FLAVONOLS AND FLAVONOL GLYCOSIDES FROM *Rhododendron irroratum*

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Rhododendron irroratum Franch. is a shrub that flowers in March to May and is widely distributed southwest of China, especially in Yunnan Province. It is one species of *Rhododendron*, which are famous decorative plants and generally used in Chinese folk medicine. Although several species of *Rhododendron*, such as *Rhododendron anthopogonoides* [1] and *Rhododendron fortunei* [2], have been reported to contain flavonols and flavonol glycosides, the chemical constituents in the flower of *R. irroratum* have been less studied.

Flowers of *R. irroratum* were collected in September 2005 from Yunnan province of China and identified by Prof. Changqin Zhang, Kunming Institute of Botany, Chinese Academy of Sciences.

Dry pieces of flowers (5 kg) were refluxed with 80% EtOH at 80°C and then concentrated. The residue was partitioned between H_2O and petroleum ether, $CHCl_3$, EtOAc, and *n*-BuOH, successively. The EtOAc fraction (95g) was subjected to silica gel column chromatography, which was eluted with $CHCl_3$–MeOH (100:1→100:50). The eluate of 108 to 136 fractions (1.5 g) was chromatographed on silica gel column and then submitted to Sephadex LH-20 column to afford **1** (50 mg) and **2** (60 mg). The fractions (2.5 g) of 137 to 151 were subjected to repeated chromatography to obtain **4** (15 mg). The part (17 g) from 152 to 197 afforded **3** (10 mg), **5** (200 mg).

Their chemical structures were identified by spectral analysis using UV, IR, MS, and NMR spectrometers and were determined as kaempferol (**1**) [3], quercetin (**2**) [4], myricetin (**3**) [4], quercetin-3-*O*-*β*-D-galactopyranoside (**4**) [5], and quercetin -4′-*O*-*β*-D-galactopyranoside (**5**) [6] by comparing the data with those in the literature. They were all isolated from *R. irroratum* for the first time.

Kaempferol (1) yellow powder. UV (MeOH, λ_{max}, nm, log ε): 368 (4.3), 267 (4.2), 202(4.5); IR (KBr, ν_{max}, cm^{-1}): 3326 (OH), 1668 (C=O), 1620, 1513; ESIMS *m/z*: 285 $[M-H]^+$; ^1H NMR (500 MHz, MeOD, δ, ppm, J/Hz): 8.09 (2H, dd, J = 4.8,6.9, H-2′, H-6′), 6.91 (2H, dd, J = 4.7, 6.9, H-3′, H-5′), 6.40 (1H, d, J = 2.1, H-8), 6.19 (1H, d, J = 2.1, H-6).

Quercetin (2) yellow powder. UV (MeOH, λ_{max}, nm, log ε): 372 (4.3), 256 (4.3), 205 (4.6); IR (KBr, ν_{max}, cm^{-1}): 3408 (OH), 1663 (C=O), 1610, 1562; ESIMS *m/z*: 301 $[M-H]^+$; ^1H NMR (500 MHz, MeOD, δ, ppm, J/Hz): 7.63 (1H, dd, J = 2.2, 8.5, H-5′), 7.73 (1H, d, J = 2.2, H-2′), 6.89 (1H, d, J = 8.5, H-6′), 6.39 (1H, d, J = 2.1, H-8), 6.19 (1H, d, J = 2.1, H-6).

Myricetin (3) yellow powder. UV (MeOH, λ_{max}, nm, log ε): 375 (3.7), 254 (3.6), 210 (3.9); IR (KBr, ν_{max}, cm^{-1}): 3427 (OH), 1667 (C=O), 1623, 1523; ESIMS *m/z*: 317 $[M-H]^+$; ^1H NMR (500 MHz, acetone-d_6, δ, ppm, J/Hz): 7.42 (2H, s, H-2′, H-6′), 6.50 (1H, d, J = 2, H-8), 6.26 (1H, d, J = 2, H-6).

Quercetin-3-*O*-*β*-D-galactopyranoside (4) (hyperin) pale yellow powder. UV (MeOH, λ_{max}, nm, log ε): 360 (4.0), 257 (4.0), 206 (4.3); IR (KBr, ν_{max}, cm^{-1}): 3294 (OH), 1656 (C=O), 1605, 1559, 1502; ESIMS *m/z* : 463 $[M-H]^+$. For the ^1H and ^{13}C NMR data, see Table 1.

Quercetin-4′-*O*-*β*-D-galactopyranoside (5) yellow powder. UV (MeOH, λ_{max}, nm, log ε):364 (4.2), 257 (4.3), 205 (4.5); IR (KBr, ν_{max}, cm^{-1}): 3339 (OH), 1655 (C=O), 1605, 1561, 1503; ESIMS *m/z*: 463 $[M-H]^+$. For the ^1H and ^{13}C NMR data, see Table 1.

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TABLE 1. ^{1}H NMR and ^{13}C NMR Data of Compounds **4** and **5** (δ, ppm, J/Hz)

C atom	**4** (CD_3OD)		**5** (DMSO-d_6)	
	^{1}H	^{13}C	^{1}H	^{13}C
2		158.4		156.2
3		135.8		133.4
4		179.5		177.4
5		163.0		161.1
6	6.20 (1H, d, 2.1)	99.9	6.20 (1H, d, 1.9)	98.6
7		166.0		164.0
8	6.40 (1H, d, 2.1)	94.7	6.40 (1H, d, 1.9)	93.4
9		160.4		159.3
10		104.0		103.6
1′		122.9		121.9
2′	7.83 (1H, d, 2.2)	116.0	7.52 (1H, d, 2.1)	115.1
3′		145.8		148.4
4′		149.9		144.7
5′	6.86 (1H, d, 8.5)	117.8	6.82 (1H, d, 8.5)	115.9
6′	7.59 (1H, dd, 2.2,	122.9	7.67 (1H, dd, 2.1, 8.5)	121.0
1″	8.5)	105.4	5.36 (1H, d, 7.7)	101.8
2″	5.15 (1H, d, 7.8)	73.2		71.1
3″		75.1		73.1
4″		70.0		67.8
5″		77.2		75.8
6″		61.9		60.1

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