Geographic Variation in the Tropical Marine Sponge *Jaspis* cf. *johnstoni*: An Unexpected Source of New Terpene-Benzenoids

Leanne M. Murray, Amanda Johnson, Maria Cristina Diaz, and Phillip Crews*

Department of Chemistry and Biochemistry, University of California, Santa Cruz, California 95064

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Compounds of diverse structures have been isolated from the sponge genus *Jaspis* (Choristida, Jaspidae) which makes this an enticing organism for chemical study. The malabaricane triterpenes, first reported in 1981 by Wells, from *Jaspis stellifera*[1] have, over the years, been found from this sponge[2] as well as from *Stelleta globostellata*.[3] There has been much interest in the cyclic depsipeptide jasplakinolide (**1**) (jaspamide), first described in 1986 from *Jaspis johnstoni*.[4−6] In recent years it has been shown that **1** possesses unique conformational[7a] ionophoric[7b] and biological properties.[8−10] Furthermore, a variety of routes have been developed for the total synthesis of (+)-**1**.[11]

The results outlined in this note were unexpected and came about during our efforts to explore two very disparate circumstances pertaining to the relationship of **1** and its sponge source. Since 1986 we have made over 19 distinct collections of specimens appearing to be the same species of a *Jaspis* sponge, and all contain jasplakinolide in high yield. Due to taxonomic uncertainties, discussed further in the Experimental Section, these taxa can only be confidently identified as *Jaspis* cf. *johnstoni*. In view of our extensive results to date with this sponge it is tempting to consider **1** as a chemical marker for the species we have studied. Alternatively, there is reason to suspect that the biogenetic production of **1** might depend on involvement by microorganisms. Relevant to the latter idea is a recent eye-catching report of gliding bacteria constituents including (+)-chondramides[12] whose cyclic depsipeptide structures are quite parallel to that of (+)-**1** obtained from sponges.[4−6] Alternatively, our unsuccessful, yet limited attempts to find **1** as a metabolite of microorganisms associated with *J.* cf. *johnstoni* has not contributed to resolving this dilemma.[13] Turning to the other issue, the possibility that **1** can be employed as a chemical marker of the species *J.* cf. *johnstoni* has been undermined because this compound has been found from other sponge genera including *Auletta* cf. *constricta*,[14a] *Hemiasterella minor*,[14b] and *Cymbastela* sp.[14c,d]

Our collections of *Jaspis* cf. *johnstoni* come from numerous locations throughout the Indo-Pacific including Indonesia, Vanuatu, Fiji, Papua New Guinea, and Malaysia. These specimens have always yielded jasplakinolide (**1**) as the major component with the only exception being two collections (92215 from Fiji and 93115 from Papua New Guinea) which contained **1** accompanied by very small quantities of jasplakinolide B.[10] We now report on an additional exception in which a recent collection of *Jaspis* cf. *johnstoni* from Madang, Papua New Guinea yielded jasplakinolide (**1**) plus two new mixed biogenesis diterpene-benzenoid compounds, (−)-jaspic acid (**2**) and jaspaquinol (**3**), all as major components.

The new collection of *Jaspis* cf. *johnstoni* (coll. no. 96117) was preserved using our standard procedure as described in the Experimental Section. The crude oil obtained from MeOH extraction was successively partitioned between equal volumes of aqueous MeOH, percent adjusted to produce a biphasic solution, and hexanes followed by CH_2Cl_2. Next, Sephadex LH-20 gel filtration chromatography of the CH_2Cl_2 fraction (30:70 CH_2Cl_2/MeOH) gave six fractions. The third fraction contained jasplakinolide (**1**), whereas the fourth fraction exhibited unusual ^{1}H and ^{13}C NMR resonances so it was subjected to reversed-phase HPLC to afford (−)-jaspic acid (**2**) and jaspaquinol (**3**).

The structure elucidation of (−)-jaspic acid (**2**) began once its molecular formula, $C_{27}H_{38}O_3$, was established based on the HRFABMS m/z = 409.2743 [M − H]$^+$ (Δ 0.0 mmu of calcd). The ^{13}C and DEPT-135 NMR data gave a partial formula of $C_{27}H_{36}$, and oxygen functionalities could be identified as an OH attached to the carbon at δ 158.2 and a carboxylic acid group (δ 171.7). These moieties were proposed to be attached to the trisubstituted aromatic ring (δ 8.03, s, H17; 7.83, br d, H19; 6.78, br d, H20) which together accounted for five of the nine degrees of unsaturation. There were two additional trisubstituted double bonds (δ 5.40, br s, H7; 5.13 br t, H24) which meant that **2** also contained two additional rings. It is interesting to note that the ^{1}H NMR spectrum obtained in $CDCl_3$ is inexplicably broad compared to the same resonances when the spectrum is obtained in CD_3OD (δ 7.87, d, H17; 7.67, dd, H19; 6.76, d, H20).

