SPECIALIA

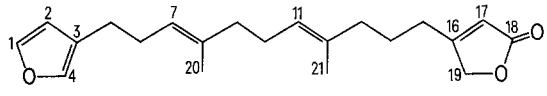
Furospongolide, a new C_{21} furanoterpene from a marine organism[1]

Y. Kashman and M. Zviely

Department of Chemistry, Tel-Aviv University, 61390-Ramat-Aviv (Israel), 7 January 1980

Summary. The structure of a new linear C_{21} furanoterpene, furospongolide (**1**), obtained from the marine sponge *Dysidea herbacea,* was determined by spectral means.

C_{21}-Furanoterpenes are among the most unusual terpenes isolated from sponges, mainly occurring in the genus *Spongia*[2]. The majority of these compounds terminate in a furane ring at both ends of the linear carbon skeleton. However, the γ-hydroxy-α,β-butenolide and β,γ-epoxybutenolide ends are not unknown[2]. In this communication we wish to report the isolation of a new C_{21}-furanoterpene, furospongolide (**1**), which coexists with several alkylated scalarins[3] in *Dysidea herbacea* collected in the Gulf of Suez (Red Sea). Freeze-dried sponge was extracted with petrol ether to give a crude extract (1.6% dry weight) from which compound **1** (0.05% dry weight of the animal) could be obtained following chromatography on Silica-gel (eluted with petrol ether and increasing amounts of ether) and on Sephadex LH-20 (eluted with petrol ether-CH_2Cl_2-MeOH in ratio of 1:1:2). Compound **1**, $C_{21}H_{28}O_3$ an oil, m/e 328 (M^+, 12%), 247 ($M^+ - C_5H_5O$, 4%) and 81 ($C_5H_5O^+$, 100%) exhibits a positive Ehrlich test, for furans, in agreement with the 81 fragment in the mass spectrum[4]. The IR-spectrum of **1** ($\nu_{max}^{CHCl_3}$ 1785(w), 1775(s), 1645, 1170, 1070, 1030, 880 cm^{-1} and $\nu_{max}^{CCl_4}$ 1785(s) and 1755(w) cm^{-1}) was consistent with the presence of a α,β-unsaturated-γ-lactone[5] and a furan moiety. The ^1H and ^{13}C-NMR spectra of **1** suggested the following structure:



Compound **1**

^1H-NMR ($CDCl_3$, 270 MHz, ppm): 7.33 brs (H-1), 6.27 brs (H-2), 7.20 brs (H-4), 5.83 t (J=2 Hz, H-17), 5.16 t (J=8.3 Hz, H-11), 5.10 t (J=8.3 Hz, H-7), 4.72 d (J=2 Hz, H-19,19'), 2.45 t (J=7.8 Hz, H-5,5'), 2.33 t (J=7.3 Hz, H-15,15'), 2.25 brq (J=8 Hz, H-6,6'), 2.05 m (6H, H-9,10 and 13), 1.68 quin (J=7.5 Hz, H-14,14') and 1.59 (CH_3-20 and 21).

^{13}C-NMR ($CDCl_3$, 22.63 MHz, ppm):

C-	1	2	3	4	5	6	7	8
δ-	142.3	110.9	124.8	138.5	24.8	27.7[a]	123.7[b]	135.3[c]
9	10	11	12	13	14	15	16	17
38.7[d]	26.2	125.5[b]	132.2[c]	39.4[d]	28.2[a]	24.8	170.4[e]	115.1
18	19	20	21					
170.0[e]	72.9	15.7	15.7					

[a–e] Assignments may be interchanged.

The signal assignment was based on intensive double resonance experiments of compound **1** and its complex with d_{27}-Eu(fod)$_3$.

The ^{13}C-chemical shift assignment was based on the peak multiplicities (SFORD), chemical-shift considerations and by comparison with structurally related compounds: butenolides, furans, linear terpenes and furano sesterterpenes[6].

The above ^1H and ^{13}C-NMR data agree with either 1 of 2 structures namely the $\Delta^{7,11}$ or the $\Delta^{8,12}$ isomers of the above formula. Differentiation between the two was achieved by an LIS experiment, vide supra ($\Delta\delta$, H-17 > H-19 ≫ H-15 > H-14 > H-13 > H-5, 11, 7, 6). This experiment confirmed a 3-(rather than 2)methylene chain to link the complexation site, that is, the butenolide terminus with the nearby double bond, confirming thereby the entire structure of the C_{10}-C_{19} segment[7]. The ^{13}C-NMR spectrum in addition to suggesting the various molecules' functional moieties also made possible the E-configuration assignment of the 2 double bonds[8,6e].

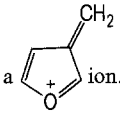
The close relationship between compound **1** and the furospongins[2] lead us to the name, furospongolide.

Finally, it is noteworthy, that although the α,β-unsaturated butenolide end is unknown in the C_{21}-furanoterpene series it is not unfamiliar in other marine metabolites; e.g. the linear hexaprenoid moqubilin[6d] terminates with such a moiety.

1 We thank Professor J. Vacelet for the identification and Dr Loya and Mr Benayahu for the collection of the sponge.

2 L. Minale, in: 'Marine Natural Products', chapter 4, p. 175. Ed. P.J. Scheuer. Academic Press, New York 1978.

3 Y. Kashman and M. Zviely, Tetrahedron Lett. *1979,* 3879.

4 An 81 m.u. fragment points on a 

ion.

5 a) K. Nakanishi, Infra-Red Absorption Spectroscopy-Practical. Holden-Day Inc., San-Francisco 1964; b) R.N. Jones, C.L. Angell, T. Ito and R.J.D. Smith, Can. J. Chem. *37,* 2007 (1959).

6 a) L. Barlow and G. Pattenden, J. chem. Soc. Perkins I *1976,* 1031; b) L. Crombie, R.W. King and D.A. Whiting, J. chem. Soc. Perkins I *1975,* 913; c) R. Tschesche and B. Streuff, Chem. Ber. *111,* 2130 (1978); d) M.B. Yunker and P.J. Scheuer, J. Am. chem. Soc. *100,* 307 (1978); e) G. Alfano, G. Cimino and S. De Stefano, Experientia *35,* 1136 (1979).

7 The missing signal of 2 double allylic protons (C-10) in the ^1H-NMR spectrum of compound **1** (2.6–2.8 ppm) excluded a possible $\Delta^{8,11}$ structure.

8 P.A. Couperus, A.D.H. Clauge and J.P.C.M. Van-Dongan, Org. Mag. Res. *8,* 426 (1976).