

## Hamigerin A and a hamigerin D decomposition product

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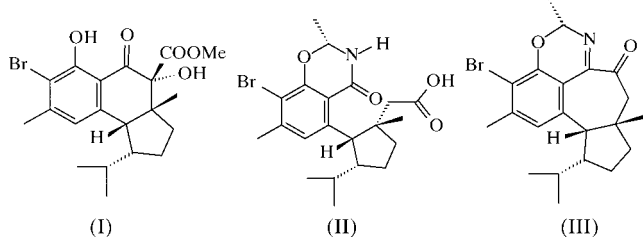
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The sponge *Hamigera tarangaensis* has yielded eight new compounds and we report here the structure of one of these compounds, hamigeran A,  $C_{20}H_{25}BrO_5$ , or methyl 7-bromo-4 $\beta$ ,6-dihydroxy-1 $\beta$ -isopropyl-3 $\alpha$ ,8-dimethyl-5-oxo-1 $\alpha$ ,3 $\alpha$ ,4,5-tetrahydrocyclopenta[*a*]naphthalene-4-carboxylate, and the decomposition product of hamigeran D,  $C_{21}H_{28}BrNO_4$ , namely 2-(8-bromo-2 $\beta$ ,7-dimethyl-4-oxo-1,3 $\alpha$ -benzoxazan-5-yl)-3-isopropylcyclopentylacetic acid.

### Comment

As part of a search for biologically active compounds from New Zealand sponges, extracts from *Hamigera tarangaensis* yielded eight new compounds. The structural elucidation, by NMR spectroscopy, of seven of the compounds and the structural revision of the eighth compound have been published elsewhere (Wellington *et al.*, 2000). In order to confirm the structure assignments and establish the absolute stereochemistries, single-crystal X-ray studies were carried out on hamigeran A, (I), and the decomposition product, (II), of hamigeran D, (III).

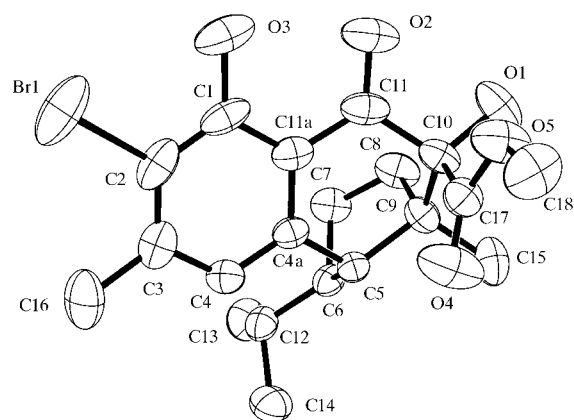


The structure of (I) is illustrated in Fig. 1 which shows the absolute stereochemistry and confirms the chemical assignment. The six- and five-membered rings are *cis* fused at the ring junction C5–C9. There is some strain in the molecule at this point evidenced by the bond lengths C5–C6 1.565 (5), C5–C9 1.562 (5) and C8–C9 1.575 (6) Å, which are slightly longer than the remaining C–C single bonds. These distances are consistent with tabulated values for a pentasubstituted C–C bond (Allen *et al.*, 1987). The C6–C12 bond is stag-

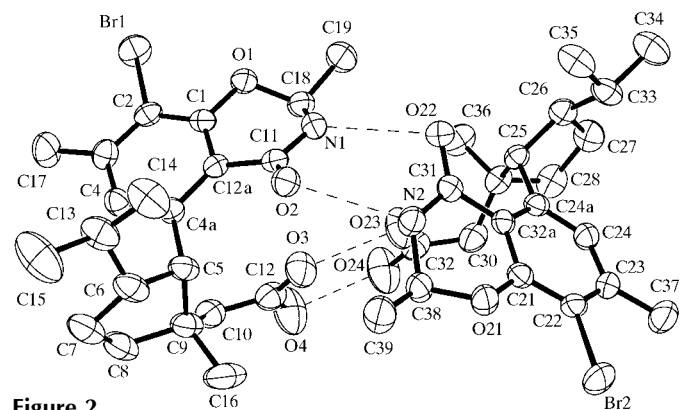
gered [C5–C6–C12–C13 172.3 (4) $^\circ$ ], orienting the isopropyl group well clear of the five-membered ring. The torsion angle C9–C10–C17–O5 is 163.3 (3) $^\circ$ , which orients the ester group so as to minimize steric interactions in this area.

There is an intramolecular hydrogen bond between the phenolic H3A atom and the carbonyl O2 atom, the O3...O2 separation is 2.580 (6) Å. The hydroxyl H1A atom does not seem to be involved in a hydrogen bond, the closest approach to an acceptor atom being 2.80 Å to O5. There are no significant intermolecular interactions.

