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New Diterpenoids from *Coleus forskohlii*

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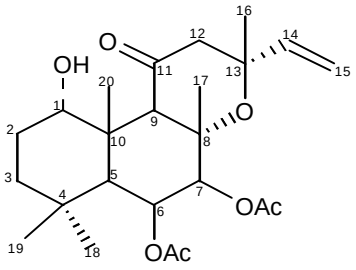
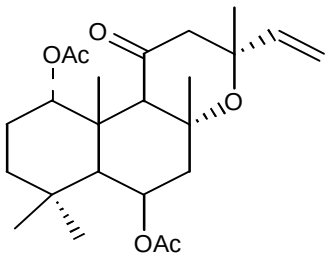
Abstract: Two new diterpenoids, forskolin G and H were isolated from the chloroform extract of the roots of *Coleus forskohlii*, and based on spectroscopic data, their structures were identified as 1α-hydroxy-6β,7β-diacetoxy-8,13-epoxylabd-14-ene-11-one (**1**), and 1α,6β-diacetoxy-8,13-epoxy labd-14-ene-11-one (**2**), respectively.

Keywords: *Coleus forskohlii*, diterpenoids, forskolin G and H.

Coleus forskohlii is only distributed in Yunnan and the southern regions of Asia. The decoction of the plant is used in local folk medicine against asthma, cough and bronchitis. It appears that the Coleus is rich source of diterpenoids with different oxygenation patterns[1,2], six diterpenoids and two new quinones have been isolated from its whole plant distributed in Yunnan[3,4]. As a continuation of our investigation on this plant, two new diterpenoids, forskolin G and H were isolated. The present paper describes the isolation and structural identification of these two new compounds.



1



2

Compound **1**, $C_{24}H_{36}O_7$, was obtained as colorless needles, showed the presence of five tertiary methyl groups, four methylene groups, six methine groups, four quaternary carbons, two olefinic carbons, one ketonic carbon and two acetoxy signals in ^{13}C and DEPT spectra. Its IR, MS, ^1H and ^{13}C NMR were very similar to those of forskolin E[1], which suggested that **1** had a typical 8,13-epoxylabd-14-ene-11-one skeleton. In addition, the HMBC showed cross peaks between δ_H 5.75 (dd, 1H, J 4.0, 2.2Hz, 6α-H) to δ_C

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33.86s (C-4), 41.89s (C-10), 46.22d (C-5), 77.98s(C-8), 78.66d(C-7) and 170.11s(OAc), δ_H 5.10 (d, 1H, J 4.0Hz, 7α-H) to δ_C 23.92q (C-17), 57.85d (C-9), 69.92d (C-6), 77.98s(C-8) and 169.84s (OAc), and δ_H 4.38 (br. s, 1H, 1β-H) to δ_C 36.30t (C-3) and 46.22d (C-5), indicating a 6β-OAc, 7β-OAc and 1α-OH in **1.** Its ^{1}H-^{1}H COSY also supported the above deduces. Therefore, **1** was elucidated as 1α-hydroxy-6β, 7β-diacetoxy-8,13-epoxylabd-14-ene-11- one, and named as forskolin G.

Compound **2**, $C_{24}H_{36}O_6$, comparing the ^{13}C NMR data of **2** with those of **1** showed that they possessed the same 8,13-epoxylabd-14-ene-11-one skeleton. In addition, the HMBC showed the correlation between δ_C 69.47d (C-6) to δ_H 2.24 (dd, 1H, J 14.6, 2.6Hz, 7-Ha), 2.03 (s, 3H, OAc) and 1.45 (d, 1H, J 2.1Hz, 5α-H), δ_C 75.07d (C-1) to $_H$ 3.21 (br. s, 1H, 9α-H), 1.94 (s, 3H, OAc), 1.45 (d, 1H, J 2.1Hz, 5α-H) and 1.40 (s, 3H, 20-Me), and signals of δ_H 5.55 (t, 1H, J 2.6 Hz, 6α-H) and 5.51 (br. s, 1H, 1β-H) in ^{1}H NMR, indicating that **2** has 1α-OAc and 6β-OAc. Its ^{1}H-^{1}H COSY also supported the above deduces. Accordingly, **2** was identified as 1α, 6β-diacetoxy-8, 13-epoxylabd-14-ene-11-one, and named as forskolin H.

