

## References and Notes

- (1) This work was performed under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy. We also wish to acknowledge the partial support of this collaborative research by the National Science Foundation (Grant No. CHE-77-22650) through a grant to J.M.W. and G.D.S. G.D.S. also acknowledges support by NSF Grant NSF-CHE-77-24964.
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- (14) We now realize that, although the C—H...Mo<sup>5</sup> and B—H...Mo<sup>4</sup> systems were both described as 2-electron 3-center bonds, there is a very important difference between them in the crystalline state. Based on the X-ray crystallographic results for the B—H...Mo<sup>4</sup> system, which appear to be very internally consistent, the derived distances for B—H<sub>1</sub> = 0.92 (6) and 0.98 (6) Å, while the bridging bonds were much longer, B—H<sub>2</sub> (to Mo) = 1.23 (4) and 1.29 (5) Å. However, the C—H...Mo system gave C—H<sub>1</sub> = 0.97 (8) Å; i.e., there was no observed C—H bond lengthening which suggests that the bridge bonds in the B—H...Mo and C—H...Mo systems are different. Therefore, the B—H...Mo interaction might be best described as a delocalized 2-electron 3-center bond, while that for the C—H...Mo case would be an incipient 2-electron 3-center bond. While there is considerable crystallographic evidence for B—H bond lengthening upon formation of a B—H...X bond, none exists for C—H.
- (15) The H...Mo distance of ~2.2 Å may be compared with the terminal (Mo—H<sub>1</sub>) distance of 1.685 (3) Å that we derived<sup>16</sup> in H<sub>2</sub>Mo(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> and the bridging (Mo—H<sub>2</sub>—Mo) distances of 1.851 (4) and 1.869 (4) Å that we obtained<sup>17</sup> for HMo<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>4</sub>(PCH<sub>3</sub>)<sub>2</sub>.
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- (20) One unusual feature was noted in the <sup>1</sup>H NMR of **1**, viz., an extreme high-field resonance at -6.54 ppm (2, br q) which was assigned to two protons associated with the C(1) and C(5) atoms. This was interpreted in terms of a "nonbonded interaction" of the two protons with the metal center and it was suggested that only one proton at a time participated in the Fe...H—C interaction. Furthermore, it was suggested<sup>18</sup> that by forming a 3-center 2-electron bond the coordinative unsaturation of the 16-electron Fe atom is relieved, resulting in an 18-electron configuration.
- (21) A single crystal of [Fe{P(OMe)<sub>3</sub>}<sub>3</sub>( $\eta^3$ -C<sub>8</sub>H<sub>13</sub>)<sub>3</sub>]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup>, weighing 30 mg, was sealed under dry N<sub>2</sub> in a Pb glass capillary for protection. A total of 3784 three-dimensional data, of which 2748 had  $F_o^2 > \sigma F_o^2$ , were collected on the Chemistry Division neutron diffractometer at the Argonne CP-5 reactor. All data were collected at 110 K, using a device based on the Strouse<sup>22</sup> design, out to  $\sin \theta/\lambda = 0.563$  ( $\lambda = 1.142$  (1) Å). A least-square fit of 23 automatically centered reflections ( $40^\circ < 2\theta < 60^\circ$ ) confirmed the monoclinic unit cell ( $P2_1/c$ ) with  $a = 8.947$  (6) Å,  $b = 18.508$  (13) Å,  $c = 16.594$  (11) Å,  $\beta = 101.71$  (7)°,  $V = 2690.7$  Å<sup>3</sup>, and  $d_{\text{calcd}} = 1.541$  g cm<sup>-3</sup> for  $Z = 4$ . All integrated intensities were corrected for absorption ( $\mu_c = 3.01$  cm<sup>-1</sup>) and the range of transmission coefficients was 0.353–0.485. Using initial nonhydrogen atom coordinates from an X-ray investigation<sup>23</sup> all atoms were located using Fourier techniques. Final anisotropic full-matrix least-squares refinement of all 75 atoms (677 parameters) on the Argonne IBM 370/195 computer gave  $R(F_o^2) = 0.142$  and  $R(F_o) = 0.156$  with a "goodness of fit" of 1.53 for all data and  $R(F_o^2) = 0.122$  and  $R(F_o) = 0.098$  for 2748 data with  $F_o^2 > \sigma F_o^2$ .
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- (32) Considering that the Mn—H<sub>1</sub> distance in HMn(CO)<sub>5</sub> is 1.60 (2) Å,<sup>33</sup> and that Mn and Fe have very similar covalent radii, then a better value for the Fe—H<sub>1</sub> distance may be ~1.60 Å. If this is the case then the observed Fe—H<sub>1</sub> distance in **1** is ~0.3 Å longer than a Fe—H<sub>1</sub> separation.