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Chart 1

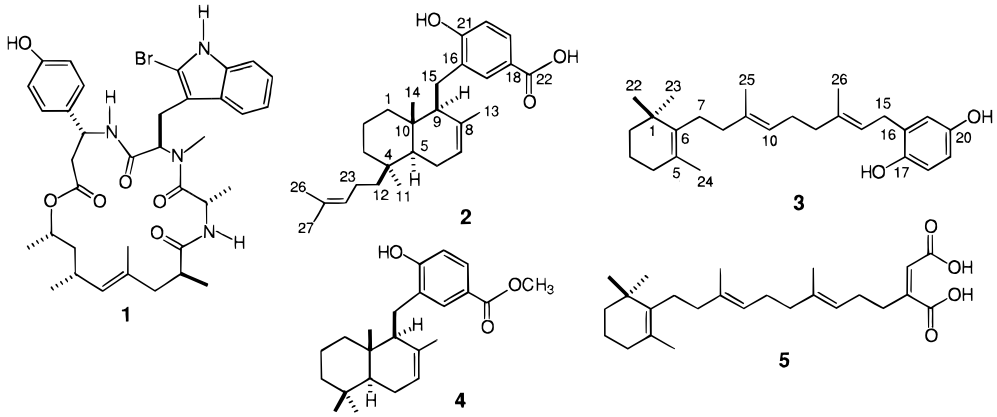

Table 1. NMR Data for Jaspic Acid (2), ($CDCl_3$ ^1H, 500/^{13}C, 62.9 MHz) and Dactylosponol (4)[15]

	2					4
atom no.	^{13}C δ (m)	^1H δ (mult, J Hz)	$^1H-^1H$ COSY	HMBC (C to H)	NOESY	carbon δ (mult)
1	39.7 (t)	1.92 (br m), Hβ	1′, 2	3, 3′, 14	15	39.4
		1.24 (m), Hα	1, 2			
2	18.7 (t)	1.49 (m)	1/1′, 3/3′			18.9
3	37.1 (t)	1.78 (br d, 14.0), Hα	2, 3′	1, 5, 11	11	42.2
		1.00 (m), Hβ	2, 3			
4	35.7 (s)			3, 5, 11		33.0
5	52.5 (d)	1.38 (t, 8.0)	6	1, 3, 7, 11, 14	9, 11	50.2
6	23.3 (t)	2.00 (br s)	5, 7	5	11	23.8
7	122.8 (d)	5.40 (br s)	6	6, 13	13	122.8
8	135.0 (s)			6, 13, 15		135.1
9	54.3 (d)	2.49 (br s)	15	5, 7, 13, 14, 15	5, 17	53.7
10	37.1 (s)			1, 5		37.0
11	28.9 (q)	0.90 (s)		3′, 5, 12	3α, 5, 6	33.2
12	32.7 (t)	1.65 (m)	12′, 23	3/3′, 5, 11	14	21.9
		1.24 (m)	12, 23			
13	22.4 (q)	1.44 (s)		7	7, 15	22.4
14	14.9 (q)	0.95 (s)		1′, 5	12, 15	13.9
15	26.0 (t)	2.67 (br m)	9	17	1β, 13, 14	26.0
16	130.1 (s)			15		129.9[a]
17	132.4 (d)	8.03 (br s)	19	19	9	131.8
18	121.7 (s)			20		*a*
19	129.4 (d)	7.83 (br d, 8.0)	17, 20	17		128.7
20	115.2 (d)	6.78 (br d, 8.0)	19			115.1
21	158.2 (s)			17, 19		157.4
22	171.7 (s)			17		169.5
23	23.0 (t)	1.86 (m)	12/12′, 24			
24	125.6 (d)	5.13 (br t, 7.0)	23	26, 27		
25	131.0 (s)			26, 27		
26	17.6 (q)	1.62 (s)		24, 27		
27	25.8 (q)	1.71 (s)		23, 26		

[a] Assignment corrected from original literature (ref 15).

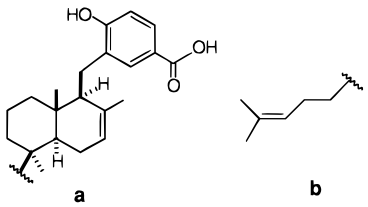

Figure 1. Substructures for (−)-jaspic acid (**2**).

