ulations concerning the biosynthetic origin of victala[2] and puts severe restrictions on the choice of a mechanism for the formation of the unusual 12-membered ring in this toxin and in its victorin cognates.

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Abbreviations used: FAB, fast atom bombardement; NOBA, 3-nitrobenzylalcohol; gly, glycerol; TFA, trifluoroacetic acid.

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Okinonellins A and B, two novel furanosesterterpenes, which inhibit cell division of fertilized starfish eggs, from the marine sponge *Spongionella* sp.[1]

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Summary. Two novel furanosesterterpenes, okinonellins A (**1**) and B (**2**), have been isolated from the sponge *Spongionella* sp. Both compounds inhibit cell division of starfish embryos.
Key words. Spongionella sp.; porifera; cell division inhibitor; starfish embryos, furanosesterterpene.

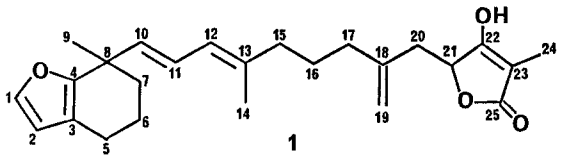
We previously reported the isolation and structural elucidation of two bioactive furanosesterterpenes, spongionellin (**3**) and dehydrospongionellin (**4**), from a marine sponge *Spongionella* sp.[2]. We have now separated two more novel sesterterpenes, named okinonellins A and B, form another species of *Spongionella*. Both compounds inhibit the development of fertilized starfish eggs.

The sponge (800 g, wet weight) was collected by SCUBA (−20 m) at Okinoshima Island in Uwa Sea, 700 km southwest of Tokyo, and stored frozen at −20 °C until processed. The frozen sponge was extracted with ethanol, whose extract was partitioned between water and ether. The organic phase was subjected to low pressure column chromatography on silica gel with dichloromethane-ethyl acetate systems. The active materials

^{1}H and ^{13}C NMR shifts for **1** and **2**

C	**1** ^{1}H δ($CDCl_3$)	^{13}C δ($CDCl_3$)	**2** ^{1}H δ($CDCl_3$)	^{13}C δ($CDCl_3$)
1	7.25 (1H, d, 1.8 Hz)	140.7 d	7.33 (1H, brs)	142.6 d
2	6.18 (1H,d, 1.8)	110.2 d	6.25 (1H, brs)	111.1 d
3		116.8 s		124.9 s
4		154.5 s	7.19 (1H, brs)	138.8 d
5	2.42 (2H, m)	22.6 t	2.39 (2H, t, 7.5)	24.9 t
6	1.72 (2H, m)	20.1 t	1.54 (2H, m)	27.8 t
7	1.79 (1H, m)	38.5 t[a]	1.35 (2H, q, 7.5)	36.9 t[c]
	1.63 (1H, m)			
8		38.7 s	2.19 (1H, m)	36.8 d
9	1.36 (3H, s)	25.8 q	1.00 (3H, d, 6.7)	20.8 q
10	5.62 (1H, brd, 15.3)	139.0 d	5.45 (1H, dd, 15.1, 7.9)	138.5 d
11	5.97 (1H, dd, 15.3, 10.7)	124.9 d	6.19 (1H, dd, 15.1, 10.7)	124.9 d[d]
12	5.79 (1H, d, 10.7)	124.9 d	5.79 (1H, d, 10.7)	125.2 d[d]
13		137.1 s		136.0 s
14	1.65 (3H, brs)	16.6 q	1.73 (3H, brs)	16.5 q
15	2.01 (2H, t, 7.7)	39.3 t[a]	2.06 (2H, m)	39.3 t[c]
16	1.55 (2H, m)	25.8 t	1.61 (2H, m)	25.8 t
17	2.04 (2H, t, 7.7)	35.9 t[a]	2.06 (2H, m)	36.1 t[c]
18		144.4 s		144.8 s
19	4.92 (1H, brs)	113.1 t	4.92 (2H, brs)	112.3 t
	4.90 (1H, brs)			
20	2.65 (1H, dd, 15.0, 3.8)	38.4 t[a]	2.63 (1H, dd, 15.0, 7.2)	34.7 t[c]
	2.27 (1H, dd, 15.0, 8.5)		2.52 (1H, dd, 15.0, 7.2)	
21	4.79 (1H, brm)	76.8 d	4.46 (1H, dt, 3.3, 7.2)	80.8 d
22		175.8 s[b]	4.36 (1H, brdd, 3.3, 4.5)	71.7 d
23		97.4 s	2.73 (1H, dq, 4.5, 7.3)	41.9 d
24	1.70 (3H, s)	6.0 q	1.27 (3H,d, 7.3)	8.0 q
25		174.6 s[b]		177.6 s

[a–d] Assignments may be interchanged.