Experimental

8.4 kg dried roots of *Coleus forskohlii* were extracted with 25 Lx3 of 95% ethanol for 15 days at room temperature. The extract was decoloured with 200 g x3 active charcoal and the solvent was removed in vacuum. The residues (395 g) were dissolved in H_2O. The aqueous solution was extracted with petroleum ether, $CHCl_3$ and *n*-butanol, the $CHCl_3$ extract was evaporated to give 85 g of residues. The residues were subjected to CC silica gel, eluted with petroleum ether-acetone (from petroleum ether to petroleum ether-acetone 1:1). The fractions were combined by monitoring with TLC to obtain fractions B 1~B 22. Then the fraction B 4 was recrystallized with acetone to give 173 mg of **2**; the fraction B 8 (4 g) was chromatographed repeatedly on silica gel eluted with $CHCl_3$-acetone and recrystallized from petroleum ether-acetone to afford 175 mg of **1**.

Compound 1: $C_{24}H_{36}O_7$, M 436, $[\alpha]_D^{17}$-62.42 ($CHCl_3$), mp. 241~243°C ;IR (KBr): 3510, 2865, 1731, 1448, 1371, 1314, 1261, 1173, 1099, 973, 949, 926, 802, 784, 752, 722, 659, 626, 419 cm^{-1}; MS (*m/z*, %): 436 (27, M^+), 421 (90, M^+-CH_3), 403 (20, M^+-H_2O-CH_3), 361 (20, M^+-HOAc-CH_3), 343 (17, 403-HOAc), 325 (77, 343-H_2O), 301 (21, M^+-2HOAc-CH_3), 283 (16, 301-H_2O), 246 (17), 231 (28), 203 (42), 175 (23), 153 (100), 139 (36), 123 (34), 109 (46), 99 (100), 95 (60), 81 (85), 69 (72), 55 (88);

Compound 2: $C_{24}H_{36}O_6$, M 420, $[\alpha]_D^{16}$-69.11 ($CHCl_3$), mp. 231~234°C ;IR (KBr): 3445, 2948, 2867, 1733, 1450, 1393, 1364, 1322, 1238, 1209, 1143, 1105, 1066, 1035, 948, 913 cm-1; MS (*m/z*, %): 420 (5, M^+), 405 (12, M^+-CH_3), 377 (40, M^+-CH_3CO), 360 (100, M^+-HOAc), 345 (9, 360-CH_3), 310 (28), 300 (49, M^+-2HOAc), 285 (72, 300-CH_3), 247 (70), 232 (32), 215 (76), 190 (48), 173 (45), 163 (26), 147 (22), 135 (18), 119 (25), 109 (32), 95 (35), 81 (33), 69 (37), 55 (49);

Table 1 The ^{13}C NMR of **1** and **2** ($CDCl_3$, δ in ppm)

Carbon	**1**	**2**	Carbon	**1**	**2**
1	71.01	75.07	12	49.73	49.06
2	25.50	21.72	13	74.84	74.55
3	36.30	36.90	14	145.78	146.71
4	33.86	33.73	15	112.72	112.33
5	46.22	49.06	16	31.48	31.68
6	69.92	69.47	17	23.92	29.47
7	78.66	46.21	18	32.63	32.86
8	77.98	75.72	19	22.81	22.88
9	57.85	58.22	20	17.76	17.37
10	41.89	40.46	OAc	170.11, 21.28	169.81, 21.72
11	207.00	206.19	OAc	169.84, 20.83	169.50, 21.68

Table 2 The ^{1}H NMR data of **1** and **2** ($CDCl_3$, δ_H in ppm, J Hz)

