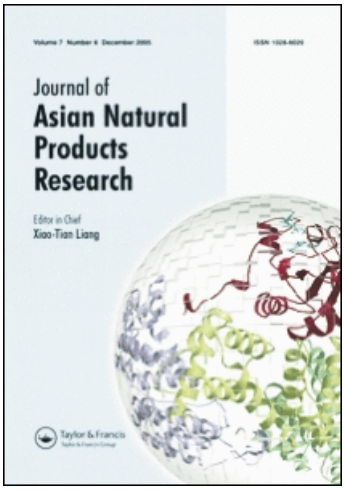

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Note: A new compound from *Rhododendren anthopogonosides* maxim

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Note

A new compound from *Rhododendren anthopogonosides* maxim

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A new compound, (2*R*)-4-phenyl-2-*O*-[β-D-xylopyranosyl(1 → 6)-β-D-glucopyranosyl]butane (**1**), has been isolated from the aerial parts of *Rhododendren anthopogonoides*, together with two known compounds, fraxin (**2**), and lyoniside (**3**). Their structures were determined by means of physico-chemical evidence and spectral analyses, including UV, IR, HR-FABMS, ^{1}H and ^{13}C NMR, and 2D NMR data.

Keywords: *Rhododendren anthopogonoides* Maxim; (2*R*)-4-Phenyl-2-*O*-[(β-D-xylopyranosyl(1 → 6)-β-D-glucopyranosyl]butane; (2*R*)-4-Phenyl-2-butanol

1. Introduction

Rhododendren anthopogonoides Maxim. is a shrub, commonly growing on the damp sides of mountains, and is distributed throughout western regions widely in China. Its stems and leaves have traditionally been used as a folk medicine to treat coughes, bronchitis, asthma and so on [1]. In our investigation of biologically active substances from *Rhododendren anthopogonoides*, we examined the constituents of the plant systematically, and led to the isolation of a new glycoside. We describe here the isolation, structure elucidation, and absolute stereochemistry of the new compound, (2*R*)-4-phenyl-2-*O*-[β-D-xylopyranosyl(1 → 6)-β-D-glucopyranosyl]butane (**1**).

2. Results and discussion

Compound **1** was obtained as a white powder, $[\alpha]_D^{17}$ −81.0 (*c*, 0.10, in 80% EtOH). It showed a quasi-molecular ion peak at *m/z* 445.2 $[M + H]^+$, and 467.1 $[M + Na]^+$ in the FAB, and the HRFAB mass spectrum displayed a quasi-molecular ion peak at *m/z* 467.1903 $[M + Na]^+$,

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corresponding to the molecular formula $C_{21}H_{32}O_{10}$. According to the molecular formula, six degrees of unsaturation were calculated, accounted for by a benzene ring, a glucopyranose and a xylopyranose on the basis of analyses below.

The IR spectrum showed absorption bands at 1454, 1496, 1600 and 3430 cm^{-1}, suggesting an aromatic ring and hydroxy group. The ^{13}C NMR and DEPT spectrum (table 1) of compound **1** gave 18 carbon signals, including 1 methyl, 4 methylenes, 12 methines and 1 quaternary carbon, of which the carbon signals at δ 142.31, 128.38, 128.23 and 125.54 were attributed to a mono-substituted phenyl moiety. Based on the DEPT, HMQC and HMBC data (table 1), the relative high-field carbon signals at δ 19.72, 31.26, 38.66 and 72.71 were deduced to be the structural fragment-CH_2–CH_2–CH–CH_3. Moreover, HMBC correlations between H-3 (δ 1.73) and C-1′(δ 142.31), as well as H-4 (δ 2.62) and C-2′ or C-6′ (δ 128.23) (figure 1), indicated that the fragment [–CH_2–CH_2–CH–CH_3] must be attached to C-1′ of the phenyl group.

