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Two New *O*-terpenoidal Coumarins, Excavacoumarin A and B from *Clausena excavata*

Hong Ping HE, Yue Mao SHEN, Guo Ying ZUO, Wei Ming ZHU,
Xiao Sheng YANG, Xiao Jiang HAO*

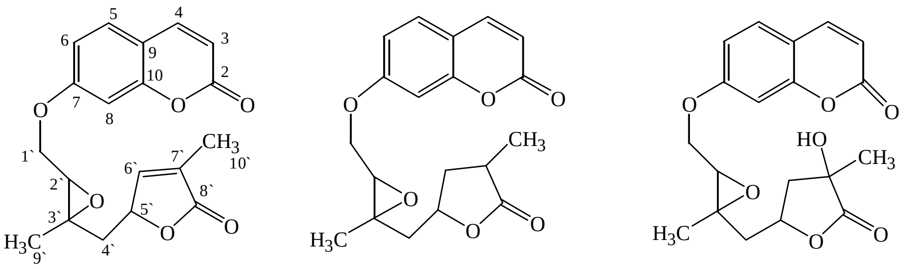
Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences,
Kunming, Yunnan 650204

Abstract: Two new *O*-terpenoidal coumarins named excavacoumarin A (**2**), B (**3**), and a known one **1** were isolated from the leaves of *Clausena excavata* Burm. f. (Rutaceae) collected in Xishuangbanna, Yunnan. Structure elucidation and unambiguous NMR assignments for the title compounds were carried out on the basis of 1D and 2D NMR experiments.

Keywords: Coumarin, *Clausena excavata*, excavacoumarin A, excavacoumarin B.

Clausena excavata Burm. f. (Rutaceae) is a bush widely distributed in Yunnan, China. Leaves and barks of this plant have been used as folk medicine for the treatment of dysentery，enteritis，and urethra infection[1]. *Clausena* species are known to be the rich sources of carbazole alkaloids and coumarins[2-3]. The constituents of *C. excavata* collected in Xishuangbanna have been studied[4] and this paper describes the isolation and structure elucidation of two new *O*-terpenoidal coumarins, excavacoumarin A (**2**) and excavacoumarin B (**3**), and the ^{13}C NMR spectral data assignments for a known coumarin **1** for the first time.

Figure 1. Chemical structure of three *O*-terpenoidal coumarins



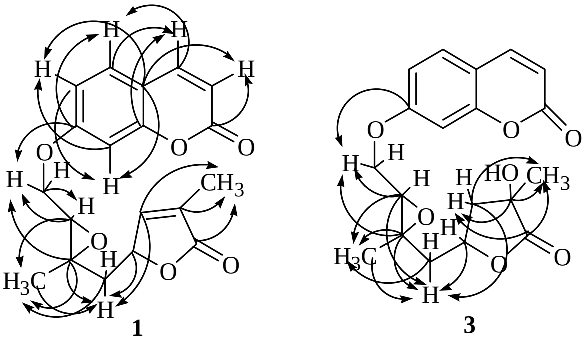
1 **2** **3**

Compound **1**, a white amorphous powder, $[\alpha]_D^{26.1}$ +3.75 (c 2.0, $CHCl_3$). The molecular formula was determined as $C_{19}H_{18}O_6$ by high-resolution EIMS (at *m/z* 342.1105 $[M]^+$, calc.: 342.1103). The presence of a coumarin lactone was evident from the ^1H NMR spectrum which showed a typical AB system characteristic signals at δ_H

6.18, 7.60 (each 1H, d, 9.5) assigned to H-3, H-4 (**Table 1**). The ^{13}C NMR spectrum (**Table 1**) revealed the presence of a 10-carbon moiety besides the coumarin chromophore. The other characteristic proton signals [δ_H 7.34 (d, 8.6), δ_C 128.8 (d); δ_H 6.83 (dd, 8.6, 2.4), δ_C 112.6 (d); δ_H 6.76 (d, 2.4), δ_C 101.7 (d)] of ring B indicated the 10-carbon side chain at C-6 or C-7. Furthermore, the ^{1}H-^{13}C long-range correlation (**Figure 2**) between δ_H 7.34 (d, 8.6) and δ_C 143.2 (C-4), and δ_H 6.83 (dd, 8.6, 2.4) and δ_C 112.8 (C-9) suggested that the side chain was at C-7, rather than at C-6.

The structure elucidation of the 10-carbon side chain was performed on the basis of HMQC, HMBC, and ^{1}H-^{1}H COSY experiment. The long-range correlation were observed between H-1' (δ 4.29, dd, 1H, 11.2, 3.6; 4.02, dd, 1H, 11.2, 6.6) and C-2' (δ 61.0d), C-3' (δ 58.1s); H-9' (δ 1.44s, 3H) and C-2', C-3', C-4' (δ 42.5t); H-4' (δ 1.73-1.89, m, 2H) and C-3', C-5' (δ 77.9, d), C-6' (δ 148.4, d), C-9' (δ 16.9, q); H-10' (δ 1.85, s, 3H) and C-6', C-7' (δ 129.9, s), C-8' (δ 173.5, s). Although the ^{1}H-^{13}C long-range correlations between H-5' with C-4' and C-6' were not observed in HMBC, the correlations between H-5' with H-4' and H-6' were obvious in the ^{1}H-^{1}H COSY spectrum. The signals at δ 61.0 (d) and δ 58.1 (s) attributed to C-2' and C-3', respectively, showed that an epoxide was between C-2' and C-3' of the side chain[5]. This structure of the side chain was also supported by the ^{1}H and ^{13}C NMR spectra of 2',3'-epoxyanisolactone[5-6] which had the same side chain as **1**. Based on those analyses, the structure of this compound, which had similar ^{1}H NMR spectral data as the literature lactone[7], was identified as **1**. All proton and carbon resonances (**Table 1**) were assigned by analyzing of the ^{1}H-^{1}H COSY, HMQC, and HMBC spectra.

