

A BROMINATED BISACETYLENIC ACID FROM THE  
MARINE SPONGE XESTOSPONGIA TESTUDINARIA

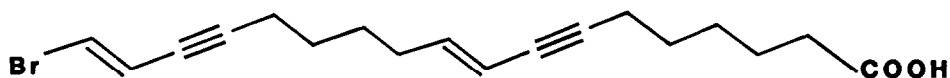
Ronald J. Quinn\* and David J. Tucker  
School of Science, Griffith University, Nathan  
Queensland 4111, Australia

**ABSTRACT:** A brominated bisacetylenic acid, 18-bromooctadeca-9(E),17(E)-dien-7,15-dienoic acid, has been isolated from the marine sponge Xestospongia testudinaria and its structure elucidated by NMR including 2D homonuclear spectroscopy.

Marine sponges of the genus Xestospongia have recently been reported to contain a new class of 1-oxaquinolizidines possessing vasodilative activity<sup>1</sup> and earlier had been found to contain the first example of a dibrominated straight-chain C<sub>16</sub> acetylenic acid<sup>2</sup>. Our studies of Xestospongia testudinaria (from Pandora Reef, 18° 49'S, 146° 25'E near Townsville, Queensland, Australia) have resulted in the isolation of further straight chain metabolites and we report herein the structure of a monobrominated bisacetylenic acid.

Dichloromethane extraction of the freeze-dried sponge, chromatography on silica (40-63  $\mu$ m, 10% ethyl acetate in chloroform) followed by repeated HPLC (partisil-10, ODS-3, 20% water in methanol) gave a low melting acid (1) ( $\sim$ 0.1% of wet sponge) mp 66-67° (recrystallised from aqueous methanol). A molecular formula of C<sub>18</sub>H<sub>23</sub>O<sub>2</sub>Br was established by a C.I. (NH<sub>3</sub>) mass spectrum which gave ions at m/z 368/370 (M + NH<sub>4</sub>)<sup>+</sup> and high resolution E.I. data (M<sup>+</sup>-Br: 271.16966, calcd. for C<sub>18</sub>H<sub>23</sub>O<sub>2</sub> 271.16979)<sup>3</sup>. The <sup>13</sup>C NMR spectra<sup>3</sup> showed 1 quaternary carbon ( $\delta$  179.3), 4 methine olefinic carbons ( $\delta$  142.4 - 111.3), 4 quaternary acetylenic carbons ( $\delta$  93.0 - 78.0), 7 methylene carbons ( $\delta$  33.8 - 24.4) and 2 methylene carbons ( $\delta$  19.5, 19.3) adjacent to acetylenes<sup>4</sup>. The 300 MHz <sup>1</sup>H NMR spectrum showed an E-disubstituted double bond ( $\delta$  6.55 J = 14 Hz,  $\delta$  6.14 J = 14, 2.3, 2.3 Hz) which was coupled on one side only to a two proton signal at  $\delta$  2.24 (J = 6, 6, 2.3 Hz) which was further coupled to a methylene in an eight proton multiplet at  $\delta$  1.5. The small 2.3 Hz coupling was indicative of a 5 bond coupling with an acetylene between the olefin and the methylene<sup>5</sup> and established part structure -CH=CH-C $\equiv$ C-CH<sub>2</sub>- (A). A second E-disubstituted double bond ( $\delta$  6.00 J = 15.8, 7,

7 Hz,  $\delta$  5.43 J = 15.8, 1.7, 1.7, 0.7, 0.7 Hz) was substituted on one side with a methylene ( $\delta$  2.08, J = 7, 7, 7, 0.7 Hz) which was further coupled to a methylene in the 8H multiplet and which showed coupling (0.7 Hz) to the other olefinic proton at  $\delta$  5.43. This second olefinic proton was coupled with a small 1.7 Hz coupling to a methylene ( $\delta$  2.27, J = 7, 7, 1.7 Hz) which was coupled to a methylene in the 8H multiplet. The 1.7 Hz coupling indicated coupling across an acetylene, thus establishing the part structure  $-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}=\text{CH}-\text{CH}_2-$ . A methylene triplet at  $\delta$  2.34 (J = 7.5 Hz) was only coupled to a methylene at  $\delta$  1.63 (quintet J = 7.5 Hz) which was further coupled to a methylene in the 8H multiplet and chemical shift considerations establish that this unit is terminated by a COOH while the Br is at the end of partial structure A. Structural ambiguity was resolved by a homonuclear shift-correlated 2-D  $^1\text{H}$  NMR (COSY-45)<sup>6</sup> spectrum of **1** run in  $d_5$ -pyridine, as the 8H multiplet was resolved into two four-proton multiplets at  $\delta$  1.52 and 1.38. The spectrum indicated the absence of coupling between the two 4H multiplets establishing that the partial structures are each joined by two methylene groups. The methylene ( $\delta$  1.76)  $\beta$  to the carboxylic acid and a methylene adjacent to an acetylene ( $\delta$  2.33) were coupled to the  $\delta$  1.52 methylenes, while the allylic protons ( $\delta$  1.99) and a methylene adjacent to an acetylene ( $\delta$  2.20) were coupled to the  $\delta$  1.38 methylenes thus establishing full connectivity and the structure of **1** as 18-bromooctadeca-9(E),17(E)-dien-7,15-diynoic acid.

**1**

**Acknowledgements.** We would like to thank Dr. D. Maguire for collecting and Dr. J. Thompson for identifying the sponge, the Brisbane NMR Centre, Griffith University for use of facilities, Dr. P. Barron for the COSY spectrum, the QMASS Centre, Queensland Institute of Technology for C.I. and the Chemistry Department, University of Queensland for high resolution mass spectra. We acknowledge the award of a Commonwealth Postgraduate Research Award to DJT.

#### References.

1. M. Nakagawa, M. Endo, N. Tanaka and L. Gen-Pei, *Tetrahedron Lett.*, **25**, 3227 (1984).
2. F.J. Schmitz and Y. Gopichand, *Tetrahedron Lett.*, 3637 (1978).
3.  $^1\text{H}$  NMR (300 MHz,  $d_5$ -pyridine)  $\delta$  6.95 ( $\text{H}_{18}$ ), 6.44 ( $\text{H}_{17}$ ), 6.14 ( $\text{H}_{10}$ ), 5.66 ( $\text{H}_9$ ), 2.48 ( $\text{H}_2$ ), 2.33 ( $\text{H}_6$ ), 2.20 ( $\text{H}_{14}$ ), 1.99 ( $\text{H}_{11}$ ), 1.76 ( $\text{H}_3$ ), 1.52 ( $\text{H}_{4,5}$ ) 1.38 ( $\text{H}_{12,13}$ );  $^{13}\text{C}$  NMR (75.46 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  179.3, 142.4, 118.5, 117.3, 111.3, 93.0, 89.0, 80.0, 78.0, 33.8, 32.5, 28.8, 28.5, 28.2, 28.0, 24.4, 19.5, 19.3; IR (film) 3400-2400, 2220, 1695  $\text{cm}^{-1}$ ; MS (C.I.; NH)  $m/z$  370, 368 (M + 18), 271 (M - Br).
4. E. Breitmaier and W. Voelter,  $^{13}\text{C}$  NMR Spectroscopy, 2nd Ed., Verlag Chemie, Weinheim, 1978.
5. R.M. Silverstein, G.C. Bassler and T.C. Morrill, *Spectrometric Identification of Organic Compounds*, 4th Ed., Wiley, N.Y. 1981.
6. A. Bax and R. Freeman, *J. Mag. Res.*, **44**, 542 (1981).

(Received in UK 5 February 1985)