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New Triterpene-Ketides (Merotriterpenes), Haliclotriol A and B, from an Indo–Pacific *Haliclona* Sponge

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Abstract—Two new terpene-ketides, haliclotriol A and B (**1** and **3**), have been isolated from the Indonesian sponge *Haliclona* sp. Their structure and relative stereochemical features were determined by 1D and 2D NMR spectroscopy and by converting **1** to its corresponding triacetate **2**. The hexacyclic core of **1** and **3** appears to arise via a biosynthetic cyclization of a hexaprenylbenzoquinone type precursor and **1** has an additional C_2 functionalization on the aromatic ring. Haliclotriol B demonstrated weak antimicrobial activity against *B. subtilis* and *S. aureus*.

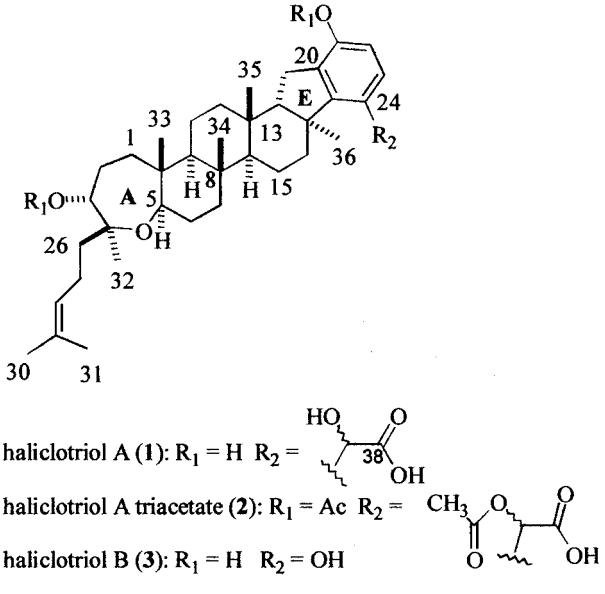
Introduction

Some taxonomic orders of marine sponges appear to be a prolific source of polycyclic terpenoids as a continuing stream of sponge-derived compounds are published each year.[1] Most of these derivatives fall within the sesqui-, di-, or sesterterpene classes. Remarkably, triterpenes, which are the subject of this report, are less commonly encountered even though their occurrence from marine sponges can be traced back to the early 1970s.[2] The Scheuer laboratory was the first, in 1978, to report on sponge-derived polycyclic head-to-tail type triterpenes, the mokupalides.[3] Interestingly, the introduction to Scheuer's paper contained a forward-looking yet still relevant observation; 'sponges … have become recognized for their synthetic virtuosity, which approaches that of microorganisms'. In part, this realization has been a continuing stimulus in our work and partially underlies the results being reported below.

We have an abiding interest in the chemistry of the *Haliclona* sponges as they seem to produce metabolites belonging to many biosynthetic classes. Recently our laboratory reported on two Indo–Pacific members of this genus that are sources of bicyclic terpenoids consisting of the cyclorenierins (sesquiterpenes) from a Vanuatu *Haliclona* sp.,[4] and helianane (a sesquiterpene) from an Indonesia *Haliclona* cf. *fascigera*.[5] By contrast, our investigation of other members of this genus have afforded polycyclic alkaloids including halicyclamine A from an Indonesia *Haliclona* sp.,[6] and a mixture of papuamine and haliclonadiamine from a Papua New Guinea *Haliclona* sp.[7] In a similar fashion, wide ranging metabolites have been discovered by other laboratories from *Haliclona* sponges which vary from steroids,[8] polyketides,[9] an enamide substituted macrolide,[10] to structurally complex alkaloids.[11] The propensity of the *Haliclona* genus to be a source of great chemodiversity made it attractive to begin work on an Indonesian (cup-like) sponge (coll. no. 96544) which initially appeared to be taxonomically similar to *Haliclona* cf. *Fascigera*.[12] We now describe the structures and the properties of a new class of triterpene polyketides, haliclotriol A (**1**) and B (**3**).

Results and Discussion

The characterization of **1** commenced once its molecular



Keywords: terpene-ketides; haliclotriol A and B; *Haliclona* sponge.
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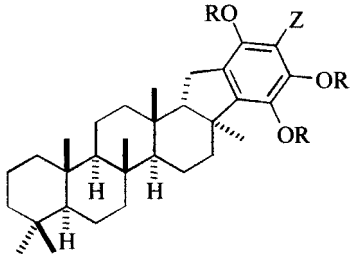
Table 1. NMR properties of haliclotriol A (**1**) and B (**3**) in CD_3OD at 500/125 MHz

