Journal of Natural Products
Vol. 57, No. 10, pp. 1416-1423, October 1994

SODWANONES A–F, NEW TRITERPENOIDS FROM THE MARINE SPONGE *AXINELLA WELTNERI*

AMIRA RUDI, YOEL KASHMAN,*

School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel

YEHUDA BENAYAHU,

Department of Zoology, Tel Aviv University, Tel Aviv 69978, Israel

and MICHAEL SCHLEYER

Oceanographic Research Institute, Durban, Republic of South Africa

ABSTRACT.—Six triterpenoids, sodwanones A–F (**1–3**, **7–9**), having three different skeletons, have been isolated from the Indo-Pacific sponge *Axinella weltneri*. The complete spectral data of the previously reported sodwanones A–C [**1–3**], together with the structure determination of the new sodwanones D–F [**7–9**], based mainly on 1D and 2D nmr spectroscopy, are the subject of this report.

The structures of three new triterpenoids, sodwanones A–C [**1–3**], from the Indo-Pacific fan sponge *Axinella weltneri* (Axinellidae), were recently reported (1). Compounds **1–3** are closely related to the previously reported sipholenols (e.g., **4**, sipholenol B) (2), siphonellinol [**5**] (3) and neviotine A (4) isolated from the Red Sea sponge *Siphonochalina siphonella*, as well as the recently reported raspacionins (e.g., **6**, raspacionin A) isolated from the Mediterranean red sponge *Raspaciona aculeata* (5–7). Interestingly, the latter sponge, like *A. weltneri*, is an Axinellidae sponge, whereas *S. siphonella* belongs to the order Haplosclerida.

All of the above triterpenoids comprise two separate cyclic systems assumed to be obtained from di- or trioxidosqualenes in two separate acid-catalyzed cyclizations (2–4). Each cyclization is suggested to be initiated by a carbonium ion obtained from protonation of either an epoxide or one of the squalene double bonds. Compounds **1–9** possess at least one perhydrobenzoxepine system derived from one half of the squalene precursor and a variety of other systems obtained from the second half of the squalene. In the previously reported sodwanones A–C [**1–3**], the second cyclic system is a substituted decalin.

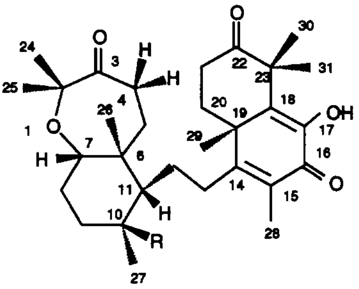
In this paper, the structure determination of three new compounds [**7–9**], designated sodwanones D, E, and F from *A. weltneri*, together with the complete spectral data and stereochemistry of both these new compounds and sodwanones A–C [**1–3**] are presented.

RESULTS AND DISCUSSION

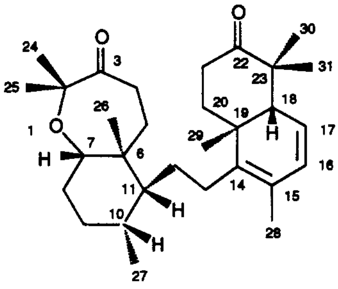
The EtOAc extract of *A. weltneri* was found to contain six triterpenoids having three different carbon skeletons. Of the six, only sodwanone A [**1**] appears in a somewhat higher concentration (0.1% dry wt) relative to the others, which exist in the sponge in minute amounts (0.01%–0.005%).

The structure of sodwanone A [**1**], $C_{30}H_{44}O_6$, suggested by analysis of the nmr and other spectral data, was secured by single crystal X-ray diffraction analysis (1).

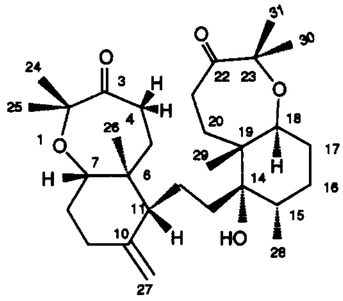
Half of the sodwanone A molecule [**1**] has the same *trans*-perhydrobenzoxepine system as compounds **4–6** but they have different substituents. The rest of the molecule of **1**, however, differs. Mono-, bi-, and tricarbocyclic systems have already been found in the second half of the molecule of the *S. siphonella* metabolites (2–4). Sodwanone A [**1**]



