Isolation and Structure of Providencin: A Highly Oxygenated Diterpene Possessing a Unique Bicyclo[12.2.0]hexadecane Ring System from the Sea Plume *Pseudopterogorgia kallos*

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List of Supporting Information:

- (1) Detailed description of experimental procedures.
- (2) Tables of crystal data for providencin (1) (crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters and hydrogen coordinates).

Experimental Section

General Experimental Procedures: 1D- and 2D-NMR spectral data were recorded with a Bruker DPX-300 FT-NMR spectrometer. Infrared and UV spectra were obtained in a Nicolet Magna FT-IR 750 and a Varian CARY 1E UV-Vis spectrometers, respectively. The optical rotation was obtained with an Autopol IV polarimeter. Column chromatography was performed on silica gel (35-75 mesh) and TLC analyses were carried out using glass precoated silica gel plates. All solvents used were either spectral grade or were distilled from glass prior to use. The percentage yield of providencin (1) is based on the weight of the crude $\text{CH}_2\text{Cl}_2/\text{MeOH}$ extract.

Collection of *Pseudopterogorgia kallos*: *P. kallos* was collected by SCUBA at depths of 83-91 ft in Old Providence Island, Colombia on March 15, 2002. A voucher specimen is stored in the Chemistry Department of the University of Puerto Rico.

Extraction and Isolation Procedure: The organism was partially sun-dried, frozen, and lyophilized prior to its extraction. The dry organism (1.07 kg) was blended using a mixture of 1:1 $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (20 x 1L). After filtration the crude extract was evaporated and stored under vacuum to yield a green gum (166 g). The crude extract was partitioned between hexane and H_2O and then the aqueous suspension was extracted with CHCl_3 (3 x 2L). The resulting extract was concentrated in vacuo to yield 39.3 g of a brown amorphous solid which was chromatographed over Si gel (673 g) and separated into 32 fractions (A-FF) on the basis of TLC analyses. Purification of fraction P (612 mg) by size exclusion chromatography on a Bio-Beads SX-3 column with toluene led to three subfractions. The second fraction (393.6 mg) was purified by column chromatography over Si gel (13 g) with 15% acetone in hexane to afford providencin (1) (20 mg, yield = 0.012 %). Providencin A was recrystallized in a mixture of 9:1 $\text{MeOH}/\text{CHCl}_3$ giving excellent quality crystals.

Providencin (1): colorless crystalline solid; $[\alpha]_D^{20} +7.9$ (c 1.2, CHCl_3); IR (neat) 3461, 3020, 2953, 2938, 2856, 2253, 1783, 1743, 1718, 1648, 1620 1220, 1577, 1442, 1376, 1235 cm^{-1} ; UV (MeOH) λ_{max} 203 (ϵ 11500), 251 (ϵ 4900); ^1H NMR (CDCl_3 , 300 MHz) and ^{13}C NMR (CDCl_3 , 75 MHz) (see Table 1); HREIMS m/z $[\text{M}]^+$ 460.1366 (calcd for $\text{C}_{23}\text{H}_{24}\text{O}_{10}$ 460.1370).

X-ray Single-Crystal Structure Determination of Providencin (1) at 298(2) K: $C_{23}H_{24}O_{10}$, $M_r = 460.42$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 9.061(2)$ Å, $b = 9.628(2)$ Å, $c = 24.800(4)$ Å, $V = 2163.5(5)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.414$ Mg m⁻³, $F_{000} = 968$, $\lambda(\text{MoK}\alpha) = 0.71073$ Å, $\mu = 0.112$ mm⁻¹. **Data collection and reduction:** crystal size, 0.13 x 0.09 x 0.08 mm, θ range 1.64–28.06°, 15255 reflections collected, 5236 independent reflections ($R_{\text{in}} = 0.0591$), final R indices ($I > 2\sigma(I)$): $R_1 = 0.0436$, $wR_2 = 0.0829$ for 302 variable parameters, GOF = 0.914.

