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A New Diterpenoid from *Hydroclathrus tenuis*

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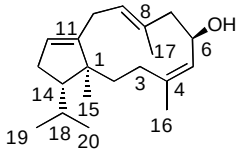
Abstract: A new dolabellane diterpene **1**, named as hydroclathrol, has been isolated from the alga *Hydroclathrus tenuis.* Its structure has been determined on the basis of spectral analysis as 1, 4, 8-trimethyl-14-isopropyl-bicyclo [9, 3, 0]-4(*Z*), 8(*E*), 11(*Z*)-tetradeca triene-6-ol.

Keywords: *Hydroclathrus tenui*, hydroclathrol, spectral analysis.

A number of diterpenoids based on the dolabellene skeleton have been isolated from marine sources, and many of them possessed remarked biological activities[1-4]. In this paper we would like to report a new Nor-dolabllane diterpene **1**, hydroclathrol, from the alga *Hydroclathrus tenuis* collected from Xisha Islands in the South China Sea.

The EtOH extract of the alga *Hydroclathrus tenuis* was partitioned between EtOAc and H_2O, and the resulted organic layer was twice chromatographed on a silica gel column to yield hydroclathrol **1**.



Hydroclathrol **1**

Hydroclathrol **1**, colorless needle crystals, mp. 124-125°C, gave a molecular ion peak in its EIMS at *m/z*: 288, and its ^{13}C-NMR DEPT spectrum was assigned to five methyls, five methenes, six methines and four quaternal carbons, corresponding to the molecular formula $C_{20}H_{32}O$, which required five degrees of the unsaturation. Its IR (KBr, ν) 1679 cm^{-1} and ^{1}H-NMR signals at δ 5.37 (brs), 5.04 (brs) and 4.74 (brs) supported the existence of three tri-substitute double bond, therefore, hydroclathrol **1** must be a bicyclic compound. The IR spectra of **1** exhibiting an absorption band at 3425 cm^{-1} indicated the presence of the hydroxyl group, and the significant ion *m/z*: 270 $(M-H_2O)^+$ also confirmed the existence of the hydroxyl group. Data of IR (KBr, ν) 1375, 13 88 cm^{-1} and MS *m/z*: 245 (M^+-43), 43 (67) showed the presence of an isopropyl group. ^{1}H-NMR showed five methyl group signals at δ_H (0.85, 0.88, 0.92, 0.94, 1.49), corresponding to 19-Me, 16-Me, 20-Me, 15-Me and 17-Me, respectively. Four separated spin-systems "$(CH_3)_2CHCHCH_2CH$=" (a), "-CH_2CH_2-" (b), "=$CHCH(OH)CH_2$-" (c) and "=$CHCH_2$-" (d) were identified by means of ^{1}H-^{1}H COSY and ^{1}H-^{13}C COSY spectra. Based on the HMBC correlations of hydroclathrol **1** (**Table 1**), the partial structure "a-d"

could be connected as structure **1**, and the 15-Me was transferred[5,6]. The 4(*Z*)-geometry of the olefinic bond was assigned on the basis of NOE correlation between H-16 and H-6, and the E- geometry of 8, 9-olefin resulted in NOE correlation between H-7 and H-9. The sterochemistry at C-6 could be deduced from the NOE correlation between H-6 and H-15, 15-α-Me was assigned from NOE correlation between H-15, H-6α and H-13α (2.08), and 14-α-isoPr was suggested from NOE correlation between H-14 and H-13β (1.19).

Table 1 NMR data of hydroclthrol **1** (500 MHz, $CDCl_3$)

Position	δ_C	δ_H	Key HMBC (C-H)
1	41.84		C-1, H-2, 3, 14, 15
2	38.92	1.88 (m, 2H)	
3	35.34	1.19 (m, 2H)	
4	138.11		C-4, H-5, 6, 3, 2, 16
5	127.05	4.74 (brs, 1H)	
6	78.46	4.20 (m, 1H)	
7	49.58	2.29 (d, 5Hz, 1H), 2.16 (d, 5Hz, 1H)	
8	134.91		C-8, H-7, 6, 9, 10, 17
9	125.81	5.37 (brs, 1H)	
10	29.32	2.76 (dd, 2.5, 1.6 Hz, 1H), 2.55 (dd, 2.5, 1.6 Hz, 1H)	
11	150.19		C-9, H-12, 13, 15, 2, 4, 9
12	123.34	5.04 (brs, 1H)	
13	32.52	1.19 (m, 1H), 2.08 (m, 1H)	
14	51.28	1.70 (m, 1H)	
15	26.18	0.94 (s, 3H)	
16	11.51	1.49 (s, 3H)	
17	16.75	0.88 (s, 3H)	
18	29.65	1.67 (m, 1H))	
19	22.28	0.85 (d, 5.8, 3H)	
20	22.18	0.92 (d, 6.1, 3H)	

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