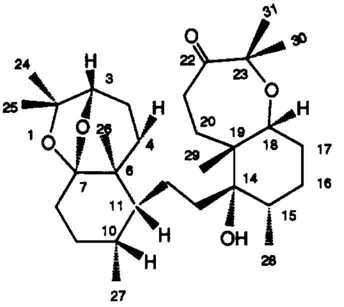
1* R=OH
2* R=H



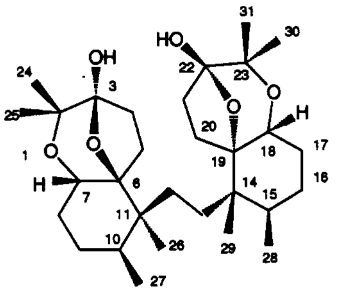
3*



7*



8*



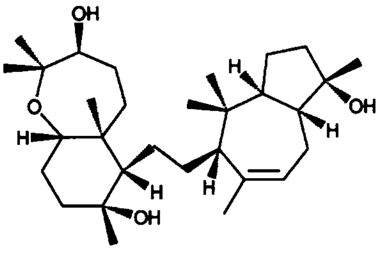
9*

contains a different bicyclic system from that of the sipholanols, namely, a substituted decalin moiety which embodies a rare α-hydroxy cross-conjugated dienone system.

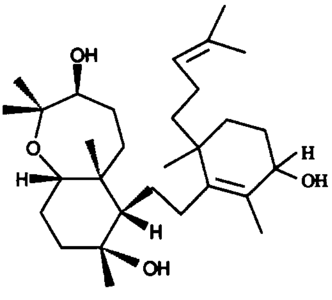
The second compound, sodwanone B [**2**], $C_{30}H_{44}O_5$, *m/z* 484, has the same decalin moiety as **1** and a very similar perhydrobenzoxepine system. The major difference in the ^{1}H-nmr spectrum of **2**, when compared to that of **1**, was that the Me-27, α- to the 10-OH group in **1**, is replaced by a doublet methyl resonating at δ_H 1.06. At the same time the tertiary C-10 OH singlet resonance (δ_C 73.5) was replaced by a new methine doublet resonance at δ 28.2, suggesting that sodwanone B [**2**] is the 10-deoxy derivative of **1**. As for the relative stereochemistry of C-6, C-7, C-10, and C-11, the ^{1}H-^{1}H coupling pattern of H-7 (δ 2.90 dd, J=10.7 and 5.1 Hz) and the chemical shifts of the oxepane C-atoms suggest that the C-6 methyl group (Me-26) and H-7 in **2** are trans diaxial as in **1**. Furthermore, nOe cross-peaks between the axial H-4 (δ_H 3.16) and methyls 25 and

---

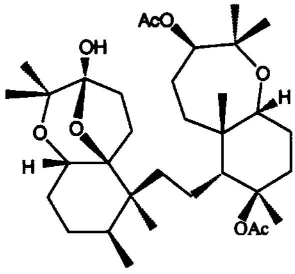
*relative stereochemistry



4



5



6

26 on one side of the ring system (the α-side), and between H-7 and methyl 24 and H-11 (δ_H 1.25 m) on the other (β) side of the system, are in good agreement with a C-6, -7 trans configuration. This also determines the α-equatorial configuration of the C-12, -13 ethylene bridge. Additionally, an nOe cross-peak between H-11 (β axial) and H-10 (δ_H 1.93 m) requires H-10 also to be β (equatorial), thus determining the configuration of Me-27 to be α, and on the same side as methyls 25 and 26.

The nmr line assignments of **2** (Table 1) were based on homo-COSY, HMQC, and HMBC experiments. The structure and stereochemistry of the perhydrobenzoxepine system of **2** was further supported by comparing its nmr data with those of sipholenol B [**4**] (2). Based on biogenetic considerations it is tentatively suggested that the relative stereochemistry of the two halves of **2**, as well as those of **3**, are the same as in **1** (having the same C-6 and C-19 configurations) where it was assured by X-ray diffraction analysis. No nOes could be measured between the two separate (by the C-12, C-13 bridge), conformationally labile, bicyclic halves of molecules **1**–**3**.

