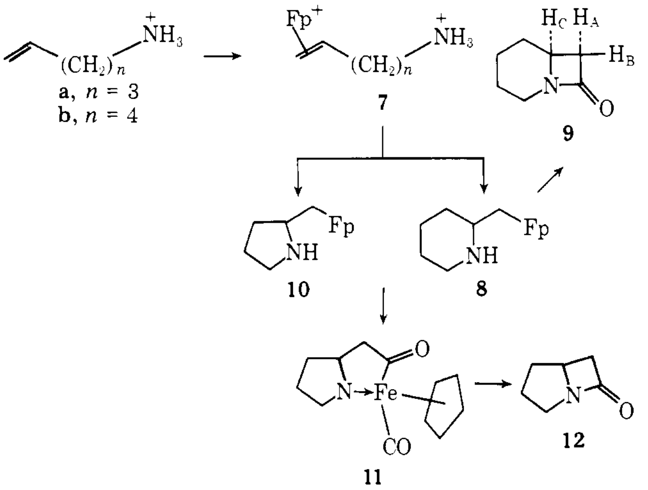
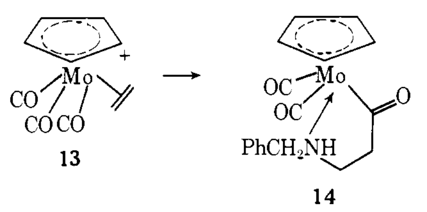
with tri-*n*-butylamine followed by potassium *tert*-butoxide gave the piperidine complex **8**, which was converted with Ag_2O (THF, 65 °C, 20 h) to the lactam **9** in 30% overall yield from the uncomplexed olefin: IR 1755 cm^{-1}; NMR ($CDCl_3$) δ 3.8 (dd, 1, J_{ab} = 14 Hz, J_{ac} = 2 Hz, H_A).[13]

A similar sequence, employing 1-pentenylammonium tetrafluoroborate gave the pyrrolidine complex **10**. An attempt to convert this directly to β-lactam by oxidation led instead to a polyamide (ν_{CO} 1590 cm^{-1}) due to the high reactivity of this lactam. However, when **10** was heated in THF for 4 h in the presence of 10 molar % of triphenylphosphine, it was smoothly converted to the chelate (**11**, ν_{CO} 1620, 1930 cm^{-1}) in 80% yield. Treatment of this with freshly precipitated Ag_2O for 5 min at 25 °C led to the disappearance of chelate carbonyl absorptions and formation of β-lactam (**12**) (ν_{CO}(THF) 1775 cm^{-1}).[14] Initial attempts to isolate this substance have led to polymerization.



Finally, these transformations are not confined to iron complexes. The closely related group 6 metal–ethylene complexes are known to add amines with ease.[15] Thus the molybdenum–ethylene complex (**13**) smoothly adds benzylamine, affording the chelate complex (**14**) directly in 90% yield. Preliminary experiments show that oxidation of this substance with Ag_2O gives the β-lactam (**3a**) in 10% yield.



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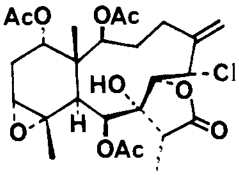
Stylatulide, a Sea Pen Toxin

Sir:

The sea pen *Stylatula* sp.[1] is a slender, whip-like coelenterate which was collected in the intertidal zone at Isla Partida, Gulf of California. The bioluminescent properties of *S. elongata* and other sea pens have been investigated,[2] but there are no other reports of secondary metabolites from sea pens. We found that extracts of *Stylatula* were toxic to larvae of the copepod *Tisbe furcata johnsonii*. We wish to report the structure of stylatulide (**1**), the major toxic metabolite of *Stylatula* sp.

