12d: The ketone (30 mg) gave a crude product which was chromatographed on silica gel (12 × 1 cm column, 10% Et_2O/PE as eluant), affording a white solid (25 mg, 83%): mp 105–106 °C; IR (KBr) 1725 (s), 1670 (s), 1620 (m), 1600 (m), 1465 (m), 1410 (m), 1330 (s), 1170 (s), 1130 (s), 1070 (s), 1020 (m), 850 (m), 760 cm^{-1} (m); ^1H NMR δ 8.0–7.0 (m, 9 H), 6.6–6.2 (highly str m, 2 H), 5.95 (dd, J = 10, 1.7 Hz, 1 H), 4.3 (s, 1 H); mass spectrum, exact mass calcd for $C_{21}H_{13}O_2F_3$ m/e 354.0868, m/e obsd 354.0859.

Thermal Rearrangement of 9b. A solution of **9b** (0.25 g, 0.93 mmol) in *o*-dichlorobenzene (10 mL) containing 2,6-di-*tert*-butylhydroquinone (2.0 mg) was degassed by three freeze–thaw cycles and heated at reflux under N_2 for 16 h, after which time TLC analysis (1:1 Et_2O/PE) indicated no remaining starting material. The solvent was removed in vacuo, and the residue was chromatographed on silica gel (6 in. × $^1/_2$ in. column, 20% EtOAc/PE as eluant) to afford **14** (0.122 g, 49%) as a clear oil: IR (NaCl) 2970 (m), 2880 (m), 1720 (br, s), 1600 (m), 1462 (m), 1412 (m), 1210 (m), 1100 (br, s), 1030 (m), 1015 (m), 960 (br, s), 925 (m), 750 cm^{-1} (m); ^1H NMR δ 7.8–7.2 (str m, 4 H), 5.95 (br s, 2 H), 5.65 (AB q with additional coupling, $\Delta\nu_{AB}$ = 35 Hz, J_{AB} = 11 Hz, 2 H), 4.0 (s, 4 H), 2.7 (q, J = 7 Hz, 1 H), 1.1 (d, J = 7 Hz, 3 H); ^{13}C NMR δ 205.7, 155.7, 135.3, 135.0, 134.5, 128.4, 127.3, 125.8, 125.7, 123.8, 65.3, 65.1, 53.1, 49.1, 9.8 (two C missing); mass spectrum, exact mass calcd for $C_{17}H_{16}O_3$ m/e 268.1100, obsd m/e 268.1084.

The structural assignment for **14** was further confirmed by hydrolysis of the ethylene glycol ketal moiety as follows. To a solution of **14** (0.018 g, 0.067 mmol) in $(CH_3)_2CO$ (10 mL) was added 5% aqueous HOAc (5 mL), and the mixture was allowed to stand at room temperature for 12 h. Next, the reaction mixture was poured into saturated aqueous $NaHCO_3$ (10 mL), and the solvent was removed in vacuo. Extractive workup using Et_2O (2 × 10 mL) gave **14** (0.015 g, 99%), mp 144–147 °C, with spectral properties identical with those previously described for **6b**.

Details for Kinetic Measurements. A detailed description and representative kinetic and Arhenius plots are given in the supplementary material. The progress for reaction of compounds **5a,b** were determined by removing sealed, degassed ampoules of **5a** (6.3×10^{-2} M) and **5b** (5.8×10^{-2} M) from a constant-temperature bath and analyzing the progress of reaction by ^1H NMR spectroscopy. The NMR analysis for the **5a** reaction was performed by integrating the relative areas of the vinyl protons at δ 4.65 vs the two methylene protons in the product at δ 2.95. For **5b** the allylic methyl resonance at δ 1.8 was integrated vs the ketone methyl resonance at δ 1.2. For the aryl substituted compounds, **12a–d**, a similar sealed tube technique was employed, except the disappearance of starting material was analyzed by UV. These concentrations for the kinetic runs were (6.7–7.7) × 10^{-4} M and the analyses performed at the indicated wavelengths: **12a** (346.5 nm); **12b** (355 nm); **12c** (350 nm); **12d** (349.5 nm) on solutions diluted so that the maximum optical density was <1.0. The kinetic determinations employing ^1H NMR spectroscopy are thought to be accurate to at least ±10% while those determined employing UV spectroscopy are probably accurate to at least ±5%.

