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Coumarins from the roots of *Prangos uloptera*

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ABSTRACT

Three new coumarins, 6-*O*-[β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranosyl]-prenyletin, 3″-*O*-[β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranosyl]-oxypeucedanin hydrate and 2″-*O*-[β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranosyl]-oxypeucedanin hydrate, together with six known coumarins, 3″-*O*-[β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranosyl]-heraclenol, 3″-*O*-(β-D-glucopyranosyl)-heraclenol, tortuoside, 3″-*O*-(β-D-glucopyranosyl)-oxypeucedanin hydrate, heraclenol and oxypeucedanin hydrate, have been isolated from the roots of *Prangos uloptera*, and the structures of these coumarins were unequivocally determined by spectroscopic means, notably UV, HRESIMS, and 1D and 2D NMR spectroscopy.

1. Introduction

Prangos uloptera DC. (family: Apiaceae *alt*. Umbelliferae) is a perennial herb native to mountain slopes of the central and western Asian countries including Turkey, Iran, Iraq, Afghanistan and Uzbekistan (Abyshev and Denisenko, 1973; Mazloomifar et al., 2004; GRIN Database, 2008). *Prangos* species, commonly known as 'Djashir' in Iran, are widely used in folk medicine as tonic, and for the treatment of flatulence, haemorrhoids, wounds and leukoplakia (Dokoric et al., 2004). Previous phytochemical studies on the aerial parts, fruits and roots of *P. uloptera* yielded various coumarins, monoterpenes and sesquiterpenes (Abyshev and Denisenko, 1973; Sefidkon and Navaii, 2001; Mazloomifar et al., 2004; Nazemiyeh et al., 2007; Razvi et al., 2008). As part of our ongoing phytochemical and bioactivity studies on Iranian medicinal plants, we report on the isolation, identification and possible chemotaxonomic significance of nine coumarins, three of which are new natural products, from the roots of *P. uloptera*.

2. Results and discussion

A combination of solid-phase extraction (SPE) on C_{18} silica cartridges, and reversed-phase preparative high performance liquid chromatography (prep-HPLC) of the methanol (MeOH) extract of the roots of *P. uloptera* yielded nine coumarins (**1**–**9**), three of which (**1**, **5** and **6**) are new (Fig. 1). The structures of all compounds were elucidated by UV, MS and extensive 1D and 2D NMR analyses, and by comparison of the spectral data with respective published data for the known compounds.

All compounds (**1**–**9**) displayed UV absorption maxima characteristic for a coumarin nucleus (Murray et al., 1982). Moreover, the UV absorption maxima for the compounds **2**, **3** and **5**–**9** suggested a linear furanocoumarin skeleton within these molecules. The ^{1}H NMR spectra of compounds **1**–**9** exhibited signals characteristic for H-3 and H-4 of a coumarin nucleus (Murray et al., 1982).

The HRESIMS of **1** gave a *pseudo*-molecular ion peak at *m*/*z* 541.1920 $[M+H]^+$, corresponding to the empirical formula, $C_{25}H_{33}O_{13}$. In the ^{1}H and ^{13}C NMR spectra of **1**, in addition to the signals associated with a 6,7-dioxygenated coumarin nucleus

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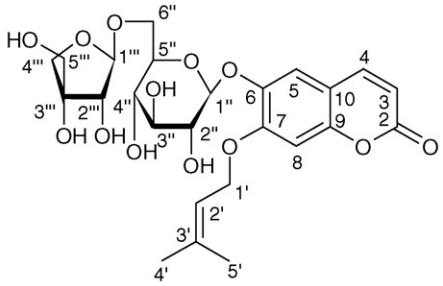

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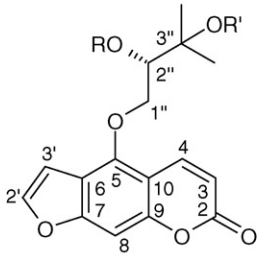

5 R = H; R' = β-D-apiofuranosyl-(1→6)-β-D-glucopyranosyl

6 R = β-D-apiofuranosyl-(1→6)-β-D-glucopyranosyl; R' = H

Fig. 1. Coumarins isolated from *P. uloptera*.