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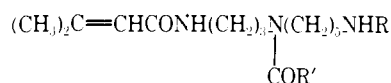
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### Polyandrocarpidines: Antimicrobial and Cytotoxic Agents from a Marine Tunicate (*Polyandrocarpa* sp.) from the Gulf of California<sup>1</sup>

Sir:

During the Illini-Trojan Baja expedition of 1976,<sup>2</sup> a red encrusting colonial tunicate was identified in our mobile laboratory as possessing potent activity against *Bacillus subtilis*. Subsequently, the tunicate was identified as a *Polyandrocarpa* sp.,<sup>3</sup> and its extracts were demonstrated to have cytotoxic (L1210<sup>4a</sup> and KB<sup>4b</sup> cells) as well as antibacterial activity. We assign here the structure of the major bioactive component of this species (polyandrocarpidine I) as **1a** (Chart I) and the minor component (polyandrocarpidine II) as **1b**. The polyandrocarpidines are remarkable, both for the occurrence of the highly strained cyclopropene ring (heretofore found in nature only in sterculic and related acids<sup>5a,b</sup> and in calysterol<sup>5c</sup>) and for their relationship to the recently discovered acarnidines (**2a-c**),<sup>6</sup> which occur in a sponge (*Acarnus erithacus*), in a



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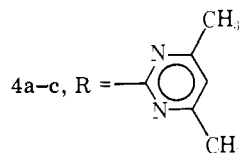
2a-c, 4a-c

2a-c, R = C(=NH)NH<sub>2</sub>

2a, R' = (CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>

b, R' = (CH<sub>2</sub>)<sub>3</sub>CH=CH(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub> (Z)

c, R' = (CH<sub>2</sub>)<sub>3</sub>(CH=CHCH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> (all-Z)



4a, R' = (CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>

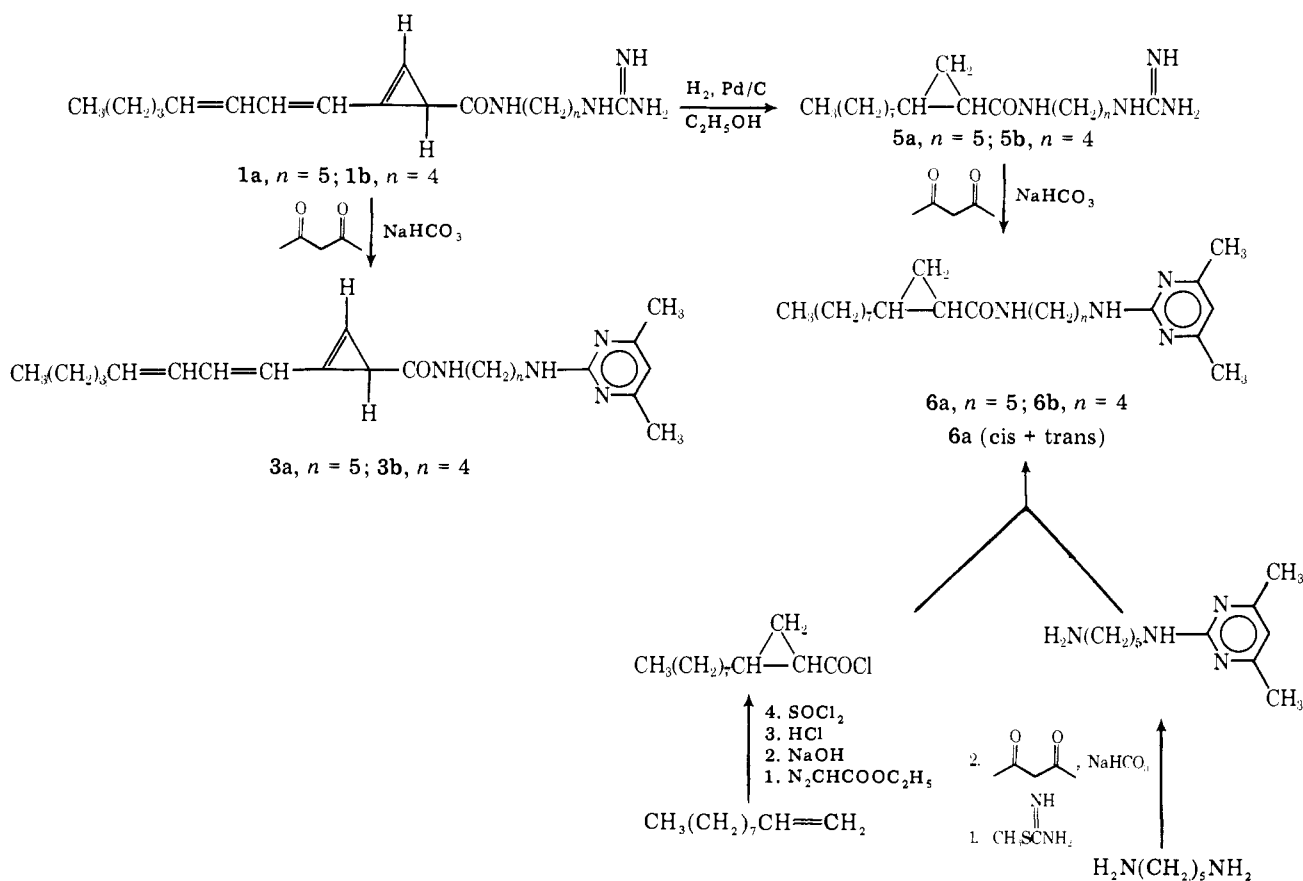
b, R' = (CH<sub>2</sub>)<sub>3</sub>CH=CH(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub> (Z)