Acknowledgment. We acknowledge generous support from the National Science Foundation.

Supplementary Material Available: Detailed description of the kinetic procedures, ^1H NMR spectra of **5a, 6a, 6b, 11a, 12a,** and **13a**, and representative kinetic and Arhenius plots (12 pages). Ordering information is given on any current masthead page.

The Baconipyrones: Novel Polypropionates from the Pulmonate *Siphonaria baconi*

Denise C. Manker and D. John Faulkner*

Scripps Institution of Oceanography, A-012F, University of California, San Diego, La Jolla, California 92093

Thomas J. Stout and Jon Clardy*

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

Received May 2, 1989

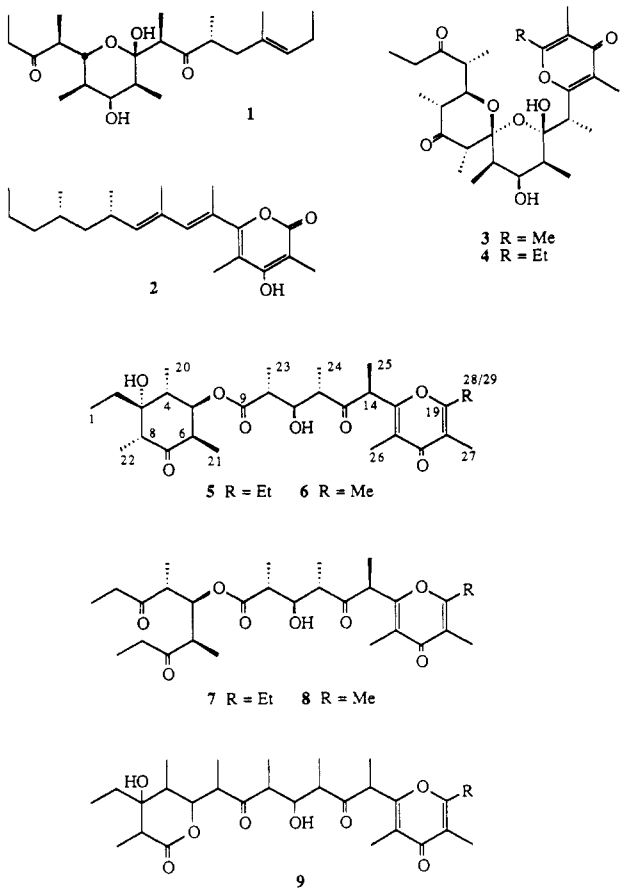
The pulmonate mollusc *Siphonaria baconi* from the south coast of Australia contains four new propionate-derived metabolites, baconipyrones A–D (**5–8**), in addition to the known compound siphonarin A (**3**). The structure of baconipyrone B (**6**) was determined by X-ray analysis. The structures of baconipyrones A (**5**), C (**7**), and D (**8**) were established by comparison of spectral data with those of baconipyrone B (**6**) and by consideration of a biosynthetic hypothesis linking the baconipyrones with the siphonarins.

The Siphonariids, or false limpets, are pulmonate molluscs that live in the intertidal zone. They possess both a gill and a primitive lung that enables them to "breathe" both above and under water. From the chemists' viewpoint, they are characterized by their ability to synthesize compounds of the polypropionate class.[1] The metabolites described previously[2] all fall into three general classes: the simple polypropionates, such as denticulatin A (**1**) from *Siphonaria denticulata*,[3] the α-pyrones, exemplified by diemenensin (**2**) from *S. diemenensis*,[4] and γ-pyrones like siphonarins A (**3**) and B (**4**) from *S. zelandica* and *S. atra*.[5] In this paper we describe four new polypropionates, baconipyrones A–D (**5–8**), that are unusual[6] because they do not contain a contiguous carbon skeleton.

