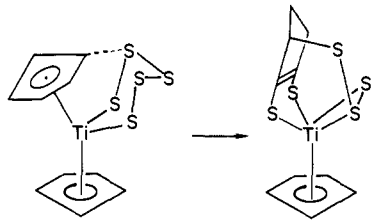
co-workers[9] in their crystallographic characterization of **1**, provides a structural basis for the initiation of the rearrangement process, i.e., C···S bond formation concomitant with lysis of S(2)-S(1) (eq 1).

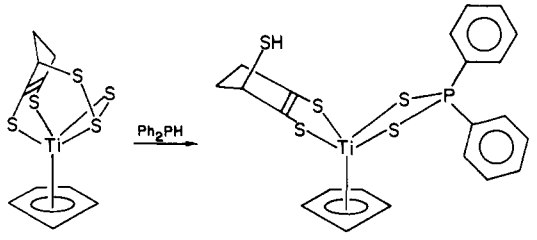


(1)

1 2

Two aspects of this reaction are particularly significant independent of the finer mechanistic details. First, the transformation provides a precedent for the *migration of* a *π-complexed organic fragment to inorganic sulfur ligands*. An associated feature of the rearrangement is that hydrogen migration accompanies the sulfiding of the C_5H_5 fragment. It is very likely that this rearrangement occurs intramolecularly.

Compound **2** cleanly adds Ph_2PH[10] to give a single diastereoisomer wherein each of the S–S bonds has been disconnected.[11] The structure of the product was assigned on the basis of NMR spectroscopy, particularly crucial was the D_2O-exchangeable doublet at 2.24 ppm attributable to the SH substituent, which we suggest is endo (eq 2).



(2)

2 3

In summary, the thermally induced rearrangement of Cp_2TiS_5 gives a novel organosulfur complex via migration of an organic ligand to coordinated sulfur atoms. Conceivably similar but more facile metal-to-sulfur migrations occur in previously reported "additions" of organic substrates to sulfido ligands.[12,13]

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Registry No. 1, 12116-82-4; **2**, 92126-84-6; **3**, 92126-85-7.

Supplementary Material Available: Structure factor tables, positional the thermal parameters, and bond distances and angles (12 pages). Ordering information is given on any current masthead page.

(10) For the related reaction of an η^2-S_2OCH_3 ligand, see: Hoots, J. E.; Rauchfuss, T. B.; Wilson, S. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1226.

(11) Anal. C, H, P, S, Ti. ^1H NMR (90 MHz, $CDCl_3$) δ 7.5 (m, 10 H), 6.4 (s, 5 H), 4.3 (q, 1 H), 3.1 (m, 2 H), 2.2 (d, 1 H), 2.0 (q, 2 H). ^1H NMR (200 MHz, $CDCl_3$, D_2O shake) δ 7.5 (m, 10 H), 6.4 (s, 5 H), 4.3 (t, 1 H), 3.1 (m, 2 H), 2.0 (q, 2 H). ^{13}C NMR (360 MHz, $CDCl_3$) δ 145.5, 145.2, 137.1 (d, J_{PC} = 74.16 Hz), 129.65 (d, J_{PC} = 12.11 Hz), 128.41 (d, J_{PC} = 13.04 Hz), 47. 697, 37.0, 33.0. $^{31}P\{^1H\}$ NMR (250 HMz, CH_2Cl_2) δ 66.05 relative to H_3PO_4 as external standard.

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Hapalindoles: New Alkaloids from the Blue-Green Alga *Hapalosiphon fontinalis*

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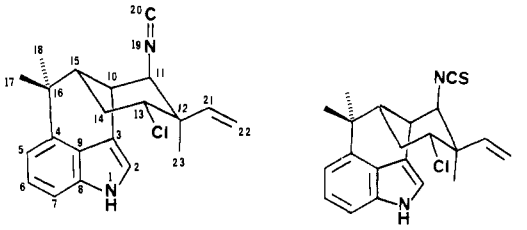
Hapalosiphon intricatus has been reported to produce an extracellular substance that inhibits the growth of another blue-green alga, an *Anabaena* sp.[1] A similar antialgal response has been reported for *H. fontinalis* toward *A. oscillarioides*.[2] In neither case has the active principle been identified.[3] In our work *H. fontinalis* was isolated from soil samples collected in the Marshall Islands in 1981. The lipophilic extract of the cultured alga showed antialgal and antimycotic activities.

