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A NEW TRISNORDITERPENE
FROM THE SPONGE *FASCIOSPONGIA CAVERNOSA*¹

Y. VENKATESWARLU* and M.A. FAROOQ BIABANI

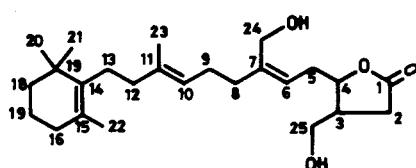
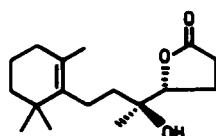
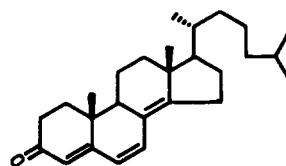
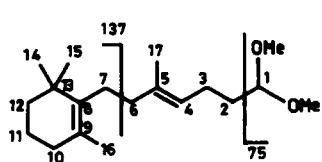
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ABSTRACT.—A new trisnorditerpene [1] and a known ketosterol [2] have been isolated from the sponge *Fasciospongia cavernosa* and characterized by spectroscopic methods.

In continuation of our search for biologically active compounds from marine organisms (1–4), we investigated the sponge *Fasciospongia cavernosa* Schmidt (Thorectidae), collected off the coast of the Andaman Islands during March 1992. A literature survey revealed that *F. cavernosa* has previously afforded the ichthyotoxic trisnorditerpene cavernosin [3] (5) and C₂₁-furanoterpenes (6). The (1:1) CH₂Cl₂-MeOH extract of this sponge was subjected to Si gel chromatography eluting with hexane, through hexane/EtOAc mixtures to EtOAc, to afford a new trisnorditerpene [1] and a known ketosterol [2] (7). Compound 2 was obtained as semi-solid, which displayed a molecular ion at *m/z* 378. A study of its ir spectrum (1660, 1640, and 1585 cm⁻¹) and characteristic ¹H-nmr signals at δ 6.60 (1H, d, *J*=9 Hz), 6.05 (1H, d, *J*=9 Hz), and 5.70 (1H, br s) led

to the identification of compound 2 as (22*E*)-cholesta-4,6,8(14),22-tetraen-3-one, which has been isolated previously from a sponge, *Dictyonella incisa* (7).

Compound 1 was obtained as an oil and analyzed for C₁₉H₃₄O₂ by microanalysis; eims *m/z* 294 (M⁺). The ¹³C-nmr spectrum of compound 1 showed the presence of a tetrasubstituted and a trisubstituted double bond (δ 137.2 s, 136.5 s, 126.9 s, and 123.5 d) and a methine carbon at δ 104.1 d. The ¹H-nmr spectrum of compound 1 displayed the presence of two quaternary methyls at δ 1.00 (6H, s) and two vinylic methyls at δ 1.61 (3H, s) and 1.55 (3H, s), and two methoxyl groups at δ 3.31 (6H, s). Further, the ¹H-nmr spectrum of compound 1 revealed the presence of a trisubstituted double bond at δ 5.19 (1H, t, *J*=7 Hz) and a methine carbon-bearing oxygen atom at δ 4.30 (1H, t, *J*=7 Hz). The signal at δ



4.30 was attributed to a dimethylacetal proton, which was supported by ^{13}C -nmr signals at δ 104.6 (d), and 52.62 ($2\times\text{q}$) respectively, for acetal carbon and methoxyl groups. Further, the ^{13}C -nmr chemical shifts of the trimethylcyclohexenyl and trisubstituted double-bond portions of compound **1** were found to be in good agreement with those of *Z*-2,3-dihydroneromanoalide [4], a sesquiterpene isolated from a sponge of the genus *Luffariella* (8). From the foregoing spectral data and the ms data [m/z 137 (100)], the structure of compound **1** was recognized as a typically alkylated cyclohexenyl derivative ($\text{C}_{10}\text{H}_{17}$) commonly found in marine sponges (9,10). Several attempts to convert compound **1** to its aldehyde form were not successful due to the formation of complex mixtures in the reaction. Compound **1** might be an artifact obtained during the isolation procedure.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—The ^1H - (200 MHz) and ^{13}C -nmr (50 MHz) spectra were recorded on a Varian Gemini 200 MHz spectrometer, using TMS as internal standard. Elemental analysis was carried out on a Perkin-Elmer 240C instrument. Chemical shifts were reported in δ values and coupling constants (J) in Hz. Mass spectra were recorded on a Finnigan-MAT 1020 mass spectrometer.

ANIMAL MATERIAL.—The sponge *Fasciospongia cavernosa* (IIC-057) was collected (400 g dry wt) from the intertidal rocks at the Andaman Islands and preserved in MeOH until workup. A voucher specimen has been deposited at the museum of the National Institute of Oceanography, Goa, India.

EXTRACTION AND ISOLATION.—The sponge was extracted with CH_2Cl_2 -MeOH (1:1) at room temperature (3×1 liter), and the combined extracts concentrated under reduced pressure to afford a predominantly aqueous suspension that was

extracted with EtOAc. Cc of the EtOAc extract (2 g) over Si gel (100–200 mesh) eluting with hexane, through hexane/EtOAc mixtures to EtOAc, yielded compound **1** (30 mg) and the ketosterol **2** (40 mg) (7). Compound **1** exhibited: *anal.* found, C, 77.25%, H, 11.83%, required for $\text{C}_{19}\text{H}_{34}\text{O}_2$, C, 77.49%, H 11.63%; ^1H nmr (CDCl_3 , 200 MHz) δ 5.19 (1H, t, $J=7$ Hz), 4.30 (1H, t, $J=7$ Hz), 3.31 (6H, s), 2.08 (8H, m), 1.95 (2H, m), 1.61 (3H, s), 1.55 (3H, s), 1.40 (4H, m), 1.00 (6H, s); ^{13}C nmr (CDCl_3 , 50 MHz) δ 137.2 s, 136.5 s, 126.9 s, 123.5 d, 104.1 d, 52.6 ($2\times\text{q}$), 40.3 t, 39.9 t, 35.0 s, 32.1 t, 28.6 ($2\times\text{q}$), 27.9 t, 26.6 t, 24.8 t, 19.8 t, 19.6 q, and 16.0 q; eims m/z 294 (2), 218 (20), 137 (100), 95 (70), 81 (60), 75 (40).

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