Figure 2. The Key ^{1}H-^{13}C long-range correlations for **1** and **3**.
HMBC were obtained at 500MHz in $CDCl_3$ and C_5D_5N for **1** and **3**, respectively.



1 **3**

2, a white amorphous powder, $[\alpha]_D^{25.9}$ +22.96 (c 3.92, $CHCl_3$). HR EIMS gave the formula as $C_{19}H_{20}O_6$ (at *m/z* 344.1261 $[M]^+$, calc.: 344.1260). The ^{1}H and ^{13}C NMR spectra were similar to those of **1** except for C-6' and C-7'. The difference in the ^{13}C NMR spectrum were the presence of two high field signals at δ_C 35.8 (d) and 37.8 (t) (**Table 1**), and the absence of two double bond signals in **1**, indicating that **2** was a saturated 1actone of **1**.

3, a white amorphous powder, $[\alpha]_D^{20.9}$ +29.41 (c 3.06, C_5H_5N). The molecular formula was obtained as $C_{19}H_{20}O_7$ based on high-resolution EIMS (at *m/z* 360.1212 $[M]^+$, calc.: 360.1209). The ^{1}H and ^{13}C NMR spectra were similar to those of **1** and **2** except for C-6' and C-7' (**Table 1**). By means of HMBC experiment (**Figure 2**), the ^{1}H-^{13}C long-range correlations between H-10' (δ_H 1.66, s, 3H) and δ_C 44.8t (C-6'), δ_C 73.1s (C-7'), δ_C 178.3s (C-8'); and between H-4' (δ_H 2.05m, 1.96m, each 1H) and δ_C 61.3d (C-2'), 58.5s (C-3'), 75.2d (C-5'), 44.8t (C-6'), 73.1s (C-7'), 17.1q (C-9') were observed, indicating that **3** was the C-7' hydroxylation of **2**.

The stereochemistry of those two new coumarins, **2**, **3**, and **1** remain to be determined. So far, the stereochemistry of this type of *O*-terpenoidal coumarins reported previously was not resolved[5-7]. Further structure elucidation on the stereochemistry pertaining to C-2', C-3', C-5' and C-7' of **1**, **2**, and **3** is in the progress.

Table 1. The ^{1}H and ^{13}C NMR assignments for compounds **1**-**3**.

Position	**1**[a]		**2**[b]		**3**[b]	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
2	/	160.8s	/	160.8s	/	160.8s
3	6.18 (d, 9.5)	113.2d	6.33 (d, 9.5)	113.5d	6.33 (d, 9.5)	113.6d
4	7.60 (d, 9.5)	143.2d	7.67 (d, 9.5)	143.8d	7.68 (d, 9.5)	143.8d
5	7.34 (d, 8.6)	128.8d	7.42 (d, 8.6)	129.6d	7.42 (d, 8.6)	129.6d
6	6.83 (dd, 8.6, 2.4)	112.6d	6.99 (dd, 8.6, 2.5)	113.1d	6.99 (dd, 8.6, 2.4)	113.1d
7	/	161.4s	/	162.2s	/	162.2s
8	6.76 (d, 2.4)	101.7d	7.04 (d, 2.5)	102.2d	7.06 (d, 2.4)	102.3d
9	/	112.8s	/	113.3s	/	113.3s
10	/	155.6s	/	156.3s	/	156.4s
1'	4.29 (dd, 11.2, 3.6) 4.02 (dd, 11.2, 6.6)	67.1t	4.48 (dd, 11.2, 3.1) 4.27 (dd, 11.2, 6.7)	68.3t	4.49 (dd, 11.1, 5.3) 4.23 (dd, 11.1, 2.6)	68.3t
2'	3.15 (dd, 6.6, 3.6)	61.0d	3.37 (dd, 6.7, 3.1)	61.3d	3.41 (dd, 5.3, 2.6)	61.3d
3'	/	58.1s	/	58.5s	/	58.5s
4'	1.73-1.89 (m)	42.5t	1.80-1.84 (m)	44.5t	1.96-2.05 (m)	44.4t
5'	5.06 (m)	77.9d	5.00 (m)	75.6d	5.15 (m)	75.2d
6'	7.07 (t, 1.6)	148.4d	1.92 (m) 1.60 (m)	37.8t	2.64 (m) 1.95 (m)	44.8t
7'	/	129.9s	2.38 (dd, 7.9, 4.7)	35.8d	/	73.1s
8'	/	173.5s	/	179.1s	/	178.3s
9'	1.44 (s)	16.9q	1.44 (s)	17.1q	1.45 (s)	17.1q
10'	1.85 (s)	10.4q	1.18 (s)	15.1q	1.66 (s)	23.8q

[a] ^{1}H and ^{13}C NMR spectra were obtained at 400 and 100 MHz, respectively, and recorded in $CDCl_3$.

[b] ^{1}H and ^{13}C NMR spectra were obtained at 400 and 100 MHz, respectively, and recorded in C_5D_5N at room temperature.

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