Specimens of *Siphonaria baconi* were collected from intertidal rock platforms near Melbourne, Australia, and were stored in acetone. The ethyl acetate soluble material from the acetone extract was chromatographed on silica gel, and fractions containing polypropionates, as judged by ^1H NMR spectroscopy, were further purified by HPLC to obtain baconipyrone A (**5**, 0.05 mg/animal), baconipyrone B (**6**, 0.046 mg/animal), baconipyrone C (**7**, 0.016 mg/animal), baconipyrone D (**8**, 0.046 mg/animal), and

(1) Manker, D. C.; Garson, M. J.; Faulkner, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1061.
(2) For recent reviews, see: Faulkner, D. J. *Nat. Prod. Rep.* **1984**, *1*, 551; **1986**, *3*, 1; **1987**, *4*, 539; **1988**, *5*, 613.
(3) Hochlowski, J. E.; Faulkner, D. J.; Matsumoto, G. K.; Clardy, J. *J. Am. Chem. Soc.* **1983**, *105*, 7413.
(4) Hochlowski, J. E.; Faulkner, D. J. *Tetrahedron Lett.* **1983**, *24*, 1917.
(5) Hochlowski, J. E.; Coll, J. C.; Faulkner, D. J.; Biskupiak, J. E.; Ireland, C. M.; Zheng, Q.; He, C.; Clardy, J. *J. Am. Chem. Soc.* **1984**, *106*, 6748.
(6) For an example of a propionate ester that may be obtained by a similar mechanism, see: Hochlowski, J. E.; Faulkner, D. J. *J. Org. Chem.* **1984**, *49*, 3838.

0022-3263/89/1954-5371$01.50/0



the known metabolite siphonarin A (**3**, 0.008 mg/animal).

Baconipyrone B (**6**) was initially obtained as an oil that slowly crystallized from ether–hexane to obtain colorless cubic crystals, mp 142–143 °C. The FAB mass spectrum produced a MH^+ peak at m/z 509.2960, which indicated that the molecular formula was $C_{28}H_{42}O_8$. The infrared spectrum contained bands at 3460 (hydroxyl), 1720 (ketone), 1655, and 1600 cm^{-1} (γ-pyrone) and the UV absorption at 259 nm (ϵ 11 700) was typical of a single γ-pyrone ring. Several isolated spin systems were identified in the ^1H NMR spectrum (Table I) of baconipyrone B (**6**). The methyl signals at δ 2.23 (s, 3 H), 2.03 (s, 3 H), and 1.94 (s, 3 H) were assigned to methyl groups on the pyrone ring by comparison of the data with those of siphonarin B (**4**) and by NOEDS experiments. The fourth substituent on the pyrone ring was an isolated $CH(CH_3)$ group [δ 4.01 (q, 1 H, J = 6.9 Hz), 1.37 (d, 1 H, J = 6.9 Hz)] that must be adjacent to a carbonyl group. Spin–spin decoupling experiments established the presence of the 2,4-disubstituted 3-pentanol system (C-23, C-10, C-11, C-12, C-24), and it was assumed from the chemical shift data that this substructure was flanked by carbonyl groups. The molecular formula required that the three remaining isolated spin systems, $CH(CH_3)CH(OCO)CH(CH_3)$, $CH(CH_3)$, and CH_3CH_2, be incorporated into a second ring that contained a tertiary alcohol [^{13}C NMR δ 76.1 (s)]. These data could be accommodated by several possible structures, the most likely of which were **6** and **9**. The structure of baconipyrone B (**6**) was therefore determined by X-ray analysis.

A computer-generated perspective drawing of the final X-ray model of baconipyrone B (**6**) is given in Figure 1. As expected, the pyrone ring is planar within experimental error, and the cyclohexanone ring is a slightly flattened twist boat. The chain connecting the two rings is not in the extended form, but neither is it so contracted as to generate close contacts between the rings. There is no hydrogen bond between O(5)H and O(4); an intermolecular hydrogen bond is formed instead. The molecular geometry agrees well with generally accepted values. A complete assignment of the ^1H NMR spectrum is given in Table I. The ^{13}C NMR spectrum is in accord with the proposed structure, but the signals could not be unambiguously assigned. The relative stereochemistry at C-4, C-6, C-10, C-11, C-12, and C-14 in baconipyrone B (**6**) is identical with that of siphonarin A (**3**), which was also determined by X-ray crystallography.[5]

