1H, t, *J* = 9.0 Hz, H-5), 2.17 (1H, m, H-6a), 1.79 (1H, m, H-6b), 1.85 (1H, m, H-7a), 1.17 (1H, m, H-7b), 5.79 (1H, s, H-9), 5.79 (1H, s, H-10), 3.46 (1H, br.q, *J* = 7.2 Hz, H-12), 3.02 (1H, d, *J* = 20.2 Hz, H-14a), 2.36 (1H, dt, *J* = 20.2, 1.6 Hz, H-14b), 1.13 (3H, s, Me-16), 1.63 (3H, s, Me-17), 1.29 (3H, d, *J* = 7.2 Hz, Me-18), 1.40 (3H, s, Me-19), 5.98 (1H, s, H-20a), 5.73 (1H, br.s, H-20b), 6.53 (1H, d, *J* = 15.9 Hz, H-2′), 7.71 (1H, d, *J* = 15.9 Hz, H-3′), 7.71 (2H,

m, Ph-*o*), 7.45 (3H, m, Ph-*m*, Ph-*p*), 2.08, 2.07, 2.02 (3 × *CH*$_3$CO-), 4.16 (1H, s, 1-OH); ^{13}C NMR (125 MHz, Acetone-D$_6$) δ 78.2 (C-1), 79.0 (C-2), 62.3 (C-3), 142.2 (C-4), 76.3 (C-5), 25.7 (C-6), 30.9 (C-7), 45.2 (C-8), 82.0 (C-9), 79.4 (C-10), 56.6 (C-11), 51.4 (C-12), 212.0 (C-13), 46.8 (C-14), 44.9 (C-15), 22.8 (C-16), 22.2 (C-17), 15.4 (C-18), 26.8 (C-19), 128.8 (C-20), 165.0 (C-1′), 118.1 (C-2′), 144.8 (C-3′), 134.6 (C-4′), 128.2 (C-5′), 128.9 (C-6′), 130.3 (C-7′), 20.3, 20.3, 19.9 (3 × *CH*$_3$CO-), 169.1, 169.9, 170.3 (3 × CH$_3$*C*O-).

Taxine B (40): ^{1}H NMR (500 MHz, Acetone-D$_6$) δ 4.09 (1H, d, *J* = 6.1 Hz, H-2), 3.22 (1H, d, *J* = 6.0 Hz, H-3), 5.04 (1H, m, H-5), 1.57 (1H, m, H-6a), 1.57 (1H, m, H-6b), 1.85 (1H, m, H-7a), 1.45 (1H, m, H-7b), 4.30 (1H, d, *J* = 9.6 Hz, H-9), 5.86 (1H, d, *J* = 9.6 Hz, H-10), 2.58 (1H, d, *J* = 19.5 Hz, H-14a), 2.86 (1H, d, *J* = 19.5 Hz, H-14b), 1.20 (3H, s, Me-16), 1.53 (3H, s, Me-17), 2.24 (3H, s, Me-18), 1.13 (3H, s, Me-19), 5.60 (1H, s, H-20a), 5.22 (1H, s, H-20b), 2.95 (1H, m, H-2′a), 2.60 (1H, m, H-2′b), 3.93 (1H, m, H-3′), 7.38 (2H, m, Ph-*o*), 7.38 (2H, m, Ph-*m*), 7.29 (1H, m, Ph-*p*), 2.05 (*CH*$_3$CO-), 2.24 (6H, s, N-(Me)$_2$); ^{13}C NMR (125 MHz, Acetone-D$_6$) δ 77.1 (C-1), 71.2 (C-2), 45.9 (C-3), 143.3 (C-4), 78.5 (C-5), 28.0 (C-6), 26.2 (C-7), 44.8 (C-8), 74.4 (C-9), 75.9 (C-10), 154.6 (C-11), 137.7 (C-12), 200.0 (C-13), 44.2 (C-14), 42.6 (C-15), 33.1 (C-16), 19.6 (C-17), 13.0 (C-18), 17.0 (C-19), 117.8 (C-20), 169.7 (C-1′), 37.6 (C-2′), 65.8 (C-3′), 128.6 (C-5′), 127.7 (C-6′), 127.4 (C-7′), 19.8 (*CH*$_3$CO-), 169.7 (CH$_3$*C*O-), 41.0 (N-Me).

