wet mixture was transfered to a reaction flask. To a stirred suspension of this mixture in dichloromethane (15 mL) was added cyclohexene (1) (0.329 g, 4 mmol) in dichloromethane (5 mL) followed by the addition of *tert*-butyl alcohol (1.0 mL). Within a few minutes the reaction mixture started to reflux for a while (5 min) and then cooled down. After stirring the reaction mixture for 0.5 h at room temperature (25 °C) it was filtered over a pad of Celite and washed thoroughly with dichloromethane. Removal of solvent gave adipoin (**2**,[15a] 0.137 g, 30%) as a dimer, mp 97-101 °C (lit.[15b] 97-102 °C).

Oxidation of Cycloheptene (3). A mixture of $KMnO_4$ (4.0 g), $CuSO_4 \cdot 5H_2O$ (2.0 g), and water (200 μL) in dichloromethane (15 mL) was treated with cycloheptene (**3**, 0.385 g, 4 mmol) in dichloromethane (5 mL) followed by *tert*-butyl alcohol (1 mL) at 25 °C. The course of the reaction was monitered by thin-layer chromatography. After 0.5 h, the reaction mixture was filtered over a pad of Celite and washed thoroughly with dichloromethane, and solvent was evaporated to afford α-hydroxycycloheptanone (**4**,[16] 0.302 g, 59%) as an oil.

Oxidation of Cyclooctene (5). A stirred mixture of $KMnO_4$ (4.0 g), $CuSO_4 \cdot 5H_2O$ (2.0 g), and water (200 μL) in dichloromethane (15 mL) was treated with cyclooctene (**5**, 0.441 g, 4 mmol) in dichloromethane (5 mL) and *tert*-butyl alcohol (1 mL). After 0.5 h, the reaction mixture was filtered, and solvent was removed to yield α-hydroxycyclooctanone (**6a**,[17a] 0.285 g, 50%) as the only product; bp 79-81 °C/2 mmHg (lit.[17b] bp 75 °C/1.5 mmHg).

Oxidation of Cyclooctene (5) to Diketone 6b. When a mixture of $KMnO_4$ (4.0 g), $CuSO_4 \cdot 5H_2O$ (2.0 g), and water (300 μL) in dichloromethane (15 mL) was treated with solid $Cu(OAc)_2 \cdot H_2O$ (1.0 g), cyclooctene (**5**, 0.220 g, 2 mmol) in dichloromethane (5 mL), and *tert*-butyl alcohol (1 mL), cyclooctane-1,2-dione (**6b**,[18] 0.134 g, 48%) was obtained after distillation; bp 130 °C/3 mmHg (lit.[19] bp 130 °C/3 mmHg); IR (thin film) 1702 cm^{-1}; NMR ($CDCl_3$) δ 1.7 (s, 8 H), 2.53-2.76 (m, 4 H).

Oxidation of Cyclododecene (7).[10b] Cyclododecene (**7**, 0.332 g, 2 mmol) under similar reaction conditions afforded cyclododecane-1,2-dione (**8**, 0.227 g, 58%) after distillation, bp 82-85 °C/0.1 mmHg, as a yellow solid: mp 42-44 °C (lit.[20] mp 43 °C); IR (thin film) 1701 cm^{-1}; NMR ($CDCl_3$) δ 1.3 (s, 16 H), 2.66-2.86 (m, 4 H).

Oxidation of Compound 9. A mixture of $KMnO_4$ (4.0 g), $CuSO_4 \cdot 5H_2O$ (2.0 g), and water (300 μL) in dichloromethane (15 mL) treated with compound **9** (0.568 g, 4 mmol) in dichloromethane (5 mL) and *tert*-butyl alcohol (1 mL) yielded, after chromatography, compound **10** (0.550 g, 79%): IR (thin film) 3450, 1720, 1705 cm^{-1}; NMR ($CDCl_3$) δ 1.43 (s, 6 H), 2.2 (s, 3 H), 2.83 (s, 4 H), 3.76 (br s, 1 H); MS, *m/e* 159 $(M + 1)^+$. Anal. Calcd for $C_8H_{14}O_3$: C, 60.76; H, 8.86. Found: C, 60.88; H, 8.94.

