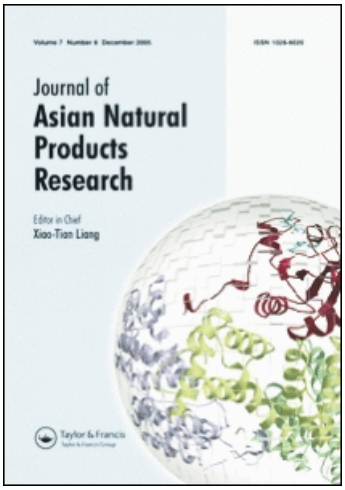


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# Three new acylated flavone *C*-glycosides from the flowers of *Trollius chinensis*

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Three new flavone *C*-glycosides with the substitution of the unusual acyl, 2″-*O*-veratroylisoswertisin (**1**), 3″-*O*-2-methylbutyrylisoswertiajaponin (**2**), and 3″-*O*-2-methylbutyrylvitexin (**3**), together with the known compounds of 2″-*O*-2-methylbutyrylisoswertisin (**4**), 3″-*O*-2-methylbutyrylisoswertisin (**5**), and trollisin I (**6**) were isolated from the antibacterial fraction of the aqueous extract of the flowers of *Trollius chinensis*. The structural elucidations of these compounds were carried out by a detailed analysis of the NMR and MS spectra.

**Keywords:** *Trollius chinensis*; Ranunculaceae; 2″-*O*-veratroylisoswertisin; 3″-*O*-2-methylbutyrylisoswertiajaponin; 3″-*O*-2-methylbutyrylvitexin



## 1. Introduction

*Trollius chinensis* Bunge (Ranunculaceae), one of the 25 species in the *Trollius* genus, is widely distributed in Hebei, Shanxi, and Liaoning Provinces of China. Its flower is used as a folk antibacterial agent for the treatment of tonsillitis, upper respiratory infection, and pharyngitis [1]. Organic acids, alkaloids, and flavone *C*-glycosides of the derivatives of vitexin and orientin have been isolated from *T. chinensis* [2–5] and *Trollius ledebouri* [6–8]. In our screening for the antibacterial effective part of *T. chinensis*, the $CHCl_3$–MeOH (100:5) eluate of the EtOAc extract, which was more potent than the $CHCl_3$ extract and the *n*-BuOH extract, on silica gel column chromatography showed significant inhibition effect on Gram-positive (*Staphylococcus aureus* and *Bacillus subtilis*) and Gram-negative (*Escherichia coli*) bacteria. Detailed isolation of this eluate by HPLC afforded three new acylated flavone *C*-glycosides, compounds **1**–**3** (Figure 1), along with the three known compounds 2″-*O*-2-methylbutyrylisoswertisin (**4**) [8], 3″-*O*-2-methylbutyrylisoswertisin (**5**) [8], and trollisin I (**6**) [4]. This paper describes the isolation and structural elucidation of the three new compounds.

## 2. Results and discussion

Compound **1** was obtained as a yellow amorphous powder, whose molecular formula was determined as $C_{31}H_{30}O_{13}$ by HR-ESI-MS at *m/z* 611.1767 $[M+H]^+$. In the $^1H$ NMR spectrum of **1**, the typical H-3 signal of a flavone at $\delta$ 6.86 (1H, s), the signals of the AA′BB′ coupling system

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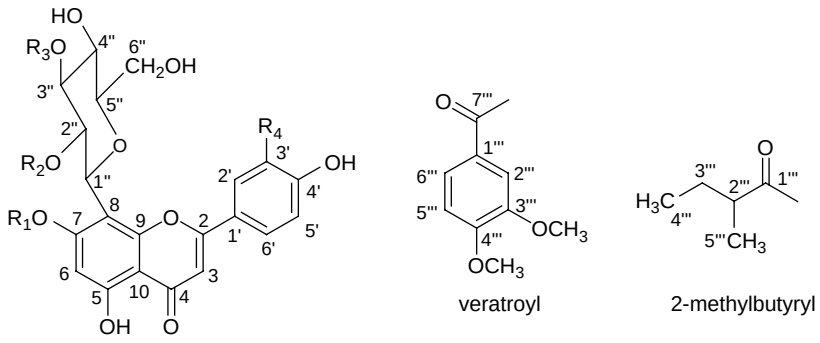


