# Briarane Diterpenes from the Gorgonian Octocoral *Erythropodium caribaeorum* from the Northern Caribbean

Darin Maharaj,[†,‡] Keith O. Pascoe,[†] and Winston F. Tinto*[,§]

*Department of Chemistry, University of the West Indies, Mona Campus, Jamaica, and Laboratory of Bioorganic Chemistry, Department of Biological and Chemical Sciences, University of the West Indies, Cave Hill Campus, Barbados*

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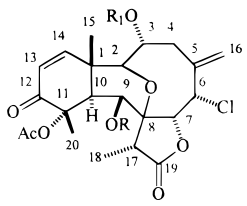
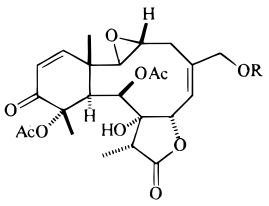
An investigation of the gorgonian octocoral *Erythropodium caribaeorum* collected off the north coast of Jamaica has yielded three new briarane diterpenes. In addition, the six known diterpenes, erythrolides A, B, D, E, F, and I were isolated. The structures of these diterpenes were established by $^1$H and $^{13}$C NMR spectroscopy utilizing DEPT, COSY, and HETCOR experiments.

Marine coelenterates of the subclass Octocorallia have been the subject of numerous chemical investigations, in part due to a wide variety of diterpenes which they possess. Some of these diterpenes were shown to display interesting biological activity.[1] *Erythropodium caribaeorum* Duchassaing & Michelotti is an encrusting gorgonian, and previous investigations of this organism has resulted in the isolation of over 10 briarane diterpenes, including erythrolides A−J.[1−3] We previously reported on the isolation and characterization of four briarane diterpenes from *E. caribaeorum* collected off the coast of Tobago in the southern Caribbean. We have now investigated specimens of *E. caribaeorum* collected off Discovery Bay, Jamaica, in the northern Caribbean and report here the isolation of nine diterpenes from this organism. Three are the new briarane compounds (**1**−**3**), while the other six, erythrolides A, B, D, E, F, and I, have been reported previously.[1−3] Compounds **1** and **2** are the acetate analogues of the closely related erythrolides E (**4**) and I (**5**), respectively, while compound (**3**) was the acetate analogue of erythrolide H (**6**).[2,3]





(**1**) R = R$_1$ = Ac

(**2**) R = (CO)CH$_2$O(CO)CH$_3$; R$_1$ = Ac

(**4**) R = Ac; R$_1$ = H

(**5**) R = (CO)CH$_2$O(CO)CH$_3$; R$_1$ = H

(**3**) R = Ac

(**6**) R = H

The known compounds were identified by comparison of their spectral data with those reported for erythrolides A−I.[2,3] Unambiguous $^1$H and $^{13}$C NMR assignments were made for all six compounds by the analysis of DEPT, COSY, and HETCOR experiments. The IR spectrum of compound **1** showed absorbances characteristic of $\gamma$-lactone (1788 cm$^{-1}$), ester (1740 cm$^{-1}$), and $\alpha,\beta$-unsaturated ketone (1689 cm$^{-1}$) functionalities. The $^1$H NMR spectrum had resonances due to two quaternary methyl groups at $\delta$ 1.47 and 1.58, a methyl doublet at $\delta$ 1.08 ($J$ = 7.0 Hz), and three acetoxy methyls at $\delta$ 2.11, 2.12, and 2.27. In addition, there were resonances due to four oxymethine protons at $\delta$ 4.15 (1H, d, $J$ = 3.2 Hz, H-2), 5.20 (1H, m, H-3), 4.39 (1H, d, $J$ = 1.8 Hz, H-7), and 5.67 (1H, d, $J$ = 2.0 Hz, H-9). A resonance at $\delta$ 4.80 (1H, d, $J$ = 1.8 Hz, H-6) was characteristic of a methine attached to a carbon-bearing chlorine.[3] Low-field resonances at $\delta$ 6.05 (1H, d, $J$ = 10.4 Hz, H-12) and 6.83 (1H, d, $J$ = 10.4 Hz, H-13) were associated with the $\alpha,\beta$-unsaturated ketone, while signals for an exomethylene group occurred at $\delta$ 5.37 (s) and 5.60 (s). A comparison of the $^1$H NMR spectrum of **1** with that of erythrolide E (**4**) showed that they were similar except for the appearance of an additional acetate methyl resonance and the downfield shift of the H-3 oxymethine proton from $\delta$ 3.96 in **4** to $\delta$ 5.20 in **1**.[3] Thus, from the NMR data (Table 1), it was concluded that compound **1** was the 3-acetate of **4**.

