

## FLAVONOIDS FROM *Callicarpa nudiflora* LEAVES

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*Callicarpa nudiflora* belongs to the genus *Callicarpa*, family Verbenaceae. The dried leaves of this plant have been used in Chinese folk medicine for antibiosis, antiphlogosis, and hemostasis. The essential oil composition of *C. nudiflora* has been studied [1]. Previous studies reported that three flavonoid glycosides (luteoloside, dracocephalosite, and juncein) were isolated from the leaves of this plant [2]. In this work, we isolated for the first time four flavonoids from this plant. Ayanin is reported for the first time from *Callicarpa* genus.

The leaves of *C. nudiflora* were collected in Hainan Province, People's Republic of China, in May, 2006. The air-dried leaves of *C. nudiflora* (3 kg) were reflux-extracted with 70% EtOH (3 × 30 L) three times (1 h each time). The extract was evaporated under vacuum to afford a residue, which was partitioned with petroleum ether, EtOAc, and *n*-BuOH successively. The EtOAc extract (62 g) was chromatographed on a series of chromatographs, using a silica gel column and Sephadex LH-20 to afford four flavonoids 1–4.

Ayanin (1), yellow crystal, mp 229–230°C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, δ, ppm, J/Hz): 3.81 (3H, s, OCH<sub>3</sub>), 3.85 (3H, s, OCH<sub>3</sub>), 3.86 (3H, s, OCH<sub>3</sub>), 6.35 (1H, d, J = 2.1, H-6), 6.76 (1H, d, J = 2.1, H-8), 6.94 (1H, d, J = 8.4, H-5'), 7.60 (1H, dd, J = 2.0, 8.5, H-6'), 7.66 (1H, d, J = 1.8, H-2'), 9.95 (1H, s, 3'-OH), 12.66 (1H, s, 5-OH). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 56.2 (7-OCH<sub>3</sub>), 55.9 (4'-OCH<sub>3</sub>), 59.3 (3-OCH<sub>3</sub>), 92.5 (C-8), 97.9 (C-6), 105.3 (C-10), 112.1 (C-5'), 115.7 (C-2'), 120.8 (C-1'), 122.4 (C-6'), 138.0 (C-3), 147.6 (C-3'), 150.0 (C-4'), 155.9 (C-2), 156.4 (C-9), 161.0 (C-5), 165.2 (C-7), 178.1 (C-4) [3–5].

Apigenin (2), yellow amorphous powder, mp 347–348°C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, δ, ppm, J/Hz): 6.20 (1H, s, H-6), 6.49 (1H, d, H-8), 6.78 (1H, s, H-3), 6.92 (2H, d, J = 9.0, H-3', 5'), 7.92 (2H, d, J = 8.4, H-2', 6'), 10.35 (1H, s, 4'-OH), 10.82 (1H, s, 7-OH), 12.97 (1H, s, 5-OH). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 94.0 (C-8), 98.9 (C-6), 102.9 (C-3), 103.8 (C-10), 116.0 (C-3', 5'), 121.3 (C-1'), 128.5 (C-22, 62), 157.4 (C-5), 161.2 (C-4'), 161.5 (C-9), 163.8 (C-7), 164.2 (C-2), 181.8 (C-4) [6, 7].

Luteolin (3), yellow amorphous powder, mp 268–270°C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, δ, ppm, J/Hz): 6.17 (1H, d, J = 2.0, H-6), 6.43 (1H, d, J = 2.0, H-8), 6.66 (1H, s, H-3), 6.86 (1H, d, J = 8.4, H-5'), 7.39 (1H, br.s, H-2'), 7.42 (1H, d, J = 2.1, H-6'), 12.97 (1H, s, 5-OH). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 94.0 (C-8), 98.9 (C-6), 103.0 (C-3), 103.8 (C-10), 116.1 (C-5'), 113.5 (C-22), 119.1 (C-6'), 121.6 (C-1), 157.4 (C-5), 161.6 (C-9), 164.0 (C-7), 164.2 (C-2), 145.8 (C-32), 149.8 (C-42), 181.8 (C-4) [8].

Quercetin (4), yellow needle crystals, mp 312–313°C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, δ, ppm, J/Hz): 6.87 (1H, d, J = 8.7, H-5'), 6.41 (1H, d, H-8), 6.19 (1H, d, H-6), 7.68 (1H, d, J = 1.8, H-2'), 7.53 (1H, d, J = 8.4, H-6'), 9.34 (2H, s, 3'-OH, 4'-OH), 12.50 (1H, s, 5-OH). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 93.4 (C-8), 98.3 (C-6), 103.1 (C-10), 115.7 (C-2'), 122.0 (C-3'), 120.16 (C-6'), 135.8 (C-3), 145.1 (C-4'), 146.9 (C-2), 147.8 (C-11), 160.8 (C-7), 156.2 (C-5), 164.0 (C-9), 179.5 (C-4) [9].

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