Comparing the ^{13}C NMR data between **2** and dactylosponol (**4**)[15] (Table 1) indicated that both molecules contained the same tricyclic substructure **a**. Comparison to the molecular formula of **2** leaves an additional C_6H_{11} which can be represented by substructure **b** (Figure 1). This framework was substantiated by $^1H-^1H$ COSY plus HMBC[16] correlations from δ 32.7 (C12) to δ 1.78 (H3) and δ 1.38 (H5) allowing attachment of **b** to **a** at C4 to complete the structure.

The relative stereochemistry of (−)-jaspic acid (**2**) was set through the use of NOESY and ^{13}C NMR chemical shift data. NOESY correlations from H5 to H9 showed these atoms are on the same face of the molecule. Similarly, a correlation from $H_2$15 to $H_3$14 indicates that these two groups are *syn* and on the opposite face to H5/H9. The ^{13}C NMR chemical shift of C11 suggests this methyl is in the equatorial position while that of C14 indicates it to be axial. Further support for these assignments comes from NOESY correlation between $H_3$14 and $H_2$12. Since the relative stereochemistry for (−)-jaspic acid (**2**) is the same as that previously reported for (−)-dactylosponol (**4**), it is possible that their absolute stereochemistry is also identical. Interestingly, other sesquiterpenoid members of this series with (−)[α]$_D$

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Table 2. NMR Data for Jaspaquinol (3), ($CDCl_3$ ^1H, 500/^{13}C, 62.9 MHz) and Dehydroluffariellolide Diacid (5)[20]

	3				5
atom no.	^{13}C δ (m)	^1H δ (mult, J Hz)	$^1H-^1H$ COSY	HMBC (C to H)	carbon δ (mult)
1	35.0 (s)			2, 22	35.0
2	39.9 (t)	1.43 (m)	3	4	39.7
3	19.6 (t)	1.70 (m)	2, 4	2, 4	19.6
		1.60 (m)			
4	32.8 (t)	1.92 (t, 6.5)	3	2, 24	32.8
5	126.9 (s)			4, 7, 24	127.0
6	137.2 (s)			4, 7, 22, 24	138.4
7	27.9 (t)	2.08 (m)		8	25.3
8	40.3 (t)	2.04 (m)		7, 25	40.4[a]
9	136.6 (s)			7 or 8, 25	136.5
10	123.3 (d)	5.13 (br t, 5.5)	11, 25[b]	8, 11 or 12, 25	121.2
11	26.4 (t)	2.14 (m)	10	12	26.2
12	39.7 (t)	2.12 (m)		11, 14, 26	39.9[a]
13	138.7[c] (s)			12, 15, 26	136.5
14	121.3 (d)	5.32 (br t, 7.5)	15, 26[b]	15, 26	123.2
15	29.8 (t)	3.32 (d, 7.5)	14	21	28.0
16	128.2 (s)			15, 18	
17	148.3 (s)			15, 19, 21	
18	116.6 (d)	6.69 (d, 8.5)	19		
19	113.8 (d)	6.59 (dd, 8.5, 2.5)	18, 21	21	
20	149.3 (s)			18	
21	116.6 (d)	6.62 (d, 2.5)	19	15, 19	
22	28.7 (q)	1.01 (s)		2	28.7
23	28.7 (q)	1.01 (s)		2	28.7
24	19.9 (q)	1.61 (s)			19.8
25	16.1 (q)	1.65 (s)	10[a]	10	16.1[d]
26	16.3 (q)	1.78 (s)	14[a]	14	16.3[d]

[a,d] Assignments corrected from original literature (ref 20). [b] Long-range correlation observed in DQF COSY. [c] ^{13}C NMR resonance only observed through HMBC correlations.

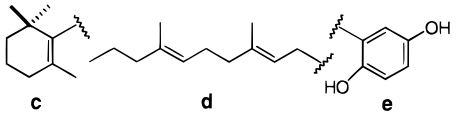

Figure 2. Substructures for jaspaquinol (**3**).

values, such as **4**, have been argued to have 9*R*,10*S* stereochemistry.[17]

