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CHEMICAL CONSTITUENTS OF *Hippophae rhamnoides* subsp. *turkestanica* FRUITS

Yinqing Li,[1,2,3,4] A. Yili,[1,2,4] Yongqiang Liu,[1,2,4] A. Kawuli,[1,2,4] and H. A. Aisa[1,2,4]*

As a subspecies of sea buckthorn, *Hippophae rhamnoides* L. subsp. *turkestanica* (Fam. Elaeagnaceae) is a deciduous shrub and is distributed widely throughout many regions of Central Asia (Xinjiang of China, northwest of India, Pakistan, Uzbekistan, etc.) [1]. The fruits of *H. rhamnoides* L. subsp. *turkestanica* were collected in October 2011 from Wushi, Xinjiang, China and identified by Prof. Guanmian Shen (Xinjiang Institute of Ecology and Geography, Chinese Academy of Sciences).

Air-dried and powdered fruits (12 kg) were extracted with MeOH (8 L × 5) at room temperature. Then the methanol extracts were combined, evaporated, and suspended in 10 L of water. The suspension was partitioned with petroleum ether, EtOAc, and *n*-BuOH. Both the EtOAc and *n*-BuOH fractions were purified by column chromatography on silica gel and Sephadex LH-20, and preparative HPLC to yield compounds **1–21**.

Compounds **1–7** were isolated from the Elaeagnaceae family for the first time. Compounds **8–14** were obtained from the species *Hippophae rhamnoides* L. subsp. *turkestanica* for the first time. Moreover, the structure of compound **4** was only postulated from the MS and ^{1}H NMR spectrum in the literature [5]. Here, compound **4** was identified as 1-*n*-propyl-6-hydroxy-l,2,3,4-tetrahydro-β-carboline by 1D and 2D NMR in combination with MS spectral data for the first time.

***cis-p*-Cinnamic acid-4-*O*-β-D-glucopyranoside (1)**, yellow amorphous powder. $C_{15}H_{18}O_8$. MS spectrum (ESI) *m/z* 327 $[M + H]^+$. ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.66 (2H, d, J = 8.4, H-2, 6), 6.99 (2H, d, J = 8.4, H-3, 5), 5.84 (1H, d, J = 12.6, H-α), 6.69 (1H, d, J = 12.6, H-β), 4.90 (1H, d, J = 7.2, H-1′). ^{13}C NMR (150 MHz, DMSO-d_6, δ, ppm): 128.8 (C-1), 131.3 (C-2, 6), 115.6 (C-3, 5), 157.6 (C-4), 120.7 (C-α), 138.0 (C-β), 168.4 (COOH), 100.1 (C-1′), 73.2 (C-2′), 76.6 (C-3′), 69.7 (C-4′), 77.0 (C-5′), 60.7 (C-6′) [2].

***trans-p*-Cinnamic acid-4-*O*-β-D-glucopyranoside (2)**, yellow amorphous powder. $C_{15}H_{18}O_8$. MS spectrum (ESI) *m/z* 349 $[M + Na]^+$. ^{1}H NMR (400 MHz, D_2O, δ, ppm, J/Hz): 7.34 (2H, d, J = 7.6, H-2, 6), 6.90 (2H, d, J = 7.6, H-3, 5), 6.15 (1H, d, J = 15.6, H-α), 7.20 (1H, d, J = 15.6, H-β), 4.94 (1H, d, J = 6.4, H-1′). ^{13}C NMR (100 MHz, D_2O, δ, ppm): 128.9 (C-1), 129.9 (C-2, 6), 116.5 (C-3, 5), 158.1 (C-4), 117.0 (C-α), 144.6 (C-β), 171.9 (COOH), 99.5 (C-1′), 72.8 (C-2′), 75.4 (C-3′), 69.3 (C-4′), 76.0 (C-5′), 60.4 (C-6′) [3].