Sodwanone C [**3**], $C_{30}H_{46}O_3$, *m/z* 454, has the same substituted perhydrobenzoxepine system as compound **2** (according to the δ_C values, Table 1), but differs in the decalin moiety. The latter moiety still has the same cyclohexanone ring, with its characteristic α-*gem*-dimethyl ketone, but instead of the conjugated dienone it has a 1,3-diene group (>CH(18)CH(17)=CH(16)-C(15)Me=C(14)CH_2(13)-; δ_H 5.90 dd (J=9.3 and 3.2 Hz) and 5.62 dd (J=9.3 and 2.7 Hz); δ_C 142.5 s, 131.0 d, 125.2 s, and 124.2 d). Based on the CH-correlations (HMBC) from CH_3s -29, -30, -31 to C-18 (δ_C 53.4 d); CH_3s-28, -29 to C-14 (δ_C 142.5 s); also from CH_3-28 to C-15, C-16, and C-17, and , as in all the series, from CH_3s -30, -31 to CO-22, the $\Delta^{14,16}$ (rather than $\Delta^{15,17}$) position was proposed. A trans geometry was determined for the decalin system of **3** based on nOe correlations between the axial 21-proton (δ_H 2.82) and methyls -29 and -30 (δ_C 22.8, δ_H 1.19) on the α-side of the decalin (the latter effect distinguishes between methyls 30 and 31), and between H-18 (δ_H 2.48) and Me-31 (δ_H 1.12) on the β-side of the ring system.

The structure of sodwanone D [**7**], $C_{30}H_{48}O_5$, *m/z* 488, is proposed to comprise two

TABLE 1. Nmr Data (125 and 500 MHz) Including CH-Correlations of Sodwanones A–C [**1–3**].[a–c]

Position	Compound						
	1				**2**	**3**	
	δ_C[b]	δ_H[b]		HMBC (C to H)	δ_C	δ_C	HMBC (C to H)
2	82.0 s			H-4a, -7, Me-24, Me-25	82.4 s	82.3 s	Me-24, -25
3	218.0 s			H-4a, -5a, Me-24, Me-25	218.0 s	218.1 s	H-4a, Me-24, -25
4a	35.0 t	3.25 ddd	13.5, 11.1, 2.6	H-5a, -5b	35.1 t	35.2 t	
4b		2.19 m					
5a	40.6 t	1.95 ddd	11.0, 6.3, 2.2	H-7, Me-26	40.5 t	40.4 t	
5b		1.38 m					
6	42.0 s			H-5a, -5b, Me-26	41.5 s	41.3 s	H-7, Me-26
7	80.9 d	2.97 dd	10.7, 5.1	H-5a, -9a, Me-26	81.9 d	82.2 d	Me-24, -25, -26
8a	24.8 t	1.62 m		H-5b	25.5 t	26.3 t	
8b		1.58 m					
9a	41.5 t	1.76 ddd	13.5, 6.5, 3.5	H-8a, -8b, -11, Me-27	29.9 t	31.2 t	
9b		1.48 m					
10	73.5 s			H-8a, -9a, -11, Me-27	28.2 d	28.3 d	
11	57.5 d	1.13 dd	5.5, 3.4	H-9a, -9b, Me-26, Me-27	51.3 d	51.3 d	Me-26, -27
12a	28.7 t	1.55 m		H-7	28.4 t	27.1 t	
12b		1.45 m					
13a	33.9 t	2.64 dd	13.0, 3.5	H-12a, -12b	31.1 t	34.3 t	
13b		2.38 dt	13.0, 5.4				
14	164.7 s			H-13a, -13b, -20a, Me-28	164.5 s	142.5 s	H-16, Me-28, -29
15	128.8 s			H-13a, -13b, Me-28	129.1 s	125.2 s	H-16, -17, Me-28
16	181.5 s			OH (17), Me-28	181.5 s	124.2 d	Me-28
17	141.8 s			OH (17), -20a	141.9 s	131.0 d	Me-28
18	137.6 s			OH (17), -20a, Me-29, Me-30, -31	137.2 s	53.4 d	H-16, -17, Me-29, Me-30, -31
19	42.9 s			H-20a, -20b, -21a, -21b, Me-29	42.7 s	40.6 s	Me-29
20a	27.6 t	2.48 dd	13.4, 6.6	H-21a, -21b, Me-29	25.8 t	26.4 t	
20b		1.75 m					
21a	32.6 t	2.74 dd	18.5, 8.9	H-20a	32.5 t	34.5 t	
21b		2.60 dd	18.5, 2.5				
22	216.0 s			H-21a, -21b, Me-30, -31	215.0 s	215.8 s	H-21a, Me-30, -31
23	49.0 s			H-20b, -21a, -21b, Me-30, Me-31	48.0 s	47.2 s	Me-30, -31
24	20.4 q	1.31 s			20.5 q	20.5 q	
25	26.3 q	1.25 s		Me-24	26.4 q	26.4 q	
26	12.1 q	0.95 s		H-5b, -7	13.4 q	13.4 q	
27	23.6 q	1.21 s			14.7 q	14.5 q	
28	12.0 q	2.02 s			11.9 q	17.7 q	
29	21.6 q	1.09 s			21.6 q	15.0 q	
30	20.8 q	1.56 s			20.8 q	22.8 q	
31	24.3 q	1.46 s		Me-30	24.4 q	24.8 q	

[a] CDCl$_3$; Bruker ARX 500 instrument, chemical shifts refer to TMS (δ_H=0) and CDCl$_3$ (δ_C=77.0).

