hydrogen atoms in the ^{1}H NMR and the presence of the eight required resonance absorptions in the ^{13}C NMR.[9]

The ultraviolet spectrum has no maximum above 200 nm (λ 230 nm: $\epsilon = 1160$ in acetonitrile).[10] The photoelectron spectrum shows three ionization bands at 8.1$_5$, 8.3$_5$, and 9.2 eV, closely spaced in comparison to those shown by *trans*-hexa-1,3,5-triene (8.3, 10.2$_5$, and 11.9 eV).[11] Both observations are in excellent agreement with the prediction that **1** is close to being a "perpendicular triene".

For the purpose of assessing the thermochemical consequences of orthogonality by studying heats of hydrogenation, the parent hydrocarbon bicyclo[5.3.2]dodeca-1,6,11-triene has the advantage of giving only a single perhydro derivative. This triene has now been prepared following closely the scheme developed for **1**, starting with acetylene instead of dimethylacetylene in the photochemical step. Support for its structure comes from the ^{1}H NMR spectrum, in which two new vinyl hydrogen atoms appear as a singlet [6.38 (s, 2 H)] in place of the two methyl groups of **1**[12] while the rest of the spectrum remains essentially unchanged.

Acknowledgment. We express our deep appreciation to Dr. James K. Bashkin and Jeremy M. Berg of this department for their skillful assistance in resolving the X-ray crystallographic data for **7** and our gratitude to the Norman Fund in Organic Chemistry for its support of J.C.S. in this work.

Supplementary Material Available: Thermal ellipsoid diagram, crystallographic data, and bond lengths and angles for compound **7** (5 pages). Ordering information is given on any current masthead page.

---

(9) IR (film) 3030 (C—H), 1660 (C═C) cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 5.18 (dd, 2 H, J = 5.5, 10.2 Hz), 1.79–2.26 (m, 9 H), 1.76 (s, 6 H), 1.56–1.70 (m, 1 H), 1.42–1.53 (m, 1 H), 1.00–1.12 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ 145.5 (s), 133.2 (s), 124.5 (d), 33.8 (t), 31.5 (t), 30.2 (t), 24.4 (t), 15.6 (q); ms, *m/e* 188.15649 (*m/e* calcd for $C_{14}H_{20}$ 188.15649).

(10) For comparison (*Z*,*Z*,*Z*)-1,3,5-cyclononatriene has λ_{max} 296 nm (ϵ = 4010, cyclohexane) [Glass, D. S.; Watthey, J. W. H.; Winstein, S. *Tetrahedron Lett.* **1965**, 377–383].

(11) The details of the PES will be published elsewhere by Professor Edgar Heilbronner to whom we express our gratitude for his active interest.

(12) IR (film) 3020 (C—H), 1650 (C═C) cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 6.38 (s, 2 H), 5.39 (dd, 2 H, J = 5.2, 10.6 Hz), 2.27–2.41 (m, 2 H), 2.10–2.18 (m, 2 H), 1.87–2.01 (m, 5 H), 1.11–1.71 (m, 3 H); ms, *m/e* 160 (calcd for $C_{12}H_{16}$ 160).

Erythrolides: Unique Marine Diterpenoids Interrelated by a Naturally Occurring Di-π-methane Rearrangement

Sally A. Look and William Fenical*

Institute of Marine Resources
Scripps Institution of Oceanography
La Jolla, California 92093

Donna Van Engen and Jon Clardy*

Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, New York 14853

Received November 23, 1983
. *Revised Manuscript Received April 9, 1984*

As part of a research program emphasizing the characterization of biologically active, novel compounds from marine sea fans and whips (Cnidaria, Octocorallia), we have recently concluded an investigation of the encrusting Caribbean octocoral *Erythropodium caribaeorum* (Duchassaing and Michelotti) (family Anthothelidae).[1,2] Unlike other organisms within this group, *E. caribaeorum* lacks the characteristic fan or tree shape of related octocorals and grows in shallow-water reef habitats as encrusting sheets exposed on rock and coral surfaces.[2] In this communication, we report the structures of two new chlorinated diterpenoids, **1** and **2**, from this source. Erythrolide A (**1**) appears to be produced in nature from diterpenoid **2** by a di-π-methane rearrangement.[3] This is the first observation of this photochemical rearrangement in the production of natural products.[4]