1-Methyl-6-hydroxy-l,2,3,4-tetrahydro-β-carboline (3), yellow amorphous powder. $C_{12}H_{14}N_2O$. MS spectrum (ESI) *m/z* 203 $[M + H]^+$. ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 10.70 (1H, s, NH-9), 8.33 (1H, s, OH), 7.11 (1H, d, J = 7.2, H-8), 6.72 (1H, s, H-5), 6.59 (1H, d, J = 7.2, H-7), 4.50 (1H, m, H-1), 3.61 and 3.13 (1H, m, H-3), 2.74 (2H, m, H-4), 1.54 (3H, t, J = 7.2, Me). ^{13}C NMR (150 MHz, DMSO-d_6, δ, ppm): 150.6 (C-6), 133.6 (C-4b), 130.3 (C-9a), 126.9 (C-8a), 111.5 (C-7), 111.3 (C-8), 104.8 (C-4a), 102.0 (C-5), 48.1 (C-1), 40.5 (C-3), 19.3 (C-4), 18.0 (Me) [4].

1-*n*-Propyl-6-hydroxy-l,2,3,4-tetrahydro-β-carboline (4), yellow amorphous powder. $C_{14}H_{18}N_2O$, MS spectrum (ESI) *m/z* 231 $[M + H]^+$. ^{1}H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 8.47 (1H, s, OH), 7.18 (1H, d, J = 8.4, H-8), 6.83 (1H, d, J = 2.4, H-5), 6.71 (1H, dd, J = 8.4, 2.4, H-7), 4.64 (1H, m, H-1), 3.71 and 3.42 (1H, m, H-3), 2.98 (2H, m, H-4), 2.19 and 1.91 (1H, m, H-1′), 1.60 (2H, m, H-2′), 1.08 (3H, t, J = 7.2, H-3′). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 152.1 (C-6), 133.8

1) Key Laboratory of Plant Resources and Chemistry of Arid Zone, Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, 830011, Urumqi, P. R. China, fax: 86 991 3838957, e-mail: haji@ms.xjb.ac.cn; 2) State Key Laboratory Basis of Xinjiang Indigenous Medicinal Plants Resource Utilization, Xinjiang; Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, 830011, Urumqi, P. R. China; 3) University of Chinese Academy of Sciences, 100049, Beijing, P. R. China; 4) Central Asia Drug Research and Development Center of Chinese Academy of Sciences, 830011, Urumqi, P. R. China. Published in *Khimiya Prirodnykh Soedinenii*, No. 2, March–April, 2014, pp. 307–308. Original article submitted May 26, 2013.

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(C-4b), 131.1 (C-9a), 128.3 (C-8a), 113.5 (C-7), 113.0 (C-8), 106.6 (C-4a), 103.5 (C-5), 55.0 (C-1), 43.3 (C-3), 35.6 (C-1′), 19.7 (C-4), 19.6 (C-2′), 14.3 (C-3′) [5].

Quercetin-3-*O*-[α-L-rhamnopyranosyl-(1→2)]-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranoside (5), yellow amorphous powder. $C_{33}H_{40}O_{20}$. MS spectrum (ESI) *m/z* 755 $[M - H]^-$. ^1H NMR (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.55 (1H, dd, J = 7.2, 1.8, H-6′), 7.50 (1H, d, J = 1.8, H-2′), 6.86 (1H, d, J = 7.8, H-5′), 6.40 (1H, s, H-8), 6.20 (1H, s, H-6), 5.55 (1H, d, J = 7.8, H-1″), 5.09 (1H, s, H-1‴), 4.37 (1H, s, H-1⁗), 0.99 and 0.83 (3H, d, J = 6.6, Me) [6].

Quercetin-3-*O*-β-D-sophoroside-7-*O*-α-L-rhamnoside (6), yellow amorphous powder. $C_{33}H_{40}O_{21}$. MS spectrum (ESI) *m/z* 771 $[M - H]^-$. ^1H NMR (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.65 (1H, dd, J = 8.4, 2.4, H-6′), 7.61 (1H, d, J = 1.8, H-2′), 6.88 (1H, d, J = 8.4, H-5′), 6.78 (1H, s, H-8), 6.43 (1H, s, H-6), 5.72 (1H, d, J = 7.8, H-1″), 5.56 (1H, s, H-1⁗), 4.63 (1H, d, J = 7.8, H-1‴), 1.16 (3H, d, J = 5.4, Me). ^{13}C NMR (150 MHz, DMSO-d_6, δ, ppm): 177.6, 161.5, 160.9, 156.1, 155.8, 148.6, 145.0, 133.3, 122.0, 120.6, 116.1, 115.4, 105.6, 104.6, 99.4, 98.4, 98.0, 94.1, 82.8, 77.6, 76.8, 76.6, 76.5, 74.4, 71.6, 70.2, 70.1, 69.8, 69.5, 69.5, 60.7, 60.6, 17.9 [7].

