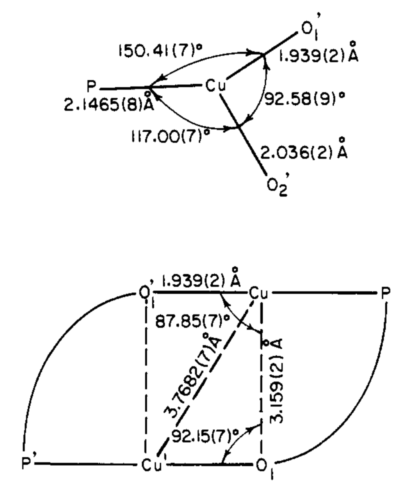


Figure 2. The in-plane and out-of-plane structural parameters for the $[Cu(acacP)]_2$ molecule; inversion related atoms are indicated by primes.

topologically equivalent ligands,[8,9] it appeared likely that the copper(I) moieties would be pseudotetrahedral as are most copper(I)–phosphine complexes. On the other hand, the values of $J(^{109}Ag,^{31}P)$ and $J(^{107}Ag,^{31}P)$ of 826 and 718 Hz measured for $[Ag(acacP)]_2$[10] are unusually large for tetracoordinated silver(I).[11] Our X-ray crystallographic study clarified this situation by demonstrating that **1** possesses a very unusual structure.

A 0.20- × 0.35- × 0.35-mm crystal obtained by slow diffusion of methanol into a CH_2Cl_2 solution of **1** with exclusion of air was used for data collection. The space group and cell data are as follows: monoclinic, space group $P2_1/n$ with $a = 9.508$ (2) Å, $b = 14.529$ (3) Å, $c = 16.001$ (5) Å, $\beta = 92.01$ (2)°, $V = 2209.2$ (9) Å^3, d(calcd) = 1.356 g cm^{-3}, d(found) = 1.34 g cm^{-3}, and $Z = 2$. Three-dimensional diffraction data (a total of 3657 independent reflections having $2\theta(\text{Cu } K\alpha) \leq 130°$) were collected on a Syntex $P2_1$ autodiffractometer by using graphite-monochromated Cu $K\alpha$ radiation. The position for the Cu atom was located by a weighted (E*F) Patterson synthesis. Subsequent difference Fourier maps revealed the positions of all remaining atoms, including all hydrogens. Least-squares refinement to convergence using anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms gave $R = 0.0388$ and $R_w = 0.0478$.[12]

The structure of **1** consists of two trigonally coordinated copper(I) units[13] related through the inversion center and bridged by the phenylene fragment of the acacP chelate (Figure 1). The coordination sphere of the copper atom is very nearly planar with the metal atom within 0.0087 (5) Å of the plane containing the PO_2 donor set. The coordination planes of the dimer are parallel since they are inversion related. As indicated in Figure 2, the two in-plane Cu–O distances differ by ~0.1 Å while a third, nonbonding oxygen is a further 1.220 Å distant from the metal center.

The present structure is geometrically related to a growing class of bimetallic complexes characterized by cofacially positioned coordinatively unsaturated, low-valent metal ions[14] ("dimetallophanes").[15] On the basis of synthetic and structural principles illustrated in this work, a range of new homo- and heterobimetallic complexes can now be anticipated by using chemically and topologically equivalent agents.[16]

Acknowledgment is made to the Dow Chemical Company and the donors of the Petroleum Research Fund, administered by the American Chemical Society. Field desorption mass spectra were obtained in part under a grant from the National Cancer Institute (CA 11388).

(8) For a general review of this area of coordination chemistry, see: Casellato, O.; Vigato, P. A.; Fenton, D. E.; Vidali, M. *Chem. Soc. Rev.* **1979**, *8*, 199.

(9) Heeg, M. J.; Mack, J. L.; Glick, M. D.; Lintvedt, R. L. *Inorg. Chem.* **1981**, *20*, 833.