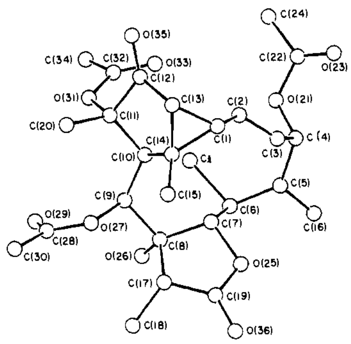
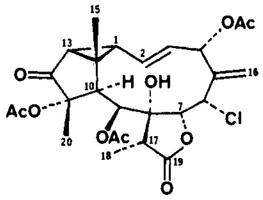
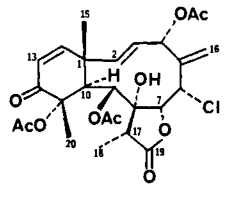


Figure 1. A computer-generated perspective drawing of erythrolide A. The absolute stereochemistry is C-1 *S*, C-4 *S*, C-6 *S*, C-7 *R*, C-8 *R*, C-9 *S*, C-10 *S*, C-11 *S*, C-13 *R*, C-14 *R*, and C-17 *R*.

Conventional chromatographic methods yielded pure samples of erythrolide A (**1**),[5] and erythrolide B (**2**),[6] from the CHCl$_3$ extract of *E. caribaeorum*. Erythrolide A was analyzed for $C_{26}H_{31}O_{10}Cl$ by high-resolution mass spectrometry, and its spectral properties suggested a structural similarity with the briarein diterpenoids recently reported from sea pens and other related octocorals.[7] The combined spectral data for **1** indicated the presence of three acetates, one ketone, a γ-lactone, two double bonds, and a single chlorine. These data combined with the molecular formula of **1** required erythrolide A to have a tricyclic carbon skeleton.



1



2

Insight into the gross structure of **1** was gained by a close examination of ^{13}C NMR data. A shielded quaternary carbon was observed at δ 28.7, suggesting the presence of a cyclopropane ring. From a gated decoupling experiment two signals at δ 37.4 (d) and 39.8 (d) were confidently assigned to a cyclopropane on the basis of their characteristically large J_{CH} values of 158.9 and 164.3 Hz. ^{1}H NMR experiments at 360 MHz yielded connectivity data for carbons 13 and 1, 1–7, and 9 and 10. On the basis of this information, structure **1**, without stereochemistry, was proposed for erythrolide A.

---

(1) This organism was collected (−20 m) at Carrie Bow Cay, Belize, in March, 1980, and April, 1981.

(2) Bayer, F. M. "The Shallow Water Octocorallia of the West Indian Region"; Nijhoff: The Hague, 1961.

(3) For a review, see: Hixon, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531.

(4) Pettus and Moore have pointed out (Pettus, J. A., Jr.; Moore, R. E. *J. Am. Chem. Soc.* **1971**, *93*, 3087–3088 and references therein) that dictyopterene A could plausibly have been formed by a di-π-methane rearrangement of *cis*,*trans*-1,4,6-undecatriene. However, this precursor has not been reported from *Dictyopteris*, nor have photochemical experiments been reported.

(5) Spectral data for Erythrolide A have been deposited as supplementary material.

(6) Spectral data for Erythrolide B have been deposited as supplementary material.

(7) (a) Burks, J. E.; van der Helm, D.; Chang, C. Y.; Ciereszko, L. S. *Acta Crystallogr. Sect. B.* **1977**, *B33*, 704. (b) Wratten, S. J.; Fenical, W.; Faulkner, D. J.; Wekel, J. C. *Tetrahedron Lett.* **1977**, *18*, 1559. (c) Wratten, S. J.; Faulkner, D. J.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1977**, *99*, 2824. (d) Grode, S. H.; James, T. R.; Cardellina, J. H., II. *Tetrahedron Lett.* **1983**, *24*, 691. (e) Ravi, B. N.; Marwood, J. F.; Wells, R. J. *Aust. J. Chem.* **1980**, *33*, 2307. (f) Grode, S. H.; James, T. R.; Cardellina, J. H., II. *J. Org. Chem.* **1983**, *48*, 5203.

