

tetrahydrofuran ring is in the envelope (C_2) conformation with C-11 as the flap. The molecular conformation observed in the solid state orients all of the isocyano groups on the same face of the molecule.

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Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances, bond angles, and torsional angles from the X-ray diffraction study of kalihinol F (11 pages). Ordering information is given on any current masthead page.

Zoanthamine: A Novel Alkaloid from a Marine Zoanthid

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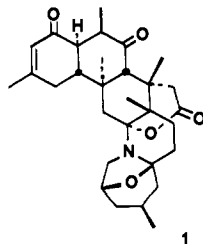
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The chemical constituents of the colonial zoanthid *Zoanthus* sp.¹ were investigated as part of a program to study toxic marine organisms from the Visakhapatnam coast of India. The colonial zoanthids, which occur as dense mats on intertidal rocks, can eject jets of water when they are disturbed. If the spray comes in contact with a victim's eyes, it causes tears followed by prolonged redness and pain.² A preliminary investigation of extracts of the whole organism has revealed the presence of a series of novel alkaloids. In this communication we report the structural determination of zoanthamine (1), the first member of the new class of alkaloids.



The ether-soluble material from an ethanolic extract of the homogenized animals was chromatographed on silica gel. The fractions eluted with 20% ethyl acetate in benzene contained zoanthamine (1, 9×10^{-4} % dry weight) that was crystallized from methanol. More polar fractions have yielded two additional alkaloids that will be reported elsewhere.

(1) The animals may be a new species of *Zoanthus*. They were first identified as *Z. sociatus*, but this species is regarded as being restricted to the Caribbean. Specimens are available from either Andhra University or Scripps Institution of Oceanography.

(2) The effects can last up to a week. Several collectors have experienced these irritant effects, and they recommend caution when handling zoanthids from any location.

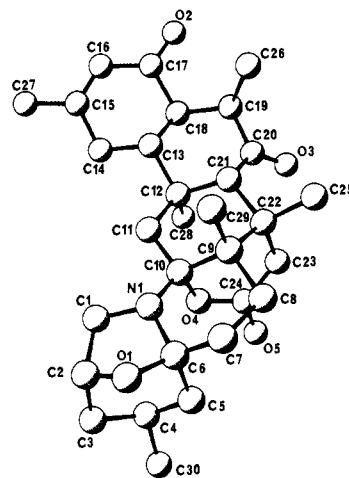


Figure 1. Computer-generated perspective drawing of zoanthamine (1).

Zoanthamine (1), $[\alpha]_D + 18^\circ$ (c 0.48 CHCl_3), was obtained as a white crystalline solid, mp 306–308 °C. The molecular formula, $\text{C}_{30}\text{H}_{41}\text{NO}_5$, was indicated by mass measurement and by the off-resonance decoupled ^{13}C NMR spectrum.³ An initial analysis of the ^{13}C NMR data of zoanthamine (1) revealed the presence of a ketone [δ 212.0 (s)], an α,β -unsaturated ketone [δ 197.2 (s), 159.9 (s), and 126.8 (d)], and an ester [δ 172.5 (s)]. The molecular formula required that zoanthamine (1) be heptacyclic and have both a fully substituted nitrogen atom and an ether linkage. The signal at δ 101.6 (s) in the ^{13}C NMR spectrum was assigned to a carbon atom bearing either two oxygen atoms or oxygen and nitrogen atoms. A search of the literature revealed that this molecule was unrelated to any known alkaloid structure.

Zoanthamine (1) crystallized in the orthorhombic crystal class with diffractometer-measured lattice constants of $a = 11.775$ (5) Å, $b = 13.88$ (1) Å, and $c = 15.877$ (6) Å. Systematic extinctions, crystal density, and optical activity were uniquely accommodated by space group $P2_12_12_1$ with one molecule of molecular weight 495 ($\text{C}_{30}\text{H}_{41}\text{NO}_5$) forming the asymmetric unit. All unique diffraction maxima with $2\theta \leq 114^\circ$ were collected on a computer-controlled four-circle diffractometer using graphite monochromated $\text{Cu K}\alpha$ radiation (1.541 78 Å) and variable-speed 1° ω -scans. Of the 2019 unique reflections measured in this fashion, 1677 (83%) were judged observed ($|F_o| \geq 3\sigma(F_o)$) after correction for Lorentz, polarization, and background effects.⁴ A phasing model was found using a multisolution tangent formula approach and tangent formula recycling of a plausible molecular fragment.⁵ Eventually all 36 non-hydrogen atoms of zoanthamine were located. The attribution of atoms types was not a simple task. Initial assignments of heteroatoms were made on the basis of the behavior of the thermal parameters and consideration of molecular geometry. They were ultimately confirmed by refining several alternative models and location of hydrogen atoms in a difference synthesis. Block-diagonal least-squares refinements with aniso-