(10) The reaction of $AgClO_4$ with HacacP and Et_3N in acetonitrile afforded $[Ag(acacP)]_2$ as photosensitive cream-colored crystals. Anal. Calcd for $C_{50}H_{48}Ag_2O_4P_2$: C, 60.60; H, 4.85; P, 6.26. Found: C, 60.25; H, 4.84; P, 6.48. Spectral data: IR (mull) 1571 (s), 1548 (s) cm^{-1}; ^{1}H NMR (90 MHz, CD_2Cl_2 solution) δ 8.74–6.7 (m, 14 H), 5.7 (s, 1 H), 1.1 (s, 9 H); $^{31}P\{^1H\}$ NMR (40.5 MHz, CD_2Cl_2 solution) 3.6 ppm upfield of 85% H_3PO_4 [$^1J(^{109}Ag,^{31}P) = 826$ Hz, $^1J(^{107}Ag,^{31}P) = 718$ Hz]; field desorption MS, m/z 990 (M^+).

(11) Pregosin, P. L.; Kunz, R. W. "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes"; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1979; Vol. 16.

(12) The function minimized was $\sum w||F_o| - |F_c||^2$, $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$.

(13) Three-coordinate metal complexes: Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1.

(14) Cofacial diporphyrin complexes: Hatada, M. H.; Tulinsky, A.; Chang, C. K. *J. Am. Chem. Soc.* **1980**, *102*, 7115. Collman, J. P.; Denisovich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. *Ibid.* **1980**, *102*, 6027 and references therein. Landrum, J. T.; Grimmett, D.; Haller, K. J.; Scheidt, W. R.; Reed, C. A. *Ibid.* **1981**, *103*, 2640.

(15) For a discussion of this terminology, see: Smith, B. H. "Bridged Aromatic Systems"; Academic Press: New York, 1964.

(16) Synthetic and structural studies relating to homo- and heterobimetallic derivatives of acacP are under way.

Synthesis of $[(C_6H_5NH)PNC_6H_5]_3$: A Participant in a Phosphorus(III)–Nitrogen Compound Trimer–Dimer Interconversion Reaction

Martin L. Thompson,[1a] Abbas Tarassoli,[1b]
R. Curtis Haltiwanger, and Arlan D. Norman*

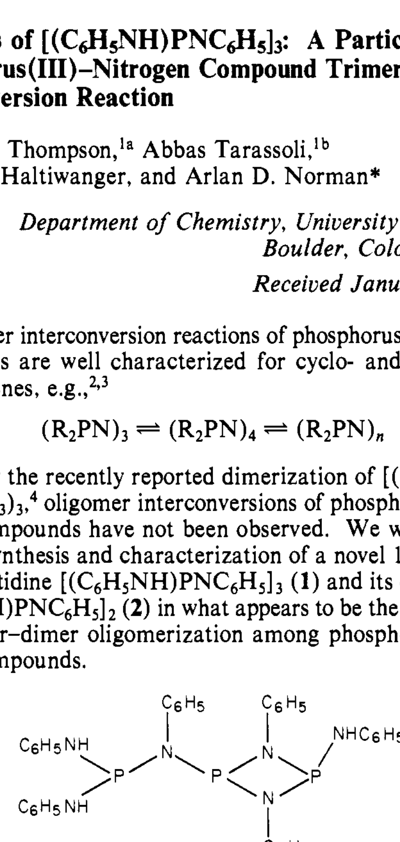
Department of Chemistry, University of Colorado
Boulder, Colorado 80309

Received January 19, 1981

Oligomer interconversion reactions of phosphorus(V)–nitrogen compounds are well characterized for cyclo- and linear polyphosphazenes, e.g.,[2,3]

$$(R_2PN)_3 \rightleftharpoons (R_2PN)_4 \rightleftharpoons (R_2PN)_n \qquad (1)$$

Except for the recently reported dimerization of $[(CH_3)_3Si]_2N$-$PNSi(CH_3)_3$,[4] oligomer interconversions of phosphorus(III)–nitrogen compounds have not been observed. We wish to report now the synthesis and characterization of a novel 1,3,2,4-diazadiphosphetidine $[(C_6H_5NH)PNC_6H_5]_3$ (**1**) and its conversion to $[(C_6H_5NH)PNC_6H_5]_2$ (**2**) in what appears to be the first example of a trimer–dimer oligomerization among phosphorus(III)–nitrogen compounds.



