Tetrahedron Letters No. 16, pp 1331 - 1332, 1976. Pergamon Press. Printed in Great Britain.

TETRADEHYDROFUROSPONGIN-1, A NEW C-21 FURANOTERPENE 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

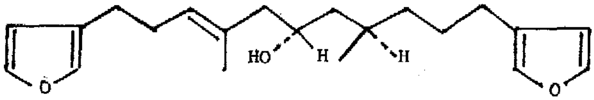
(Received in UK 17 February 1976; accepted for publication 7 March 1976)

The presence of C_{21} degraded furanoterpenes in the closely related Mediterranean sponge species Spongia officinalis, S. nitens and Hippospongia communis has been reported [1-3]. Furospongin-1 (1) exemplifies the compounds obtained from S. officinalis and H. communis[1,2] and nitenin (2), containing an extra lactone function, was obtained from S. nitens[3]. Minor metabolites with oxidised furan rings have also been reported[4].

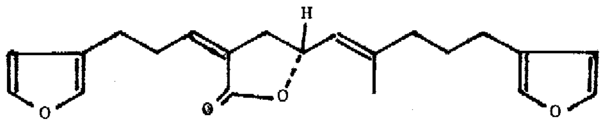
Extraction of a freeze dried sample of an Australian Spongia species, collected near Sydney, with cold petroleum ether yielded 1% of tetradehydrofurospongin-1 (3) as an air and light sensitive oil, by rapid silica gel chromatography.

The molecular formula ($C_{21}H_{26}O_3$,M^+326) of (3) was established by high resolution mass spectrometry and major fragment ions were revealed at m/e 81, 95, 97, 150, 170 and 308. The i.r. spectrum demonstrated the presence of an alcohol (ν max 3400 cm^{-1}) and (3) could be oxidised to the ketone (4) ($C_{21}H_{24}O_3$,M^+324) in 55% yield by a brief treatment with a slight excess of Jones reagent in acetone. The ready uptake of three moles of hydrogen when (3) was shaken with 5% Pd/C established the presence of three double bonds.

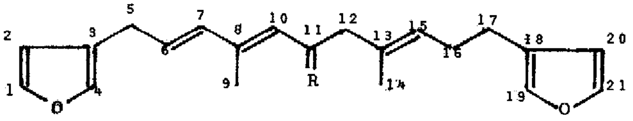
The 100 MHz. ^1H n.m.r. spectrum of (3) in carbon tetrachloride showed resonances fully in accord with the proposed structure as follows[5]:- δ 7.25-7.10 (3H,m) and 7.10 (1H, bs.) attributable to α-furan protons; 6.36 (1H, bs; C_2-H); 6.12 (1H, bs; C_{20}-H); 6.13 (1H, d, J=15Hz; C_7-H); 5.80 (1H, d of triplets, J=15 Hz, 7 Hz; C_6-H); 5.12 (1H, bd, J=7.5 Hz; C_{10}-H); 5.16 (1H, bt; C_{15}-H); 4.30 (1H, m; C_{11}-H); 2.75 (2H, bd, J=7 Hz; C_5-H); 1.64 and 1.60 (3H each, bs; C_{14}-H and C_9-H). Other resonances occurred between δ 2.5 and 2.0. Many of the assignments were supported by double resonance studies. Irradiation of the doublet of triplets at δ5.80 collapsed the broad doublet at δ2.75 to a broadened singlet; also irradiation at δ4.30 collapsed the broad doublet at δ5.12 to a singlet and a singlet also appeared at δ2.05. The mass spectral data also supported this structure and prominent peaks at m/e 150 and 176 were readily explained by a McLafferty re-arrangement of (3) with transfer of the OH proton to C_{15} and cleavage of the C_{11}-C_{12} bond.



(1)



(2)



(3) R = H, OH

(4) R = O

The ^{1}H n.m.r. spectrum of (4) supported the proposed structure. The α-furan protons were observed between δ7.30-7.10 and two β furan protons appeared at δ6.40 and 6.15. Other resonances were as follows :- δ6.22 (1H,d,J=15Hz, C_7-H); 6.01 (1H,s;C_{10}-H); 5.75 (1H, d of triplets, J=15 Hz, 7Hz; C_6-H); 5.20 (1H, bt; C_{15}-H); 2.95 (2H,s; C_{12}-H); 2.87 (2H,d,J=7Hz; C_5-H); 2.5-2.1 (4H,m; C_{16}-H + C_{17}-H); 2.10 (3H,s; C_9-H); 1.57 (3H,s;C_{14}-H). The i.r. spectrum of (4) (ν max 1685, 1615 cm^{-1}) was in accord with the presence of a conjugated-enone.

REFERENCES

1. G. Cimino, S. de Stefano, L. Minale and E. Fattorusso, Tetrahedron, 27, 4673 (1971).
2. G. Cimino, S. de Stefano, L. Minale and E. Fattorusso, Tetrahedron, 28, 267 (1972).
3. E. Fattorusso, L. Minale, G. Sodano and E. Trivellone, Tetrahedron, 27, 3909 (1971).
4. G. Cimino, S. de Stefano; L. Minale, Experientia, 30, 18 (1974).
5. For the sake of consistency the numbering system adopted in this paper follows the numbering system presented in References 1 and 2.