Novel Metabolites of Four *Siphonaria* Species

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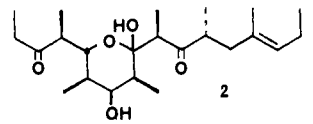
Abstract: Two novel spiroketals, siphonarin-A (**3**) and siphonarin-B (**4**), were isolated from *Siphonaria zelandica* and *S. atra*. The corresponding dihydrosiphonarins **5** and **6** were obtained from *S. normalis* and *S. laciniosa*. The structure of siphonarin-A (**3**) was determined by X-ray analysis. The acid-catalyzed degradation of dihydrosiphonarin-A (**5**) is described.

Marine pulmonates of the genus *Siphonaria* are air-breathing molluscs that resemble limpets, with which they cooccur in the intertidal zone. Previous studies of *Siphonaria* species have reported polypropionate metabolites as typical of the genus. *Siphonaria diemenensis*,[1] *S. pectinata*,[2] and *S. lessoni*[3] all contain 4-hydroxy-2-pyrones, exemplified by diemenensin (**1**). Two more

1



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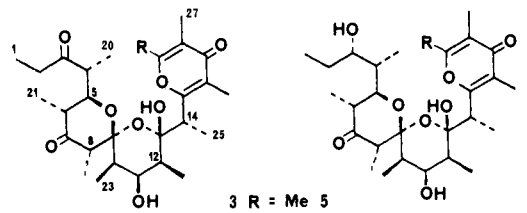
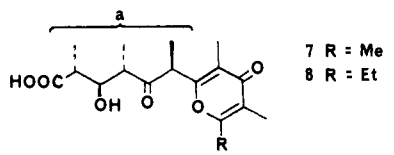


3 R = Me **5**
4 R = Et **6**



7 R = Me
8 R = Et

complex metabolites, denticulatin A (**2**) and an epimer, were isolated from *S. denticulata*.[4] In this paper we report the structural elucidation of siphonarin A (**3**) and its homologue siphonarin B (**4**) from *S. zelandica* and *S. atra* and their relationship with dihydrosiphonarin A (**5**) and dihydrosiphonarin B (**6**) from *S. normalis* and *S. laciniosa*.

The structural studies were performed using material from *S. zelandica* and *S. normalis*. *S. zelandica*, Quoy and Gaimard, 1833,[5,6] was found along the coast of New South Wales, Australia, where it cooccurred with *S. denticulata*. From the mixed bulk collections of *S.* denticulata and *S. zelandica* (~4:1) we isolated two pyrones, siphonarin A (**3**) and siphonarin B (**4**) that were subsequently found to be present in an authenticated sample of *S. zelandica*. *Siphonaria normalis* was collected at Diamond Head Beach, Oahu, HI.

Mixed collections of *S. zelandica* and *S. denticulata* from Sydney, Australia, were immersed in acetone for 2 weeks, and the solvent was decanted. The ethyl acetate soluble material from the acetone extract was chromatographed on silica gel, and a fraction eluted with 1:1 ethyl acetate–diethyl ether was separated by LC on Partisil to obtain equal quantities of siphonarin A (**3**) and siphonarin B (**4**). We estimate the yield of each metabolite to be in the region of 0.05 mg/animal on the basis of random sampling of the mixed collection.

Siphonarin A (**3**), $[\alpha]_D$ +21.7° (*c* 0.014, $CHCl_3$) was obtained as a crystalline solid, mp 164–166 °C. The molecular formula, $C_{28}H_{42}O_8$, was obtained from a high-resolution mass measurement. The γ-pyrone ring was indicated by infrared bands at 1660 and 1595 cm^{-1} and the UV absorption at 260 nm (ε 4000). The ^{13}C NMR signals at δ 180.2 (s), 166.0 (s), 161.5 (s), 122.0 (s), and 117.5 (s) were at typical chemical shifts for a fully substituted γ-pyrone,[7-9] and the ^1H NMR signals at δ 2.36 (s, 3 H) and 1.96 (s, 6 H) were assigned to three methyl groups on the γ-pyrone ring.