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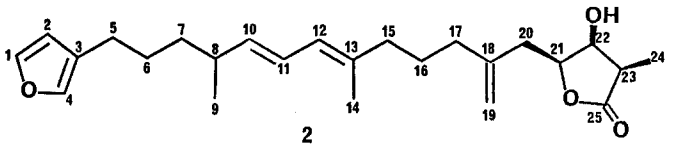

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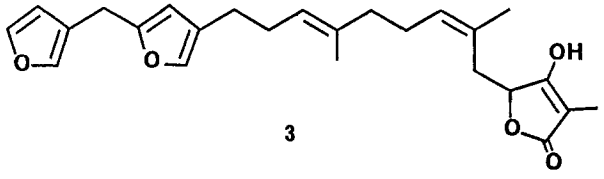

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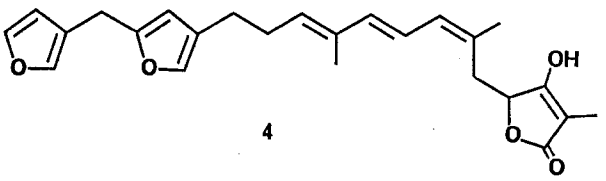

4

were repeatedly purified by HPLC on C_{18} columns with 80% acetonitrile followed by 85% methanol, to give okinonellin A(**1**) (3.5 mg) and okinonellin B(**2**) (2.0 mg). Both compounds inhibited cell division of fertilized starfish *(Asterina pectinifera)* eggs at 5 µg/ml.

Okinonellin A(**1**) is a labile colorless oil, $[\alpha]_D^{20}$ +42.5° (*c* 0.08, EtOH), positive to Ehrlich reagent. The UV spectrum showed absorption at 243 (ε 26000) nm in ethanol. The molecular formula of $C_{25}H_{32}O_4$ was established by HREIMS (M^+, obsd; *m/z* 396.2274, Δ-2.4 mmu). ^{13}C NMR signals (δ 175.8 s, 174.6 s, 97.4 s, 76.8 d, 38.4 t, 6.0 q) together with IR absorptions (ν_{max} 3300, 1750, 1660 cm^{-1}) implied the presence of a nonconjugated tetronic acid moiety[2], which was supported by ^1H NMR [δ 4.79 (1H, brm), 2.65(1H, dd, 15.0, 3.8 Hz), 2.27(1H, dd, 15.0, 8.5), 1.70 (3H, s)]. The ^1H NMR (table) also suggested that the molecule contained a 2,3-disubstituted furan ring [δ 7.25(1H, d, 1.8), 6.18(1H, d, 1.8)], a 1-methyl-1,4-disubstituted butadiene [δ 5.97(1H, dd, 15.3, 10.7), 5.79(1H, d, 10.7), 5.62(1H, brd, 15.3), 1.65(3H, brs)], an exomethylene [δ 4.92(1H, brs), 4.90(1H, brs)], and a methyl group attached to a quaternary carbon [δ 1.36(3H, s)]. In the ^{13}C NMR spectrum (table, 100 MHz) 7 additional methylene signals were observed.

Since **1** possessed 10 degrees of unsaturation, one more ring was expected to be present in the molecule. This was substantiated by 400 MHz ^1H NMR analyses including COSY[3] and NOE experiments, which led to the gross structure **1**. Cross peaks in the COSY spectrum revealed the unambiguous sequences from C-10 to C-17 and three contiguous methylenes; C-5 to C-7. The presence of a novel fused furanocyclohexene skeleton linked to a conjugated diene was evidenced by an inbeam EIMS fragment peak at *m/z* 135 (fission between C-8 and C-10 bonds) and NOE experiments: upon irradiation of H-5 methylene protons at δ 2.42, NOE enhancement was observed for H-2 proton signal at δ 6.18, while enhancement of H-10 signals at δ 5.62 was observed by irradiation of H-9 methyl protons at δ 1.36. Since a cross peak was observed between the signals at δ 2.04 (H-17) and δ 4.90 (H-19'), the exomethylene functionality can be accommodated between C-17 and C-20 methylenes, the latter of which was linked to the terminal tetronic acid moiety. The *E* geometry of the $\Delta^{10,11}$ double bond was deduced from the large coupling constant (15.3 Hz) between H-10 and H-11. On the other hand, the *E* geometry of the $\Delta^{12,13}$ double bond was secured by an NOE observed for H-14 proton signals (δ 1.65) when irradiated at the H-11 proton (δ 5.97). The absolute configurations at C-8 and C-21 remain to be determined.

The other active compound, okinonellin B(**2**), $[\alpha]_D^{20}$ +17.9°(*c* 0.15, EtOH), showed spectral data similar to those of okinonellin A. HREIMS led to the molecular formula of $C_{25}H_{36}O_4$ (M^+, obsd: *m/z* 400.2598, Δ-1.3 mmu). The presence of a diene system [UV(EtOH) 240(ε 24000) nm; δ_H 6.19(dd, 15.1, 10.7; H-11), 5.79(d, 10.7; H-12), 5.45(dd, 15.1, 7.9; H-10)] and an exomethylene group [δ_H 4.92(2H, brs), δ_C 112.3 t] was verified by spectral data. Interestingly, this compound contained a 2-methyl-3-hydroxy-γ-lactone, the 2,3-dihydroderivative of tetronic acid (λ_{max} 1760, 1170 cm^{-1}), which is rather exceptional for marine furanosesterterpenes.

^1H NMR analyses including double resonance and NOE experiments allowed the assignment of all proton signals and established the gross structure of okinonellin B(**2**). *E* geometries of both $\Delta^{10,11}$ and $\Delta^{12,13}$ double bonds were determined as mentioned above. NOE's were observed H-21(δ 4.46) and H-22 (δ 4.36) protons when irradiated at H-23 proton(δ 2.73), which were in turn enhanced on irradiation at either H-21 or H-22 protons. There findings led us to assign the relative configurations of C-21 through C-23. However, the absolute stereochemistry is not known.

Although several linear furanosesterterpenes[4] have been found in sponges of the family Thorectidae, these two compounds, which contained an exomethylene and dihydrotetronic acid functionalities in the molecule, have not been reported. The roles and biosynthesis of these compounds are interesting problems.

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