Compound **2** was isolated as a white powder, and like compound **1**, it had IR absorptions indicative of $\gamma$-lactone, ester, and $\alpha,\beta$-unsaturated ketone at 1783, 1745, and 1689 cm$^{-1}$, respectively. The $^1$H NMR spectrum had resonances for two quaternary methyl groups at $\delta$ 1.47 and 1.53, one secondary methyl at $\delta$ 1.13 ($J$ = 7.0 Hz), and three acetoxy methyls at $\delta$ 2.21, 2.13, and 2.12, as in **1**. Four oxymethine protons had resonances at $\delta$ 4.17 (1H, $J$ = 4.0 Hz, H-2), 5.19 (1H, m, H-3), 4.44 (1H, d, $J$ = 1.5 Hz, H-7), and 5.73 (1H, s, H-9), while an oxymethylene group had a resonance at $\delta$ 4.71 (2H, s). A comparison of the $^1$H and $^{13}$C NMR spectra of **2** with those of erythrolide I (**5**) showed that they were almost indentical. The differences previously noted in the comparison of **1** and **4** were also observed between **2** and **5**. In this respect, a signal at $\delta$ 4.00 corresponding to H-3 in **5** was replaced by the downfield signal at $\delta$ 5.19 in **2**, in addition to an acetoxy methyl resonance at $\delta$ 2.13. Compound **2** is therefore 3-acetylerythrolide I.[2]

Compound **3** was isolated as a white amorphous powder. The IR spectrum showed strong absorbances characteristic of hydroxyl (3460 cm$^{-1}$), $\gamma$-lactone (1790 cm$^{-1}$), ester (1740 cm$^{-1}$), and $\alpha,\beta$-unsaturated ketonic (1692 cm$^{-1}$) functionalities. The $^1$H NMR spectrum of **3** revealed the presence of two oxymethine protons at $\delta$ 5.18 (1H, d, $J$ = 10.0 Hz, H-7) and 5.71 (1H, d, $J$ = 3.0 Hz, H-9). A trisubsubstituted double bond had an olefinic proton signal at $\delta$ 5.58 (1H,d, $J$ = 10.0 Hz, H-6) and associated carbon resonances at $\delta$ 143.2 (s) and 122.3 (d). There were $^1$H NMR signals for three acetoxy methyl groups at $\delta$ 2.24, 2.11, and 2.04. An oxymethylene group had a resonance at $\delta$ 4.48 (2H, s) while

* To whom correspondence should be addressed. Tel: (246) 417-4357. Fax: (246) 425-1327. E-mail: wtinto@uwichill.edu.bb.
† Department of Chemistry, Mona Campus.
‡ Deceased February 4, 1996.
§ Laboratory of Bioorganic Chemistry, Cave Hill campus.

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**Table 1.** $^{13}C$ and $^{1}H$ NMR Assignments for Compounds **1**−**3** ($J_{HH}$/Hz in Parentheses)

