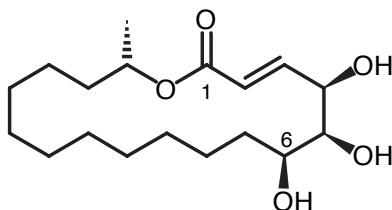


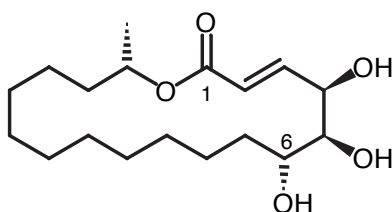
### 6-*epi*-Aspicilin



To fully protected 6-*epi*-aspicilin (5mg, 0.01mmol) was added TFA/water 9:1 (500 $\mu$ l) and the reaction was stirred for 30mins. Concentration *in vacuo* followed by purification by flash column chromatography (ether) gave 6-*epi*-aspicilin as a crystalline white solid (1.4mg, 44%);

$R_f$  0.16 (ether); mp 116°C;  $[\alpha]_D^{29} + 23.0$  (c 0.14, CHCl<sub>3</sub>);  $\delta_H$  (600 MHz, CDCl<sub>3</sub>) 6.99 (1H, dd,  $J$  6 and  $J$  16, 3-H), 6.10 (1H, dd,  $J$  1 and  $J$  16, 2-H), 5.01-5.09 (1H, m, 17-H), 4.68 (1H, m, 4-H), 3.72 (1H, m, 5-H), 3.60 (1H, m, 6-H), 2.68 (1H, brs, OH), 2.49 (1H, brs, OH), 1.66 (1H, brs, OH), 1.34-1.55 (20H, m, (CH<sub>2</sub>)<sub>10</sub>), 1.25 (3H, d,  $J$  6, CH<sub>3</sub>);  $\delta_C$  (100.6 MHz, CDCl<sub>3</sub>) 165.5 (C-1), 144.5 (C-3), 123.2 (C-2), 76.7, 72.5, 71.8, 71.0 (C-4, C-5, C-6, C-17), 36.0, 32.2, 27.74, 27.70, 27.5, 27.4, 26.6, 26.4, 24.09, 24.08 (C7-C16), 20.4 (CH<sub>3</sub>);  $m/z$  (EI) 351(MNa<sup>+</sup>, 60%), 249 (50); (Found: 351.2147. C<sub>18</sub>H<sub>32</sub>O<sub>5</sub>Na requires 351.2140).

### Aspicilin



To fully protected aspicilin (78mg, 0.16mmol) in DCM (10ml) was added ethanedithiol (121 $\mu$ l, mmol) and the solution cooled to 0°C. BF<sub>3</sub>.OEt<sub>2</sub> (166 $\mu$ l, mmol) was then added and the solution warmed to RT and left stirring for 14h. The reaction was diluted with EtOAc, washed with saturated NaHCO<sub>3</sub> solution and the organic layer was dried (MgSO<sub>4</sub>). Concentration *in vacuo* followed by purification by flash column chromatography (5% MeOH in ether) gave aspicilin as a crystalline white solid (38mg, 73%);

$R_f$  0.16 (ether); mp 150-155°C;  $[\alpha]_D^{28} + 35.0$  (c 0.20, CHCl<sub>3</sub>);  $\nu_{max}$ (CHCl<sub>3</sub> solution) 3500 br, 3016s, 2931s, 2858s, 1773w, 1709s, 1460m, 1379m, 1360w, 1278m, 1232m, 1180s, 1124s, 1082s, 1040s, 1010s, 985s;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 6.90 (dd,  $J$  16, 5, 1H, 3-H), 6.12 (dd,  $J$  16, 2, 1H, 2-H), 5.02-5.08 (m, 1H, 17-H), 4.53-4.59 (m, 1H,

4-H), 3.77-3.80 (m, 1H, 5-H), 3.59 (dd, *J* 3, 7, 1H, 6-H), 3.10 (d, *J* 7, 1H, 4-OH), 2.95 (d, *J* 7, 1H, 5-OH), 2.35 (d, *J* 3, 1H, 6-OH), 1.08-1.60 (m, 23H, (CH<sub>2</sub>)<sub>10</sub>, CH<sub>3</sub>CH); δ<sub>c</sub> (100.6 MHz, CDCl<sub>3</sub>) 165.3 (C-1), 144.4 (C-3), 123.1 (C-2), 74.8, 73.2, 71.1, 69.9 (C-4, C-5, C-6, C-17), 35.7, 32.2, 28.3, 27.8, 27.6, 27.3, 27.1, 26.4, 24.3, 23.6 (C7-C16), 20.5 (CH<sub>3</sub>); *m/z* (EI) 351(MNa<sup>+</sup>, 100%), 292 (50), 224 (28); (Found: 351.2166. C<sub>18</sub>H<sub>32</sub>O<sub>5</sub>Na requires 351.2148).