Tetrahedron Letters, Vol. 34, No. 21, pp. 3371-3372, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

ERYTHRODIENE: A NEW SPIROBICYCLIC SESQUITERPENE OF A RARE SKELETAL CLASS FROM THE CARIBBEAN GORGONIAN CORAL *ERYTHROPODIUM CARIBAEORUM*

Charles Pathirana and William Fenical*

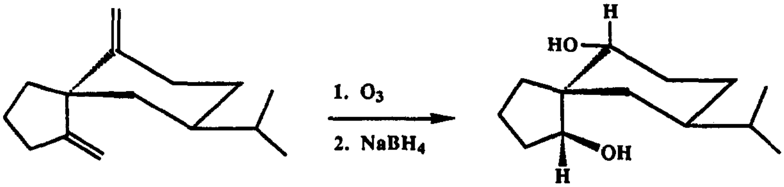
Scripps Institution of Oceanography
University of California at San Diego
La Jolla, CA 92093-0236

Ethan Corcoran and J. Clardy

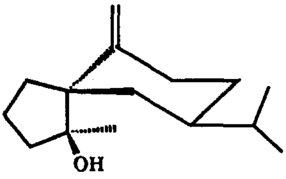
Department of Chemistry—Baker Laboratory
Cornell University
Ithaca, NY 14853-1301

Summary - Erythrodiene (1), a new sesquiterpene hydrocarbon of a rare structural class, has been isolated from the encrusting Caribbean gorgonian coral *Erythropodium caribaeorum*. The structure of the new compound was assigned on the basis of spectral studies and through an X-ray analysis of a reduced ozonolysis product, the diol 2.

The Caribbean gorgonian octocoral *Erythropodium caribaeorum* (Duchassaing & Michelloti) grows aggressively, forming thin sheets over hard corals to gain substrate.[1a] Despite their exposure and their lack of a hard coral's calcareous exoskeleton, these animals are relatively free of predation.[1b] As part of our interest in the chemical adaptations of this group of soft-corals, we recently investigated the chemical basis for predator avoidance of *E. caribaeorum*.[1c] The majority of the deterrence noted toward predatory reef fishes was derived from a mixture containing two chlorine-containing diterpenoids, erythrolides B and D. While the non-polar fractions were inactive, it was noted that a single sesquiterpene hydrocarbon, erythrodiene (1), comprised over 60% of these mixtures. We now wish to report the structure determination of this compound as a member of a rare spirobicyclo[5.4]decane terpenoid skeleton. The first terrestrial example of this class, spirojatamol (3), was recently discovered in root extracts of the roots of the Indian medicinal plant *Nardostachys jatamansi*.[2] Erythrodiene, the first marine hydrocarbon representative of this structure class, possesses the identical relative stereochemistry as that observed in spirojatamol.



1, erythrodiene **2**



3, spirojatamol

Erythrodiene (1) was isolated by standard silica vacuum flash chromatography, and subsequent silica HPLC, from the condensed CH_2Cl_2 extracts of *E. caribaeorum* collected at Chub Cay, Bahamas, in June, 1989. Erythrodiene was analysed for $C_{15}H_{24}$ by combined HRMS and ^{13}C NMR methods. The molecular formula and the observation of four olefinic carbons in the ^{13}C NMR spectrum of erythrodiene, showed that the new sesquiterpene possessed two carbocyclic rings. The observed double bonds were assigned as terminal exocyclic olefins on the basis of their ^{1}H and ^{13}C NMR characteristics.[3] In addition, ^{1}H NMR COSY experiments illustrated that two methyl doublets (δ 0.89 and 0.86), each showing $J = 7$ Hz couplings, were coupled to a one-proton multiplet at δ 1.45. On the basis of this observation, erythrodiene possessed an isopropyl group.

The spectral data, although clear, did not suggest that erythrodiene belonged to a common sesquiterpenoid group. In an attempt to prepare a crystalline derivative, erythrodiene was ozonized and the resulting crude ketone mix reduced with $NaBH_4$ in methanol to yield the crystalline diol 2. The diol showed typical spectral characteristics,[4] but failed to yield significant structural data from its NMR spectra. However, since diol 2 was crystalline, the structure was solved by X-ray methods.

