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STELLETTIN A, A NEW TRITERPENOID PIGMENT
FROM THE MARINE SPONGE *STELLETTA TENUIS*

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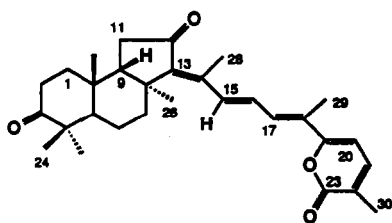
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ABSTRACT.—A new isomalabaricane triterpenoid, stellettin A [**1**], was isolated from the sponge *Stelletta tenuis* collected off Hainan Island, People's Republic of China. Its structure and stereochemistry were established by analysis of its spectral data and reference to related compounds.

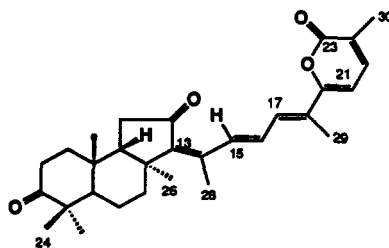
Chemical investigations of sponges in the genus *Stelletta* have resulted in the isolation of steroids, alkaloids, and triterpenoids (1–3). The triterpenoids belong to the rare isomalabaricane class which has only been reported from *Stelletta* and *Jaspis* species (4–6) of sponges, and several isomalabaricanes have been reported to inhibit significantly the growth of L1210 and KB cancer cells. Malabaricane-type triterpenes were first isolated from the wood of the tree *Ailanthus malabarica* (7). Recently, in our research on the sponge *Stelletta tenuis* Lindgren (Stellettidae), we have isolated a new cytotoxic isomalabaricane designated stellettin A [**1**]. The structure was deduced from comparison of its spectral data with that of a closely related known compound.

An EtOH extract of dried *S. tenuis* was partitioned between EtOAc and H₂O. Si gel chromatography of the EtOAc extract afforded **1**, which was obtained as yellow needles, mp 235–235° [α]_D²⁰ + 28.8° (*c* = 0.16, MeOH). The high-resolution fabms, *m/z* 463.2874 [M+H]⁺

revealed the molecular formula C₃₀H₃₈O₄, and the uv spectrum (see Experimental) revealed an extended conjugated system like that of **2**, an isomalabaricane-type triterpenoid isolated from a *Stelletta* sp. (3). Its ir spectrum showed the presence of three types of carbonyl groups (1732, 1712, 1685 cm⁻¹), just as in **2**. Comparison of the ¹H-nmr data of **1** (see Table 1) and **2** revealed the two sets of data to be nearly identical except that the signal for H-28 of **1** was observed at lower field (δ 2.35 instead of δ 2.07) and that of H-15 was observed at higher field (δ 6.99 instead of δ 8.26). This indicated that H-28 was deshielded by the C-12 keto group in **1** and so must be *cis*- to it while H-15 is *trans*- to the ketone. Thus structure **1**, with stereochemistry identical to that of **2** except that the configuration at C-13,14 is *E*, was assigned to this new triterpene. Unfortunately, a ¹³C-nmr spectrum was not obtained due to decomposition of the sample. The instability of these types of compounds has been noted earlier (3).



1



2

TABLE 1. $^1\text{H-Nmr}$ Data of **1** and **2** in CDCl_3 .

Proton	Compound	
	1	2 ^a
H ₃ -24	1.12 (3H, s)	1.12 (3H, s)
H ₃ -25	1.42 (3H, s)	1.41 (3H, s)
H ₃ -26	1.03 (3H, s)	1.06 (3H, s)
H ₃ -27	0.83 (3H, s)	0.86 (3H, s)
H ₃ -28	2.35 (3H, s)	2.07 (3H, s)
H ₃ -29	2.03 (3H, s)	2.03 (3H, s)
H ₃ -30	2.12 (3H, s)	2.12 (3H, s)
H-15	6.99 (1H, d, $J=15$ Hz)	8.26 (1H, d, $J=15$ Hz)
H-16	6.94 (1H, dd, $J=15$ and 12 Hz)	6.97 (1H, dd, $J=15$ and 11 Hz)
H-17	7.27 (1H, d, $J=12$ Hz)	7.26 (1H, d, $J=11$ Hz)
H-20	6.22 (1H, d, $J=7.0$ Hz)	6.22 (1H, d, $J=6.6$ Hz)
H-21	7.14 (1H, d, $J=7.0$ Hz)	7.14 (1H, d, $J=6.6$ Hz)

