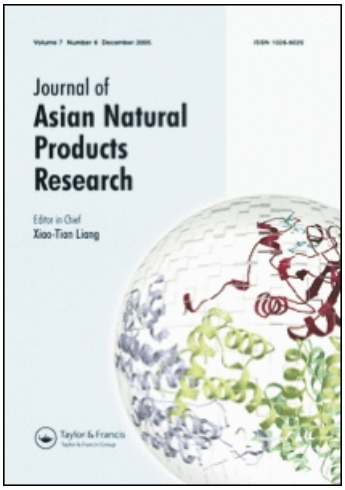


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# Flavonoid Glycosides from *Thalictrum przewalskii*

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# FLAVONOID GLYCOSIDES FROM *THALICTRUM PRZEWALSKII*

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A new flavonoid glycoside, 5,7-dihydroxy-4′-methoxyflavone-7-O-[6-O-(4-O-acetyl-α-L-rhamnosyl)-3-O-β-D-glucosyl]-6-O-acetyl-β-D-glucoside and three known flavonoid glycosides, 5,7-dihydroxy-4′-methoxyflavone-7-O-[6-O-(4-O-acetyl-α-L-rhamnosyl)]-β-D-glucoside, 3,5,7,4′-tetrahydroxyflavonol-3-O-β-D-glucoside and 5,7-dihydroxy-4′-methoxyflavone-7-O-(6-O-α-L-rhamnosyl)-β-D-glucoside were isolated from the whole plant of *Thalictrum przewalskii*. Their structures were determined on the basis of spectroscopic evidences.

*Keywords: Thalictrum*; *Thalictrum przewalskii*; Flavonoid glycoside; 5,7-dihydroxy-4′-methoxyflavone-7-O-[6-O-(4-O-acetyl-α-L-rhamnosyl)-3-O-β-D-glucosyl]-6-O-acetyl-β-D-glucoside

## INTRODUCTION

*Thalictrum* (Ranunculaceae) is a large genus of herb, which occurs widely in the world. In China there are 67 species and nearly half of them have been used in Chinese herbal medicine mainly for the treatment of hepatitis, dysentery and conjuctival congestion [1]. Chemical investigation of this genus has led to the isolation of more than 200 components; most of them are alkaloids and only a few are triterpene glycosides and flavonoids.

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*T. przewalskii*, distributed in north-west and north-east of China, is a Chinese folk medicine used in treatment of hepatitis. Based on available literature, no chemical investigation has been carried out on this plant. In continuation of our study on *Thalictrum*, oriented to obtain biologically active compounds and influenced by a chemotaxonomic interest in this genus, we investigated the chemical constituents in the methanol extract of this plant and isolated four flavonoid glycosides including one new compound.

## RESULTS AND DISCUSSION

The methanolic extract of the dried whole plant of *T. przewalskii* was extracted with 5.0% HOAc and the aq. HOAc was extracted with ethyl acetate. The ethyl acetate fraction was purified and four flavonoid glycosides (**1**–**4**) were obtained, one of which was a new compound (**1**).

Compound **1**, white powder, gave a molecular formula of $C_{38}H_{46}O_{21}$ based on its EI-MS (*m/z* 284 $M^+$ of aglycone), positive MALDI-TOF-HRMS ($M^+ + 1$ *m/z* 839.2610, calcd. for $C_{38}H_{46}O_{21}$, 839.2604), $^1H$ NMR and $^{13}C$ NMR spectra. The UV (MeOH) bands at 268 and 328 nm suggested a flavonoid skeleton. Its IR (KBr) spectrum showed absorption at 3440 (OH), 2950 (saturated CH), 1735 (ester C=O), 1650 ($\alpha,\beta$-unsaturated C=O), 1615 (C=C), 1590, 1515, 1500 $cm^{-1}$ (aromatic system).