Oxidation of Citronellol Acetate (11). To a mixture of $KMnO_4$ (4.0 g), $CuSO_4 \cdot 5H_2O$ (2.0 g), and water (300 μL) in dichloromethane (15 mL) was added citronellol acetate (**11**, 0.792, 4 mmol) in dichloromethane (5 mL) and *tert*-butyl alcohol (1 mL) and stirred for 2 h. On purification by chromatography the epoxy compound **12a** (0.342 g, 40%) and ketol acetate **12b** (0.368 g, 40%) were obtained.

12a: IR (thin film) 1735 cm^{-1}; NMR ($CDCl_3$) δ 0.93 (d, 3 H), 1.33 (d, 6 H), 1.43-1.83 (m, 7 H), 2.06 (s, 3 H), 2.66-2.83 (t, 1 H), 4.0-4.3 (t, 2 H); MS, *m/e* 194 (M^+). Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.29; H, 10.28. Found: C, 67.38; H, 10.35.

12b: IR (thin film) 3450, 1735, 1710 cm^{-1}; NMR ($CDCl_3$) δ 0.9 (d, 3 H), 1.34 (s, 6 H), 1.43-1.83 (m, 5 H), 2.0 (s, 3 H), 2.40-2.56 (t, 2 H), 3.7 (br s, 1 H), 4.0-4.2 (t, 2 H); MS, *m/e* 231 $(M + 1)^+$. Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.61; H, 9.56. Found: C, 62.82; H, 9.68.

Oxidation of 1,2-Dihydronaphthalene (13). When a mixture of $KMnO_4$ (4.0 g), $CuSO_4 \cdot 5H_2O$ (2.0 g), and water (200 μL) in dichloromethane (15 mL) was treated as above with compound **13** (0.260 g, 2 mmol) in dichloromethane (5 mL) and *tert*-butyl alcohol (1 mL), 2-hydroxy-1-tetralone (**14**, 0.178 g, 55%), mp 36-37 °C (lit.[21] mp 36-36.5 °C), was obtained after chromatography on silica gel; IR (thin film) 3460, 3060, 1680, 1600 cm^{-1}; NMR ($CDCl_3$) δ 1.76-2.73 (br m, 2 H), 3.06-3.26 (m, 2 H), 3.8 (br s, 1 H), 4.26-4.56 (dd, 1 H), 7.26-7.66 (m, 3 H), 8.0-8.23 (m, 1 H).

Oxidation of Cholesteryl Acetate (15). Cholesteryl acetate (**15**, 0.857 g, 2 mmol) was treated under similar conditions with $KMnO_4$ (4.0 g), $CuSO_4 \cdot 5H_2O$ (2.0 g), water (400 μL), and *tert*-butyl alcohol (1 mL) to give β-epoxy compound **16** (0.820 g, 92%), mp 110-112 °C (lit.[22] mp 111-112 °C).

Oxidation of *trans*-Stilbene (17). *trans*-Stilbene (**17**, 0.720 g, 4 mmol) was allowed to react with a mixture of $KMnO_4$ (4.0 g), $CuSO_4 \cdot 5H_2O$ (2.0 g), water (300 μL), and *tert*-butyl alcohol (1 mL), to give benzaldehyde (**18**, 0.780 g, 92%), found to be identical with an authentic sample.

Oxidation of 1-Decene (19). A mixture of $KMnO_4$ (4.0 g), $CuSO_4 \cdot 5H_2O$ (2.0 g), and water (300 μL) was treated under similar conditions with 1-decene (**19**, 0.560 g, 4 mmol) and *tert*-butyl alcohol (1 mL), to yield nonanoic acid (**20**, 0.455 g, 72%), found to be identical with an authentic sample.