The ^{13}C NMR spectrum of siphonarin A (**3**) also contained two ketone carbonyl signals at δ 213.4 (s) and 206.5 (s), two ketal or hemiketal carbons at δ 105.1 (s) and 103.4 (s), two carbons bearing one oxygen at δ 77 (d)[10] and 74.6 (d), and 10 methyl carbon signals. The ^1H NMR spectrum could be assigned (Table I) to a bicyclic ketal structure after partial structures had been defined by spin-decoupling experiments.[11] Since we could not define the stereochemistry at several of the chiral centers, an X-ray diffraction experiment was performed. A computer-generated drawing of the final X-ray model is given in Figure 1. The X-ray experiment defined only the relative stereochemistry of siphonarin A (**3**) so the enantiomer shown is an arbitrary choice.

Siphonarin B (**4**), $[\alpha]_D$ +13.2° (*c* 0.014, $CHCl_3$), was very closely related to siphonarin A (**3**); the molecular formula, $C_{29}H_{44}O_8$, indicated that siphonarin B (**4**) was a homologue. The ^1H NMR spectra were nearly identical (Table I) except that the methyl signal at δ 2.36 (s, 3 H) in **3** was replaced by signals for an ethyl group at δ 2.79 (q, 2 H, J = 7 Hz) and 1.20 (t, 3 H, J = 7 Hz) in **4**. From a biosynthetic rationale it was most likely that the methyl group in the α-position of the pyrone ring had

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(6) The taxonomy of *S. zelandica* has recently been redefined after years of confusion. Jenkins, B. W. *J. Malac. Soc. Aust.* **1983**, *6*, 1.
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(9) Ireland, C.; Scheuer, P. J. *Science (Washington, D.C.)* **1979**, *205*, 922.
(10) The signal was obscured in the proton-decoupled spectrum but observed as a doublet in the off-resonance decoupled spectrum.
(11) For details, see: Hochlowski, J. E. Ph.D. Thesis, University of California, San Diego, 1983.

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Table I. ^{1}H NMR Spectra of Siphonarin A (**3**), Siphonarin B (**4**), Dihydrosiphonarin A (**5**), and Dihydrosiphonarin B (**6**)

