EtOAc (1 mL), filtered, and rinsed through a short (1-in.) column of silica gel with EtOAc. The solvent was removed and the peroxide mixture analyzed by NMR.

Peroxides from 7c. Ozonation of **7c** (72 mg) provided 97 mg (92%) of a mixture of **24c**, **25c**, and **26c** in a 41:29:30 ratio by NMR: ^{1}H NMR (in CDCl$_3$, after shake with D$_2$O to remove interfering OH signal) δ 5.20 (m, **26c**, 0.30 H), 4.69 (m, **24c** and **25c**, 0.70 H), 4.1–3.5 (m, 1 H), 3.48–3.39 (5 s, 3 H), 2.16 (s, **25c**, 0.88 H), 2.1–1.6 (m, 4 H), 1.45–1.15 (5 s, **24c** and **26c**, 2.10 H), 0.19–0.09 ppm (3 s, 9 H). Treatment of this mixture with excess (CH$_3$)$_2$S caused conversion to **27c** over a 20-h period: ^{1}H δ 9.77 (t, J = 1.3 Hz, 1 H), 4.05 (t, J = 6.5 Hz, 1 H), 2.52 (t, J = 7.6 Hz, 2 H), 2.18 (s, 3 H), 2.00 (m, 2 H), 0.14 ppm (s, 9 H).

Peroxides from 7e. Ozonation of 44 mg (0.32 mmol) of **7e** provided 54 mg (77%) of a peroxide mixture containing **24e**, **25e**, and **26e** in a 41:40:19 ratio by NMR: ^{1}H δ 5.28 (m, **26e**, 0.19 H), 5.03 (m, **24e** and **25e**, 0.81 H), 4.9–4.7 (m, 1 H), 3.5–3.3 (6 s, 3 H), 2.21–2.05 (6 s, OAc for all and CH$_3$ for **25e**, 4.2 H), 2.1–1.7 (m, 4 H), 1.5–1.2 ppm (6 s, **24e** and **26e**, 1.8 H). Exposure of this mixture to excess (CH$_3$)$_2$S overnight led to ketoaldehyde **27e**: ^{1}H δ 9.78 (br s, 1 H), 5.02 (dd, J = 7.5, 5.1 Hz, 1 H), 3.46 (s, 3 H), 2.61 (t, J = 7.3 Hz, 2 H), 2.20 (s, 3 H), 2.14 (s, 3 H), 2.13 ppm (m, 2 H).

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Notes

Rare Phenazine L-Quinovose Esters from a Marine Actinomycete

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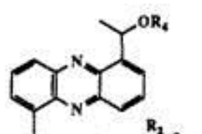
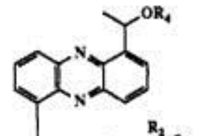
Although soil-derived bacteria have proven to be the major source for commercial antibiotics and related bioactive metabolites, similar microorganisms found in marine habitats have been almost totally ignored.[1] This has been due, in part, to the diversity of unique bacteria in marine habitats and the fact that many of these microorganisms are not readily brought into culture. As part of a continuing program to explore the nutritional requirements, distributions, and secondary metabolites produced by marine bacteria,[2] we have initiated several studies of bacteria from bay and estuarine environments. A study of the shallow sediments in Bodega Bay, CA, resulted in the isolation of a filamentous bacterium (isolate CNB-253, an unknown *Streptomyces* sp.) which was found to produce compounds with broad-screen antibacterial activity. Subsequent fermentation in saltwater-based media, followed by EtOAc extraction of the whole broth, vacuum flash chromatographic purification of the extract, and HPLC purification led to the isolation of four new alkaloid esters of the rare phenazine class (**1–4**, Chart I).[3] In addition, minor quantities of the known compounds 6-acetylphenazine-1-carboxylic acid (**7**) and saphenic acid (**8**) were also isolated.[4]

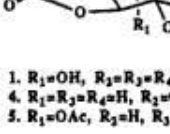
Chart I



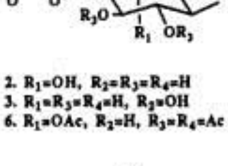
1. R$_1$=OH, R$_2$=R$_3$=R$_4$=H
4. R$_1$=R$_3$=R$_4$=H, R$_2$=OH
5. R$_1$=OAc, R$_2$=H, R$_3$=R$_4$=Ac



2. R$_1$=OH, R$_2$=R$_3$=R$_4$=H
3. R$_1$=R$_3$=R$_4$=H, R$_2$=OH
6. R$_1$=OAc, R$_2$=H, R$_3$=R$_4$=Ac



7. R= =O
8. R=H, OH



Revealing their isomeric relationships, all four phenazine alkaloid esters (**1–4**) showed identical molecular ions at m/z 414 amu (LREIMS), which was analyzed by high-resolution methods for $C_{21}H_{22}N_2O_7$. The ^{1}H NMR spectra for all four compounds (Table I) showed six aromatic protons and those from a hexose sugar pyranose functionality. The ^{1}H NMR spectrum of the major compound, **2**, resolved the aromatic resonances, and decoupling experiments revealed that they belonged to two isolated spin systems each involving three contiguous protons. All four compounds also showed a methyl group at δ 1.8 ppm (d, J = 6.5 Hz) that was coupled to a deshielded methine proton at δ 5.8 ppm (dq, J = 2.0, 6.5 Hz) which simplified to a quartet upon changing the NMR solvent from pure

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(1) (a) Faulkner, D. J. *Nat. Prod. Rep.* **1991**, *8*(2), 97 and earlier reviews in the same journal. (b) Fenical, W.; Jensen, P. R. In *Advances in Marine Biotechnology*, Zaborsky, O. K., Attaway, D. A., Eds.; Plenum Press: New York, Vol. 1, in press.

(2) (a) Gil-Turnes, M. S.; Hay, M. E.; Fenical, W. *Science* **1989**, *246*, 116. (b) Gustafson, K.; Roman, M.; Fenical, W. *J. Am. Chem. Soc.* **1989**, *111*, 7519. (c) Pathirana, C.; Tapiolas, D. M.; Jensen, P. R.; Dwight, R.; Fenical, W. *Tetrahedron Lett.* **1991**, *32*(21), 2323. (d) Tapiolas, D. M.; Roman, M.; Fenical, W.; Stout, T. J.; Clardy, J. *J. Am. Chem. Soc.* **1991**, *113*, 4682.

(3) (a) Berger, J. In *Encyclopedia of Chemical Technology*, Mark, H. E., Othmer, D. F., Overberger, C. G., Seaborg, G. T., Eds.; Wiley Interscience: New York, 1978; Vol. 3, pp 1–21. (b) Gerber, N. N. *J. Heterocycl. Chem.* **1969**, *6*, 297.

(4) Geiger, A.; Keller-Schierlein, W.; Brandl, M.; Zahner, H. *J. Antibiotics* **1988**, *41*, 1542.

0022-3263/92/1957-0740$03.00/0