| | | | | |
|---|---|---|---|---|
| **1** | $R_1 = CH_3$ | $R_2$ = veratroyl | $R_3$ = H | $R_4$ = H |
| **2** | $R_1 = CH_3$ | $R_2$ = H | $R_3$ = 2-methylbutyryl | $R_4$ = OH |
| **3** | $R_1$ = H | $R_2$ = H | $R_3$ = 2-methylbutyryl | $R_4$ = H |
| **4** | $R_1 = CH_3$ | $R_2$ = 2-methylbutyryl | $R_3$ = H | $R_4$ = H |
| **5** | $R_1 = CH_3$ | $R_2$ = H | $R_3$ = 2-methylbutyryl | $R_4$ = H |
| **6** | $R_1 = CH_3$ | $R_2$ = 2-methylbutyryl | $R_3$ = H | $R_4$ = OH |

Figure 1. The structures of compounds **1**–**6**.

in ring-B at $\delta$ 8.13 (2H, d, $J = 8.4$ Hz) and 6.92 (2H, d, $J = 8.4$ Hz), and a singlet of ring-A at $\delta$ 6.33 (1H, s) were observed. Additionally, a conjugated hydroxyl signal of 5-OH at $\delta$ 13.28 (1H, br s), a methoxyl signal at $\delta$ 3.78 (3H, s), and a distinct anomeric proton signal at $\delta$ 5.04 (1H, d, $J = 10.4$ Hz) were further shown. The $^{13}$C NMR spectrum displayed 31 carbon signals, in which 15 signals of the flavone aglycone, a methoxyl carbon at $\delta$ 56.6, and the six carbons of a hexose ranging from $\delta$ 60.9 to 82.2 characteristic of a *C*-glycoside, were observed. The HMBC experiment (Figure 2) confirmed the flavone skeleton and the aromatic proton at $\delta$ 6.33 (1H, s) showed the long-range correlations with the carbons at $\delta$ 104.2 (C-10), 103.3 (C-8), 162.5 (C-7), and 161.4 (C-5) designating it as H-6. Furthermore, the methoxyl group was assigned by the long-range correlation between the methoxy at $\delta$ 3.78 with the carbon at $\delta$ 162.5 (C-7), and the hexose was determined to be linked at C-8 by a C—C bond by the cross-peaks observed between the anomeric proton at $\delta$ 5.04 with the carbons of ring-A at $\delta$ 162.5 (C-7), 103.3 (C-8),

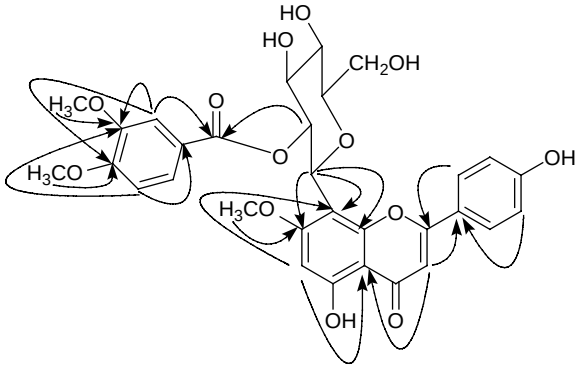


Figure 2. The key HMBC correlations (H → C) of compound **1**.

and 155.3 (C-9) in the HMBC spectrum (Figure 2). Thus, isoswertisin was determined as a part of the structure of **1** by the comparison of its NMR spectral data with those reported [2] and the anomeric proton of the glucose was determined to be β-orientated by the analysis of its coupling constant.