position	3	4	5	6
1	0.94 (t, J = 7 Hz)	0.94 (t, J = 7 Hz)	0.88 (t, J = 7 Hz)	0.88 (t, J = 7 Hz)
2a	2.25 (dq, J = 18.5, 7 Hz)	2.25 (dq, J = 18.5, 7 Hz)	1.32 (ddq, J = 14, 7, 7 Hz)	1.32 (ddq, J = 14, 7, 7 Hz)
2b	2.48 (dq, J = 18.5, 7 Hz)	2.48 (dq, J = 18.5, 7 Hz)	1.61 (ddq, J = 14, 7, 3 Hz)	1.62 (ddq, J = 14, 7, 3 Hz)
3			3.23 (dt, J = 7, 3 Hz)	3.24 (dt, J = 7, 3 Hz)
4	2.62 (br, q, J = 7 Hz)	2.61 (br q, J = 7 Hz)	1.42 (ddq, J = 7, 3, 1 Hz)	1.40 (ddq, J = 7, 3, 2.5 Hz)
5	3.89 (br d, J = 10.5 Hz)	3.88 (br d, J = 10.5 Hz)	3.73 (dd, J = 10.5, 1 Hz)	3.72 (dd, J = 10.5, 2.5 Hz)
6	2.28 (dq, J = 10.5, 6.5 Hz)	2.28 (dq, J = 10.5, 6.5 Hz)	2.35 (dq, J = 10.5, 7 Hz)	2.34 (dq, J = 10.5, 7 Hz)
8	2.64 (q, J = 6.5 Hz)	2.66 (q, J = 6.5 Hz)	2.61 (q, J = 7 Hz)	2.61 (q, J = 7 Hz)
10	1.83 (qd, J = 7, 2 Hz)	1.83 (qd, J = 7, 2 Hz)	1.93 (qd, J = 7, 2.4 Hz)	1.92 (qd, J = 7, 2.4 Hz)
11	3.81 (br s)	3.81 (br s)	3.68 (dd, J = 3, 2.4 Hz)	3.68 (dd, J = 3, 2.4 Hz)
12	2.04 (qd, J = 7, 2.5 Hz)	2.04 (qd, J = 7, 2.5 Hz)	2.04 (qd, J = 7, 3 Hz)	2.05 (qd, J = 7, 3 Hz)
14	3.26 (q, J = 7 Hz)	3.28 (q, J = 7 Hz)	3.23 (dt, J = 7, 3 Hz)	3.34 (q, J = 7 Hz)
20	1.07 (d, J = 7 Hz)	1.07 (d, J = 7 Hz)	0.89 (d, J = 7 Hz)	0.89 (d, J = 7 Hz)
21	0.77 (d, J = 6.5 Hz)	0.76 (d, J = 6.5 Hz)	0.72 (d, J = 7 Hz)	0.71 (d, J = 7 Hz)
22	1.07 (d, J = 6.5 Hz)	1.07 (d, J = 6.5 Hz)	1.10 (d, J = 7 Hz)	1.10 (d, J = 7 Hz)
23	1.21 (d, J = 7 Hz)	1.21 (d, J = 7 Hz)	1.26 (d, J = 7 Hz)	1.26 (d, J = 7 Hz)
24	1.25 (d, J = 7 Hz)	1.25 (d, J = 7 Hz)	1.25 (d, J = 7 Hz)	1.25 (d, J = 7 Hz)
25	1.15 (d, J = 7 Hz)	1.18 (d, J = 7 Hz)	1.23 (d, J = 7 Hz)	1.24 (d, J = 7 Hz)
26	1.96 (s)	1.98 (s)	1.93 (s)	1.95 (s)
27	1.96 (s)	2.00 (s)	1.98 (s)	1.99 (s)
28	2.36 (br s)	2.79 (q, J = 7 Hz)	2.35 (s)	2.78 (q, J = 7 Hz)
29		1.20 (t, J = 7 Hz)		1.22 (t, J = 7 Hz)
OH	5.19 (s)	5.14 (s)	5.49 (br s)	
OH	3.08 (br s)	3.11 (br s)	3.95 (br s)	

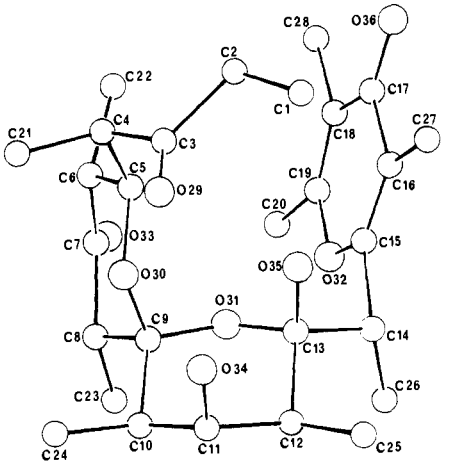

Figure 1. Computer-generated perspective drawing of siphonarin A (**3**). Hydrogens are omitted for clarity.

been replaced by an ethyl group. This was confirmed by the ^{13}C NMR data which revealed that the furthest downfield methyl signal at δ 17.7 (q) was replaced by ethyl signals at δ 11.4 (q) and 24.7 (t)

The chloroform-soluble material from an isopropyl alcohol extract of *Siphonaria normalis* was chromatographed on silica gel. Selected fractions were purified by LC on ODS-3 and Partisil-10 to obtain dihydrosiphonarin A (**5**, 0.21 mg/animal) and dihydrosiphonarin B (**6**, 0.05 mg/animal) together with the degradation products **7** and **8**.