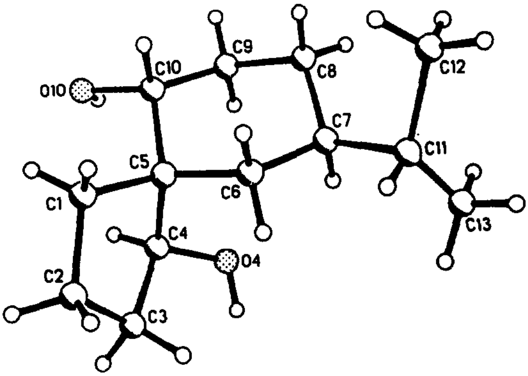


Figure. Computer-generated drawing of diol 2.

Diol 2 crystallized from $CHCl_3$ in space group $P2_12_12_1$ with $a = 6.385(1)$, $b = 10.908(2)$, $c = 17.987(3)$ and one molecule of $C_{13}H_{24}O_2$ per asymmetric unit. A total of 1014 independent reflections were measured using Cu K$\bar{\alpha}$ and $2\theta:\theta$ scans between $0° \leq 2\theta \leq 116°$, and 1008 (99%) were judged observed ($|F_o| \geq 3\sigma(|F_o|)$). The structure was successfully solved and refined with anisotropic heavy atoms and riding hydrogens to a final R-factor of 7.5%. Coordinates have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgements

This research is a result of financial support from the National Science Foundation, Chemistry and Oceanography Divisions, under grant CHE90-08621 to WF and New York State Sea Grant to JC. We also appreciate receiving NSF ship support funding for the operation of the research vessel *Columbus Iselin*.

References

1. a) Bayer, F. M.,*The Shallow Water Octocorallia of the West Indian Region*, Nijhoff, The Hague, **1961**, 373 pp.; b) Pawlik, J. R., Burch, M. T., Fenical, W., *J. exp. mar. Biol. Ecol.*, **108**, 55, (1987); c) Fenical, W., Pawlik, J. R., *Mar. Ecol. Prog. Ser.*, **75**, 1 (1991).

2. Bagchi, A., Oshima, Y., Hikino, H., *Tetrahedron*, **46**, 1523, (1990).

3. For erythrodiene (1): an oil, $[\alpha]_D = -30.8°$ (c 0.24, $CHCl_3$); LREIMS *m/z* 204 (M^+), 189 (23), 161 (66), 133 (56), 105 (57), 97 (75), 91 (85), 83 (76), 79 (50), 71 (81), 69 (89), 57 (100), 43 (65); HREIMS : M^+ *m/z* = 204.1851 calc. for $C_{15}H_{24}$ 204.1879; ^{1}H NMR (360 MHz, $CDCl_3$) δ 4.97 (s, 1H), 4.87 (s, 1H), 4.79 (s 1H), 4.75 s 1H), 2.40 (m, 2-3H), 2.28 (m), 2.1 (m), 1.8 (m), 1.7 (m), 1.6 (m), 1.45 (m), 1.10 (m), 0.92 (m, 1H), 0.89 (d, $J = 7$ Hz, 3H), 0.85 (d, $J = 7$ Hz, 3H); ^{13}C NMR (50 MHz; $CDCl_3$): δ 158.0 C, 152.8 C, 106.7 CH2, 109.9 CH2, 51.3 C, 41.1 C, 39.7 CH, 39.6 CH2, 33.8 CH2, 33.0 CH2, 32.5 CH, 31.1 CH2, 20.8 CH3, 20.1 CH3, 19.7 CH3.

4. For synthetic diol 2: IR (film) 3400, 2959, 2980, 1750, 1450, 1370 cm^{-1}; LREIMS *m/z* 194, $M^+ - H_2O$, 176, $M^+ -2H_2O$, 133, 107, 91, 67 amu; ^{1}H NMR (360 MHz, $CDCl_3$): δ 4.30 (m, 1H), 3.49 (dd, 1H), 1.4 - 2.1 (m, 14 H), 0.92 (d, $J = 7$ Hz, 3H), 0.88 (d, $J = 7$ Hz).

(Received in USA 15 February 1993)