C no.	**1**			**3**		
	δC (m)	δH (mult, *J*, Hz)	HMBC	δC (m)	δH (mult, *J*, Hz)	HMBC
1	36.6 t	1.50 m	H3, H33	36.6 t	1.50 m	H3, H33
1′		1.40 m			1.36 m	
2	26.9 t	1.92 m		26.9 t	1.92 m	H3
2′		1.68 m			1.72 m	
3	75.9 d	3.75 d, *J*=6.5	H32, H26, H26′	75.8 d	3.75 d, *J*=6.5	H32
4	81.2 s		H5, H32, H26, H26′	81.2 s		H5, H32
5	78.1 d	3.50 dd, *J*=11.5, 4.5	H33	78.1 d	3.50 dd, *J*=11.5, 4.5	H33
6	28.0 t	1.57 m		28.1 t	1.66 m	
6′		1.37 m			1.34 m	
7	39.8 t	1.65 m	H34	39.8 t	1.70 m	H34
7′		0.96 m			0.90 m	
8	37.9 s		H34	38.0 s		H34
9	58.7 d	0.88 m	H33, H34	58.8 d	0.85 m	H33, H34
10	42.1 s		H33	42.1 s		H33
11	19.8 t	1.70 m		19.4 t	1.72 m	
11′		1.65 m			1.64 m	
12	43.2 t	1.70 m	H35	43.3 t	1.67 m	H35
12′		1.12 m			1.10 m	
13	38.3 s		H35	38.3 s		H35
14	62.4 d	0.93 m	H34, H35, H16, H16′	62.9 d	0.90 m	H34, H35, H16, H16′
15	18.6 t	1.54 m		18.6 t	1.55 m	
15′		1.24 m			1.19 m	
16	40.3 t	2.43 m	H36	38.7 t	2.57 m	H36
16′		1.94 m			1.76 m	
17	49.8 s		H19, H19′, H36	49.6 s		H19, H19′, H36
18	65.3 d	1.70 m	H19, H19′, H35, H36	65.8 d	1.61 m	H19, H19′, H35,H36
19	25.3 t	2.61 dd, *J*=14.5, 6.5		25.8 t	2.57 dd, *J*=14.0, 6.0	
19′		2.43 t, *J*=14.5			2.44 t, *J*=14.0	
20	129.4 s		H19, H19′, H22	130.3 s		H19, H19′, H22,
21	154.4 s		H23	147.2 s		H23, H19, H19’
22	114.1 d	6.53 d, *J*=8.5		113.9 d	6.47 d, *J*=8.5	
23	127.4 d	6.95 d, *J*=8.5	H37	120.6 d	7.13 d, *J*=8.5	
24	126.4 s		H22, H37	142.1 s		H22, H23
25	155.1 s		H19, H19′, H37, H23, H36	151.2 s		H23
26	42.4 t	1.37 m	H3, H32	42.4 t	1.38 m	H3, H32
26′		1.28 m			1.29 m	
27	24.1 t	2.05 m		24.0 t	2.05 m	
27′		1.92 m			1.95 m	
28	125.8 d	5.10 t, *J*=7.0		125.8 d	5.09 t, *J*=7.0	H30, H31
29	131.9 s		H30, H31	131.9 s		H30, H31
30	17.6 q	1.61 s		17.9 q	1.59 s	
31	25.8 q	1.66 s	H30	25.8 q	1.66 s	
32	19.1 q	1.15 s		19.1 q	1.15 s	
33	14.2 q	0.83 s		14.2 q	0.82 s	
34	16.8 q	0.92 s		16.8 q	0.90 s	
35	17.7 q	1.08 s		17.6 q	1.05 s	
36	22.4 q	1.16 s		21.3 q	1.12 s	
37	69.2 d	5.47 s	H23			
38	177.1 s		H37			

formula of $C_{38}H_{56}O_6$, was established. The formula was supported by data including: negative ion LRESIMS *m/z* 607.5 $[M-H]^-$, positive ion HRFABMS *m/z* 591.4055 $[MH-H_2O]^+$ (Δ 0.4 mmu of calcd.), and the DEPT-135 ^{13}C NMR carbon types, $7CH_3+11CH_2+9CH+11C$, for a count of $C_{38}H_{52}$. While the presence of four OH groups was implied by comparing the MS and NMR formulas, additional insights about their exact nature as well describing the other functional groups required the analysis of 1D and 2D NMR spectra. The 1D NMR data confirmed that six of the 11 degrees of unsaturation consisted of a carboxylic acid (δ_C 177.1 s), a trisubstituted phenol (δ_C 154.4 s, 155.1 s, 129.4 s, 127.4 d, 126.4 s, 114.1 d; δ_H 6.53 d, 6.95 d), and a trisubstituted double bond (δ_C 131.9 s, 125.8 d; δ_H 5.10 t). Distinctive among the aliphatic residues were the four oxygen bearing sp^3 carbons (δ_C/δ_H 81.2 s, 78.1 d/3.50 dd,



