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Two new pyranoanthraquinones from the root of *Rennellia elliptica* Korth. (Rubiaceae)

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ABSTRACT

Two new pyranoanthraquinones, rennellianone A (**1**) and rennelianone B (**2**) along with four known compounds, alizarin-1-methyl ether (**3**), scopoletin (**4**), 4-hydroxy-3,5-dimethoxybenzaldehyde (**5**) and 3b-acetateoleanan-13b, 28-lactone (**6**) were isolated and characterized from the root extract of *Rennellia elliptica*. The structures were established based on spectroscopic data including HR-ESI–MS, 1D and 2D NMR. Triterpenoid lactone (**6**) is reported for the first time from family Rubiaceae.

1. Introduction

Rennellia elliptica is a member of the family Rubiaceae and native to South East Asia. It is a small tropical shrub that can be found in the lowlands of tropical rainforests. *R. elliptica* is locally known as 'segemuk' and popularly dubbed as Malaysian Ginseng due to the appearance of its yellow root and its many medicinal uses. The decoction of the root is taken by the locals for the treatment of body aches, as after-birth tonic and as an aphrodisiac (Mat Salleh and Latiff, 2002). We previously reported the presence of *Rubia*-type anthraquinones in the root of *R. elliptica* (Osman et al., 2010) similar to those reported in *Morinda* and *Prismatomeris* species (Ee et al., 2009; Hao et al., 2011; Ismail et al., 1997; Krohn et al., 2007; Sittie et al., 1999; Tuntiwachwuttikul et al., 2008; Xiang et al., 2008). The root extract of *R. elliptica* is a potent antiplasmodial agent (IC_{50} = 4.04 μg/mL) in which many of the anthraquinones isolated were active plasmodial inhibitors with IC_{50} values of less than 1 μM (Osman et al., 2010).

In continuation of phytochemical investigation focusing on the minor constituents incorporating modern chromatographic techniques had resulted in the isolation of two interesting pyranoanthraquinones along with an anthraquinone, a coumarin, a phenolic compound and a lactone triterpenoid from *R. elliptica*. Their structures were elucidated as rennellianone A (**1**) and rennellianone B (**2**), alizarin-1-methyl ether (**3**), scopoletin (**4**), 4-hydroxy-3,5-dimethoxybenzaldehyde (**5**) and 3b-acetateoleanan-13b, 28-lactone (**6**) (Al-Hazimi et al., 1987; Imai et al., 1989; Katai et al., 1983; Pereda-Miranda and Gascón-Figueroa, 1988) (Fig. 1). The triterpenoid lactone is reported for the first time from the family Rubiaceae. Herein, we reported the structural elucidation of the two new pyranoanthraquinones, rennellianone A (**1**) and rennellianone B (**2**).

2. Result and discussion

Compound **1** was obtained as a light yellow solid. Its molecular formula was established as $C_{24}H_{20}O_8$ by HRESIMS which showed a pseudomolecular ion peak $[M+H]^+$ at *m/z* 437.1232 (calcd 437.1231). The ^{13}C NMR revealed the presence 24 carbons which included 3 carbonyls, 3 oxygenated carbons, 9 quaternary carbons, 3 methoxy carbons, 6 methine carbons and 2 methylene carbons (Table 1). ^1H NMR of compound **1** showed the characteristic signals of 9,10-anthraquinone with unsubstituted ring A (Derksen and Van Beek, 2002) exemplified by the presence of four sets of hydrogen centered at δ_H 8.23 (*ddd*, J_o = 7.3 Hz, J_m = 3.2 Hz, J_p = 1.8 Hz, 1H), δ_H 8.19 (*ddd*, J_o = 7.3 Hz, J_m = 3.2 Hz, J_p = 1.8 Hz, 1H), δ_H 7.70 (*td*, J_o = 7.5 Hz, J_m = 2 Hz, 1H) and δ_H 7.74 (*td*, J_o = 7.5 Hz, J_m = 2 Hz, 1H) in the aromatic region assigned to H-5, H-8 and H-6, H-7, respectively. Two singlets resonating at δ_H 7.24 (*s*, 1H) and δ_H 13.24 (*s*, 1-OH) were assigned to H-4 and 1-OH, respectively.

In the upfield region, six signals were observed: a methine proton (δ_H 5.35, *s*, 1H), axial and equitorial methylene protons

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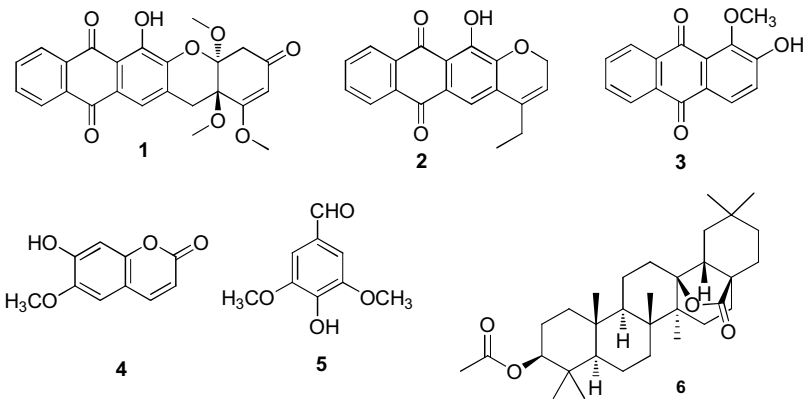