Dihydrosiphonarin A (**5**), $[\alpha]_D$ −24.9° (c 0.99, CH_2Cl_2), $C_{28}H_{44}O_8$ (high-resolution FABMS of MH^+, obsd 509.3136, $C_{28}H_{45}O_8$ reqiures 509.3114), exhibited spectral data characteristic of a fully substituted γ-pyrone ring bearing three methyl groups [IR 1646, 1595 cm^{-1}; ^{13}C NMR δ 179.8 (s), 162.0 (s), 161.4 (s), 121.9 (s), 118.2 (s); ^{1}H NMR δ 2.35 (s, 3 H), 1.98 (s, 3 H), 1.93 (s, 3 H)], a saturated ketone [IR 1717 cm^{-1}; ^{13}C NMR δ 208.1 (s)], two ketal groups [^{13}C NMR δ 105.2 (s), 102.7 (s)], and two secondary hydroxyl groups [^{13}C NMR δ 74.0 (d), 73.9 (d)]. All of these data suggested the dihydrosiphonarin A structure. Further evidence for structure **5** having a hydroxyl at C-3 was provided by proton-decoupling studies which defined a 1-methyl-2-hydroxybutyl end group together with overall similarities in the ^{1}H NMR spectra of **3** and **5** (Table I). The relationship between **3** and **5** was confirmed by oxidation of dihydrosiphonarin A (**5**) with pyridinium chlorochromate (PCC) in refluxing benzene to obtain siphonarin A (**3**), identical in all respects with the natural product. Two additional minor products were obtained which appear to be the alternate monooxidation product and the dioxidation product. The C-3 hydroxyl was assigned the S^* stereochemistry on the basis of coupling constants and conformational analysis. In the crystalline state, the side chain of siphonarin A is positioned such that the terminal methyl group is held in close proximity to the pyrone ring by hydrogen bonding between the 13-hydroxyl group and the 3-ketone. ^{1}H NMR data provide evidence for a similar solution conformation for both siphonarin A (**3**) and dihydrosiphonarin A (**5**). The terminal methyl groups in the side chain of **3** (δ 0.94) and **5** (δ 0.88) resonate at higher field than the comparable signal in denticulatin A (**2**) (δ 1.03) due to deshielding by the pyrone ring. The adjacent methylene protons are diastereotopic indicating that the side chain is held rigid and the coupling between protons at C-4 and C-5 (J = 1 Hz for both **3** and **4**) is that predicted from the X-ray conformation. Assuming the X-ray conformation for the side chain of **5**, the substituents at C-3 and C-4 must exist in a priority anti-reflective (parf) relationship[12] to obtain a 7-Hz coupling between protons at C-3 and C-4.

Dihydrosiphonarin B (**6**), $[\alpha]_D$ −32.6° (c 0.33, CH_2Cl_2), $C_{29}H_{46}O_8$ (high-resolution FABMS of MH^+, obsd 523.3284, $C_{29}H_{47}O_8$ requires 523.3271) exhibited spectral data so similar to that of **5** that it could only be a homologue. The ^{1}H NMR spectrum of **6** was nearly superimposable on that of **5** except that the methyl signal at δ 2.35 (s, 3 H) in **5** was replaced by ethyl signals at δ 1.12 (t, 3 H, J = 7 Hz) and 2.78 (q, 2 H, J = 7 Hz), indicating that the relationship between **5** and **6** was the same as that between **3** and **4**.

Two minor metabolites **7** ($C_{17}H_{24}O_6$) and **8** ($C_{18}H_{26}O_6$) from *S. normalis* were also homologues of each other. The ^{1}H NMR spectra of **7** and **8** contained signals assigned to a 2,3,5-trimethylpyrone [δ 2.26 (s, 3 H), 2.14 (s, 3 H), 1.95 (s, 3 H)] and a 2-ethyl-3,5-dimethylpyrone [δ 2.60 (q, 2 H, J = 7 Hz), 2.16 (s, 3 H), 1.95 (s, 3 H), 1.17 (t, 3 H, J = 7 Hz)], respectively. The remaining signals in the ^{1}H NMR spectra were identical for **7** and **8** and were assigned to partial structure a. The IR bands at 3600, 1723, and 1700 cm^{-1} were assigned to the alcohol, acid, and ketone functionalities. Careful reexamination of the crude extract of *S. normalis* indicated that **7** and **8** were artifacts of silica gel chromatography using ethyl acetate. It is assumed that the ketal rings of **5** and **6** open to give β-diketones that undergo a retro-Claisen reaction to give **7** and **8**. Acid-catalyzed hydrolysis

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of dihydrosiphonarin A (**5**) gave the acid **7** in good yield, lending support to this proposal.