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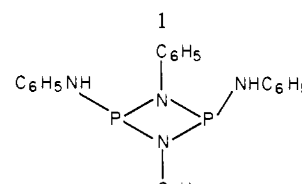

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(1) (a) Department of Chemistry, Lake Forest College, Lake Forest, IL 60045. (b) Department of Chemistry, Jundi Shapur University, Ahwaz, Islamic Republic of Iran.

(2) Shaw, R. A. *Phosphorus Sulfur* **1978**, *4*, 101.

(3) Emsley, J.; Hall, D. "The Chemistry of Phosphorus"; Harper and Row: London, 1976.

(4) Niecke, E.; Flick, W.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 309.

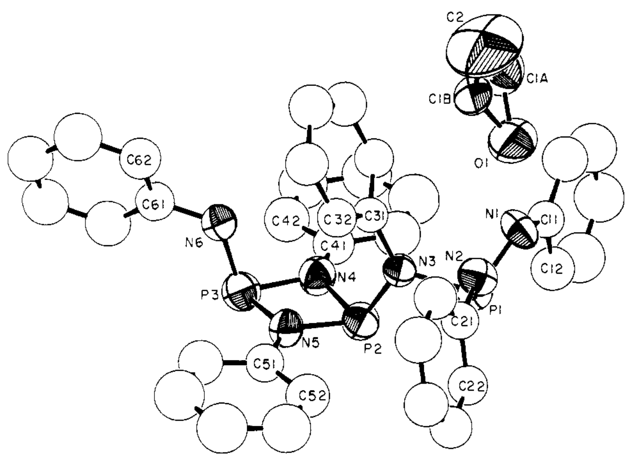


Figure 1. Molecular structure of $[(C_6H_5NH)PNC_6H_5]_3{\cdot}C_2H_5OH$ and labeling of atom positions. Hydrogen atoms omitted for clarity.

Compound **1** is formed in greater than 80% yield from $[(C_6H_5NH)_2P]_2NC_6H_5$[5] thermolysis (2 h, 80 °C) in toluene (eq 2)

$$3[(C_6H_5NH)_2P]_2NC_6H_5 \rightarrow 2[(C_6H_5NH)PNC_6H_5]_3 + 3C_6H_5NH_2 \quad (2)$$

or from reaction of PCl_3 with $C_6H_5NH_2$ (1:6 mole ratio, 2 h, 0 °C) in methylene chloride (eq 3). Filtration of either reaction

$$3PCl_3 + 15C_6H_5NH_2 \rightarrow 9C_6H_5NH_3Cl + [(C_6H_5NH)PNC_6H_5]_3 \quad (3)$$

mixture, evaporation of solvent in vacuo, and recrystallization from CH_2Cl_2 or benzene yields pure microcrystalline **1** (mp 180–181 °C). Anal. Calcd for $C_{36}H_{33}N_6P_3$: C, 67.28; H, 5.18; N, 13.08; P, 14.46. Found: C, 66.87; H, 5.17; N, 13.15; P, 14.58. Spectral data for **1**: IR (KBr pellet) characteristic NH and PN ring absorptions[6] at 3160 and 835 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.55–6.66 (complex multiplet, area 30, phenyl), 4.43 (d, $^2J_{HP} = 6.5$ Hz, area 2, NH), and 3.50 (d, $^2J_{HP} = 6.3$ Hz, area 1, NH); ^{31}P NMR (^1H decoupled, C_6D_6, relative to H_3PO_4, ABX spectrum[7]) δ −109.6 (P_2), −106.9 (P_3), −62.0 (P_1), $^2J_{P_1P_2} = 363 \pm 2$ Hz and $^2J_{P_2P_3} = 12.3 \pm 0.2$ Hz. Compound **1** oxidizes slowly in air and reacts with water to form $C_6H_5NH_2$ and $(C_6H_5NH)_2P(O)H$.[8]

