ethanol (3 equiv) and aniline (2 equiv) in ether, a monoanilinium salt of 1-hydroxy-1-methyl-2-chloroethylphosphonic acid (**8a**) was obtained in 99% yield (**8a**, mp 156–157 °C). In a similar manner, **8b** and **8f** were obtained in 98 and 87% yields, respectively. Therefore, the reactions of **1** with alkyl-substituted α-halocarbonyl compounds provide the first method[7] for the synthesis of free 1-hydroxy-2-haloalkylphosphonic acids. However, from **2c**, **2d**, and **2g**, the desired products were obtained only as crude materials because of the difficult separation from simultaneously formed by-products. From **3k**, a newly classified half ester, a monoanilinium salt of ethoxycarbonylmethylphosphonic acid (**9**) was obtained in 94% yield (**9**, mp 136–137 °C). Furthermore, it was of particular interest that *a quite unstable enolphosphate* (**10**) *was for the first time isolated as the crystalline form* from **4h** in 81% yield by treatment of **4h** with aniline-containing ethanol at room temperature for 2.5 h. Finally, it was shown that the carbonyl adducts could be converted to bis(trimethylsilyl) esters of 1,2-epoxyalkylphosphonic acids by treatment with sodium methoxide in methanol followed by retrimethylsilylation with trimethylsilyl chloride in dry THF. Thus, for instance, bis(trimethylsilyl) 1-methyl-1,2-epoxyethylphosphonate (**11**) bp (68–77 °C (0.10–0.12 mmHg)) was obtained from **5a** in 58% yield. **11** was readily converted to the corresponding free salt (**12**) (mp 126–127 °C).

$$H_2C \overset{O}{\underset{CH_3}{\diagdown}} C \overset{O}{\underset{O^-}{\overset{\|}{-}}} P \overset{OH}{\underset{H_3\overset{+}{N}C_6H_5}{\diagup}}$$

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This facile conversion of 1-silyloxy-2-halo-alkylphosphonates to 1,2-epoxyalkylphosphonates reported here is noteworthy in the context of interest in the synthesis of such free epoxyalkylphosphonates[8] following discovery of a naturally occurring free epoxyalkylphosphonate, phosphonomycin,[9] which is a wide-spectrum antibiotic.

Extensions of this work are now in progress.

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(4) In our early work,[1e] the product from the reactions of **1** with **2a** was reported as the enolphosphate **4a** (the structure is now corrected as described in the text): NMR (CDCl₃) δ 0.22 (s, 9 H, CH₃SiOC), 0.33 (s, 18 H, CH₃SiOP), 1.37 (d, 3 H, J_{H-P} = 16 Hz, CH₃CP), 3.58 (d, J_{H-P} = 5 Hz, ClCH₂CP); IR (no absorption at 1600–1800 cm⁻¹).
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Tridachione, a Propionate-Derived Metabolite of the Opisthobranch Mollusc *Tridachiella diomedea*

Sir:

As part of a research program to study the relationship between the secondary metabolites of opisthobranch molluscs and dietary constituents,[1] we have investigated the secondary metabolites of *Tridachiella diomedea* (Bergh), commonly known as the Mexican Dancer.[2] *Tridachiella* was of particular interest because it is one of a group of sacoglossans which contain functional chloroplasts derived from siphonous marine algae.[3] In this communication we wish to report the structural elucidation of tridachione (**1**), the major secondary metabolite of *T. diomedea*.

The ether-soluble fraction of acetone extracts of homogenized *T. diomedea* was chromatographed on silica gel to obtain tridachione (**1**) as a colorless oil (~1 mg per animal). Trichachione (**1**), $C_{22}H_{30}O_4$, gave the following spectral data: IR 1660, 1590 cm⁻; UV 257 nm (ε 6000); ¹H NMR (CDCl₃) δ 0.68 (t, 3 H, *J* = 7 Hz), 1.32 (s, 3 H), 1.36 (s, 3 H), 1.60 (s, 3 H), 1.80 (s, 3 H), 2.01 (s, 3 H), 2.07 (s, 3 H), 2.91 (s, 1 H), 3.11 (s, 1 H), 3.93 (s, 3 H), 5.18 (t, 1 H, *J* = 7 Hz), 6.00 (s, 1 H); ¹³C NMR (CDCl₃) 181.1 (s), 161.0 (s), 160.1 (s), 132.5 (s), 131.6 (d), 129.0 (d), 128.5 (s), 118.4 (s), 97.8 (s), 60.5 (s), 57.6 (q), 55.3 (s), 54.7 (d), 46.7 (d), 31.2 (t), 21.8 (q), 21.5 (q), 20.2 (q), 12.9 (q), 12.0 (q), 11.6 (q), 6.1 (q) ppm. The presence of eight methyl groups in a molecule containing only 22 carbon atoms indicated that **1** had a novel carbon skeleton.