1		**2**	
H	δ_H	H	δ_H
1β-H	4.38 (br.s, 1H)	1α-H	5.51 (br.s, 1H)
5α-H	1.63 (d, 1H, 2.2)	5α-H	1.45 (d, 1H, 2.1)
6α-H	5.75 (dd, 1H, 4.0, 2.2)	6α-H	5.55 (t, 1H, 2.6)
7α-H	5.10 (d, 1H, 4.0)	7-Ha	2.24 (dd, 1H, 14.6, 2.6)
9α-H	3.60 (br.s, 1H)	7-Hb	1.88 (dd, 1H, 14.6, 2.6)
12-Ha	2.71 (d, 1H, 18.2)	9α-H	3.21 (br.s, 1H)
12-Hb	2.58 (d, 1H, 18.2)	12-Ha	2.64 (d, 1H, 18.6)
14-H	5.97 (dd, 1H, 17.4, 10.7)	12-Hb	2.58 (d, 1H, 18.6)
15-Ha	5.21 (d, 1H, 17.4)	14-H	5.90 (dd, 1H, 17.3, 10.7)
15-Hb	5.05 (d, 1H, 10.7)	15-Ha	5.17 (d, 1H, 17.3)
16-H	1.24 (s, 3H)	15-Hb	5.02 (d, 1H, 10.7)
17-H	1.51 (s, 3H)	16-H	1.24 (s, 3H)
18-H	0.98 (s, 3H)	17-H	1.44 (s, 3H)
19-H	0.93 (s, 3H)	18-H	0.95 (s, 3H)
20-H	1.40 (s, 3H)	19-H	0.97 (s, 3H)
OAc	2.08 (s, 3H)	20-H	1.40 (s, 3H)
OAc	2.07 (s, 3H)	OAc	2.03 (s, 3H)
		OAc	1.94 (s, 3H)

Table 3 HMBC and H-H COSY spectral data of **1**

HMBC		**H-H COSY**	
H	Correlative C	H	Correlative H
1α-H	C-1, C-2, C-5, C-9, C-10, C-20	1α-H	1β-H, 2β-H, 2α-H
1β-H	C-2, C-3, C-5, C-9, C-10, C-20	1β-H	1α-H, 2β-H, 2α-H
2α-H	C-2	2α-H	1α-H, 1β-H, 2β-H
2β-H	C-1, C-2	2β-H	1α-H, 1β-H, 18-H, 2α-H
5α-H	C-2, C-3, C-4, C-5, C-6, C-9, C-10	5α-H	6-H, 19-H, 18-H
6α-H	C-7, C-8, C-10	6α-H	5α-H, 6β-OH, 7β-H
7β-H	C-5, C-6, C-8, C-9, C-14	7β-H	6α-H, 7α-OH
15-Ha	C-12, C-13, C-14, C-16, C-17	15-Ha	15-Hb, 16-H
15-Hb	C-12, C-13, C-14, C-16, C-17	15-Hb	15-Ha, 16-H
16-H	C-13, C-15, C-21	16-H	15-Ha, 15-Hb, 17-H
17-H	C-16	17-H	16-H
18-H	C-3, C-4, C-5	18-H	2α-H, 2β-H, 5α-H, 19-H
19-H	C-2, C-3, C-4, C-5	19-H	1β-H, 18-H
20-H	C-1, C-5, C-9, C-10	20-H	1β-H, 2β-H, 2α-H
6β-OH	C-5, C-6, C-7	6β-OH	6α-H
7α-OH	C-6, C-7, C-8	7α-OH	7β-H
21-H	C-16, C-22	21-H	22-H
22-H	C-21	22-H	21-H

Table 4. HMBC and H-H COSY spectral data of **2**

HMBC		H-H COSY	
H	Correlative C	H	Correlative H
1α-H	C-2, C-9, C-10, C-20	1α-H	1β-H, 2α-H, 2β-H
1β-H	C-2, C-3, C-5, C-9, C-10, C-20	1β-H	1α-H, 2α-H, 2β-H
2α-H	C-1	2α-H	1α-H, 2β-H
2β-H	C-3, C-4, C-10	2β-H	1α-H, 2α-H
5α-H	C-3, C-4	5α-H	6α-H, 18-H,19-H
6α-H	C-4, C-5, C-7, C-8, C-10	6α-H	5α-H, 7β-H
7β-H	C-5, C-6, C-8, C-9, C-14	7β-H	6α-H
12-H	C-9, C-13, C-14, C-16	12-H	no correlation
16-Hb	C-12, C-13, C-14 , C-15, C-17	15-H	16-Ha, 16-Hb
16-Ha	C-13, C-14 , C-15, C-17	16-Ha	16-Hb, 15-H
17-H	C-12, C-13, C-15, C-16	16-Hb	16-Ha, 15-H
18-H	C-3, C-4, C-5	17-H	15-H
19-H	C-2, C-3, C-4	18-H	2α-H,2β-H,5α-H, 19-H
20-H	C-1, C-5, C-9, C-10	19-H	18-H, 5α-H
		20-H	1β-H, 2α-H

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