Table I. ^1H NMR Data (360 MHz, $CDCl_3$) for Baconipyrones A (**5**) and B (**6**)[a]

H no.	δ (**5**)		δ (**6**)
1	0.86	(t, 3 H, J = 7.5 Hz)	0.85
2	1.54	(dq, 1 H, J = 14, 7.5 Hz)	1.53
2	1.66	(dq, 1 H, J = 14, 7.5 Hz)	1.65
4	2.13	(dq, 1 H, J = 6.9, 6.3 Hz)	2.13
5	5.05	(dd, 1 H, J = 6.3, 4.7 Hz)	5.01
6	3.00	(qd, 1 H, J = 7.2, 4.7 Hz)	2.95
8	2.60	(q, 1 H, J = 6.8 Hz)	2.60
10	2.65	(qd, 1 H, J = 7.2, 3.4 Hz)	2.62
11	3.68	(ddd, 1 H, J = 9.6, 8.6, 3.4 Hz)	3.63
OH	3.43	(d, 1 H, J = 9.6 Hz)	3.34
12	2.84	(dq, 1 H, J = 8.6, 6.9 Hz)	2.78
14	4.09	(q, 1 H, J = 6.9 Hz)	4.01
20	1.06	(d, 3 H, J = 6.9 Hz)	1.06
21	1.00	(d, 3 H, J = 7.2 Hz)	0.99
22	1.07	(d, 3 H, J = 6.8 Hz)	1.07
23	1.29	(d, 3 H, J = 7.2 Hz)	1.29
24	0.91	(d, 3 H, J = 6.9 Hz)	0.92
25	1.38	(d, 3 H, J = 6.9 Hz)	1.37
26	2.05	(s, 3 H)	2.03
27	1.95	(s, 3 H)	1.94
28	2.60	(m, 2 H)/(s, 3 H)	2.23
29	1.16	(t, 3 H, J = 7.5 Hz)	

[a] Chemical shifts in ppm from TMS; the multiplicities and coupling constants for most signals are identical in the two spectra.

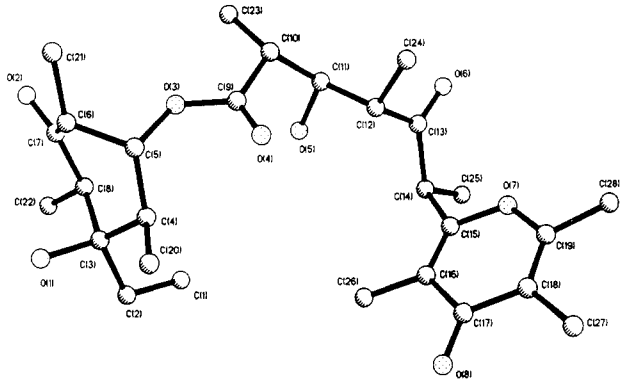


Figure 1. A computer generated perspective drawing of the X-ray model of baconipyrone B (**6**). Hydrogens are omitted for clarity, and the absolute configuration drawn is an arbitrary choice.

The spectral data of baconipyrone A (**5**) were very similar to those of baconipyrone B (**6**) and differed only by the replacement of the terminal C-28 methyl group by an ethyl group. The FAB mass spectrum of **5** has a MH^+ peak at m/z 521.3126 that requires the molecular formula $C_{29}H_{44}O_8$. In the ^{13}C NMR spectrum there is one additional CH_2 signal, and in the ^1H NMR spectrum the methyl signal at δ 2.23 (s, 3 H) is replaced by ethyl signals at δ 2.60 (m, 2 H) and δ 1.16 (t, 3 H, J = 7.5 Hz). A similar replacement of the terminal methyl group by ethyl, resulting in similar differences in the NMR spectra, had been observed in the siphonarin series.[5]

The structures of baconipyrones A (**5**) and B (**6**) are almost unique among the polypropionates from species of *Siphonaria*[6] because they do not contain the normal contiguous polypropionate backbone. The co-occurrence of

