Supporting Information

for

The marine sponge *Agelas citrina* as a source of the new pyrrole–imidazole alkaloids citrinamines A–D and *N*-methylagelongine

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**NMR data**

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Citrinamine A (1)

**Figure S1.** 1D $^1$H NMR spectrum of citrinamine A (1) in DMSO-$d_6$, 303 K, 400 MHz.

**Figure S2.** 1D $^{13}$C-NMR spectrum of citrinamine A (1) in DMSO-$d_6$, 303 K, 850 MHz.
Citrinamine B (2)

Figure S3. 1D $^1$H-NMR spectrum of citrinamine B (2) in DMSO-$d_6$, 303 K, 400 MHz.

Figure S4. 1D $^{13}$C-NMR spectrum of citrinamine B (2) in DMSO-$d_6$, 303 K, 850 MHz.
Citrinamines C (3) and D (4)

**Figure S5.** $^1$H,$^{13}$C-HMBC and the structure of citrinamine C (3) (key correlations and bonds in red).
Table S1. $^1$H, $^{13}$C, and $^{15}$N chemical shifts of citrinamines C (3) and D (4) (600 MHz, DMSO-$d_6$).*

<table>
<thead>
<tr>
<th>Position</th>
<th>citrinamine C (3)</th>
<th>citrinamine D (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta_{H}$, mult. (J/Hz)</td>
<td>$\delta_{C}$ / $\delta_{N}$</td>
</tr>
<tr>
<td>1-NH</td>
<td>11.81, s (161)</td>
<td>11.78, s (161)</td>
</tr>
<tr>
<td>2</td>
<td>6.98, m</td>
<td>121.2</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>94.9</td>
</tr>
<tr>
<td>4</td>
<td>6.86, m</td>
<td>111.1</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>126.6</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>159.9</td>
</tr>
<tr>
<td>7-NH</td>
<td>8.22, t (5.8)</td>
<td>(102)</td>
</tr>
<tr>
<td>8</td>
<td>3.45$^b$; 2.96, m</td>
<td>42.2</td>
</tr>
<tr>
<td>9</td>
<td>3.72, m</td>
<td>80.8</td>
</tr>
<tr>
<td>10</td>
<td>4.09, d (4.8)</td>
<td>34.5</td>
</tr>
<tr>
<td>11</td>
<td>-</td>
<td>117.6</td>
</tr>
<tr>
<td>12-NH</td>
<td>9.66, s</td>
<td>(127)</td>
</tr>
<tr>
<td>13</td>
<td>-</td>
<td>154.6</td>
</tr>
<tr>
<td>14-NH</td>
<td>9.74, s</td>
<td>(131)</td>
</tr>
<tr>
<td>15</td>
<td>6.38, s</td>
<td>106.4</td>
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<td>16</td>
<td>3.31, s</td>
<td>58.5</td>
</tr>
<tr>
<td>1’-NH</td>
<td>11.81, s</td>
<td>(161)</td>
</tr>
<tr>
<td>2’</td>
<td>6.98, m</td>
<td>121.2</td>
</tr>
<tr>
<td>3’</td>
<td>-</td>
<td>94.9</td>
</tr>
<tr>
<td>4’</td>
<td>6.86, m</td>
<td>111.1</td>
</tr>
<tr>
<td>5’</td>
<td>-</td>
<td>126.6</td>
</tr>
<tr>
<td>6’</td>
<td>-</td>
<td>159.3</td>
</tr>
<tr>
<td>7’-NH</td>
<td>8.37, t (5.7)</td>
<td>(106)</td>
</tr>
<tr>
<td>8’</td>
<td>3.93, m</td>
<td>40.8</td>
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<tr>
<td>9’</td>
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<td>127.4</td>
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<tr>
<td>10’</td>
<td>6.35, d (16.0)</td>
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<tr>
<td>11’</td>
<td>-</td>
<td>121.3</td>
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<tr>
<td>12’-NH</td>
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<td>(130)</td>
</tr>
<tr>
<td>13’</td>
<td>-</td>
<td>147.1</td>
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</table>

*a $^1$H and $^{13}$C chemical shifts are referenced to the DMSO-$d_6$ signal (2.50 ppm and 39.5 ppm, respectively). $^{15}$N NMR shifts were not calibrated with an external standard. Therefore, the $\delta$ value has an accuracy of about 1 ppm in reference to NH$_3$ (0 ppm) and the $^{15}$N NMR shifts are given without decimals.

*b No multiplicity information could be given because of overlapped signals.
**N-Methylgalangolone (5)**

Figure S6. 1D $^1$H-NMR spectrum of N-methylgalangolone (5) in DMSO-$d_6$, 303 K, 600 MHz.

Figure S7. 1D $^{13}$C-NMR spectrum of N-methylgalangolone (5) in DMSO-$d_6$, 303 K, 600 MHz.