In its $^1H$ NMR (500 MHz, DMSO-$d_6$), the aromatic protons at $\delta$ 8.02 (2H, brd, $J = 8.5$ Hz), 7.12 (2H, brd, $J = 8.9$ Hz), 6.92 (1H, s), 6.75, 6.48 (each 1H, brs) and the methoxyl singlet at $\delta$ 3.85 ppm suggested the presence of 5,7-dihydroxy-4′-methoxyflavonoid as the aglycone of **1** and should be assigned to H-2′, 6′, H-3′, 5′, H-3, H-8, H-6 and 4′-OMe, respectively [2]. In the $^{13}C$ NMR (DMSO-$d_6$, 125 MHz) of **1**, the characteristic glycosylation shift −2.0 ppm was observed for C-7, indicating the locations of the sugar moiety to be in the C-7, while the chelated hydroxy signal at $\delta$ 12.89 (1H, br) was due to 5-OH. From the $^1H$ and $^{13}C$ NMR spectra, this compound also contained the signals attributed to two $\beta$-D-glucoses, an $\alpha$-L-rhamnose and two acetyl groups. The nature of these groups was also investigated by using HMBC (see Fig. 1) spectroscopic technique. The anomaric proton signals at $\delta$ 5.25 (1H, d, $J = 6.8$ Hz, H-1″) correlated to C-7, 4.52 (1H, d, $J = 7.8$ Hz, H-1‴) to C-3″ (82.9, glycosylation shift *ca.* +7.8 ppm) and 4.60 (1H, br, H-1⁗) to C-6‴ (65.8, glycosylation shift *ca.* +4.0 ppm) and the MALDI-TOF-HRMS also gave an ion peak at *m/z* 651.1903 ($C_{30}H_{35}O_{16}$, $M^+$-acetylrhamnosyl). Whereas the acetylation shifts for C-6″ (*ca.* +2.5 ppm) and C-4⁗ (*ca.* +2.0 ppm) were also observed, respectively [2]. Thus, the acetylated sugar

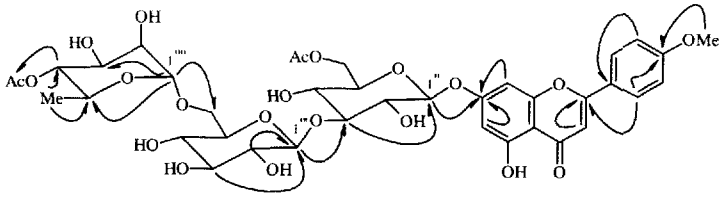

FIGURE 1 Key interactions of **1** in its HMBC spectrum.

moiety at C-7 was determined as 7-O-[6-O-(4-O-acetyl-α-L-rhamnosyl)-3-O-β-D-glucosyl]-6-O-acetyl-β-D-glucoside. Consequently, the whole structure of **1** was concluded to be 5,7-dihydroxy-4′-methoxyflavonoid 7-O-[6-O-(4-O-acetyl-α-L-rhamnosyl)-3-O-β-D-glucosyl]-6-O-acetyl-β-D-glucoside which is in agreement with its $^{13}C$ NMR spectral data.

Compounds **2–4** were identified as 5,7-dihydroxy-4′-methoxyflavone-7-O-[6-O-(4-O-acetyl-α-L-rhamnosyl)]-β-D-glucoside (**2**) [2], 3,5,7,4′-tetrahydroxyflavonol-3-O-β-D-glucoside (**3**) [3] and 5,7-dihydroxy-4′-methoxyflavone-7-O-(6-O-α-L-rhamnosyl)-β-D-glucoside (**4**) [2], respectively, by spectroscopic analysis.



## EXPERIMENTAL SECTION

### General Experimental Procedures

All mps are uncorr. $^1H$, $^{13}C$ NMR and 2D NMR spectra were recorded on a Bruker AM 500 spectrometer with TMS as int. standard. UV spectra were obtained on a Philips PYE Union PU8800 spectrophotometer, and IR spectra on a Perkin–Elmer 983G instrument. EI-MS (70 eV) and MALDI-TOF-HRMS were determined on a KYKY-ZSP-50 and BIPLEX III mass spectrometer. Chromatographic separations were carried out on silica gel H, polyamide and Sephadex LH-20, TLC on silica gel G and polyamide film.

### Plant Material

Whole plant of *T. przewalskii* Maxim was collected from Sichuan province, China, in July, 1996. Voucher specimens are deposited in Institute of Medicinal Plant Development, Chinese Academy of Medical Sciences, Beijing, P.R. China.

## Extraction and Isolation

Air-dried whole plant of *T. przewalskii* (4.0 kg) was extracted with hot MeOH three times. The methanolic extract was extracted with 3000 ml of 5.0% HOAc and then the aq. HOAc was extracted with ethyl acetate. The EtOAc fr. (42 g) was chromatographed on silica gel column using a step-gradient $CHCl_3$–MeOH and gave fourteen frs. 1–14. Fr. 8 was chromatographed on polyamide (MeOH–$H_2O$) and followed by purification on Sephadex LH-20 (MeOH) to give **1** (120 mg) and **4** (200 mg). Fr. 6 was rechromatographed on polyamide (MeOH–$H_2O$) and Sephadex LH-20 (MeOH) to give **2** (70 mg) and **3** (30 mg).

