Zyzzyanones B−D, Dipyrroloquinones from the Marine Sponge *Zyzzya fuliginosa*

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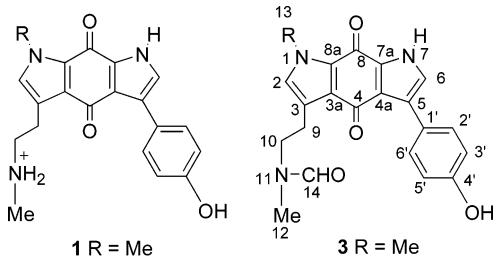
Zyzzyanones B, C, and D (**2**−**4**), three new dipyrroloquinones with a pyrrolo[3,2-*f*]indole-4,8(1*H*,7*H*)-dione skeleton, have been isolated from the Australian marine sponge *Zyzzya fuliginosa*. The known zyzzyanone A, makaluvamines C, E, G, H, and L, damirones A and B, 3,7-dimethylguanine, and 4-hydroxybenzoic acid were also isolated. The structures of the new compounds **2**−**4** were established by extensive NMR spectroscopic data. Compounds **2**−**4** showed moderate cytotoxic activity against mouse Ehrlich carcinoma cells (IC_{50} 25 μg/mL).

The marine sponge *Zyzzya fuliginosa* (order Poecilosclerida) is a rich source of alkaloids bearing a pyrrolo[4,3,2-*de*]quinoline skeleton:[1] makaluvamines,[2−6] damirones,[2,3,7] veiutamine,[8] batzellines,[9] isobatzellines,[9] and discrhabdins.[10] Moreover, makaluvic acids,[11] ring-opened examples of pyrrolo[4,3,2-*de*]quinolines, and purines[11,12] were isolated from this sponge. Recently, we have reported the isolation and structure elucidation of zyzzyanone A (**1**), the first pyrrolo[3,2-*f*]indole-4,8(1*H*,7*H*)-dione alkaloid from the Australian marine sponge *Zyzzya fuliginosa* (Carter, 1879).[13] The tricyclic dipyrroloquinone skeleton of zyzzyanone A (**1**) is a seco-derivative of a tetracyclic dipyrroloquinoline core of tsitsikammamines A and B, isolated from the South African latrunculid sponge.[14,15] To obtain more of zyzzyanone A to evaluate biological activities, we reinvestigated the aqueous EtOH extract of the same sponge and have isolated in addition to zyzzyanone A three new minor dipyrroloquinones: zyzzyanone B (**2**), an N_1-demethyl analogue of zyzzyanone A; zyzzyanone C (**3**), an N_{11}-formyl analogue of zyzzyanone A; and zyzzyanone D (**4**), an N_{11}-formyl analogue of zyzzyanone B. The known makaluvamines C (**9**),[2] E (**7**),[2] G (**5**),[6] H (**8**),[3] and L (**6**),[3] damirones A (**10**) and B (**11**),[7] 3,7-dimethylguanine,[12] and 4-hydroxybenzoic acid[11] were also isolated. The known compounds were identified by comparison of their spectral data with published values. In this paper we report the structure determination of the new compounds **2**−**4**.

The freeze-dried sponge was extracted with 50% EtOH at room temperature. The extract was separated as described in the Experimental Section to obtain compounds **2** (0.002%), **3** (0.001%), and **4** (0.001%).

Compound **2**, named zyzzyanone B, was obtained as a purple TFA salt. The UV spectrum of zyzzyanone B was similar to that of the known compound zyzzyanone A (**1**).[13] Compound **2** gave a protonated molecular ion at *m/z* 336 by FABMS analysis, 14 atomic mass units less than **1**. HRFABMS measurements of the protonated pseudomolecular ion (*m/z* 336.1339) suggested the molecular formula $C_{19}H_{18}N_3O_3$. The ^{13}C NMR and DEPT spectra revealed signals for 19 carbon atoms and indicated the presence of one methyl, two methylenes, six methines, and 10 quaternary carbons (Table 1). These data suggested the difference between **2** and **1** was a single methyl group. The ^1H NMR spectrum of **2** (Table 2) contained proton signals of the *para*-substituted phenol, two doublet signals in the aromatic region (δ 7.02 and δ 7.19) coupled with exchangeable protons at δ 12.50 and 12.69, respectively; a triplet signal from the only *N*-methyl group coupled with a broad signal from two exchangeable protons at δ 8.42; and a pair of triplets from two mutually coupled methylene groups, as shown by the $^1H-^1H$-COSY spectrum.