Oxidation of 2-Octene (21). When compound **21** (0.448 g, 4 mmol) was treated as above with $KMnO_4$ (4.0 g), $CuSO_4 \cdot 5H_2O$ (2.0 g), water (300 μL), and *tert*-butyl alcohol (1.0 mL), hexanoic acid (**22**, 0.324 g, 78%) was obtained, found to be identical with an authentic sample.

Oxidation of Diphenylacetylene (23). Compound **23** (0.356 g, 2 mmol) was treated with a mixture of $KMnO_4$ (4.0 g), $CuSO_4 \cdot 5H_2O$ (2.0 g), water (300 μL), and *tert*-butyl alcohol (1 mL) under similar conditions of oxidation to afford benzil (**24**, 0.407 g, 97% mp 94-95 °C) as a yellow solid, found to be identical with an authentic sample.

Acknowledgment. We express our thanks to the Ministry of Defence, New Delhi, and C.S.I.R., New Delhi, for financial assistance.

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5-Isothiocyanatopupukeanane from a Sponge of the Genus *Axinyssa*

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Marine sponges of the order Halichondrida have provided an unprecedented array of sesquiterpene isonitriles, isothiocyanates, and formamides.[1] These metabolites are thought to inhibit feeding by omnivorous browsers, but they do not deter nudibranches that are specific predators on the sponges. In 1975, the Scheuer group[2] reported the isolation of 9-isocyanopupukeanane (1) from both the

(1) For recent reviews, see: Faulkner, D. J. *Nat. Prod. Rep.* **1984**, *1*, 551; **1986**, *3*, 1; **1987**, *4*, 539. Edenborough, M. S.; Herbert, R. B. *Nat. Prod. Rep.* **1988**, *5*, 229.

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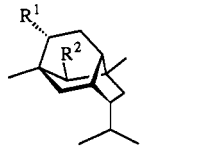
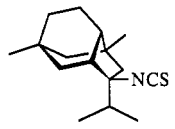
nudibranch *Phyllidia varicosa* and a sponge of the genus *Hymeniacidon*. The same group subsequently isolated 2-isocyanopupukeanane (**2**) from the same sponge[3] and reported, without details, that the isonitrile was accompanied by the corresponding isothiocyanate (**3**) and formamide (**4**).[4] In this paper we report the isolation and structural elucidation of 5-isothiocyanatopupukeanane (**5**) from a sponge of the genus *Axinyssa*.

Specimens of a species of *Axinyssa* were collected at Gun Beach, Guam. The hexane extract of the lyophilized sponge was chromatographed on silica to obtain a nonpolar fraction that was purified by HPLC to obtain 5-isothiocyanatopupukeanane (**5**, 0.08% dry wt) and the known metabolites 10-isothiocyanato-4-amorphene (**6**, 0.018% dry wt),[5] calamanene (**7**, 0.0025% dry wt),[6] and zizanene (**8**, 0.004% dry wt).[7] The sponge also contained an isonitrile fraction that was subsequently lost through evaporation under high vacuum.[8]





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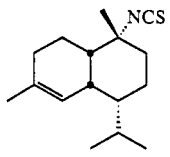
1 R^1 = NC R^2 = H
2 R^1 = H R^2 = NC
3 R^1 = H R^2 = NCS
4 R^1 = H R^2 = NHCHO



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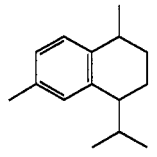

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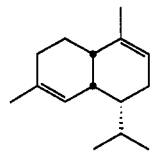

8

5-Isothiocyanatopupukeanane (**5**) was obtained as crystals from hexane, mp 87–88 °C. The molecular formula, $C_{16}H_{25}NS$, was established by EI high-resolution mass spectrometry. The infrared band at 2100 (br) cm^{-1} was assigned to an isothiocyanate group; however, the characteristic isothiocyanate carbon signal in the ^{13}C NMR spectrum was too weak to be clearly observed. The ^{13}C NMR spectrum contained only aliphatic carbon signals,

