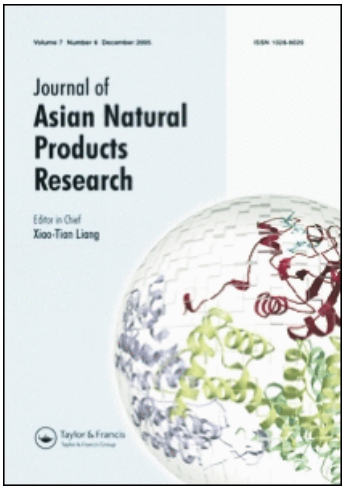

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Arylglycerol glucosides from *Dracocephalum forrestii*

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Three new arylglycerol glucosides, *threo*-guaiacylglycerol 3-*O*-(6-*O*-*p*-hydroxybenzoyl)-β-D-glucopyranoside (**1**), *threo*-guaiacylglycerol 3-*O*-[6-*O*-(*E*)-*p*-coumaroyl]-β-D-glucopyranoside (**2**) and *threo*-guaiacylglycerol 3-*O*-[6-*O*-(*Z*)-*p*-coumaroyl]-β-D-glucopyranoside (**3**), together with seven known compounds were isolated from the whole plants of *Dracocephalum forrestii* and their structures were determined on the basis of spectroscopic evidences.

Keywords: *Dracocephalum forrestii*; Labiatae; Arylglycerol glucosides

1. Introduction

Dracocephalum forrestii (Labiatae) is a wild perennial plant growing in Lijiang and Diqing regions of Yunnan province, China [1]. It has been used as astringent, diuretic and antipyretic agent in traditional Tibetan medicine [2]. To our knowledge, no phytochemical investigation on this species has so far been reported. In phytochemical investigation of the n-BuOH-soluble fraction of EtOH extraction of *Dracocephalum forrestii*, we isolated three new arylglycerol glucosides (**1**–**3**), together with seven known compounds. The present paper deals with structural elucidation of these compounds.

2. Results and discussion

Compound **1** was obtained as an amorphous solid. The possible molecular formula of **1** was inferred to be $C_{23}H_{28}O_{12}$ from its quasi-molecular ion at *m*/*z* 495 $[M\text{-}H]^-$ in negative ion FAB-MS, and ^{13}C NMR (with DEPT) spectral data (table 1). The molecular composition of $C_{23}H_{28}O_{12}$ was finally determined by HRESI-MS at *m*/*z* 495.1481 $[M\text{-}H]^-$ (calcd. for $C_{23}H_{27}O_{12}$, 495.1502). The presence of hydroxyl groups, carbonyl group and aromatic rings could be proposed in the structure of **1** based on the absorption bands at 3419, 1697, 1607,

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Table 1. ^{13}C (125 MHz) and ^{1}H NMR (500 MHz) spectral data of compounds **1**, **2**, and **3** [CD_3OD, δ (ppm), *J* (Hz) in parentheses].

