pair on bismuth in a cluster of only 1– charge. In support of this is the observation that when **2** is oxidized with Cu^+, $Bi_2Fe_3(CO)_9$ is produced along with $Fe(CO)_5$ and $Fe_3(CO)_{12}$.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, F_{obsd} and F_{calcd}, and bond angles and distances for $[Et_4N][Bi_2Fe_2Co(CO)_{10}]$ and $Me_4N]_3[Bi_2Fe_4(CO)_{13}]Cl$ (56 pages). Ordering information is given on any current masthead page.

Calyculin A, a Novel Antitumor Metabolite from the Marine Sponge *Discodermia calyx*[1]

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Marine sponges have proved to be a rich source of metabolites possessing novel structural features as well as interesting biological activities,[2,3] as, e.g., okadaic acid[4] and related compounds,[5,6] tedanolide[7] and the latrunculins.[8] In the course of our search for bioactive metabolites from Japanese marine invertebrates, we encountered a sponge *Discodermia calyx*[9] whose lipophilic extract showed strong activity in the starfish egg assay[10] and in the cytotoxicity test, which led us to isolate the active constituents. The major active constituent, calyculin A, is a novel spiro ketal of an unprecedented skeleton bearing phosphate, oxazole, nitrile, and amide functionalities.

The sponge (1 kg wet weight) was collected in the Gulf of Sagami by SCUBA (–5 to –15 m) and extracted with ethanol; this extract was partitioned between water and dichloromethane. The organic layer was subjected to low-pressure column chromatography on silica gel (CH_2Cl_2/MeOH), followed by reversed-phase HPLC (ODS, 80% MeOH) to give calyculin A (**1**) (150 mg, 0.15% wet weight), colorless needles, $[\alpha]_D^{15}$ +59.8° (*c* 0.12, EtOH). Calyculin A was not only inhibitory against development of starfish (*Asterina pectinifera*) embryos at 0.01 μg/mL but also strongly cytotoxic against L1210 cells (IC_{50} 1.75 × 10^{-3} μg/mL). The UV maxima at 342 (ϵ 12 000) and 230 (19 000) nm and IR bands at 3500, 3300, 3150, 2250, 1640, 1260, 1100, and 1060 cm^{-1} indicated the presence of two conjugated systems and hydroxyl, amide, nitrile, and phosphate functions. ^{13}C NMR spectra[11] revealed 50 carbon signals, which are assignable to one amide, one nitrile, one ketal, one oxazole, nine oxymethines, two methoxys, two *N*-methyls, ten olefins, five methines, six methylenes, nine methyls, and one sp^3 quaternary carbon. ^{31}P NMR[12,13] (–1.3 ppm, J_{POCH} 10.5 Hz) implied that **1** contained a phosphate ester linked to a methine carbon. These data and FABMS [m/z 1009 (MH^+)] together with combustion analysis [N 5.46% (calcd 5.55%)] led to the molecular formula of $C_{50}H_{81}N_4O_{15}P$. Detailed 500-MHz NMR analyses[14] including COSY[15] and C–H shift correlation experiments[16] (^1J and long range) allowed us to construct a gross structure, in which two major portions were combined via two contiguous quaternary carbons. However, the position of two ether linkages remained ambiguous.

The structure including relative stereochemistry was deduced by single-crystal X-ray diffraction. Repeated crystallization from a mixture of *n*-hexane, diethyl ether, and acetone afforded colorless needles (mp 247–249 °C) belonging to the orthorhombic space group $P2_1P2_1P2_1$ with a = 18.173 (3) Å, b = 20.138 (4) Å, c = 15.574 (3) Å and Z = 4. Intensities were measured in the $\omega/2\theta$ scan mode on a Rigaku AFC-5R diffractometer, using graphite-monochromated Cu Kα radiation (λ = 1.541 84 Å). Correction was made for Lorentz and polarization factors but not for absorption. Of 5001 independent reflections with $2\theta < 120°$, 3094 reflections with $F_0 < 2\sigma$ were considered to be zero reflections.

The structure was determined by direct methods coupled with the MULTAN 78[17] program and successive Fourier syntheses. Its parameters were refined by the blocked-diagonal least-squares method with isotropic temperature parameters to the current residual of 0.12 (R_w = 0.083) for 1626 reflections. The atomic identifications were carefully made on the basis of both their peak heights and isotropic thermal parameters. The structure thus

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[11] 125-MHz ^{13}C NMR ($CDCl_3$) δ 176.2 (C-33), 169.8 (C-29), 156.3 (C-3), 144.5 (C-8), 137.3 (C-27), 134.7 (C-7), 133.8 (C-5, 28), 132.6 (C-25), 132.4 (C-9), 128.2 (C-4), 123.7 (C-6), 117.3 (C-1), 116.1 (C-26), 108.7 (C-19), 94.6 (C-2), 84.8 (C-16), 81.9 (C-17), 80.7 (C-11), 77.3 (C-15), 74.9 (C-13), 73.4 (C-34), 71.4 (C-21), 68.9 (C-35), 67.1 (C-23), 65.6 (C-37), 63.7 (C-36), 60.9 (C-45), 58.9 (C-38), 50.1 (C-18), 44.3, 37.4 (C-39,40), 42.1 (C-12), 38.3 (C-14), 37.7 (C-22), 35.9 (C-24), 35.8 (C-10), 34.4 (C-32), 33.6 (C-31), 29.6 (C-20), 28.4 (C-30), 22.4, 17.5 (C-43, 44), 19.2 (C-50), 17.9 (C-47), 17.5 (C-41), 13.9 (C-49), 13.7 (C-48), 12.7 (C-46), 10.8 (C-42).

