FLAVONOIDS IN *Luculia pinceana*

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Luculia pinceana is a medicinal plant to treat tracheitis, tuberculosis, and rheumaric diseases in China [1]. The stems of *L. pinceana* contain essential oils, paeonol, and triterpenoid saponins, which have been studied [2–4]. However, the flavonoids of this plant have not been reported. We isolated five flavonoids from the *n*-BuOH extract of the stem of *L. pinceana*. Results are presented here.

The stem of *L. pinceana* was collected in July 2001 from Dali, Yunnan province of China. The plant was identified by Prof. H. Peng. A voucher specimen (KUN No. 0358685) was deposited in the Herbarium of the Department of Taxonomy, Kunming Institute of Botany, Chinese Academy of Sciences.

Dried stem of *L. pinceana* Hook. (20 kg) was extracted three times with ethanol under reflux. After evaporation of the solvent in vacuo, the concentrated extract was suspended in water and extracted successively with EtOAc and *n*-BuOH. The *n*-BuOH extract (150 g) was chromatographed over a silica-gel column separately with gradient elution by chloroform–methanol (20:1–7:3). There were flavonoids in the chloroform–methanol (8:2–7:3) fractions. All the fractions were combined to obtain 1.8 g flavonoids, and the flavonoids were chromatographed over RP-18 with water-methanol (6:4) and Sephadex LH-20 with methanol to afford compounds **1–5**. These compounds were identified using UV, MS, and NMR spectrum, chemical transformations, and comparison with authentic samples and were isolated from *L. pinceana* for the first time.

Kaempferol 3-*O*-α-L-rhamnoside (1), $C_{21}H_{20}O_{10}$, mp 172–174°C. Negative FAB-MS *m/z* (%): 431 (M-1, 100), 325 (18), 311 (9), 285 (55). ^{1}H NMR (400 MHz, C_5D_5N, δ, ppm, J/Hz): 7.73 (2H, dd, J = 2.8, 11.6, H-2′, 6′), 6.89 (2H, dd, J = 2.8, 11.6, H-3′, 5′), 6.37 (1H, d, J = 1.6, H-8), 6.17 (1H, d, J = 1.6, H-6), 5.28 (1H, br.s, H-1″), 0.77 (3H, d, J = 6.0, H-6′). ^{13}C NMR (100 MHz, C_5D_5N, δ, ppm): 156.5 (C-2), 134.2 (C-3), 177.6 (C-4), 161.3 (C-5), 98.9 (C-6), 164.9 (C-7), 93.8 (C-8), 157.0 (C-9), 103.8 (C-10), 120.5 (C-1′), 130.5 (C-2′), 115.4 (C-3′), 159.9 (C-4′), 115.4 (C-5′), 130.5 (C-6′), 101.8 (C-1″), 74.2 (C-2″), 76.4 (C-3″), 70.6 (C-4″), 75.8 (C-5″), 17.2 (C-6″) according to previously published spectral data [5, 6].

Kaempferol 3-*O*-rutinoside (2), $C_{27}H_{30}O_{15}$, mp 185–190°C. UV (λ_{max}, nm): 205, 266, 295, 350. IR (KBr, ν_{max}, cm^{-1}): 3424, 1658, 1608, 1560, 1508, 1453, 1362, 1286, 1260, 1208, 1183, 1142, 1092, 971, 912, 834. ^{1}H NMR (500 MHz, C_5D_5N, δ, ppm, J/Hz): 12.55 (1H, s, 5-OH), 7.96 (2H, d, J = 8.8, H-2′, 6′), 6.66 (2H, d, J = 8.8, H-3′, 5′), 6.39 (1H, d, J = 2.0, H-8), 6.18 (1H, d, J = 2.0, H-6), 5.30 (1H, d, J = 7.6, H-1″), 4.38 (1H, s, H-1‴), 0.96 (3H, d, J = 6.4, H-6‴). ^{13}C NMR (125 MHz, C_5D_5N, δ, ppm): 156.4 (C-2), 133.2 (C-2), 177.3 (C-4), 161.1 (C-5), 98.6 (C-6), 164.1 (C-7), 93.6 (C-8), 156.7 (C-9), 103.9 (C-10), 120.8 (C-1′), 130.7 (C-2), 115.0 (C-3), 159.8 (C-4), 115.0 (C-5), 130.7 (C-6), 101.3 (C-1″), 74.1 (C-2″), 76.4 (C-3″), 70.6 (C-4″), 75.8 (C-5″), 66.8 (C-6″), 100.6 (C-1‴), 70.3 (C-2‴), 69.9 (C-3‴), 71.8 (C-4‴), 68.1 (C-5‴), 17.6 (C-6‴), according to previously published spectral data [5].

