JOURNAL OF NATURAL PRODUCTS

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J. Nat. Prod., **1994**, 57 (4), 539-540• DOI:
10.1021/np50106a019 • Publication Date (Web): 01 July 2004

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Journal of Natural Products
Vol. 57, No. 4, pp. 539-540, April 1994

A SESQUITERPENE QUINONE AND HYDROQUINONE FROM THE SOUTHERN AUSTRALIAN MARINE SPONGE, *THORECTA CHOANOIDES*

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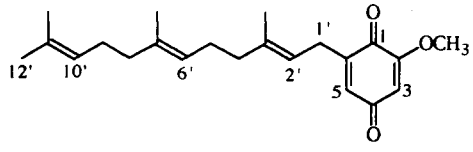
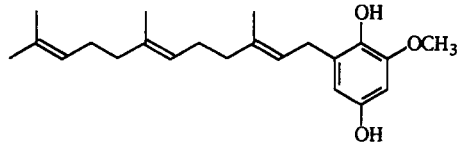
ABSTRACT.—This report describes the isolation and structure elucidation of a new sesquiterpene quinone [**1**] and its corresponding hydroquinone [**2**], from the southern Australian marine sponge, *Thorecta choanoides*.

Metabolites of mixed sesquiterpene and quinone or hydroquinone biosynthesis are common to marine brown algae and sponges. Numerous examples of this structure class have been reported, including those where the sesquiterpene unit exists in an acyclic, monocyclic, bicyclic, or tricyclic form. Further to this, structural variation can focus around the degree of oxygenation and substitution to the aromatic unit. In this report we describe the isolation of two new acyclic examples of this structure class, 6-(3,7,11-trimethyl-2,6,10-dodecatrienyl)-2-methoxy-*p*-quinone [**1**] and 6-(3,7,11-trimethyl-2,6,10-dodecatrienyl)-2-methoxy-*p*-hydroquinone [**2**], from the sponge *Thorecta choanoides* Bowerbank 1872 (Dictyoceratida: Thorectidae) collected from Port Phillip Bay, Victoria, Australia.[1]

Compound **1**, a stable yellow oil ($C_{22}H_{30}O_3$), displayed uv (264 nm) and ir (1650 and 1680 cm^{-1}) absorptions consistent with a *p*-quinone, which was further revealed by ^{1}H-nmr data, in particular meta-coupling between two aromatic



1



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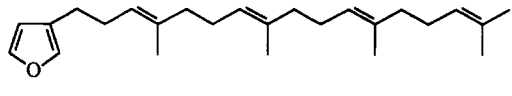

3

[1]A type specimen of the sponge has been lodged with the Queensland Museum (Registry Number: G301314).

protons at δ 6.45 (d, J=2.4 Hz) and 5.86 (d, J=2.4 Hz), to be 2,5-disubstituted. One substituent was attributed to a methoxy moiety [δ 3.81 (s); 56.3 ppm (q)], and the other to a farnesyl (3,7,11-trimethyl-2,6,10-dodecatrienyl) moiety [δ 5.14 (t, J=7.4 Hz), 5.08 (2t, J=6 Hz), 1.67 (s), 1.63 (s), 1.59 (2s), 140.1 (s), 135.4 (s), 132.8 (d), 131.3 (s), 124.8 (d), 123.7 (d), 25.7 (q), 17.7 (q), 16.2 (q), 16.0 (q)], with shielded ^{13}C-nmr chemical shifts for the olefinic methyls defining the *E*-geometry about the two asymmetrically substituted double bonds.

Compound **2**, also a stable yellow oil ($C_{22}H_{32}O_3$), was spectroscopically similar to **1**. Compound **2** did not display carbonyl absorptions in the ir spectrum, but instead exhibited two hydroxyl absorptions (3854 and 3286 cm^{-1}). These observations were taken to imply that **2** was the corresponding *p*-hydroquinone to the *p*-quinone **1**. Confirmation of this assignment was provided by oxidative (Ag_2O) interconversion of **2** to **1**. Attempts to convert **2** to **1** through aerial oxidation proved unsuccessful. Despite this, it could not be entirely discounted that **1** was an oxidative artifact of **2**, brought on during storage and/or handling.

