Supporting information:

Isolation procedure. 480 g of flowerheads of *Borreria verticillata* were extracted with MeOH. The methanolic extract (7.8 g) was submitted to flash chromatography. The fraction eluted with $CHCl_3$:MeOH (80:20 v/v) was submitted to chromatography on Sephadex LH-20 and yielded a crude iridoid mixture. This mixture was submitted to preparative HPLC.

The conditions used were the following: Column: Merck Lichrocart ODS2 cartridge, 15 cm X 4.6 mm. A linear gradient of B in A from 0 to 100% in 30 min. Eluent A was water. Eluent B was MeOH/water (50:50). Detector: Diode array, 200-350 nm. The chromatograms were monitored at 240 and 210 nm. Flow: 1 ml/min. The extract was dissolved in water and 5 injections of 200 ul each were done. Borreriagenin (**1**) eluted at 5.7 min, asperuloside (**2**) at 18.0 min and daphylloside (**3**) at 24.0 min.

Borreriagenin (**1**, 8.0 mg) was obtained as a white foam. $[\alpha]^{25}_{D}$ -1.3° (c, 0.79 in MeOH). EIMS (70 eV): *m/z* (relative intensity) 214 ($[M]^{\cdot+}$, absent), 178 ($[M]^{\cdot+}$ - $2H_2O$, 4), 166 (20), 148 (60), 136 (90), 120 (30), 107 (25), 104 (27), 91 (100).

Borreriagenin (**1**) ^{1}H NMR (CD_3OD) δ 3.78 (dd, *J* = 11.3, 4.4 Hz, H-1a), 3.71 (dd, J= 11.3, 6.7 Hz, H-1b) , 3.89 (dd, J= 10.8, 4.6 Hz, H-3a), 3.83 (dd, J= 10.8, 3.9 Hz, H-3b), 2.95 (ddd, J= 6.1, 4.6, 3.9 Hz, H-4), 3.32 (ddd, J= 8.3, 7.8, 6.1 Hz, H-5), 5.39 (ddddd, 7.8, 2, 1.5, 1.5, 1 Hz, H-6), 5.83 (dddd, J= 2, 2, 1.5, 1.5 Hz, H-7), 3.10 (m, H-9), 4.21 (dddd, J= 14.9, 1.5, 1, 1 Hz, H-10a), 4.15 (dddd, J= 14.9, 1.5, 1.5, 1.5 Hz, H-10b).

Asperuloside (**2**) ^{1}H NMR (D_2O) δ 5.98 (s, H-1), 7.40 (d, *J*= 2.4 Hz, H-3), 3.71 (ddd, *J*= 6.8, 6.0, 2.4 Hz, H-5), 5.69 (d, *J*= 6.8 Hz, H-6), 5.80 (s, H-7), 3.40 (dbr, *J*=6.0 Hz, H-9), 4.80 (d, *J*=14.2 Hz, H-10^a), 4.70 (d, *J*=14.2 Hz, H-10b), 4.87 (d, *J*= 8.7 Hz, H-1'), 3.31 (dd, *J*= 8.8, 8.7 Hz, H-2'), 3.52 (dd, *J*= 9.3, 8.8 Hz, H-3'), 3.41 (dd, *J*= 9.3, 9.3 Hz, H-4'), 3.56 (ddd, *J*= 9.3, 6.4, 2.4 Hz, H-5'), 3.96 (dd, *J*= 12.2, 2.4 Hz, H-6'a), 3.75 (dd, *J*=12.2, 6.4 Hz, H-6'b), 2.12 (3H, s, Ac).

Daphylloside (**3**) ^{1}H NMR (D_2O) δ 5.02 (d, *J*= 9.0 Hz, H-1), 7.74 (d, *J*= 1.7 Hz, H-3), 3.17 (ddd, *J*= 7.7, 6.1, 1.7 Hz, H-5), 4.9-5.0 (3H, m, H-6, H-10a, H-10b), 6.12 (sbr, H-7), 2.78 (dd, *J*=9.0, 7.7 Hz, H-9), 4.86 (d, *J*= 8.0 Hz, H-1'), 3.3-3.4 (3H, m, H-2', H-4', H-5'), 3.52 (dd, *J*= 9.3, 8.8 Hz, H-3'), 3.89 (dd, *J*= 12.4, 1.9 Hz, H-6'a), 3.70 (dd, *J*=12.4, 5.7 Hz, H-6'b), 3.78 (3H, s, OMe), 2.16 (3H, s, Ac).