The structure elucidation of jaspaquinol (**3**) proceeded rapidly once the molecular formula of $C_{26}H_{38}O_2$ was established from the HRFABMS m/z = 381.2795 [M − H]$^+$ (Δ +0.15 mmu of calcd). The ^{13}C and DEPT-135 NMR data gave a partial formula of $C_{26}H_{36}$ which indicated the presence of two hydroxy groups when compared to the MS-based formula. Examination of the ^1H NMR spectrum again indicated the presence of a trisubstituted aromatic ring (δ 6.69, d, H18; 6.59, dd, H19; 6.62, d, H21), two additional trisubstituted double bonds (δ 5.32, br t, H14; 5.13, br t, H10), and a tetrasubstituted double bond (δ 126.9, s; 137.2, s), accounting for seven of the eight degrees of unsaturation. One ring, substructure **c**, was assigned using $^1H-^1H$ COSY, HMQC,[18] DEPT-135, and HMBC data (Table 2). Interestingly, C13 (δ 138.7) could only be seen from the strong HMBC correlations to H12, H15, and $H_3$26. The remaining substructures, **d** and **e**, (Figure 2) could be established through $^1H-^1H$ COSY and HMBC correlations (Table 2). Correlations from δ 126.9 (C5) to δ 2.08 ($H_2$7) allowed attachment of **c** to **d** through a connection between C6 and C7. The aromatic ring, substructure **e**, was attached from C16 to the partial structure **d** and justified by correlations from δ 128.2 (C16), δ 148.3 (C17), and δ 116.6 (C21) to δ 3.32 ($H_2$15). A comparison of the ^{13}C NMR data to that previously reported for prenylated *p*-quinols[19] supported substitution of the hydroxy groups at C17 and C20 on the aromatic ring. Furthermore, the ^{13}C NMR data for the terpene portion of the molecule is in good agreement with assignments we previously reported for dehydroluffariellolide diacid (**5**)[20] (Table 2). The geometry of the C9−C10 and C13−C14 double bonds could be deduced as *E* from the upfield chemical shift of the olefinic methyl resonances for C25 (δ 16.1) and C26 (δ 16.3).[21]

The types of secondary metabolites reported from sponges of the *Jaspis* genus seem especially disparate. There are other structurally diverse compounds from this genus in addition to the malabaricane-type terpenoids and jasplakinolide-type cyclic depsipeptides mentioned above. These others range from mixed biogenesis compounds such as the bengamides[22] and the bengazoles,[23] nucleosides,[24] purine bases,[25,26] and styryl sulfates,[25,27−29] to the macrolides jaspisamides A-C.[30] To date there have been no reports of terpenoid-derived natural products

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from sponges classified as *Jaspis* cf. *johnstoni*. The diterpene-benzenoid (−)-jaspic acid (**2**) is more closely related to the sesquiterpene-benzenoids, such as dactylosponol (**4**), more commonly isolated from *Smenospongia* and *Dactylospongia* sp., and it is the first diterpene-benzenoid from the *Jaspis* genus. The closest structure analog to jaspaquinol (**3**) is the sesterterpene dehydroluffariellolide diacid (**5**), previously reported from *Fascaplysinopis reticulata*. Of special note is that jaspaquinol (**3**) represents the first example of a monocyclic diterpene-benzenoid from a natural source.

Experimental Section

General Experimental Procedures. The NMR spectra were recorded at 250 or 500 MHz for ^{1}H and 62.9 MHz for ^{13}C. Multiplicities of ^{13}C NMR peaks were determined from DEPT experiments. Standard pulse sequences were employed for the DEPT, HMQC, and HMBC experiments. NOESY spectra were measured with a mixing time (t_m) of 500 ms. Low and high resolution FAB mass spectra were obtained from the University of Illinois spectrometry facilities. Size exclusion chromatography was performed using Sephadex LH-20. High performance liquid chromatography (HPLC) was performed on 10 μm ODS columns.

Collection and Identification. The sponge (coll. no. 96117) was collected in Madang, Papua New Guinea. The specimen was preserved in methanol. Voucher specimens and photographs are archived at U. C. Santa Cruz. This sponge as well as other related collections were identified as *Jaspis* cf. *johnstoni* (order Choristida, family Jaspisidae) as follows. The vouchers of sponges investigated here are assigned as an undetermined species of the genus *Jaspis* Gray 1897,[31,32] closer to *Jaspis johnstoni* Schmidt 1862. Our specimens are similar to a species from Papua New Guinea reported by Braeckman in 1987[6] as a source of jasplakinolide, and taxonomically assigned as *Jaspis johnstoni* Schmidt 1862 (= *Zaplethea digonoxea* De Laubenfels 1950).[33] Our specimens also resemble one that has been indicated to be *Dorypleres splendens*,[34] but a more appropriate descriptor might be *Jaspis splendens* considering the current taxonomic status of these genera.[31,32]