Despite the extensive range of sesquiterpene quinone structural variants known from marine sources (>100), the oxygenation pattern demonstrated by both **1** and **2** is quite rare. Although compounds of this general structure class have been reported to inhibit both bacteria growth and HIV replication, neither **1** or **2** demonstrated such activity.[2]

[2]We also take this opportunity to note the isolation of 2-(3,7,11-trimethyl)-2,6,10-dodecatrienyl-*p*-hydroquinone, from an unidentified southern Australian marine sponge. Although a known algal metabolite (1), to the best of our knowledge the current report represents the first account of this metabolite from a sponge. It is noteworthy that 2-(3,7,11-trimethyl)-2,6,10-dodecatrienyl-*p*-hydroquinone is the most likely precursor to all marine metabolites of mixed sesquiterpene and quinone or quinol biosynthesis.

EXPERIMENTAL

ANIMAL MATERIAL AND EXTRACTION AND FRACTIONATION.—A specimen of the sponge was collected from Port Phillip Bay, Victoria, Australia, by scuba at a depth of 25 m in March 1991. The sponge was transported to the laboratory, diced and steeped in EtOH at −20° for 15 months. The crude EtOH extract was decanted, concentrated under reduced pressure, and the CH_2Cl_2-soluble portion fractionated by silica hplc (2 ml/min 40% EtOAc/hexane, Phenomonex 5 μm silica 10×250 mm) to yield **1** (16.7 mg, 0.25%) and **2** (39.2 mg, 0.58%), along with the known marine metabolite furospinosulin-1 [**3**] (10.9 mg, 0.16%) (2,3).

*6-(3,7,11-Trimethyl-2,6,10-dodecatrienyl)-2-methoxy-*p*-quinone* [**1**].—A stable yellow oil; ir (film) ν max 1680, 1650 cm^{-1}; uv (EtOH) λ max 264 nm (ε 1300); ^{1}H nmr (400 MHz, $CDCl_3$) δ 1.59 (2s, 3′ and 7′-CH_3), 1.63 (s, 11′-CH_3), 1.67 (s, 12′-H_3), 3.13 (d, J=7.3 Hz, 1′-H_2), 3.81 (s, -OCH_3), 5.08 (2t, J=6 Hz, 6′ and 10′-H), 5.14 (t, J=7.4 Hz, 2′-H), 5.86 and 6.45 (2d, J=2.4 Hz, 3 and 5-H); ^{13}C nmr (100 MHz, $CDCl_3$) 16.0 (q), 16.2 (q), 17.7 (q), 25.7 (q), 26.4 (t), 26.7 (t), 26.9 (t), 27.1 (t), 39.6 (t), 56.3 (q), 107.1 (d), 117.7 (d), 123.7 (d), 124.8 (d), 131.3 (s), 132.8 (d), 135.4 (s), 140.1 (s), 146.4 (s), 158.9 (s), 182.2 (s), 187.7 (s); hreims (70 eV) *m/z* 342.2193 ($C_{22}H_{30}O_3$ requires 342.2195).

*6-(3,7,11-Trimethyl-2,6,10-dodecatrienyl)-2-methoxy-*p*-hydroquinone* [**2**].—A stable yellow oil; ir (film) ν max 3854, 3286 cm^{-1}; uv (EtOH) λ max 288 (ε 4100), 201 nm (ε 43000); ^{1}H nmr (400 MHz, $CDCl_3$) δ 1.59 (2s, 3′ and 7′-CH_3), 1.67 (s, 11′-CH_3), 1.71 (s, 12-H_3), 3.31 (d, J=7.3 Hz, 1′-H_2), 3.84 (s, -OCH_3), 5.11 (m, 6′ and 10′-H), 5.31 (m, 2′-H), 6.21 and 6.31 (2d, J=2.4 Hz, 3 and 5-H); ^{13}C nmr (100 MHz, $CDCl_3$) 16.0 (q), 16.1 (q), 17.7 (q), 25.7 (q), 26.5 (t), 26.7 (t), 27.8 (t), 27.9 (t), 39.7 (t), 56.0 (q), 107.5 (d), 107.6 (d), 121.8 (d), 124.2 (d), 124.4 (d), 127.8 (s), 131.3 (s), 135.0 (s), 136.6 (s), 137.3 (s), 146.8 (s), 148.5 (s); hreims (70 eV) *m/z* 344.2356 ($C_{22}H_{32}O_3$ requires 344.2351).

ACKNOWLEDGMENTS

We gratefully acknowledge the taxonomic expertise of J.N.A. Hooper, and the financial support of the Australian Research Council.

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Received 15 October 1993