[b] Assignments aided by HMQC, HMBC, homo-COSY, TOCSY, and NOESY experiments.

[c] Ha the lower field proton in a geminal pair, and Hb the higher field proton in a geminal pair.

perhydrobenzoxepine systems based on its 1D and 2D nmr data. The 3-oxo-2,2,6- and 22-oxo-19,23,23-trimethylated oxepanes are characteristic of these two systems. These were in full agreement with the proton and carbon chemical shifts of **1–6** (Tables 1 and 2), and exhibited the expected 2D nmr COSY, HMQC, and HMBC correlations. HMQC and HMBC correlations between the various methyl protons and their neighboring C atoms (Table 2) were of special importance. Two other functionalities in **7** were an exocyclic methylene (δ_C 145.3 s, 103.3 t) and a tertiary hydroxyl group (δ_C 78.0 s). The existence of an exo methylene group explained the presence of only seven rather than the expected eight methyl groups in **7**, and accounts, with the other functionalities, for the seven degrees of unsaturation within the molecule. The locations of the $\Delta^{10(27)}$ double bond in one half of **7** and the C-14 position of the hydroxyl group in the second half were proposed in part on the basis of a COSY experiment which showed correlations between H-4a, H-4b and H-5a, H-5b and between H-7, H-8a, H-8b, H-9a and H-9b for one half

TABLE 2. Nmr Data (125 and 500 MHz) Including CH-Correlations of Sodwanones D–F [**7**–**9**].[a,b]

Position	Compound								
	7			**8**			**9**		
	δ_C	δ_H	HMBC (C to H)	δ_C	δ_H	HMBC (C to H)	δ_C	δ_H	HMBC (C to H)
2	81.8 s		H-7, Me-24, -25	78.9 s		Me-24, -25	76.7 s		Me-24, -25
3	218.0 s		H-4a,- 5a ,-5b, Me-24, -25	80.6 d	3.97 d	Me-24, -25	105.7 s		H-5b, Me-24, -25
4	35.8 t	3.18 dt 2.14 m		29.9 t	1.95 m 1.58 m		24.2 t	1.85 m 1.85 m	
5	39.3 t	1.95 m 1.30 m	Me-26	32.1 t	1.55 m 1.40 m	H-3, Me-26	32.3 t[c]	2.30 m 1.12 m	
6	42.5 s		Me-26	41.3 s		H-5a, -5b, Me-26	89.3 s		H-5a, H-7, Me-26
7	80.3 d	3.05 dd		110.1 s		H-3, H-5a, -5b, Me-26	70.6 d	4.20 dd	
8	32.5 t	1.70 m 1.50 m		22.7 t	2.02 m 1.62 m		26.7 t	1.78 m 1.38 m	
9	35.3 t	2.28 dd 1.88 m	H-27a, -27b	28.0 t	2.05 m 1.35 m		28.5 t	1.32 m 1.32 m	Me-27
10	145.3 s			29.7 d	1.92 m	Me-26	39.2 d	1.13 m	Me-26, -27
11	54.2 d	1.45 m		48.1 d	1.46 m	H-5a, -5b, Me-26, Me-27	40.9 s		Me-26, -27
12	20.1 t	1.42 m 1.42 m		20.5 t	1.22 m 1.22 m		29.7 t	1.88 m 1.18 m	H-13a
13	36.0 t	1.88 m 1.08 m		35.1 t	1.75 m 1.26 m		29.9 t	2.60 m 1.88 m	Me-29
14	78.0 s		Me-28, -29	77.6 s		Me-28, -29	42.0 s		H-13a, Me-28, -29
15	33.6 d	1.82 m		33.3 d	1.89 m	Me-28	33.5 d	1.75 m	Me-28, -29
16	28.2 t	1.35 m 1.35 m	Me-28	28.7 t	1.40 m 1.40 m	Me-28	26.5 t	1.35 m 1.12 m	H-18, Me-28
17	30.0 t	1.53 m 1.53 m		30.5 t	1.58 m 1.58 m	H-18	27.9 t	1.65 m 1.55 m	
18	76.1 d	3.52 dd	Me-29	76.1 d	3.52 dd	H-17a, -17b, Me-29	71.2 d	4.36 dd	
19	45.3 s		Me-29	45.4 s		H-21a, -22b, Me-29	88.4 s		H-18, H-20a, Me-29
20	32.7 t	2.00 m 1.52 m	H-18, Me-29	32.9 t	2.08 m 1.65 m		33.5 t[c]	2.30 m 1.12 m	
21	35.2 t	3.12 m 2.15 m		35.4 t	3.20 dt 2.25 dd		24.4 t	1.88 m 1.60 m	
22	217.6 s		Me-30, -31	215.8 s		Me-30, -31	104.4 s		H-20b, Me-30, -31
23	82.2 s		H-18, Me-30,- 31	81.6 s		H-21a, Me-30, -31	77.1 s		H-20a, Me-30, -31
24	20.3 q	1.28 s		20.7 q	1.39 s		19.2 q	1.65 s	
25	26.9 q	1.22 s	Me-24	28.2 q	1.29 s		24.6 q	1.38 s	Me-24
26	11.2 q	0.83 s		18.6 q	1.04 s		18.9 q	1.15 s	
27	108.3 t	4.94 s 4.57 s		14.7 q	0.97 d		15.4 q	0.80 d	
28	15.3 q	0.80 d		15.5 q	0.86 d		15.8 q	0.86 d	
29	14.0 q	1.04 s	H-18	14.4 q	1.15 s	H-18	17.2 q	1.18 s	
30	20.4 q	1.31 s	Me-31	20.4 q	1.34 s		18.9 q	1.57 s	
31	26.6 q	1.23 s		26.7 q	1.27 s		24.6 q	1.37 s	Me-30