^aData taken from McCabe *et al.* (3).

Stellettin A [**1**] was quite toxic to P388 leukemia cells, exhibiting an ED₅₀ value of 0.001 $\mu\text{g/ml}$.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—The mp (uncorrected) was measured on a X4 microscale melting point apparatus. The specific rotation was measured with a Rudolph Autopol III automatic polarimeter. The ir spectrum was obtained on a Nicolet 205 Ft-ir spectrophotometer; the uv spectrum on a Hewlett-Packard spectrophotometer, the nmr spectrum at 300 MHz on a Varian VMR 300 instrument; and the mass spectrum on a VG ZAB mass spectrometer.

ANIMAL MATERIAL.—The sponge *Stelletta tenuis* was collected off Hainan Island, People's Republic of China, in April 1991. A voucher specimen (No. 91-6) was deposited in the Research Center of Organic Natural Products, Zhongshan University, Guangzhou, People's Republic of China.

EXTRACTION AND ISOLATION.—Chopped, sun-dried specimens (2.5 kg) were extracted with EtOH. The extract was evaporated *in vacuo* to give a dark brown syrup (246 g). This was partitioned between EtOAc and H₂O. The EtOAc-soluble fraction (56.8 g) was subjected to vacuum flash chromatography over Si gel, using solvents of gradually increasing polarity. From the fraction eluted with EtOAc-petroleum ether (7:3), 15 mg of **1** was obtained as yellow needles [after crystallization from EtOAc-petroleum ether (1:1)], mp 234–5°; $[\alpha]_D^{20} + 28.8^\circ$ ($c=0.16$, MeOH). Ir (KBr) ν max 2975, 2950, 2870, 1732, 1713, 1685, 1608, 1400, 1385, 1180, 1100 cm^{-1} ; uv (MeOH) λ max (ϵ) 396 (30200), 312 (12780), 302 (11720), 248 (4188) nm; hrfabms m/z 463.2874 $[\text{M}+\text{H}]^+$

(calcd for $\text{C}_{30}\text{H}_{30}\text{O}_4$, 463.2848), lrfabms m/z 463 $[\text{M}+\text{H}]^+$ (100), 309 (18.4), 292 (24.8), 273 (27.2), 242 (20.5), 169 (21.1), 151 (22.7), 107 (98.5); $^1\text{H-nmr}$ data in CDCl_3 are reported in Table 1; $^1\text{H-nmr}$ (C_6D_6) δ 0.53 (3H, s), 1.00 (3H, s), 1.03 (3H, s), 1.09 (3H, s), 1.63 (3H, s), 1.90 (3H, s), 2.64 (3H, s), 5.52 (1H, d, $J=7$ Hz), 6.28 (1H, d, $J=7$ Hz), 6.85–7.05 (2H, m), 7.57 (1H, d, $J=11$ Hz); $^1\text{H-nmr}$ ($\text{Me}_2\text{CO}-d_6$) δ 0.86 (3H, s), 1.01 (3H, s), 1.12 (3H, s), 1.49 (3H, s), 2.04 (3H, s), 2.11 (3H, s), 2.35 (3H, s), 6.47 (1H, d, $J=7$ Hz), 7.00–7.25 (3H, m), 7.35 (1H, d, $J=12$ Hz).

ACKNOWLEDGMENTS

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