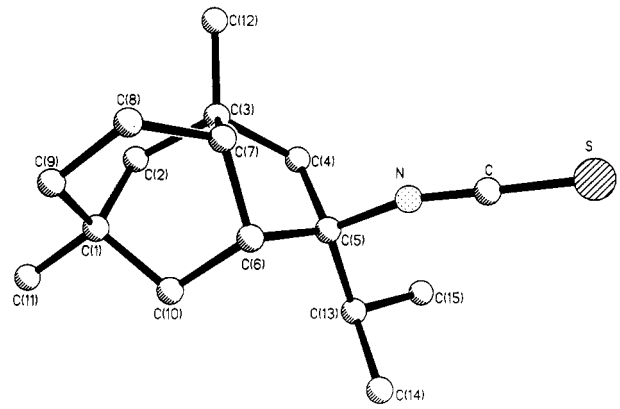

Figure 1. A computer-generated perspective drawing of the final X-ray model of 5-isothiocyanatopupukeanane (**5**). Hydrogens are omitted for clarity.

indicating the isothiocyanate was tricyclic. The ^1H NMR spectrum contained methyl signals at δ 0.74 (s, 3 H), 0.92 (d, 3 H, J = 7.5 Hz), 1.00 (d, 3 H, J = 7.5 Hz), and 1.04 (s, 3 H). Although the remaining signals overlapped so badly in all solvents that the spectrum could not be interpreted, we deduced from the COSY spectrum that two of the methyl groups were part of an isolated isopropyl group that was probably adjacent to the isothiocyanate group.

The structure of 5-isothiocyanatopupukeanane (**5**) was determined by single-crystal X-ray analysis. A computer-generated perspective drawing is given in Figure 1. The absolute configuration shown is arbitrary but is drawn to conform with that determined for 1.[3] The C5–N–C bond angle of the isothiocyanate is 160.0 (6)°, and the N–C–S angle is 177.7 (5)°. The conformation of the five-membered ring (C3, C4, C5, C6, and C7) is approximately Cm or envelope with C7 as the flap. The conformations of the three six-membered rings (C1, C2, C3, C7, C8, C9; C1, C9, C8, C7, C6, C10; and C1, C2, C3, C7, C6, C10) are almost ideal boats.

The sponge *Axinyssa* sp. was examined because its crude extracts deterred feeding in the common pufferfish *Canthigaster solandri*. However, when tested at a relatively high concentration, 5-isothiocyanatopupukeanane (**5**), which was the only constituent of the sponge to be available in sufficient quantities for the bioassay, failed to deter feeding.[10]

Experimental Section

Collection, Extraction, and Isolation. Specimens of a species of *Axinyssa* were collected by hand using SCUBA (–3 m) at Gun Beach, Guam and were immediately frozen. The frozen sponge was cut into small portions and lyophilized, after which the sponge was allowed to soak in hexane (2 × 500 mL, 2 days). The combined hexane extracts were dried over anhydrous sodium sulfate and filtered, and the solvent was evaporated to obtain an oil (3.0 g). The oil was chromatographed on a silica gel flash column using an elution gradient from hexane to chloroform. The least polar fractions were combined and rechromatographed by LC on a Partisil column using 2% chloroform in hexane as eluant to obtain 5-isothiocyanatopupukeanane (**5**, 160 mg, 0.08% dry wt), 10-isothiocyanato-4-amorphene (**6**, 35 mg, 0.018% dry wt), calamene (**7**, 5 mg, 0.0025% dry wt), and zizanene (**8**, 8 mg, 0.004% dry wt).

