

Assignments for **1** (shinorine): ESI-MS: m/z 333.11 $[M+H]^+$; 1H -NMR (D_2O): δ_H 4.48 (1H, dd, $J=4.8, 6.4$, H-1 \prime); 4.18 (2H, d, $J=3.1$, H-9); 4.02 (1H, dd, $J=3.6, 12.0$, H-3 \prime); 3.96 (1H, dd, $J=6.4, 12.0$, H-3 \prime); 3.67 (3H, s, H-8); 3.57 (2H, s, H-7); 2.93 (1H, d, $J=17.8$, H-6); 2.84 (1H, d, $J=17.8$, H-4); 2.79 (1H, d, $J=17.8$, H-4); 2.79 (1H, d, $J=17.8$, H-6); ^{13}C -NMR (D_2O): δ_C 174.03 (C-2 \prime); 173.43 (C-10); 160.46 (C-3); 159.69 (C-1); 125.58 (C-2); 73.92 (C-5); 71.13 (C-3 \prime); 70.20 (C-7); 67.25 (C-1 \prime); 62.22 (C-8); 49.50 (C-9); 36.13 (C-6); 35.67 (C-4); 22.22 (C-4 \prime).

Assignments for **2** (palythine): ESI-MS: m/z 244.98 $[M+H]^+$; 1H -NMR (D_2O): δ_H 4.03 (2H, s, H-9); 3.64 (3H, s, H-8); 3.57 (2H, s, H-7); 2.95 (1H, d, $J=17.8$, H-6); 2.83 (1H, d, $J=17.8$, H-4); 2.75 (1H, d, $J=17.8$, H-4); 2.68 (1H, d, $J=17.8$, H-6).

Assignments for **3** (asterina-330): ESI-MS: m/z 289.07 $[M+H]^+$; 1H -NMR (D_2O): δ_H 4.02 (2H, s, H-9); 3.77 (2H, d, $J=5.3$ Hz, H-1 \prime); 3.65 (3H, s, H-8); δ_H 3.60 (2H, d, $J=5.3$ Hz, H-2 \prime); 3.59 (2H, s, H-7); 2.91 (2H, s, H-6); 2.82 (1H, d, $J=17.8$ Hz, H-4); 2.74 (1H, d, $J=17.8$ Hz, H-4).

Assignments for **4** (porphyra-334): ESI-MS: m/z 347.12 $[M+H]^+$; 1H -NMR (D_2O): δ_H 4.30 (1H, dq, $J=4.6, 6.4$ Hz, H-3 \prime); 4.07 (1H, d, $J=4.4$ Hz, H-1 \prime); 4.05 (2H, d, $J=3.8$ Hz, H-9); 3.70 (3H, s, H-8); 3.58 (2H, s, H-7); 2.94 (1H, d, $J=17.8$ Hz, H-6); 2.83 (1H, d, $J=17.8$ Hz, H-4); 2.77 (1H, d, $J=17.8$ Hz, H-4); 2.75 (1H, d, $J=17.8$ Hz, H-6); 1.26 (3H, d, $J=6.4$ Hz, H-4 \prime); ^{13}C -NMR (D_2O): δ_C 178.18 (C-2 \prime); 177.73 (C-10); 163.41 (C-3); 162.03 (C-1); 128.53 (C-2); 73.92 (C-5); 71.13 (C-3 \prime); 70.20 (C-7); 67.25 (C-1 \prime); 62.22 (C-8); 49.50 (C-9); 36.13 (C-6); 35.67 (C-4); 22.22 (C-4 \prime).

Assignments for **5** (aplysiapalythine A): ESI-MS: m/z 303.10 $[M+H]^+$; 1H -NMR (D_2O): δ_H 4.02 (2H, d, $J=0.9$ Hz, H-9); 4.01 (1H, m, H-2 \prime); 3.63 (3H, s, H-8); 3.59 (2H, s, H-7); 3.49 (1H, dd, $J=14.0$ Hz, 4.0, H-1 \prime); 3.43 (1H, dd, $J=14.0$ Hz, 7.3, H-1 \prime); 2.89 (2H, s, H-6); 2.82

(1H, d, J=17.8 Hz, H-4); 2.74 (1H, d, J=17.8 Hz, H-4); 1.23 (3H, d, J=6.4 Hz, H-3'); ¹³C-NMR (D₂O): δ_C 177.84 (C-10); 162.01 (C-3); 162.83 (C-1); 127.85 (C-2); 73.62 (C-5); 70.35 (C-7); 69.55 (C-2'); 61.67 (C-8); 52.72 (C-1'); 49.42 (C-9); 35.61 (C-6); 35.14 (C-4); 21.91 (C-3').

