

**THIOFURODYSININ, A SULFUR-CONTAINING
FURANOSQUITERPENE FROM THE MARINE SPONGE
DYSIDEA AVARA**

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Marine natural products incorporating sulfur are rare and are usually confined to those metabolites derived from sulfur-containing amino acids. Thiofurodysin acetate [**1**] and thiofurodysin acetate [**2**], reported (1) from an Australian *Dysidea* sp. were considered to be the first natural terpene thiol derivatives. Despite numerous reports of the related compounds furodysin [**3**] and furodysin [**4**] from *Dysidea* spp. (2) and the nudibranches *Cadlina luteomarinata* (3,4), *Hypseloderis californiensis* (5), *Hypseloderis porterea* (5), and *Hypseloderis zebra* (6), the unacetylated thiols remain undetected.

Our investigations of a specimen of *Dysidea avara* Schmidt have resulted in the isolation of furodysin [**3**] (0.081%), furodysin [**4**] (0.16%), thiofurodysin acetate [**2**] (0.023%), and the previously undescribed thiofurodysin [**5**] (0.14%).

The ms of **5** displayed a molecular ion corresponding to the composition $C_{15}H_{20}OS$ (m/z 248.1231) as well as a base peak at m/z 122, characteristic of the retro-Diels Alder derived ion common to [**1-4**]. The 1H nmr ($CDCl_3$) 1.18, 1.21 (2s, 14- and 15- CH_3), 1.44 (t, $J=8.0$ Hz, D_2O exchangeable, SH), 3.11 (d, $J=8.0$ Hz, 16- CH_2), 5.85 (d, $J=6.0$ Hz, 10-H), 6.24 (d, $J=2.0$ Hz,

3-H, 7.22 (bs, 2-H); and ^{13}C nmr ($CDCl_3$) 19.0 (t, C-7), 26.2 (q, C-14), 27.2, 28.2 (2t, C-8 and C-12), 31.1 (d, C-11), 31.2 (t, C-16), 32.8 (q, C-15), 33.1 (s, C-5), 44.4 (d, C-6), 108.1 (d, C-3), 124.6 (s, C-4), 128.0 (d, C-10), 136.5 (s, C-9), 140.5 (d, C-2), 146.8 (s, C-13); spectra of **5** were consistent with the assigned structure. Particularly diagnostic was the presence of a very sharp D_2O exchangeable one proton triplet at δ 1.44 coupled to a deshielded methylene doublet at δ 3.11. These signals were attributed to the thiomethylene moiety.

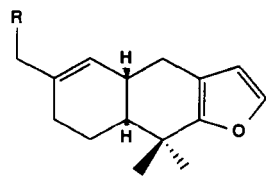
Acetylation of **5** ($[\alpha]_D +49.3$, c 12.0, $CHCl_3$) with Ac_2O /pyridine at room temperature returned a quantitative yield of a thiol acetate identical in all respects, including optical activity, to **2**.

EXPERIMENTAL

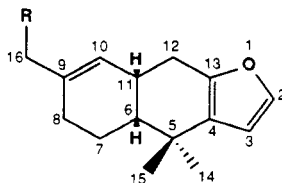
GENERAL EXPERIMENTAL PROCEDURES.—These have been previously reported (7).

COLLECTION.—A specimen of *D. avara* (Australian Museum Registry Number Z4977) was collected by SCUBA at a depth of 20 m off Black Rock, Batemans Bay, on the New South Wales coast. The diced sponge was steeped in EtOH, packed in dry ice, and transported to the laboratory where it was stored at -20° .

EXTRACTION AND ISOLATION.—After decanting, the EtOH extract was evaporated to dryness and triturated with CH_2Cl_2 to yield a lipid



1 R=SAc
3 R=H



2 R=SAc
4 R=H
5 R=SH

soluble extract. Rapid silica filtration (hexane to EtOAc) followed by hplc (Waters 10 μ silica [0.8 \times 10 cm] radial compression cartridge [1% EtOAc/hexane]) yielded **2-5** as shown. Full details are available on request.

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