Zoanthoxanthin, a Heteroaromatic Base from *Parazoanthus cfr. axinellae* (Zoantharia): Structure Confirmation by *X*-Ray Crystallography

By LUCIO CARIELLO, SPARTACO CRESCENZI, and GIUSEPPE PROTA*
(*Stazione Zoologica, Napoli and Istituto di Chimica Organica, Università di Napoli, Italy*)
and FEDERICO GIORDANO and LELIO MAZZARELLA
(*Istituto Chimico, Università di Napoli, Italy*)

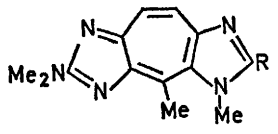
Summary Zoanthoxanthin (I), a novel metabolite containing a previously unknown heterocyclic system, was isolated from *Parazoanthus cfr. axinellae*, and its structure was determined from chemical and spectral data and by *X*-ray crystallographic analysis of a derivative (II).

DURING a study on the flavin-like metabolites of the Mediterranean zoanthid *Parazoanthus cfr. axinellae* (O. Schmidt, 1862), a yellowish-green fluorescent pigment, zoanthoxanthin, has been isolated by chromatography of the ethanolic extracts on a Dowex 50W (X-2, 100—200 mesh) column.

Zoanthoxanthin, $C_{13}H_{16}N_6$, yellow needles, m.p. 275—276° (decomp.) (methanol) has λ_{max} (MeOH) 427 and 293 nm (log ϵ 4·35 and 4·52), M^+ at *m/e* 256 (base peak) and fragments at *m/e* 241, 227, and 186, the latter suggesting the presence in the molecule of a $-N=\overset{|}{C}-NMe_2$ grouping. The n.m.r. spectrum [60 MHz, $(CD_3)_2SO$] exhibited a broad signal at δ8·05 (2H, D_2O-exchangeable), a singlet at 7·93 (2H) for two equivalent heteroaromatic protons, and three methyl singlets at 3·90 (3H), 3·20 (6H), and 3·13 (3H) assigned, respectively, to a methyl group on cyclic nitrogen, NMe_2, and CMe (supported by Kuhn–Roth analysis; Found/calc., 4·75/5·86%) at unusually low field.[1]

Zoanthoxanthin was stable to acid, alkali, and various oxidizing agents; with acetic anhydride it gave an amorphous monoacetyl derivative, M^+ at *m/e* 298, δ [$(CD_3)_2SO$] 2·21 (3H), λ_{max} (MeOH) 428 and 290 nm (log ϵ 4·10 and 4·29). When treated with sodium nitrite and 2N-HCl at 4°, zoanthoxanthin yielded a chloro-compound,[2] $C_{13}H_{14}N_5Cl$ (II), m.p. 192° (decomp.), M^+ at *m/e* 275, and similarly by diazotisation in hydrobromic acid[3] it gave the bromo-analogue, $C_{13}H_{14}N_5Br$ (III); in both cases the primary amino-group of zoanthoxanthin was replaced by the corresponding halogen atom (i.r., n.m.r.). Mild alkaline treatment of either halogen compound afforded the same hydroxy-derivative, $C_{13}H_{15}N_5O$ (IV) (M^+ at *m/e* 257), yellow-orange prisms, m.p. 304—306° (decomp.) (ethanol).

Because of the stability of zoanthoxanthin and the consequent difficulty in obtaining conclusive information about the chromophore of zoanthoxanthin by degradative studies, and as material was limited, the structure was determined by single-crystal *X*-ray diffraction.



(I) R = NH_2
(II) R = Cl
(III) R = Br
(IV) R = OH

Suitable crystals of (II), $C_{13}H_{14}N_5Cl,3H_2O$, (from aqueous ethanol) were monoclinic, space group $P2_1/c$ with a = 7·282, b = 8·408, c = 25·422 Å, β = 94·52°, D_m = 1·43 g cm^{-3}, Z = 4.

The intensities of 2623 reflexions were recorded on an automatic Siemens diffractometer. The structure was solved by direct methods, using the computer programme MULTAN (Main, Woolfson, Germain). The structure was refined by least-squares and the hydrogen atoms were located from a difference Fourier map. The final disagreement index R was 0·041.

Within experimental error, the molecule is planar and the packing is stabilized by hydrogen bonds involving the water molecules and the ring nitrogens at positions 1, 5, and 7.

The structure derived for (II) by *X*-ray diffraction analysis allows the assignment of structure (I) to zoanthoxanthin. It is one of a group of closely related pigments occurring in the Zoanthidae (a group of marine animals related to sea anemones and stony corals). As the classification of these animals is difficult, even at genus levels (*P. axinellae* is not identified with certainty), the distribution of these pigments may be of taxonomic value since we have found that two closely related species (as judged by the usual morphological criteria) have a completely different pigment pattern.

We thank Prof. R. H. Thomson for helpful discussions and Dr. Lucia Rossi, University of Turin, for advice on the taxonomical problem. This work was supported in part by Consiglio Nazionale delle Ricerche.

(*Received*, 31*st October* 1972; *Com.* 1846.)

[1] J. C. N. Ma and E. W. Warnhoff, *Canad. J. Chem.*, 1965, **43**, 1849.
[2] F. Kögl, G. M. Want, and C. A. Salemink, *Rec. Trav. chim.*, 1948, **67**, 29.
[3] D. D. Bly and M. G. Mellon, *J. Org. Chem.*, 1962, **27**, 2945.