disidein (4a*): Z = R = H
chlorodisidein triacetate (4b*): Z = Cl, R = $COCH_3$

* Designates absolute stereochemistry

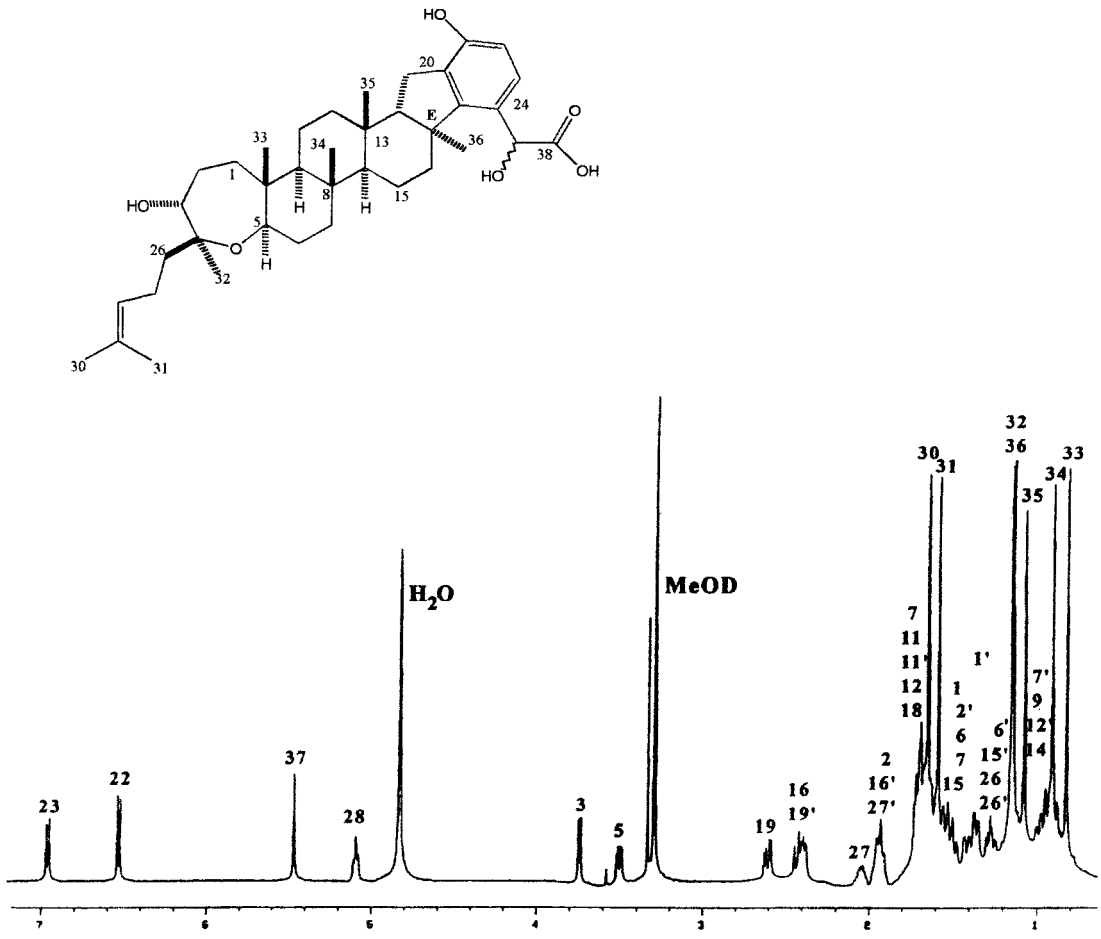
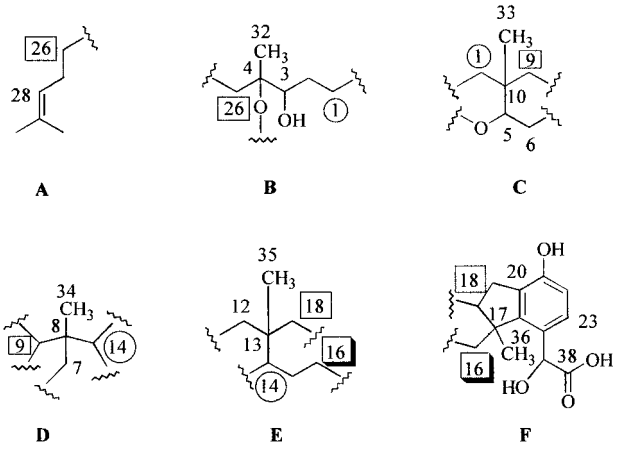


Figure 1. ^{1}H NMR of haliclotriol A (**1**), 500 MHz (CD_3OD).

