

## CHEMICAL CONSTITUENTS FROM THE LEAVES OF *Sorbus tianschanica*

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*Sorbus tianschanica* Ruper., which is widely distributed in Xinjiang of China, has been used in folklore medicine to treat asthma, ventricular myocytes, dyspnea, and gastritis [1, 2]. Previous phytochemical studies on *Sorbus tianschanica* have reported the identification of flavonoids, cyanogenic glycosides such as amygdalin, and phenolic acids [3–6]. In the course of our investigation on the chemical constituents of Chinese liverworts, eight compounds were obtained and identified as hexacosanoic acid (**1**), ursolic acid (**2**), quercetin (**3**), kaempferol-3-*O*- $\beta$ -D-glucoside (**4**), hyperin (**5**), rutin (**6**), amygdalin (**7**), and prunasin (**8**) from *Sorbus tianschanica*. Compounds **1**, **2**, **4**, **6**, and **8** were isolated from the plant for the first time.

**Plant Material.** The leaves of *Sorbus tianschanica* were collected in July 2001 in Tianshan Mountain in Urumqi of China and were identified by Chief Pharmacist Sulayiman Khalik at the Xinjiang Uyghur Autonomous Regional Institute for Food and Drug Control. A voucher specimen is deposited in the herbarium of the Institute for Material Medica of Xinjiang.

**Sample Preparation.** The air-dried leaves (1.8 kg) were extracted twice with boiling ethanol (78%) under reflux for 2 h and concentrated *in vacuo* to afford a crude extract (330 g), which was then dissolved in H<sub>2</sub>O and partitioned successively with petroleum ether (PE), CHCl<sub>3</sub>, and *n*-BuOH. The solvents were evaporated to produce PE (15.0 g), CHCl<sub>3</sub> (23.0 g), and *n*-BuOH (51.0 g) fractions. The CHCl<sub>3</sub> fraction (10 g) was subjected to repeated column chromatography over silica-gel (200–300 mesh) eluted with PE-acetone gradient (100:0 to 0:100) to obtain compounds **1** (30 mg), **2** (93 mg), and **3** (57 mg). The *n*-BuOH extract (21 g) was subjected to repeated column chromatography over silica-gel [eluted with CHCl<sub>3</sub>-MeOH, (100:0 to 60:40)] and semi-preparative HPLC [eluted by MeOH-H<sub>2</sub>O (15:5 to 65:35) and CH<sub>3</sub>CN-H<sub>2</sub>O (25:75)] to provide compounds **4** (27 mg), **5** (32 mg), **6** (47 mg), **7** (73 mg), and **8** (31 mg), and then identified by comparison of their physical data (UV, <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS) with reported values in the literature [7–19].

**Hexacosanoic Acid (1).** White powder, CH<sub>3</sub>(CH<sub>2</sub>)<sub>24</sub>COOH, mp 79–81°C. UV spectrum (MeOH,  $\lambda_{\max}$ , nm): 232. EI-MS *m/z*: 395 [M – H]<sup>+</sup>, 388, 360, 337 and 312. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm, J/Hz): 2.35 (2H, t,  $J$  = 7.4,  $\alpha$ -CH<sub>2</sub>), 1.20–1.57 (44H, m, CH<sub>2</sub> × 22), 0.98 (3H, t,  $J$  = 6.4, CH<sub>3</sub>) [7, 8].