(Table 1), there were signals corresponding to a prenyloxy group (δ_H 5.38, 4.79 and 1.62; δ_C 128.8, 111.9, 65.6, 24.3 and 23.9), a glucosyl unit (δ_H 4.84 and 3.34–3.82; δ_C 104.5, 78.1, 77.4, 74.9, 72.0 and 69.8) and an apiosyl moiety (δ_H 5.01 and 3.60–3.88; δ_C 109.5, 77.5, 80.7, 74.9 and 65.5). The NMR signals associated with the coumarin nucleus and the prenyloxy group were in good agreement with the published data for prenyletin (Chiang et al., 1982; Cardona et al., 1992; Nuñez-Alarcón and Quińones, 1995), thus leaving the sugar molecules to be linked to C-6. Similarly, the NMR signals corresponding to the coumarin nucleus and the sugar moieties were in good agreement with the published data for aesculetin 6-*O*-β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside (Matsuda and Kikuchi, 1995), thus leaving the prenyloxy group to be linked to C-7. These linkages as well as the 1 → 6 link between apiose and glucose were confirmed from ^{1}H-^{13}C HMBC long-range correlations (Table 1). The ^3J correlation between the oxymethylene protons (H_2-1′, δ 4.79) of the prenyloxy group and C-7 (δ 151.9) of the coumarin nucleus confirmed that the prenyloxy was at C-7, and a similar correlation between the glucose anomeric proton (H-1″, δ4.84) and C-6 (δ 153.0) established glycosylation at C-6. A ^3J correlation between H-6″ (δ 3.72 and 3.82) and the anomeric carbon of apiose (C-1‴, δ 109.5), and from H-1‴ (δ 5.01) to C-6″ (δ 69.8) confirmed the 1 → 6 link between these two sugars. In the ^{1}H-^{1}H NOESY the one interaction between H_2-1′ and H-8, further confirmed that the prenyloxy group, was in close proximity of H-8, and was linked to C-7. Thus compound **1** was identified unambiguously as 6-*O*-[β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranosyl]-prenyletin.

The HRESIMS analyses of **5** and **6** revealed a *pseudo*-molecular ion peak at *m*/*z* 599.1976 $[M+H]^+$ corresponding to the empirical formula $C_{27}H_{34}O_{15}$ for both compounds. In the ^{1}H and ^{13}C NMR spectra of **5** and **6** (Table 2), in addition to displaying signals corresponding to oxypeucedanin hydrate (**9**, Hiermann et al., 1996; Ishihara et al., 2001; Tesso et al., 2005), there were signals attributable to a β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranosyl moiety as in **1**. The attachment of this disaccharyl

Table 1
^{1}H NMR (500 MHz, coupling constant *J* in Hz in parentheses), ^{13}C NMR (125 MHz) data, and ^{1}H-^{13}C HMBC key long-range correlations in **1**

Position	Chemical shift (δ) in ppm		^{1}H-^{13}C HMBC long-range correlation	
	^{1}H	^{13}C	^2J	^3J
Coumarin nucleus				
2	–	162.9	–	–
3	6.26, *d* (9.5)	111.9	C-2, C-4	C-10
4	7.93, *d* (9.5)	145.3	C-3, C-10	C-2, C-5, C-9
5	7.67, *s*	116.4	C-6, C-10	C-4, C-7, C-9
6	–	153.0	–	–
7	–	151.9	–	–
8	6.83, *s*	113.9	C-7, C-9	C-6, C-10
9	–	153.0	–	–
10	–	112.5	–	–
Prenyl unit				
1′	4.79, *d* (2.5)	65.6	C-2′	C-7, C-3′
2′	5.38, *t* (2.4)	111.9	C-1′, C-3′	3′-Me
3′	–	128.8	–	–
3′-Me	1.62, *s*	23.9	C-3′	3′-Me
3′-Me	1.62, *s*	24.3	C-3′	3′-Me
Glucosyl unit				
1″	4.84, *d* (7.8)	104.5	C-2″	C-6, C-3″, C-5″
2″	3.40[a]	74.9	C-1″, C-3″	
3″	3.34 t (9.5)	78.1	C-2″, C-4″	
4″	358[a]	72.0	C-3″, C-5″	
5″	3.80[a]	77.4	C-4″, C-6″	C-1″
6″	3.72[a], 3.82[a]	69.8	C-5″	C-4″, C-1‴
Apiosyl unit				
1‴	5.01, *d* (2.6)	109.5	C-2‴	C-6″, C-3‴
2‴	3.88[a]	77.5	C-1‴, C-3‴	
3‴	–	80.7	–	–
4‴	3.70[a], 3.92[a]	74.9	C-3‴	
5‴	3.60[a]	65.5	C-3‴	C-2‴, C-4‴

[a] Overlapped peaks.