Kaempferol 3-*O*-β-D-glucopyranoside-7-*O*-α-L-rhamnoside (3), $C_{27}H_{30}O_{15}$, mp 251–253°C. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.55 (1H, s, 5-OH), 7.95 (2H, d, J = 9.0, H-2′, 6′), 6.87 (2H, d, J = 9.0, H-3′, 5′), 6.30 (1H, d, J = 2.0, H-8), 6.20 (1H, d, J = 2.0, H-6), 5.78 (1H, d, J = 7.6, H-1″), 4.38 (1H, s, H-1‴), 0.98 (3H, d, J = 6.4, H-6‴), ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm):156.4 (C-2), 133.2 (C-2), 177.3 (C-4), 161.1 (C-5), 98.6 (C-6), 164.1 (C-7), 93.6 (C-8), 156.7 (C-9), 103.9 (C-10), 120.8 (C-1′), 130.7 (C-2′), 115.0 (C-3′), 159.8 (C-4′), 115.0 (C-5′), 130.7 (C-6′), 101.5 (C-1″), 74.3 (C-2″), 76.4 (C-3″), 70.0 (C-4″), 77.1 (C-5″), 61.8 (C-6″), 98.9 (C-1‴), 70.3 (C-2‴), 70.6 (C-3‴), 71.8 (C-4‴), 70.0 (C-5‴), 17.5 (C-6‴) according to previously published spectral data [7].

Kaempferol 3-*O*-rutinoside-7-*O*-α-L-rhamnoside (4). $C_{33}H_{40}O_{19}$, $[\alpha]_D^{25.9}$ –101.3° (*c* 0.032, MeOH). UV (λ_{max}, nm): 205, 264, 295, 346. IR (KBr, ν_{max}, cm^{-1}): 3418, 2931, 1653, 1610, 1506, 1456, 1362, 1300, 1278, 1208, 1179, 1136, 1085,

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1054, 979, 839, 813. Negative FAB-MS *m/z* (%): 739 (M-1, 100), 593(10), 285(90). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.55 (1H, s, 5-OH), 7.95 (2H, d, J = 9.0, H-2′, 6′), 6.87 (2H, d, J = 9.0, H-3′, 5′), 6.30 (1H, d, J = 2.0, H-8), 6.20 (1H, d, J = 2.0, H-6), 5.78 (1H, d, J = 7.6, H-1″), 4.38 (1H, s, H-1‴), 0.98 (3H, d, J = 6.4, H-6‴) according to previously published spectral data [7, 8].

7,8,3′,4′-Tetrahydroxy-3-methoxyflavone (5), mp 255–256°C. EI-MS *m/z* (%): 316 (M, 15), 281 (5), 221 (5), 175 (8), 147 (12), ^{1}H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 8.13 (1H, d, J = 7.9, H-5), 7.23 (1H, d, J = 7.9, H-6), 7.90 (1H, s, H-2′), 7.35 (1H, d, J = 8.1, H-5′), 7.79 (1H, d, J = 8.1, H-6′), 3.87 (3H, s, OMe). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 147.8 (C-2), 138.1 (C-3), 173.8 (C-4), 125.4 (C-5), 98.3 (C-6), 162.3 (C-7), 154.3 (C-8), 160.5 (C-9), 108.4 (C-10), 123.4 (C-1′), 116.6 (C-2′), 145.4 (C-3′), 148.0 (C-4′), 116.7 (C-5′), 121.7 (C-6′) according to previously published spectral data [9].

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