

## CHEMICAL CONSTITUENTS OF THE FLOWER OF *Fritillaria thunbergii*

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*Fritillaria thunbergii* Miq., belonging to the Liliaceae family, is widely distributed in China. It has been used as an important crude drug for its antitussive, antiasthmatic, and expectorant effects. Previous phytochemical investigations of *F. thunbergii* showed the presence of steroid saponins, isosteroidal alkaloids, and steroidal alkaloids [1, 2]. Most previous study of *F. thunbergii* focused on the bulbs but not other parts because of the traditional and customary use of this plant. To the best of our knowledge, there have been no reports on the chemical components of extracts of the flower of *F. thunbergii*. In this study of the chemical constituents of the flower of *F. thunbergii*, eight compounds were isolated and identified. All compounds were obtained from this plant for the first time.

The dried and powdered flowers of *F. thunbergii* were extracted and refluxed three times (each extraction period lasted 2 h) with 75% ethanol aqueous solution. The solution was concentrated and partitioned with solvents starting with petroleum ether, ethyl acetate, and *n*-butanol. By using a series of chromatographic techniques, such as silica gel (200–300 mesh) and Sephadex LH-20 column chromatography, and PTLC, we isolated compounds **1–8**.

The compounds were identified using their mass and NMR spectra, and all data were in good agreement with the literature data.

**1-Heptadecanol (1).** C<sub>17</sub>H<sub>36</sub>O, colorless oil; identification of compound **1** was performed by comparison of <sup>1</sup>H NMR and <sup>13</sup>C NMR data with those reported in [3].

**Monoheptadecanoic acid (2).** C<sub>20</sub>H<sub>40</sub>O<sub>4</sub>, white powder; identification of compound **2** was performed by comparison of <sup>1</sup>H NMR and <sup>13</sup>C NMR data with those reported in [4].

**5,7-Dihydroxy-2-(4-hydroxy-3-methoxyphenyl)-3-methoxy-4H-chromen-4-one (3).** C<sub>17</sub>H<sub>14</sub>O<sub>7</sub>, yellow powder. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>, δ, ppm, J/Hz): 12.69 (1H, s, OH), 10.9 (1H, s, OH), 9.93 (1H, s, OH), 7.64 (1H, d, J = 1.5, H-2'), 7.58 (1H, dd, J = 1.5, 8.5, H-6'), 6.96 (1H, d, J = 8.5, H-5'), 6.48 (1H, d, J = 1.5, H-8), 6.20 (1H, d, J = 1.5, H-6), 3.86 (3H, s, OCH<sub>3</sub>), 3.80 (3H, s, OCH<sub>3</sub>). <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>, δ, ppm): 177.92 (C-4), 164.13 (C-7), 161.16 (C-5), 156.29 (C-9), 155.38 (C-2), 149.71 (C-3'), 147.40 (C-4'), 137.86 (C-3), 122.13 (C-1'), 120.72 (C-6'), 115.58 (C-5'), 111.99 (C-2'), 98.51 (C-10), 93.76 (C-6), 59.65 (C-8), 55.67 (OCH<sub>3</sub>), 48.51 (OCH<sub>3</sub>) [5].

**Isorhamnetin (4).** C<sub>16</sub>H<sub>12</sub>O<sub>7</sub>, yellow powder. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>, δ, ppm, J/Hz): 12.49 (1H, s, OH), 10.91 (1H, s, OH), 9.79 (1H, s, OH), 9.49 (1H, s, OH), 7.73 (1H, d, J = 1.5, H-2'), 7.72 (1H, dd, J = 1.5, 8.5, H-6'), 6.95 (1H, d, J = 8.5, H-5'), 6.49 (1H, d, J = 1.5, H-8), 6.21 (1H, d, J = 1.5, H-6), 3.86 (3H, s, OCH<sub>3</sub>). <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>, δ, ppm): 175.87 (C-4), 163.91 (C-7), 160.70 (C-5), 156.16 (C-9), 148.81 (C-2), 147.36 (C-3'), 146.62 (C-4'), 135.82 (C-3), 121.98 (C-1'), 121.72 (C-6'), 115.55 (C-5'), 111.75 (C-2'), 103.03 (C-10), 98.21 (C-6), 93.59 (C-8), 55.78 (OCH<sub>3</sub>) [6].

