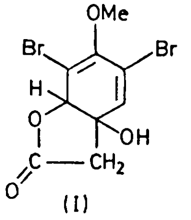
Aeroplysinin-2, a Dibromolactone from Marine Sponges *Aplysina* (*Verongia*) *aerophoba* and *Ianthella* sp.

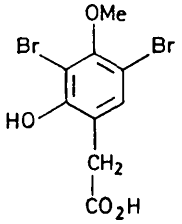
By L. MINALE* and G. SODANO
(*Laboratorio per la Chimica e Fisica di Molecole di Interesse Biologico del C.N.R., Via Toiano, 2 Arco Felice, Naples, Italy*)

and W. R. CHAN and A. M. CHEN
(*Chemistry Department, University of The West Indies, Kingston 7, Jamaica*)

Summary Absolute structure (VIII) has been assigned to aeroplysinin-2, a new bromo-compound from the sponges *Aplysina* (*Verongia*) *aerophoba* and *Ianthella* sp.

RECENTLY,[1–4] a number of related bromo-compounds have been isolated from *Verongia* spp. sponges; in addition, both enantiomorphic isomers of one of these have been isolated from *Ianthella* spp.[5] After further examination of the solvent extracts from *Verongia* (*Aplysina*) *aerophoba* and *Ianthella* sp., we have now isolated a related minor dibromo-constituent, aeroplysinin-2 (I).


(I)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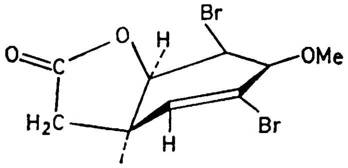
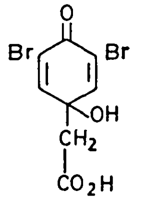
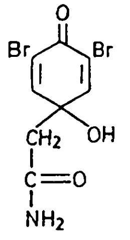
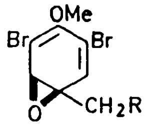

(III)


(IV)


(V)


(VI)

Aeroplysinin-2 (I), $C_9H_8Br_2O_4$ (elemental analysis and mass spectrum), has been obtained as the optically active form, m.p. 106—108°, [α] + 22° (*c* 3 in MeOH) from *Verongia aerophoba* and as the racemate, m.p. 127—128°, from *Ianthella* sp. It shows u.v. absorption at 284 nm [ε 4900 in MeOH; *cisoid* diene; *cf.* aeroplysinin-1[3]], i.r. bands ($CHCl_3$) at 3400br (OH) and 1785 (CO, γ-lactone) cm^{-1} and n.m.r. signals at δ ($CDCl_3$) 2·88 (2H, ABq, *J* 18 Hz, CH_2), 3·38br (1H, OH), 3·79 (3H, s, OMe), 5·20 (1H, d, *J* 0·7 Hz, CHO), and 6·36 (1H, d, *J* 0·7 Hz, C=CH) p.p.m.

On acetylation (I) afforded a monoacetate (oil), *m/e* 380, 382, 384 (M^+), 320, 322, and 324 (strong, M^+ − AcOH); ν_{max} (liquid film) 1795 (γ-lactone-CO) and 1745 (acetyl-CO); δ 2·10 ($MeCO_2$) p.p.m., which, on treatment with cold dilute alkali, gave the acetic acid (II), identified by comparison of its methyl ester with an authentic sample.[3] This result, along with the spectral evidence, leads to the structure (I) for aeroplysinin-2. We propose that its stereochemistry is as represented in structure (III) for the following reasons.† Dreiding models show that the hydroxy- and acyloxy-groups must be *trans*. The small coupling (0·7 Hz) between the olefinic and methine protons suggests a **W**[6] relationship for these two protons, indicating a quasi-equatorial orientiation for the methine proton and accordingly, a quasi-diaxial orientation for the hydroxy- and acyloxy-groups. The c.d. curve [(MeOH), Δε 284 ± 2] indicated a right-handed helicity for the diene[7] and, therefore, confirms the absolute configuration as depicted in (III).

When set aside, aeroplysinin-2 sometimes yielded the hydroxy-dienoic acid (IV) (identified by direct comparison with an authentic sample[2]), probably by a photochemical reaction. Such an easy transformation suggests that the natural amide (V) could be derived biogenetically from the lactone (I) or more directly from an epoxide (VI) which seems a likely precursor[3,8] of aeroplysinin-2 and of all the *Verongia* bromo-metabolites.

We thank Professor M. Sará (University of Genoa) for identifying the sponges. Two of us (L.M. and G.S.) also thank the Zoological Station (Naples) for collection of *Verongia aerophoba* samples, Professor G. Geraci (Laboratorio di Embriologia Molecolare del C.N.R., Naples) for c.d. measurements, and Mr. A. Milone for mass measurements.

(*Received*, 13*th March*, 1972; *Com.* 420.)

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† Fulmor *et al.*,[5] following the same criteria, assigned the absolute configuration of the (−)-isomer of aeroplysinin-I; this configuration was later confirmed by *X*-ray analysis (D. B. Cosulich and F. M. Lovell, *Chem. Comm.*, 1971, 397.)

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