Crystallization of **1** from a saturated CH_2Cl_2 solution by dropwise addition of C_2H_5OH yields crystals of monosolvated $\mathbf{1}{\cdot}C_2H_5OH$ suitable for single-crystal X-ray analysis. Crystal data[9] for $\mathbf{1}{\cdot}C_2H_5OH$ are space group $C2/c$, $a = 23.156$ (9) Å, $b = 14.533$ (5) Å, $c = 22.243$ (8) Å, $\beta = 100.63$ (3)°, $V = 7357$ (5) Å^3, $\rho_{calcd} = 1.16$ g/cm^3 ($Z = 8$), $\rho_{obsd} = 1.17$ g/cm^3, μ (Mo Kα) = 2.04 cm^{-1}. The molecular structure of $\mathbf{1}{\cdot}C_2H_5OH$ is shown in Figure 1. Significant interatomic bond distances and angles are summarized in Table I.

Table I. Selected Structural Parameters in $[(C_6H_5NH)PNC_6H_5]_3{\cdot}C_2H_5OH$[a]

Bond Lengths, Å			
P(1)–N(1)	1.682 (7)	P(2)–N(5)	1.712 (8)
P(1)–N(2)	1.690 (8)	P(3)–N(4)	1.732 (8)
P(1)–N(3)	1.727 (7)	P(3)–N(5)	1.714 (8)
P(2)–N(3)	1.694 (7)	P(3)–N(6)	1.675 (8)
P(2)–N(4)	1.720 (8)	C–N (mean)	1.410 (9)
Bond Angles, deg			
N(1)–P(1)–N(2)	93.2 (4)	N(4)–P(3)–N(6)	102.8 (4)
N(1)–P(1)–N(3)	103.8 (4)	N(5)–P(3)–N(6)	105.1 (4)
N(2)–P(1)–N(3)	103.3 (4)	P(1)–N(3)–P(2)	115.5 (4)
N(3)–P(2)–N(4)	106.4 (4)	P(1)–N(3)–C(31)	122.1 (5)
N(3)–P(2)–N(5)	105.5 (4)	P(2)–N(3)–C(31)	122.3 (5)
N(4)–P(2)–N(5)	79.5 (4)	P(2)–N(4)–P(3)	99.7 (4)
N(4)–P(3)–N(5)	79.1 (4)	P(2)–N(5)–P(3)	100.7 (4)

[a] Standard deviations in the least significant figures are given in parentheses.

The structure of **1** consists of a four-membered 1,3,2,4-diazadiphosphetidine ring, with C_6H_5NH- and $(C_6H_5NH)_2P(NC_6H_5)$ moieties attached to rign phosphorus atoms in a cis disposition relative to the nearly planar P_2N_2 ring. The dihedral angle between perpendiculars to planes N(1), N(2), N(3) and N(3), N(4), N(5) is only 10.1°, making the phosphorus lone pair electrons of P(1) and P(2) approximately eclipsed. The principal structural parameters (Table I), distances, mean ring P–N (1.72 Å) and mean N(exo)–P (1.69 Å), and angles, mean ring P–N–P (100°), mean ring N–P–N (79°), ring N–P (exo)–N (105°), P–N(C_6H_5)–P (115°), are remarkably consistent with those reported recently for the dinuclear 1,3,2,4-diazadiphosphetidine $[(C_6H_5NH)P_2(NC_6H_5)_2]_2NC_6H_5$,[11] $[(C_6H_5NH)_2P]_2NC_6H_5$,[5] and $[(C_6H_5)_2PN(CH_3)P(C_6H_5)N\textit{t}C_4H_9]_2$.[12]

