Table I. Electrochemical and Spectroscopic Data

Compound	$E_{p,red}$[a]	$E_{p,ox}$[a]	E_T, eV	$\Delta H°$,[b] eV	$h\nu$, nm
Eu(DBM)$_3$.pip	−1.94	n.o.[c]		2.78	612[f]
Eu(DNM)$_3$.pip	−1.68	n.o.[c]		2.52	610[f]
TPTA	n.r.[c]	1.00	2.9[d]		
BP	−1.75	n.o.[c]	2.97[e]	2.59	~490 to 700[g]
DBMH	−1.43	n.o.[c]	2.77[e]	2.27	~550 to 730[g]

[a] Solutions contained about 1.0 m*M* depolarizer and 0.1 *M* TBAP in acetonitrile. Potentials *vs.* Ag reference electrode. [b] For reaction of reduced form with TPTA·$^+$, calculated from $-\Delta H° = E_{p,red} - E_{ox} + 0.16$ eV.[12] [c] n.r. = not reduced, n.o. = not oxidized, in region of interest. [d] From ref 8. [e] From ref 13. [f] Emission peak obtained by optical excitation. [g] Ecl emission from the electron transfer reaction of TPTA·$^+$ and corresponding anions; λ_{max} values were 581 nm for (TPTA·$^+$–BP·$^-$) and 665 nm for (TPTA·$^+$–DBMH·$^-$).

−1.80 V are probably due to free ligand (DBMH), which cannot be removed from the chelate even by several recrystallizations and sublimation. A cyclic voltammogram of the reduction in a similar solution containing TPTA and BP (Figure 1b) shows that BP can be reduced without reduction of the Eu(III) complex. When the potential of the platinum electrode is pulsed, with a pulse length of 1 sec, from −1.81 V (BP·$^-$ production) to +1.06 V (TPTA·$^+$ production) the exciplex emission observed in the absence of Eu chelate (a broad band with a maximum at 581 nm) is replaced by a narrow band at 612 nm (Figure 1c); this emission corresponds to the luminescence observed from the chelate alone upon photoexcitation (Figure 1d). Note that the electron transfer reaction between TPTA·$^+$ and the reduced Eu(III) chelate does not produce ecl emission (although the energy of the reaction is sufficient to produce an excited chelate species), so that the observed emission cannot be attributed to this source (*e.g.*, from trace amounts of reduced complex formed at the foot of its wave). Moreover trivial excitation of the chelate by the emitted light from the exciplex cannot occur, since the absorption maximum of the complex is at 2.95 eV and excitation at wavelengths of exciplex emission (*ca.* 2.14 eV) fails to produce chelate emission. Finally excited states of TPTA and BP cannot be formed in the electron transfer reaction since the energy of the reaction ($\Delta H° \simeq 2.59$ eV) is significantly below the triplet energies of these species. The results are consistent with the formation of exciplex, reaction 2, followed by energy transfer.

$$^1(A^-D^+)^* + EuL_3 \longrightarrow A + D + EuL_3^* \quad (4)$$

$$EuL_3^* \longrightarrow EuL_3 + h\nu \quad (5)$$

Very similar results are obtained with the TPTA-DBMH-Eu(DNM)$_3$·piperidine system. In the absence of chelate the electron transfer reaction between TPTA·$^+$ and DBMH·$^-$ ($\Delta H° \simeq 2.27$ eV) produces exciplex emission (a band at 615-665 nm) and is energetically incapable of producing excited states of the parent species. When Eu(DNM)$_3$·piperidine is added, only emission from the Eu chelate is observed.

The results suggest that the energy transfer reaction between exciplex and chelate must be a very rapid one, since the exciplex emission is quenched by millimolar amounts of chelate. Since there is essentially no overlap between the exciplex emission and chelate absorption spectra, a long range Förster-type dipole–dipole interaction is improbable, and a diffusion-controlled collisional transfer appears more probable. One possibility, suggested by a reviewer,[14] is that the EuL$_3$ facilitates intersystem crossing of $^1(A^-D^+)$ to the triplet exciplex. Energy transfer from the triplet exciplex to the chelate then produces EuL$_3$*. Finally we should point out the unique advantage of ecl or cl methods in a sensitization study of this sort. The selective formation of exciplex *via* the A·$^-$/D·$^+$ reaction avoids the production of excited states of A and D, required in photoexcitation experiments, which complicate the interpretation of the results.[15]

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(14) We are indebted to Dr. Peter D. Wildes (Boston University) for this suggestion.
(15) Support of this research by the Army Research Office-Durham is gratefully acknowledged.