**Ursolic Acid (2).** White powder, mp 285–287°C,  $[\alpha]_D$  +69.2° (c 0.7, CHCl<sub>3</sub>). UV spectrum (MeOH,  $\lambda_{\max}$ , nm): 210. IR (KBr,  $\nu_{\max}$ , cm<sup>−1</sup>): 3420 (OH), 2928 (CH<sub>3</sub>), 1691 (C=O), 1392, and 1377. EI-MS *m/z*: 456 [M]<sup>+</sup>, 438, 248, 207, 203, 189, 175, 133. <sup>1</sup>H NMR (400 MHz, Py-d<sub>5</sub>,  $\delta$ , ppm, J/Hz): 5.40 (1H, t,  $J$  = 3.2, H-12), 3.39 (1H, dd,  $J$  = 9.6 and 5.2, H-3), 1.86 (2H, br.s, H-2 $\alpha$  and H-2 $\beta$ ), 1.30 (3H, s, H-23), 1.22 (6H, s, H-26 and 27), 0.98 (3H, s, H-24), 0.92 (3H, d,  $J$  = 6.4, H-30), 0.80 (3H, d,  $J$  = 6.0, H-29), 0.74 (3H, s, H-25). <sup>13</sup>C NMR (100 MHz, Py-d<sub>5</sub>,  $\delta$ , ppm): 38.8 (C-1), 28.1 (C-2), 78.5 (C-3), 39.4 (C-4), 56.2 (C-5), 18.9 (C-6), 33.8 (C-7), 39.7 (C-8), 48.3 (C-9), 37.6 (C-10), 23.3 (C-11), 126.0 (C-12), 139.6 (C-13), 42.7 (C-14), 29.0 (C-15), 24.3 (C-16), 48.3 (C-17), 53.9 (C-18), 39.2 (C-19), 39.7 (C-20), 31.4 (C-21), 37.8 (C-22), 29.2 (C-23), 17.0 (C-24), 16.0 (C-25), 17.6 (C-26), 24.16 (C-27), 180.2 (C-28), 17.9 (C-29), 21.8 (C-30) [9, 10].

**Quercetin (3).** Yellow powder, mp 310–312°C. UV spectrum (MeOH,  $\lambda_{\max}$ , nm, lg $\epsilon$ ): 373 (2.80), 257 (2.81), 207. EI-MS *m/z*: 302 [M]<sup>+</sup>, 274 [M – CO]<sup>+</sup>. The <sup>1</sup>H and <sup>13</sup>C NMR spectral data of compound **3** were in accord with the reported values in the literature [11, 12].

**Kaempferol-3-*O*- $\beta$ -D-glucoside (4).** Yellow powder, mp 178–180°C. ESI-MS *m/z* 447 [M + H]<sup>+</sup>. The <sup>1</sup>H and <sup>13</sup>C NMR spectral data of compound **4** were in accord with the reported values in the literature [11, 13].

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**Hyperin (5).** Yellow powder, mp 235–237°C. UV spectrum (MeOH,  $\lambda_{\max}$ , nm, lg ε): 362 (4.20), 257 (4.33). ESI-MS  $m/z$  464 [M]<sup>+</sup>. <sup>13</sup>C NMR (100 MHz, Py-d<sub>5</sub>, δ, ppm): 156.3 (C-2), 134.1 (C-3), 177.6 (C-4), 161.7 (C-5), 98.6 (C-6), 164.6 (C-7), 93.2 (C-8), 156.7 (C-9), 103.9 (C-10), 122.0 (C-1'), 116.0 (C-2'), 145.1 (C-3'), 149.0 (C-4'), 116.3 (C-5'), 121.8 (C-6'), glucosyl: 101.6 (C-1''), 74.5 (C-2''), 77.2 (C-3''), 70.5 (C-4''), 77.4 (C-5''), 61.5 (C-6'') [11].

**Rutin (6).** Yellow powder, mp 185–187°C. UV spectrum (MeOH,  $\lambda_{\max}$ , nm, lg ε): 361 (3.98), 259 (4.31). ESI-MS  $m/z$ : 610 [M]<sup>+</sup>, 465, 391, 303, 302, 219, 133, 115. The <sup>13</sup>C NMR spectral data of compound **6** were in accord with the reported values in the literature [14].

**Amygdalin (7).** White powder, mp 206–209°C,  $[\alpha]_D$  +34.1° (c 0.2, MeOH). UV spectrum (MeOH,  $\lambda_{\max}$ , nm): 269, 261, 257, 252, 209; ESI-MS  $m/z$ : 479.9 [M + Na]<sup>+</sup>, 458.3 [M]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, δ, ppm, J/Hz): 7.68 (2H, m, H-2 and H-6), 7.50 (2H, m, H-3 and H-5), 7.47 (1H, m, H-4), 5.97 (1H, s, H-7), 4.60 (1H, d, J = 8.0, H-1' of Glc), 4.42 (1H, d, J = 7.8, H-1'' of Glc) [15–17].