Assignments for **6** (mycosporine-glycine): ESI-MS: m/z 245.95 [M+H]⁺; ¹H-NMR (D₂O): δ_H 3.98 (2H, s, H-9); 3.59 (3H, s, H-8); 3.53 (2H, s, H-7); 2.83 (1H, d, J=17.8 Hz, H-6); 2.68 (1H, d, J=17.8 Hz, H-6); 2.67 (1H, d, J=17.8 Hz, H-4) 2.43 (1H, d, J=17.8 Hz, H-4); ¹³C-NMR (D₂O): δ_C 188.24 (C-1); 178.85 (C-10); 161.93 (C-3); 132.44 (C-2); 74.82 (C-5); 70.15 (C-7); 62.39 (C-8); 44.12 (C-6); 43.95 (C-9); 35.44 (C-4).

Assignments for **7** (mycosporine-alanine-glycine): ESI-MS: m/z 317.11 [M+H]⁺; ¹H-NMR (D₂O): δ_H 4.24 (1H, q, J=7 Hz, H-1'); 4.02 (2H, d, J=3.6 Hz, H-9); 3.65 (3H, s, H-8); 3.57 (2H, s, H-7); 2.94 (1H, d, J=17.8 Hz, H-6); 2.80 (1H, d, J=17.8 Hz, H-4); 2.74 (1H, d, J=17.8 Hz, H-4); 2.72 (1H, d, J=17.8 Hz, H-6); 1.26 (3H, d, J=7 Hz, H-3'); ¹³C-NMR (D₂O): δ_C 181.66 (C-2'); 178.35 (C-10); 163.41 (C-3); 163.16 (C-1); 128.03 (C-2); 73.36 (C-5); 70.06 (C-7); 57.48 (C-1'); 61.82 (C-8); 49.41 (C-9); 36.28 (C-6); 35.95 (C-4); 21.12 (C-3').

Assignments for **8** (aplysiapalythine B): ESI-MS: m/z 273.07 [M+H]⁺; ¹H-NMR (D₂O): δ_H 4.03 (2H, s, H-9); 3.46 (1H, q, J=7 Hz, H-1'); 3.64 (3H, s, H-8); 3.62 (2H, s, H-7); 2.75-2.94 (4H, d, J=17.8 Hz, H-4 and H-6); 1.27 (3H, t, J=7 Hz, H-2').

Assignments for **9** (mycosporine-methylamine threonine): ESI-MS: m/z 303.10 [M+H]⁺; ¹H-NMR (D₂O): δ_H 4.29 (1H, dq, J= 4.3, 6.3 Hz, H-3'); 4.03 (1H, d, J=4.3 Hz, H-1'); 3.65 (3H, s, H-8); 3.59 (2H, s, H-7); 3.09 (3H, s, H-9); 2.88 (2H, s, H-6); 2.87 (1H, d, J=17.8 Hz, H-4); 2.72 (1H, d, J=17.8 Hz, H-4); 1.24 (3H, d, J=6.3 Hz, H-4'); ¹³C-NMR (D₂O): δ_C 175.46 (C-2'); 161.60 (C-3); 158.67 (C-1); 125.07 (C-2); 71.40 (C-5); 68.15 (C-3'); 67.64 (C-7); 64.50 (C-1'); 58.58 (C-8); 33.48 (C-6); 33.48 (C-4); 30.65 (C-9); 19.77 (C-4').

Assignments for **10** (usujirene): ESI-MS: m/z 285.07 $[M+H]^+$; $^1\text{H-NMR}$ (D_2O): δ_{H} 6.41 (1H, dd, $J=1.3, 7.7$ Hz, H-1'); 5.43 (1H, dq, $J=7.4, 7.7$ Hz, H-2'); 4.11 (2H, s, H-9); 3.72 (3H, s, H-8); 3.63 (2H, s, H-7); 2.83-2.96 (4H, s, H-4 and H-6); 1.79 (3H, dd, $J=1.3, 7.4$ Hz, H-3').

Assignments for **11** (palythene): ESI-MS: m/z 285.07 $[M+H]^+$; $^1\text{H-NMR}$ (D_2O): δ_{H} 6.59 (1H, dd, $J=1.3, 13.7$ Hz, H-1'); 5.76 (1H, dq, $J=6.9, 13.7$ Hz, H-2'); 4.09 (2H, s, H-9); 3.66 (3H, s, H-8); 3.63 (2H, s, H-7); 2.79-2.93 (4H, s, H-4 and H-6); 1.78 (3H, dd, $J=1.3, 6.9$ Hz, H-3').