0002-7863/84/1506-5026$01.50/0

The structure of **1**, which included the absolute stereochemistry at 11 chiral centers, was obtained by X-ray crystallographic methods (Figure 1).[8] The rearranged structure and the presence of the 2-ketobicyclo[3.1.0]hexane fragment suggested that **1** may have been photochemically produced from a cyclohexenone precursor. To pursue this notion, the remaining metabolites of *E. caribaeorum* were examined. Erythrolide B (**2**), another major metabolite, was readily recognized[6] to possess a cyclohexenone group and thus to be a potential precursor of **1**. Irradiation of **2** under a variety of conditions[9] yielded **1** as the sole product. Working backward from the secure structure of **1** to assign the structure of **2** showed that the photochemical interconversion did *not* involve a typical cyclohexenone rearrangement but was instead consistent with a di-π-methane rearrangement.[10]

The possibility that erythranes **1** and **2** were artifacts of isolation was explored. Samples of fresh *E. caribaeorum* were extracted immediately following their collection from several habitats and locales. TLC analysis of the extract consistently showed **1** and **2** as the major components. While we cannot completely rule out the possibility that the conversion of **2** to **1** is an enzyme-mediated process, the measured half-life for the sunlight-induced conversion[9] is consistent with a slow photochemical process occurring within the illuminated tissues of *E. caribaeorum*.[12]

Acknowledgment. This report is contribution No. 129 of the IMSWE (Inshore Marine Shallow Water Ecosystem) Reef and Mangrove Investigation in Carrie Bow Cay, Belize. The IMSWE program is sponsored by the Smithsonian Institution and supported, in part, by the Exxon Corp. We thank Dr. Klaus Reutzler, program director, for the kind invitation to participate. Mass spectra were kindly provided by the Mass Spectrometry Resource Center, School of Pharmacy, University of California, San Francisco (A. L. Burlingame, Director) which is supported by NIH Grant RR00719. Support for this research at the Scripps Institution was kindly provided by the National Science Foundation, Chemistry Division, under Grant CHE81-11907. Research at Cornell University was supported by the NIH both through a training grant to D.V.E. and through Grant CA24487 to J.C. and by the New York State Sea Grant Program. We wish to thank Dr. Frederick M. Bayer at the Smithsonian Institution for his identification of *E. caribaeorum*.

Registry No. 1, 89999-14-4; **2**, 89999-15-5; **3**, 89999-16-6.

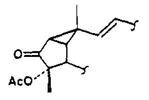
Supplementary Material Available: Description of the X-ray diffraction determination of **1**, tables of fractional coordinates, thermal parameters, bond distances, bond angles, and observed and calculated structure factors, and spectral data for **1** and **2** (20 pages). Ordering information is given on any current masthead page.

---

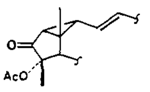
[8] We suggest the name "erythrane" and the numbering shown in **1** for this new rearranged diterpenoid skeleton. Experimental details and results of the X-ray diffraction experiment have been deposited as supplementary material.

[9] Irradiation of **2** in benzene (quartz) using a medium-pressure Hg lamp yielded **1** (87% conversion in 3 h). Irradiation of **2** in 5% methanolic seawater (glass) with sunlight yielded **1** (37% conversion in 8 days).

[10] A typical cyclohexenone photorearrangement of **2**, i.e., C-2 to C-4 and C-3 to C-5 bonding (cyclohexenone numbering), would be expected to yield partial structure i. The conversion of **2** to partial structure ii indicates the participation of the C-2–C-3 olefinic bond in a di-π-methane rearrangement with the C-13, C-14 olefin.[11]



i



ii

[11] The di-π-methane rearrangement is also classified as a photochemically allowed ${}_{\sigma}2_a + {}_{\pi}2_a$ cycloaddition reaction: see: Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie GmbH, Academic Press: NewYork, 1970.

[12] Most octocorals found in the Caribbean Sea contain symbiotic algae known as "zooxanthellae", which, through photosynthesis and carbon transfer, provide a large portion of the nutrient requirements of the octocoral. Hence, for proper nutrition and growth the octocorals must occupy habitats exposed to sunlight.