Table: Crystal data and structure refinement for **1**

Providencin	
Empirical formula	$C_{23}H_{24}O_{10}$
Formula weight	460.42
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (No.19)
Unit cell dimensions	
a (Å)	9.061(2)
b (Å)	9.628(2)
c (Å)	24.800(4)
α (deg)	90
β (deg)	90
γ (deg)	90
Volume (Å ³)	2163.5(5)
Z	4
Density (calc.) (Mg m ⁻³)	1.414
Absorption coefficient (mm ⁻¹)	0.112
F(000)	968
Crystal size (mm)	0.13 x 0.09 x 0.08
θ range for data collection (deg)	1.64 to 28.06
Index ranges	$-11 \leq h \leq 8, -11 \leq k \leq 12, -32 \leq l \leq 32$
Reflections collected	15255
Independent reflections	5236 [$R(\text{int}) = 0.0591$]
Independent reflections [$I > 2\sigma(I)$]	2543 [$R(\text{int}) = 0.0849$]
Max. and min. transmission	
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5236 / 0 / 302
Goodness-of-fit on F^2	0.914
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0436, wR2 = 0.0829$
R indices (all data)	$R1 = 0.1244, wR2 = 0.1046$

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&!Table 1. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for ar030. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

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	x	y	z	U(eq)
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O(1)	10221(3)	7407(2)	10109(1)	63(1)
O(2)	7712(2)	6986(2)	8896(1)	42(1)
O(3)	10604(3)	10789(3)	8587(1)	107(1)
O(4)	11666(2)	9153(2)	9080(1)	63(1)
O(5)	4651(2)	8223(2)	8080(1)	65(1)
O(6)	4255(2)	4799(2)	9005(1)	60(1)
O(7)	5741(2)	2506(2)	8638(1)	57(1)
O(8)	5998(2)	4732(2)	9635(1)	54(1)
O(9)	8427(2)	2944(2)	8224(1)	42(1)
O(10)	10511(2)	4086(2)	8014(1)	61(1)
C(1)	9430(3)	5019(3)	9462(1)	38(1)
C(2)	10129(3)	6335(3)	9199(1)	39(1)
C(3)	9127(3)	7444(3)	8990(1)	41(1)
C(4)	9242(4)	8769(3)	8815(1)	48(1)
C(5)	7815(3)	9163(3)	8601(1)	53(1)
C(6)	6937(3)	8064(3)	8652(1)	50(1)
C(7)	5420(3)	7641(3)	8537(1)	53(1)
C(8)	5054(3)	6765(3)	8071(1)	52(1)
C(9)	3769(3)	5762(4)	8113(1)	63(1)
C(10)	4052(3)	4445(4)	8435(1)	60(1)
C(11)	5423(3)	3674(3)	8290(1)	49(1)
C(12)	6480(3)	3821(3)	8729(1)	41(1)
C(13)	8137(3)	3924(3)	8650(1)	40(1)
C(14)	9132(3)	3698(3)	9140(1)	43(1)
C(15)	10713(3)	5047(3)	9851(1)	44(1)
C(16)	11467(4)	4094(4)	10102(1)	69(1)
C(17)	11001(3)	6565(3)	9738(1)	48(1)
C(18)	10534(4)	9684(3)	8811(1)	59(1)
C(19)	6230(3)	6449(3)	7649(1)	60(1)
C(20)	5644(3)	4504(3)	9180(1)	45(1)
C(21)	12953(4)	10054(4)	9115(1)	76(1)
C(22)	9644(3)	3170(3)	7921(1)	45(1)
C(23)	9711(4)	2170(4)	7468(1)	73(1)

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&!Table 2. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for ar030.

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O(1)-C(17)	1.416(3)
O(2)-C(3)	1.376(3)
O(2)-C(6)	1.391(3)
O(3)-C(18)	1.203(4)
O(4)-C(18)	1.326(3)
O(4)-C(21)	1.457(4)
O(5)-C(7)	1.443(3)
O(5)-C(8)	1.451(4)
O(6)-C(20)	1.361(3)
O(6)-C(10)	1.466(3)
O(7)-C(11)	1.446(3)
O(7)-C(12)	1.450(3)
O(8)-C(20)	1.194(3)
O(9)-C(22)	1.351(3)
O(9)-C(13)	1.442(3)
O(10)-C(22)	1.203(3)
C(1)-C(15)	1.511(4)
C(1)-C(14)	1.525(3)
C(1)-C(2)	1.560(4)
C(2)-C(3)	1.494(4)
C(2)-C(17)	1.568(4)
C(3)-C(4)	1.352(4)
C(4)-C(5)	1.447(4)
C(4)-C(18)	1.466(4)
C(5)-C(6)	1.331(4)
C(6)-C(7)	1.461(4)
C(7)-C(8)	1.469(4)
C(8)-C(9)	1.516(4)
C(8)-C(19)	1.524(4)
C(9)-C(10)	1.521(4)
C(10)-C(11)	1.491(4)
C(11)-C(12)	1.456(4)
C(12)-C(20)	1.503(4)
C(12)-C(13)	1.517(4)
C(13)-C(14)	1.529(3)
C(15)-C(16)	1.303(4)
C(15)-C(17)	1.510(4)
C(22)-C(23)	1.481(4)