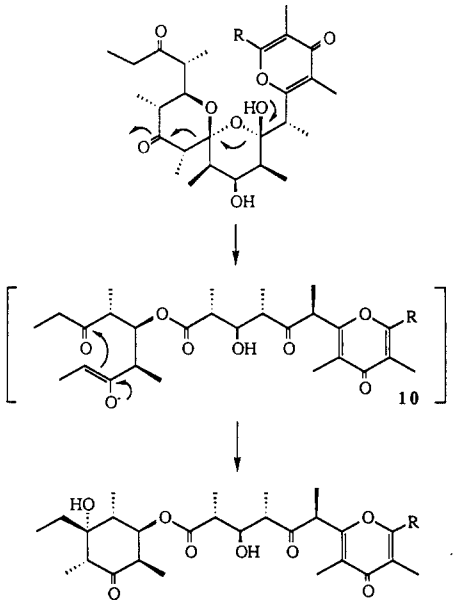


Figure 2. A proposed mechanism for the generation of the baconipyrones from the siphonarins.

siphonarin A (**3**) in *Siphonaria baconi* led to the proposal that baconipyrone B (**6**) could be derived from siphonarin A (**3**) by the mechanism shown in Figure 2. This mechanism is of interest because protonation of the enolate intermediate **10** leads to a triketone (baconipyrone D) that has a prochiral center at C-5, and that can, in principal, cyclize to give two epimers of baconipyrone B (**6**). The fact that only one epimer was observed indicates that the ketone groups at C-3 and C-7 may be differentiated during the transformation.

Baconipyrones C (**7**) and D (**8**) are isomers of baconipyrones A (**5**) and B (**6**), respectively. The most significant differences in the spectral data were found in the ^{13}C NMR spectra of **7** and **8**, both of which contain a new carbonyl signal and one additional methylene carbon signal in place of the tertiary alcohol carbon signal and one of the methine carbon signals in the spectra of **5** and **6**. The ^1H NMR spectra of both baconipyrones C (**7**) and D (**8**) contain signals due to two ethyl ketone moieties. If one accepts the hypothesis that baconipyrones C (**7**) and D (**8**) are derived from the siphonarins as shown in Figure 2, then the two 2-alkyl-3-pentanone chains (C-1 to C-20 and C-22 to C-21) in **7** and **8** are identical in all respects, including the absolute configurations at C-4 and C-6, but their attachment to a prochiral carbon allows the spectral data for corresponding atoms to differ considerably. For example, in the ^1H NMR spectrum of baconipyrone C (**7**), the C-1 and C-22 methyl groups gave rise to signals at δ 0.91 (t, 3 H, J = 7.2 Hz) and 1.01 (t, 3 H, J = 7.3 Hz). Although baconipyrones C (**7**) and D (**8**) are expected as intermediates in the conversion of the siphonarins to baconipyrones A and B, according to the mechanism shown in Figure 2 they could also be derived from **5** and **6** by a retro-aldol reaction. In the absence of any conflicting data, it has been assumed that the relative stereochemistry at all chiral centers in baconipyrones C and D are the same as in baconipyrones A and B.

Experimental Section

Collection, Extraction, and Chromatography. A total of 403 specimens of *Siphonaria baconi* were collected from the rocky intertidal platforms at Sorrento Beach, Victoria, Australia. The animals were extracted in acetone for 1 week, after which time the solvent was decanted and evaporated in vacuo to obtain an aqueous phase that was extracted with ethyl acetate (4 × 100 mL). The combined organic extracts were dried over sodium sulfate, and the solvent was evaporated to give a brown oil (703 mg). A portion (400 mg) of the crude extract was chromatographed on silica gel using a solvent gradient of increasing polarity from hexane to ethyl acetate. The most polar, UV-active fractions were combined (194 mg) and further purified by HPLC on Partisil (9:9:2 hexane–ethyl acetate–2-propanol) to obtain five UV-active fractions. The least polar fraction consisted of baconipyrone A (**5**, 20.0 mg). A second fraction was rechromatographed by LC on reversed-phase C-18 silica, using 30% water in methanol as eluant, to obtain baconipyrone B (**6**, 19.6 mg). A third fraction was subjected to reversed-phase HPLC (25% water in methanol) to separate baconipyrone C (**7**, 6.4 mg) from siphonarin A (**3**, 3.3 mg). The most polar fraction was purified by reversed-phase HPLC using 20% water in methanol as eluant to yield baconipyrone D (**8**, 8.9 mg).