Besides the above data, the $^1$H NMR spectrum of **1** showed also the protons of an ABX coupling system at $\delta$ 7.15 (1H, br s), 6.98 (1H, d, $J = 8.4$ Hz), and 7.32 (1H, br d, $J = 8.4$ Hz) and two methoxyl signals at $\delta$ 3.78 and 3.73. According to the left nine carbon signals in the $^{13}$C NMR spectrum, and the loss of a veratric acid from $[M-H]^-$ at *m/z* 427.0, a veratroyl moiety was established, whose substitution pattern was determined by comparison with those reported [7,8] and the corresponding HMBC correlation. If an acyl was substituted at C-2 of the glucose moiety in the flavone-8-*C*-glycoside, a downfield-shifted triplet ($J = ca.$ 10 Hz) of H-2 ranging from $\delta$ 5.30 to 5.55 was prominent in the $^1$H NMR spectrum, while if the acyl was at C-3 of the glucose moiety, the triplet ($J = ca.$ 10 Hz) of H-3 downfield-shifted to $\delta$ 4.88 [8]. The H-2″ of compound **1** was observed at $\delta$ 5.50 (1H, t, $J = 10.4$ Hz). The downfield-shift of C-2″ by 2.0 chemical shift and upfield-shifts of C-1″ (from $\delta$ 73.1 to 70.8) and C-3″ (from $\delta$ 78.3 to 75.7) compared to those of isoswertisin [2], and the HMBC correlation of H-2″ at $\delta$ 5.50 with the carbonyl signal of the veratroyl moiety at $\delta$ 164.3 (Figure 2) showed finally that the veratroyl moiety was substituted at C-2″. Thus, **1** was established as 2″-*O*-veratroyl-isoswertisin.

Compound **2** was a yellow amorphous powder with the molecular formula of $C_{27}H_{30}O_{12}$ confirmed by the HR-ESI-MS data at *m/z* 547.1814 $[M+H]^+$. The $^1$H and $^{13}$C NMR spectra of **2** established that it has a 5-hydroxy-7-methoxyflavone-8-*C*-glucoside, which was similar to **1** except for the ABX coupling system in the ring-B at $\delta$ 7.49 (1H, br s, H-2′), 6.87 (1H, d, $J = 8.4$ Hz, H-5′), and 7.57 (1H, br d, $J = 8.4$ Hz) in **2** instead of an AA′BB′ coupling system in **1**. Comparison of the NMR spectral data of **2** with those of isoswertiajaponin [9] exhibited the downfield-shift of H-3 of the glucose moiety at $\delta$ 4.87 (1H, t, $J = 10.0$ Hz) by 1.50 chemical shifts, along with the downfield-shift of C-3″ (from $\delta$ 78.6 to 78.8) and the significant upfield-shifts of C-2″ (from $\delta$ 70.6 to 68.5) and C-4″ (from $\delta$ 70.5 to 68.5). Additionally, the signals of a 2-methylbutyryl group [8] at $\delta$ 2.30 (1H, m, H-2‴), 1.51 (1H, m, H-3‴a), 1.34 (1H, m, H-3‴b), 0.78 (3H, t, $J = 7.2$ Hz, $CH_3$-4‴), and 1.03 (3H, d, $J = 6.8$ Hz, $CH_3$-5‴) in the $^1$H NMR spectrum, along with the five carbon signals at $\delta$ 175.1, 40.3, 26.4, 11.2, and 16.6, were observed. Analysis of the NMR spectral data of the 2-methylbutyryl group at C-2″ or C-3″ of the flavone-8-*C*-glucosides [8] showed that the two methyl proton signals of $CH_3$-4‴ ($\delta$ 0.78) and $CH_3$-5‴ ($\delta$ 1.03) of the 2-methylbutyryl group substituted at C-3″ were more downfielded than those of $CH_3$-4‴ ($\delta$ 0.59) and $CH_3$-5‴ ($\delta$ 0.70) of the 2-methylbutyryl group at C-2″. According to the acylation shifts described above and the long-range correlation of H-3″ at $\delta$ 4.87 with the carbonyl signal of the 2-methylbutyryl group at $\delta$ 175.1, the structure of **2** was elucidated to be 3″-*O*-2-methylbutyryl-isoswertiajaponin.

