Chemistry of Natural Compounds, Vol. 50, No. 3, July, 2014 [Russian original No. 3, May–June, 2014]

CHEMICAL CONSTITUENTS OF *Apocynum lancifolium* FLOWERS

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The perennial plant *Apocynum lancifolium* (Apocynaceae) is broadly distributed in Central Asia, western and eastern Siberia, Mongolia, Iran, and China [1]. It flowers in June-July and fruits in August-September. It grows among bushes along valleys and banks of rivers and lakes and occasionally in alkaline meadows.

Flowers of *A. lancifolium* are known in China as Luobuma and are used in Chinese folk and contemporary medicine as a medicinal tea and effective treatment for hypertension and neurasthenia and possess hypolipidemic, hepatotropic, antioxidant, antiviral, and nephritic activity. The flowers are popular in Japan as a health drink and are sold as rejuvenating food additives in the battle with hypercholesterolemia and as antihypertensive sedative agents [2–5].

Ground air-dried flowers of *A. lancifolium* that were collected in Xinjiang A. R., PRC, were extracted with EtOH (70%) at room temperature. The combined extract was evaporated *in vacuo*, diluted with H_2O (1:1), and extracted successively with hexane, $CHCl_3$, EtOAc, and *n*-BuOH. The EtOAc extract was chromatographed over a column of silica gel using a $CHCl_3$–MeOH gradient. Elution by $CHCl_3$–MeOH (50:1–1:1) isolated sterol and phenolic compounds **1**–**15**. The structures of the isolated compounds were elucidated using spectral data (PMR, ^{13}C NMR, DEPT, HSQC, HMBC, COSY, and mass spectrometry) and comparisons with the literature and authentic samples.

Ergost-5-en-3-ol (1), $C_{28}H_{48}O$, $[M]^+$ 400.680. Identified by GC-MS: 39 (8), 41 (56), 43 (100), 55 (75), 57 (69), 69 (48), 77 (12), 79 (36), 81 (57), 95 (50), 97 (28), 99 (6), 107 (47), 119 (28), 133 (26), 145 (37), 159 (31), 173 (13), 187 (9), 199 (11), 213 (27), 231(14), 240 (7), 247 (5), 255 (18), 273 (15), 281 (6), 289 (29), 301 (5), 315 (25), 340 (6), 367 (21), 382 (25), 385 (18), 400 (43).

Lupeol (2), $C_{30}H_{50}O$, $[M]^+$ 426. Identified by GC-MS: 41 (70), 43 (100), 55 (90), 57 (48), 68 (96), 77 (22), 81 (75), 83 (22), 95 (75), 109 (70), 212 (58), 135 (50), 147 (38), 161 (30), 175 (25), 189 (52), 203 (25), 207 (55), 218 (46), 234 (20), 247 (12), 257 (16), 272 (10), 283 (8), 297 (6), 315 (7), 339 (6), 357 (5), 365 (4), 383 (4), 393 (4), 411 (10), 426 (25).

***β*-Sitosterol (3)**, $C_{29}H_{50}O$, mp 131–132°C. Identified by comparison with an authentic sample.

***p*-Hydroxybenzoic acid (4)**, $C_7H_6O_3$, mp 159.5°C [6].

3,4-Dihydroxybenzoic acid methyl ester (5), $C_8H_8O_4$, mp 137–138°C [6].

Caffeic acid (6), $C_9H_8O_4$. ^1H NMR spectrum (400 MHz, CD_3OD, δ, ppm, J/Hz): 7.53 (1H, d, J = 16.9, H-8), 7.03 (1H, d, J = 1.8, H-2), 6.93 (1H, dd, J = 1.8, 8.0, H-6), 6.77 (1H, d, J = 8.0, H-5), 6.21 (1H, d, J = 16.9, H-7). ^{13}C NMR spectrum (100 MHz, CD_3OD, δ, ppm): 127.79 (C-1), 115.07 (C-2), 146.79 (C-3), 149.44 (C-4), 116.47 (C-5), 122.84 (C-6), 115.51 (C-7), 147.02 (C-8), 171.09 (C-9).

Esculetin (7), $C_9H_6O_4$, mp 268–270°C. ^1H NMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.87 (1H, d, J = 9.2, H-4), 6.97 (1H, s, H-5), 6.73 (1H, s, H-8), 6.15 (1H, d, J = 9.2, H-3), 3.41 (1H, br.s, 6-OH), 9.80 (1H, br.s, 7-OH). ^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 160.76 (C-2), 111.46 (C-3), 144.42 (C-4), 112.27 (C-5), 142.85 (C-6), 150.40 (C-7), 102.61 (C-8), 148.48 (C-9), 110.71 (C-10) [7].

***β*-Sitosterol-D-glucopyranoside (8)**, $C_{35}H_{60}O_6$, mp 275–277°C [6].

Kaempferol (9), $C_{15}H_{10}O_6$, yellow crystals, mp 276–277°C. PMR and ^{13}C NMR spectra agreed with those published [6].

Quercetin (10), $C_{15}H_{10}O_7$, light-yellow crystals, mp 305–307°C. Spectral data and a comparison with the literature identified **10** as quercetin [6, 8].

Quercetin was isolated earlier from *A. lancifolium* leaves [6, 9].

Astragalin (11), $C_{21}H_{20}O_{11}$, mp 209–211°C. Spectral data agreed with those published [9].

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Isoquercitrin (12), $C_{21}H_{20}O_{12}$, mp 248–250°C [10]. Acid hydrolysis of **12** produced quercetin and D-glucose.

Hyperoside (13), $C_{21}H_{20}O_{12}$, mp 231–232°C [11]. Both quercetin and D-galactose were identified after acid hydrolysis.

Nicotiflorin (14), light-yellow crystals, $C_{27}H_{30}O_{15}$, mp 182–186°C. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 8.23 (2H, dd, J = 8.4, 2.0, H-2′, 6′), 6.86 (2H, dd, J = 8.4, 2.0, H-3′, 5′), 6.29 (1H, d, J = 1.8, H-8), 6.10 (1H, d, J = 1.8, H-6), 5.27 (1H, d, J = 7.2, H-1″), 4.40 (1H, br.s, H-1‴), 3.16–3.43 carbohydrate protons, 1.06 (3H, d, J = 6.0, CH_3), 12.57 (1H, br.s, 5-OH) [12].

Acid hydrolysis of **14** produced kaempferol, D-glucose, and L-rhamnose [9].

Rutin (15), $C_{27}H_{30}O_{16}$, mp 193–195°C [9]. Acid hydrolysis of **15** produced quercetin, D-glucose, and L-rhamnose.

Ergost-5-en-3-ol, caffeic acid, esculetin, and nicotiflorin were isolated for the first time from plants of the genus *Apocynum*.

ACKNOWLEDGMENT

The work was supported by the Program for International Collaboration and Exchange of the National Foundation for Natural Sciences of China (No. 31110103908) and the Foundation for International Scientific and Technical Collaboration of Xinjiang-Uygur A. R. (No. 20126023).

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