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A NEW FURANOSESQUITERPENE FROM THE MEDITERRANEAN ALCYONACEAN *ALCYONUM PALMATUM*

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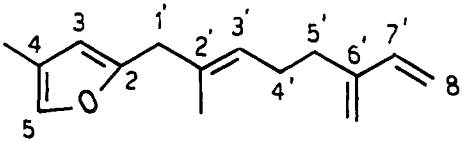
Organisms belonging to the order Alcyonacea (subclass Octocorallia) are widely distributed on tropical coral reefs and have offered to marine chemists the possibility of discovering an impressive series of new molecules (1-3). In the bay of Naples few species of this order are present and, until now, they have not been chemically studied as, living in deep water, they are not easy to collect. In this paper we wish to report the first chemical result obtained from the study of a Mediterranean alcyonacean, *Alcyonum palmatum* Pall.

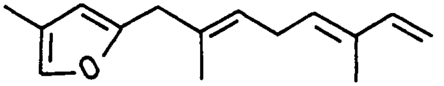
A. palmatum was collected in the bay of Naples by dredging. The Et_2O-soluble fraction, from the Me_2CO extracts of the fresh material, was chromatographed on a silica gel column (light petroleum ether), yielding an Ehrlich positive substance.

The new compound showed a molecular composition $C_{15}H_{20}O$ determined by hrms on the molecular peak at *m/z* 216. Assuming a sesquiterpenoid carbon skeleton for **1** the pmr spectra suggested a linear structure having at the ends of the molecule a 2,4-disubstituted furan ring (δ 7.09, H-5; δ 5.9, H-3; δ 2.0, CH_3-4) and a diene group (δ 6.4, H-7′; δ 5.25 and 5.07, C-8′ H's; δ 5.04 and 5.01, CH_2-6′). The last structural feature was further supported by the highly diagnostic (4) signals (113.0 t, 115.7 t, 138.9 d, 146.0 s) in the cmr spectra. The pmr spectrum showed in addition a vinyl methyl signal (δ 1.62, CH_3-2′) long-range coupled to an olefinic proton resonating at δ 5.29. The remaining resonances, observed at δ 3.25 (2H, s) and 2.26 (4H), were assigned to the doubly allylic protons of C-1′ and to those of the carbons 4′ and 5′, respectively. All these assignments were supported by decoupling experiments and fully agreed with the structure **1**. The cmr spectra confirmed the proposed structure and also allowed assignment of the *E* stereochemistry to the isolated double bond on the basis of the diagnostic (4) chemical shift of the methyl carbon (δ 15.9) in the chain.

A series of sesquiterpenes, e.g., (**2**) closely related to **1** have been recently reported (3) from two species of Australian soft corals (*Sinularia capillosa* and *Sinularia stricta*), while some related cyclic compounds, e.g., **3**, were previously found (5) in some soft corals of the family Xeniidae. All these findings could give taxonomical significance to the 2,4-disubstituted furanosesquiterpenes in the Alcyonacea order.



1



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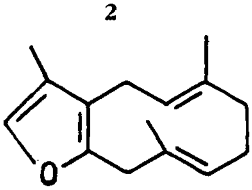

3

EXPERIMENTAL

Equipment used.—Pmr: Bruker WX 250; cmr: Varian XL-100; ms: A.E.I. MS 30; ir: Perkin-Elmer Infracord 257; uv: Shimadzu Bausch & Lomb, Spectronic 210.

ISOLATION OF COMPOUND **1**.—*A. palmatum* (identified by Prof. D. Zavodnik, Center for Marine Research "R. Bošković," Roviny, Yugoslavia) was collected in the bay of Naples in September 1981 by dredging. The fresh material (dry weight 132 g) was extracted with Me_2CO (room temperature, 5 liters$\times$3); after concentration in vacuo the aqueous residue was extracted with Et_2O (200 ml$\times$3). The ethereal extracts were taken to dryness to give 2.4 g of an oil which was chromatographed on a silica gel column (light petroleum ether 40-60°).

After tlc monitoring (SiO_2, light petroleum ether) the Ehrlich positive fractions (Rf 0.3) were combined to give **1** (40 mg, 0.033% yield).

PHYSICAL DATA.—Ms *m/z* 216 (M^+, 25%), 189 (21%), 120 (71%), 95 (38%), 81 (45%), 57 (100%); ir (liquid film) ν max 2920, 2850, 1590, 1450, 1370, 1110, 980, 940, 890 cm^{-1}; uv (CH_3OH) λ max 222 nm (ϵ 11.700); pmr ($CDCl_3$) δ 7.09 (1H, bs, H-5), 6.4 (1H, dd, J=10.7 and 18 Hz, H-7'), 5.9 (1H, bs, H-3), 5.29 (1H, t, J=6 Hz, H-3'), 5.25 (1H, d, J=18 Hz, H-8'), 5.07 (1H, d, J=10.7 Hz, H-8'), 5.04 and 5.01 (2 one-proton singlets, CH_2-6'), 3.25 (2H, s, C-1' H's), 2.26 (4H, apparent broad singlet, A_2B_2 system coupled with the signal at 5.29; C-4' and C-5' H's), 2.0 (3H, s, CH_3-4), 1.62 (3H, s, CH_3-2'); cmr ($CDCl_3$) δ 154.4 (s, C-2), 146.0 (s, C-6'), 138.9 (d, C-7'), 137.7 (d, C-5), 132.2 (s, C-2'), 126.4 (d, C-3'), 120.5 (s, C-4), 115.7 (t, C-8'), 113.0 (t, CH_2-6'), 108.8 (d, C-3), 38.5 (t, C-1'), 31.3 (t, C-5'), 26.8 (t, C-4'), 15.9 (q, CH_3-2'), 9.8 (q, CH_3-4).

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