Compound **3**, a yellow amorphous powder, was assigned the molecular formula of $C_{26}H_{28}O_{11}$ by the HR-ESI-MS data at *m/z* 517.1713 $[M+H]^+$. The $^1$H NMR spectral data of **3** showed the signals of a 2-methylbutyryl moiety similar to those of **2** at $\delta$ 2.32 (1H, m, H-2‴), 1.52 (1H, m, H-3‴a), 1.34 (1H, m, H-3‴b), 0.80 (3H, t, $J = 7.0$ Hz, $CH_3$-4‴), and 1.03 (3H, d, $J = 6.8$ Hz, $CH_3$-5‴). Along with the corresponding signals at $\delta$ 175.0, 40.3, 26.4, 11.2, and 16.6 in the $^{13}$C NMR spectrum, the acyl moiety in **3** was characterized as 2-methylbutyryl. Additionally, the NMR

spectra displayed the signals assignable to vitexin [2], which is abundant in several plants of the *Trollius* genus. For the similar signal of H-3‴ to compound **2** at $\delta$ 4.88 (1H, t, $J = 9.6$ Hz) and the acylation shifts of C-2‴ (from $\delta$ 70.8 to 68.4) and C-4‴ (from $\delta$ 70.5 to 68.0), together with the long-range correlation of H-3″ at $\delta$ 4.88 with the carbonyl signal of the 2-methylbutyryl group at $\delta$ 175.0, compound **3** was deduced to be 3″-*O*-2-methylbutyrylvitexin.

Flavone 8-*C*-glycosides with the acyl groups of 2-methylbutyryl or veratroyl are characteristic secondary metabolites in the *Trollius* genus, which were first reported from *T. ledebouri* [8] and showed moderate antivirus and anti-inflammatory activities. While, little work has been done for *T. chinensis* [4] and most of the compounds isolated are acylated at C-2″ of the glucose moiety. This is the first report on the isoswertisin derivative with a veratroyl group at C-2″ (compound **1**), and the flavone *C*-glycosides with an acyl group at C-3″ (compounds **2**, **3**, and **5**) from *T. chinensis*.



## 3. Experimental

### 3.1 General experimental procedures

Optical rotations were recorded on a Perkin-Elmer 241 MC polarimeter. ESI-MS spectra were recorded on an Agilent 1100SL spectrometer and HR-ESI-MS data were measured on a Bruker micro-TOFQ instrument in the positive mode. The 1D and 2D NMR spectra were recorded in DMSO-$d_6$ on a JEOL JNM-AL 400 spectrometer with TMS as an internal standard. HPLC was performed on a Hitachi L-6200 intelligent pump with a Hitachi L-4000 UV detector and a Hitachi D-2500 chromato-integrator. The separation was carried out on a Shiseido CAPCELL PAK $C_{18}$ column (UG 80 Å, 5 μm, 250 mm × 10 mm i.d.). The detector wavelength was set at 254 nm and the flow rate was 2 ml/min in all cases. The mobile phase was MeOH–$H_2O$ or $CH_3CN$–$H_2O$ system. For the opening column chromatography, ODS (100–200 mesh) was purchased from Fuji Silysia Chemical Ltd, Kasugai, Japan and Sephadex LH-20 was produced by GE Healthcare, Piscataway, NJ, USA.

### 3.2 Plant material

The flowers of *T. chinensis* were purchased from Tongrentang drugstore, Shenyang, China, in November 2005. The sample was identified by Prof. Qishi Sun of the Department of Medicinal Plants, Shenyang Pharmaceutical University. A voucher specimen (JLH-200530) is deposited in the Herbarium of Shenyang Pharmaceutical University.

### 3.3 Extraction and isolation

The air-dried flowers of *T. chinensis* (5.0 kg) were decocted with water for three times, 50 l in each time. The extract was concentrated ($\rho = 1.5$ g/ml) and added to EtOH until the concentration of EtOH was *ca.* 80%. After being laid aside for 12 h, the supernatant was evaporated *in vacuo* to give an extract (920 g). Half of the residue (460 g) was dissolved in $H_2O$ (900 ml) and partitioned successively with $CHCl_3$ (2.7 l), EtOAc (2.7 l), and *n*-BuOH (2.7 l). Part of the EtOAc extract (20.0 g) was chromatographed on silica gel eluted with $CHCl_3$–MeOH (100:5–0:100) to give the four fractions (E1–E4). The fraction E1 (100:5, 9.6 g) was further subjected to an opening ODS column chromatography (65.0 g) eluted with $H_2O$ and MeOH in gradient to afford the five fractions from E1-1 to E1-5. The fraction E1-4 (60% MeOH) was put on a Sephadex LH-20 column chromatography (20.0 g) eluted with MeOH to give the eight fractions from E1-4-1 to E1-4-8. The fraction E1-4-5 (30–50 ml) was separated by HPLC with Shiseido CAPCELL PAK $C_{18}$ column (5 μm, 250 mm × 10 mm i.d.)