Subsequent to the completion of structural studies, one of us (J.C.C.) isolated the siphonarins **3** and **4** from *S. atra* and the dihydrosiphonarins **5** and **6** from *S. laciniosa*, both collected at Townsville, Australia. A sample of *S. atra* collected at Newport, NSW, Australia, did not contain the siphonarins and was the only sample of *Siphonaria* that we have examined that did not contain polypropionate metabolites.

Experimental Section

Collection and Extraction of *S. zelandica*. Over 1000 specimens of a mixture of *Siphonaria denticulata* and *Siphonaria zelandica* were collected by hand in the intertidal zone at Bottle and Glass Rocks in Sydney Harbor, Australia, in April 1983. The animals were steeped in acetone at ambient temperature for 2 weeks. The acetone was decanted and evaporated to obtain an aqueous suspension that was extracted with ethyl acetate (3 × 300 mL). The combined extracts were dried over sodium sulfate and the solvent evaporated to obtain a dark green oil (350 mg). The oil was chromatographed on silica gel using eluants of increasing polarity from hexane through ether to ethyl acetate. The fraction eluted with ether contained denticulatin A (**2**) (80 mg) and denticulatin B (80 mg).[4] Fractions eluted with 50% ethyl acetate in ether were rechromatographed by LC using 2:1 ethyl acetate/ether as eluant to obtain siphonarin A (**3**, 6 mg) and siphonarin B (**4**, 6 mg).

Siphonarin A (3): mp 161–166 °C $[\alpha]_D$ +21.7° (*c* 0.0143, $CHCl_3$); UV (MeOH) 260 nm (ϵ 4000); IR ($CHCl_3$) 3530, 3035, 2995, 1725, 1660, 1595, 1460, 1390 cm^{-1}; ^1H NMR ($CDCl_3$) (see Table I; ^{13}C NMR ($CDCl_3$) δ 213.4 (s), 206.5 (s), 180.2 (s), 166.0 (s), 161.5 (s), 122.0 (s), 117.5 (s), 105.1 (s), 103.4 (s), 74.6 (d), 50.0 (d), 46.0 (d), 45.3 (d), 42.1 (d), 38.7 (d), 38.2 (d), 35.6 (t), 17.7 (q), 13.0 (q), 12.6 (q), 12.0 (q), 10.9 (q), 9.9 (q), 9.2 (q), 8.6 (q), 8.1 (q), 7.4 (q) (1 signal obscured by solvent); HR MS, obsd *m/z* 506.2910, $C_{28}H_{42}O_8$ requires 506.2880).

Siphonarin B (4): $[\alpha]_D$ +13.2° (*c* 0.01361, $CHCl_3$); UV (MeOH) 260 nm (ϵ 2600); IR ($CHCl_3$) 3460, 2995, 1725, 1655, 1600, 1470, 1390 cm^{-1}; ^1H NMR ($CDCl_3$) see Table I; ^{13}C NMR ($CDCl_3$) δ 213.3 (s), 206.4 (s), 179.8 (s), 165.5 (s), 161.6 (s), 121.6 (s), 117.2 (s), 105.1 (s), 103.1 (s), 74.6 (d), 50.0 (d), 46.0 (d), 45.3 (d), 42.4 (d), 38.7 (d), 38.4 (d), 35.6 (t), 24.7 (t), 13.0 (q), 12.6 (q), 11.9 (q), 11.4 (q), 10.9 (q), 9.4 (q), 9.3 (q), 8.6 (q), 8.2 (q), 7.4 (q) (1 signal obscured by solvent); HR MS, obsd *m/z* 520.3065, $C_{29}H_{44}O_8$ requires 520.3036.