c, R' = (CH<sub>2</sub>)<sub>3</sub>(CH=CHCH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> (all-Z)

phylum (Porifera) very distant from that of the tunicates (Chordata).

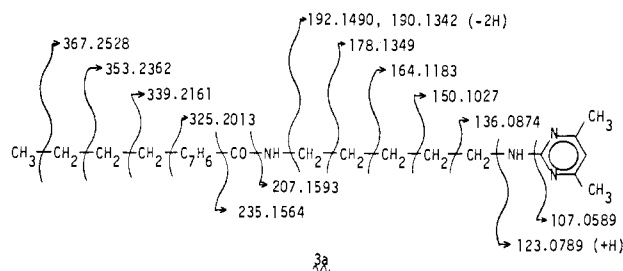
A sample of the *Polyandrocarpa* species was homogenized in the ethanol in which it had been stored and the chloroform-soluble fraction of the concentrated ethanol extract was chromatographed over a silica gel column. Elution with chloroform-methanol (3:2) gave a mixture consisting of 90%

Chart I. Polyandrocarpidines I and II (1a, 1b), Their Derivatives, and the Synthetic Route to a Derivative (6a)



polyandrocarpidine I ( $\text{C}_{18}\text{H}_{30}\text{N}_4\text{O}$ )<sup>7a</sup> and 10% polyandrocarpidine II ( $\text{C}_{17}\text{H}_{28}\text{N}_4\text{O}$ ).<sup>7a</sup> The mixture inhibits *Bacillus subtilis* (16-mm zone size from 100  $\mu\text{g}$ ), *Staphylococcus aureus* (15 mm), *Streptococcus pyogenes* (24 mm), and *Mycobacterium avium* (15 mm);<sup>4c</sup> inhibits L1210 cells ( $\text{ID}_{50}$  4.8  $\mu\text{g}/\text{mL}$ );<sup>4a</sup> is cytotoxic toward monkey kidney tissue culture (CV-1 cells, 14-mm zone size from 200  $\mu\text{g}$ );<sup>4d</sup> and shows slight antiviral activity against Herpes virus, type I.<sup>4d</sup>

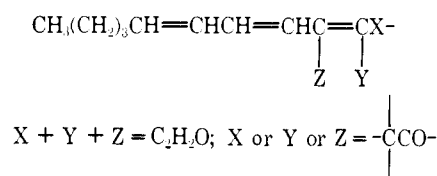
A positive Sakaguchi test and a  $^{13}\text{C}$  NMR absorption at 157.3 ppm suggested a guanidine group<sup>6</sup> and the complex was, accordingly, converted to a mixture of 4,6-dimethylpyrimidine derivatives<sup>6,8</sup> (Chart I, 3a,  $\text{C}_{23}\text{H}_{34}\text{N}_4\text{O}$ , and 3b,  $\text{C}_{22}\text{H}_{32}\text{N}_4\text{O}$ )<sup>7b</sup> by treatment with acetylacetone and sodium bicarbonate. The high resolution electron impact mass spectrum of 3a shows a series of peaks from  $m/e$  107 to 235, which establishes the 1-acylamino-5-(4,6-dimethyl-2-pyrimidylamino)pentane unit like that found in the corresponding derivatives (4a-c) of the acarnidines,<sup>6</sup> and another series of peaks from  $m/e$  325 to 367 ( $\text{M} - \text{C}_4\text{H}_9$  to  $\text{M} - \text{CH}_3$ ), which establishes a terminal *n*-butyl group. The amide group is



