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CYCLOPRODIGIOSIN FROM BENECKEA GAZOGENES

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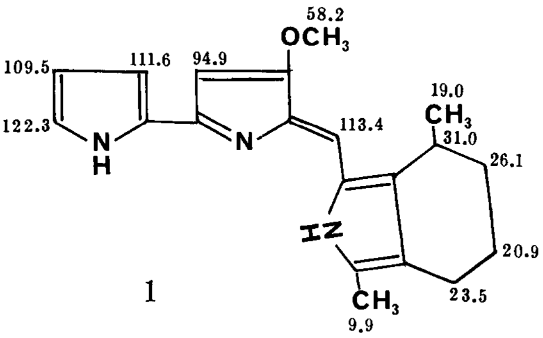
Abstract: The cyclic prodigiosin from Beneckea gazogenes has been shown to be 1.

Beneckea gazogenes, a red facultatively anaerobic marine bacterium isolated from salt-water marsh mud was reported to produce prodigiosin[1]. We had found that the prodigiosin-like pigment from the marine isolate, Alteromonas rubra, was a difficultly separable mixture of prodigiosin and a new cyclic isomer[2]. Examination of the pigment from B. gazogenes also disclosed two components whose chromatographic properties, electronic absorption and mass spectra were identical with those from prodigiosin and the cyclic isomer from A. rubra.

Since pigment yields were significantly higher from B. gazogenes than from A. rubra, and satisfactory separation of the two components was achieved by column chromatography on slightly alkaline silica, 18 mg of the cyclic pigment was obtained for ^{13}C-NMR spectroscopy. Signals from the quaternary carbons were not successfully resolved but the chemical shift values of the aliphatic carbons which are shown in the figure, suggested structure 1 rather than 2 which had been chosen previously for the cyclic prodigiosin



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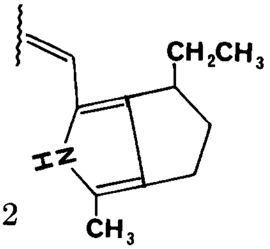

2

from A. rubra.[3] Chemical shift values in the literature[4,5] for various kinds of terminal methyl carbons in prodiginine pigments also suggested structure 1.

The ^{1}H-NMR spectrum of the free base showed a pattern of peaks in the aromatic region like that of the cyclic pigment from A. rubra. However, absorption at δ 0.95 was negligible; three sharp bands at δ 1.28, 1.31 and 1.36 were observed which collapsed to a broad singlet on irradiation of the ArCH resonance at 2.75. This established the methyl group as shown in 1. The third peak in the δ 1.3 region is due evidently to long alkyl chain impurities which, in retrospect, probably accounted for the asymmetric triplet previously reported[2] at δ 0.95 and the choice of structure 2.

Attempts, using A. rubra ATCC 29570, to produce enough of its cyclic pigment for similar ^{13}C-NMR and/or decoupling experiments were unsuccessful. Since there are prodiginine pigments which differ only as to which carbon of their aliphatic chain is attached to the chromophore[6] and which are impossible to resolve chromatographically, isomeric cycloprodigiosins such as 1 and 2 could exist. However in the accompanying paper, the structure of the cycloprodigiosin from A. rubra is demonstrated to be 1, thus confirming that the two compounds are identical.

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FOOTNOTES AND REFERENCES

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(4) R.J. Cushley, R.J. Sykes, C-K. Shaw and Harry H. Wasserman, Can. J. Chem., 1975, 53 148. Note necessary conversion: $\delta_{TMS} = \delta_{HMDS} - 2.34$.
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