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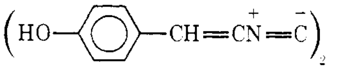
Received August 19, 1974

Cooccurrence of a Terpenoid Isocyanide–Formamide Pair in the Marine Sponge *Halichondria* sp.

Sir:

Prior to the recent isolation of two sesquiterpenoid isocyanides from marine sponges,[1,2] an isocyanide had only once been reported as a naturally occurring function, namely in xanthocillin (**1**),[3] a mold metabolite of *Penicillium notatum.* The postulate of a formamide precursor of this unique natural product seemed an attractive idea, but Achenbach and Grisebach's[4] attempt at illuminating the biogenesis of the isocyanide function in xanthocillin failed. We now have in hand strong presumptive evidence that formamides are precursors of isocyanides in the marine sponge of the genus *Halichondria,* by isolating from this animal two isocyanide–formamide pairs, one a sesqui- (80%) and the other a diterpene (20%). The structures of the sesquiterpenoids are the subject of this report.



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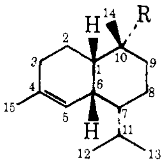
In the course of our program on antimicrobial constituents of marine sponges, we examined the active extract of *Halichondria* sp., which was collected by trawling at a depth of 200 m off the north shore of Oahu. Methanol extraction of the sponge, followed by ether–water partition of the residue, furnished 2.3% (based on dry weight of the animal) of an oil which was separable by preparative tlc on silica gel (methylene chloride–hexane 1:1, visualized with long wavelength uv light). The major portion of the oil consists of functional derivatives **2–4** of the sesquiterpene 4-amorphene (**5**) in addition to two nonfunctionalized dienes, ole-



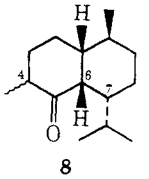
2, R = $\overset{+}{N}\overset{-}{C}$
3, R = NCS
4, R = NHCHO
5, R = H
6, R = NHMe

finic isomers about C-10 (5% of mixture), which we did not rigorously separate. Isocyanide **2** (42%) (mp 40-42°; $[\alpha]_D$ −75° (*c* 5.0, CCl_4); $C_{16}H_{25}N$; ν_{max} 2130 cm^{-1}) was purified by repeated tlc. Isothiocyanate **3** (10%) (oil; $[\alpha]_D$ −63° (*c* 7.4, CCl_4); $C_{16}H_{25}NS$; λ_{max} 214 (1800), 243 (940) nm; ν_{max} 2250, 2100 cm^{-1}) could be separated from its diterpenoid counterpart by tlc (silica gel, hexane) only after allowing the mixture to react with aniline at room temperature, which left **3** unreacted, presumably because of the hindered nature of the isothiocyanate. Formamide **4** (43%) ($C_{16}H_{27}NO$; $[\alpha]_D$ −50° (*c* 5.1, CCl_4); ν_{max} 1680 cm^{-1}) was always contaminated with an equal amount of aliphatic material from which it could be completely freed by LAH reduction of **4** to **6**. Mass and nmr spectra made it at once apparent that these compounds differed only by their functionality at C-10. This was proven by converting **4** to **2** (py and $C_6H_5SO_2Cl$), **2** to **4** (glacial HOAc), and **2** to **3** (S, 120°, 16 hr).

The cadalene (1,6-dimethyl-4-isopropylnaphthalene, **7**) skeleton for the *Halichondria* terpenoids was proven by direct Pd-C conversion of **4** to **7**, or better by Li-$EtNH_2$ treatment of **2**, followed by Pd-C, resulting in **7**, which had expected spectral properties and formed orange picrate, mp 113-115° (lit.[5] 115°).