Single-Crystal X-ray Diffraction Determination of Siphonarin A. Preliminary X-ray photographs of siphonarin A displayed orthorhombic symmetry. Precise lattice constants, determined from a least-squares fit of 15 diffractometer measured 2θ-values, were a = 8.976 (3) Å, b = 10.663 (4) Å, and c = 29.286 (9) Å. Systematic extinctions, crystal density, and the presence of chirality were uniquely accommodated by space group $P2_12_12_1$ with one molecule of composition $C_{28}H_{40}O_8$ forming the asymmetric unit. All unique diffraction maxima with $2\theta \leq 114°$ were measured on a computer-controlled four-circle diffractometer using a variable speed, 1° ω-scan and graphite monochromated Cu Kα (1.54178 Å) radiation. After correction for Lorentz, polarization and background effects, 1626 (75%) were judged observed ($|F_o| \geq 3\sigma(F_o)$) and used in subsequent calculations.[13] The structure was solved uneventfully using a multisolution tangent formula approach. Block-diagonal least-squares refinements with 36 anisotropic nonhydrogens and 40 isotropic hydrogens have converged to a standard crystallographic residual of 0.0939 for the observed reflections. Additional crystallographic details are available and are described in the supplementary material.

Collection and Extraction of *S. normalis*. *Siphonaria normalis* ($N \simeq 200$) were collected at Diamond Head Beach, Oahu, HI, and stored in isopropyl alcohol at 5 °C for 1 week. The resulting extract was concentrated in vacuo and partitioned between brine (100 mL) and chloroform (100 mL × 3), and the combined chloroform layers were dried over magnesium sulfate and evaporated to give 1.517 g of organic oil. Column chromatography (silica gel 62; EtOAc) gave a UV absorbing oil (128 mg). HPLC [ODS-3, H_2O/MeOH (30:70) and Partisil, TMP/EtOAc, (30:70)] of a portion (64 mg) of this oil gave dihydrosiphonarin A (**5**) (21.3 mg), dihydrosiphonarin B (**6**) (5.2 mg), **7** (1.9 mg), and **8** (0.9 mg).

Dihydrosiphonarin A (5): $C_{28}H_{45}O_8$ (HR FABMS, obsd 509.3136, calcd 509.3114), $[\alpha]_D$ -24.9 (*c* 0.9925, CH_2Cl_2); IR (CH_2Cl_2) 3460, 3370, 2933, 1716, 1646, 1595 cm^{-1}; ^1H NMR ($CDCl_3$) see Table I; ^{13}C NMR ($CDCl_3$) δ 208.1 (s), 179.8 (s), 162.0 (s), 161.4 (s), 121.9 (s), 118.2 (s), 105.2 (s), 102.7 (s), 74.0 (d), 73.9 (d), 73.4 (d), 50.4 (d), 45.6 (d), 42.7 (d), 39.6 (d), 39.5 (d), 37.9 (d), 27.4 (t), 17.6 (q), 12.9 (q), 12.8 (q), 12.1 (q), 11.0 (q), 9.8 (q), 9.4 (q) (2 C), 9.1 (q) (2 C).

Dihydrosiphonarin B (6): $C_{29}H_{47}O_6$ (HR FABMS, obsd 523.3289, calcd 523.3271), $[\alpha]_D$ -32.6° (*c* 0.331, CH_2Cl_2); IR (CH_2Cl_2) 3463, 3367, 2935, 1717, 1645, 1593 cm^{-1}; ^1H NMR ($CDCl_3$) see Table I.

(7): $C_{17}H_{24}O_6$ (HR EI MS, obsd 324.1567, calcd 324.1573), $[\alpha]_D$ -116.8° (*c* 0.113, CH_2Cl_2); IR (CH_2Cl_2) br 3600–2200, 2937, 1723, 1653, 1578 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.15 (q, 1 H, J = 7 Hz), 3.63 (dd, 1 H, J = 2.5, 2.5 Hz), 2.87 (dq, 1 H, J = 7, 2.5 Hz), 2.74 (dq, 1 H, J = 7, 2.5 Hz), 2.26 (s, 3 H), 2.14 (s, 3 H), 1.95 (s, 3 H), 1.38 (d, 3 H, J = 7 Hz), 0.97 (d, 3 H, J = 7 Hz), 0.93 (d, 3 H, J = 7 Hz).