Isotaxine B (41): ^{1}H NMR (500 MHz, Acetone-D$_6$) δ 4.17 (1H, d, *J* = 6.1 Hz, H-2), 3.24 (1H, d, *J* = 6.1 Hz, H-3), 5.02 (1H, m, H-5), 1.57 (1H, m, H-6a), 1.57 (1H, m, H-6b), 1.63 (1H, m, H-7a), 1.63 (1H, m, H-7b), 5.78 (1H, d, *J* = 10.1 Hz, H-9), 5.06 (1H, d, *J* = 10.1 Hz, H-10), 2.59 (1H, d, *J* = 19.6 Hz, H-14a), 2.85 (1H, d, *J* = 19.6 Hz, H-14b), 1.29 (3H, s, Me-16), 1.69 (3H, s, Me-

17), 2.10 (3H, s, Me-18), 0.92 (3H, s, Me-19), 5.62 (1H, s, H-20a), 5.22 (1H, s, H-20b), 2.95 (1H, m, H-2'a), 2.60 (1H, m, H-2'b), 3.93 (1H, m, H-3'), 7.38 (2H, m, Ph-*o*), 7.38 (2H, m, Ph-*m*), 7.29 (1H, m, Ph-*p*), 2.05 (*CH*$_3$CO-), 2.24 (6H, s, N-(Me)$_2$); ^{13}C NMR (125 MHz, Acetone-D$_6$) δ 77.7 (C-1), 71.2 (C-2), 45.9 (C-3), 142.9 (C-4), 78.4 (C-5), 28.0 (C-6), 27.3 (C-7), 43.9 (C-8), 77.7 (C-9), 70.3 (C-10), 158.5 (C-11), 135.6 (C-12), 200.0 (C-13), 44.2 (C-14), 42.6 (C-15), 33.8 (C-16), 19.4 (C-17), 12.9 (C-18), 16.8 (C-19), 118.3 (C-20), 169.7 (C-1'), 37.6 (C-2'), 65.8 (C-3'), 128.6 (C-5'), 127.7 (C-6'), 127.4 (C-7'), 19.8 (*CH*$_3$CO-), 170.0 (CH$_3$*C*O-), 41.0 (N-Me).

2-Deacetyltaxine B (43): ^{1}H NMR (500 MHz, Acetone-D$_6$) δ 2.32 (1H, m, H-1), 4.28 (1H, br.m, H-2), 3.61 (1H, br.d, *J* = 4.3 Hz, 2-OH), 3.04 (1H, d, *J* = 5.9 Hz, H-3), 5.00 (1H, m, H-5), 1.57 (1H, m, H-6a), 1.57 (1H, m, H-6b), 1.84 (1H, m, H-7a), 1.45 (1H, m, H-7b), 4.22 (1H, d, *J* = 9.5 Hz, H-9), 4.57 (1H, br., 9-OH), 5.81 (1H, d, *J* = 9.5 Hz, H-10), 2.40 (1H, d, *J* = 19.7 Hz, H-14a), 2.76 (1H, d, *J* = 19.6 Hz, H-14b), 1.11 (3H, s, Me-16), 1.60 (3H, s, Me-17), 2.24 (3H, s, Me-18), 1.11 (3H, s, Me-19), 5.67 (1H, s, H-20a), 5.18 (1H, s, H-20b), 2.98 (1H, m, H-2'a), 2.64 (1H, m, H-2'b), 3.94 (1H, br.m, H-3'), 7.39 (2H, m, Ph-*o*), 7.35 (2H, m, Ph-*m*), 7.28 (1H, m, Ph-*p*), 2.05 (*CH*$_3$CO-), 2.26 (6H, s, N-(Me)$_2$); ^{13}C NMR (125 MHz, Acetone-D$_6$) δ 51.9 (C-1), 68.0 (C-2), 44.2 (C-3), 143.5 (C-4), 78.7 (C-5), 28.2 (C-6), 25.9 (C-7), 44.9 (C-8), 74.8 (C-9), 76.3 (C-10), 152.4 (C-11), 135.8 (C-12), 199.9 (C-13), 35.8 (C-14), 37.6 (C-15), 36.1 (C-16), 25.1 (C-17), 13.2 (C-18), 17.2 (C-19), 117.7 (C-20), 169.8 (C-1'), 37.8 (C-2'), 66.0 (C-3'), 128.8 (C-5'), 127.9 (C-6'), 127.6 (C-7'), 19.9 (*CH*$_3$CO-), 169.7 (CH$_3$*C*O-), 41.1 (N-Me).