Spectral data (^1H and ^{31}P NMR) shows conclusively that **1** in solution is a 1,3,2,4-diazadiphosphetidine, as it is in the solid. The two low-field resonances of the ABX pattern of **1** at δ −109.6 and −106.9 are in the region observed previously for *cis*-1,3,2,4-diazadiphosphetidines.[2,12] The higher field resonance at δ −62.0 occurs close to that of $[(C_6H_5NH)_2P]_2NC_6H_5$ (δ −67.8),[5] supporting strongly the presence of the triaminophosphorus moiety in **1**. No evidence is obtained for the presence of other isomeric forms of **1** in solution. Thus, the *cis*-diazadiphosphetidine structural type seems to dominate any tendency of the system to form an isomeric, six-membered ring structure analogous to what has been reported recently for $(C_2H_5NPCl)_3$ and $(CH_3NPX)_3$ (X = Cl, Br).[13,14] However, since the latter structures are deduced largely from ^1H NMR spectral data, the interesting possibility that they can exist as 1,3,2,4-diazadiphosphetidine structural types must be considered.

Thermolysis of **1** in toluene at temperatures above 80 °C results in the slow conversion of **1** to a mixture of **1** and the previously characterized dimer $[(C_6H_5NH)PNC_6H_5]_2$ (**2**)[15] according to

$$\underset{\mathbf{1}}{2[(C_6H_5NH)PNC_6H_5]_3} \rightleftharpoons \underset{\mathbf{2}}{3[(C_6H_5NH)PNC_6H_5]_2} \quad (4)$$

After 3 h at 110 °C, a mixture of **1** and **2** in an approximately 1:10 molar ratio results. This appears to represent the equilibrium position for the trimer–dimer reaction at this temperature. So far, attempts to measure reliably equilibrium constants for the reaction have been frustrated by the slow decomposition of reaction

(5) Tarassoli, A.; Haltiwanger, R. C.; and Normal, A. D. *Inorg. Chem.*, in press.

(6) Grapov, A. F.; Mel'nikov, N. N.; Razvodovskaya, L. V. *Russ. Chem. Rev.* (*Engl. Transl.*) **1970**, *39*, 1 and references cited therein.

(7) Abraham, R. J. "The Analysis of High Resolution NMR Spectra"; Elsevier: New York, 1971.

(8) Thompson, M. L.; Tarassoli, A.; Haltiwanger, R. C.; Coons, E.; Norman, A. D. *Inorg. Chem.*, in press.

(9) Intensity data were collected by using the θ–2θ scan technique ($2\theta_{max}$ = 40.0°) on a Syntex P$\bar{1}$ automated diffratometer with graphite monochromatized Mo Kα radiation. The structure was solved by direct methods using MULTAN 78 and refined by full-matrix least-squares techniques. All phenyl rings were treated as groups with individual isotropic thermal parameters. Nongroup atoms were refined anisotropically. Hydrogen atoms, except those associated with the disordered ethanol solvate, were located and included in fixed idealized positions. Refinement on 1850 significant reflections converged with $R_f = \sum||F_o| - |F_c||/\sum|F_o| = 0.070$ and $wR_f = [w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0.080$.[10]

(10) All calculations were carried out on the University of Colorado's dual 6400's by using programs contained in or based on Iber's Northwestern University Crystallographic Computing Package, the MULTAN 78 package, and Syntex's data reduction routines. The scattering factors used were for neutral atoms ("International Table for X-ray Crystallography"; Kynoch Press: Birmingham, 1974; Vol. 4). A complete description of the crystallographic details and the refinement and solution of structure $\mathbf{1}{\cdot}C_2H_5OH$ will be published later.

(11) Thompson, M. L.; Haltiwanger, R. C.; Norman, A. D. *J. Chem. Soc., Chem. Commun.* **1979**, *647*.

(12) Harvey, D. A.; Keat, R.; Keith, A. N.; Muir, K.; Rycroft, D. S. *Inorg. Chim. Acta* **1979**, *34*, L201.

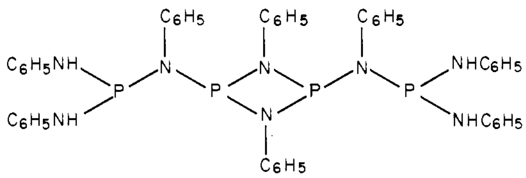
(13) Jefferson, R.; Nixon, J. F.; Painter, T. M.; Keat, R.; Stobbs, L. *J. Chem. Soc., Dalton Trans.* **1973**, 1414.