[a] $CDCl_3$ for **7** and **8** and C_6D_6 for **9**; Bruker ARX 500 instrument, chemical shifts refer to TMS (δ_H=0) and $CDCl_3$ (δ_C=77.0).
[b] Assignments aided by HMQC, HMBC, homo-COSY, TOCSY, and NOESY experiments.
[c] May be interchangeable.

of **7** and between H-20a, H-20b, H-21a, and H-21b, and between Me-28, H-15, H-16a, H-16b, H-17a, H-17b, and H-18 for the second half of **7**. In addition, HMBC correlations (CH_3-26 to C-7 and C-11; H-27a, H-27b to C-9 and C-11; CH_3s -28 and -29 to C-14 (δ_C 78.0); and CH_3-29 to C-18) supported this assignment. An nOe cross-peak between the axial H-7 and H-11 showed that H-11 is also axial and is on the same side as H-7; H-7 also showed an nOe correlation with CH_3-24. Hence, C-11 in **7** has the same relative stereochemistry as in sodwanones A–C [**1**–**3**]. Further support for the trans C-6, -7 ring junction, as in **1**–**3**, came from the multiplicity of H-7 (Experimental) and nOe correlations between the axial H-4 (δ_H 3.18 dt, J=3.0 and 11.3 Hz) and methyls -25 and -26, and between H-11 and H-5 on the other side of the ring system. The pattern of H-18, the C-atom resonances of C-14–C-23 (Table 2) as well as an nOe between H-18 and Me-30 (δ_C 20.4, δ_H 1.31), established the C-18, -19 trans configuration for the second ring system of **7**. The latter trans ring junction was further supported by nOe correlations between the axial H-21 (δ_H 3.12) and methyls -29 (δ_C 14.0, δ_H 1.04) and -31 (δ_C 26.6, 1.23). Two other nOe correlations between Me-29 and H-15 (δ_H 1.82) and between Me-29 and H_2-12 (δ_H 1.42) determined the H-15 β-configuration as well as the β-orientation (towards C-14) of the ethylene bridge (i.e., 14α-OH).

Another compound that was obtained in small amounts (2.5 mg, 0.005% dry wt) was sodwanone E [**8**], $C_{30}H_{50}O_5$, *m/z* 490. Comparison of the nmr data of **8** with those of the above compounds suggested that one half of the molecule (C-14–C-23) had the same 14-hydroxy-22-oxo-perhydrobenzoxepine as sodwanone D [**7**] (Table 2). The absence of sp^2 carbon resonances for the second half of **8** indicated it to be tricyclic. A single carbon resonating at δ_C 110.1 s, which most likely bears two oxygen atoms, together with two additional C-atoms bearing a single oxygen each (δ_C 78.9 s and 80.6 d), could be best explained by the presence of an internal ketal group.

