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$13^2,17^3$-CYCLOPHEOPHORBIDE ENOL, THE FIRST PORPHYRIN ISOLATED FROM A SPONGE

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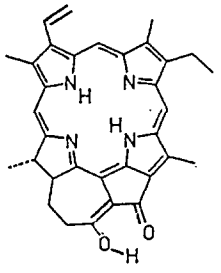
Summary $13^2,17^3$-Cyclopheophorbide enol (1) a non-metalated chlorophyll A derivative has been isolated from Darwinella oxeata (Bergquist) and its structure determined by physical and X-ray measurements.

During investigation of Darwinella oxeata (Bergquist) a hexane extract of the freeze-dried sponge deposited a solid which after column chromatography on silica gel (ethyl acetate-hexane, 3:17), h.p.l.c. (Merck Si60, 7 μm; ethyl acetate-hexane, 1:4), and repeated crystallizations by slow evaporation of hexane-dichloromethane solutions yielded lustrous black needles, m.p. > 360°. The u.v. spectrum (λ_{max} 287, 359, 426, 452, 626, 686 nm; ε 4300, 4800, 4800, 4700, 4000, 4500) indicated a chlorin type structure. Examination of crystals under an electron probe and observing the scattered X-rays, indicated that no elements heavier than oxygen were present and thus the porphyrin was non-metalated. The mass spectrum gave the molecular ion ($M^{+\cdot}$ 516) as the base peak and high resolution mass matching indicated the molecular formula $C_{33}H_{32}N_4O_2$. The i.r. spectrum contained absorptions corresponding to pyrrole hydrogens (ν_{max} 3390, 3180 cm^{-1}) and a ketone (ν_{max} 1655 cm^{-1}). Owing to its intense absorption in the red and ultraviolet region an accurate optical rotation could not be obtained but a specific rotation, $[\alpha]_D$ -2000° ± 1000°, for a very dilute solution indicated that the compound was chiral. Insufficient material was available for n.m.r. measurements but crystals were just suitable for X-ray structure determination.[2] Fig. 1 illustrates the molecular structure. Bond lengths and angles appear normal, but the standard deviations are comparatively large and this precludes meaningful comparisons with other porphyrin systems.

Although it has not hitherto been obtained from natural sources, $13^2,17^3$-cyclopheophorbide enol has been synthesized from methylpyropheophorbide-a (2) during a study of the ring E enolization of chlorophyll derivatives.[1] The current X-ray analysis shows that in the solid state the β-diketone is almost fully enolized with the seven membered ring bearing the enol.

The enol (1) is probably produced by the sponge from dietary chlorophyll A.



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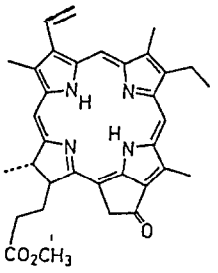

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References

1. H. Falk, G. Hoornaert, H-P. Isenring, and A. Eschenmoser, Helv. Chim. Acta, 58, 2347 (1975).

2. Crystal data for (1): $C_{33}H_{32}N_4O_2$, M 516.65, monoclinic, a = 22.048(6), b = 16.053(3), c = 15.166(2) Å, β = 92.40(1)°, V = 5363.18 Å^3, Z = 8, D_c = 1.28 g cm^{-3}, Mo Kα radiation, λ = 0.71069 Å, Zr filter, μ = 0.88 cm^{-1}. The correct space group is $P2_1$.(C_2^2 No. 4) containing 4 distinct molecules per asymmetric unit. However the great majority of the atoms are related in pairs through a non-crystallographic centre of symmetry and it has only proven practical to refine the structure as though there are in fact two distinct molecules in space group $P2_1/c$. Such a refinement requires that atoms not lying on the molecular plane be included as pairs of half-weighted atoms. Because of the large number of parameters (even in space group $P2_1/c$) and the general paucity of data, all atoms have been assigned isotropic temperature factors. Where possible, hydrogen atoms have been placed in calculated positions. The final R value is 0.104.

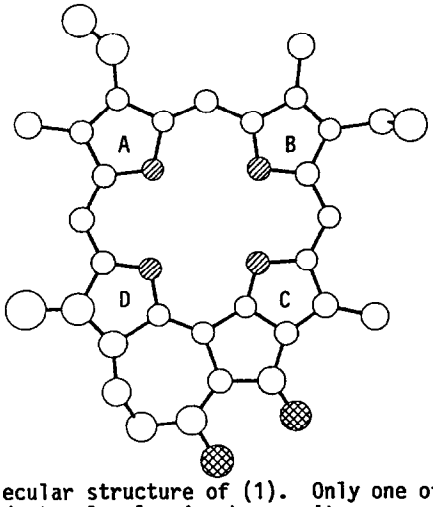

Fig. 1: The molecular structure of (1). Only one of the four independent molecules is shown. Atoms are drawn to sizes proportional to their isotropic temperature factors. The relative stereochemistry of ring D is trans.

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