Tetrahedron Letters,Vol.29,No.50,pp 6655-6656,1988
Printed in Great Britain

0040-4039/88 $3.00 + .00
Pergamon Press plc

EILATIN, A NOVEL ALKALOID FROM THE MARINE TUNICATE EUDISTOMA SP.

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Abstract: Eilatin (4), dibenzotetraazaperylene, is a novel highly symmetric heptacyclic aromatic compound isolated from the marine tunicate Eudistoma sp.

We recently reported the isolation of three novel alkaloids, segoline A (1), isosegoline A (2) and nor-segoline (3), from the Red Sea tunicate Eudistoma sp.[1]. All three compounds have in common the same diazatetracyclic aromatic ring system which was first described by Schmitz as part of amphimedin[2] and has most recently been reported from several other marine organisms[3].

Besides compounds 1-3 we have isolated from Eudistoma sp. several other related alkaloids. Herewith we wish to report the structure of eilatin (4) a bright yellow alkaloid which was isolated in small amounts (up to 0.001% dry wt.) from the tunicate collected in the Gulf of Eilat (July 1985).

Eilatin (4) was purified by several chromatographies and at last crystallized from chloroform-methanol-water; mp>310°C, λ_{max} MeOH 242(48200), 286(36700), 366(11500), 388(21000), 408(30400 and 434(27000)[4].

The molecular formula $C_{24}H_{12}N_4$ for 4 implying 21 degrees of unsaturation, was determined by HREIMS(m/e 356.1062 Δmu +6, m/e 178 M/2). The ^1H NMR spectrum showed only six aromatic protons which were assigned to four adjacent protons (δ 8.70d, J=8.0Hz;8.68d, J=7.2Hz; 8.00t, J=8.0Hz and 7.87t, J=7.2Hz) on a ortho-disubstituted benzene ring and two protons (δ 9.32d, J=5.5Hz and 8.57d, J=5.5hz) on a trisubstituted pyridine ring. The ^{13}C NMR spectrum, exhibiting only 12 carbon lines (6 methines and 6 non-protonated ones)[4] point clearly to a dimer structure. 2D-NMR correlation spectroscopy alone, failed, because of the high symmetry of the molecule, to solve the structure.

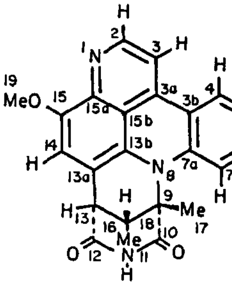
Eilatin (4) crystallized in the monoclinic crystal class with diffractometer-measured lattice constants of a=9.258(4)Å, b=10.994(6)Å, c=16.768(7)Å, β =92.74(3)°, V=1704.7Å^3 and d_c=1.459g.cm^{-3}. Diffraction data were measured at ca 20°C on a CAD4 diffractometer equipped with a graphite monochromator, using MoKα (λ=0.7107Å) radiation. The structure was solved by direct methods (SHELXS-86)[5]. Its refinement was carried out by large-block least-squares (SHELX-76)[6] including the positional and anisotropic thermal parameters of all the nonhydrogen atoms. The final refinement was based on 899 intensity data above the intensity threshold of 2σ. At convergence, R=0.086, wR=0.077, goodness-of-fit=1.04e, $|\Delta\rho_{max}|$=0.33eA^{-3}. The compound crystallized as a 1:1 hydrate. In the crystal, each water is in contact with the concave surfaces of two adjacent aromatic molecules, forming possible hydrogen bonds with the surrounding nitrogen sites N(6), N(13) and N(14)[7].

As expected from a 1,10-phenathroline moiety eilatin shows UV shifts in the presence of cations like Ni^{+2} but gives no red complex with iron salts[3].

Eilatin is the first fused heptacyclic aromatic marine alkaloid and it represents a unique highly symmetrical structure.

Compound 4 embodies the same tetracyclic hetero ring system as 1-3 and several other marine metabolites[3] and they all possess most intriguing biosynthetic pathways.

AKNOWLEDGEMENT We thank Prof. F.J. Schmitz, Oklahoma, for the HRMS spectrum and Mrs. Y. Abudi for her technical assistance.



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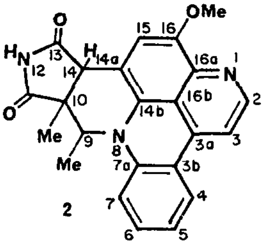

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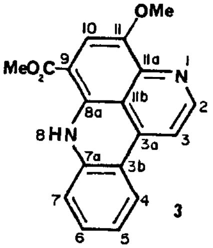

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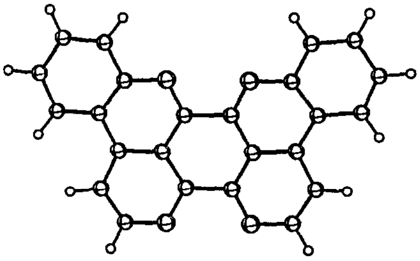

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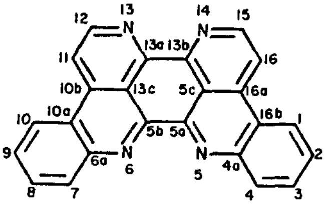

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REFERENCES AND NOTES

1. A. Rudi, Y. Benayahu, I. Goldberg and Y. Kashman, Tet. Letters, 29, 3861 (1988).

2. F.J. Schmitz, S.K. Agarwal, S.P. Gunasekara, P.G. Schmidt and J.N. Shoolery, J. Am. Chem. Soc. 105, 4835 (1983).

3.a) G. Cimino, A. Crispino, S. De Rosa, S. De Stefano, M. Gavagnin and G. Sodano, Tet. 43, 4023 (1987); b) S.J. Bloor and F.J. Schmitz, J. Am. Chem. Soc. 109, 6134 (1987); c) J. Kobayashi et al. Tet. Letters, 29, 1177 (1988); d) J. Kobayaski et al. J. Org. Chem. 53, 1800 (1988); e) T.F. Molinski, E. Fahy, D.J. Faulkner, G.D. van Dayne and J. Clardy, J. Org. Chem. 53, 1341 (1988); f) G.P. Gunawardana, S. Kohmoto, S.P. Gunasekera, O.J. McConnell and F.E. Koehn, J. Am. Chem. Soc. 110, 4856 (1988).

4. Eilatin (4), $\nu_{max}(CHCl_3)$3000, 1240, 1200, 1120, 970 cm^{-1}, $\lambda_{max}(MeOH,H^+)$305(39800), 440(21500), $(MeOH+Ni^{+2})$296(38700), 368(7300), 404(18300), 426(22500), 450(19900) $\delta_c(CDCl_3)$ 150.2s, 149.7d, 148.8s, 146.1s, 138.8s, 132.1d, 131.7d, 129.3d, 122.5d, 122.5s, 118.7s, 117.1d.

5. G.M. Sheldrick, in "Crystallographic Computing 3" Eds. G.M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, 1985 pages 175-189.

6. G.M. Sheldrick, Program for Crystal Structure Determination, University of Cambridge, England 1976.

7. O(17)...N(13)3.104(11)Å,O(17)...N(14)3.021(12)Å,&O(17)...N(16)(at x,0.5-y,z-0.5)3.132(11)Å.

(Received in UK 19 September 1988)