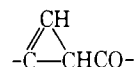
confirmed by an infrared band at  $1660\text{ cm}^{-1}$  and a  $^{13}\text{C}$  NMR absorption at 176.6 ppm in polyandrocarpidine.

Hydrogenation of polyandrocarpidine complex over palladium/charcoal in ethanol gave a mixture of hexahydro derivatives (Chart I, 5a,  $\text{C}_{18}\text{H}_{36}\text{N}_4\text{O}$ ; 5b,  $\text{C}_{17}\text{H}_{34}\text{N}_4\text{O}$ )<sup>7a</sup> which was converted by acetylacetone to the dimethylpyrimidyl derivatives (6a,  $\text{C}_{23}\text{H}_{40}\text{N}_4\text{O}$ ; 6b,  $\text{C}_{22}\text{H}_{38}\text{N}_4\text{O}$ ).<sup>7c</sup> The major component (6a) showed a GC-mass spectral fragmentation pattern similar to that of 3a, but indicating a terminal *n*-octyl group ( $\text{M} - \text{CH}_3$  through  $\text{M} - \text{C}_8\text{H}_{17}$ ).

The ultraviolet spectrum (EtOH) of polyandrocarpidine contains a maximum at 275 nm indicative of a conjugated triene not further conjugated to a carbonyl group.<sup>9</sup> The acyl group ( $\text{C}_{12}\text{H}_{15}\text{O}$ ) is thus defined as



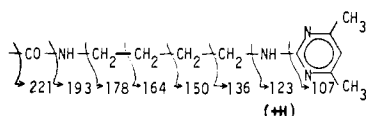
by the mass spectral data cited for 3a (*n*-butyl group) and 6a (*n*-octyl group) and partially confirmed by osmium tetroxide-periodate oxidation of polyandrocarpidine to give pentanal and glyoxal, identified by isolation of their 2,4-dinitrophenylhydrazone derivatives. The  $^{13}\text{C}$  NMR spectrum of 1a indicates five  $=\text{CH}-$  carbons and one  $=\text{C}<$  carbon (doublets and singlet in the off-resonance spectrum, respectively); an allene grouping,  $-\text{CH}=\text{C}=\text{CHCO}-$ , is missing in the infrared spectrum. Thus, only one arrangement is possible for C-2 through C-4 of the acyl group, a cyclopropene ring:



In agreement with the cyclopropene structure is the appearance of one of the =CH carbons and the  $\alpha$ -C—H- carbon at abnormally high fields, 102.8 and 28.9 ppm, respectively.<sup>10</sup>

Structure **1a** also agrees with its selective uptake of 3 mol of hydrogen, noted above, which would give an alkylcyclopropanecarboxamide (**5a**). The dimethylpyrimidyl derivative (**6a**) of **5a** was synthesized from 1-decene by the route shown in Chart I. The cis and trans isomers of **6a** were separated and analyzed by GC-mass spectrometry; the more abundant (presumably the trans isomer)<sup>11</sup> cochromatographed with **6a** and gave the same mass spectrum as **6a** prepared from the natural product.

The structure of the minor homologue, polyandrocarpine II, was assigned as **1b** (Chart I) by its molecular formula (C<sub>17</sub>H<sub>28</sub>N<sub>4</sub>O)<sup>7a</sup> and those of its derivatives (**3b**, **5b**, **6b**),<sup>7a,b</sup> all with formulas CH<sub>2</sub> less than their polyandrocarpine I analogues. The GC-mass spectral fragmentation pattern of **2b** locates the missing -CH<sub>2</sub>- group in the guanidinoalkylamine group, since **2b** gives peaks from *m/e* 107 through 221, as shown.



