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A New Oxygenated Furano Sesquiterpene from the Sponge *Dysidea fragilis*#

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Abstract – A new oxygenated furano sesquiterpene [**1**] has been isolated from the sponge *Dysidea fragilis* collected from Mandapam coast, Tamilnadu, India and its structure was determined by analysis of spectral data.

Key words – *Dysidea fragilis*, furano sesquiterpene and monocyclo farnesane.

Introduction

In continuation of our search for biologically active compounds from marine organisms (Venkateswarlu *et al.*, 1993, 1996), we investigated a sponge *Dysidea fragilis* (Montagu) family *Dysideidae* collected from Mandapam coast during October 1997. The genus *Dysidea* is a prolific source for sesquiterpenoids (Guella *et al.*, 1985) and sesquiterpene hydroquinones (Minale *et al.*, 1974), which were biologically active and structurally interesting. Previously, we reported a new sesquiterpene isolated from *D. herbacea* (Venkateswarlu *et al.*, 1994). Recently, dysidiolide, a new rearranged sesterterpene lactone, has been isolated from Caribbean sponge *D. etheria* (Gunasekera *et al.*, 1996) and was found to inhibit protein phosphatase.

Experimental

Optical rotation was measured with JASCO DIP-370 polarimeter using 1dm cell. IR spectrum recorded on Perkin Elmer 1310 spectrophotometer. ^{1}H-NMR and ^{13}C NMR spectra were recorded on Varian Gemini 200 MHz spectrometer using TMS as internal standard and coupling constant (*J*) were reported in Hz. High-resolution mass spectra was recorded on VG-AUTO SPEC-M instrument.

Collection, Extraction and Isolation – The sponge *D. fragilis* was collected in October, 1997 at a depth of 20 feet by skin diving near Mandapam coast. A voucher specimen (IIC-306) has been lodged at the museum of National Institute of Oceanography, Goa, India. The specimens were soaked in MeOH at the site of collection until work up. The MeOH was decanted, concentrated *in vacuo* to obtain an aqueous suspension that was lyophilized to give solid residue. The specimens (15 g dry wt.) were then lyophilized and extracted with MeOH-CH_2Cl_2 (1:1, 2×0.5 L) and concentrated to obtain viscous gummy residue. The combined residues were extracted with ethyl acetate (3×100 mL) and the concentrated extract (2 g) was subjected to gel filtration on Sephadex LH-20, (1:1 MeOH-CH_2Cl_2) followed by silica gel chromatography eluting with hexane through hexane-ethyl acetate mixtures and finally with ethyl acetate to afford compound **1** (8 mg).

Compound **1**: Colorless oil; $[\alpha]_D$ −17.9 (c=

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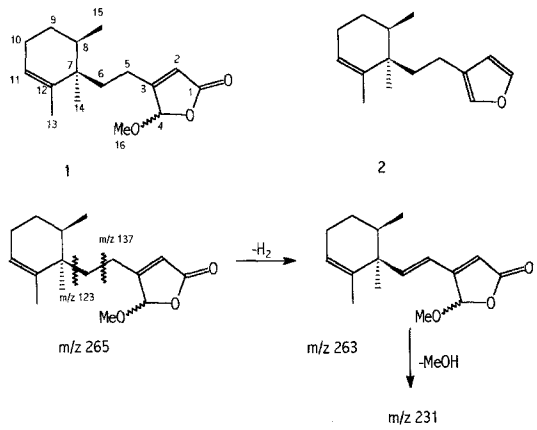
0.5; $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz) δ 5.82 (s, 1H), 5.78 (s, 1H), 5.34 (m, 1H), 3.12 (s, 3H), 2.85 (t, J=6 Hz, 1H), 2.40 (m, 1H), 2.18 (m, 1H), 1.78 (m, 1H), 1.64 (s, 3H), 1.60 (m, 2H), 1.25 (m, 2H), 1.05 (s, 3H) and 0.84 (d, J=7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.2 (C-1), 148.0 (C-3), 139.0 (C-12), 123.8 (C-11), 120.1 (C-2), 93.2 (C-4), 50.6 (C-16), 43.7 (C-7), 38.2 (C-6), 31.1 (C-8), 29.6 (C-10), 25.7 (C-5), 24.3 (C-9), 21.3 (C-15), 21.28 (C-14) and 20.7 (C-13); FABMS (m/z) 265 (8), 263 (100), 231 (28), 137 (32), 123 (25), 107 (26); HREIMS m/z 264.3573 (calcd 264.3648; for $C_{16}H_{24}O_3$).

Results and Discussion

The 1:1 dichloromethane-methanol extract of the sponge was subjected to gel filtration chromatography followed by silica gel column chromatography afforded a new oxygenated furano sesquiterpene [**1**]. Compound **1** was obtained as an oil $[\alpha]_D$ -17.9 (c=0.5; $CHCl_3$) and assigned molecular formula $C_{16}H_{24}O_3$ by its ^1H NMR and HREIMS data. Its IR spectrum showed a band corresponding to a α,β-unsaturated γ-lactone at 1680 cm^{-1}. The ^1H NMR spectrum of compound **1** contained signals corresponding to two trisubstituted double bond protons at δ 5.82 (s, 1H), and δ 5.34 (m, 1H), a methine proton corresponding to hemiacetal at δ 5.78 (s, 1H), a vinylic methyl at δ 1.64 (s, 3H), a methoxy signal at δ 3.12 (s, 3H), a secondary methyl at δ 0.84 (d, 3H), and a tertiary methyl signal at δ 1.05 (s, 3H), respectively. Further, the ^{13}C NMR spectrum of compound **1** supported the presence of α,β-unsaturated γ-lactone carbon at δ 170.2 and its olefinic carbons at δ 148.0 and 120.1, a hemiacetal methine carbon at δ 93.2, a methoxy carbon at δ 50.3 and a trisubstituted double bond carbons at δ 139.0 and 123.8 respectively. A literature survey and the foregoing spectral data revealed that the structure of the new sesquiterpene



as **1**, a photo oxygenated product of microcionin-2 [**2**] isolated from *Microciona toxystila* (Cimino *et al.*, 1975). Its EIMS showed base peak at m/z 123, further supported the proposed rearranged monocyclo farnesane skeleton as indicated in **1** (Cimino *et al.*, 1975).

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