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3 R = Me
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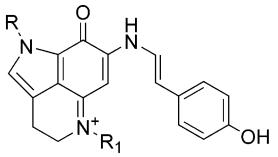
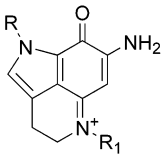
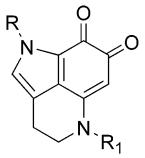


5 R = R_1 = Me
6 R = H, R_1 = Me
7 R = Me, R_1 = H



8 R = R_1 = Me
9 R = H, R_1 = Me



10 R = R_1 = Me
11 R = H, R_1 = Me

Comparison of the ^1H and ^{13}C NMR data of **2** with those of **1** showed strong structural similarities between the two molecules and suggested that compound **2** was an N_1-demethyl analogue of zyzzyanone A (**1**). Signals of the *para*-substituted phenol in the ^1H and ^{13}C NMR spectra of **2** fully coincided with those of **1**. The presence of the protonated methylaminoethyl chain in **2** was evident from the $^1H-^1H$ COSY correlations in the proton spin system comprising H_2-9 (δ 3.00), H_2-10 (δ 3.13), H_2-N_{11} (δ 8.42), and H_3-12 (δ 2.55). Full ^1H and ^{13}C NMR assignments were readily

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Table 1. ^{13}C NMR Data for Compounds **1**−**4** (DMSO-d_6)

no.	**1**[a]	**2**	**3**	**4**
2	130.3 CH	125.0 CH[b]	130.4 CH, 130.0*[c] CH	125.0 CH, 124.6* CH
3	119.6 C	120.6 C	121.5 C, 122.0* C	122.5 C, 123.0* C
3a	125.4 C	125.9 C	125.4 C, 125.5* C	125.9 C, 126.0* C
4	180.4 C	179.8 C	180.4 C, 180.3* C	179.8 C, 179.7* C
4a	121.4 C	121.2 C	121.4 C	121.2 C
5	126.6 C	126.9 C	126.5 C, 126.4* C	126.8 C, 126.7* C
6	123.9 CH	124.2 CH	123.8 CH, 123.7* CH	124.1 CH, 124.0* CH
7a	133.3 C	133.3 C	133.3 C	133.4 C
8	168.7 C	169.4 C	168.6 C, 168.7* C	169.3 C, 169.4* C
8a	129.5 C	131.5 C	129.4 C, 129.2* C	131.4 C, 131.2* C
9	22.0 CH_2	22.3 CH_2	24.2 CH_2, 22.6* CH_2	24.5 CH_2, 22.9* CH_2
10	48.1 CH_2	48.2 CH_2	48.6 CH_2, 43.2* CH_2	48.7 CH_2, 43.3* CH_2
12	32.6 CH_3	32.7 CH_3	29.0 CH_3, 34.0* CH_3	29.1 CH_3, 34.1* CH_3
13	35.8 CH_3		35.8 CH_3	
14			162.2 CH, 162.3* CH	162.3 CH, 162.4* CH
1′	124.0 C	124.0 C	124.0 C	124.0 C
2′	129.8 CH	129.9 CH	129.8 CH	129.9 CH
3′	114.6 CH	114.6 CH	114.6 CH	114.6 CH
4′	156.7 C	156.7 C	156.9 C	156.8 C
5′	114.6 CH	114.6 CH	114.6 CH	114.6 CH
6′	129.8 CH	129.9 CH	129.8 CH	129.9 CH

[a] Published data[13] are given for comparison. [b] Multiplicities determined by DEPT. [c] Asterisks indicate additional signals of lower intensity due to geometrical isomers.

Table 2. ^1H NMR and HMBC Data for Compounds **2**−**4** (DMSO-d_6)