(3) $[\alpha]_D + 18^\circ$ (c 0.4, CHCl_3); IR (CHCl_3) 1720 (br), 1660 cm^{-1} ; UV (CH_2CN) 233 nm (ϵ 11 000); ^1H NMR (CDCl_3) see text; ^{13}C NMR (CDCl_3) δ 212.0 (s), 197.2 (s), 172.5 (s), 159.9 (s), 126.8 (d), 101.6 (s), 89.9 (s), 74.2 (d), 53.8 (d), 48.0 (d), 48.0 (d), 47.2 (t), 45.8 (d), 44.4 (t), 41.9 (t), 40.1 (s), 39.5 (s), 38.8 (t), 35.9 (t), 35.9 (s), 30.6 (t), 29.9 (t), 24.5 (d), 23.7 (t), 22.9 (q), 21.8 (q), 20.7 (q), 18.4 (q), 18.3 (q), 13.8 (q); HRMS, obsd $m/z = 495.2969$, $\text{C}_{30}\text{H}_{41}\text{NO}_5$ requires 495.2985.

(4) All crystallographic calculations were done on a PRIME 850 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were: Leonowicz, M. E.; REDUCE and UNIQUE, data reduction programs, Cornell University, Ithaca, NY, 1978. Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M., MULTAN 78, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson syntheses), University of York, England, 1978. Hirotsu, K.; Arnold, E., BLS78A, an anisotropic block diagonal least-squares refinement, Cornell University, Ithaca, NY, 1980. Motherwell, W. D. S., PLUTO78, a crystallographic illustration program, Cambridge Crystallographic Data Centre, 1978. Hirotsu, K., BOND, a program to calculate molecular parameters and prepare tables, Cornell University, Ithaca, NY, 1978.

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tropic non-hydrogen atoms and isotropic hydrogens have converged to a standard crystallographic residual of 0.058 for the observed reflections. Additional crystallographic details are available and are described in the supplementary material.

Figure 1 is a computer-generated perspective drawing of the final X-ray model of zoanthamine. Hydrogens are omitted for clarity, and, since the absolute configuration was not determined, the enantiomer shown is an arbitrary choice.

The spectral data for zoanthamine (1)³ are all compatible with the proposed structure. The ¹H NMR spectrum was assigned from decoupling data as follows: δ 0.92 (d, 3 H, *J* = 7 Hz, C-30), 0.98, 1.00, 1.20 (all s, 3 H, C-25, C-28, C-29), 1.10 (t, 1 H, *J* = 13 Hz, C-5), 1.17 (d, 3 H, *J* = 7 Hz, C-26), 1.48 (ddd, 1 H, *J* = 13, 12, 2 Hz, C-3), 1.56 (br, dd, 1 H, *J* = 12, 4 Hz, C-3), 1.55-1.90 (m, 4 H, C-7, C-8), 1.92 (d, 1 H, *J* = 14 Hz, C-11), 2.01 (s, 3 H, C-27), 2.10 (dd, 1 H, *J* = 13, 4 Hz, C-5), 2.17 (d, 1 H, *J* = 14 Hz, C-11), 2.23 (m, 2 H, C-14), 2.27 (m, 1 H, C-4), 2.37 (d, 1 H, *J* = 20 Hz, C-23), 2.42 (m, 1 H, C-13), 2.66 (dd, 1 H, *J* = 13, 5 Hz, C-18), 3.02 (qd, 1 H, *J* = 7, 5 Hz, C-19), 3.22 (s, 1 H, C-21), 3.24 (dd, 1 H, *J* = 7, 6 Hz, C-1), 3.29 (br d, 1 H, *J* = 7 Hz, C-1), 3.67 (d, 1 H, *J* = 20 Hz, C-23), 4.56 (m, 1 H, C-2), 5.92 (s, 1 H, C-16).