Principal evidence for the tertiary nature of the functional group rests on the absence of pmr signals in **2** between δ 2.5 and 5.5 and on a cmr triplet at δ 57.6 assigned to C-10, which is coupled to ^{14}N (J = 4 ± 1 Hz)[6] and becomes a broad singlet in the off-resonance spectrum. C-7 was eliminated as a possible locus of the functionality, since a low-field methyl singlet (δ 1.42) in **2** had to be on the carbon bearing the isocyanide while the isopropyl signals (δ 0.91, 0.97, d, J = 6.5 Hz) showed no isocyanide influence.

To distinguish between structure **2** for the isocyanide and an equally plausible alternate with functionality at C-4 and a 9,10-double bond, the isocyanide function was removed with Li-$EtNH_2$, yielding hydrocarbon **5**, $[\alpha]_D$ +11° (*c* 9, CCl_4), the pmr spectrum of which had lost the methyl signal at δ 1.42 but had retained a broad methyl singlet at δ 1.61 for the C-4 methyl. Treatment of **5** with *m*-chloroperbenzoic acid furnished the 4,5-epoxide (C-4 methyl, s, δ 1.25, H-5, s, δ 2.52), which on treatment with BF_3-etherate yielded **8** (mp 50-52°, $[\alpha]_D$ +85° (*c* 2, CCl_4), ν_{max} 1710 cm^{-1}, C-4 methyl, δ 1.18, d (J = 7 Hz), H-6, t, δ 2.95 (J = 4 Hz)). Reaction of **8** with methyllithium, followed by treatment with formic acid and dehydrogenation with Pd-C, led without isolation of intermediates to 5-methylcadalene (1,5,6-trimethyl-4-isopropylnaphthalene), picrate mp 100-102° (lit.[7] 102.5-103.5°).



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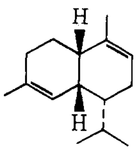

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Ketone **8** not only served to place the functionality unambiguously at C-10 but also provided key evidence for the assigned stereochemistry. The small equal coupling (J = 4 Hz) of H-6 (δ 2.95, t) with H-1 and H-7 is consistent only with axial-equatorial protons in a *cis*-decalone system,[8] as trans diaxial coupling should be 10 Hz. On the reasonable assumption of an equatorial C-7 isopropyl because of its bulk, the *Halichondria* sesquiterpenes possess amorphane (**5**) stereochemistry at C-1, 6, and 7. Both amorphane enantiomers are known natural products.[9,10] They may be distinguished by CD as the octant rule predicts a positive Cotton effect for **8**.[10] We confirmed the stereochemical assignment by a positive Cotton effect of **8** (Φ_{302} +4173, θ_{302} +9264), and by partial epimerization of C-6 of **8** in base to the trans ketone (oil; $[\alpha]_D$ +55° (*c* 2, CCl_4)) exhibiting a weak positive (Φ_{320} +191) and a somewhat stronger negative (Φ_{290} −407) Cotton effect.[10]

Finally, stereochemistry at C-10 was inferred from LAH reduction of **4** to **6** followed by MeI quaternization and Hofmann degradation with Ag_2O. The resulting hydrocarbon mixture, $[\alpha]_D$ +101° (*c* 0.74, CCl_4), has only weak ir absorption and no nmr signals for an exocyclic double bond and must therefore be a mixture of Δ^1 and Δ^9 olefins. These olefins can only have arisen from an axial amine by diaxial elimination, thereby proving stereochemical assignments as shown in **2–6**. The olefinic mixture was subjected to glc (6 ft × ⅛ in., 3% OV-17 on Gas-Chrom Q, column t 95°). When an authentic sample[11] of (+)-α-amorphene (zizanene, **9**) was coinjected, its glc peak coincided with the major component of the Hofmann mixture.

Acknowledgment. We are grateful to Dr. T. R. Erdman for initial extraction of the sponge, to Dr. Ole Tendal for preliminary taxonomic identification, to Professor V. Herout, Dr. K. Adachi, and Dr. N. H. Andersen for comparison samples, and to Professor L. Minale for preprints of ref 1 and 2.

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Received July 31, 1974

Oscillations in Chemical Systems. VII.[1] Effects of Light and of Oxygen on the Bray–Liebhafsky Reaction

Sir:

The first established oscillating chemical reaction in a homogeneous system was the iodate catalyzed decomposition of hydrogen peroxide reported by Bray[2] over 50 years ago. It has recently been studied extensively by Liebhafsky