	2		**3**		**4**	
no.	δ H (J)	HMBC	δ H (J)	HMBC	δ H (J)	HMBC
2	7.02 d (2.2)	3, 3a, 8a, 9	6.99 s	3, 3a, 4, 8, 8a, 9, 13	6.95 s	3, 3a, 4, 8, 8a, 9
			7.01*[a] s		6.97* s	
6	7.19 d (2.7)	4a, 5, 7a, 1′	7.17 bs	4, 4a, 5, 7a, 8	7.17 bs	4, 4a, 5, 7a, 8
9	3.00 t (7.5)	2, 3, 3a, 10	2.89 m	2, 3, 3a, 10	2.90 m	2, 3, 3a, 10
10	3.13 m	3, 9, 12	3.45 m	3, 9, 12, 14	3.46 m	3, 9, 12, 14
12	2.55 t (5.1)	10	2.76 s	10, 14	2.75 s	10, 14
			2.88* s		2.87* s	
13			3.89 s	2, 8a		
14			7.78 s	10, 12	7.78 s	10, 12
			7.95*		7.95*	
N_1H	12.50 d (2.2)	3, 3a			12.49 bs	
N_7H	12.69 d (2.7)	4a, 5	12.60 bs		12.69 bs	
$N^+_{11}H_2$	8.42 m					
OH	9.45 s		9.42 s	3′, 4′, 5′	9.42 s	3′, 4′, 5′
2′	7.55 d (8.9)	5, 4′, 6′	7.56 d (8.7)	5, 4′, 6′	7.56 d (8.7)	5, 4′, 6′
3′	6.74 d (8.9)	1′, 4′, 5′	6.75 d (8.7)	1′, 4′, 5′	6.75 d (8.7)	1′, 4′, 5′
5′	6.74 d (8.9)	1′, 3′, 4′	6.75 d (8.7)	1′, 3′, 4′	6.75 d (8.7)	1′, 3′, 4′
6′	7.55 d (8.9)	5, 2′, 4′	7.56 d (8.7)	5, 2′, 4′	7.56 d (8.7)	5, 2′, 4′

[a] Asterisks indicate additional signals of lower intensity due to geometrical isomers.

obtained from HSQC and HMBC correlations and by comparison with zyzzyanone A (Table 2). The doublet resonance at δ 7.02 from the pyrrole proton, attached to a carbon at δ 125.0 ($^1J_{CH}$ = 184 Hz), exhibited HMBC correlations with all the carbons of the first pyrrole ring (δ 120.6, 125.9, 131.5) and with the methylene carbon C-9 (δ 22.3) of the methylaminoethyl chain, indicating the attachment of the chain to this ring. The key HMBC correlation from the protons H_2-10 (δ 3.13) to the carbon atom of the pyrrole ring at δ 120.6 pointed to the position of the methylaminoethyl chain being at C-3. The second doublet resonance at δ 7.19 from the pyrrole proton, attached to a carbon at δ 124.2 ($^1J_{CH}$ = 184 Hz), exhibited HMBC correlations with all the carbons of the second pyrrole ring (δ 121.2, 126.9, 133.3) and with the quaternary carbon C-1′ (δ 124.0) of the *para*-substituted phenol, indicating the attachment of the *p*-hydroxyphenyl moiety to this pyrrole ring. The key HMBC correlations from the protons H-2′(6′) at δ 7.55 of the phenol ring to the carbon at δ 126.9 of the second pyrrole ring indicated the attachment of the phenol moiety to this carbon (δ 126.6) and have allowed assignment of this carbon as C-5. Comparison of chemical shifts of carbonyl atoms C-4 and C-8 of **2** with those of **1** showed that the chemical shift of the carbonyl atom C-4 at δ 179.8 is diagnostic for a pyrrolo[3,2-*f*]indole-4,8(1*H*,7*H*)-dione skeleton,[13] and this allowed to ascribe structure **2** to zyzzyanone B.

To confirm the structure of zyzzyanone B (**2**), we prepared it from makaluvamine L (**6**). Treatment of an EtOH solution of **6** with aqueous NH_3 at room temperature for 20 h gave a mixture of products. Chromatography of the reaction mixture yielded hydrolysis products of **6**, damirone B (**11**), makaluvamine C (**9**), and *p*-hydroxybenzoic acid, and a cyclized product **2**, the spectral and physical data of which were identical with those for zyzzyanone B. Thus the structure of **2** was confirmed.