Evidence for a Single Transition State in the Intermolecular Transfer of a Sulfonyl Group between Oxyanion Donor and Acceptors[1]

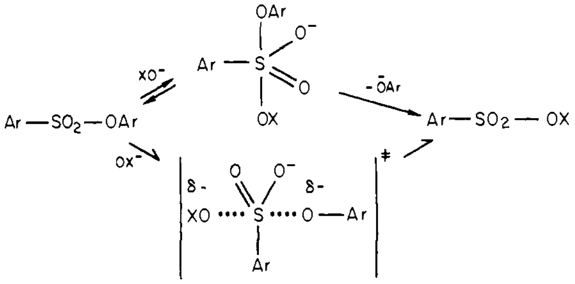
Peter D'Rozario, Richard L. Smyth, and Andrew Williams*

University Chemical Laboratories
Canterbury, Kent, England

Received February 23, 1984

We describe a linear Brønsted-type relationship for the transfer of a sulfonyl group to a series of oxyanions with basicities both smaller and larger than the donor 4-nitrophenolate group. This evidence is consistent with a mechanism with only one transition state which must therefore be concerted.

Displacement reactions of oxyanions with a sulfonate ester yield a symmetrical reaction when the difference between donor and acceptor basicities (ΔpK) is zero. If a stepwise mechanism (eq 1) is followed, a change in rate-limiting step should occur as the acceptor becomes more or less basic than the leaving 4-nitrophenolate ion. A nonlinear Brønsted relationship with a break at $\Delta pK = 0$ is thus expected for the stepwise mechanism which has two electronically distinct transition states. A concerted process, with a single transition state, will give a linear or gently curving Brønsted correlation. Whereas we can predict the breakpoint in the present reaction for the stepwise process, this is not possible for previous studies of sulfonyl group transfer.[2a-d] Recent work where the breakpoint pK can be predicted and is spanned by the pK's of a range of similar nucleophiles is that on the related but completely distinct phosphoryl ($-PO_3^{2-}$)[2e,f] and sulfate ($-SO_3^-$)[2g] group-transfer reactions.



(1)

The reactivity of oxyanions with 4′-nitrophenyl 4-nitrobenzenesulfonate obeys the equation $\log k_{XO^-}/q = (0.64 \pm 0.11)(pK_{XOH} + \log(p/q)) - (7.8 \pm 0.3)$ ($r = 0.986$). Acetate ion, succinate dianion, and hexafluoroisopropoxide ion are very close in reactivity to phenolate ions of similar pK, and it is therefore assumed that trifluoroethoxide ion, which fits the line, should also be included in the correlation. Ortho fluorine substituents are assumed to have similar steric requirements to hydrogen; increase in steric factors could only reduce the reactivity of the two fluorine-substituted phenols. In several diverse reactions, under conditions where only one transition state is involved throughout, carboxylate, phenolate, and alcoholate leaving groups fit a single linear free energy relationship.[3] It is usually unsafe to use a multiplicity of structural types in a linear free energy relationship but oxyanions excluding α-effect nucleophiles and sterically hindered species should be sufficiently well-behaved to reveal changes in transition-state structure caused by a change in rate-limiting step.

---

[1] We are grateful to the S.E.R.C. and N.A.T.O. (RG 115.80) for support of this work.

[2] (a) Suttle, N. A.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1563. (b) Deacon, T.; Farrar, C. R.; Sikkel, B. J.; Williams, A. *J. Am. Chem. Soc.* **1978**, *100*, 2525. (c) Kice, J. L.; Legan, E. *Ibid.* **1973**, *95*, 3912. (d) Deacon, T.; Steltner, A.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1778. (e) Skoog, M. T.; Jencks, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 3356. (f) Bourne, N.; Williams, A.; *Ibid.* **1983**, *105*, 3357. (g) Hopkins, A. Bourne, N.; Williams, A. *Ibid.* **1983**, *105*, 3358.

[3] (a) Gerstein, J.; Jencks, W. P. *J. Am. Chem. Soc.* **1964**, *86*, 4655. (b) Jencks, W. P.; Gilchrist M. *Ibid.* **1964**, *86*, 4651. (c) Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1244. (d) Kirby, A. J.; Varvoglis, A. G. *J. Am. Chem. Soc.* **1967**, *89*, 415.

0002-7863/84/1506-5027$01.50/0