75.9 d/3.75 d, 69.2 d/5.47 s), two geminal vinylic methyls (δ_C/δ_H 25.8 q/1.66 s, 17.6 q/1.61 s), and five methyls attached to quaternary sp^3 carbons (δ_C/δ_H 22.4/1.16, 19.1/1.15, 17.7/1.08, 16.8/0.92, 14.2/0.83). These moieties were used as input for dereplication leading to the conclusion that the B, C, D, E, and F rings of haliclotriol A (**1**) were similar to those of disidein (**4a**).[10]

In order to utilize the features and physical properties of **4** as a seed, precise NMR assignments were required for **1** and these were made by analysis of the 2D NMR data sets. Further rationalized below is that the ^{1}H-^{1}H COSY NMR correlations pinpointed the presence of six individual aliphatic spin systems and two distinct vinylic spin systems. Furthermore, the HMBC NMR data established the nature of the aliphatic groups attached to each of the five quaternary sp^3 carbons bearing a methyl group. Complete NMR assignments for haliclotriol A are shown in Table 1 and its ^{1}H NMR spectrum appears in Fig. 1.

The task of unraveling the ^{1}H–^{1}H COSY NMR data for the aliphatic residues was complicated because the upfield region (δ 0.9–1.9), as seen in Fig. 1, contained overlapping resonances for approximately 19 hydrogens further obscured by the seven intense singlet methyls. None the less, the six separate spin systems were identified in part from 2D NMR data, by assigning resonances at δ 2.05 (H27), δ 3.75 (H3), δ 3.50 (H5), δ 0.88 (H9), δ 2.43 (H16), δ 2.61 (H19) each of which were subsequently used as anchor points for developing the connectivites of substructures **A**–**F**, respectively shown in Fig. 2. Thus, the



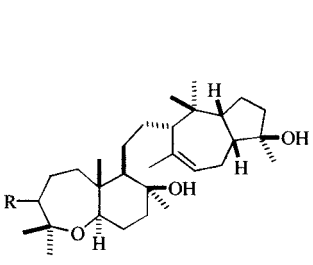
Important HMBC correlations
B: Me32 ⟶ C3, C4, C26; $H_2$1 ⟶ C3
C: Me33 ⟶ C1, C10, C5, C9
D: Me34 ⟶ C7, C8, C9, C14
E: Me35 ⟶ C12, C13, C14, C18; $H_2$16 ⟶ C14
F: Me36 ⟶ C16, C17, C18, C25; $H_2$19 ⟶ C17, C18, C20, C25; H22 ⟶ C20, C24; H37 ⟶ C23, C24, C25, C38; H23 ⟶ C21, C37

Figure 2. Substructures **A**–**F** emphasizing common atoms.

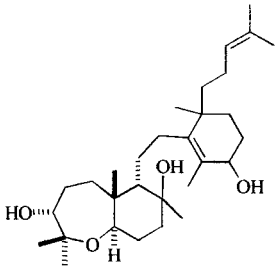
4-methyl-3-pentenyl substructure (**A**) was elaborated based on the assignment of allylic protons $H_2$27 that were in turn coupled to the vinylic H28 (δ 5.10 t, J=7.0 Hz), and the diagnostic shifts of the geminal vinylic methyls at δ 1.66 (C31) and δ 1.61 (C30). Long range ^{1}H–^{1}H COSY correlations from $H_3$30 and $H_3$31 to H28 completed the assignment of **A**.

Elucidation of the remaining substructures required 2D ^{13}C–^{1}H NMR data. In a straightforward manner the one bond C–H NMR assignments, shown in Table 1 and derived from an HMQC spectrum, provided the basis to interpret the HMBC spectrum. Attention was first focused on the five upfield singlet methyl protons and Fig. 2 summarizes the correlations from each of these methyl groups to their neighboring carbons. The simplest situation involved the three HMBC correlations observed from Me32 to C3, C4 and C26 plus the correlation observed from $H_2$1 to C3 which together fully defined substructure **B**. Similarly, the individual sets of four HMBC correlations to methyl group protons Me33, Me34, Me35 along with the relationships shown in Fig. 2 justified substructures **C**, **D** and **E**. Substructure **F** was derived by initially establishing the juxtaposition of Me36 to C16, C17, C18 and C25. This latter carbon was part of the tetrasubstituted phenol ring which contained the ortho coupled protons H22 (δ 6.53) and H23 (δ 6.95). The additional atoms within or attached to the aromatic ring were pinpointed by the HMBC correlations from $H_2$19 to C17, C18, C20 and C25; from H37 to C23, C24, C25, C38; and from H23 to C21, C37. Collectively these correlations supported the indane ring system with an OH substitutent at C21, and the α-hydroxyl carboxylate at C24 shown in substructure **F**. At this juncture it was clear that the termini of haliclotriol A were moieties **A** and **F**. Finally, it was possible to establish the entire connectivity sequence of **A**–**B**–**C**–**D**–**E**–**F** because each substructure possessed one or more atoms in common as shown by the codes in Fig. 2.

