1,1-Dimethyl-5,6-dihydroxyindolinium chloride from a deep water marine sponge, *Dercitus* sp.

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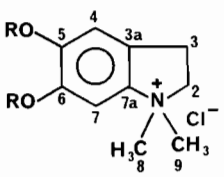
Summary. 1,1-Dimethyl-5,6-dihydroxyindolinium chloride (**1a**) was identified from a deep water sample of the marine sponge, *Dercitus* sp., and its structure was elucidated by spectral methods.
Key words. 1,1-Dimethyl-5,6-dihydroxyindolinium chloride; marine natural products; *Dercitus*; marine sponge.

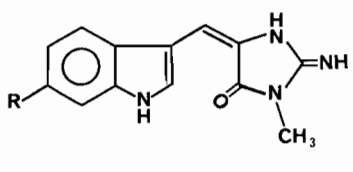
Numerous nitrogen-containing metabolites have been isolated from marine sponges[3–5], but only a small percentage of these metabolites contain a quaternary ammonium functionality. In this note, we report the isolation and identification of 1,1-dimethyl-5,6-dihydroxyindolinium chloride (**1a**), a new marine natural product from a deep water sponge, *Dercitus* sp. Gray, 1867[6]. Two tryptophan derivatives, 2'-de-N-methyl-aplysinopsin (**2a**) and 6-bromo-2'-de-N-methyl-aplysinopsin (**2b**), have been reported from a shallow water sample of *Dercitus* sp.[7].

The sponge was collected northwest of Goulding Cay, Bahamas, in August, 1985, at a depth of 215 m using the Harbor Branch Oceanographic Institution's submersible, the Johnson Sea-Link II. Sequential solvent extraction of the fresh frozen sponge (97 g) with EtOAc and MeOH yielded crude extracts (0.15 g and 2.7 g, respectively). From a portion of the MeOH extract (2 g), **1a** (118 mg) was purified with multilayer planetary coil CCC[8] using a solvent system of $CHCl_3-MeOH-H_2O$ (5/10/6), followed by recrystallization from $MeOH-CHCl_3$ (m.p. 244 °C).

The molecular formula of **1a** was deduced as $C_{10}H_{14}NO_2Cl$ from elemental analysis of the monohydrate of the chloride salt (calculated for $C_{10}H_{16}NO_3Cl$: C, 51.5; H, 6.86; N, 6.00; Cl, 15.0; found: C, 51.58; H, 6.96; N, 6.02; Cl, 15.62) and high resolution FABMS (m/z of $C_{10}H_{14}NO_2$, 180.1021, Δ 0.4 nm). The presence of a 1,2,4,5-tetrasubstituted benzene ring in **1a** was suggested by the ^1H NMR singlets (d_4-MeOH) at δ 6.81 (H-4) and 7.09 (H-7), the chemical shifts and multiplicities of the sp^2 carbons (from proton decoupled and DEPT ^{13}C NMR experiments in d_4-MeOH: δ 124.9 (C-3a, s), 112.5 (C-4, d), 149.5 (C-5, s), 147.7 (C-6, s), 104.4 (C-7, d), and 139.5 (C-7a, s), and the relationship of these ^{13}C NMR doublets with the ^1H NMR singlets (from a C–H correlation experiment[9]). The presence of two phenolic hydroxyls in **1a** was suggested by the ^{13}C NMR singlets with chemical shifts of δ 147.7 and 149.5, IR bands at 3360 and 3140 cm^{-1}, the absence of a carbonyl band in the IR spectrum, and the formation of a diacetate (**1b**) upon treatment of **1a** with pyridine and acetic anhydride (**1b**:



1a, R = H
1b, R = Ac



2a, R = H
2b, R = Br

LREIMS, m/e 249 (10%, $M^+ - CH_3$), ^1H NMR singlets at δ 2.30 and 2.31 (3 H each), ^{13}C NMR signals at δ 169.5 (s × 2) and 20.3 (q × 2), and an IR band at 1775 cm^{-1}). As expected for phenols, a bathochromic shift was observed in the UV spectrum upon addition of base (λ_{max} (MeOH, nm) 206 (ε 12 200), 223 (sh, ε 3800) and 289 (ε 3700) shifted to 209 (ε 16 500), 248 (ε 5800) and 303 (ε 5100)). Still to be accounted for are 10 protons, 4 carbons and 1 nitrogen. Based on the remaining ^{13}C and ^1H NMR data (δ 3.45 (6 H, s)/55.3 (q), 3.25 (2 H, t, J = 7.2)/27.5 (t) and 4.15 (2 H, t, J = 7.2)/(70.0 (t)), the final partial structure in **1a** must be N,N,N-dimethylethylamine where the nitrogen and β-carbon of the ethyl group are attached to ortho positions on the aromatic ring. Complete carbon assignments in the aromatic ring were made based on a long range C–H correlation NMR experiment (J = 10 Hz) which emphasizes three-bond coupling (H 8 and H 9 (δ 3.45) – C 2 (70.0), C 7a (139.5); H 2 (4.15) – C 8 and C 9 (55.3), C 3a (124.9); H 3 (3.25) – C 4 (112.5); H 4 (6.81) – C 6 (147.7), C 7a (139.5); H 7 (7.09) – C 3a (124.9), C 5 (149.5)). Assemblage of the partial structures suggested by these data yields 1,1-dimethyl-5,6-dihydroxyindolinium chloride as the proposed structure **1a**, and the corresponding diacetate as **1b**.

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2 To whom reprint requests should be addressed.
3 Christophersen, C., in: The Alkaloids, vol. 24, chapt. 2, p. 25. Ed. A. Brossi. Academic Press, Orlando, FL 1985.
4 Faulkner, D. J., Nat. Prod. Rep. *1* (1984) 551.
5 Faulkner, D. J., Nat. Prod. Rep. *3* (1986) 1.
6 The sponge identification was made by S. Pomponi per the description for *Dercitus* sp. Gray, 1867; family Pachastrellidae Carter, 1875; order Choristida. Gray, J. E., Proc. zool. Soc. London (1867) 492.
7 Djura, P., and Faulkner, D. J., J. org. Chem. *45* (1980) 735.
8 Ito, Y., Sandlin, J., and Bowers, W. G., J. Chromat. *244* (1982) 247.
9 Bax, A., and Morris, G., J. magn. Res. *42* (1981) 501.

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