Fumaric acid monomethyl ester (7), white amorphous powder. $C_5H_6O_4$. MS spectrum (ESI) *m/z* 131 $[M + H]^+$. ^1H NMR (400 MHz, pyridine-d_5, δ, ppm, J/Hz): 6.58 (1H, s, H-3), 6.53 (1H, s, H-2), 3.86 (3H, s, Me). ^{13}C NMR (100 MHz, pyridine- d_5, δ, ppm): 166.4 (C-4), 164.4 (C-1), 97.1 (C-3), 94.8 (C-2), 52.6 (Me) [8].

Isorhamnetin-3-*O*-β-D-sophoroside-7-*O*-α-L-rhamnoside (8), yellow amorphous powder. $C_{34}H_{42}O_{21}$. MS spectrum (ESI) *m/z* 785 $[M - H]^-$. The ^1H NMR and ^{13}C NMR data agreed with those reported in the literature [9].

Isorhamnetin-3-*O*-β-D-glucopyranoside-7-*O*-α-L-rhamnoside (9), yellow amorphous powder. $C_{28}H_{32}O_{16}$. MS spectrum (ESI) *m/z* 623 $[M - H]^-$. The MS and NMR data agreed with those reported in the literature [9].

Isorhamnetin-3-*O*-β-D-glucopyranoside (10), yellow amorphous powder. $C_{22}H_{22}O_{12}$. MS spectrum (ESI) *m/z* 479 $[M + H]^+$. The MS and NMR data agreed with those reported in the literature [10].

Quercetin-3-*O*-β-D-glucopyranoside (11), yellow amorphous powder. $C_{21}H_{20}O_{12}$. MS spectrum (ESI) *m/z* 463 $[M - H]^-$. The MS and NMR data agreed with those reported in the literature [10].

Quercetin-7-*O*-β-D-glucopyranoside (12), yellow amorphous powder. $C_{21}H_{20}O_{12}$. MS spectrum (ESI) *m/z* 463 $[M - H]^-$. The MS and NMR data agreed with those reported in the literature [10].

Ethyl-β-D-glucopyranoside (13), white needles, mp 78–79°C. $C_8H_{16}O_6$. MS spectrum (ESI) *m/z* 207 $[M - H]^-$. The NMR data agreed with those reported in the literature [11].

Isorhamnetin-3-*O*-rutinoside (14), yellow needle crystals, mp 181–183°C. $C_{28}H_{32}O_{16}$. MS spectrum (ESI) *m/z*: 625 $[M + H]^+$, 647 $[M + Na]^+$. The NMR and MS data were in agreement with those reported in the literature [10].

Kaempferol (15), yellow needle crystals, mp 275–279°C. The compound was compared with a standard sample by HPLC.

Isorhamnetin (16), yellow amorphous powder, mp 306–307°C. $C_{16}H_{12}O_7$. MS spectrum (ESI) *m/z* 315 $[M - H]^-$. The NMR and MS data were in agreement with those reported in the literature [12].

Protocatechuic acid (17), white needle crystals, decompose at 194–197°C. $C_7H_6O_4$. MS spectrum (ESI) *m/z* 153 $[M - H]^-$. The MS and NMR data agreed with those reported in the literature [12].

Rutin (18), yellow needle crystals, mp 176–178°C. $C_{27}H_{30}O_{16}$. MS spectrum (ESI) *m/z* 609 $[M - H]^-$. The MS and NMR data agreed with those reported in the literature [12].

Quinic acid (19), white needle crystals, mp 161–162°C. $C_7H_{12}O_6$. MS spectrum (ESI) *m/z* 191 $[M - H]^-$. The MS and NMR data agreed with those reported in the literature [12].

Oleanic acid (20), white amorphous powder. The NMR data agreed with those reported in the literature [12].

Daucosterol (21), white amorphous powder, mp 276–280°C. The NMR and MS data were in agreement with those reported in the literature [12].

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