The paucity of coupling between signals in the ¹H NMR spectrum prevented structural elucidation by interpretation of spectral data. Fortunately, treatment of **1** with boron trifluoride etherate in dry ether at 0 °C gave a crystalline isomeric diketone **2**: mp 194–197 °C; IR 1650, 1590 cm⁻¹; UV 251, 240 nm; ¹H NMR (CDCl₃) δ 0.98 (t, 3 H, *J* = 7 Hz), 1.00 (d, 3 H, *J* = 7 Hz), 1.25 (s, 3 H), 1.57 (s, 3 H), 1.84 (s, 3 H), 1.88 (s, 3 H), 2.06 (m, 2 H), 2.07 (s, 3 H), 2.43 (d, 1 H, *J* = 12 Hz), 2.65 (m, 1 H), 3.82 (s, 3 H), 5.36 (t, 1 H, *J* = 7 Hz), 6.50 (s, 1 H).

The structure of the rearranged product **2** was clarified with a single crystal x-ray diffraction experiment. The diketone **2** crystallized in the orthorhombic crystal class with cell constants, determined by a least-squares fitting of 15 moderate angle reflections, of *a* = 7.821 (2), *b* = 12.880 (3), and *c* = 20.359 (5) Å. Systematic extinctions and the known chirality required space group $P2_12_12_1$ and an observed density of ~1.16 g/cm³ indicated one molecule of $C_{22}H_{30}O_4$ per asymmetric unit. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a computer-controlled four-circle diffractometer using graphite monochromated Cu Kα (1.54178 Å) x-rays. Of the 1637 maxima surveyed, 1342 (82%) were considered

Figure 1. A computer-generated perspective drawing of the diketone **2**. Hydrogens are omitted for clarity, and no absolute stereochemistry is implied.

observed ($F_o{}^2 \le 3\sigma(F_o{}^2)$) after correction for Lorentz, polarization, and background effects.

The angular dependence of the scattering was eliminated as the diffraction data were converted to normalized structure factors.[4] Phases were assigned to the 200 largest E values by a multiple solution, weighted tangent formula approach.[5] The weighted E synthesis from the "best" set of phases showed most of the nonhydrogen atoms. The complete nonhydrogen atom structure was revealed by recycling[6] this plausible fragment through tangent formula refinement with all E values ≥ 1.00. Hydrogen atoms were located in difference density syntheses.[7] Full-matrix least-squares refinement with anisotropic temperature factors for nonhydrogen atoms and isotropic temperature factors for hydrogens have converged to a conventional crystallographic residual of 0.049 for the observed data. Further crystallographic details can be found in the supplemental material.

A perspective drawing of the final x-ray model less hydrogens is given in Figure 1. The diketone **2** has an essentially perpendicular arrangement of a γ-pyrone ring and a cyclohexenone ring. The γ-pyrone ring is planar, with the OCH$_3$ group rotated to move C(23) H$_3$ 0.125 Å out of the ring plane, away from C(21) H$_3$. As expected, the cyclohexenone ring is quite flat, with C(7), C(8), C(9), and C(10) forming a plane. The dihedral angle about the C(8)–C(9) bond is ~5°. Atom C(6) lies 0.28 Å away from this plane, and C(11) is 0.78 Å away on the same side, so that the entire ring might be described as a very flat boat. The methyl substituents at C(10) and C(6) are cis to each other, as are the substituted γ-pyrone at C(6) and the 1-methylbutenyl fragment at C(11). With the exception of bond lengthening around C(6), presumably due to steric crowding, and bond shortening in the ethyl fragment, due to large thermal motions, all bond distances and angles agree well with generally accepted values.

The boron trifluoride catalyzed rearrangement of cyclic epoxides to ketones has been shown to be a highly stereospecific reaction.[8] We propose that tridachione (**1**) must have the stereochemistry shown, such that the rearrangement occurred with a suprafacial migration of a proton from C(9) to C(10), causing inversion at C(10). The presence of the epoxide functionality, which gave rise to ^{13}C signals at 60.5 and 54.7 ppm, has been confirmed by a series of reactions which will be reported in detail elsewhere.

Although the α-methoxy-γ-pyrone ring occurs in spectabilin,[9] a fungal metabolite, the carbon skeleton of **1** has not previously been reported. The carbon skeleton appears to be

derived from a polyketide condensation of seven "propionate" units.

At present, we do not know the original source of **1**. Most opisthobranchs are known to obtain secondary metabolites from dietary sources.[1] However, the presence of functional chloroplasts in *T. diomedea* could provide an alternative source of secondary metabolites. **1** might be synthesized by the chloroplasts alone or by a symbiotic pathway in which the mollusc modifies metabolites produced by the chloroplasts. Unlike those of *Aplysia californica*[10] and some other opisthobranchs, the metabolites of *Tridachiella diomedea* were always the same, no matter where the animals were collected in the Gulf of California.

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**Metal–Metal Interactions in Binuclear
Rhodium(I) Complexes Derived from the
7,16-Dihydro-6,8,15,17-tetramethyldibenzo[b,i]-
[1,4,8,11]tetraazacyclotetradecinato
Macrocyclic Ligand**

Sir:

Considerable interest exists in polynuclear metal complexes, especially from their potential role in homogenous catalysis,[1-4] as well as investigating the fundamental nature associated with uncommon metal–metal interactions.[5-8] In this context, it is