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22) If the N^+-O bond of **8** is homolytically cleaved, amine radical cation and $[FeO]^{2+}$ is formed. The same intermediate (**8**), therefore, may be formed in mechanism A.

Faculty of Pharmaceutical Sciences,
University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo, 113,
Japan

NAOKI MIYATA
HIROKO KIUCHI
MASAAKI HIROBE*

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Foliaspongin, an Antiinflammatory Bishomosesterterpene from the Marine Sponge *Phyllospongia foliascens* (PALLAS)

An antiinflammatory bishomosesterterpene named foliaspongin has been isolated from the Okinawan marine sponge *Phyllospongia foliascens* (PALLAS) and the structure (**1**) of a new scalarane-type has been proposed on the basis of chemical and physicochemical evidence.

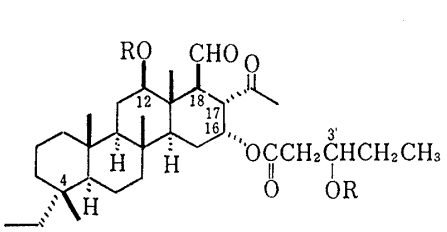
Keywords——marine sponge; *Phyllospongia foliascens*; scalarane-type bishomosesterterpene; foliaspongin; CI-MS; ^{1}H NMR; ^{13}C-NMR; UV

Scalarane-type sesterterpenes have been revealed to occur in some species of marine sponge by several groups in recent years.[1-3] As a continuing study in search of bioactive substances from marine natural products,[4,5] we have been investigating chemical constituents of the marine sponge *Phyllospongia foliascens* (PALLAS) (order Ketatosa),[6] collected in Okinawa Prefecture. Recently, we isolated from this sponge a new scalarane-type bishomosesterterpene named foliaspongin which showed an antiinflammatory activity. This paper deals with evidence supporting the structure (**1**).

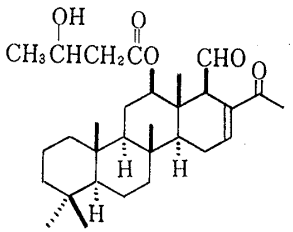
The MeOH extract of the fresh sponge (28 kg) was partitioned into an EtOAc-water mixture and chromatographic purification of the EtOAc soluble portion furnished foliaspongin (**1**) (120 mg), $C_{32}H_{52}O_6 \cdot H_2O$,[7] mp 186—189° (MeOH), $[\alpha]_D$ +44° ($CHCl_3$), CI(NH_3)-Mass: *m/z*

550 [25%, $(M+NH_4)^+$], UV (MeOH): transparent above 210 nm, IR (KBr): 3430 (OH), 1710 (CO) cm^{-1}. The CD spectrum (MeOH) of foliaspongin (**1**) shows a positive maximum: $[\theta]_{286}$ +19000, ascribable to an $n\rightarrow\pi^*$ transition of a carbonyl group. The ^{13}C NMR spectrum shows signals due to a methylketone moiety [δ_c 208.6 (s), 28.5 (q)], an aldehydic carbon [204.1 (d)], an ester carbonyl carbon [171.9 (s)], three carbinyl carbons [79.7 (d), C-12; 69.7 (d), C-3′; 68.9 (d), C-16], four quaternary carbons (45.5, 37.5, 36.9, 36.1, all s), five tertiary carbons (58.7, 58.5, 58.2, 51.5, 50.5, all d), ten methylene carbons (42.0, 41.7, 40.2, 36.6, 29.7, 28.9, 27.5, 25.4, 24.5, 18.3, all t), and six methyl carbons (18.0, 17.1, 17.0, 10.1, 9.9, 8.6, all q).

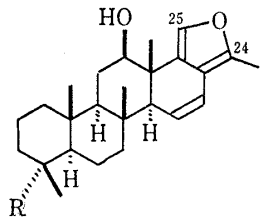
On pyrolysis (240°, 2 min, under a N_2 atmosphere), foliaspongin (**1**) furnished a furanoid derivative (**4**), $C_{27}H_{40}O_2$ (high mass), mp 157—159° (MeOH), $[\alpha]_D$ −120° (MeOH), as was reported in the pyrolytic conversion from a scalarane-type homosesterterpene (**2**) to a furanoid compound (**3**).[2] The UV spectrum (MeOH) of the furan (**4**) shows absorption maxima at 223 nm (ε=8500), 230 (9900), and 240 (11000) which are very similar to those of **3**.[2,8] Furthermore, the ^1H NMR spectrum supports the presence of a conjugated α-methylfuran moiety by signals at δ 2.23 (3H, s, 24-CH_3), 5.67 (1H, d.d, J=10, 2 Hz, 16-H), 6.38 (1H, d.d, J=10, 2.5 Hz, 15-H), and 7.24 (1H, s, 25-H),[9] and also shows the presence of a 12β-OH group and a 4-ethyl moiety by a signal at δ 3.84 (1H, d.d, J=11, 4 Hz) and a triplet at δ 0.72 (3H, J= 7 Hz), together with four C-methyl groups (δ 0.77, 0.86, 0.98, and 1.01, each 3H, all s).[2] The