**Prunasin (8).** White powder, mp 145–148°C,  $[\alpha]_D$  -53.4° (c 0.10, MeOH). UV spectrum (MeOH,  $\lambda_{\max}$ , nm): 275, 225; ESI-MS  $m/z$ : 296 [M + H]<sup>+</sup>, 268 [M – HCN]<sup>+</sup>. The <sup>1</sup>H and <sup>13</sup>C NMR spectral data of compound **8** were in accord with the reported values in the literature [18, 19].

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## REFERENCES

- Editorial Committee for Flora of China, *Flora of China*, Vol. **36**, Beijing, Science Press (1974), p. 316.
- W. Fu, T. Liu, C. Y. Yang, T. Wang, Q. Sh. Zheng, H. Tang, and Z. H. Wang, *Chin. Pharmacol. Bull.*, **26**, 251 (2010).
- L. Li, H. Tang, T. Wu, and C. Z. Yu, *Chem. Nat. Comp.*, **46**, 811 (2010).
- G. G. Zapesochnaya, A. I. Ban'kovskii, and I. A. Gubanov, *Chem. Nat. Comp.*, **5**, 104 (1969).
- G. G. Zapesochnaya, R. Kh. Aitbaeva, and A. I. Ban'kovskii, *Chem. Nat. Comp.*, **9**, 112 (1973).
- J. W. Zang and Q. Y. Xiao, *Handbook of Bioactive Components in Medicinal Plants*, Beijing, People's Medical Publishing House (1986), 49.
- A. P. Deshmukh, B. Chefetz, and P. G. Hatcher, *Chemosphere*, **45**, 1007 (2001).
- W. Y. Jin, B. S. Min, J. P. Lee, Ph. Th. Thuong, H. K. Lee, K. S. Song, Y. H. Seong, and K. H. Bae, *Arch. Pharm. Res.*, **30**, 172 (2007).
- R. W. Kriwacki and T. P. Pitner, *Pharm. Res.*, **6**, 531 (1989).
- X. F. Cai, I. S. Lee, G. H. Shen, N. T. Dat, J. J. Lee, and Y. H. Kim, *Arch. Pharm. Res.*, **27**, 825 (2004).
- L. M. Dai, Ch. Ch. Zhao, H. Z. Jin, J. Tang, Y. H. Shen, H. L. Li, C. Y. Peng, and W. D. Zhang, *Arch. Pharm. Res.*, **31**, 1325 (2008).
- C. N. He, C. L. Wang, S. X. Guo, J. S. Yang, and P. G. Xiao, *China J. Chin. Mater. Med.*, **30**, 761 (2005).
- X. J. Xu, L. X. Zuo, W. H. Qi, and W. Wang, *Chem. Ind. Times.*, **20**, 45 (2006).
- D. Q. Chen, *Operating Manual of Chemical Reference Substances from Traditional Chinese Medicine*, Beijing, China Medical Science Press (2000), p. 119.
- J. Y. Koo, E. Y. Hwang, S. Cho, J. H. Lee, Y. M. Lee, and S. P. Hong, *J. Chromatogr. B*, **814**, 69 (2005).
- G. F. Pauli, *J. Nat. Prod.*, **63**, 834 (2000).
- G. Widmalm, K. Jansson, G. Pellijeff, and D. Sandstrom, *J. Phys. Chem. B*, **107**, 11794 (2003).
- M. Ch. Song, H. J. Yang, T. S. Jeong, K. T. Kim, and N. I. Baek, *Arch. Pharm. Res.*, **31**, 573 (2008).
- S. K. Ling, T. Tanaka, and I. Kouno, *J. Nat. Prod.*, **65**, 131 (2002).