An edaphic form of *Hapalosiphon fontinalis* (Ag.) Bornet (Stigonemataceae), strain number V-3-1, was isolated by repeated subculture on solidified media.[4] The alga was cultured in 25-L glass bottles containing an inorganic medium[5] modified by replacing citrate buffer with 3 mM 3-morpholinopropanesulfonic acid (pH 7) and by supplementing the medium with a comprehensive minor and trace element mixture.[6] Cultures were illuminated continuously at an incident intensity of 330 μEinstein m^{-2} s^{-1} from banks of cool-white fluorescent tubes. Cultures were vigorously aerated with 1% CO_2 in air and incubated at 24 ± 1 °C. The alga was harvested by filtration; yields typically were 0.4–0.5-g dry weight of cells per liter of culture. The freeze-dried alga (360 g) was extracted with 1:1 *i*-PrOH/CH_2Cl_2 and the oily extract (15.1 g) was subjected to gel filtration on Sephadex LH-20 with 1:1 *i*-PrOH/CH_2Cl_2 and rapid chromatography on silica gel (TLC grade) with hexane, 1:1 hexane/CH_2Cl_2, CH_2Cl_2, CH_2Cl_2/EtOAc, EtOAc, and EtOAc/EtOH. The fraction that was eluted with 1:1 hexane/CH_2Cl_2 was purified by HPLC on Whatman Partisil with 1:1 hexane/CH_2Cl_2 to give 2.1 g (0.58%) of hapalindole A (**1**), mp 160–167 °C dec and $[\alpha]^{25}_D$ −78°



1 2

(CH_2Cl_2, *c* 1.2) after crystallization from hexane/CH_2Cl_2 and sublimation at 125 °C (0.1 mm). Hapalindole A was responsible for most of the antialgal and antimycotic activity of *H. fontinalis*.

Compound **1** exhibited a UV spectrum [λ_{max} (ϵ) 222 (38 000), 280 (7000), 291 nm (5800)] typical of an indole and IR and ^{13}C NMR peaks [ν_{max} 2145 cm^{-1}; $\delta_{^{13}C}$ 157.40] characteristic of an isonitrile. A molecular formula of $C_{21}H_{23}N_2Cl$ could be deduced for the alkaloid from detailed analyses of the ^1H and ^{13}C NMR spectra (Table I) and a high-resolution EI mass spectrum (M^+ observed at *m/z* 338.1595; mmu error 4.6).[7]

The indole system appeared to be 3,4-disubstituted since the

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(7) The EI MS of **1** does not show an ion peak for loss of HCN from the molecular ion. In the mass spectra of isonitriles, the M–HCN ion peak is generally very intense. The characteristic 3:1 isotopic cluster is observed at *m/z* 338,340 for the chlorine-containing molecular ion.

0002-7863/84/1506-6456$01.50/0

Table I. NMR Data for Hapalindole A (**1**) in $CDCl_3$

^{13}C $\delta^{a,b}$		^1H δ^c	^{13}C $\delta^{a,b}$		^1H δ^c
157.40 s[d]	20		63.59 d[d]	11	4.373 br d
142.99 d	21	6.100 dd	62.99 d	13	4.360 dd
137.52 s	8		44.39 d	15	2.317 ddd
133.17 s	4		43.86 s	12	
123.58 s	9		37.76 s	16	
123.21 d	6	7.190 m	36.80 d	10	3.875 br m
118.48 d	2	6.878 t	31.64 q	18	1.193 s
115.90 t	22	5.346 dd	30.82 t	14	2.142[e] dtd
		5.236 dd			1.472[f] q
113.65 d	5	6.969 m	24.07 q	17	1.553 s
110.14 s	3		18.60 q	23	0.878 s
108.33 d	7	7.199 m		1	8.085 br

$J_{H,H}$ (Hz): 1,2 = 2; 1,7 = ~0.5;[g] 2,6 = ~0.5;[g] 2,10 = 2; 5,6 = 7.2;[g,h] 5,7 = 0.6;[g,h] 6,7 = 8.2;[g,h] 10,11 = 1.6;[g] $10,14_{eq}$ = 1.2; 10,15 = 4.6; $13,14_{ax}$ = 12.4; $13,14_{eq}$ = 4.0; $14_{ax},14_{eq}$ = -13.5; 14_{ax},15 = 13.0; 14_{eq},15 = 3.8; trans 21,22 = 17.4; cis 21,22 = 10.9; gem 22,22 = 0.5

[a] 75 MHz; $CDCl_3$ as internal reference = 76.90. [b] ^1H-^{13}C connectivities determined using a phase-cycled 16-step heteronuclear chemical shift correlation map (CSCM) experiment.[9] [c] 300 MHz; residual $CHCl_3$ as internal reference = 7.25. [d] Broad 1:1:1 triplet in proton-noise-decoupled spectrum, $J_{^{13}C^{14}C}$ ~ 5 Hz. [e] Equatorial. [f] Axial. [g] Determined in benzene-d_6. [h] From simulation of ABX spectrum shown by protons on C-5, C-6, and C-7.