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C(3)-O(2)-C(6)	107.8(2)
C(18)-O(4)-C(21)	114.8(3)
C(7)-O(5)-C(8)	60.99(18)
C(20)-O(6)-C(10)	112.1(2)
C(11)-O(7)-C(12)	60.37(17)
C(22)-O(9)-C(13)	116.8(2)
C(15)-C(1)-C(14)	119.0(2)
C(15)-C(1)-C(2)	86.5(2)
C(14)-C(1)-C(2)	122.1(2)
C(3)-C(2)-C(1)	118.6(2)
C(3)-C(2)-C(17)	120.1(2)
C(1)-C(2)-C(17)	87.88(18)
C(4)-C(3)-O(2)	108.6(2)
C(4)-C(3)-C(2)	137.6(3)
O(2)-C(3)-C(2)	113.3(2)

C(3)-C(4)-C(5)	107.3(3)
C(3)-C(4)-C(18)	129.1(3)
C(5)-C(4)-C(18)	123.6(3)
C(6)-C(5)-C(4)	106.9(3)
C(5)-C(6)-O(2)	109.5(3)
C(5)-C(6)-C(7)	139.9(3)
O(2)-C(6)-C(7)	110.6(3)
O(5)-C(7)-C(6)	120.0(3)
O(5)-C(7)-C(8)	59.76(17)
C(6)-C(7)-C(8)	121.8(2)
O(5)-C(8)-C(7)	59.25(18)
O(5)-C(8)-C(9)	114.9(2)
C(7)-C(8)-C(9)	119.0(3)
O(5)-C(8)-C(19)	112.3(3)
C(7)-C(8)-C(19)	119.8(3)
C(9)-C(8)-C(19)	117.2(3)
C(8)-C(9)-C(10)	115.9(2)
O(6)-C(10)-C(11)	104.1(2)
O(6)-C(10)-C(9)	109.5(3)
C(11)-C(10)-C(9)	115.4(3)
O(7)-C(11)-C(12)	59.96(17)
O(7)-C(11)-C(10)	114.2(3)
C(12)-C(11)-C(10)	108.7(2)
O(7)-C(12)-C(11)	59.67(17)
O(7)-C(12)-C(20)	105.3(2)
C(11)-C(12)-C(20)	105.5(2)
O(7)-C(12)-C(13)	119.6(2)
C(11)-C(12)-C(13)	124.1(2)
C(20)-C(12)-C(13)	124.5(2)
O(9)-C(13)-C(12)	103.4(2)
O(9)-C(13)-C(14)	112.5(2)
C(12)-C(13)-C(14)	118.1(2)
C(1)-C(14)-C(13)	113.7(2)
C(16)-C(15)-C(1)	134.1(3)
C(16)-C(15)-C(17)	132.9(3)
C(1)-C(15)-C(17)	91.8(2)
O(1)-C(17)-C(15)	110.3(2)
O(1)-C(17)-C(2)	112.5(2)
C(15)-C(17)-C(2)	86.3(2)
O(3)-C(18)-O(4)	122.3(3)
O(3)-C(18)-C(4)	125.2(3)
O(4)-C(18)-C(4)	112.5(3)
O(8)-C(20)-O(6)	120.8(3)
O(8)-C(20)-C(12)	130.5(3)
O(6)-C(20)-C(12)	108.7(2)
O(10)-C(22)-O(9)	123.0(3)
O(10)-C(22)-C(23)	126.5(3)
O(9)-C(22)-C(23)	110.5(3)

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&H Symmetry transformations used to generate equivalent atoms:&N

