

A New Isomalabaricane Triterpenoid from Sponge *Jaspis sp.*

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Abstract: From the marine sponge *Jaspis sp.*, a new isomalabaricane triterpenoid 22, 23-dihydrostelletin D (**1**) was isolated, and its structure was established on the basis of IR, MS and extensive 2D NMR spectroscopic analysis. It is a unique skeleton compound rarely obtained from Chinese marine organisms.

Keywords: *Jaspis sp.*, 22, 23-dihydrostelletin D, structural elucidation.

Isomalabaricane-type triterpenoids are a rare group of triterpenoids with unique skeleton mainly discovered in some genus of marine sponges¹⁻⁷. Some of isomalabaricanes possessed potential anti-tumor activities¹⁻⁵. For searching antitumor compounds from marine organisms, the marine sponge *Jaspis sp.* was collected at Hainan Island. A detailed silica gel column chromatographic separation of the dichloromethane extract led to a new isomalabaricane triterpenoid 22, 23-dihydrostelletin D **1**. This report intends to describe the structural elucidation of compound **1**.

Compound **1** was obtained as a pale yellow amorphous powder, its molecular formula C₃₂H₄₄O₅ was established by HRESIMS spectrum (*m/z* 509.3236 [M+1]⁺, calcd. for C₃₂H₄₅O₅ 509.3267). The IR absorptions at 1725, 1692, 1600 cm⁻¹ suggested the presence of two conjugated carbonyl groups. ¹H NMR spectrum exhibited eight methyl singlets at δ_H 0.80 (s, Me), 1.00 (s, Me), 1.04 (s, Me), 1.13 (s, Me), 1.82 (s, Me), 1.90 (s, Me), 1.95 (s, Me), and 1.89 (s, Me), of which three signals (δ_H 1.82, 1.90, 1.95) were attributed to olefinic methyls, and one (δ_H 1.89) was assigned for acetyl methyl group. Moreover, there were two oxygenated methine protons at δ_H 4.22 (dd, J=3.5, 12.5 Hz, H-21), 4.72 (dd, J=5.0, 11.5 Hz, H-3), and four olefinic protons at δ_H 8.75 (d, J=15.5 Hz), 6.83 (dd, J=11.0, 15.5 Hz), 6.13 (d, J=11.0 Hz) and 5.72 (br) in ¹H NMR spectrum. The ¹H NMR features were characteristic of isomalabaricane-type terpenoid, close to those of stelletin D¹. The ¹³C NMR and DEPT spectra showed the signals for 32 carbons which were attributed to eight methyls, six methylene groups, four methine carbons and ten

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quaternary carbons (**Table 1**). The gross structure of **1** was established on the basis of extensive 2D NMR analysis. A COSY spectrum connected three olefinic protons (δ_{H} 8.75, 6.83, 6.13) as ABX spin system and their coupling constants allowed to determine the geometries of double bonds at side chain, and the most down-field shift of proton H-15 (δ_{H} 8.75, d, $J=15.5$ Hz) indicated that H-15 was toward to the deshielding zone of the carbonyl group and the geometry of double bond C-13/C-14 was thus assigned in Z form. Additionally, the COSY correlations between H-21/H-22 (δ_{H} 1.89, 1.29), H-22/H23 (δ_{H} 5.72) in association with HMBC correlations of δ_{H} 1.95 (brs, Me-27) to δ_{C} 138.8 (d, C-24), 129.4 (s, C-25) and 166.4 (s, C-26), and of methine proton H-21 to C-26, C-24, C-23 (δ_{C} 29.2, t), C-20 (δ_{C} 138.0, s) and C-21 (δ_{C} 13.2, q) strongly suggested a partial structure α , β -unsaturated α -methyl- δ -lactone annexed to quaternary carbon C-20. The stereochemistry of C-22 could be suggested as β -configuration on the basis of coupling constants of H-22 (3.5, 12.5 Hz) with methylene protons H-23 that implied an axial-axial and axial-equatorial coupling. An acetoxy group (δ_{H} 1.89, s; 21.8, q; 171.0, s) which was confirmed to locate at C-3 due to the HMBC correlation between H-3 (δ_{H} 4.72, dd) and δ_{C} 171.0 (s), and the NOE correlation between H-3 and methyl protons H-28 (δ_{H} 1.04, s) indicated the α -configuration for H-3. Accordingly, the structure of **1** was determined as 22,23-dihydrostellettin D. The ^1H and ^{13}C NMR data were assigned in **Table 1**.

