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Phenolic Components from *Rhododendron latoucheae*

Part 5 in the series "Chemical Studies on Ericaceae Plants"

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Abstract: From the leaves of *Rhododendron latoucheae* (Ericaceae), two new natural phenolic compounds named (+)-rhodolatouchol **1** and isoepirhododendrin **4** were identified. Six other known compounds, (+)-rhododendrol, epirhododendrin, 4-[3'-O-β-D-glucopyranosyl-4'-hydroxyphenyl]-2-butanone, 4-(4'-O-β-D-glucopyranosylphenyl)-2-butanone, benzyl-O-β-D-glucopyranoside and arbutin were also obtained.

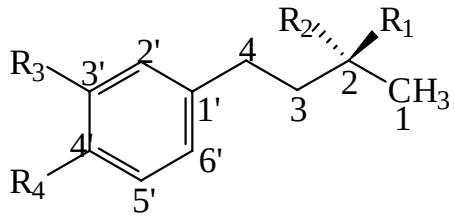
Keywords: *Rhododendron latoucheae*; Ericaceae, (+)-rhodolatouchol; isoepirhododendrin.

Chemical components of the genus *Rhododendron* with various bioactivities, such as antitussive and antitracheitis have been identified before[1]. To the best of our knowledge, the plant *Rhododendron latoucheae* Finet *et* Franch of the genus has not been studied chemically up to now. We herein report the structural elucidation of two new natural phenolic compounds named (+)-rhodolatouchol **1** and isoepirhododendrin **4** from the leaves of *R. latoucheae*. Besides, six other known compounds, (+)-rhododendrol **2**, epirhododendrin **3**, 4-(3'-O-β-D-glucopyranosyl-4'-hydroxyphenyl)-2-butanone **5**, 4-(4'-O-β-D-glucopyranosylphenyl)-2-butanone **6**, benzyl-O-β-D-glucopyranoside **7** and arbutin **8** were also isolated from the plant.

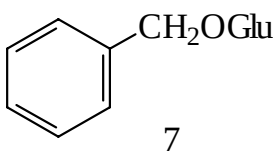
Compound **1** was obtained as light yellow oil. In ^{13}C NMR spectrum of **1** (**Table 1**), 10 carbon signals were observed as one methyl, two methylenes, four methines and three quaternary carbon signals. A benzene ring should exist in the structure of **1** according to ^{13}C NMR data. EI mass spectrum of **1** exhibited a molecular ion signal at *m/z* 182 [M^+]. The molecular formula of **1** was thus deduced to be $C_{10}H_{14}O_3$. Three hydroxy groups exist in the structure of **1**, among them, one should be connected to the methine carbon and the other two should be connected to the aromatic ring on the basis of chemical shifts of relevant carbon signals.

Analysis of ^1H-^1H COSY spectrum of **1** enabled the deduction of a fragment CH_3-CH(OH)-CH_2-CH_2-. This fragment should be linked to the benzene ring according to ^1H-^{13}C long range correlation signals between C-1' at δ 134.5 and the two H-4 protons at δ 2.85 and 2.95 in HMBC spectrum of **1**.

Figure 1. Structures of Compounds **1-8.**



	R 1	R 2	R 3	R 4
1	OH	H	OH	OH
2	OH	H	H	OH
3	OGlu	H	H	OH
4	OH	H	H	OGlu
5	O		OGlu	OH
6	O		H	OGlu



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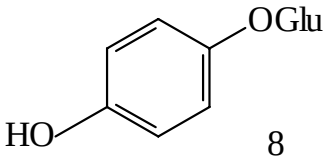

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Three aromatic protons at δ 7.25 (br, s), δ 7.18 (d, 8.0) and δ 6.72 (br, d, 8.0) indicated a 1,3,4-substitution pattern of the benzene ring. In NOESY spectrum of **1**, correlation signals were observed between proton at δ 7.25 (H-2') and the two H-4 protons, and also between proton at δ 6.72 (H-6') and the two H-4 protons.

On the basis of above evidences, the structure of **1** was established as 4-(3',4'-dihydroxyphenyl)-2-butanol as shown in **Figure 1**. A known compound, (-)-4-(3',4'-dihydroxyphenyl)-2-butanol with identical relative configuration to that of **1** has been

reported before[2]. Optical rotation value of (-)-4-(3',4'-dihydroxyphenyl)-2-butanol was $[\alpha]_D^{25}$ -18.1 (EtOH, *c* 0.12), and absolute configuration of C-2 was determined to be R. While the optical rotation value of compound **1** was $[\alpha]_D^{20}$ +11.8 (EtOH, *c* 0.85). Therefore, absolute configuration of C-2 of **1** was deduced to be S. Compound **1** is a new natural phenolic compound named (+)-rhodolatouchol.

Compound **4** was obtained as amorphous powder with $[\alpha]_D^{15}$ –28.1 (EtOH, *c* 0.32). FAB mass spectrum of **4** exhibited a quasimolecular ion signal at *m/z* 329 $[M+H]^+$. Acidic hydrolysis of **4** yielded glucose and an aglycone, and **4** was thus a glucoside. In ^{1}H NMR spectrum of **4**, an anomeric proton signal was found at δ 5.67 (1H, *d*, 7.8), therefore, the glycosidic linkage should be in β configuration. The aglycone of **4** was identified to be 4-(4'-hydroxyphenyl)-2-butanol using similar methods as mentioned above. The absolute configuration of C-2 of **4** was determined to be S according to similar optical rotation values between **2** {$[\alpha]_D^{15}$ +11.8 (EtOH, *c* 0.40); Lit. $[\alpha]_D^{20}$ +13.6 (EtOH, *c* 0.41)} and the aglycone of **4** {$[\alpha]_D^{15}$ +10.5 (EtOH, *c* 0.44)}[3]. The structural difference between **4** and **3** might just lie in linking position of their sugar moieties, which can be confirmed by comparison of their ^{13}C NMR data (**Table 1**)[4]. The HMBC spectrum of **4** showed correlation signal between the anomeric proton signal of the glucose and C-4' signal of the benzene ring, therefore, the glucose moiety should be connected to C-4'. Compound **4** was therefore identified to be 4-(4'-O-β-D-glucopyranosylphenyl)-2(S)-butanol. It is a new natural phenolic compound named isoepirhododendrin.

Table 1. ^{13}C-NMR data of compounds **1**, **3** and **4** (C_5D_5N, 75MHz).

C	**1**	**3**[#]	**4**
1	24.2, q	22.3, q	23.9, q
2	66.4, d	75.8, d	66.0, d
3	42.3, t	39.5, t	41.8, t
4	32.2, t	30.9, t	31.5, t
1'	134.5, s	133.3, s	136.3, s
2'	116.9, d	130.0, d	129.4, d
3'	147.0, s	116.2, d	116.7, d
4'	145.0, s	156.7, s	156.4, s
5'	116.4, d	116.2, d	116.7, d
6'	119.8, d	130.0, d	129.4, d
G-1		104.5, d	102.1, d
G-2		75.5, d	74.6, d
G-3		78.6, d	78.4, d
G-4		71.7, d	71.0, d
G-5		78.2, d	78.1, d
G-6		62.9, t	62.0, t

Data was taken from Reference 4.

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