Compound **3**, named zyzzyanone C, was obtained as a brownish-red solid, which gave a sodiated molecular ion at *m/z* 400.1279 $(M + Na)^+$ by HRFABMS analysis, consistent with the molecular formula $C_{21}H_{19}N_3O_4$. Analysis of NMR spectra of **3** showed that compound **3** was structurally very similar to zyzzyanone A (**1**). The signals of a *p*-hydroxyphenyl moiety in the ^1H and ^{13}C NMR spectra coincided with those for zyzzyanone A (Tables 1 and 2). Except for the signals of the *para*-substituted phenol, the NMR data for **3** were relatively complicated in

contrast to the NMR data for **1**. Most of the ^{1}H and ^{13}C resonances were doubled, indicating the presence of a 2:1 mixture of two isomers. Furthermore, the ^{13}C NMR spectrum of **3**, in contrast to **1**, displayed additional carbon signals of different intensities at δ 162.2 and 162.3 (Table 1). The ^{1}H NMR spectrum of **3** (Table 2), in turn, differed from the spectrum of **1** in the absence of a signal at δ 8.51 from two exchangeable protons and in the presence of two singlet signals in a 2:1 ratio from one proton at δ 7.78 and 7.95. This finding correlated in the HSQC spectrum to the carbon signals at δ 162.2 and 162.3, respectively, and had coupling constants $^1J_{CH}$ = 192 Hz, measured in gated decoupling experiments, characteristic of an aldehyde group. The assumption that this aldehyde group has to be an *N*-formyl group was based on the presence of **3** as a mixture of two isomers. In the ^{1}H NMR spectrum of **3** recorded in DMSO-d_6 at 150 °C, all doubled signals of protons merged: δ 7.93 (1H, s, C*H*O), 7.05 (1H, s, H-6), 6.88 (1H, s, H-2), 3.50 (2H, t, J = 7 Hz, CH_2-10), 2.97 (2H, t, J = 7 Hz, CH_2-9), 2.83 (3H, bs, CH_3-12).

The signals of the ^{1}H and ^{13}C NMR spectra were visually differentiated and assigned to the major or minor isomers. Comparison of the ^{13}C NMR spectra of **3** and **1** showed that significant differences in ^{13}C chemical shifts occurred at C-3 and carbons C-9, C-10, and C-12 of the side chain, which strongly indicated that the formyl group had to be at N_{11}. This was supported by the HMBC correlations from the proton of the formyl group at δ 7.78 to the carbon atom at δ 48.6 (C-10) and to the carbon atom of the methyl group at δ 29.0 (C-12) and from the protons at δ 3.45 (H_2-10) and at δ 2.76 (Me-12) to the carbon atom of the formyl group at δ 162.2 of the major isomer (Table 2). The same correlations were observed for signals of the minor isomer. Detailed NMR spectroscopic analysis (DEPT, HSQC, and HMBC) allowed the assignment of all the proton and carbon values reported in Table 1 and Table 2. Thus, the structure of zyzzyanone C (**3**) was determined as the N_{11}-formyl analogue of zyzzyanone A.

Compound **4**, named zyzzyanone D, was obtained as a brownish-red solid; it gave a sodiated molecular ion at *m/z* 386.1124 $(M + Na)^+$ by HRFABMS analysis, consistent with the molecular formula $C_{20}H_{17}N_3O_4$. Like that of zyzzyanone C (**3**), most ^{1}H and ^{13}C resonances of zyzzyanone D (**4**) were also doubled, indicating the presence of a 2:1 mixture of two isomers**.** Comparison of the NMR data of **4** with the NMR data of **3** showed that compound **4** differed only in the absence of one N_1-methyl group. There was an additional exchangeable proton signal at δ 12.49 in the ^{1}H NMR spectrum of **3** instead of a singlet signal of the N_1-Me group at δ 3.89 of compound **4** (Table 1). The significant upfield chemical shift of C-2 ($\sim\Delta$ 5.4 ppm) in the ^{13}C NMR spectrum of **4** in comparison with the C-2 chemical shift of **3** supported the lack of the methyl group at N_1. Thus, the substitution pattern of a dipyrroloquinone core of **4** was the same as that of zyzzyanone B (**2**). The assignment of all the proton and carbon values was made on the basis of detailed NMR spectroscopic analysis (DEPT, HSQC, and HMBC). Thus, the structure of zyzzyanone D (**4**) was determined as the N_{11}-formyl analogue of zyzzyanone B.

The presence of an *N*-formyl group in marine metabolites is common. Examples include *N*-formyl-1,2-dihydrorenierone from a marine sponge *Reniera* sp.[16] and flustrabromine from the marine bryozoan *Flustra foliacea*,[17] which were isolated as physically inseparable mixtures of two geometrical isomers.