Florisil chromatography of an acetone extract of homogenized *Stylatula* resulted in the isolation of one major (0.8% of dry weight) and five minor metabolites. The major metabolite, stylatulide (**1**), crystallized from 1:1 hexane:dichloromethane, mp 179–181 °C, $[\alpha]_D$ +65° (*c* 1.8). Stylatulide (**1**) had the molecular formula $C_{26}H_{35}O_{10}Cl$.[3] The ^1H NMR spectrum contained three acetate signals at δ 1.95, 2.00, and 2.27 ppm which, together with an IR band at 1740 cm^{-1}, indicated that stylatulide was a diterpene triacetate. The IR spectrum also contained bands at 3500 cm^{-1} (hydroxyl) and 1780 cm^{-1} (γ-lactone). All signals in the richly detailed ^1H NMR spectrum have been assigned: δ ($CDCl_3$) 1.10 (3 H, s, 15-H), 1.29 (3 H, s, 20-H), 1.31 (3 H, d, J = 7 Hz, 18-H), 1.70 (1 H, m, 3-H), 2.10 (1 H, d, J = 18 Hz, 13-H), 2.27 (1 H, m, 13-H), ~2.4 (2 H, m, 4-H), 2.59 (1 H, m, 3-H), 2.97 (1 H, d, J = 4 Hz, 12-H), 3.04 (1 H, s, 10-H), 3.18 (1 H, q, J = 7 Hz, 17-H), 3.36 (1 H, s, -OH), 4.63 (1 H, td, 6-H), 4.71 (1 H, d, J = 4 Hz, 7-H), 4.90 (1 H, d, J = 6.5, 14-H), 5.50 (1 H, s, 9-H), 5.79 (1 H, bs, 16-H), 5.93 (1 H, d, J = 9, 2-H) and 6.00 (1 H, bs, 16-H). The structure of stylatulide (**1**) was determined by single-crystal x-ray diffraction analysis.



1

Preliminary x-ray photographs showed tetragonal symmetry for stylatulide. Accurate lattice constants, determined by least-squares fitting of 15 accurately measured 2θ values, were $a = b$ = 11.543 (4) and c = 20.293 (7) Å. The systematic extinctions ($00l$, absent if $l \neq 4n$) conformed to the tetragonal space group $P4_1$ (or its enantiomorph $P4_3$) and the density indicated four molecules of $C_{26}H_{35}ClO_{10}$ in the unit cell or one per asymmetric unit. All unique diffraction maxima with $2\theta \leq 114.1°$ were recorded on a computer-controlled four-circle diffractometer using graphite monochromated Cu Kα (1.541 78Å) radiation. Of the 1889 reflections surveyed, 1844 (98%) were judged observed ($F_o^2 \geq 3\sigma(F_o^2)$) after correction for Lorentz, polarization, and background effects.

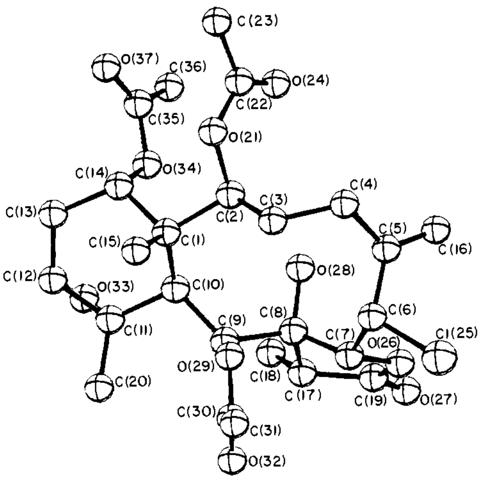


Figure 1. A computer-generated perspective drawing of **1**. Hydrogens are not shown, and no absolute stereochemistry is implied.

The structure factors were converted to normalized structure factors and phases were assigned by a multisolution, weighted tangent formula approach.[4] All nonhydrogen atoms were located in successive electron density syntheses and hydrogens in a final difference electron density synthesis. Full-matrix least-squares refinements with anisotropic temperature factors for nonhydrogen atoms and isotropic temperature factors for hydrogen have converged to a final crystallographic residual of 0.046 for the observed reflections.[5] Additional crystallographic details can be found in the supplemental material; see paragraph at end of paper.