	1		*2*		*3*	
NO.	*δC*	*δH*	*δC*	*δH*	*δC*	*δH*
1	75.5	4.54 d (6.4)	75.5	4.56 d (6.3)	75.6	4.52 d (6.5)
2	76.1	3.85 m	76.2	3.85 m	76.2	3.85 m
3	72.5	3.80 dd (10.3, 3.0) 3.31 dd (10.3, 3.4)	72.6	3.76 dd (10.3, 3.0) 3.32 dd (10.3, 3.8)	72.6	3.80 dd (10.3, 3.2) 3.31 dd (10.3, 3.3)
1′	134.4	–	131.3	–	131.3	–
2′	111.6	6.97 d (1.8)	111.5	6.97 d (1.8)	111.6	6.98 d (1.8)
3′	148.8	–	148.3	–	148.3	–
4′	147.1	–	147.1	–	146.9	–
5′	115.9	6.72 d (8.1)	115.9	6.75 d (8.2)	115.9	6.74 d (8.2)
6′	120.7	6.18 dd (8.1, 1.8)	120.7	6.80 d (8.2, 1.8)	120.7	6.79 dd (8.2, 1.8)
OCH_3	56.4	3.81 s	56.4	3.82 s	56.4	3.82 s
1″	104.9	4.25 d (7.8)	105.0	4.23 d (7.7)	104.9	4.19 d (7.8)
2″	75.1	3.25 dd (7.8, 9.3)	75.1	3.26 dd (7.7, 9.3)	75.0	3.24 dd (7.8, 9.3)
3″	77.7	3.39 m	77.7	3.34 m	77.7	3.34 m
4″	71.7	3.39 m	71.7	3.36 m	71.6	3.35 m
5″	75.4	3.52 m	75.4	3.47 m	75.2	3.43 m
6″	64.7	4.57 dd (11.9, 2.0) 4.34 dd (11.9, 5.7)	64.5	4.47 dd (11.9, 1.9) 4.27 dd (11.9, 5.7)	64.5	4.41 dd (11.8, 2.0) 4.20 dd (11.8, 5.8)
1‴	122.2	–	127.1	–	127.6	–
2‴, 6‴	132.9	7.87 d (8.7)	131.3	7.46 d (8.7)	133.8	7.62 d (9.0)
3‴, 5‴	116.2	6.83 d (8.7)	116.8	6.80 d (8.7)	115.9	6.75 d (9.0)
4‴	163.5	–	161.3	–	160.1	–
7‴	168.0	–	146.9	7.61 d (16.0)	145.4	6.88 d (12.8)
8‴			114.9	6.33 d (16.0)	116.2	5.71 d (12.8)
9‴			169.1	–	168.1	–

1516 and 1277 cm^{-1} in its IR spectrum. The UV absorption at λ_{max} 288 nm was also indication of a phenolic moiety. In the ^{1}H NMR spectrum of **1**, the coupling patterns of the aromatic proton signals at δ_H 6.97 (1H, d, $J = 1.8$ Hz), 6.72 (1H, d, $J = 8.1$ Hz) and 6.18 (1H, dd, $J = 1.8, 8.1$ Hz), and aromatic proton signals at δ_H 6.83 (2H, d, $J = 8.7$ Hz) and 7.87 (2H, d, $J = 8.7$ Hz), suggested the presence of a 1,3,4-trisubstituted benzene ring and a 1,4-disubstituted benzene ring. The glucose moiety was assigned as β-configuration based upon the coupling constant of the anomeric proton δ_H 4.25 (d, $J = 7.8$ Hz), which was attached to the C-3 judged from the correlation between C-3 and the anomeric proton in HMBC spectrum (figure 2), and the NOE correlation between C-3 and the anomeric proton in ROESY spectrum. The methoxyl group was located at C-3′ based on observed ROESY correlation between OMe (δ 3.81) and H-2′ (δ 6.97). The ^{13}C NMR data of C-3 (δ 72.5) and C-2 (δ 76.1) were in accordance with those reported in literature [3]. The relative stereochemistry of the glycerol portion was expected to be *threo*-form from the coupling constant ($J = 6.4$ Hz) of the proton at the C-1 position [4,5,6]. In the ^{13}C NMR spectrum of **1**, C-6″ of the glucose moiety showed a downfield shift at δ 64.7 while the slightly shielded C-5″ resonance was at δ 75.4. These shifts clearly indicated that C-6″ of the glucose was bonded to the *p*-hydroxybenzoyl. The HMBC correlation between H-6″ and C-7‴ (δ 168.0) confirmed this result. Therefore, The structure of compound **1** was elucidated to be *threo*-guaiacylglycerol 3-*O*-(6-*O*-*p*-hydroxybenzoyl)-β-D-glucopyranoside (figure 1).