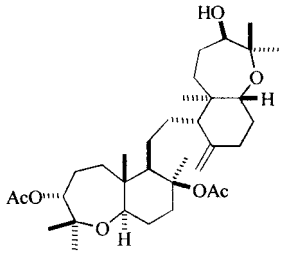
Many additional atom connections could now be made to unambiguously establish the nature of the remaining four rings. Three fused six-membered rings further annulated to the indane substructure (**F**) were proposed based on parallelisms between the ^{13}C NMR shifts of chlorodisidein triacetate **4b**[13] and **1** as shown in Fig. 3. Particularly striking was that the δ values for many C and CH_2 groups in rings B/C/D/E were similar between these two compounds. The last step in fully assembling ring C in **1** was to insert the missing CH_2 (see Fig. 2) at δ 19.8 t (C11) between C9 and C12. The A-ring constitution was established by the HMBC correlation observed from H5 to C4 which required the sequence –C4–O–CH5– thereby allowing substructures **B** and **C** to be joined in an oxepane ring. Additional evidence in



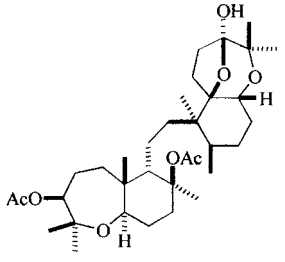
sipholenol A (**5a***): R = αOH
epi-sipholenol A (**5b***): R = βOH



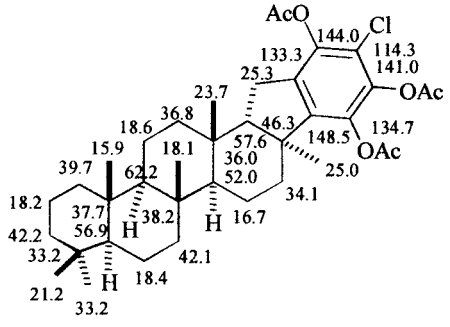
siphonellinol (**6**)



raspocionin (**7**)



raspacionin A (**8**)



4b[13]

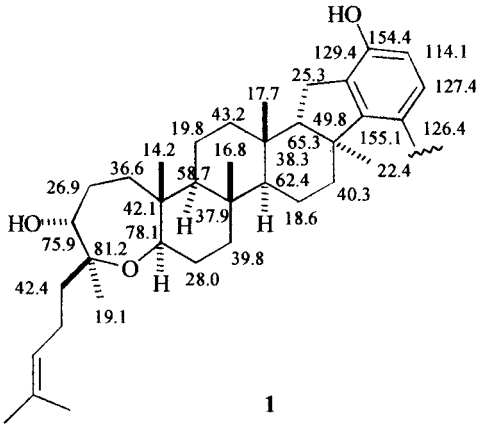


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Figure 3. Parallel ^{13}C NMR shifts of disidein derivative **4b** and haliclotriol A (**1**).

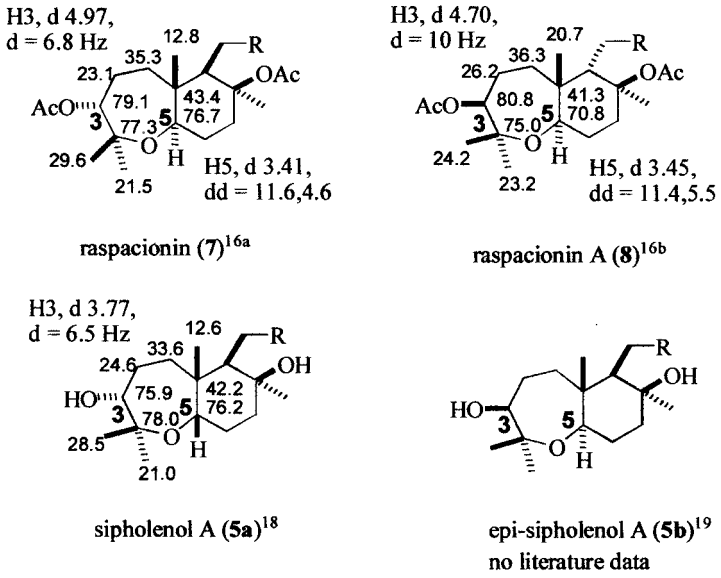


Figure 4. Sensitivity of NMR data to C3 stereochemical changes.

