FLAVONOIDS OF *Cynara scolymus*

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Heads of *Cynara scolymus* L. (*Artichoke*) are eaten as a popular vegetable and leaves of *C. scolymus* have been used for hepatoprotection as a choleretic, diuretic, liver-protective, and lipid-lowering agent in traditional European medicine since Roman times [1, 2].

The dried leaf powder of *C. scolymus* (1.5 kg) was collected from the Yandi Agricultural Company Experiment Station, Kunming, China, in the summer of 2003, and extracted with 75% ethanol (5 L × 3) at 90°C.

The alcohol extract was evaporated in vacuum at 50°C. The condensed solution was diluted with water and successively treated with chloroform, ethyl acetate, and *n*-butanol.

The *n*-butanol extract (35 g) was subjected to Sephadex LH-20 column chromatography. The column was continuously eluted with a methanol gradient in water and fractions (**1–6**) were collected. Fraction **3** was subjected to silica gel column chromatography and eluted with ethyl acetate–methanol–water (8:1:1) to isolate and purify compounds **1** (30 mg) and **2** (45 mg). Fraction **4** was first purified with a silica gel column. Further purification was by semipreparative HPLC [(Shimatzu Zorbax ODS (9.4 × 250 mm); acetonitrile–0.1% acetic acid (2:5) as a mobile phase; flow rate, 3.0 ml/min; UV detector, 330 nm)] to afford compounds **3** (20 mg) and **4** (12 mg). These compounds were identified using UV, IR, ESI-MS, MS/MS, and NMR spectra and by comparison with reported spectral data in the literature.

Luteolin-7-O-α-*L*-rhamnosyl(1→6)-β-D-glucopyranoside (1), $C_{27}H_{30}O_{15}$, mp 186–189°C, UV spectrum (MeOH, λ_{max}, nm): 256, 266sh, 348. Nagative ESI-MS spectrum (70 eV): *m/z* 593.3 $[M–H]^–$; MS/MS fragments: *m/z* 326.9, 284.9.

^{1}H NMR (CD_3OD, 400 MHz, δ, ppm, J/Hz): 7.45 (1H, dd, J = 2.0, J = 8.0, H-6), 7.44 (1H, d, J = 2.0, H-2′), 6.94 (1H, d, J = 8.0, H-5′), 6.81 (1H, d, J = 2.0, H-8), 6.63 (1H, s, H-3), 6.51 (1H, d, J = 2.0, H-6), 5.03 (1H, d, J = 6.9, glc-1), 4.71 (1H, br.s, rham-1), 1.18–3.90 (m, sugar protons) [3–5].

Luteolin-7-O-β-D-glucopyranoside (cynaroside) (2), $C_{21}H_{20}O_{11}$, mp 240–243°C, UV spectrum (MeOH, λ_{max}, nm): 255, 267sh, 349. Nagative ESI-MS spectrum (70 eV): *m/z* 447.6 $[M–H]^–$; MS/MS fragments: *m/z* 284.9.

^{1}H NMR (CD_3OD, 400MHz, δ, ppm, J/Hz): 7.43 (1H, dd, J = 2.0, J = 8.0, H-6′), 7.41 (1H, d, J = 2.0, H-2′), 6.90 (1H, d, J = 8.0, H-5′), 6.79 (1H, d, J = 2.0, H-8), 6.73 (1H, s, H-3), 6.43 (1H, d, J = 2.0, H-6), 5.07 (1H, d, J = 7.0, glc-1), 3.17–3.88 (m, glucose protons) [3, 5, 6].

Apigenin-7-O-α-L-rhamnosyl(1→6)-β-D-glucopyranoside (apigenin-7-rutinoside) (3), $C_{27}H_{30}O_{14}$, mp 245–248°C, UV spectrum (MeOH, λ_{max}, nm): 254, 266 sh, 348. The IR spectrum (KBr, ν, cm^{-1}) shows characteristic absorption bands of hydroxyls (3384, 3301), carbonyl of γ-pyrone (1659), aromatic ring (1576, 1516, 826), and C-O of sugar (1077, 1060, 1018). Nagative ESI-MS spectrum (70 eV): *m/z* 577.3 $[M–H]^–$; MS/MS fragments: *m/z* 326.9, 268.9.

^{1}H NMR (CD_3OD, 400 MHz, δ, ppm, J/Hz): 7.92 (2H, d, J = 8.4, H-2′, H-6′), 6.96 (2H, d, J = 8.3, H-3′, H-5′), 6.78 (1H, d, J = 2.0, H-8), 6.70 (1H, s, H-3), 6.48 (1H, d, J = 2.0, H-6), 5.10 (1H, d, J = 7.5, glc-1), 4.75 (1H, br.s, rham-1), 1.18–3.92 (m, sugar protons) [5, 7].

Acid or enzyme hydrolysis of compound **3** produced apigenin, L-rhamnose, and D-glucose.

Apigenin-7-O-β-D-glucopyranoside (4), $C_{21}H_{20}O_{10}$, mp 229–232°C, UV spectrum (MeOH, λ_{max}, nm): 255, 267 sh, 350. The IR spectrum (KBr, ν, cm^{-1}) shows characteristic absorption bands of hydroxyls (3380, 3256, 3245), carbonyl of γ-pyrone (1653), aromatic ring (1572, 1509, 834), and C–O of glycosides (1092, 1040). Negative ESI-MS spectrum (70 eV): *m/z* 431.6 $[M–H]^–$, MS/MS fragments: *m/z* 268.9 [8].

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^{1}H NMR (CD_3OD, 400 MHz, δ, ppm, J/Hz): 7.88 (2H, d, J = 8.4, H-2′, H-6′), 6.96 (2H, d, J = 8.3, H-3′, H-5′), 6.82 (1H, d, J = 2.0, H-8), 6.70 (1H, s, H-3), 6.50 (1H, d, J = 2.0, H-6), 5.12 (1H, d, J = 7.0, glc-1), 3.34–3.92 (m, glucose protons). Acid or enzyme hydrolysis of compound **4** produced apigenin and *D*-glucose.

Flavonoids **3** and **4** are isolated for the first time from the leaves of *C. scolymus*.

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