The observation of CH-correlations (HMBC experiment) between the protons of methyls -24 and -25 (δ_H 1.39 and 1.29, α to an oxygen atom) and C-2 and C-3; between H-3 and C-7, and between CH_3-26 and C-7, established the position of the proposed ketal as being between the single oxygen-bearing C-2 and C-3 to the doubly oxygenated C-7. NOe cross-peaks between Me-26 and Me-27, H-8 (axial) (δ_H 2.02) and H-5 (axial) (δ_H 1.55), and between Me-24 and H-5, suggested the relative stereochemistry shown for **8**. Furthermore, the appearance of H-3 as a doublet at δ_H 3.97 ppm suggested either a twisted conformation of the oxepane ring, or a strong influence of the oxygen atoms on one of the H-3 coupling constants which becomes close to zero.

Both sodwanones D and E [**7** and **8**] have the same carbon skeleton as the siphonellinols (e.g., siphonellinol, **5**) (3) and raspacionin A [**6**] (5–7).

Sodwanone F [**9**], $C_{30}H_{50}O_6$, *m/z* 506 (six degrees of unsaturation), contains only sp^3 hybridized carbon atoms and hence must be hexacyclic. In **9**, as in the other sodwanones, two geminal pairs of methyls were observable. According to CH-correlations (Table 2) both pairs were positioned between an oxygen and a proposed hemiketal group. For better resolution, the nmr data of **9** were taken in C_6D_6 and for comparison with raspacionin A [**6**] (5–7) in $CDCl_3$ (see below). HMBC correlations between C-6 and H-7 and CH_3-26, and between CH_3-26, and C-10 and C-11 suggested that one perhydrooxepine-hemiketal system of sodwanone F [**9**] was identical to that in raspacionin A [**6**] (6,7). Indeed, comparison of the nmr data of **9** with those of **6** (6,7) [δ 4.05 (dd, J=11.2 and 5.2 Hz, H-7), 1.32 (s, Me-24) and 1.25 (s, Me-25) for **9** against δ 4.05 (dd, J=10.8 and 5.2 Hz), 1.31 s and 1.25 s, respectively, for **6**, and very similar ^{13}C-nmr chemical shifts, even in C_6D_6] clearly pointed to the identification of half of **9** (C-2–C-11) as the same as that of the corresponding half in raspacionin A [**6**] (6). The second half of **9** (C-14–C-23) is proposed to consist of a very similar tricyclic system to that of **6** based on similar δ_C values, except for the resonance of C-15, which is shifted about 7 ppm upfield in comparison to C-10. We conclude that the two halves differ in the stereochemistry at C-14 and/or C-15. Extensive overlap in the ^{1}H-nmr spectra made nOe measurements very difficult.

The multiplicity of H-18 and the carbon resonances of C-18–23 and C-30 and C-31 unequivocally confirmed the dioxabicyclo[3.2.1]octane system. Furthermore, an nOe correlation between Me-29 and one of the C-20 methylene protons determined the methyl group to be in the β- configuration (opposite to the oxygen bridge and H-18), and in the same equatorial configuration as Me-26. These differences in the chemical shifts of the two halves of **9** (Table 2) would require the inversion of C-15 (in comparison to C-10, i.e., Me-28 must be axial). Indeed, a 1D-TOCSY nmr experiment confirmed the equatorial configuration of H-15 (all J values around 5 Hz). A Dreiding model of this molecule suggests that the cyclohexane ring, C-14–19, is in a twisted chair conformation.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Ir spectra were recorded on a Nicolet 205 Ft-ir spectrophotometer. Low-resolution mass spectra were recorded on a Finnigan-4021 mass spectrometer and high-resolution mass spectra (hrms) were obtained on a VG70 VSEQ instrument. ^{1}H- and ^{13}C-nmr spectra were recorded on Bruker AMX-360 and ARX-500 spectrometers. All chemical shifts are reported with respect to TMS ($\delta_H=0$). Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter using a 1-cm microcell.