(14) Zeiss, W.; Barlos, K. *Z. Naturforsch. B* **1979**, *34B*, 423.

(15) Characterization of **2**, reported tentatively by Trishin et al. (Trishin, Yu. G.; Christokletov, V. N.; Kosovtsev, V. V.; Petrov. A. A. *Zhur. Org. Khim.* **1975**, *11*, 1750) has been established finally in our laboratories on the basis of its chemical and spectral (^1H and ^{31}P NMR, IR, and mass) properties.

materials at temperatures at which the rate of trimer-dimer interconversion is appreciable. Experiments to find species which might catlyze the **1** ⇌ **2** interconversion reaction or to discover differently substituted aminophosphine systems in which the equilibrium is more facile are in progress currently.

Compounds **1** and **2**, through their relationship as shown in eq 4, represent two members of a novel oligomerization series involving species of the general formula $[(C_6H_5NH)PNC_6H_5]_n$. So far, no evidence for the monomer (n = 1) has been obtained. If the tendency toward formation of 1,3,2,4-diazaphosphetidine rings persists in the series, the series is limited and can exhibit besides the monomer (n = 1), dimer (n = 2), and trimer (n = 3), only tetramer (n = 4) $[(C_6H_5NH)PNC_6H_5]_4$ (**3**). Species of higher



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n cannot exist unless structures which contain bond arrangements other than 1,3,2,4-diazadiphosphetidine rings occur. Intensive study of the conditions under which **3** might be formed and isolated seems warranted.

Acknowledgment. Support of this work in the form of sabbatical leaves for M.L.T. (Lake Forest College) and A.T. (Jundi Shapur University) and grants from the National Science Foundation (CHE 76-04290 and CHE 79-09497) and the University of Colorado Computer Center is gratefully acknowledged.

Supplementary Material Available: Tables of positional and thermal parameters for nongroup atoms and rigid group atoms (3 pages). Ordering information is given on any current masthead page.

Sceptrin, an Antimicrobial Agent from the Sponge *Agelas sceptrum*

Roger P. Walker and D. John Faulkner*

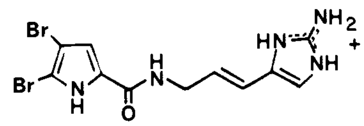
Scripps Institution of Oceanography
La Jolla, California 92093

Donna Van Engen and Jon Clardy*

Department of Chemistry, Cornell University
Ithaca, New York 14853

Received July 17, 1980

During a study of Caribbean sponges, we have examined several sponges of the genus *Agelas*, all of which gave ethanolic extracts having antimicrobial activity, in agreement with previous reports.[1] Prior studies by Minale et al.[2] resulted in the identification of 4,5-dibromo-2-cyanopyrrole as the antimicrobial constituent of the Mediterranean sponge *Agelas oroides*. *A. oroides* also contained 4,5-dibromopyrrole-2-carboxylic acid,[3] the corresponding amide, and oroidin (**1**).[4] In this communication, we report the structural elucidation of sceptrin (**2**), the major antimicrobial constituent of *Agelas sceptrum* (Lamarck).



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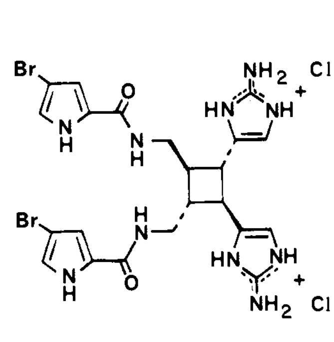