(8): $C_{18}H_{26}O_6$ (HR EI MS, obsd 338.1731, calcd 338.1729), $[\alpha]_D$ -86.5° (*c* 0.052, CH_2Cl_2): IR (CH_2Cl_2) br 3600–2200, 2933, 1722, 1647, 1578 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.17 (q, 1 H, J = 7 Hz), 3.63 (dd, 1 H, J = 7, 2.5 Hz), 1.39 (d, 3 H, J = 7 Hz), 1.36 (d, 3 H, J = 7 Hz), 1.17 (t, 3 H, J = 7 Hz), 0.92 (d, 3 H, J = 7 Hz).

Oxidation of Dihydrosiphonarin A (5). PCC (2 mg) and sodium acetate (10 mg) were added to benzene (5 mL), and the mixture was brought to reflux. A solution of **5** (4 mg) in benzene (2 mL) was added and reflux continued for 4.5 h. The reaction mixture was evaporated *in vacuo* and filtered through a silica gel pad to give an oil. HPLC of the oil (Partisil, TMP/EtOAc 30:70) gave **3** (1 mg, 25% yield), $[\alpha]_D$ +19.4° (*c* 0.108, CH_2Cl_2).

Hydroylsis of Dihydrosiphonarin A. 5 (2 mg) was dissolved in THF (10 mL). HCl_{aq}, 30% (1 mL), was added and the mixture stirred for 48 h at room temperature. The reaction mixture was evaporated in vacuo and the crude products were purified by HPLC (Partisil, TMP/EtOAc 30:70) to give **7** (0.7 mg, 55% theoretical yield).

Collection and Extraction of *Siphonaria atra* and *Siphonaria laciniosa*. *Siphonaria atra* and *Siphonaria laciniosa* were collected at Townsville, Australia, and freeze-dried prior to shipment.

Siphonaria atra (~100 specimens) was extracted with acetone and the extract evaporated to obtain an oil (150 mg). The oil was chromatographed on TLC grade silica gel, and fractions containing UV-absorbing compounds (~50 mg) were recombined and rechromatographed by LC on μ-Porasil using 2:1 ethyl acetate/ether as eluant to obtain siphonarin A (**3**), the minor component, and siphonarin B (**4**), the major component. Examination of spectral data confirmed that these samples were identical with those isolated from *S. zelandica*.

Siphonaria laciniosa specimens were extracted with dichloromethane, and the solvent was evaporated to obtain a yellow oil (140 mg). Chromatography of the oil as described above gave a UV-absorbing material (22.5 mg). Examination of the material by ^1H NMR spectroscopy revealed that it was a mixture of dihydrosiphonarin A (**5**) and dihydrosiphonarin B (**6**) in an approximately 85:15 ratio.

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Supplementary Material Available: Tables of fractional coordinates, bond distances, bond angles, and observed and calculated structure factors for Siphonarin A (17 pages). Ordering information is given on any current masthead page.

(13) All crystallographic calculations were done on a PRIME 850 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were the following: REDUCE and UNIQUE, data reduction programs Leonowicz, M. E. Cornell University, Ithaca, NY, 1978), MULTAN 78, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, locally modified to perform all Fourier calculations including Patterson syntheses (Main, P.; Hull, S. E.; Lessinger, L. Germain, G.; Declercq, J. P.; Woolfson, M. M. University of York, England, 1978), BLS78A, an anisotropic block-diagonal least-squares refinement (Hirotsu, K.; Arnold, E. Cornell University, Ithaca, NY, 1980), PLUTO78, a crystallographic illustration program (Motherwell, W. D. S. Cambridge Crystallographic Data Centre, 1978), BOND, a program to calculate molecular parameters and prepare tables (Hirotsu, K. Cornell Univeristy, Ithaca, NY, 1978).