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&!Table 3. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for ar030. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [(h a^* \sin^2 \theta)^2 U_{11} + \dots + 2 h k a^* b^* U_{12}]$

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	U11	U22	U33	U23	U13	U12
O(1)	92(2)	50(1)	46(1)	-8(1)	-7(1)	-4(1)
O(2)	45(1)	41(1)	40(1)	4(1)	-6(1)	6(1)
O(3)	99(2)	58(2)	163(3)	50(2)	-20(2)	-5(2)
O(4)	68(2)	54(1)	66(1)	9(1)	-9(1)	-9(1)
O(5)	63(1)	79(2)	52(1)	4(1)	-11(1)	30(1)
O(6)	42(1)	83(2)	57(1)	-2(1)	6(1)	9(1)
O(7)	49(1)	54(1)	68(1)	-11(1)	0(1)	-10(1)
O(8)	59(1)	61(1)	42(1)	-6(1)	4(1)	3(1)
O(9)	39(1)	44(1)	43(1)	-11(1)	2(1)	-2(1)
O(10)	52(1)	64(2)	69(1)	-1(1)	2(1)	-19(1)
C(1)	38(2)	40(2)	36(1)	-2(1)	-5(1)	1(1)
C(2)	42(2)	41(2)	35(1)	1(1)	-6(1)	2(1)
C(3)	46(2)	42(2)	34(1)	-1(1)	-3(1)	5(2)
C(4)	64(2)	39(2)	39(2)	1(1)	-1(2)	5(2)
C(5)	64(2)	47(2)	47(2)	5(2)	0(2)	16(2)
C(6)	55(2)	54(2)	42(2)	0(2)	-3(2)	17(2)
C(7)	50(2)	65(2)	43(2)	10(2)	-7(1)	15(2)
C(8)	44(2)	68(2)	44(2)	-3(2)	-5(1)	17(2)
C(9)	40(2)	87(3)	60(2)	-9(2)	-5(2)	8(2)
C(10)	41(2)	85(3)	54(2)	-7(2)	-4(2)	-5(2)
C(11)	39(2)	56(2)	52(2)	-8(2)	-4(2)	-5(1)
C(12)	39(2)	44(2)	41(2)	-7(1)	-2(1)	2(1)
C(13)	40(2)	39(2)	40(2)	-9(1)	-3(1)	-1(1)
C(14)	49(2)	36(2)	43(2)	0(1)	-11(1)	2(1)
C(15)	52(2)	42(2)	38(1)	3(1)	-8(1)	1(2)
C(16)	81(2)	57(2)	69(2)	6(2)	-33(2)	2(2)
C(17)	44(2)	48(2)	53(2)	-1(2)	-13(2)	-6(1)
C(18)	73(2)	44(2)	61(2)	9(2)	-10(2)	5(2)
C(19)	54(2)	78(3)	48(2)	-2(2)	1(2)	12(2)
C(20)	45(2)	44(2)	48(2)	3(1)	5(2)	2(2)
C(21)	69(2)	81(3)	79(2)	-9(2)	1(2)	-16(2)
C(22)	35(2)	52(2)	47(2)	3(1)	-2(1)	-1(2)
C(23)	66(2)	91(3)	61(2)	-27(2)	12(2)	1(2)

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&!Table 4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ar030.

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H(1)	10399	8227	10048	94
H(1A)	8529	5288	9654	46
H(2)	10816	6053	8914	47
H(5)	7562	10021	8455	63
H(7)	4805	7484	8856	63
H(9A)	3475	5499	7751	75
H(9B)	2943	6248	8275	75
H(10)	3201	3823	8399	72
H(11)	5769	3668	7916	59
H(13)	8349	4853	8508	47
H(14A)	8673	3020	9376	51
H(14B)	10065	3316	9020	51
H(16A)	11234	3161	10054	83
H(16B)	12237	4345	10330	83
H(17)	12043	6809	9692	58
H(19A)	6813	7266	7585	90
H(19B)	5762	6169	7319	90
H(19C)	6854	5714	7776	90
H(21A)	12683	10908	9289	114
H(21B)	13315	10247	8759	114
H(21C)	13710	9601	9321	114
H(23A)	10638	2266	7284	109
H(23B)	8919	2354	7221	109
H(23C)	9620	1241	7605	109

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&!Table 5. Torsion angles [$^{\circ}$] for ar030.&H

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