The molecular formula of compound **2** was deduced as $C_{25}H_{30}O_{12}$ from HRESI-MS at *m/z* 521.1640 $[M-H]^-$ (calcd. for $C_{25}H_{29}O_{12}$, 521.1659). The ^{1}H and ^{13}C NMR data of **2** were similar to those of **1** in glycerol and sugar moieties. Its IR spectrum (ν_{max} 3413, 1695, 1604, 1515 and 1272 cm^{-1}) showed the presence of hydroxyl groups, carbonyl group and aromatic

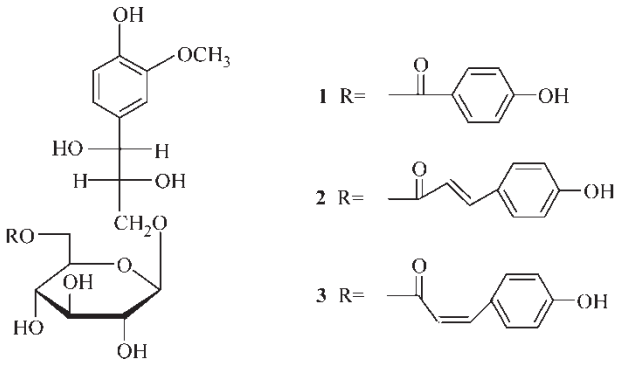

Figure 1. Structures of compounds **1**–**3**.

rings. The UV absorption at λ_{max} 315 nm was in accordance with a substituted aromatic ring. Its ^{1}H NMR spectrum showed two olefinic protons at δ 7.61 and 6.33 with a large coupling constant (d, $J = 16.0$ Hz). The HMBC correlations of **2** (figure 2) revealed that it contains a *trans*-*p*-coumaroyl function attached to C-6″ of glucose moiety. The relative stereochemistry of the glycerol portion was also expected to be *threo*-form from the coupling constant ($J = 6.3$ Hz) of the proton at the C-1 position. Thus, compound **2** was assigned as *threo*-guaiacylglycerol 3-*O*-[6-*O*-(*E*)-*p*-coumaroyl]-β-D-glucopyranoside.

Compound **3** was found to have the same molecular formula determined by HRESI-MS as that of **2**. The other spectroscopic data were also similar to those of **2**, except for the coupling constants of two olefinic protons, δ_H 6.88 (d, $J = 12.8$ Hz) and 5.71 (d, $J = 12.8$ Hz), from which a *cis*-form double bond in the *p*-coumaroyl function was assumed. Thus, compound **3** was elucidated to be *threo*-guaiacylglycerol 3-*O*-[6-*O*-(*Z*)-*p*-coumaroyl]-β-D-glucopyranoside.

The structures of seven other known compounds were established by comparison with data from the literature as 3,7-dimethyloct-1-ene-3,6,7-triol 3-*O*-β-D-glucopyranoside [7], sayaendoside [8], 2-hydroxy-5-(2-hydroxyethyl)phenyl β-D-glucopyranoside [9], 3-(3,4-dihydroxyphenyl)acrylic acid 1-(3,4-dihydroxyphenyl)-2-methoxycarbonylethyl ester [10], benzyl-α-L-xylopyranosyl(1–6)-β-D-glucopyranoside [11], apigenin [12] and 3-(3,4-dihydroxyphenyl)-2-propenoic acid methyl ester [13].

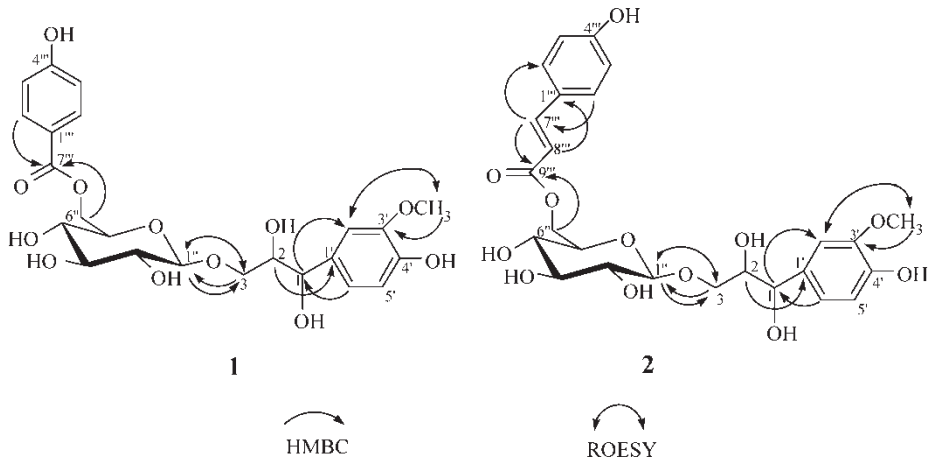

Figure 2. Selected HMBC and ROESY correlations for compounds **1** and **2**.