supporting this conclusion was obtained by converting **1** to its triacetate (**2**). As expected the key differences in the ^{1}H NMR between **1** and **2** were at H3 (**1**: δ 3.75; **2**: 4.92), and H37 (**1**: δ 5.47; **2**: 6.31) and in the ^{13}C NMR at C3 (**1**: δ 75.9; **2**: 78.6), C21 (**1**: δ 154.4; **2**: 148.8), and C37 (**1**: δ 69.2; **2**: 73.2). Finally the B-ring ^{13}C NMR shifts were similar to those of the fused oxepane–cyclohexane rings of sponge metabolites including the sipholenols (**5a**),[14] siphonellinols (**6**),[15] raspacionins (**7**–**8**),[16] and the sodwanones.[17]

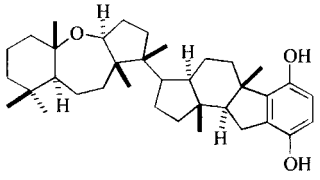
Attention was shifted next to defining the relative stereochemical relationships for each of the 11 chiral centers present in haliclotriol A (**1**). The data of Fig. 3 shows that the relative upfield ^{13}C NMR shifts of the four axial methyls (Me33, Me34, Me35, Me36) of dysidein (**4**), shown by X-ray analysis to have all trans-fused rings, are similar to those of haliclotriol A (**1**). Consequently, these parallelisms implicate that **1** and **4** have the same relative geometry across each of the fused rings. In addition, there were slight differences between these two compounds in the shifts of ring D carbons and of Me35 and Me36. These intimate slightly variations in the conformation of the D-ring, which adopts a boat conformation in **4b**.[13b] The Me32 shift of δ 19.1 in **1** indicates it is axial which is analogous to the shifts of the ring A axial Me32 (δ 21.2) in **4b** and the ring A axial Me32 (δ 21.0) in sipholenol A (**5a**) and in raspacionin (**7**). The presence of a pseudo equatorial C3 hydroxyl in **1** is based on the sensitivity of NMR data in a *trans* fused oxepane–cyclohexane to changes in the C3-OH stereochemistry as shown in Fig. 4. Model data for a pseudo-axial OH/OAc is provided by sipholenol A (**5a**) (δ_H 3.77 J=6.5 Hz)[18] and raspacionin (**7**) (the CH(OH) group at δ_C/δ_H 77.0/3.83 J=5 Hz, and CH(OAc) group at δ_C/δ_H 79.1/4.97 J=6.8 Hz,)[16a] and whereas data for a pseudo-equatorial OAc is represented by raspacionin A (**8**) (δ_C/δ_H 80.8/4.70 J=10 Hz)[16b] and by epi-sipholenol A (**5b**).[19] Only the former data set is similar to that of **1** (δ_C/δ_H 75.9/3.75 J=6.5 Hz). The final structure depicts all of the relative stereochemical details proposed at all chiral centers except C37 for haliclotriol A (**1**). Attempts to obtain additional stereochemical information were thwarted because efforts to form MTPA esters[19] of **1** were unsuccessful.

Structure elucidation of haliclotriol B (**3**) was greatly facilitated by making comparisons to the properties of **1**. The molecular formula of **3** was established as $C_{36}H_{54}O_4$ from the HRFABMS m/z=573.3915 $[M+Na]^+$ (Δ −0.5 mmu of calcd). Chemical shift data in Table 1 indicated that substructures **A**–**E** (Fig. 2) were identical in both **1** and **3**. Alternatively, it was clear that the major differences in these two compounds were in substructure **F** because the largest differences in ^{13}C NMR data between **1** and **3** included: C21 (**1**: δ 154.4; **3**: 147.2), C23 (**1**: δ 127.4; **3**: 120.6), C24 (**1**: δ 126.4; **3**: 142.1), and C25 (**1**: δ 155.1; **3**: 151.2). The $C_2H_2O_2$ difference in the formulas between **1** and **3** was consistent with the α-hydroxyl acetic acid substitutent at C24 in **1** being replaced by an OH in **3**. The supporting data for this conclusion were the downfield shift of 15.7 ppm at C24 in **3** versus that in **1** and the absence of the chemical shifts in **1** of δ 69.2 (C37) and δ 177.1 (C38). The ^{1}H NMR spectrum of **3** showed the familiar ortho coupling pattern (J=8.5 Hz) for the aromatic protons H22 (δ 6.47) and H23 (δ 7.13), giving evidence for a tetra substituted benzene ring. Also consistent with the aromatic ring substructure were the HMBC correlations from C20 to H19/19′ and H22 and from C24 to H22 and H23. In summary, the overall structure including relative stereochemical details shown for **3** is based on analogies to the arguments advanced above for **1**.