^{13}C NMR chemical shifts were comparable with those of skatole and 4-methylindole.[8] Futhermore, the ^1H-^1H coupling constants associated with the aromatic protons were consistent with this substitution pattern. The signal for the C-2 proton was a triplet, showing small vicinal coupling to the NH proton and allylic coupling to a methine (H on C-10) attached to C-3; in benzene-d_6 this signal was a broader triplet due to long-range zig-zag coupling to the proton on C-6. Two-dimensional spectra for determining the homonuclear ^1H (COSY/16) and heteronuclear ^1H-^{13}C connectivities (CSCM)[9] and selected proton spin-spin decoupling experiments strongly suggested that C-10 was in a X-$CH_{eq\ or\ ax}$-(C-10)H_{eq}-$CH_{ax}H_{eq}$-CH_{ax}-Y unit (where X and Y were CN and Cl, respectively) located in a six-membered ring. The ^{13}C signals for the C=NCH group were broad 1:1:1 triplets in the proton-noise-decoupled spectrum due to ^{13}C-^{14}N coupling. The ^1H signal for the C=NCH group was broad whereas the ^1H signal for the Cl-CH group was sharp.

Remaining for total assemblance of the structure were the placements of two quaternary carbon atoms along with three Me groups and a vinyl group which obviously had to be attached to the two quaternary carbons. One of the quaternary carbons was in the six-membered ring bearing the isocyano and chloro substituents.

The final structure, including relative stereochemistry, was decided from three ^1H-^1H NOE experiments. Irradiation of the Me signal at δ 0.878 produced strong NOE enhancements of the signals at δ 6.878 (C-2 H), 6.100 (C-21 H), 5.236 (C-22 H trans to C-21 H), 4.373 (C-11 H), and 1.472 (axial H on C-14). These NOEs indicated that (1) the irradiated Me group was on the C-12 quaternary carbon and axially disposed, (2) the H on C-11 was equatorial, (3) the vinyl group was on the same carbon as the irradiated methyl group, and (4) the remaining quaternary carbon with two Me groups had to bridge C-4 and the six-membered ring at C-15. The alkaloid therefore had to possess structure **1**. This was verified by irradiation of the Me signals at δ 1.193 [strong NOE enhancement of signals at δ 3.875 (C-10 H), 2.317 (C-15 H), and 1.553 (3H on C-17)] and δ 1.553 [strong NOE enhancement of signals at δ 6.969 (C-5 H), 2.317 (C-15 H), and 2.142 (equatorial H on C-14)].

Hapalindole A is accompanied by smaller amounts of several related compounds. One of these compounds is the corresponding isothiocyanate **2**[10] (EI MS: M^+ observed at m/z 370.1243).

The biogenesis of **1** apparently involves the fusion of tryptophan and monoterpene units. The origin of the isonitrile carbon, however, is unknown.[11] Recently glycine has been shown to serve as a satisfactory precursor of the *N*-formyl carbon in tuberin and possibly the isocyano carbons in xanthocillin X dimethyl ether from *Aspergillus clavatus*.[12]

Acknowledgment. This research was supported by NSF Grant CHE83-03996. High-frequency NMR studies at the University of Hawaii were made possible by NSF Grant CHE81-00240.

Registry No. 1, 92219-95-9; **2**, 92219-96-0.

Supplementary Material Available: 300-MHz ^1H NMR spectrum of **1** in dimethyl-d_6 sulfoxide and difference NOE spectra resulting from irradiation of the three quaternary methyl groups (1 page). Ordering information is given on any current masthead page.

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Models of Photosynthetic Chromophores. Molecular Structure and Aggregation of a Bacteriochlorin

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The recent crystallizations of reaction centers (RC's) containing bacteriochlorophyll *a* (BChl *a*, **1**)[1] and BChl *b*[2] (**2**) only emphasize the sparsity of structural information available for BChls.[3] The structure of a metal-free bacteriochlorin (**3**)[4] has been determined

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