Figure 1 is a perspective drawing of the final x-ray model of stylatulide. All bond distances generally agree well with accepted values. The intra-ring bond angles in the ten-membered ring are all larger than normal tetrahedral angles. This presumably is a consequence of relief of steric strains across the ring. There are short contacts between O(28)-C(2) of 2.89 Å, C(9)-C(2) of 3.28 Å, and C(8)-C(5) of 3.21 Å. The torsional angles around the ten-membered ring range widely, but there exists an approximate twofold axis which bisects the C(1)-C(10) and C(5)-C(6) bonds. The γ-lactone ring has an envelope conformation with C(8) serving as the flap. Since the torsional angles about the C(11)-C(12) and C(12)-C(13) bonds are essentially 0, the cyclohexane ring has a 1,2-diplanar conformation. There are no intermolecular contacts less than the van der Waals distance, save one C—OH···O=C distance of 2.93 Å.

Although chlorine-containing diterpenes were known to exist for more than 10 years,[6] the structures have been slow to appear. The structures of the "briareins", metabolites of the gorgonian coral *Briareum asbestinum* have recently been determined.[7] Briarein-A, whose structure was also determined by x-ray analysis,[8] has the same ring system with a similar substitution pattern. The structure of the toxin from the sea pen *Ptilosarcus gurneyi* (or *P. quadrangularis*)[9] is also related to stylatulide (**1**) and briarein-A.[10] In the copepodite assay, stylatulide (**1**) was toxic (LD_{100}) at concentrations greater than 0.5 ppm.

Acknowledgments. The copepodite assay was performed by Ms. M. S. Wolfe in our laboratory. Comparison of the voucher sample with materials in the SIO invertebrate collection was carried out by S. Luke. Collections of *Stylatula* were made during a cruise of R/V Dolphin funded by the National Science Foundation (BMS75-07659). S.J.W. wishes to thank the National Science Foundation for a graduate fellowship.

Supplementary Material Available: Fractional coordinates (Table 1), bond distances (Table 2), bond angles (Table 3), and observed and calculated structure factors (Table 4) (14 pages). Ordering information is given on any current masthead page.

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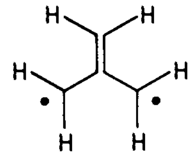
Trimethylenemethane. A Reversible, Temperature Dependent Transformation from Higher to Lower Symmetry as Observed by Electron Spin Resonance Spectroscopy

Sir:

Trimethylenemethane[1a] (I), in its ground triplet state,[1b] is characterized by a four-line electron spin resonance spectrum.[2] The presence of four lines, rather than six, is a consequence of the D_{3h} symmetry[1b] of the triplet I. In this, and in other instances of threefold or higher symmetry, the molecular x and y axes[3] are equivalent and the lines corresponding to them coincide forming a pair of xy lines, for instance, the inner two lines in the spectrum of trimethylenemethane-d_6 (I-d_6) in Figure 1a. In molecules of lower symmetry, C_{2v} for example, the xy lines are split into their component x and y lines giving rise to four inner lines,[2-4] instead of two. The outer two lines in the spectrum of Figure 1a are the z lines;[2-4] their presence is not dependent upon the molecular symmetry.



I
I-d_6, H=D

Examination of the electron spin resonance spectrum of trimethylenemethane-d_6 (I-d_6) has revealed an extremely facile apparent interconversion of states of different symmetry of the triplet I. Thus, irradiation of methylenecyclopropane-d_6[5] with γ-rays,[7] at the boiling point of liquid nitrogen, gives rise to the spectrum of the triplet state of trimethylenemethane-d_6 (I-d_6) shown in Figure 1a. As the temperature is raised from