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Two new compounds from *Coriaria nepalensis*

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Abstract

Two new compounds, corialins A (**1**) and B (**2**) were isolated from *Coriaria nepalensis* Wall. These new compounds were established as 7-hydroxy-3-[2,3-acetonide-(3-methylbutane)] coumarin (**1**) and 3-*O*-*β*-D-glucopyranosyl-3,4,5-trihydroxy-1-(3-methyl-2-butenyl)-benzene (**2**), on the basis of 1D and 2D NMR techniques.

Keywords: *Coriaria nepalensis*; Corialin A; Corialin B; NMR techniques

Coriaria nepalensis Wall, mainly distributed in the southern and southwestern parts of China, has been used to treat numbness, toothache, traumatic injury, and acute conjunctivitis [1]. The family Coriariaceae is a rich source of sesquiterpene lactones [2–6] which have been used to treat schizophrenia [7]. During our investigation on chemical constituents of *C. nepalensis*, one new coumarin was isolated from the ripe fruits of this plant, another new phenolic glucoside from the leaves of this plant. In this paper, the isolation and structural elucidation of these two new compounds were reported (Fig. 1).

The ripe fruits of *C. nepalensis* were collected in Dali State, Yunnan Province, China, in August 2008. The leaves of *C. nepalensis* were collected in Wenshan State,Yunnan Province, China, in May 2009, and identified by Prof. Xi-Wen Li. Voucher specimens (KIB 20081006 and 20091011) were deposited at the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Dry ripe fruits of *C. nepalensis* (2.7 kg) were extracted with 70% aq. acetone (3 × 10 L) at room temperature and concentrated in vacuo to yield a residue, which was partitioned between H_2O and EtOAc. The EtOAc extract (100 g) was chromatographed over a silica gel, eluted in a step gradient manner with $CHCl_3$–$(CH_3)_2CO$ (1:0–0:1) to afford fractions A–F. Fraction C (5 g) was subjected to RP-18 column chromatography (40–80% gradient CH_3OH–H_2O) to give fractions C1–C4. Fraction C3 (90 mg) afforded compound **1** (14 mg) by semipreparative HPLC (70% MeOH–H_2O). Dry leaves of *C. nepalensis* (3.5 kg) were extracted with 70% aq. acetone (3 × 15 L) at room temperature and concentrated in vacuo to yield a residue. The residue was partitioned between H_2O and EtOAc, and EtOAc extract (120 g) was chromatographed over silica gel, eluted in a step gradient manner with $CHCl_3$–$(CH_3)_2CO$ (1:0–0:1) to

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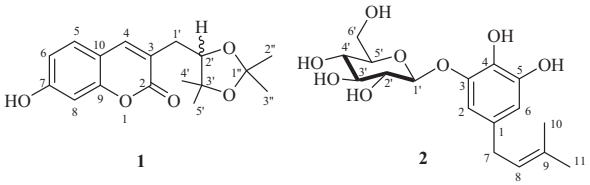

Fig. 1. Structures of compounds **1** and **2**.

afford fractions A–G. Fraction C (6 g) was submitted to chromatography over silica gel (petroleum ether–acetone, from 9:1 to 1:1), to give fractions C1–C5. Fraction C3 (120 mg) afforded compound **1** (31 mg) by RP-18 column chromatography (30–60% MeOH–H_2O) and semipreparative HPLC (40% MeOH–H_2O).

Corialin A (**1**), $[\alpha]_D^{25}$ −100.2 (*c* 0.17, CH_3OH), was obtained as a white solid, and its HR-ESI-MS (*m/z* 327.1216 $[M+Na]^+$, calcd. 327.1208) gave the molecular formula, $C_{17}H_{20}O_5$, indicating eight degrees of unsaturation. The ^1H NMR and ^{13}C NMR spectra (Table 1) showed characteristic signals for a coumarin skeleton, showing resonances at δ_H 7.78 (s), 7.47 (d, J = 8.5 Hz), 6.83 (dd, J = 8.5, 2.1 Hz), and 6.74 (d, J = 2.1 Hz), and at δ_C 162.1 (s), 161.5 (s), 156.0 (s), 141.5 (d), 129.8 (d), 122.4 (s), 113.9 (d), 113.1 (s), and 102.9 (d), and a 2,3-diol-isopentyl unit due to a set of carbon signals at δ_C 81.4 (d), 80.6 (s), 31.3 (t), 26.2 (q), 23.2 (q). Four downfield singles at δ_H 7.78 (s), 7.47 (d, J = 8.5 Hz), 6.83 (dd, J = 8.5, 2.1 Hz), and 6.74 (d, J = 2.1 Hz) in the ^1H NMR spectrum suggested that **1** was a disubstituted coumarin. Three carbon signals including a quaternary carbon [δ_C 107.3 (C-1″)] and two methyls at [δ_C 28.9 (C-2″) and 27.2 (C-3″)] indicated the presence of an acetone ketal linked to the C-2′ and C-3′, which was proven by the HMBC correlations of H-2′ with C-1″, and of H_3-3″ and H_3-2″ with C-1″ (Fig. 2). Therefore, another substitute in the structure of **1** should be a hydroxyl group based on its molecular formula, which was assigned at C-7 based on the HMBC correlations of H-6 with C-7 and C-10, and of H-8 with C-6, C-7, C-9 and C-10. The HMBC correlations of H-1′ with C-2 (δ_C 162.1), C-3 (δ_C 122.4) and C-4 (δ_C 141.5) suggested the location of 2,3-diol-isopentyl at the C-3

Table 1
^1H and ^{13}C NMR data of corialins A (**1**) and B (**2**) (δ ppm).