Table 1. $^{1}$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectral data of compounds **1**–**3** in DMSO-$d_6$.

| | **1** | | **2** | | **3** | |
|---|---|---|---|---|---|---|
| Position | $\delta_H$ (multiplicity, $J$ in Hz) | $\delta_C$ | $\delta_H$ (multiplicity, $J$ in Hz) | $\delta_C$ | $\delta_H$ (multiplicity, $J$ in Hz) | $\delta_C$ |
| 2 | | 164.3 | | 164.2 | | 163.7 |
| 3 | 6.86 (s) | 102.4 | 6.70 (s) | 102.4 | 6.77 (s) | 102.0 |
| 4 | | 182.0 | | 182.0 | | 181.9 |
| 5 | | 161.4 | | 161.3 | | 161.0 |
| 6 | 6.33 (s) | 94.7 | 6.52 (s) | 94.9 | 6.24 (s) | 97.2 |
| 7 | | 162.5 | | 163.2 | | 161.1 |
| 8 | | 103.3 | | 104.6 | | 102.5 |
| 9 | | 155.3 | | 155.1 | | 156.0 |
| 10 | | 104.2 | | 104.6 | | 103.6 |
| 1′ | | 121.2 | | 121.8 | | 121.6 |
| 2′ | 8.13 (d, 8.4) | 129.1 | 7.49 (br s) | 114.0 | 8.04 (d, 8.4) | 128.9 |
| 3′ | 6.92 (d, 8.4) | 115.8 | | 145.8 | 6.89 (d, 8.4) | 115.8 |
| 4′ | | 161.4 | | 149.6 | | 160.4 |
| 5′ | 6.92 (d, 8.4) | 115.8 | 6.87 (d, 8.4) | 115.6 | 6.89 (d, 8.4) | 115.8 |
| 6′ | 8.13 (d, 8.4) | 129.1 | 7.57 (br d, 8.4) | 119.4 | 8.04 (d, 8.4) | 128.9 |
| 5-OH | 13.28 (br s) | | 13.34 (br s) | | 13.16 (br s) | |
| 7-$OCH_3$ | 3.78 (s) | 56.6 | 3.88 (s) | 56.5 | | |
| 1″ | 5.04 (d, 10.4) | 70.8 | 4.79 (d, 10.0) | 73.4 | 4.77 (d, 9.6) | 73.3 |
| 2″ | 5.50 (t, 10.4) | 72.8 | 3.96 (t, 10.0) | 68.5 | 3.99 (m) | 68.4 |
| 3″ | 3.63 (m) | 75.7 | 4.87 (t, 10.0) | 78.8 | 4.88 (t, 9.6) | 78.7 |
| 4″ | 3.55 (m) | 70.4 | 3.57 (m) | 68.5 | 3.57 (m) | 68.0 |
| 5″ | 3.40 (m) | 82.2 | 3.34 (m) | 82.0 | 3.38 (m) | 81.5 |
| 6″ | 3.63 (m), 3.82 (m) | 60.9 | 3.77 (m), 3.57 (m) | 61.0 | 3.72 (m), 3.57 (m) | 60.6 |
| 1‴ | | 121.6 | | 175.1 | | 175.0 |
| 2‴ | 7.15 (br s) | 111.4 | 2.30 (m) | 40.3 | 2.32 (m) | 40.3 |
| 3‴ | | 148.0 | 1.51 (m), 1.34 (m) | 26.4 | 1.52 (m), 1.34 (m) | 26.4 |
| 4‴ | | 152.6 | 0.78 (t, 7.2) | 11.2 | 0.80 (t, 7.0) | 11.2 |
| 5‴ | 6.98 (d, 8.4) | 110.8 | 1.03 (d, 6.8) | 16.6 | 1.03 (d, 6.8) | 16.6 |
| 6‴ | 7.32 (br d, 8.4) | 122.8 | | | | |
| 7‴ | | 164.3 | | | | |