5-Isothiocyanatopupukeanane (5): colorless prisms from hexane; mp 87–88 °C; $[\alpha]_D$ +33.5° (*c* 7.6, $CHCl_3$); IR ($CHCl_3$) 2920, 2860 (br), 2100 (br), 1445 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 0.74 (s, 3 H), 0.92 (d, 3 H, J = 7.5 Hz), 1.00 (d, 3 H, J = 7.5 Hz), 1.04 (s, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 77.8 (s), 57.2 (t), 52.9 (t), 47.6 (d), 41.2 (d), 39.3 (s), 34.2 (t), 33.9 (t), 33.8 (d), 28.5 (s), 28.0

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(6) Identified by comparison of ^1H NMR data with those reported by Andersen, N. H.; Syrdal, D. D.; Graham, C. *Tetrahedron Lett.* **1972**, 905. The chemical shifts of the methyl signals are appropriate for *cis*-calamanene.

(7) Identified by analysis of the ^1H and ^{13}C NMR data and by comparison with those reported by Andersen, N. H. *Tetrahedron Lett.* **1970**, 4651. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 135.9 (s), 133.7 (s), 123.9 (d), 119.5 (d), 45.0 (d), 38.6 (d), 36.0 (d), 28.8 (d), 27.1 (t), 26.4 (t), 25.3 (t), 24.0 (q), 21.5 (q), 20.8 (q), 20.6 (q).

(8) This isonitrile has spectral data that are compatible with those expected of 9-isocyanopupukeanane (**1**). Despite the publication of the structural elucidation[2] and two total syntheses,[9] no useful spectral data have been reported for **1**.

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(10) Paul, V. J. Manuscript in preparation.

(q), 26.8 (q), 17.9 (q), 17.6 (t), 17.6 (q); HRMS obsd m/z 263.1703, $C_{16}H_{25}NS$ requires 263.1709.

Single-Crystal X-ray Diffraction Analysis of 5. A suitable single crystal was glued to a glass fiber, and preliminary X-ray photographs were taken. Compound **5** had orthorhombic symmetry with a = 9.543 (2), b = 10.371 (2), and c = 15.373 (3) Å. Systematic absences, a calculated density, and the compound's optical activity were uniquely accommodated by space group $P2_12_12_1$ with one molecule of composition $C_{16}H_{25}NS$ forming the asymmetric unit. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a computer-controlled four-circle diffractometer using Cu Kα radiation and variable speed 1° ω-scans. Of the 1206 unique reflections collected this way, 948 (79%) were judged observed after correction for Lorentz, polarization, and background effects.[11] The structure was phased using direct methods, and the initial maps clearly revealed the heavy atom structure. Hydrogen atoms were located in a ΔF-synthesis after partial refinement of the heavy atoms. Block-diagonal least-squares refinements with anisotropic heavy atoms and fixed isotropic hydrogens have converged to a conventional crystallographic residual of 0.063. Additional crystallographic information is available in the supplementary material.

Acknowledgment. The sponge was collected by Dr. Valerie Paul (University of Guam) and identified by Dr. Rob van Soest. This research was supported by grants from the National Institutes of Health (AI11969 to D.J.F. and CA24487 to J.C.) and the New York State and California (R/MP40) Sea Grant College Programs.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, interatomic distances, interatomic angles, and torsional angles for 5-isothiocyanatopupukeanane (**5**) (5 pages). Ordering information is given on any current masthead page.

(11) All crystallographic calculations were done on a PRIME 850 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed: Leonowicz, M. E. REDUCE and UNIQUE, data reduction programs, Cornell University, 1978. Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. MULTAN 78, MULTAN 80, and RANTAN 80, systems 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, 1979 and 1980. Beurskens, P. T.; et al. DIRDIF, University of Nijmegen, The Netherlands, 1981. Gilmore, C. J. MITHRIL, an automatic solution package, University of Glasgow, Scotland, 1983. Hirotsu, K. K.; Arnold, E. BLS78A, an anisotropic block-diagonal least-squares refinement, Cornell University, 1980. Motherwell, W. D. S. PLUTO78, a crystallographic illustration program, Cambridge Data Centre, 1978. Hirotsu, K. BOND, a program to calculate molecular parameters and prepare tables, Cornell University, 1978.

