Isolation of a Diterpenoid Isonitrile from a Marine Sponge

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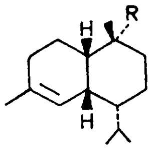
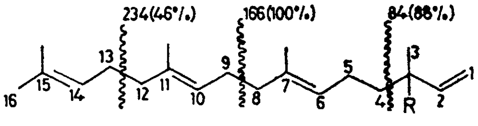
Summary The isonitrile analogue of geranyl-linalo-ol and its corresponding formamide and isothiocyanate have been isolated from a marine sponge of the genus *Halichondria*.

Our recent isolation[1] from a marine sponge (*Halichondria sp.*†) of an amorphane sesquiterpenoid isonitrile (**1**) with its corresponding formamide (**2**), and accompanied by an isothiocyanate (**3**), is strong evidence that a formamide is the biogenetic precursor of the rare isonitrile function. We now report that, remarkably, the same sponge also elaborates a diterpenoid functionalized by the same three groups.

Preparative t.l.c. (silica gel; hexane) of the organic sponge extract furnished (**1**) and a second isonitrile which was further purified by t.l.c. (silica gel; hexane-CH_2Cl_2; 1 : 1) and isolated as an oil (*ca.* 20% of the isonitriles, 0·1% of dry sponge), $[\alpha]_D + 15°$ (*c* 2·8, CCl_4); ν_{max} 2140 (NC), 990, and 930 ($C{=}CH_2$) cm^{-1}; *m/e* (20 eV) 299 (23%) for a composition of $C_{21}H_{33}N$. The ^{13}C n.m.r. spectrum (from Me_4Si) of the second isonitrile displayed signals at 155·6 p.p.m. for the isonitrile carbon and an off-resonance singlet at 62·5 p.p.m. for C-3, in addition to 8 olefinic resonances at 114·0—138·1 p.p.m., consistent with an acyclic tetraene. The ^1H n.m.r. spectrum of (**4**) showed signals at δ 1·59—1·67 (12H, 3 s, 4 =CMe), 1·47 (3H, t, *J* 1·5 Hz, 3-Me, weakly coupled to isonitrile $^{14}N^2$), 1·99br (s, 5 allylic CH_2), 5·1—5·5 (6 =CH, including 3 vinyl-H) and *ca.* 1·2 (2H, unresolved, 4-CH_2). These data, coupled with lack of conjugation (u.v. end absorption only), suggested structure (**4**) for this sponge



(1) R = $\overset{+}{N}\overset{-}{C}$
(2) R = NHCHO
(3) R = NCS



(4) R = $\overset{+}{N}\overset{-}{C}$
(5) R = NHCHO
(6) R = NHMe
(7) R = NCS

metabolite; this structure is the isonitrile analogue of the known[3] jasmine constituent geranyl-linalo-ol. The postulated structure was confirmed by ozonolysis and reductive

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† Collected by trawling at 200 m north of Oahu; taxonomic determination by Dr. Ole Tendal.

work-up of (**4**), leading to 2,4-diphenylhydrazone derivatives of formaldehyde, acetone, and 4-oxopentanal, and by transformation into the formamide (**5**) (HOAC; room temp.), followed by $LiAlH_4$ reduction of (**5**) to the methylamine (**6**). The mass spectrum of (**6**) showed in addition to M^+ at m/e 303 (11%) major fragmentation resulting from allylic cleavage as shown.

The formamide (**5**) is also a sponge constituent, but is cleanly separable from (**2**) only after treatment of the mixture with benzenesulphonyl chloride in pyridine leading to (**4**) and (**1**). Similarly, the isothiocyanate (**7**) (m/e 331, M^+) can be separated from its sesquiterpenoid counterpart (**3**) only after treating the mixture with aniline at room temperature, which left the more hindered (**3**) unchanged.

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[1] B. J. Burreson, C. Christophersen, and P. J. Scheuer, *J. Amer. Chem. Soc.*, in the press.

[2] I. D. Kuntz, Jr., P. von R. Schleyer, and A. Allerhand, *J. Chem. Phys.*, 1961, **35**, 1533.

[3] E. Demole and E. Lederer ,*Bull. Soc. Chim., France*, 1958, 1128.