## Identification of Components

*5,7-dihydroxy-4′-methoxyflavone-7-O-[6-O-(4-O-acetyl-α-L-rhamnosyl)-3-O-β-D-glucosyl]-6-O-acetyl-β-D-glucoside* (**1**) White amorphous powder, m.p. 262–264°C, UV$\lambda_{max}^{MeOH}$ (nm): 268, 328; +NaOMe: 288, 370; +$AlCl_3$: 230 (sh), 274, 298, 344, 380 (sh); +$AlCl_3$+HCl: 228 (sh), 274, 298, 336, 376 (sh); +NaOAc: 268, 328; +NaOAc+$H_3BO_3$: 268, 330; IR$\nu_{max}^{KBr}$ ($cm^{-1}$): 3440 (HO), 2950 (saturated CH), 1735 (C=O), 1650 (α,β-unsaturated C=O), 1615 (C=C), 1515, 1500, 1440, 1380, 1260, 1190, 1085, 1055; $^1$H NMR (500 MHz, DMSO-$d_6$) δ: 12.89 (1H, br, 5-OH), 8.02 (2H, brd, $J$ = 8.5 Hz, H-2′, 6′), 7.12 (2H, brd, $J$ = 8.9 Hz, H-3′, 5′), 6.92 (1H, s, H-3), 6.75, 6.48 (each 1H, brs, H-8, 6), 5.25 (1H, d, $J$ = 6.8 Hz, H-1″), 4.60 (1H, br, H-1‴), 4.52 (1H, d, $J$ = 7.8 Hz, H-1‴), 3.85 (3H, s, 4′-OMe), 1.97 (3H, s, 6″-COMe), 1.94 (3H, s, 4‴-COMe), 0.92 (3H, d, $J$ = 6.8 Hz, H-6‴); $^{13}$C NMR of **1** in DMSO-$d_6$ (125 MHz, δ in ppm): 181.9 (C-4), 170.2 (6″-MeC=O), 169.9 (4‴-MeC=O), 163.9 (C-2), 162.7 (C-7), 162.4 (C-4′), 161.1 (C-5), 156.8 (C-9), 128.3 (C-2′, 6′), 122.6 (C-1′), 114.6 (C-3′, 5), 105.4 (C-10), 104.6 (C-1″), 103.8 (C-3), 100.0 (C-1‴), 99.6 (C-6), 98.1 (C-1‴), 94.9 (C-8), 82.9 (C-3‴), 75.9 (C-5‴), 75.6 (C-5″), 75.1 (C-3″), 74.5 (C-2‴), 73.9 (C-2″), 73.7 (C-4‴), 70.2 (C-2‴), 69.7 (C-4‴), 69.1 (C-4″), 68.2 (3-4‴), 65.8 (C-6‴), 65.6 (C-5‴), 63.5 (C-6″), 55.5 (4′-OMe), 20.8 (6″-MeC=O), 20.4 (4‴-MeC=O), 17.2 (C-6‴); EI-MS $m/z$ (%): 284 $[M]^+$ of aglycone (100), 256 (4.9), 241 (11.2), 213 (4.0), 152 (9.8), 132 (32.0); MALDI-TOF-HRMS: 839.2610 ($M^+$+1), 651.1903 ($C_{30}H_{35}O_{16}$), 285.0755 ($C_{16}H_{13}O_5$).

*5,7-dihydroxy-4′-methoxyflavone-7-O-[6-O-(4-O-acetyl-α-L-rhamnosyl)]-β-D-glucoside* (**2**) White amorphous powder, m.p. 245–247°C, UV$\lambda_{max}^{MeOH}$ (nm): 268, 324; +NaOMe: 288, 368; +$AlCl_3$: 228 (sh), 276, 300, 342, 380 (sh); +$AlCl_3$+HCl: 228 (sh), 276, 298, 336, 374 (sh); +NaOAc: 268, 324;

NaOAc + $H_3BO_3$: 268, 326; IR$\nu_{max}^{KBr}$ ($cm^{-1}$): 3440 (HO), 2950 (saturated CH), 1730 (C=O), 1660 ($\alpha,\beta$-unsaturated C=O), 1620 (C=C), 1500, 1460, 1380, 1305, 1280, 1260, 1190, 1110, 1080, 1050; $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 12.87 (1H, br, 5-OH), 8.01 (2H, brd, $J$ = 8.5 Hz, H-2′, 6′), 7.11 (2H, brd, $J$ = 8.5 Hz, H-3′, 5′), 6.90 (1H, s, H-3), 6.79, 6.45 (each 1H, brs, H-8, 6), 5.09 (1H, d, $J$ = 7.2 Hz, H-1″), 4.60 (1H, br, H-1‴), 3.84 (3H, s, 4′-OMe), 1.97 (3H, s, 6‴-COMe), 0.91 (3H, d, $J$ = 6.1 Hz, H-6‴); $^{13}$C NMR (500 MHz, DMSO-$d_6$) $\delta$: 181.9 (C-4), 169.9 (4‴-MeC=O), 163.8 (C-2), 162.8 (C-7), 162.4 (C-4′), 161.1 (C-5), 156.9 (C-9), 128.3 (C-2′, 6′), 122.6 (C-1′), 114.6 (C-3′, 5), 105.4 (C-10), 103.8 (C-3), 100.1 (C-1‴), 99.8 (C-1″), 99.6 (C-6), 94.9 (C-8), 76.3 (C-5″), 75.4 (C-3″), 73.9 (C-4‴), 73.1 (C-2″), 70.3 (C-2‴), 69.5 (C-4″), 68.2 (C-3‴), 65.9 (C-5‴), 65.8 (C-6″), 55.5 (4′-OMe), 20.8 (4‴-MeC=O), 17.2 (C-6‴); EI-MS $m/z$ (%): 284 $[M]^+$ of aglycone (100).