Figure 1 The structure of 22, 23-dihydrostellettin D **1**

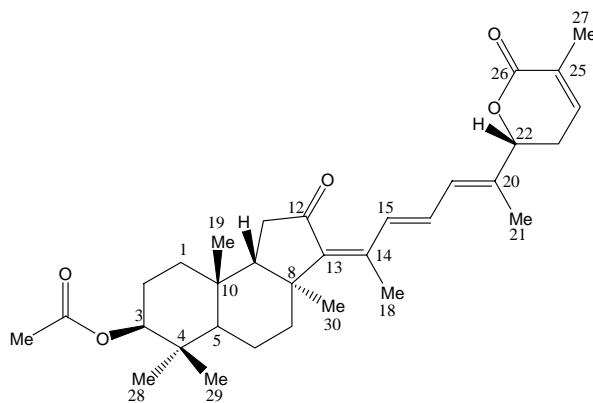


Figure 2 The main NOE correlations of 22, 23-dihydrostellettin D (**1**)

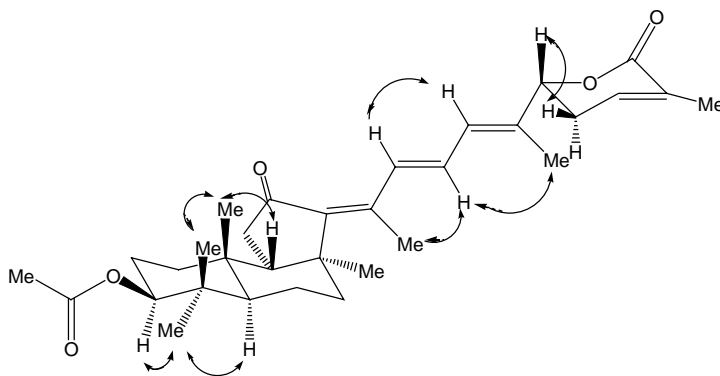


Table 1 ^1H and ^{13}C NMR data of compound **1** (500 MHz, in C_6D_6)

position	δ_{H} (ppm)	δ_{C} (ppm)	HMBC (H \rightarrow C)
1	1.04, m ; 1.29, m	33.9, t	
2	1.71, m ; 1.93, m	26.3, t	
3	4.72, dd, 5.0, 11.5	81.3, d	C-2, C-4, C-28, C-29, $\text{O}\underline{\text{C}}\text{OCH}_3$
4		39.3, s	
5	1.65, brd	47.7, d	
6	1.51, m; 1.24, m	19.2, t	
7	1.75, m; 1.89, m	39.2, t	
8		45.3, s	
9	1.56, m	51.2, d	C-1, C-8, C-19, C-30
10		36.0, s	
11	2.11, m; 2.14, m	37.8, t	C-8, C-12, C-13
12		205.9, s	
13		148.7, s	
14		141.5, s	
15	8.75, d, 15.5	135.3, d	C-13, C-17, C-18
16	6.83, dd, 15.5, 11.0	130.1, d	C-14, C-17, C-20
17	6.13, d, 11.0	129.0, d	C-15, C-16, C-21, C-22
18	1.90, brs	16.9, q	C-13, C-14, C-15
19	0.80, s	23.0, q	C-1, C-5, C-9, C-10
20		138.0, s	
21	1.82, brs	13.2, q	C-17, C-20, C-22
22	4.22, dd, 3.5, 12.5	82.2, d	C-20, C-21, C-26, C-23, C-24
23	1.42, m; 1.97, m	29.2, t	
24	5.72, br	138.8, d	C-22, C-26, C-27
25		129.4, s	
26		166.4, s	
27	1.95, brs	18.2, q	C-24, C-25, C-26
28	1.04, s	30.0, q	C-3, C-4, C-5, C-29
29	1.00, s	18.1, q	C-3, C-4, C-5, C-28
30	1.13, s	25.4, q	C-7, C-8, C-9, C-13
OCOCH_3	1.89, s	21.8, q	$\text{O}\underline{\text{C}}\text{OCH}_3$
OCOC H_3		171.0, s	

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