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Antimicrobial assays of the crude extracts of six *Agelas* samples revealed the presence of active compounds in all samples. When the crude extracts were partitioned between ethyl acetate and water, *A. sceptrum* was distinguished by the strong antimicrobial activity of the aqueous phase. *Agelas sceptrum*, collected at Glover Reef, Belize, was maintained frozen until required. The lyophilized sponge was extracted sequentially with hexane, dichloromethane, and methanol. The acetone-insoluble portion of the methanolic extract was twice chromatographed on Sephadex LH-20 by using first methanol and then 1:1 methanol/chloroform as eluants to obtain a fraction containing the antimicrobial material. This fraction was chromatographed on a LiChrosorb DIOL column by using 1:1 methanol/chloroform as eluant to obtain oroidin (**1**, 0.5% dry weight) and sceptrin (**2**, 2.1% dry weight). Traces of a colored impurity were removed by passing an aqueous solution of sceptrin through Sephadex G-10, after which sceptrin (**2**) (as the dihydrochloride) was crystallized from water. Sceptrin (**2**), mp 215-225 °C dec, $[\alpha]_D$ -7.4° (c 1.2, MeOH), had the molecular formula $C_{22}H_{24}Br_2N_{10}O_2 \cdot 2HCl \cdot nH_2O$.[5] The electron impact mass spectrum did not show a molecular ion, but the field desorption mass spectrum contained a triplet at m/z 619, 621, 623 $(C_{22}H_{25}Br_2N_{10}O_2)^{+\cdot}$. The following spectral data indicated that sceptrin (**2**) was a symmetrical dimer of the 2-debromo derivative of oroidin (**1**): IR (KBr) 3350, 1680, 1625 cm^{-1}; UV (MeOH) 265 nm (ϵ 20850); ^{1}H NMR (Me_2SO-d_6) δ 2.29 (br s, 1 H), 3.10 (d, 1 H, J = 8 Hz), 3.42 (br s, 2 H), 6.66 (s, 1H), 6.97 (s, 1 H), 6.99 (s, 1 H), 7.33 (br s, 2 H), 8.59 (br t, 1 H, $J \simeq$ 5 Hz); ^{13}C NMR (D_2O) δ 160.8 (s), 145.7 (s), 123.9 (s), 121.6 (d), 111.6 (d), 108.3 (d), 95.2 (s), 41.6, 40.9, 36.9.

Sceptrin (**2**) formed small crystals in the monoclinic class, and accurate cell constants determined by a least-squares fit of 15 high angle reflections were a = 19.788 (8) Å, b = 13.337 (4) Å, c = 13.725 (7) Å, and β = 122.69 (2)°. Systematic extinctions ($h + k = 2n$), a calculated density of 1.63 g/cm^3, and the presence of chirality were uniquely accomodated by the space group $C2$, with four molecules of $C_{22}H_{26}Br_2Cl_2N_{10}O_2 \cdot 3H_2O$ per unit cell. All unique diffraction maxima with $2\theta \leq 100°$ were collected on a computer-controlled four-circle diffractometer using graphite monochromated Cu Kα (1.54178 Å) radiation and a variable speed ω-scan technique. Of the 2172 unique reflections surveyed in this fashion, 1697 (78%) were judged observed $[F_o \geq 3\sigma(F_o)]$ after correction for Lorentz, polarization, and background effects.

A phasing model was achieved by standard heavy-atom procedures.[6] The deconvolution of the Patterson synthesis gave the

(1) Burkholder, P. R. In "Biology and Geology of Coral Reefs, Biology I"; Jones, O. A., Endean, R., Eds.; Academic Press: New York, 1973; p 144 and references cited therein.

(2) Minale, L.; Cimino, G.; de Stefano, S.; Sodano, G. *Prog. Chem. Nat. Prod.* **1976**, *33*, 1.

(3) Forenza, S. L.; Minale, L.; Riccio, R.; Fattorusso, E. *Chem. Commun.* **1971**, 1129.

(4) After some confusion, the structure of oroidin (**1**) was accepted to be that shown.[2] An interest in solid-state photodimerization reactions prompted us to carry out a single-crystal X-ray diffraction analysis of oroidin. This study reconfirmed the structure shown and details can be found in the supplementary material.

(5) The elemental analysis of a sample dried at 110 °C over P_2O_5 required one molecule of water per sceptrin molecule while the X-ray study indicated three water molecules per sceptrin.