*3,5,7,4′-tetrahydroxyflavonol-3-O-β-D-glucoside* (**3**) Yellow amorphous powder, m.p. 282–284°C, UV$\lambda_{max}^{MeOH}$ (nm): 264, 348; +NaOMe: 274, 324, 398; +$AlCl_3$: 230 (sh), 273, 302, 350, 392; +$AlCl_3$ + HCl: 230 (sh), 274, 302, 346, 392; +NaOAc: 272, 384; +NaOAc + $H_3BO_3$: 266, 352; IR$\nu_{max}^{KBr}$ ($cm^{-1}$): 3450 (HO), 2920 (saturated CH), 1665 ($\alpha,\beta$-unsaturated C=O), 1630 (C=C), 1510, 1370, 1190, 1070, 1020; $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 12.58 (1H, br, 5-OH), 8.02 (2H, brd, $J$ = 9.5 Hz, H-2′, 6′), 6.88 (2H, brd, $J$ = 8.9 Hz, H-3′, 5′), 6.42, 6.20 (each 1H, d, $J$ = 1.7 Hz, H-8, 6), 5.43 (1H, d, $J$ = 7.3 Hz, H-1″); $^{13}$C NMR (500 MHz, DMSO-$d_6$) $\delta$: 177.4 (C-4), 164.1 (C-7), 161.2 (C-9), 159.8 (C-4′), 156.3 (C-5), 156.2 (C-2), 133.2 (C-3), 130.8 (C-2′, 6′), 120.9 (C-1′), 115.0 (C-3′, 5), 104.0 (C-10), 100.9 (C-1″), 98.6 (C-6), 93.6 (C-8), 77.4 (C-5″), 76.4 (C-3″), 74.1 (C-2″), 69.9 (C-4″), 60.8 (C-6″); EI-MS $m/z$ (%): 286 $[M]^+$ of aglycone (100).

*5,7-dihydroxy-4′-methoxyflavone-7-O-(6-O-α-L-rhamnosyl)-β-D-glucoside* (**4**) White amorphous powder, m.p. 274–276°C, UV$\lambda_{max}^{MeOH}$ (nm): 266, 326; NaOMe: 266, 368; +$AlCl_3$: 226 (sh), 278, 304, 344, 382 (sh); +$AlCl_3$ + HCl: 230 (sh), 278, 298, 334, 376 (sh); +NaOAc: 266, 324; +NaOAc + $H_3BO_3$: 268, 326; IR$\nu_{max}^{KBr}$ ($cm^{-1}$): 3450 (HO), 2940 (saturated CH), 1650 ($\alpha,\beta$-unsaturated C=O), 1610 (C=C), 1510, 1370, 1270, 1240, 1190, 1100, 1080, 1040; $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 12.89 (1H, br, 5-OH), 8.03 (2H, brd, $J$ = 8.4 Hz, H-2′, 6′), 7.13 (2H, brd, $J$ = 8.5 Hz, H-3′, 5′), 6.92 (1H, s, H-3), 6.78, 6.45 (each 1H, brs, H-8, 6), 5.05 (1H, d, $J$ = 7.0 Hz, H-1″), 4.55 (1H, br, H-1‴), 3.84 (3H, s, 4′-OMe), 1.07 (3H, d, $J$ = 5.8 Hz, H-6‴); $^{13}$C NMR (500 MHz, DMSO-$d_6$) $\delta$: 181.9 (C-4), 163.9 (C-2), 162.9 (C-7), 162.4 (C-4′), 161.1 (C-5), 156.9 (C-9), 128.4 (C-2′, 6′), 122.6 (C-1′), 114.6 (C-3′, 5), 105.4 (C-10), 103.8 (C-3), 100.5 (C-1″), 100.0 (C-1‴), 99.6 (C-6), 94.8 (C-8), 76.2 (C-5″), 75.6 (C-3″), 73.0 (C-2″), 72.0 (C-4‴), 70.7 (C-2‴), 70.3 (C-3‴), 69.6

(C-4″), 68.3 (C-5‴), 66.1 (C-6‴), 55.5 (4′-OMe), 17.7 (C-6‴); EI-MS *m/z* (%): 284 $[M]^+$ of aglycone (100).

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