Our material occurs as a thickly encrusting sponge (1−2 cm thick) with lobate protrusions (1−2 cm high and thick), orange in and out, with a smooth surface, and compressible in consistency. Its spiculation consists of a combination of large oxeas (500−1100 × 5−25 μm, length by width), smaller oxeas (100−240 × 5−8 μm, length by width), smooth calthropses with 4−5 rays (rays 15−30 × 2−5 μm, length by width), spined oxyasters (15−20 μm in diameter), and chiasters (6−12 μm in diameter). All of a dozen or more collections of this sponge species in our repository showed greater differences to *J. splendens*[35] than to *J. johnstoni* Schmidt 1862.[6] The sponge *J. splendens* is described as having a strongly conulose surface, and it seems to lack the calthrop-like spicules found in the species studied here. Although *Jaspis johnstoni* Schmidt 1862 also seems to lack the calthrops spicule type, it possesses the smooth surface as found in our specimens. For now, we refer to this species as *Jaspis* cf. *johnstoni* and defer a definitive specific assignation until a comprehensive comparative study of the holotypes of these species plus the samples studied by various authors can be completed.

Extraction and Isolation. The specimen was preserved by soaking in a 50:50 ethanol/H_2O solution. After approximately 24 h this solution was decanted and discarded. The damp organism (0.8 kg) was placed in bottles and shipped back to the home lab at ambient temperature. Next, 100% MeOH was added, and the sponge was soaked for 24 h. This procedure was repeated two more times. The crude oil was then successively partitioned between equal volumes of aqueous MeOH, percent adjusted to produce a biphasic solution, and hexane followed by CH_2Cl_2. The remaining water solubles were extracted with *sec*-BuOH. The workup of coll. no. 96117 was as follows. The CH_2Cl_2 fraction was subjected to Sephadex LH-20 gel filtration chromatography in 30:70 CH_2Cl_2/MeOH giving six fractions. The third fraction contained jasplakinolide (**1**) (86 mg, 0.1% dry weight of sponge), and half of the fourth fraction was then subjected to reversed-phase HPLC, (95:5 MeOH/H_2O), to afford (−)-jaspic acid (**2**) (26 mg, 0.03% dry weight of sponge) and jaspaquinol (**3**) (14 mg, 0.02% dry weight of sponge).

(−)-Jaspic Acid (2). A yellow oil (26 mg); $[\alpha]^{22}_D = -22.9°$ (c = 0.8, EtOH); UV [λ_{max}] 216, 258, 290; IR (film) 3300, 2923, 1685, 1603, 1275 cm^{-1}; LRFABMS, positive ion, m/z (relative intensity %) 409 [M − H]$^+$ (48), 275 (27), 215 (28), 145 (71), 119 (100); HRFABMS 409.2743 [M − H]$^+$ = $C_{27}H_{37}O_3$ requires 409.2743; ^{1}H NMR (500 MHz, $CDCl_3$) see Table 1; ^{1}H NMR (500 MHz, CD_3OD) δ 7.87 (d, J = 1.5 Hz, H17), 7.67 (dd, J = 8.0, 1.5 Hz, H19), 6.76 (d, J = 8.0 Hz, H20), 5.35 (br m, H7), 5.12 (br t, J = 5 Hz, H24), 2.71 (dd, J = 15.5, 9.5 Hz, H15), 2.57 (dd, J = 15.5, 2.5 Hz, H15′), 2.45 (br d, J = 9.5 Hz, H9), 1.96 (m, $H_2$6), 1.93 (m, H1), 1.90 (m, H23), 1.83 (m, H23′), 1.79 (m, H3), 1.67 (s, $H_3$27), 1.63 (m, H12), 1.60 (s, $H_3$26), 1.54 (m, H2), 1.44 (m, H2′), 1.41 (s, $H_3$13), 1.34 (t, J = 8.5 Hz, H5), 1.24 (br m, H1′/H12′), 0.98 (m, H3′), 0.94 (s, $H_3$14), 0.90 (s, $H_3$11); ^{13}C NMR, see Table 1.

Jaspaquinol (3). A yellow oil (14 mg); UV [λ_{max}] 217, 290; IR (film) 3300, 2927, 1652 cm^{-1}; LRFABMS, positive ion, m/z (relative intensity %) 381 [M − H]$^+$ (10), 275 (6), 243 (88), 203 (10), 137 (100); HRFABMS 381.2795 [M − H]$^+$ = $C_{26}H_{37}O_2$ requires 381.2794; ^{1}H NMR and ^{13}C NMR see Table 2.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of (−)-jaspic acid (**2**) and jaspaquinol (**3**) (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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