Zoanthamine (1) is the first example of a new class of alkaloids of unknown biosynthetic origin. Although there are some elements that suggest a triterpenoid origin, the carbon skeleton is far from a normal polyisoprenoid system. Two related metabolites have been isolated from the same organism and will be described in a future paper.⁶

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Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances, bond angles, and torsional angles for zoanthamine (1) (8 pages). Ordering information is given on any current masthead page.

(6) Zoanthamine was inactive as a skin irritant⁷ and is being reisolated for screening as an eye irritant.

(7) We thank Dr. Robert S. Jacobs, U. C. Santa Barbara, for these data.

Electron Transfer in Mixed-Valence, Oxo-Centered, Trinuclear Iron Acetate Complexes: Effect of Statically Disordered to Dynamically Disordered Transformation in the Solid State

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During the last decade there has been considerable interest in mixed-valence transition-metal complexes.^{1,2} In the case of many such complexes the electron-transfer rate for a *solution-state* species has been determined indirectly and to some degree qualitatively by analyzing the energy and line shape of the intervalence-transfer (IT) electronic absorption band in the near-IR. For certain mixed-valence complexes such as mixed-valence bi-

(1) "Mixed-Valence Compounds, Theory and Applications in Chemistry, Physics, Geology, and Biology"; Brown, D. B., Ed.; Reidel Publishing Co.: Boston, 1980.

(2) Day, P. *Int. Rev. Phys. Chem.* **1981**, *1*, 149.

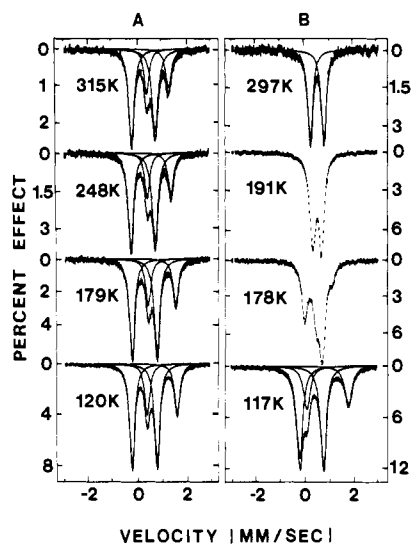


Figure 1. Variable-temperature ⁵⁷Fe Mössbauer spectra for [Fe₃O(O₂CCH₃)₆(py)₃] (left panel) and [Fe₃O(O₂CCH₃)₆(py)₃](py) (right panel).

ferrocenes³⁻⁷ the electron-transfer rate in the *solid state* has been characterized relatively directly with various spectroscopic and physical techniques. In this communication we report several observations that strongly suggest that electron-transfer rates for mixed-valence complexes in the *solid state* are determined, at least in part, by dynamic disorder of coordinated ligands or solvate molecules.

The mixed-valence, oxo-centered, basic iron acetates with general composition [Fe₃O(O₂CR)₆(base)₃](solvate) have been characterized^{8,9} to have appreciable electron-transfer rates in spite of weak antiferromagnetic exchange interactions. Our observations on these complexes and the results of single-crystal X-ray structures of [Fe₃O(O₂CCH₃)₆(4-Etpy)₃](4-Etpy) (1) at 163 and 298 K are summarized herein.

One of the two main discoveries that we made concerning the basic iron acetates is that the solvate molecule has a dramatic effect on the electron-transfer rate for a given mixed-valence complex. Several new series (different substituted pyridines used for each series) of trinuclear iron acetates have been prepared in which only the solvate molecule differs. For example, in the series [Fe₃O(O₂CCH₃)₆(py)₃](solvate), the solvate molecule can be pyridine (py), benzene, or nothing. As can be seen in Figure 1, the variable-temperature ⁵⁷Fe Mössbauer characteristics of [Fe₃O(O₂CCH₃)₆(py)₃] and [Fe₃O(O₂CCH₃)₆(py)₃](py) are different. All of the mixed-valence iron acetates give a Mössbauer spectrum at temperatures of ~100 K or lower that is characteristic of a localized electronic structure with one Fe^{II} ion and two Fe^{III} ions. The nonsolvated complex does *not* show any evidence of a change in the electron-transfer rate as the temperature is increased to 315 K. On the other hand, in the case of the pyridine solvate complex the electron-transfer rate increases as the tem-

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