COLLECTION AND ISOLATION PROCEDURES.—*Axinella weltneri* (Von Lendenfeld) (class Demospongiae, order Halichondria, family Axinellidae) (No. TASA-92) was collected in Sodwana Bay, South Africa by scuba during the summer of 1992. A voucher sample is deposited in the Zoological Department at Tel Aviv University. The freshly collected sponge was immediately frozen at −25°. The freeze-dried sponge (50 g) was then extracted with EtOAc to give a brown gum (2 g). The latter gum was chromatographed first on a Sephadex LH-20 column, eluted with MeOH-$CHCl_3$-hexane (1:1:2) and then several times on Si gel columns eluted with hexane/EtOAc mixtures to afford: **1** (50 mg, 0.1%), **2** (0.01%), **3** (0.01%), **7** (0.01%), **8** (0.005%), and **9** (0.005%). R_f values (EtOAc-hexane, 1:1) are **1** 0.25, **9** 0.80 and all others approximately 1.0; (EtOAc-hexane, 2:8), **2** 0.18, **3** 0.22, **7** 0.25, **8** 0.35, **9** 0.05.

Sodwanone A [**1**].—Mp 253° (Me_2CO); $[\alpha]_D$ −9°; (c=0.1, $CHCl_3$); ir ν max (neat) 3520, 3400, 2975, 1715, 1613 cm^{-1}; ^{1}H and ^{13}C nmr, see Table 1; COSY, H-4a/-4b, -5a, -5b; H-4b/-5a, -5b, Me-24; H-7/-8a, -9a, Me-24; H-8a/-9a, -9b; H-9a/-9b; H-11/-12a, -12b, Me-27; H-12a/-13a, -13b; H-13a/Me-28, -29; H-20a/-20b, -21a, -21b, Me-29; H-20b/21a, -21b, Me-29; Me-24/-25; Me-30/-31; eims m/z 500 (M$^+$, 40), 482 (M−H_2O, 15), 260 ($C_{16}H_{20}O_3$, decalin part, 15), 246 ($C_{15}H_{18}O_3$, decalin moiety, 100), 234 (m/z 246-H_2O, 62).

Sodwanone B [**2**].—Glass; $[\alpha]_D$ −6° (c=0.1, $CHCl_3$); ir ν max (neat) 3400, 2950, 1713, 1625 cm^{-1}; ^{13}C nmr, see Table 1; ^{1}H nmr δ_H 3.16 ddd (J=13.5, 11.1, and 2.6 Hz, H-4a), 2.90 dd (J=10.7 and 5.1 Hz, H-7), 2.77 dd (J=18.5 and 8.9 Hz, H-21a), 2.62 dt (J=18.5 and 9.4 Hz, H-21b), 2.01 (Me-28), 1.93 m (H-10), 1.55 s (Me-30), 1.52 s (Me-31), 1.35 s (Me-24), 1.30 s (Me-25), 1.25 m (H-11), 1.15 s (Me-29), 1.06 d (J=7.5 Hz, Me-27), 1.04 s (Me-26); COSY, same correlations as for **1**; eims m/z 484 (M$^+$, 91), 248 ($C_{15}H_{20}O_3$, decalin moiety, 50), 234 ($C_{14}H_{18}O_3$, decalin part, m/z 248-CH_2, 100), 188 (80); hreims m/z 484.3188 (calcd m/z 484.3177 for $C_{30}H_{44}O_5$).

Sodwanone C [**3**].—Amorphous powder; $[\alpha]_D$ −35° (c=0.15, $CHCl_3$); ir ν max (neat) 2950, 1715 cm^{-1}; ^{13}C nmr, see Table 1; ^{1}H nmr δ_H 5.90 dd (J=9.3 and 3.2 Hz, H-16), 5.62 dd (J=9.3 and 2.7 Hz, H-17), 3.17 dt (J=3.0 and 11.3 Hz, H-4a), 2.97 dd (J=4.3 and 11.6 Hz, H-7), 2.82 dt (J=5.7 and 14.2 Hz), 1.78 s (Me-28), 1.30 s (Me-24), 1.25 s (Me-25), 1.19 s (Me-30), 1.12 s (Me-31), 1.03 s (Me-29), 0.99 s (Me-26), 0.96 d (J=7.5 Hz, Me-27); COSY, in addition to the correlations of the perhydrobenzoxepine and oxepane moieties, as in **1**, the following correlations were observed: H-16/Me-28; H-17/Me-30, -31; eims m/z 454 (M$^+$, 32), 306 (32), 217 ($C_{15}H_{21}O$, decalin moiety, 24), 203 ($C_{14}H_{19}O$, decalin part, m/z 217−CH_2, 100), 147 (m/z 217−70, 10), 133 (m/z 203−70, 26); hreims m/z 454.3425 (calcd 454.3435).