Table II. ^1H NMR Data (360 MHz, $CDCl_3$) for Baconipyrones C (7) and D (8)[a]

H no.	δ (7)		δ (8)
1	0.91	(t, 3 H, J = 7.2 Hz)	0.92
2	2.34	(dq, 1 H, J = 18.3, 7.2 Hz)	2.33
2	2.56	(dq, 1 H, J = 18.3, 7.2 Hz)	2.53
4	2.83	(m, 1 H)	2.83
5	5.46	(dd, 1 H, J = 9.0, 3.5 Hz)	5.46
6	2.83	(m, 1 H)	2.83
8	2.39	(dq, 1 H, J = 18.1, 7.2 Hz)	2.39
8	2.76	(dq, 1 H, J = 18.1, 7.2 Hz)	2.76
10	2.55	(qd, 1 H, J = 7.2, 2.7 Hz)	2.55
11	3.54	(ddd, 1 H, J = 10.5, 9.0, 2.7 Hz)	3.55
OH	3.64	(d, 1 H, J = 10.5 Hz)	3.39
12	2.86	(dq, 1 H, J = 9.0, 7.2 Hz)	2.86
14	4.16	(q, 1 H, J = 6.9 Hz)	4.13
20	0.85[b]	(d, 3 H, J = 6.8 Hz)	0.87[b]
21	1.02[b]	(d, 3 H, J = 6.9 Hz)	1.01[b]
22	1.01	(t, 3 H, J = 7.2 Hz)	1.00
23	1.22	(d, 3 H, J = 7.2 Hz)	1.22
24	1.09	(d, 3 H, J = 7.2 Hz)	1.08
25	1.38	(d, 1 H, J = 6.9 Hz)	1.37
26	2.03	(s, 3 H)	2.07
27	1.93	(s, 3 H)	1.92
28	2.56	(q, 2 H, J = 7.6 Hz)/(s, 3 H)	2.22
29	1.16	(t, 3 H, J = 7.6 Hz)	

[a] Chemical shifts in ppm from TMS; the multiplicities and coupling constants for most signals are identical in the two spectra. [b] Assignments may be reversed.

Baconipyrone A (5): oil; $[\alpha]_D$ −82.0° (c 0.47, $CHCl_3$); IR ($CHCl_3$) 3460 (broad), 1720, 1650, 1600 cm^{-1}; UV (MeOH) 260 (ϵ 12 700), 220 nm (ϵ 10 300); ^1H NMR ($CDCl_3$) see Table I; ^{13}C NMR ($CDCl_3$) δ 7.3 (q), 8.8 (q), 9.5 (q), 9.9 (q), 11.3 (q), 11.5 (q), 11.9 (q), 12.9 (q), 14.2 (q), 15.1 (q), 24.7 (t), 30.1 (t), 37.8 (d), 41.4 (d), 44.7 (d), 46.2 (d), 48.1 (d), 51.1 (d), 77.0 (s), 77.1 (d), 77.3 (d), 118.4 (s), 120.3 (s), 160.3 (s), 164.8 (s), 174.7 (s), 179.6 (s), 210.2 (s), 221.4 (s); FABMS m/z 521.3126, $C_{29}H_{45}O_8$ (MH^+) requires 521.3114.

Baconipyrone B (6): oil; $[\alpha]_D$ −65.9° (c 0.66, $CHCl_3$); IR ($CHCl_3$) 3500 (broad), 1720, 1655, 1600 (broad) cm^{-1}; UV (MeOH) 259 (ϵ 11 700), 218 nm (ϵ 8900); ^1H NMR ($CDCl_3$) see Table I; ^{13}C NMR ($CDCl_3$) δ 7.8 (q), 8.7 (q), 9.8 (q), 10.0 (q), 11.5 (q), 11.8 (q), 13.0 (q), 14.2 (q), 15.0 (q), 17.5 (q), 30.2 (t), 37.9 (d), 41.6 (d), 44.7 (d), 46.2 (d), 48.1 (d), 51.1 (d), 76.1 (d), 77.2 (d), 77.4 (d), 119.3 (s), 120.4 (s), 160.4 (s), 160.5 (s), 174.7 (s), 179.3 (s), 210.1 (s), 211.2 (s); FABMS m/z 507.2960, $C_{28}H_{43}O_8$ (MH^+) requires 507.2958.

