

Two New Diterpenoids from *Hedychium forrestii*

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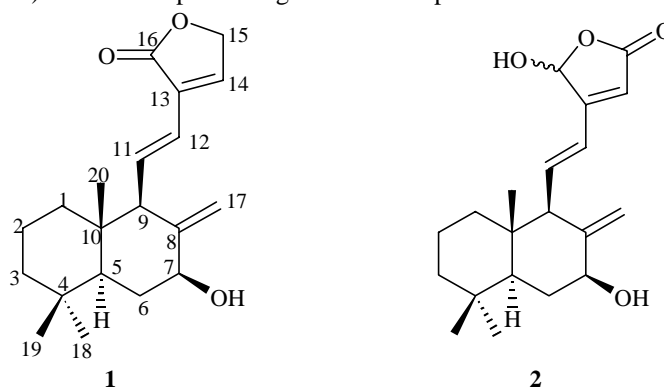
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Abstract: Two new labdane diterpenes isolated from the rhizomes of *Hedychium forrestii* were determined by spectroscopic evidence to be labda-8(17), 11, 13-trien-7 β -hydroxyl-15(16)-olide (**1**, hedyforrestin B) and labda-8(17), 11, 13-trien-7 β ,16-dihydroxyl-16(15)-olide (**2**, hedyforrestin C).

Keywords: *Hedychium forrestii*, diterpene, hedyforrestin B and C.

Previous studies on the genus *Hedychium* resulted in obtaining some labdane-type diterpenoids which showed significant cytotoxic activities against V-79 and KB cells¹⁻³. Recently, we studied the chemical constituents of *H. forrestii* in the continuation of this research, and two new labdane-type diterpenoids were obtained.

Hedyforrestin B (**1**), needles (from petroleum-ethyl acetate), $[\alpha]_D^{23} = +14.30$ (c 0.402, CHCl₃), HREIMS established its molecular formula to be C₂₀H₂₈O₃ (316.2029, calcd 316.2038). The IR spectrum gave an absorption band due to α,β -unsaturated



γ -lactone (1752 cm⁻¹), and hydroxyl group (3350 cm⁻¹). The ¹H NMR spectra indicated the presence of three methyl groups (δ_H 0.85, 0.87, 0.92) and an *exo*-methylene (δ_H 4.72, 5.14), which were characteristic of labdane-type diterpenoids, and confirmed by the characteristic EIMS fragment ion peak at *m/z* 137. The ¹³C NMR spectra (DEPT) gave

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20 carbon signals, including one carbonyl carbon (δ_C 172.24). In the ^1H NMR spectra, signals for two *trans* olefinic proton signals were observed at δ_H 6.12 (d, $J = 16.0$ Hz) and δ_H 6.92 (dd, $J = 10.5, 16.0$ Hz), respectively. The latter one was downfield shifted because the *trans* olefinic group was linked directly to the α, β -unsaturated γ -lactone¹. The comparison of ^1H and ^{13}C NMR spectra of **1** with those of coronarin A¹ showed that the difference was the six-carbon moiety at C-9 (namely, C11~16 moiety). The ^1H and ^{13}C NMR assignments were determined from ^1H - ^1H COSY, HMQC and HMBC. The ^1H - ^{13}C long-range correlation between H-12 (δ_H 6.12) and the carbonyl carbon (δ_C 172.24) indicated that this functional group was located at C-16 rather than at C-15. The α -axial orientation of H-9 and H-5 was elucidated by the cross-peak between H-9 and H-5 in ROESY. Therefore, the side chain at C-9 was determined to be β -form. Furthermore, the α -axial orientation of H-7 was confirmed by the cross-peaks between H-7 and H-9, and between H-7 and H-5 in ROESY, which indicated the hydroxyl group at C-7 to be β -form. Therefore, the structure of **1** was elucidated to be labda-8(17), 11, 13-trien-7 β -hydroxyl-15(16)-olide.