The ^1H NMR spectrum of **1** shows two anomeric proton signals, at δ 4.15 (1H, d, $J = 7.8$ Hz), and 4.23 (1H, d, $J = 7.5$ Hz), and the corresponding anomeric carbon signals at δ 100.69, 104.82 were assigned by HMQC experiment; these data suggested that **1** contains two sugar moieties. By comparing the NMR spectral data of **1** with those reported for the sugar moieties [2], the two sugar moieties were deduced to be glucose and xylose, which were further supported by comparison with authentic samples on TLC after hydrolysis. The *J* values (table 1) of the anomeric protons indicate the two sugar units are β-oriented. In the HMBC spectrum, the long-range correlation between the anomeric proton at δ 4.15 (Glu. H-1) and carbon signal at δ 72.71 (C-2) suggest that the glucose unit is connected with aglycone at C-2, while the long-range correlation between the anomeric proton at δ 4.23 (xyl. H-1) and the carbon signal at δ 68.37 (Glu. C-6) shows that the xylose unit is connected to the glucose at C-6″.

Table 1. NMR data of compound **1** (300 MHz for ^1H and 75 MHz for ^{13}C NMR in DMSO).

Position	*^1H (J, Hz)*	*^{13}C*	*DEPT*	*HMBC*
1	1.09 (3H, d, 3.3)	19.72	CH_3	C-2, C-3
2	3.80 (1H, m)	72.71	CH	C-3, C-4, C-1″
3	1.73 (2H, m)	38.66	CH_2	C-1′, C-1, C-2, C-4
4	2.62 (2H, m)	31.26	CH_2	C-1′, C-2′, C-6′
1′		142.31	C	
2′	7.22 (1H, m)	128.23	CH	C-4, C-4′
3′	7.25 (1H, m)	128.38	CH	C-1′
4′	7.19 (1H, m)	125.54	CH	C-2′, C-6′
5′	7.25 (1H, m)	128.38	CH	C-1′
6′	7.22 (1H, m)	128.23	CH	C-4′, C-4
2-glc				
1″	4.15 (1H, d, 7.8)	100.69	CH	C-2, C-2″, C-5″
2″	2.94 (1H, m)	73.33	CH	
3″	3.10 (1H, m)	76.76	CH	
4″	3.08 (1H, m)	69.91	CH	
5″	3.09 (1H, m)	76.56	CH	
6″ a	3.56 (1H,dd, 5.1,10.2)	68.37	CH_2	
b	3.90 (1H, br d, 10.2)			
6-xyl				
1‴	4.23 (1H, d, 7.5)	104.82	CH	C-6″, C-2‴, C-5‴
2‴	2.94 (1H, m)	73.33	CH	
3‴	3.26 (1H, m)	75.74	CH	
4‴	3.24 (1H, m)	69.53	CH	
5‴ a	2.96 (1H, m)	65.66	CH_2	
b	3.66 (1H,dd, 5.4, 11.4)			

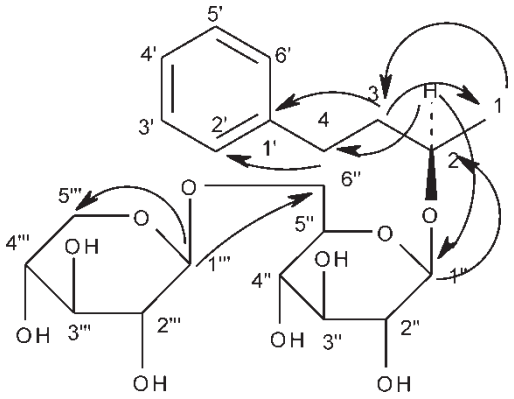

Figure 1. Key HMBC correlations for compound **1**.

Previously [3], the optical rotation of (−)-4-phenyl-2-butanol was given as $[\alpha]_D^{26}$ −32 (*c*, 6.2, in C_6H_6), and its absolute configuration at C-2 as *R*. Through hydrolysis, **1** yielded 4-phenyl-2-butanol, the optical rotation of which was $[\alpha]_D^{19}$ −30 (*c*, 5.9, in C_6H_6), which is in accord with the value mentioned above. Therefore, the absolute configuration of compound **1** at C-2 is assigned as *R*.

Taking the above data into account, **1** was determined to be (2*R*)-4-phenyl-2-*O*-[β-D-xylopyranosyl(1 → 6)-β-D-glucopyranosyl]butane (figure 2).

Besides the new compound, other constituents isolated from this plant were identified as fraxin (**2**) and lyoniside (**3**) (figure 2) by spectral analyses and comparison of physical data with those of the literature [4,5].