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[14] 500-MHz ^1H NMR ($CDCl_3$) δ 13.80 (br s, OH), 12.11 (br s, OH), 8.18 (br d, amide NH), 7.69 (br s, OH), 7.31 (1 H, s, H-28), 6.98 (1 H, dd, 15.0, 12.0 Hz; H-5), 6.93 (1 H, m, H-25), 6.82 (1 H, d, 15.0; H-4), 6.51 (1 H, br s, OH), 6.34 (1 H, d, 12.0; H-6), 6.21 (1 H, d, 9.0; H-9), 6.12 (1 H, d, 9.0, OH), 6.11 (1 H, dd, 16.5, 2.0; H-26), 5.94 (1 H, br s, OH), 5.29 (1 H, s, OH), 5.05 (1 H, br s; H-2), 4.48 (1 H, d, 10.5; H-34), 4.32 (1 H, m, H-23), 4.07 (1 H, m, H-17), 4.04 (2 H, m, H-32, H-36), 4.00 (1 H, dd, 10.0, 3.0; H-16), 3.95 (1 H, dd, 13.0, 10.5; H-37), 3.85 (1 H, m; H-21), 3.75 (1 H, br t, 10.0; H-15), 3.69 (1 H, dd, 13.0, 3.0; H-37), 3.59 (1 H, br m; H-35, 3.57 (1 H, dd, 10.5, 3.0; H-11), 3.50 (3 H, s; H-45), 3.44 (1 H, m; H-13), 3.40 (3 H, s; H-38), 3.21 (1 H, m; H-30), 3.02 (1 H, m; H-32′), 2.87, 2.79 (3 H, s each; H-39, H-40), 2.75 (1 H, m; H-10), 2.47 (1 H, br t, 13.0; H-24), 2.03 (6 H, s; H-49, H-50), 1.95 (1 H, m; H-24′), 1.92 (1 H, m; H-31), 1.86 (3 H, s; H-48), 1.80 (2 H, m; H-14, H-20), 1.76 (1 H, m; H-31′), 1.70 (1 H, m; H-22), 1.59 (1 H, dd, 10.5, 3.0; H-20′), 1.56 (1 H, m, H-14′), 1.45 (1 H, m; H-12), 1.31 (3 H, d, 5.5; H-41), 1.24, 0.91 (3 H, s each; H-43, H-44), 1.06 (3 H, d, 5.5; H-47), 0.87 (3 H, d, 5.5; H-42), 0.60 (3 H, d, 5.5; H-46).

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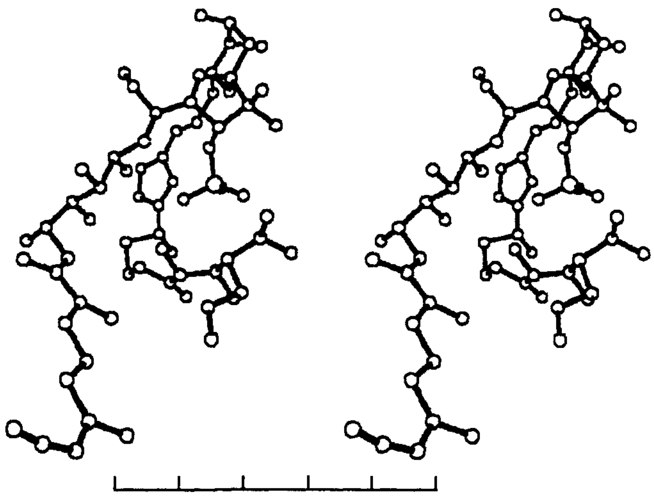
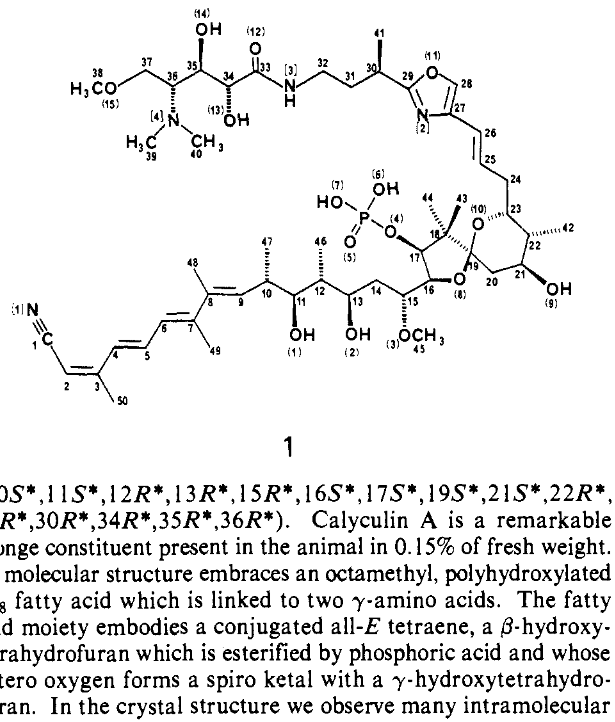