The structure of (II) contains two independent molecules in the unit cell which are linked into a dimer through hydrogen bonds. Fig. 2 shows the structure of the dimeric unit. The numbering of the O and C atoms of the second molecule are obtained by adding 20 to those of the first molecule. The crystal structure confirms the structural assignment and establishes the absolute configuration. The two molecules have a remarkably similar conformation, even though there is the possibility of free rotation about the C4A–C5, C6–C13 and C9–C10 bonds. The torsion angles within the two molecules are 65.2 (3) and 72.9 (3) $^\circ$  for C5–C9–C10–C12, and –63.1 (3) and –60.1 (3) $^\circ$  for C5–C6–C13–C14, respec-



**Figure 1**  
The structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.



**Figure 2**  
The structure of (II) showing the hydrogen bonding with the non-H atoms shown with 50% probability displacement ellipsoids. H atoms and the label for C29, which is bonded to C25 and C28, have been omitted to avoid crowding.

tively. The same bond lengthening around the pentasubstituted C5—C9 bond as shown in (I) is seen again here [C5—C6 1.568 (4) and 1.576 (3) Å; C5—C9 1.576 (4) and 1.573 (4) Å; C8—C9 1.553 (4) and 1.551 (4) Å], even though the constraint on the configuration imposed by the ring junction is absent.

The two independent molecules are linked by intermolecular hydrogen bonds. There is a strong interaction between the carboxylic acid groups: O4···O24 2.599 (4) Å and O3···O23 2.643 (3) Å. There is a somewhat weaker interaction between the amide groups; N1···O22 2.903 (3) Å and N2···O2 2.858 (3) Å, as evidenced by the longer approach.

## Experimental

The title compounds were obtained from extracts of *Hamigera tara-gaensis* as previously described (Wellington *et al.*, 2000). Hamigarin D underwent a spontaneous decomposition in CDCl<sub>3</sub> solvent in the NMR tube yielding the decomposition product. Crystals suitable for X-ray diffraction studies were obtained from methanol.

### Compound (I)

#### Crystal data

C<sub>20</sub>H<sub>25</sub>BrO<sub>5</sub>  
*M<sub>r</sub>* = 425.31  
 Orthorhombic, *P*<sub>2</sub><sub>1</sub><sub>2</sub><sub>1</sub><sub>2</sub><sub>1</sub>  
*a* = 7.0958 (13) Å  
*b* = 16.050 (3) Å  
*c* = 16.856 (4) Å  
*V* = 1919.7 (7) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.472 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 6757 reflections  
 $\theta = 2\text{--}26^\circ$   
 $\mu = 2.17 \text{ mm}^{-1}$   
*T* = 203 (2) K  
 Needle, yellow  
 0.32 × 0.16 × 0.10 mm

#### Data collection

Siemens SMART diffractometer  
 Area-detector  $\omega$  scans  
 Absorption correction: multi-scan (Blessing, 1995)  
 $T_{\min} = 0.544$ ,  $T_{\max} = 0.812$   
 8269 measured reflections  
 3020 independent reflections

2738 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.041$   
 $\theta_{\text{max}} = 26.0^\circ$   
 $h = -6 \rightarrow 6$   
 $k = 0 \rightarrow 19$   
 $l = 0 \rightarrow 20$   
 Intensity decay < 2%

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.107$   
 $S = 1.07$   
 3020 reflections  
 239 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 1.6200P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.003$   
 $\Delta\rho_{\text{max}} = 0.38 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.47 \text{ e } \text{Å}^{-3}$   
 Absolute structure: Flack (1983)  
 Flack parameter = 0.000 (13)

**Table 1**

Selected geometric parameters (Å, °) for (I).

Br1—C2	1.902 (4)	C5—C6	1.565 (5)
O1—C10	1.404 (5)	C6—C7	1.526 (6)
O2—C11	1.235 (5)	C6—C12	1.528 (5)
O3—C1	1.364 (6)	C7—C8	1.513 (6)
O4—C17	1.172 (6)	C8—C9	1.575 (6)
O5—C17	1.318 (5)	C9—C15	1.525 (6)
O5—C18	1.462 (5)	C9—C10	1.549 (5)
C5—C9	1.562 (5)		
C5—C6—C12—C13	172.3 (4)	C6—C5—C9—C8	34.9 (4)
C9—C10—C17—O5	163.3 (3)	C4a—C5—C9—C10	28.7 (5)

**Table 2**

Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O3—H3A···O2	0.92 (6)	1.75 (6)	2.580 (6)	149 (7)