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## References and Notes

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- Biological activity data were provided by (a) Dr. L. H. Li and Ms. S. L. Kuentzel, The Upjohn Co.; (b) Dr. L. P. Hager and Mr. J. Nemanich, University of Illinois; (c) Dr. J. J. Vavra and Mr. G. E. Zurenko, The Upjohn Co.; and (d) Dr. R. G. Hughes, Roswell Park Memorial Institute.
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- In agreement with the indicated molecular formula are (a) high resolution field desorption mass spectral data on M + H ions; (b) high resolution electron impact mass spectral data; or (c) gas chromatographic low resolution mass spectral data.
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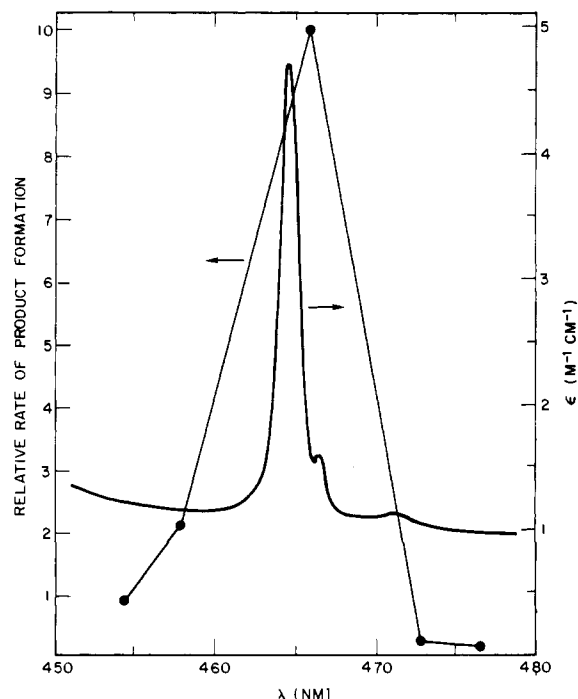
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## Lanthanide Photochemistry Initiated in f-f Transitions

Sir:

There have been few studies concerning photochemical reactions of the lanthanides (Ln) and all have involved photo-



**Figure 1.** A portion of the absorption spectrum for Eu(thd)<sub>3</sub> in acetone (right-hand scale). The large feature is due to the <sup>7</sup>F<sub>0</sub> → <sup>5</sup>D<sub>2</sub> transition and is split owing to its hypersensitivity. The slight hump at 472 nm is due to <sup>7</sup>F<sub>1</sub> → <sup>5</sup>D<sub>2</sub> thermally excited-state absorption. The photochemical rate of appearance of product, monitored spectrophotometrically, and normalized by total incident energy, is given on the left-hand scale. Error bands at each wavelength are ±20% of the rate at that wavelength.

redox processes in charge transfer or f-d bands in Ce(III,IV)<sup>1,2</sup> and Eu(III,II).<sup>3,4</sup> The line-like intrashell f-f absorption features<sup>5</sup> found in the lanthanides (Figure 1) occur throughout the ultraviolet to near-infrared spectral regions and have been ignored with respect to photochemical reactivity, since the 4f electrons are presumably effectively shielded from interactions with the chemical environment.<sup>6</sup> However, it is well known that energy can be efficiently exchanged between electronic states of complexing ligands and excited Ln 4f levels.<sup>7,8</sup> Under the appropriate conditions, such energy-transfer processes could result in photochemistry. This communication reports the first demonstration that energy absorbed in an f-f transition can result in a photochemical change, photosubstitution.

Since complexes of lanthanides are much less stable than those of most transition metals, strongly chelating ligands are required in any study of photosubstitution reactions, in order to reduce thermal reactions.<sup>9</sup> In the experiments presented here, the bidentate β-diketonate, 2,2,6,6-tetramethyl-3,5-heptanedionate (thd), was used. Complexes<sup>10</sup> of either Pr(III), Eu(III), or Ho(III) were dissolved in an appropriate solvent to give solutions 0.01 M in Ln(III) for most experiments. The samples, 0.5-1.0 mL, were irradiated and spectrophotometrically analyzed in stoppered 1-cm fused silica spectrophotometer cells. The photolytic source was an argon ion laser, line tunable over ten transitions in the blue to green region of the spectrum. The 100-200 mW laser beam was passed through the cells without focussing, using a 1.5-mm-diameter spot size.

Irradiation results in the formation of a broad absorption peak (see Figure 2) and the rate of formation is observed to be linear in both laser power and irradiation time, hence linear in incident energy. This effect is observed with all three Ln(thd)<sub>3</sub>, but only in coordinating solvents, such as pyridine, ethanol and acetone.<sup>11</sup> No effect is observed in poorly coordinating CCl<sub>4</sub> or hexane. Furthermore, little effect is seen when solutions are deaerated before photolysis by bubbling with argon gas. The spectra of the products also includes structure