Figure 1. Computer-generated perspective drawing of calyculin A. No absolute configuration is implied.



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obtained was compatible with that derived by the NMR and other spectral studies. The relative configuration and numbering scheme are shown in formula 1 and Figure 1 (10*S**,11*S**,12*R**,13*R**,15*R**,16*S**,17*S**,19*S**,21*S**,22*R**,23*R**,30*R**,34*R**,35*R**,36*R**). Calyculin A is a remarkable sponge constituent present in the animal in 0.15% of fresh weight. Its molecular structure embraces an octamethyl, polyhydroxylated C_{28} fatty acid which is linked to two γ-amino acids. The fatty acid moiety embodies a conjugated all-*E* tetraene, a β-hydroxytetrahydrofuran which is esterified by phosphoric acid and whose hetero oxygen forms a spiro ketal with a γ-hydroxytetrahydropyran. In the crystal structure we observe many intramolecular short contacts, one of which between O(1) and N(3) measures 2.99 (2) Å and forms a pseudoring. Others are with oxygen atoms of the phosphate group: O(5) and O(2) of 2.69 (2) Å, O(7) and N(4) of 2.57 (3) Å, and O(6) and N(2) of 2.81(2) Å. They contribute to a much folded molecular conformation, which may account for the resistance of the phosphate ester to either acid or enzymatic hydrolysis.

Calyculin A is an extraordinary sponge metabolite with a rich array of functional groups. The biological role and the biosynthesis of this new natural product raise interesting questions.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra and tables of additional X-ray crystallographic data (9 pages). Ordering information is given on any current masthead page.

Metal-Metal Excited-State Emission from Binuclear Platinum(III) Complexes

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Electronic emission from d^7–d^7 complexes containing metal–metal single bonds is rare; to our knowledge, the only previously reported emissions are from species with low-lying metal-to-ligand charge-transfer excited states.[1] For most d^7–d^7 compounds, the lowest electronic states involve population of the dσ* (M_2) level and are extremely short-lived,[2] precluding perceptible electronic emission.

We now report that the d^7–d^7 complexes $Pt_2(pop)_4X_2^{4-}$ (pop = $(HO_2P)_2O$; X = Cl, Br, SCN) and $Pt_2(pop)_4(py)_2^{2-}$ exhibit strong red luminescence at 77 K (Figure 1; Table I).[3] The emissions are long-lived (probably triplet → singlet) and both cation- and solvent-sensitive. Importantly, the excitation spectra for the emissions in an EtOH/MeOH glass are identical with the absorption spectra of the various complexes in the glass (Figure 2); thus we can rigorously exclude impurities (e.g., PtX_6^{2-} and PtX_4^{2-} complexes) as the source of the emission.[4]

Several of these compounds have also been examined at liquid helium temperature. One of them, $K_4[Pt_2(pop)_4Br_2]\cdot 2H_2O$, exhibits vibronic structure in its emission at this temperature (Figure 3). A long (>20 members) progression with an average vibrational interval of 125 cm^{-1} is observed. The electronic origin is not established by our data. The shortest wavelength feature we observe is at ~654 nm, but intensities are decreasing so rapidly along the progression that the true origin could well be at a still shorter wavelength.

Comparison to published[5] vibrational data for the $Pt_2(pop)_4Br_2^{4-}$ ion in room temperature aqueous solution indicates that the 125-cm^{-1} interval is energetically much too small to be a Pt–P or Pt–Br stretching frequency. The agreement with the assigned $\nu(Pt_2)$ of 134 cm^{-1} is acceptably close, considering the different conditions of the two experiments. Thus, the emissive excited state is indicated to be very strongly (because of the length of the progression) distorted along the Pt–Pt coordinate. The cation and solvent sensitivity of the emission is consistent with this type of distortion. Taken together, our data show that the emissive excited state has dσ* character, and reasonable possibilities are the triplet states derived from dσ → dσ* or dπ → dσ* excitations.[6]

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(6) The intense bands near 285 and 350 nm in the absorption spectrum of $Pt_2(pop)_4Cl_2^{4-}$ (Figure 2) have been assigned to dσ → dσ* and dπ → dσ* singlet–singlet transitions[3a].

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