Sodwanone D [**7**].—Oil; $[\alpha]_D$ +19° (c=0.30, $CHCl_3$); ir ν max (neat) 2960, 1715, 980 cm^{-1}; ^{13}C nmr, see Table 2; ^{1}H nmr δ_H 4.94 s (H-27a), 4.57 s (H-27b), 3.25 dd (J=10.5 and 5.1 Hz, H-18), 3.18 dt (J=3.0 and 11.3 Hz, H-4a), 3.12 m (H-21a), 3.05 dd (J=11.2 and 4.7 Hz, H-7a), 2.28 dd (J=12.7 and 2.2 Hz, H-9a), 1.31 s (Me-30), 1.28 s (Me-24), 1.23 s (Me-31), 1.22 s (Me-25), 1.04 s (Me-29), 0.83 s (Me-26), 0.80 d (J=6.6 Hz, Me-28); eims m/z 488 (M$^+$, 8), 306 ($C_{20}H_{34}O_2$, $C_{15}H_{23}O_2$ left part or right part after water elimination, +C_5H_9, 100); hreims m/z 488.3497 (calcd 488.3489).

Sodwanone E [**8**].—Oil; $[\alpha]_D$ +3° (c=0.1, $CHCl_3$); ^{13}C nmr, see Table 2; ^{1}H nmr, δ_H 3.97 d (J=3.2 Hz, H-3), 3.52 dd (J=10.5 and 5.1 Hz, H-18), 3.20 dt (J=11.3 and 3.0 Hz, H-21a), 2.25 dd (J=11.3 and 2.2 Hz, H-21b), 1.95 m (H-4a), 1.92 m (H-10), 1.89 m (H-15), 1.39 s (Me-24), 1.34 s (Me-30), 1.29 s (Me-25), 1.27 s (Me-31), 1.15 s (Me-29), 1.04 s (Me-26), 0.97 d (J=7.5, Me-27), 0.86 d (J=7.5 Hz, Me-28); COSY, H-3/-4a, -4b, Me-24; H-21a/-21b, -20a, -20b; cims (CH_4) m/z 491 (MH$^+$, 100), 473 (M−OH, 55), 455 (M−OH−H_2O, 20); eims m/z 490 (5), 404 (M−86, 60), 308 (100); hreims m/z 490.3632 (calcd 490.3645).

Sodwanone F [**9**].—Oil; $[\alpha]_D$ −4° (c=0.1, $CHCl_3$); ^{13}C nmr, see Table 2; ^{1}H nmr (C_6D_6) δ_H 4.16 dd (J=12.0 and 4.9 Hz, H-18), 4.06 dd (J=11.2 and 5.2 Hz, H-7), 1.75 m (H-15), 1.65 s (Me-24), 1.57 s (Me-30), 1.38 s (Me-25), 1.37 s (Me-31), 1.18 s (Me-29), 1.15 s (Me-26), 0.86 d (J=7.5 Hz, Me-28), 0.80

d (J=7.5 Hz, Me-27); cims (CH_4) *m/z* 507 (MH^+, 10), 489 (M−OH, 90), 471 ($M-OH-H_2O$, 100); hreims *m/z* 506.3585 (calcd 506.3594).

ACKNOWLEDGMENTS

We would like to thank Professor R.W.M. van Soest, University of Amsterdam, the Netherlands, for the identification of the sponge, PharmaMar, Madrid, for financial support, and Mrs. Y. Aboudi for technical assistance.

LITERATURE CITED

1. A. Rudi, I. Goldberg, Z. Stein, Y. Benayahu, M. Schleyer, and Y. Kashman, *Tetrahedron Lett.*, **34**, 3943 (1993).
2. S. Carmely and Y. Kashman, *J. Org. Chem.*, **48**, 3517 (1983).
3. S. Carmely, Y. Loya, and Y. Kashman, *Tetrahedron Lett.*, **24**, 3673 (1983).
4. S. Carmely and Y. Kashman, *J. Org. Chem.*, **51**, 784 (1986).
5. G. Cimino, A. Crispino, C.A. Mattia, L. Mazzarella, R. Puliti, E. Trivellone, and M. Uriz, *Tetrahedron Lett.*, **31**, 6565 (1990).
6. G. Cimino, A. Crispino, R. de A. Epifanio, A. Madaio, C.A. Mattia, L. Mazzarella, R. Puliti, E. Trivellone, and M. Uriz, *Tetrahedron*, **48**, 9013 (1992).
7. G. Cimino, A. Crispino, A. Madaio, and E. Trivellone, *J. Nat. Prod.*, **56**, 534 (1993).

Received 24 March 1993