3. Experimental

3.1 General experimental procedures

Melting points were determined on an XT_4-100x micro-melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. IR

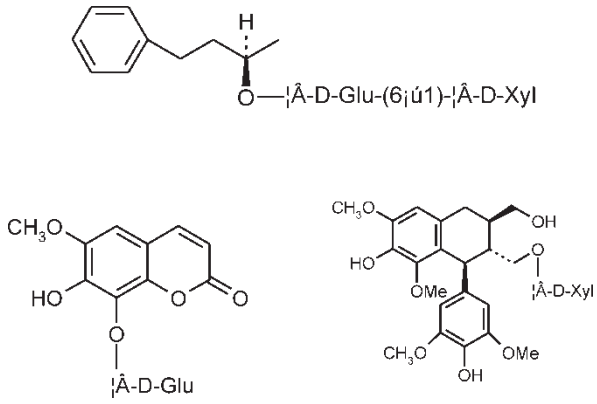

Figure 2. Chemical structures of **1**–**3**.

spectra were obtained with KBr on a Perkin-Elmer 683 infrared spectrometer. NMR spectra were run on a Mercury 300 spectrometer with TMS as internal standard. FABMS were recorded on an Autospec-Ultima ETOF MS spectrometer. Column chromatography and TIC were performed using silica gel (200–300, mesh, produced by Qing Dao Hai Yang Chemical group co. Qing Dao). The polyamide and Sephadex LH-20 used were purchased from the Beijing Chemical Factory (Beijing, China).

3.2 Plant material

The air-dried stems and leaves of *Rhododendren anthopogonoides* were collected from Qinghai (Qinghai Province of China), and were identified by Professor Duojie (Institute of Tibetan Medicine of Qing Hai Province, China). A voucher specimen of the plant has been deposited in the Herbarium of the Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing, China.

3.3 Extraction and isolation

The air-dried stems and leaves of *Rhododendren anthopogonoides* (9.0 Kg) were extracted three times with EtOH under reflux. The combined EtOH extract was concentrated to give a residue (1.1 kg) under reduced pressure, which was dispersed in water and partitioned with light petroleum, EtOAc and n-BuOH to give three fractions. The EtOAc fraction (409.2 g) was subjected to polyamide column chromatography, eluting with H_2O–EtOH (9:1, 7:3, 5:5, EtOH), to give four fractions (1–4). Fraction 1 (17.5 g) was repeatedly subjected to silica gel column and Sephadex LH-20 column, eluting with a gradient mixture of $CHCl_3$–MeOH (95:5, 90:10, 80:20, v/v) and EtOH–H_2O (1:9, 3:7, 5:5, 7:3, v/v) respectively, to afford compounds **1** (28 mg), **2** (56 mg) and **3** (129 mg).

3.4 (2R)-4-Phenyl-2-*O*-[β-D-xylopyranosyl(1 → 6)-β-D-glucopyranosyl] butane (1)

White powder, mp 180–182°C, $[\alpha]_D^{17}$ −81.0 (*c*, 0.10, in 80% EtOH). IR (KBr) ν(cm^{-1}): 1600, 1496, 1454, 1078, 1039, 144, 698. ^1H (300 MHz, in DMSO-d_6) and ^{13}C (75 MHz, in DMSO-d_6) NMR data see table 1. FABMS *m/z* 445.2 $[M + H]^+$, 467.1 [M + Na]. HR-FABMS *m/z* 467.1903 $[M + Na]^+$(calcd. for $C_{21}H_{32}O_{10}Na$, 467.1893).

3.5 (2R)-4-Phenyl-2-butanol

Compound **1** was boiled under reflux with 1 M HCl (10 ml) for 3 h. The reaction mixture was then extracted with Et_2O, and the Et_2O layer was washed and evaporated *in vacuo* to dryness. (2*R*)-4-Phenyl-2-butanol in the residue was identified with an authentic sample [on TLC with light petroleum–CH_3OCH_3 (9:1)], and by its optical rotation, $[\alpha]_D^{19}$ − 30 (*c*, 5.9 in C_6H_6), which is in accordance with that reported in literature [3]. Moreover, the ^{1}HNMR signals at δ 7.19 (m, 5H), 3.75 (m, 1H), 1.5–2.5 (m, 4H) and 1.06 (d, 3H,CH_3) were the same as the data reported in the literature [3].

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