### Compound (II)

#### Crystal data

C<sub>21</sub>H<sub>28</sub>BrNO<sub>4</sub>  
*M<sub>r</sub>* = 438.35  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>  
*a* = 10.0979 (1) Å  
*b* = 20.5473 (2) Å  
*c* = 10.7452 (1) Å  
 $\beta = 106.685 (1)^\circ$   
*V* = 2135.60 (4) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.363 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 8192 reflections  
 $\theta = 2\text{--}26^\circ$   
 $\mu = 1.95 \text{ mm}^{-1}$   
*T* = 203 (2) K  
 Irregular fragment, colourless  
 0.60 × 0.35 × 0.31 mm

#### Data collection

Siemens SMART diffractometer  
 Area-detector  $\omega$  scans  
 Absorption correction: multi-scan (Blessing, 1995)  
 $T_{\min} = 0.388$ ,  $T_{\max} = 0.583$   
 13334 measured reflections  
 8833 independent reflections

6885 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.021$   
 $\theta_{\text{max}} = 28.2^\circ$   
 $h = -12 \rightarrow 12$   
 $k = -26 \rightarrow 27$   
 $l = 0 \rightarrow 14$   
 Intensity decay < 2%

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.030$   
 $wR(F^2) = 0.065$   
 $S = 0.85$   
 8833 reflections  
 500 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2)]$   
 $(\Delta/\sigma)_{\text{max}} = 0.003$   
 $\Delta\rho_{\text{max}} = 0.27 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.26 \text{ e } \text{Å}^{-3}$   
 Absolute structure: Flack (1983)  
 Flack parameter = 0.007 (4)

**Table 3**

Selected geometric parameters (Å, °) for (II).

Br1—C2	1.895 (2)	Br2—C22	1.894 (2)
N1—C11	1.342 (3)	N2—C31	1.356 (3)
N1—C18	1.438 (3)	N2—C38	1.433 (3)
O1—C1	1.373 (3)	O21—C21	1.376 (3)
O1—C18	1.434 (3)	O21—C38	1.434 (3)
O2—C11	1.233 (3)	O22—C31	1.245 (3)
O3—C12	1.238 (3)	O23—C32	1.265 (4)
O4—C12	1.289 (4)	O24—C32	1.239 (3)
C4a—C5	1.529 (3)	C24a—C25	1.533 (3)
C5—C6	1.568 (4)	C25—C29	1.573 (4)
C5—C9	1.576 (4)	C25—C26	1.576 (3)
C6—C13	1.525 (4)	C26—C33	1.524 (4)
C6—C7	1.551 (4)	C26—C27	1.545 (4)
C7—C8	1.531 (4)	C27—C28	1.522 (4)
C8—C9	1.553 (4)	C28—C29	1.551 (4)
C9—C10	1.523 (4)	C29—C30	1.540 (4)
C9—C16	1.556 (4)	C29—C36	1.540 (4)
C10—C12	1.487 (4)	C30—C32	1.489 (4)
C11—C12a	1.504 (3)	C31—C32a	1.493 (3)
C4—C4a—C5—C6	-49.4 (3)	C5—C9—C10—C12	65.2 (3)
C24—C24a—C25—C26	-51.6 (3)	C25—C29—C30—C32	72.9 (3)
C4—C4a—C5—C9	67.4 (3)	C5—C6—C13—C14	-63.1 (3)
C24—C24a—C25—C29	65.7 (3)	C25—C26—C33—C34	-60.1 (3)

**Table 4**  
Hydrogen-bonding geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...O22 <sup>i</sup>	0.75 (3)	2.18 (3)	2.903 (3)	163 (3)
O4—H4...O24 <sup>i</sup>	0.94 (4)	1.67 (4)	2.599 (4)	170 (4)
N2—H2A...O2 <sup>ii</sup>	0.83 (3)	2.06 (3)	2.858 (3)	160 (3)
O23—H23...O3 <sup>ii</sup>	0.78 (4)	1.87 (4)	2.643 (3)	171 (4)

Symmetry codes: (i)  $2 - x, \frac{1}{2} + y, -z$ ; (ii)  $2 - x, y - \frac{1}{2}, -z$ .

H atoms were located geometrically and initially refined using a riding model. In the final refinement, the coordinates of the H atoms involved in hydrogen bonding were allowed to refine with their displacement parameters tied to the carrier atom. Final refinement allowed the fraction contribution of the inverted enantiomer to vary (Flack, 1983), the absolute structure parameter quoted being the refined value of this contribution. In both structures, the contribution of the inverted enantiomer is negligible.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995);

program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1599). Services for accessing these data are described at the back of the journal.

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