2-Deacetylisotaxine B (44): ^{1}H NMR (500 MHz, Acetone-D$_6$) δ 2.32 (1H, m, H-1), 4.37 (1H, br.m, H-2), 3.70 (1H, br.d, *J* = 4.8 Hz, 2-OH), 3.06 (1H, d, *J* = 6.0 Hz, H-3), 5.00 (1H, m, H-5),

1.57 (1H, m, H-6a), 1.57 (1H, m, H-6b), 1.63 (1H, m, H-7a), 1.63 (1H, m, H-7b), 5.71 (1H, o.d, H-9), 5.00 (1H, o.m, H-10), 4.60 (1H, br., 10-OH), 2.40 (1H, d, J = 19.7 Hz, H-14a), 2.76 (1H, d, J = 19.7 Hz, H-14b), 1.19 (3H, s, Me-16), 1.73 (3H, s, Me-17), 2.09 (3H, s, Me-18), 0.90 (3H, s, Me-19), 5.69 (1H, s, H-20a), 5.18 (1H, s, H-20b), 2.98 (1H, m, H-2′a), 2.64 (1H, m, H-2′b), 3.94 (1H, br.m, H-3′), 7.39 (2H, m, Ph-*o*), 7.35 (2H, m, Ph-*m*), 7.28 (1H, m, Ph-*p*), 2.05 (*CH*$_3$CO-), 2.26 (6H, s, N-(Me)$_2$); ^{13}C NMR (125 MHz, Acetone-D$_6$) δ 51.9 (C-1), 68.0 (C-2), 44.2 (C-3), 143.5 (C-4), 78.7 (C-5), 28.0 (C-6), 27.3 (C-7), 44.0 (C-8), 78.2 (C-9), 70.4 (C-10), 156.2 (C-11), 133.9 (C-12), 199.9 (C-13), 35.8 (C-14), 37.6 (C-15), 37.3 (C-16), 24.7 (C-17), 13.2 (C-18), 16.9 (C-19), 118.2 (C-20), 169.8 (C-1′), 37.8 (C-2′), 66.0 (C-3′), 128.8 (C-5′), 127.9 (C-6′), 127.6 (C-7′), 19.9 (*CH*$_3$CO-), 169.9 (CH$_3$*C*O-), 41.1 (N-Me).

Taxine II salt (45): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.23 (1H, m, H-1), 5.51 (1H, br.dd, J = 6.4, 1.0 Hz, H-2), 3.11 (1H, d, J = 6.4 Hz, H-3), 4.96 (1H, br.s, H-5), 1.56 (1H, m, H-6a), 1.69 (1H, m, H-6b), 1.56 (1H, m, H-7a), 1.69 (1H, m, H-7b), 5.85 (1H, d, J = 10.2 Hz, H-9), 5.98 (1H, d, J = 10.2 Hz, H-10), 2.40 (1H, o.d, H-14a), 2.85 (1H, o.m, H-14b), 1.16 (3H, s, Me-16), 1.75 (3H, s, Me-17), 2.26 (3H, s, Me-18), 0.85 (3H, s, Me-19), 5.23 (1H, s, H-20a), 4.85 (1H, s, H-20b), 3.39 (1H, br.d, J = 16.4 Hz, H-2′a), 3.29 (1H, br.dd, J = 16.4, 9.9 Hz, H-2'b), 4.49 (1H, br.m, H-3′), 7.60 (2H, m, Ph-*o*), 7.45 (2H, m, Ph-*m*), 7.45 (1H, m, Ph-*p*), 2.05 (2 × *CH*$_3$CO-), 2.08 (*CH*$_3$CO-), 2.92 (3H, br.s, N-Me), 2.72 (3H, br.s, N-Me), 12.65 (1H, br. NH$^+$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 48.5 (C-1), 69.3 (C-2), 43.0 (C-3), 144.2 (C-4), 79.8 (C-5), 27.5 (C-6), 27.4 (C-7), 44.3 (C-8), 75.5 (C-9), 73.2 (C-10), 152.3 (C-11), 137.5 (C-12), 199.8 (C-13), 36.0 (C-14), 37.8 (C-15), 37.5 (C-16), 25.0 (C-17), 14.1 (C-18), 17.3 (C-19), 118.0 (C-20), 35.9 (C-2′), 66.3 (C-3′), 129.6 (C-5′), 129.2 (C-6′),

130.2 (C-7′), 21.3 (*CH*$_3$CO-), 20.6 (2 × *CH*$_3$CO-), 169.9 (CH$_3$*C*O-), 169.2 (2 × CH$_3$*C*O-), 42.0 (N-Me), 40.1 (N-Me).