| | **1** | | **2** | | **3** | |
|---|---|---|---|---|---|---|
| carbon | $\delta_C$ | $\delta_H$ | $\delta_C$ | $\delta_H$ | $\delta_C$ | $\delta_H$ |
| 1 | 37.0 | | 37.0 | | 40.8 | |
| 2 | 85.6 | 4.15 (3.2) | 85.2 | 4.17 (4.0) | 63.7 | 2.70 (2.5) |
| 3 | 73.0 | 5.20 (m) | 73.2 | 5.19 (m) | 45.7 | 3.49 (6.0, 2.5) |
| 4 | 38.4 | 2.80 (15.8, 4.2) | 38.3 | 2.83 (15.8, 6.0) | 28.7 | 2.96 (16.0, 6.0) |
| | | 2.55 (15.8) | | 2.52 (15.8) | | 2.37 (16.0) |
| 5 | 138.5 | | 138.6 | | 143.2 | |
| 6 | 60.4 | 4.80 (1.8) | 60.7 | 4.79 (br s) | 122.3 | 5.58 (10.0) |
| 7 | 83.2 | 4.39 (1.8) | 83.2 | 4.44 (1.5) | 69.2 | 5.18 (10.0) |
| 8 | 82.9 | | 82.7 | | 81.6 | |
| 9 | 69.2 | 5.67 (2.0) | 70.7 | 5.73 (s) | 77.9 | 5.71 (3.0) |
| 10 | 41.6 | 3.21 (2.0) | 41.7 | 3.25 (s) | 41.4 | 3.57 (3.0) |
| 11 | 80.5 | | 80.5 | | 81.7 | |
| 12 | 194.3 | | 194.2 | | 195.0 | |
| 13 | 125.2 | 6.04 (10.4) | 125.4 | 6.05 (10.4) | 124.4 | 6.01 (10.5) |
| 14 | 153.4 | 6.83 (10.4) | 153.5 | 6.83 (10.4) | 153.3 | 6.67 (10.5) |
| 15 | 21.3 | 1.58 (s) | 21.1 | 1.53 (s) | 14.4 | 0.95 (s) |
| 16 | 122.3 | 5.60 (s) | 122.5 | 5.61 (s) | 67.6 | 4.48 (s) |
| | | 5.37 (s) | | 5.38 (s) | | 4.48 (s) |
| 17 | 48.3 | 2.57 (7.0) | 48.3 | 2.53 (7.0) | 43.9 | 2.48 (7.5) |
| 18 | 7.5 | 1.08 (7.0) | 7.7 | 1.13 (7.0) | 7.0 | 1.24 (7.5) |
| 19 | 174.4 | | 174.2 | | 175.9 | |
| 20 | 22.0 | 1.47 (s) | 21.9 | 1.47 (s) | 21.6 | 1.48 (s) |
| $OAc_1$ | 170.4 | | 170.3 | | 171.2 | |
| | 21.2 | 2.27 (s) | 21.3 | 2.21 (s) | 21.4 | 2.24 (s) |
| $OAc_2$ | 169.9 | | 170.1 | | 169.0 | |
| | 21.1 | 2.12 (s) | 21.1 | 2.13 (s) | 20.9 | 2.11 (s) |
| $OAc_3$ | 169.8 | | 170.0 | | 169.0 | |
| | 21.1 | 2.11 (s) | 20.3 | 2.12 (s) | 21.4 | 2.04 (s) |
| $(CO)OCH_2$− | | | 167.4 | | | |
| | | | 60.7 | 4.71 (s) | | |
| 8-OH | | | | | | 3.73 (s) |

an epoxide had two proton resonances at $\delta$ 2.70 (1H, d, $J$ = 2.5 Hz, H-2) and 3.49 (1H, dd, $J$ = 6.0, 2.5 Hz, H-3) with associated carbon resonances at $\delta$ 63.7(d) and 45.7 (d), respectively. The foregoing evidence indicated that compound **3** was the C-16 acetyl analogue of erythrolide H (**6**). A careful comparison of the $^{1}H$ and $^{13}C$ NMR data of compound **3** with those of **6** revealed that **3** had an additional acetoxy group.[2] The present study has revealed that the chemistry of *E. caribaeorum* from the northern Caribbean is quite similar to that obtained from the southern Caribbean.[3]

## Experimental Section

**General Experimental Procedures.** Infrared spectra were recored on a Pye-Unicam SP3 200 spectrometer and a Perkin-Elmer 1600 FTIR spectrometer in chloroform solutions. NMR spectra were recorded on a Bruker 200 MHz spectrometer in $CDCl_3$ solutions with TMS as internal standard.

**Animal Material.** Specimens of *E. caribaeorum* were collected off Discovery Bay, Jamaica, at −12 m in November 1991. The samples were identified by Dr. Jeremy D. Woodley, Centre for Marine Sciences, University of the West Indies, Mona, Jamaica, where a voucher specimen was lodged.

**Extraction and Isolation.** The animal material (528 g, wet weight) was macerated, extracted with acetone, and evaporated in vacuo to an aqueous suspension, which was taken up into EtOAc to yield a dark brown gum (10.9 g). A portion of the gum (7.0 g) was resolved by vacuum liquid chromatography on silica gel using hexane, $CH_2Cl_2$/EtOAc (1:1), and EtOAc successively as eluents. The fractions eluting with $CH_2Cl_2$/EtOAc (1:1) were further purified by repeated PLC on silica gel to give compounds **1**−**9**. Compounds **4**−**9** were identified by comparison of their $^{1}H$ and $^{13}C$ NMR spectra with literature data.[1−3]

**Compound (1)**: colorless glass (9.1 mg); IR $\nu_{max}$ 1788, 1740, 1689, 1380, 1220 $cm^{-1}$; $^{1}H$ and $^{13}C$ NMR data, see Table 1.

**Compound (2)**: white powder (6.1 mg); IR $\nu_{max}$ 1783, 1745, 1689, 1385, 1220 $cm^{-1}$; $^{1}H$ and $^{13}C$ NMR data, see Table 1.

**Compound (3)**: white powder (7.0 mg); IR $\nu_{max}$ 3460, 3025, 1790, 1740, 1692 $cm^{-1}$; $^{1}H$ and $^{13}C$ NMR data, see Table 1.

## References and Notes

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