Tetrahedron Letters No. 16, pp 1333 - 1334, 1976. Pergamon Press. Printed in Great Britain.

TWO NEW UNSYMMETRICALLY OXYGENATED C_{21} FURANOTERPENES FROM A SPONGE

R. Kazlauskas, P.T. Murphy, R.J. Quinn and R.J. Wells
Roche Research Institute of Marine Pharmacology, P.O. Box 255,
Dee Why, N.S.W. Australia 2099.

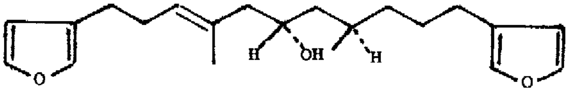
(Received in UK 17 February 1976; accepted for publication 7 March 1976)

Degraded C_{21} furanoterpenes have been reported from three sponge species of the genus Spongia and from the closely related Hippospongia communis[1]. A feature common to all structure described to date has been oxygenation at the centre of the prenyl chain (e.g. furospongin-1 (1) oxygenated at C_{11})[2]. We now report two new C_{21} furanoterpenes, furospongenol (2) and furospongenone (3), isolated from an Australian Spongia species collected near Sydney, which have unsymmetrical oxygenation at C_{12}.

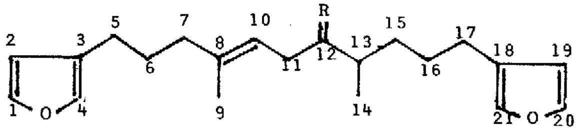
Percolation of the freeze dried sponge material with cold petroleum ether gave a 1.3% extract which yielded (2) (80%) and (3) (4%) as oils after chromatography on silica gel, together with minor amounts of lipids and sterols.

The i.r. spectrum of furospongenol (2) indicated the presence of an alcohol group and this was established by acetylation to a monoacetate and oxidation with Jones reagent to give the monoketone (3) identical with natural furospongenone. Hydrogenation of (2) with Pd/C in ethyl acetate indicated the presence of one isolated double bond.

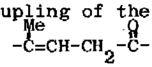
The molecular formula of (2) ($C_{21}H_{30}O_3$) was suggested by high resolution mass spectroscopy and major fragment ions which occurred at m/e 167, 164, 149, 135, 107, 94, 82 and 81 were in accord with a linear prenyl difuran[1]. This was supported by the 100 MHz ^1H n.m.r. spectrum of (2) which demonstrated the presence of two β-disubstituted furan moieties (δ7.2 (2H,bs; C_1-H, C_{20}-H); 7.08 (2H,bs; C_4-H, C_{21}-H); 6.14 (2H,bs; C_2-H,C_{19}-H)). Other resonances included a secondary methyl group at δ 0.89 (3H,d, J=6.5Hz; C_{14}-H), a proton on a carbon bearing the hydroxy group at δ3.36 (1H,m; C_{12}-H) and a $-CH_2-CH=\underset{Me}{C}-$ group was also implied by resonances at 5.08 (1H,bt, J=7Hz;C_{10}-H) and 1.60 (3H,bs; C_9-H).



(1)



(2) R = H, OH
(3) R = O

Furospongenone (3) ($C_{21}H_{28}O_3$) showed major fragment ions at m/e 166, 149, 138, 136, 120, 107, 95 and 81 in the mass spectrum and i.r. (ν max 1705 cm^{-1}) and u.v. spectra revealed that the ketone was not conjugated. The ^1H n.m.r. spectrum in CCl_4 indicated the presence of a doubly allylic methylene group at δ 3.02 (2H,d,J=7Hz; C_{11}-H) and a vinyl proton at δ5.25 (1H,bt,J=7Hz; C_{10}-H). The mutual coupling of these resonances was demonstrated by irradiation and the partial structure  $-\overset{Me}{\overset{|}{C}}=CH-CH_2-\overset{O}{\overset{\|}{C}}-$ in (3) was demanded. Successive additions of Euroshift F to this ^1H n.m.r. sample separated some resonances. The site of pseudocontact interaction was the carbonyl group as evidenced by the order of shift of separate protons ($C_{11}-H > C_{13}-H > C_{10}-H > C_{14}-H \sim C_{15}-H_a > C_{15}-H_b > C_9-H$). The protons on C_{13} and C_{15} were separated as complex multiplets and identified by irradiation experiments. Other shifts gave further information; the furan proton pairs on C_4,C_{21};C_2,C_{19} and C_1,C_{20} were unequal in accord with unsymmetrical oxygenation at C_{12} and C_7-H was observed as the expected two proton triplet.

Five Australian Spongia species investigated[1,3,4] have yielded different major metabolites:- furospongin-1 (1)[4], tetradehydrofurospongin -1[1], a series of tetracyclic diterpenefurans[3] and the compound (2) described here. The taxonomic identification of Spongia and related species have caused many problems which may well be resolved by further chemical work.

REFERENCES

1. R. Kazlauskas, P.T. Murphy, R.J. Quinn and R.J. Wells - preceding paper and references therein.
2. Number system used follows that in reference 1 and previous reference quoted.
3. R. Kazlauskas, P.T. Murphy, R.J. Quinn and R.J. Wells, Manuscript in preparation.
4. *Ibid.* Unpublished observations.