The biological activity properties of the triterpenes isolated in this study were investigated. This was in part stimulated by the cytotoxicity associated with the other sponge derived triterpenes **5**–**8**. No cytotoxicity responses were obtained for **1** and **3** in the Corbet–Valariote soft agar screen.[20] Alternatively, weak antimicrobial activity was observed for haliclotriol B (**3**) at 1 mg disk against *B. subtilis* and *S. aureus*, respectively.

Conclusions

The major structural portion of haliclotriols A and B is derived from the cyclization of a hexaprenoid precursor. Remarkably, the scant number of sponge derived triterpenes reported to date are derived from the biosynthetic cyclization of a squalene epoxide,[21] somewhat analogous to the circumstance for terrestrial triterpenes.[22] There are no close analogies in the literature to the entire structure of **1**, which combines a polycyclized prenylated hexaprenoid with an aromatic ring further functionalized by a two carbon containing moiety. The squalene epoxide derived triterpene triols including the sipholanes, the siphonellanes and the raspacionanes, all possessing a fused oxepane–cyclohexane ring system, are only distantly related to **1**. Alternatively the sponge derived triterpenes arising from hexaprenoid hydroquinone epoxide frameworks such as shaagrockols B and C,[23a] the toxicols A–C[23b] (**9**), or adocisulfate-2[24] are closer analogies to **3** but are structurally quite different. The overall details of the biogenesis of these non-squalene derived merotriterpenoids could be along the pathways elucidated by Simpson[25] for highly rearranged merosesquiterpenes.



toxicol B (**9**)

Experimental

General experimental procedures

NMR spectra were recorded at 500 MHz (^{1}H) and 125 MHz (^{13}C) in CD_3OD and $CDCl_3$. Carbon multiplicities were determined using DEPT-135 data. Atom connectivities were determined using HMQC, HMBC, and ^{1}H–^{1}H COSY data. Low resolution electrospray ionization mass spectrometry (ESIMS) and high resolution fast atom bombardment mass spectrometry (FABMS) were employed. Optical rotations were determined on a digital polarimeter in CH_2Cl_2 or MeOH. Flash chromatography was carried out on Si gel (200-400 mesh) and size exclusion chromatography was performed using Sephadex LH-20 (gel permeation).

Animal materials

The sponge (0.13kg dry wt., coll. no. 96544) was collected using SCUBA from the Indonesian Island of Mayu (site #1 N1° 20.854′ E126° 23.482′; site #2 N1° 19.699′ E 126° 25.129′). The specimen was identified as *Haliclona* sp. (family Chalinidae; order Haplosclerida) by Dr M. C. Diaz (UCSC). The sponge was soft in consistency and shaped as a cup or tube, with thin walls (<5 mm in thickness). Its color is pink externally and tan-pinkish internally. The surface is spiky (thin spikes 2–4 mm high separated for

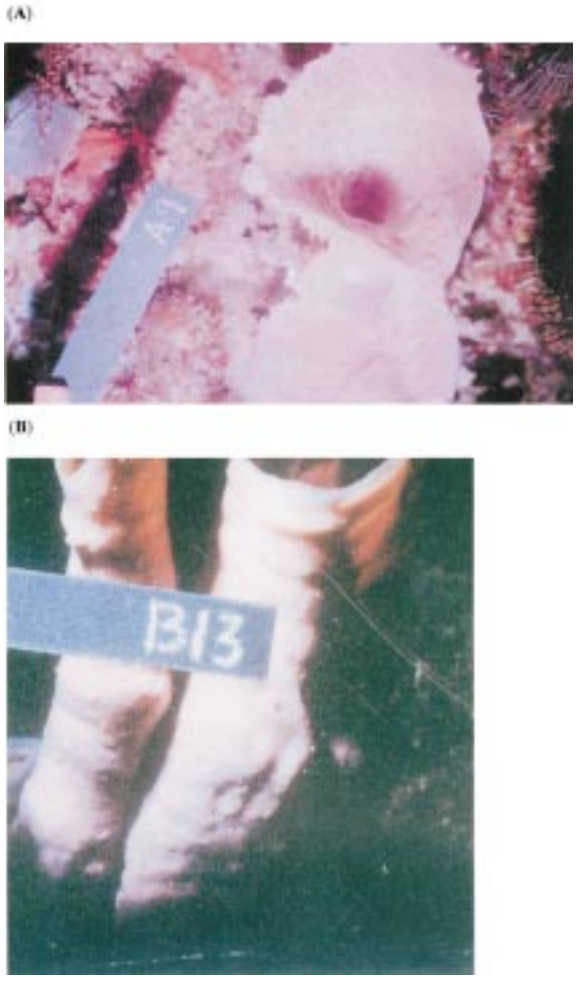


Figure 5. Underwater photos of (A) *Haliclona sp.* (coll. No. 96544) and (B) *Haliclona* cf. *Fascigera* (coll. No. 95503).