Zyzzyanones B−D described in this work deepen our knowledge of the chemistry and biosynthetic capabilities of marine organisms and add to the structural diversity of alkaloids in marine sponges. Zyzzyanones A and B could arise from makaluvamines G and L, respectively, by intramolecular cyclization at the benzylic position with a concomitant hydrolysis of an imino bond in hypothetical analogues of tsitsikammamines. Zyzzyanones can be seen to have a plausible interrelationship with the makaluvamines and with the tsitsikammamines. However, a facile conversion of makaluvamines G and L to zyzzyanones A and B in the presence of NH_3 tentatively suggests a possible formation of zyzzyanones during storage or isolation.

Zyzzyanones B−D showed moderate cytotoxic activity against mouse Ehrlich carcinoma cells with IC_{50} values of 25 μg/mL. These data support the earlier suggestion that the intact pyrroloiminoquinone moiety enhances cytotoxicity.[2,11]

Experimental Section

General Experimental Procedures. UV spectra were recorded on an UV-mini 1240 spectrophotometer (Shimadzu). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE DRX-500 NMR spectrometer at 125 and 500 MHz, respectively. Chemical shifts were referenced to the solvent peak (DMSO-d_6, 2.50 for ^{1}H and 39.6 for ^{13}C; CD_3OD, 3.30 for ^{1}H and 49.6 for ^{13}C). HMBC spectra were optimized for 10 Hz coupling. HRFABMS were performed on an AMD-604 S mass spectrometer employing a glycerol matrix. Sorbfil plates coated with Si gel (Sorbpolimer, Krasnodar, Russia) were used for TLC; Sephadex LH-20 (Pharmacia Fine Chemicals) and Polychrome-1 (powder Teflon, Olaine, Latvia) were used for column chromatography. All solvents were distilled prior to use.

Animal Material. The sponge *Z. fuliginosa* was collected by hand using scuba at Mid Islet, Eastern Australia, at a depth of 10 m in July 1989 during the ninth scientific cruise of *R/V Academik Oparin*. The sponge was freeze-dried and stored in a refrigerator until used. The sponge was taxonomically identified by Dr. V. B. Krasokhin. A voucher specimen (09-407a) is held at Pacific Institute of Bioorganic Chemistry.

Extraction and Isolation. The freeze-dried sponge (200 g) was extracted with *n*-hexane to obtain the hexane solubles (2 g), which were not examined. The sponge was then extracted with 50% EtOH (1 L × 3) at room temperature, and the solvent was concentrated under reduced pressure to yield a dark red residue. This residue was triturated with $CHCl_3$ to yield 1.2 g, which was chromatographed on a Sephadex LH-20 column in $CHCl_3$ to obtain in order of elution zyzzyanones D (**4**) (2 mg, 0.001% to the sponge dry weight) and C (**3**) (2 mg, 0.001%) and damirones A (90 mg) and B (70 mg). A $CHCl_3$–insoluble solid was subjected to column chromatography on a Polychrome-1 column with a solvent elution gradient from H_2O to EtOH. Dark red fractions eluted with 25−40% EtOH gave makaluvamines C (10 mg, 0.005%) and H (34 mg, 0.017%) and an additional quantity of damirones A (10 mg, 0.05%) and B (10 mg, 0.04%) after chromatography on a Sephadex LH-20 column in $CHCl_3$−EtOH−TFA (4:1:0.1%). A brownish-green fraction eluted with 50% EtOH was repeatedly chromatographed on a Sephadex LH-20 column in $CHCl_3$−EtOH−TFA (3:1:0.1%) to yield makaluvamines E (8 mg, 0.004%), G (110 mg, 0.055%), and L (16 mg, 0.008%), 3,7-dimethylguanine (9 mg, 0.0045%), zyzzyanone A (12 mg, 0.006%), and new zyzzyanone B (**2**) (4 mg, 0.002%). Fractions eluted with EtOH gave 4-hydroxybenzoic acid (7 mg, 0.0035%) after chromatography on a Sephadex LH-20 column in EtOH.