Baconipyrone C (7): oil; $[\alpha]_D$ −19.0° (c 0.90, MeOH); IR ($CHCl_3$) 3480 (broad), 1720, 1650, 1600 (broad) cm^{-1}; UV (MeOH) 260 nm (ϵ 11 800), 218 nm (ϵ 8900); ^1H NMR ($CDCl_3$) see Table II; ^{13}C NMR ($CDCl_3$) δ 7.2 (q), 7.7 (q), 9.5 (q), 9.6 (q), 9.9 (q), 11.3 (q), 13.1 (q), 13.8 (q), 14.1 (q), 15.0 (q), 24.7 (t), 35.1 (2 t), 41.1 (d), 45.7 (d), 47.2 (d), 48.6 (d), 50.9 (d), 73.7 (d), 77.5 (d), 118.2 (s), 120.4 (s), 160.6 (s), 164.7 (s), 174.0 (s), 179.7 (s), 210.4 (s), 210.9 (s), 211.9 (s); FABMS m/z 521.3111, $C_{29}H_{45}O_8$ (MH^+) requires 521.3114.

Baconipyrone D (8): oil; $[\alpha]_D$ −61.7° (c 1.17, MeOH); IR ($CHCl_3$) 3450 (broad), 1720, 1655, 1600 (broad) cm^{-1}; UV (MeOH) 260 (ϵ 12 600), 218 nm (ϵ 9600); ^1H NMR ($CDCl_3$) see Table II;

^{13}C NMR ($CDCl_3$) δ 7.3 (q), 7.6 (q), 9.6 (q), 9.8 (q), 10.0 (q), 13.1 (q), 13.4 (q), 14.2 (q), 15.0 (q), 17.5 (q), 35.1 (2 t), 41.1 (d), 45.8 (d), 47.2 (d), 48.6 (d), 51.1 (d), 73.8 (d), 77.6 (d), 119.1 (s), 120.4 (s), 160.3 (s), 160.8 (s), 173.9 (s), 179.4 (s), 210.4 (s), 210.9 (s), 211.8 (s); FABMS m/z 507.2945, $C_{28}H_{43}O_8$ (MH^+) requires 507.2958.

Single-Crystal X-ray Analysis of Baconipyrone. A clear, colorless, and roughly cubic (0.35 × 0.3 × 0.3 mm) crystal of baconipyrone B (**6**) was selected for all crystallographic measurements. Preliminary photographs showed monoclinic symmetry, and accurate lattice constants of a = 12.663 (3) Å, b = 8.958 (2) Å, c = 13.279 (3) Å, and β = 94.38 (2)° were determined from a least-squares analysis of 15 diffractometer measured 2θ-values. Systematic extinctions and density considerations indicated one molecule of composition $C_{28}H_{42}O_8$ formed the asymmetric unit in space group $P2_1$. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a four-circle diffractometer using Cu Kα radiation (1.541 78 Å) and θ:2θ scans of 1.0° plus the Kα separation. Backgrounds were measured at the beginning and end of each scan for 30% of the total scan time. A total of 2188 unique reflections were collected in this manner, and after correction for Lorentz, polarization, and background effects, 2118 (97%) were judged observed. No corrections for absorption or decomposition were judged necessary. A phasing model was found using direct methods and full-matrix least-squares refinements with anisotropic nonhydrogen atoms and fixed isotropic riding hydrogens have converged to a conventional discrepancy index of 0.056 for the observed data. Additional X-ray data are available and are described in the supplementary material paragraph at the end of this manuscript.

Acknowledgment. We thank Dr. Ted Molinski for assistance in collecting the animals. This research was supported by grants from the National Science Foundation (CHE86-03091 to D.J.F.), the National Institutes of Health (CA24487 to J.C.) and the New York State Sea Grant Program.