up to 1 cm). The oscules are round and simple (1–2 mm in diameter) and are regularly distributed in the inner wall. The skeleton consisted of a typical isotropic unispicular reticulation with multispicular tracts (50–120 μm in diameter) running longitudinally to the sponge body. The spicules were oxeas (120–150)×(4–6) mm in length and width. As can be seen in Fig. 5, the sponge is overall very similar to *Haliclona fascigera*,[12b] however, the spiky surface is atypical for *fascigera*,[12a] and is therefore classified as a different, undescribed species. A voucher is in the UCSC sponge collection archives and underwater photos are shown in Fig. 5.

Extraction and isolation

The sponge was preserved and processed according to our standard procedures.[26] The CH_2Cl_2 (2.01 g) and 50% aqueous methanol (1.08 g) soluble fractions were subjected to Sephadex column chromatography (100% MeOH) to afford 257.4 mg of **1** (0.002% yield of dry sponge) and 29.5 mg of **3** (0.0002% yield of dry sponge), respectively.

Haliclotriol A (1). A brown powder: $[\alpha]_D^{25}=-39.4$ (c=7.63, MeOH); UV (MeOH) λ_{max} 278, 226, 214; IR ($CHCl_3$) ν_{max} 3383, 2934, 2854, 1720, 1588, 1447, 1386, 1222, 1061, 787, 728, 670 cm^{-1}; LRESIMS, negative ion,

m/z $[M-H]^-$ 607.5; HRFABMS *m/z* $[MH-H_2O]^+$ 591.4055 (cald. for $C_{38}H_{55}O_5$, 591.4051); ^1H and ^{13}C NMR data are shown in Table 1.

Haliclotriol B (3). A white powder: $[\alpha]_D^{25}=-9.5$ (c=1.86, MeOH); UV (MeOH) λ_{max} 278, 226, 214; IR ($CHCl_3$) ν_{max} 3462, 2944, 2838, 1602, 1224, 1016, 786, 740, 666 cm^{-1}; LRESIMS, negative ion, *m/z* 573.4 $[M+Na]^+$; HRFABMS *m/z* $[M+Na]^+$ 573.3915 (cald. for $C_{36}H_{54}O_4Na$, 573.3915); ^1H and ^{13}C NMR data are shown in Table 1.

Conversion of 1 to 2. Approximately 20.0 mg of **1** was dissolved in 0.5 mL of pyridine and 1.0 mL of Ac_2O. The mixture was stirred overnight at room temperature followed by rotoevaporation with toluene to afford pure **2** in quantitative yield as a tan solid: LRESIMS, positive ion, *m/z* 757.3 $[M+Na]^+$;^1H NMR (CD_3OD, 500 MHz) 7.23 (1H, d, J=8.5 Hz, H23), 6.80 (1H, d, J=8.5 Hz, H22), 6.31 (1H, s, H37), 5.08 (1H, t, J=7.0 Hz, H28), 4.92 (1H, d, J=6.5 Hz, H3), 3.35 (1H, dd, J=11.5, 4.5 Hz, H5), 2.49 (1H, m, H19) 2.40 (1H, m, H19′), 2.5–0.8 (23H, m), 2.26 (3H, s, Ac), 2.09 (3H, s, Ac), 1.97 (3H, s Ac), 1.67 (3H, s), 1.60 (3H, s), 1.08 (3H, s), 1.08 (3H, s), 1.06 (3H, s), 0.92 (3H, s), 0.85 (3H, s), ^{13}C NMR (CD_3OD, 125 MHz) 176.2 s (C38), 156.3 s (C25), 148.8 s (C21), 136.1 s (C20), 132.3 s (C31), 130.0 s (C24), 129.1 d (C23), 125.4 d (C30), 120.2 d (C22), 80.2 s (C4), 79.2 d (C5), 78.6 d (C3), 73.2 d (C37), 64.9 d (C18), 62.0 d (C14), 58.8 d (C19), 49.6 s (C17), 43.0 t (C12), 42.2 t (C26), 42.0 s (C10), 39.6 t (C16), 39.3 t (C7), 38.3 s (C13), 37.9 s (C8), 37.4 t (C1), 27.9 t (C6), 26.1 t (C2), 25.8 q (C31), 24.5 t (C19), 23.7 t (C27), 21.9 q (C31), 19.6 t (C11), 18.8 q (C32), 18.5 t (C15), 17.6 q (C30), 17.6 q (C35), 16.8 q (C34), 13.9 q (C33), three acetate carbonyls 172.3 s, 171.9 s, 170.4 s, three acetate methyls 21.1 q, 20.7 q, 20.9 q.

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