Tetrahedron Letters No. 30, pp 2637 - 2638, 1976. Pergamon Press. Printed in Great Britain.

A NOVEL PEROXYKETAL FROM A SPONGE

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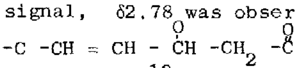
(Received in UK 14 May 1976; accepted for publication 14 June 1976)

A sponge of the genus Chondrilla, although not abundant, is widely distributed on the Great Barrier Reef. Extraction of a small freeze-dried sample of the sponge collected east of Townsville yielded a 10% petroleum ether extract from which chromatography on silica gel gave Chondrillin (1) as a viscous pale yellow oil, which slowly solidified to a wax, m.p. 30°. Pure Chondrillin was stable and was only slowly decomposed by acids but was extremely sensitive to inorganic bases and amines.

Elemental analysis of (1) indicated the formula $C_{24}H_{44}O_5$ whereas high resolution mass spectrometry gave no molecular ion. Major fragment ions occurred at m/e 380 ($C_{24}H_{44}O_3$; M^+-O_2); 364 ($C_{23}H_{40}O_3$; M^+-CH_3OH-O); 321 ($C_{22}H_{41}O$; $M^+-O_2-CH_3OCO$). Attempted distillation or gas chromatographic analysis resulted in extensive decomposition.

The 100 MHz ^1H NMR spectrum in deuterochloroform showed resonances corresponding to 44 protons as follows:- δ6.22 (1H, d of d, J=10Hz, 4.5Hz; C_4-H); 5.68 (1H, d of d, J=10Hz, 1.5Hz; C_5-H); 4.76 (1H, m; C_3-H); 3.70 (3H, s; OMe); 3.38 (3H, s; OMe); 2.78 (2H, eight lines, J=16Hz, 8Hz; C_2-H); 1.60 (2H, bt; C_7-H); 1.25 (28H, bs; $(CH_2)_{14}$); 0.89 (3H, bt, J=7Hz; C_{22}-H). Irradiation at δ4.76 collapsed the quartets at δ6.22 and 5.68 to doublets (J=10Hz) and the signal, δ2.78 was observed as an AB quartet (J=16Hz). Thus the partial structure



$-C-CH=CH-\overset{O}{\overset{|}{C}}H-CH_2-\overset{O}{\overset{\|}{C}}$ was indicated.

The ^{13}C NMR spectrum in deuterochloroform confirmed the presence of an ester carbonyl (170 ppm, s; C_1), two vinyl carbon atoms (129.4 and 126 ppm, each a doublet; C_4 and C_5), two methoxyl groups (51.8 and 51.1 ppm) and a CH-O- group (73.7 ppm, d; C_3). A singlet at 100.5 ppm confirmed the presence of a tetrasubstituted carbon atom (C_6) bound to two oxygen atoms.

The structure of (1) was further confirmed by chemical reactions. Hydrogenation in ethyl acetate with a 5% Pd/C catalyst gave a 9:1 mixture of (2) and (3). (2) was oxidised to (3) in high yield by Jones reagent. Although (3) was a β-keto ester it existed solely in the ketonic form in deuterochloroform. Deoxygenation of (1) with triphenyl phosphine at 100° for ten minutes gave a mixture of (4), (5) and (6) in high overall yield. Chromatography on silica gel gave pure (4) as the major product (70%); (5) and (6) could not be separated but ^1H NMR, MS, IR and UV data on the mixed isomers were consistent with these structures. Reduction of (1) with zinc-acetic acid was very rapid at 50° and produced the furan (7) in almost quantitative yield.

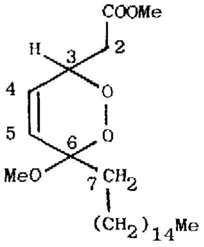
Perhaps the most interesting reaction of (1) was the almost quantitative formation of the chloro-enone (8) which was produced slowly (ca. 7 days at room temperature) when (1) was shaken with an equivolume mixture of diethyl ether and 10 M aqueous HCl. This reaction can be rationalised by the ionic mechanism shown in Scheme 1.

Peroxy-compounds of the type (1) have been prepared by photoaddition of oxygen to enol acetates or enol ethers of enones and the production of compounds of type (4) and (8) from such photoadducts is under investigation.

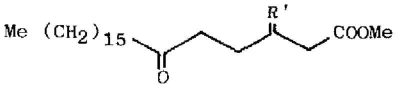
The optical activity of (1) ($[\alpha]_{20}^{D}$ + 144°) indicated that it was formed in the sponge by an enzyme mediated process and was not an artifact formed by oxygen addition to a diene. Circular dichroism and ORD studies on the hydroxyketone (2) suggested that the absolute configuration at the -OH group was R and thus the absolute configuration of (1) at C_3 was S. No information on the relative configuration at C_6 could be obtained because of the destruction of asymmetry at this centre in all reactions.

Acknowledgments.

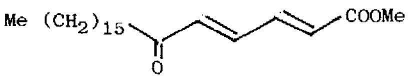
The author wishes to thank Drs.W. Vetter, K. Noack and G. Englert; F.Hoffmann-La Roche, Basel, Switzerland for MS,CD- ORD and ^{13}C NMR data respectively, and to Dr. W.Hofheinz for discussions. We thank Professor P. Bergquist for sponge identification.



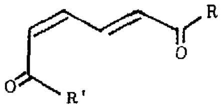
(1)



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



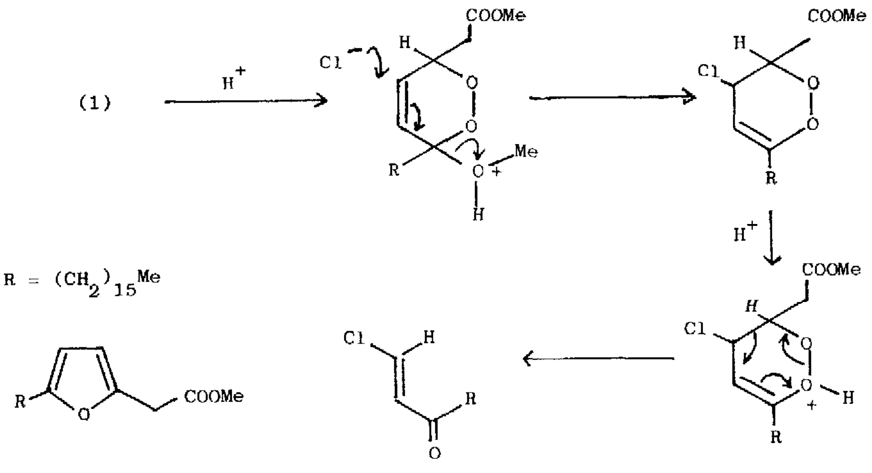
(4)



(5) R = $(CH_2)_{15}Me$, R' = OMe

(6) R = OMe, R' = $(CH_2)_{15}Me$

Scheme 1



(7) (8)