

A Brominated Metabolite from the Red Alga *Vidalia spiralis*

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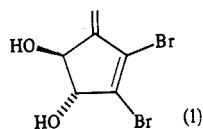
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Abstract

3,4-Dibromo-5-methylenecyclopent-3-ene-1,2-diol has been isolated from a Western Australian collection of the red alga *Vidalia spiralis*.

Introduction

In our investigations of marine organisms as potential sources of pharmacologically active compounds, we screened extracts of the red alga *Vidalia spiralis* Lamouroux (family Rhodomelaceae, order Ceramiales). The crude dichloromethane extract exhibited hypotensive activity¹ and the methanol extract demonstrated stimulant activity of the central nervous system.² In an attempt to obtain the substance responsible for the hypotensive activity, the dichloromethane extract was fractionated on silica gel. A new halogenated diol (1) was obtained from the more polar fractions and forms the subject of this communication.



Discussion

3,4-Dibromo-5-methylenecyclopent-3-ene-1,2-diol (1) separated as a fine crystalline powder from the more polar fractions from chromatography of the dichloromethane extract. The molecular formula $C_6H_6Br_2O_2$ was established by high-resolution mass measurements and the ¹H n.m.r. spectrum in $(CD_3)_2SO/D_2O$ showed two one-proton doublets and a broad two-proton singlet. The ¹³C n.m.r. spectrum indicated the presence of one tetrasubstituted double bond, an exocyclic methylene (δ 149.5, s; 107.2, t), and two secondary hydroxyl-bearing carbons at δ 82.3 (d) and 78.3 (d). Compound (1) was therefore monocyclic, and the u.v. spectrum (λ_{max} 250 nm) demanded that the double bonds were conjugated.

These spectral data allowed (1) as the only possible structure for this metabolite. The orientation of the diol was inferred to be *trans* by the failure of (1) to react with periodate, which readily cleaves only *cis*-diols. Compound (1) did, however, slowly react with lead tetraacetate to give a complex mixture of products. Attempts

¹ Marwood, J. F., personal communication.

² Baird-Lambert, J. A., personal communication.

to selectively monoacylate the diol (1) failed, thus precluding any determination of absolute configuration by Horeau's method.

The diol (1) was not the compound responsible for the hypotensive activity of the crude extract.¹

Experimental

Instruments used to acquire spectral data have been listed elsewhere.³

Isolation of 3,4-Dibromo-5-methylenecyclopent-3-ene-1,2-diol (1)

The freeze-dried alga (2.25 kg) (RRIMP museum specimen number FN 1983/000/02), collected at Yanchep Sun City, W.A., was powdered and percolated with dichloromethane to give the extract as an oil (5.6 g). This was chromatographed on silica gel (Kieselgel H) and eluted with dichloromethane/ethyl acetate mixtures followed by ethyl acetate/methanol mixtures. Concentration of ethyl acetate/methanol fractions gave a gum which was dissolved in dichloromethane from which compound (1) (200 mg) was deposited as a fine crystalline powder; the powder was recrystallized from methanol to give *needles*, m.p. 112–116° (dec.). The compound decomposed suddenly after 7 days storage at –10° with evolution of hydrogen bromide. $[\alpha]_D^{25} + 124^\circ$ (c, 0.15 in methanol). U.v. spectrum: λ_{\max} (methanol) 250 nm (log ϵ 4.21). ^1H n.m.r. spectrum: δ [(CD₃)₂SO] 5.96, 1H, d, J 7 Hz; 5.80, 1H, d, J 7 Hz; 5.12, 2H, s; 4.34, 2H, m (becoming a singlet on D₂O exchange). $\{^1\text{H}\}^{13}\text{C}$ n.m.r. spectrum: [(CD₃)₂SO] 149.5 (s), 134.7 (s), 124.7 (s), 107.2 (t), 82.3 (d), 78.3 (d) ppm. Mass spectrum: m/e 272 (4%), 270 (13), 268 (7), 255 (5), 253 (10), 251 (4), 191 (50), 189 (51), 145 (12), 143 (13), 135 (5), 133 (11), 131 (7), 110 (30), 109 (22), 81 (40), 79 (38), 53 (100), 51 (55), 50 (30). High-resolution mass measurement: m/e 269.8748. C₆H₆⁷⁹Br⁸¹BrO₂ requires mol. wt 269.8716.

Treatment of (1) with Sodium Periodate and Lead Tetraacetate

(A) Compound (1) (5 mg) in methanol (10 ml) was treated with a solution of sodium periodate (20 mg) in water (2 ml), and the mixture allowed to stand at room temperature for 24 h. Dilution with water, extraction with ether and evaporation of the ethereal layer gave a gum which showed only unchanged starting material by t.l.c. (ethyl acetate).

(B) To a solution of (1) (2 mg) in methanol (2 ml) was added lead tetraacetate (20 mg) in acetic acid (5 ml). After 3 h, the mixture was partitioned between water and ether, and t.l.c. of the ether layer showed that starting material was replaced by numerous less polar products.

Acknowledgment

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³ Kazlauskas, R., Marwood, J. F., and Wells, R. J., *Aust. J. Chem.*, 1980, 33, 1799.