**Dihydroapigenin (5).** C<sub>15</sub>H<sub>12</sub>O<sub>5</sub>, yellow powder. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD, δ, ppm, J/Hz): 7.28 (2H, d, J = 8.5, H-2' and H-6'), 7.80 (2H, d, J = 1.5, 8.1, H-3' and H-5'), 5.87 (2H, d, J = 3.5, H-6 and H-8), 5.30 (1H, dd, J = 2.5, 13.0, H-2), 3.08 (1H, dd, J = 13.0, 17.0, H-3β), 2.65 (1H, dd, J = 17.0, 2.5, H-3α). <sup>13</sup>C NMR (150 MHz, CD<sub>3</sub>OD, δ, ppm): 198.05 (C-4), 168.62 (C-7), 165.74 (C-5), 165.13 (C-9), 159.29 (C-4'), 131.37 (C-1'), 129.31 (C-2' and C-6'), 116.61 (C-3' and C-5'), 103.64 (C-10), 97.35 (C-6), 96.46 (C-8), 80.72 (C-2), 44.30 (C-3) [7].

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**Kaempferol-3-O- $\alpha$ -L-rhamnoside (6).** C<sub>21</sub>H<sub>20</sub>O<sub>10</sub>, yellow powder. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm, J/Hz): 7.72 (2H, d, J = 8.7, H-2' and H-6'), 6.91 (2H, d, J = 8.7, H-3' and H-5'), 6.31 (1H, J = 1.5, H-8), 6.10 (1H, d, J = 1.5, H-6), 5.36 (1H, d, J = 1.1, H-1''), 4.23 (1H, d, J = 1.3, H-5''), 3.72 (1H, m, H-2''), 3.31 (2H, m, H-3'' and H-4''), 0.92 (3H, d, J = 5.5, CH<sub>3</sub>). <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 179.77 (C-4), 165.97 (C-7), 163.35 (C-5), 161.70 (C-9), 159.43 (C-4'), 158.69 (C-2), 136.46 (C-3), 132.16 (C-2' and C-6'), 122.89 (C-1'), 116.73 (C-3' and C-5'), 106.18 (C-1''), 103.72 (C-10), 100.08 (C-6), 95.04 (C-8), 73.49 (C-2''), 72.39 (C-5''), 72.24 (C-4''), 72.18 (C-3''), 17.92 (C-6'') [8].

**Kaempferol-3-O- $\alpha$ -L-glucoside (7).** C<sub>21</sub>H<sub>20</sub>O<sub>11</sub>, yellow powder. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm, J/Hz): 12.39 (1H, s, OH), 10.94 (1H, s, OH), 10.35 (1H, s, OH), 8.05 (2H, d, J = 8.0, H-2' and H-6'), 6.89 (2H, d, J = 8.0, H-3' and H-5'), 6.45 (1H, s, H-8), 6.22 (1H, s, H-6), 5.45 (1H, d, J = 7.5, H-1''), 5.32–3.09 (10H, H-2''–6'', 4  $\times$  OH). <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 177.48 (C-4), 164.13 (C-7), 161.24 (C-5), 159.95 (C-9), 156.39 (C-4'), 156.28 (C-2), 133.22 (C-3), 130.89 (C-2' and C-6'), 120.92 (C-1'), 115.11 (C-3' and C-5'), 104.03 (C-1''), 100.90 (C-10), 98.69 (C-6), 93.65 (C-8), 77.49 (C-2''), 76.44 (C-5''), 74.23 (C-4''), 69.92 (C-3''), 60.86 (C-6'') [9].

**Kaempferitrin (8).** C<sub>27</sub>H<sub>30</sub>O<sub>14</sub>, yellow powder. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm, J/Hz): 7.79 (2H, d, J = 8.7, H-2' and H-6'), 6.93 (2H, d, J = 8.7, H-3' and H-5'), 6.77 (1H, J = 1.9, H-8), 6.44 (1H, d, J = 1.9, H-6), 5.44 (1H, s, H-1''), 5.31 (1H, d, J = 1.1, H-1'''), 1.14 (1H, d, J = 6.1, CH<sub>3</sub>), 0.82 (1H, d, J = 5.4, CH<sub>3</sub>). <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 177.95 (C-4), 161.73 (C-7), 160.97 (C-5), 160.20 (C-9), 157.82 (C-4'), 156.12 (C-2), 134.57 (C-3), 1130.72 (C-2' and C-6'), 120.38 (C-1'), 115.47 (C-3' and C-5'), 105.83 (C-1''), 104.57 (C-1'''), 101.89 (C-10), 99.48 (C-6), 98.49 (C-8), 94.60 (C-4''), 71.66 (C-5'''), 71.18 (C-2''), 70.70 (C-4'''), 70.40 (C-3'''), 70.31 (C-5''), 70.12 (C-2''), 69.85 (C-3''), 17.95 (C-6''), 17.51 (C-6'') [10].

All these compounds were isolated from *F. thunbergii* for the first time.

Phytochemical studies of the flower of *F. thunbergii* are continuing.

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