Table 1 The ^1H NMR(500MHz) and ^{13}C NMR(125MHz) data for **1** and **2** (CDCl_3 , δ , ppm)

C	1		2	
	δ_C	δ_H	δ_C	δ_H
1	40.33		40.51,40.38	
2	18.99		18.98	
3	41.91		41.86	
4	33.44		33.44	
5	52.51	1.16 dd(1.5, 12.5)	52.49	1.14 br.d(12.1)
6	33.15		32.93	
7	73.22	4.08 dd(5.5, 11.0)	73.12	4.07 dd(5.4, 11.0)
8	151.26		150.53,150.25	
9	60.38	2.32 d(10.5)	60.34	2.38 d(10.0)
10	39.26		39.53,39.64	
11	135.44	6.92 dd(10.5, 16.0)	142.36	6.57 dd(10.0, 15.9); 6.56 dd(10.1, 15.9)
12	121.01	6.12 d(16.0)	123.08	6.33 d(15.9); 6.34 d(15.9)
13	129.34		161.47	
14	142.87	7.18 s	115.77	5.85 s, 5.84s
15	69.59	4.82 s	171.77	
16	172.24		98.04	6.26 s; 6.28 s
17a	105.22	4.72 s	106.07,105.68	4.67 s; 4.58s
17b		5.14 s		5.14 s; 5.12s
18	33.49	0.85 s	33.50	0.84s
19	21.81	0.87 s	21.85	0.85s
20	14.99	0.92 s	15.13	0.91s

Coupling constants(Hz) in parentheses.

Hedyforrestin C (**2**) was obtained as colorless oil, $[\alpha]_D^{23} = +21.37$ (c 0.386, CHCl_3). HREIMS established its molecular formula to be $\text{C}_{20}\text{H}_{28}\text{O}_4$ (332.1983, calcd 332.1988).

The IR spectrum gave an absorption band due to an α,β -unsaturated γ -lactone (1734 cm^{-1}), and hydroxyl group (3392 cm^{-1}). The comparison of ^1H and ^{13}C NMR spectra (DEPT) of **2** with those of **1** indicated the same skeleton for both **2** and **1** (Table 1), the difference was the structure of α,β -unsaturated γ -lactone at C-12. The ^{13}C NMR signals of **2** assigned to C-1, C-8, C-10 and C-17 appeared in pairs, indicating that **2** was a mixture of two epimers at C-16 hydroxyl group which could not be chromatographically separated from each other. Furthermore, The ^1H NMR signals of **2** assigned to H-11 and H-12 seemed to be complicated, and H-14, H-16, H-17a, and H-17b appeared in pairs. The only difference between **2** and yunnancoronarin³ C was the hydroxyl substitution at C-7 in the former and at C-6 in the latter. The NMR assignments for **2** were carried out on the basis of ^1H - ^1H COSY, HMQC and HMBC. The HMBC showed the ^1H - ^{13}C long-range correlation between H-12 (δ 6.33 and 6.34) and the hemi-acetal carbon (δ 98.04), indicating that the hemi-acetal group was located at C-16, and the carbonyl group at C-15. The three cross peaks between H-9 and H-7, H-9 and H-5, H-7 and H-5 in ROESY suggested the α -axial orientation of H-9, H-7 and H-5. Thus the side chain at C-9 was determined to be β -form, and the C-7 hydroxyl group was β -form. Therefore, the structure of **2** was determined to be labda-8(17),11,13-trien-7 β ,16-dihydroxyl-16(15)-olide. Similar to the known compound yunnancoronarin³ C, the C-16 hydroxyl group in **2** was either α - or β -orientated..

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References

1. Q. Zhao, X. J. Hao, Y. Z. Chen, *et al.*, *Acta Pharmaceutica Sinica*, **1995**, 30(2), 119.
2. Q. Zhao, X. J. Hao, Y. Z. Chen, *et al.*, *Chemical Journal of Chinese Universities*, **1995**, 7(1), 25.
3. Q. Zhao, X. J. Hao, Y. Z. Chen, *et al.*, *Acta Botanica Sinica*, **1999**, 41(5), 528.

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