3. Experimental

3.1 General experimental procedures

IR spectra were taken on Nicolet AVATAR-360. The UV spectra were recorded on Shimadzu-2501PC spectrophotometer. Optical rotations were taken on Perkin-Elmer-341 polarimeter. The 1D and 2D NMR spectra were recorded on Bruker DRX-500 spectrometer. FAB-MS was performed on VG-Autospec-3000 spectrometer. HRESI-MS was performed on API Qstar Pulsar spectrometer. Column chromatography: silica gel (200–300 mesh, Qingdao, China), RP-18 (Merck). TLC: silica gel (GF_{254}, Qingdao, China).

3.2 Plant material

The plant material was collected in xianggelila county, Yunnan province, China, in September 2002, and identified as *Dracocephalum forrestii* by Mr. A Dou (Deqin Tibetan hospital). A voucher specimen was deposited in School of Pharmacy, Yunnan University.

3.3 Extraction and isolation

The air-dried and powered plant (4.5 kg) was extracted with 70% EtOH (4 × 10 L) at room temperature for 48 h each time. The residue was suspended in water, and then extracted with petroleum ether, EtOAc and n-BuOH, successively. The n-BuOH extract (72 g) was chromatographed on silica gel (1.5 kg, 200–300 mesh) and eluted with $CHCl_3$ containing increasing amounts of MeOH ($CHCl_3$—MeOH, 95:5–50:50). Fraction C (obtained with $CHCl_3$—MeOH 100:15) was chromatographied over RP-18 with 40% MeOH to afford compound **1** (41 mg). Fraction D (obtained with $CHCl_3$—MeOH 100:20) was chromatographied over RP-18 with 35% MeOH to afford compounds **2** (9 mg) and **3** (5 mg).

3.3.1 Compound (1). *threo*-guaiacylglycerol 3-*O*-(6-*O*-*p*-hydroxybenzoyl)-β-D-glucopyranoside. amorphous power, $[\alpha]_D^{19}$ −2.9 (*c* 0.4, MeOH); UV (MeOH) λ_{max} nm (log ϵ) 288(3.68), 237(3.22), 207(3.42); IR (KBr) ν_{max} 3419, 2925, 1697, 1607, 1516, 1277, 1048, 854, 771 cm^{-1}; ^1H and ^{13}C NMR data, see Table 1; HRESI-MS *m/z*: 495.1481 $[M-H]^-$ (calcd. for $C_{23}H_{27}O_{12}$, 495.1502).

3.3.2 Compound (2). *threo*-guaiacylglycerol 3-*O*-[6-*O*-(*E*)-*p*-coumaroyl]-β-D-glucopyranoside. amorphous solid, $[\alpha]_D^{19}$ 0 (*c* 0.1, MeOH); UV (MeOH) λ_{max} nm (log ϵ) 315(4.23), 225(4.42); IR (KBr) ν_{max} 3413, 2924, 1695, 1604, 1515, 1272, 1168, 1032, 882 cm^{-1}; ^1H and ^{13}C NMR data, see Table 1; HRESI-MS *m/z*: 521.1640 $[M-H]^-$ (calcd. for $C_{25}H_{29}O_{12}$, 521.1659).

3.3.3 Compound (3). *threo*-guaiacylglycerol 3-*O*-[6-*O*-(*Z*)-*p*-coumaroyl]-β-D-glucopyranoside. amorphous solid, $[\alpha]_D^{19}$ 0 (*c* 0.4, MeOH); UV (MeOH) λ_{max} nm (log ϵ) 315(4.11), 212(3.67); IR (KBr) ν_{max} 3413, 2923, 1695, 1631, 1604, 1515, 1272, 1169, 1033, 882 cm^{-1}; ^1H and ^{13}C NMR data, see Table 1; HRESI-MS *m/z*: 521.1678 $[M-H]^-$ (calcd. for $C_{25}H_{29}O_{12}$, 521.1659).

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