Zyzzyanone B (2): purple solid; UV−vis (MeOH) λ_{max} (log ϵ) 240 (3.99), 281 (3.64), 328 (3.33), 483 (3.08) nm; UV−vis (MeOH/KOH) λ_{max} (log ϵ) 241 (4.01), 281 (3.66), 332 (3.34), 503 (3.09) nm; ^{1}H NMR (CD_3OD) δ 7.54 (2H, d, J = 8.6 Hz, H-2′, 6′), 7.04 (1H, s, H-6), 6.95 (1H, s, H-2), 6.77 (2H, d, J = 8.6 Hz, H-3′, 5′), 3.26 (2H, t, J = 6.4 Hz, CH_2-10), 3.09 (2H, t, J =

6.4 Hz, C*H*$_2$-9), 2.69 (3H, s, C*H*$_3$-12); ^{13}C NMR (CD_3OD) δ 183.9 (C, C-4), 170.3 (C, C-8), 158.6 (C, C-4′), 135.3 (C, C-7a), 134.3 (C, C-8a), 131.7 (CH, C-2′, 6′), 129.8 (C, C-5), 126.9 (C, C-3a), 126.6 (C, C-1′), 126.3 (CH, C-2), 125.5 (CH, C-6), 124.1 (C, C-4a), 122.2 (C, C-3), 116.2 (CH, C-3′, 5′), 51.4 (CH_2, C-10), 34.4 (CH_3, C-12), 24.5 (CH_2, C-9); ^{1}H and ^{13}C NMR (DMSO-d_6) data, see Tables 1 and 2; HRFABMS *m/z* 336.1339 (calcd for $C_{19}H_{18}N_3O_3$, 336.1343).

Zyzzyanone C (3): brownish-red solid; UV−vis (MeOH) λ_{max} (log ϵ) 242 (3.67), 294 (3.24), 349 (2.94), 486 (2.85) nm; UV−vis (MeOH/KOH) λ_{max} (log ϵ) 244 (3.63), 287 (3.22), 340 (2.93), 511 (2.86) nm; ^{1}H and ^{13}C NMR (DMSO-d_6) data, see Tables 1 and 2; HRFABMS *m/z* 400.1279 (M^+ + Na) (calcd for $C_{21}H_{19}N_3O_4$ + Na, 400.1273).

Zyzzyanone D (4): brownish-red solid; UV−vis (MeOH) λ_{max} (log ϵ) 241 (3.67), 288 (3.23), 337 (2.95), 487 (2.84) nm; UV−vis (MeOH/KOH) λ_{max} (log ϵ) 243 (3.62), 282 (3.22), 326 (2.92), 510 (2.84) nm; ^{1}H NMR (CD_3OD) δ 7.96* and 7.79 (1H, each s, C*H*O), 7.54 (2H, d, J = 8.7 Hz, H-2′, 6′), 7.01 and 7.00* (1H, each s, H-6), 6.87* and 6.85 (1H, each s, H-2), 6.77 (2H, d, J = 8.7 Hz, H-3′, 5′), 3.58 (2H, m, C*H*$_2$-10), 2.98* and 2.89 (3H, each s, C*H*$_3$-12), 3.01 (2H, m, C*H*$_2$-9) (asterisks indicate additional signals of the minor isomer); ^{13}C NMR (CD_3OD) δ 183.8 and 183.6* (C, C-4), 170.4 and 170.3* (C, C-8), 165.7 and 165.5* (CH, *C*HO-14), 158.5 (C, C-4′), 135.1 (C, C-7a), 134.1 (C, C-8a), 131.7 (CH, C-2′, 6′), 129.8 (C, C-5), 126.9 (C, C-3a), 126.8 (C, C-1′), 126.4 and 126.0* (CH, C-2), 125.4 and 125.3* (CH, C-6), 124.5 and 124.3* (C, C-3), 124.3 (C, C-4a), 116.2 (CH, C-3′, 5′), 51.8 and 46.2* (CH_2, C-10), 36.0* and 30.7 (CH_3, C-12), 26.3 and 24.7* (CH_2, C-9) (asterisks indicate additional signals of the minor isomer); ^{1}H and ^{13}C NMR (DMSO-d_6) data, see Tables 1 and 2; HRFABMS *m/z* 386.1124 (M^+ + Na) (calcd for $C_{20}H_{17}N_3O_4$ + Na, 386.1117).

Preparation of 2 from Makaluvamines L (6). A mixture of **6** (27.8 mg), EtOH (20 mL), and aqueous 17% NH_3 (3 mL) was stirred at room temperature for 20 h. After evaporation of the solvent the residue was chromatographed on a Sephadex LH-20 column in $CHCl_3$−EtOH−TFA (4:1:0.1%) to yield damirone B (12.7%), makaluvamine C (4%), *p*-hydroxybenzoic acid (10.4%), and the cyclized product **2** (4%). The UV, HRFABMS, and ^{1}H and ^{13}C NMR data of **2** were identical with those for zyzzyanone B.

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