No. C	**1**[a]		**2**[b]	
	δ_C	δ_H	δ_C	δ_H
1			134.1 (s)	
2	162.1 (s)		111.8 (d)	6.43 (d, 1.4)
3	122.4 (s)		146.8 (s)	
4	141.5 (d)	7.78 (s)	134.3 (s)	
5	129.8 (d)	7.47 (d, 8.5)	147.2 (s)	
6	113.9 (d)	6.83 (dd, 8.5, 2.1)	110.1 (d)	6.59 (d, 1.4)
7	161.5 (s)		34.7 (t)	3.20 (d, 7.2)
8	102.9 (d)	6.74 (d, 2.1)	124.8 (d)	5.31 (m)
9	156.0 (s)		133.0 (s)	
10	113.1 (s)		26.0 (q)	1.77 (s)
11			17.9 (q)	1.74 (s)
1′	31.3 (t)	2.72 (dd, 14.7, 3.0) 2.55 (dd, 14.7, 9.6)	104.5 (d)	4.79 (d, 7.3)
2′	81.4 (d)	4.08 (dd, 9.6, 3.0)	74.9 (d)	3.55 (overlap)
3′	80.6 (s)		77.6 (d)	3.53 (overlap)
4′	23.2 (q)	1.16 (s)	71.2 (d)	3.52 (overlap)
5′	26.2 (q)	1.24 (s)	78.2 (d)	3.50 (overlap)
6′			62.4 (t)	3.94 (dd, 12.0, 1.8) 3.81 (dd, 12.0, 3.6)
1″	107.3 (s)			
2″	28.9 (q)	1.36 (s)		
3″	27.2 (q)	1.24 (s)		

[a] Recorded in $(CD_3)_2CO$, 500 MHz.
[b] Recorded in CD_3OD, 500 MHz.

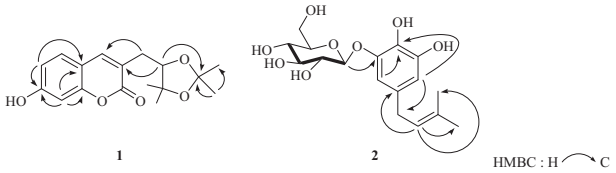

Fig. 2. Key HMBC correlations of **1** and **2**.

position of the coumarin skeleton. Thus, compound **1** was identified as 7-hydroxy-3-[2,3-acetonide-(3-methylbutane)] coumarin, and was given trivial name corialin A.

Corialin B (**2**), $[\alpha]_D^{25}$ −68.6 (*c* 0.13, CH_3OH), was isolated as a white solid. The molecular formula was established as $C_{17}H_{24}O_8$ by HR-ESI-MS (*m/z* 379.1372 $[M+Na]^+$, calcd. 379.1368), which was supported by ^{13}C NMR and DEPT spectroscopic data. The ^1H NMR spectrum showed resonances for two aromatic protons [δ_H 6.59 (d, 1H, J = 1.4 Hz, H-6), 6.43 (d, 1H, J = 1.4 Hz, H-2)], with signals at δ_C 134.1 (s), 111.8 (d), 146.8 (s), 134.3 (s), 147.2 (s), 110.1 (d), indicating the presence of a 1,3,4,5-tetrasubstituted benzol moiety. ^1H NMR signals at δ_H 3.20 (d, 2H, J = 7.2 Hz), 5.31 (m, 1H), 1.77 (s, 3H) and 1.74 (s, 3H) were attributable to one isopentenyl group based on the HMBC correlations of H_2-7 with C-8 and C-9, and of H-8 with C-10 and C-11 [8]. A series of sugar signals were also exhibited at δ_H 3.50–3.94, with an anomeric proton at δ_H 4.79 (d, 1H, J = 7.3 Hz, H-1′). The ^{13}C NMR spectrum indicated a glucose unit due to a set of carbon signals at δ_C 104.5 (d), 78.2 (d), 77.6 (d), 74.9 (d), 71.2 (d), 62.4 (t). The β-anomeric configuration for the glucose was determined based on the coupling constant (J = 7.3 Hz) of H-1′ [9]. The HMBC correlation between H-8 (δ_H 5.31) and C-1 (δ_C 134.1, s) suggested the location of isopentenyl group at C-1. And the glycosidic linkage between C-1′ and C-3 was determined by the presence of the HMBC correlation between the glucose anomeric proton H-1′ and C-3 (δ_C 146.8, s). Thus, compound **2** was identified as 3-*O*-β-D-glucopyranosyl-3,4,5-trihydroxy-1-(3-methyl-2-butenyl)-benzene, and was given trivial name corialin B.

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