Table 1 – *continued*

| | **1** | | **2** | | **3** | |
|---|---|---|---|---|---|---|
| Position | $\delta_H$ (multiplicity, *J* in Hz) | $\delta_C$ | $\delta_H$ (multiplicity, *J* in Hz) | $\delta_C$ | $\delta_H$ (multiplicity, *J* in Hz) | $\delta_C$ |
| 3″-$OCH_3$ | 3.73 (s) | 55.4 | | | | |
| 4″-$OCH_3$ | 3.78 (s) | 55.6 | | | | |

eluted by 55% MeOH in $H_2O$ to give the five fractions from E1-4-5-1 to E1-4-5-5. The fraction E1-4-5-1 (15–18 min) was further isolated by HPLC eluted with 30% $CH_3CN$ in $H_2O$ to give compounds **3** (27.68 min, 5 mg) and **2** (31.58 min, 8 mg). The fraction E1-4-5-2 (18–21 min) was further isolated by HPLC eluted with 30% $CH_3CN$ in $H_2O$ to give compound **1** (35.52 min, 10 mg). The mixture of the fractions E1-4-5-3 (21–25 min) and E1-4-5-4 (25–27 min) was further isolated by HPLC eluted with 27% $CH_3CN$ in $H_2O$ to give compounds **6** (59.02 min, 5 mg) and **5** (76.51 min, 7 mg). The fraction E1-4-5-5 (27–33 min) was further purified by HPLC with the mobile phase of 55% MeOH in $H_2O$ to afford compound **4** (29.31 min, 8 mg).

### *3.3.1 2″-O-Veratroylisoswertisin (**1**)*

A yellow amorphous powder; $[\alpha]_D^{20}$ −120.5 ($c = 0.1$, MeOH); $^1$H NMR (400 MHz, DMSO-$d_6$) and $^{13}$C NMR (100 MHz, DMSO-$d_6$), see Table 1; ESI-MS *m/z*: 611.2 $[M+H]^+$, 633.2 $[M+Na]^+$, 609.0 $[M-H]^-$, 427.0 [M − H-veratric acid]$^-$, 394.9 [M − H-veratric acid − $CH_3OH]^-$; HR-ESI-MS *m/z*: 611.1767 $[M+H]^+$ (calcd for $C_{31}H_{31}O_{13}$, 611.1765).

### *3.3.2 3″-O-2-Methylbutyryl-isoswertiajaponin (**2**)*

A yellow amorphous powder; $[\alpha]_D^{20}$ −24.8 ($c = 0.1$, MeOH); $^1$H NMR (400 MHz, DMSO-$d_6$) and $^{13}$C NMR (100 MHz, DMSO-$d_6$), see Table 1; ESI-MS *m/z*: 547.2 $[M+H]^+$, 569.2 $[M+Na]^+$, 445.2 [M + H-2-methylbutyric acid]$^+$, 545.1 $[M-H]^-$, 443.0 [M − H-2-methylbutyric acid]$^-$; HR-ESI-MS *m/z*: 547.1814 $[M+H]^+$ (calcd for $C_{27}H_{31}O_{12}$, 547.1816).

### *3.3.3 3″-O-2-Methylbutyrylvitexin (**3**)*

A yellow amorphous powder; $[\alpha]_D^{20}$ −34.0 ($c = 0.1$, MeOH); $^1$H NMR (400 MHz,

DMSO-$d_6$) and $^{13}C$ NMR (100 MHz, DMSO-$d_6$), see Table 1; ESI-MS *m/z*: 517.2 $[M+H]^+$, 539.2 $[M+Na]^+$, 415.1 [M+H-2-methylbutyric acid]$^+$, 515.1 $[M-H]^-$, 413.0 [M−H-2-methylbutyric acid]$^-$; HR-ESI-MS *m/z*: 517.1713 $[M+H]^+$ (calcd for $C_{26}H_{29}O_{11}$, 517.1710).

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