Effect of Acid on the Peracid Oxidations of 3-Methyltetrahydrobenzofuran

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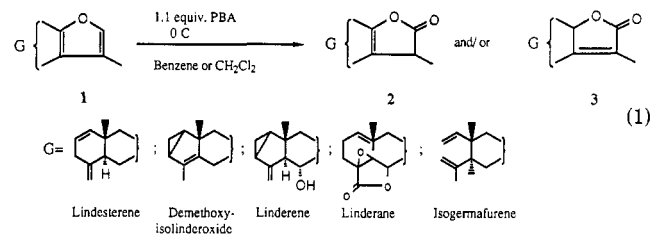
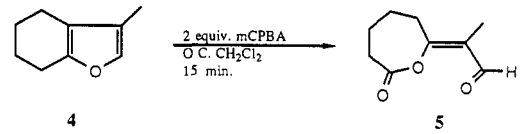
Prior to recent work in this laboratory on the peracid oxidations of tetrahydrobenzofuran derivatives, Takeda reported on the oxidations of lindesterene,[1] demethoxyisolinderoxide,[2] isogermafurene,[3] linderene,[3] and linderane,[4] which are shown in a generic type of reaction sequence as eq 1. It appears from this literature that the unconjugated γ-lactone is the primary product while the conjugated isomer results from subsequent isomerization during isolation.



(1)

In 1981, we reported[5] on the *m*-chloroperbenzoic acid (mCPBA) oxidation of a simpler system, 3-methyltetrahydrobenzofuran **4**, as shown in eq 2. In this case and with

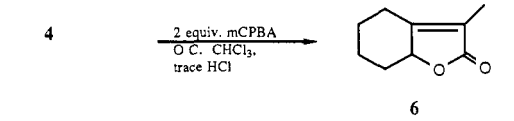


(2)

other derivatives, 2 equiv of peracid were required,[6] and the sole product was the ϵ-lactone aldehyde **5**. The same result was observed with perbenzoic acid (PBA) and with *p*-nitroperbenzoic acid (pNPBA).[7] Moreover, with use of the conditions reported by Takeda,[1] **5** was still the only product *observed*.[7] In this note, we wish to report the resolution to this apparent dichotomy.

Results

Inadvertantly, in our laboratory substrate **4** was reacted with impure mCPBA that apparently contained a small but unspecified amount of HCl. In this experiment, we obtained butenolide **6** as shown in eq 3. Repetition of the



(3)

experiment with a trace of concentrated aqueous HCl led to the same result. In another experiment, **4** was dissolved in ethanol-free $CHCl_3$, and a trace of aqueous HCl added. The light pink color that developed in the reaction mixture dissipated quickly when 1.4 equiv of PBA were added. The γ-lactone product **6** was obtained in better than 90% yield. The concentration of PBA was determined not to be a factor since both 2 and 1.4 equiv gave the same product in the same concentration.

Further investigation revealed that any one of the peracids PBA, mCPBA, or pNPBA gave the γ-lactone product in the presence of catalytic amounts of aqueous HCl. Moreover, the solvent may be CH_2Cl_2, THF, benzene, ether, or $CHCl_3$. Finally, in addition to HCl (aq), H_2SO_4, *p*-TsOH, HOAc, and HCl (g) catalyzed the formation of **6**.

With use of an even simpler substrate **7**, further insight into the pathway of this reaction was obtained (eq 4). In this reaction, **7** was reacted with 1.1 equiv of PBA in *acid-free* CH_2Cl_2 at room temperature, yielding **8**. Subsequent treatment of **8** with a catalytic amount of aqueous

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(6) If less than 2 equiv is used, one obtains only **5** and unreacted **4**. One equivalent leads to a 50:50 mixture of **4** and **5**.
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