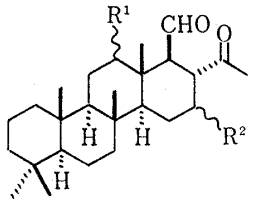
1 : R=H
1a : R=Ac



2



3 : R=CH_3
4 : R=CH_2CH_3



5 : R^1=α-OH, R^2=α-OAc
6 : R^1=β-OH, R^2=β-OAc

Chart 1

TABLE I. ^{1}NMR Data for **1**, **1a**, **3**, **5** and **6**

	12-H	16-H	17-H	18-H
1	3.79[a]	5.63 (m)	3.27 (d.d, J=3, 12)	2.93 (d, J=12)
1a	4.89 (d.d, J=4, 11)	5.65 (m)	3.24 (d.d, J=3, 12)	2.95 (d, J=12)
2	4.86 (d.d, J=4, 11)	—	—	—
5	—	5.62 (q, J=*ca.* 2)	3.13 (d.d, J=10.8, 2.7)	3.45 (br. d, J=10.8)
6	3.69 (d.d, J=10, 5)	4.66 (d.d.d, J=5, 11, 11)	3.21 (d.d, J=11, 11)	2.65 (d.d, J=11, 1)

a) The coupling pattern is unclear due to its overlapping with a signal due to 3′-H.

high resolution mass spectrum of **4** not only shows the close relationship between structures of **4** and **3**, but also suggests that **4** comprises one more methylene moiety in its A or B ring moiety as compared to **3**. Thus, it gives an ion peak of $C_{27}H_{38}O$ (M^+-H_2O) and a fragment ion peak of *m/z* 205, which is derivable from the A/B ring and contains 14 mass-unit more than the corresponding ion peaks from **3**, together with ion peaks at *m/z* 175, 172, 159, 148, 147 (base peak), and 146, all of which also occur in the mass spectrum of **3**.[10] Based on these evidence and a biogenetic consideration that the marine sponge of same kind collected in Australia were known to produce four scalarane-type compounds having a 4α-ethyl moiety in their structures,[2] the furan derivative (**4**) has been presumed to be a 4α-ethyl homolog of **3**. Consequently, foliaspongin (**1**) has been shown to be an acylated derivative of a scalarane-type bishomosesterterpene possessing a 4α-ethyl moiety.

Reduction of foliaspongin (**1**) with lithium aluminum hydride liberated pentane-1,3-diol,[11] thus the presence of a 3-hydroxypentanoate moiety being substantiated. Acetylation of foliaspongin (**1**) yielded a diacetate (**1a**), $C_{36}H_{56}O_8$, mp 175—176° (MeOH), $[\alpha]_D$ +45° ($CHCl_3$), CI(NH_3)–Mass: *m/z* 634 [16%, $(M+NH_4)^+$], IR (CCl_4): no hydroxyl, 1740 (ester CO), 1720 (CO) cm^{-1}.

Finally, examinations including decoupling experiments of the ^1H NMR spectra of **1** and **1a** in comparison with those of **5**,[1] **2**, and **6**,[2] have revealed the location of an acyloxyl function and configurations at C-16, C-17, and C-18 (Table I).

The above-described evidence has now led us to propose the structure **1** for foliaspongin. The biological activities of foliaspongin will be reported elsewhere.

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Tokyo Research Laboratories,
Fujisawa Pharmaceutical Co., Ltd.,
3-8-3, Nukuikitamachi, Koganei,
Tokyo, 184, Japan

Hiroyuki Kikuchi
Yasumasa Tsukitani
Iwao Shimizu

Faculty of Pharmaceutical Sciences,
Osaka University,
133-1, Yamada-kami, Suita,
Osaka 565, Japan

Motomasa Kobayashi
Isao Kitagawa*

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