Registry No. **3**, 92125-67-2; **5**, 123003-45-2; **6**, 123003-46-3; **7**, 123003-47-4; **8**, 123003-48-5.

Supplementary Material Available: Tables of fractional coordinates, interatomic distances, interatomic angles, and thermal parameters for baconipyrone B (5 pages). Ordering information is given on any current masthead page.

Vallartanones A and B, Polypropionate Metabolites of *Siphonaria maura* from Mexico

Denise C. Manker and D. John Faulkner*

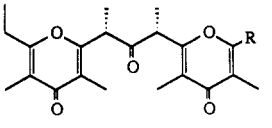
Scripps Institution of Oceanography, A-012F, University of California, San Diego, La Jolla, California 92093

Received May 2, 1989

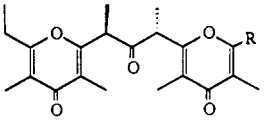
Specimens of *Siphonaria maura* collected near Puerto Vallarta, Mexico, contained two new metabolites of the polypropionate class. Vallartanones A (**6**) and B (**7**) were identified by interpretation of spectral data. Interpretation of the CD spectrum of vallartanone A (**6**) by application of exciton coupling theory provided the absolute configuration. The metabolites of *S. maura* vary according to the collection location.

Pulmonate molluscs of the genus *Siphonaria*, known commonly as false limpets, are intertidal gastropods that are amphibious in that they possess both gills and lungs. The secondary metabolite chemistry of *Siphonaria* species is dominated by compounds of the polypropionate class.[1] An earlier study of the metabolites of *Siphonaria maura* from Costa Rica resulted in the isolation of four closely related pyrones, maurapyrones A–D (**1**–**4**) and the unrelated polypropionate maurenone (**5**).[2] The major problem encountered in the structural elucidation of polypropionates such as maurenone (**5**) has been to define the stereochemistry of noncrystalline compounds, particularly those with noncontiguous chiral centers. In this paper, we report the structural elucidation of two new polypropionate metabolites, vallartanones A (**6**) and B (**7**), by using a combination of spectral and chemical methods.

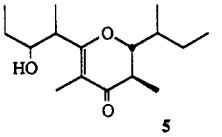
Specimens of *Siphonaria maura* collected at Sayulita, near Puerto Vallarta, Mexico, were stored in acetone. The ethyl acetate soluble material from the acetone extract was purified by flash chromatography on silica followed by LC on Partisil using 45% ethyl acetate in hexane as eluant to obtain vallartanone A (**6**, 29.8 mg, 0.08 mg/animal) and vallartanone B (**7**, 5.6 mg, 0.015 mg/animal).



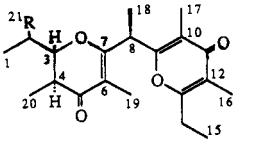
1 R = n-C_5H_{11}
3 R = i-C_4H_9



2 R = n-C_5H_{11}
4 R = i-C_4H_9



5



6 R = CH_3 **7** R = H

The molecular formula of vallartanone A (**6**), $C_{21}H_{30}O_4$, was determined from the EIMS molecular ion observed at m/z 346.2145. The presence of the γ-pyrone was indicated by infrared bands at 1645 and 1600 cm^{-1} as well as a UV absorption at 264 nm. The ^1H NMR spectrum contained two methyl singlets at δ 1.96 and 1.94, typical of those on a pyrone ring, and an olefinic methyl singlet at δ 1.75. In addition, four methyl doublets and one methyl triplet were observed. Two methyl doublets at δ 0.84 and 1.08 were coupled to a one proton signal at δ 1.85 which was coupled to a methine signal at δ 3.79 (dd, 1 H, J = 12.9, 2.6 Hz). This signal was further coupled (J = 12.9 Hz) to a signal at δ 2.38, which was also coupled to a methyl

(1) Faulkner, D. J. *Nat. Prod. Rep.* **1984**, *1*, 551; **1986**, *3*, 1; **1987**, *4*, 539; **1988**, *5*, 613.
(2) Manker, D. C.; Faulkner, D. J.; Xe, C.-F.; Clardy, J. *J. Org. Chem.* **1986**, *51*, 814.

0022-3263/89/1954-5374$01.50/0