Fig. 1. Structures of compounds **1-6.**

Table 1
NMR data for compounds **1** and **2.**

Position	**1** ($CDCl_3$)		**2** ($CDCl_3$)	
	δ_H	δ_C	δ_H	δ_C
1	–	162.2	–	nd
2	–	156.1	–	156.0
3	–	114.7	–	113.8
4	7.24, *s*,1H	108.4	7.27, *s*, 1H	108.2
5	8.23, *ddd*,J_o = 7.3 Hz, J_m = 3.2 Hz, J_p = 1.8 Hz, 1H	125.8	8.22, *ddd*, J_o = 9.3 Hz, J_m = 2.3 Hz, J_p = 0.76 Hz, 1H	125.7
6	7.70, *td*, J_o = 7.5 Hz, J_m = 2 Hz, 1H	133.3	7.70, *td*, J_o = 7.5 Hz, J_m = 2.2 Hz, 1H	133.2
7	7.74, *td*, J_o = 7.5 Hz, J_m = 2 Hz, 1H	133.2	7.74, *td*, J_o = 7.5 Hz, J_m = 2.2 Hz, 1H	133.2
8	8.19, *ddd*, J_o = 7.3 Hz, J_m = 3.2 Hz, J_p = 1.8 Hz, 1H	126.4	8.21, *ddd*, J_o = 9.3 Hz, J_m = 2.3 Hz, J_p = 0.72 Hz, 1H	126.4
9	–	187.3	–	nd
10	–	182.0	–	nd
11	–	nd	–	nd
12	–	nd	–	nd
13	–	111.3	–	nd
14	–	114.3	–	nd
1-OH	13.24, *s*, 1H	161.2	13.00, *s*, 1H	nd
1′	–	–	–	–
2′	–	74.1	5.00,*d*, *J* = 16 Hz, 1H 4.84, *d*, *J* = 16 Hz, 1H	62.1
3′	–	99.7	5.00, *t*, 1H	100.5
4′	2.82, *d*, *J* = 16 Hz, 1H 3.85, *d*, *J* = 16 Hz, 1H	18.7	–	nd
5′	–	171.9	1.83, *q*, 2H	22.6
6′	5.35, *s*, 1H	102.5	1.03, *t*, 3H	6.7
7′	–	192.8	–	–
8′	3.05, *s*, 2H	39.1	–	–
2′-OCH_3	3.34, *s*, 3H	49.1	–	–
3′-OCH_3	3.38, *s*, 3H	51.6	–	–
5′-OCH_3	3.59, *s*, 3H	55.5	–	–
5′-CH_2-	–	–	1.83, *q*, 2H	22.6
6′-CH_3	–	–	1.03, *t*, 3H	6.7

nd-not detected.

(δ_H 3.83, *d*, *J* = 16 Hz, 1H; δ_H 2.82, *d*, *J* = 16 Hz, 1H), methylene protons (δ_H 3.05, *s*, 2H) and three methoxy protons (δ_H 3.58 *s*, 3H; δ_H 3.38, *s*, 3H; δ_H 3.34, *s*, 3H).The HMBC correlations of H-4 (δ_H 7.24), 1-OH (δ_H 13.24), H-4′ (δ_H 3.83 and δ_H2.82) with quaternary carbons C-2 (δ_C 156.1) and C-3 (δ_C 114.3) suggested that a pyran ring is fused next to the 9,10-anthraquinone moiety (Fig. 2). The methylene protons (δ_H 2.82, δ_H 3.83) were assigned at C-4′ (δ_C 18.7) based on their HMBC correlations with C-2 (δ_C 156.1), C-3 (δ_C 114.3), C-2′ (δ_C 74.1) and C-3′ (δ_C 99.7). H-4′, H-6′ (δ_H = 5.35) and H-8′ (δ_H = 3.05) gave similar HMBC correlations with C-2′ (δ_C 74.1) and C-3′ (δ_C 99.7) suggesting the presence of another ring fused next to the pyran ring. H-6′ (δ_H = 5.35) and H-8′ (δ_H = 3.05) showed HMBC cross-peaks with C-7′ (δ_C 192.8) suggesting the ring is a cyclohexanone. A methoxy group (δ_H 3.59) was assigned at C-5′ (δ_C 171.9) based on its ^3J HMBC correlation with the methine proton (H-6′) and its NOESY correlation with H-6′. The olefinic proton (δ_H 5.35, *s*, 1H) was placed at C-6′ based on its HMBC correlations with C-2′ (δ_C 74.1), C-5′ (δ_C 171.9), C-7′ (δ_C 192.8) and C-8′ (δ_C 39.1). The remaining methoxy groups resonating at δ_H 3.34 (*s*, 3H) and δ_H 3.59 (*s*, 3H) were assigned to C-2′ (δ_C 74.1) and C-3′ (δ_C 99.7), respectively, based on their ^3J HMBC correlations with the quaternary carbons. The structural elucidation was supported by the presence of its major fragments observed at *m*/*z* 253.0495 due to the fragmentation at C-2′ and C-3′ (Fig. 3) to give a 1-hydroxy-9,10-anthraquinone and cyclohexanone moieties.

The relative configurations of chiral centers at C-2′ and C-3′ were assigned as 2′-*S* and 3′-*R* based on the NOESY correlations observed (Fig. 4). Analysis of spectral data suggested that this compound is rennellianone A (3-(2′,3′,5′-trimethoxycyclohex-5′,6′-en-7′-one)pyrano-1-hydroxy-9,10-anthraquinone).Based on