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CHEMICAL CONSTITUENTS FROM *Saussurea deltoidea*

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Saussurea deltoidea (DC.) C. B. Clarke, a two-year herbage widely distributed in China, is commonly used in folk medicine in the treatment of tumours, rheumatism, diarrhea, dysentery, and inflammation [1]. In order to find the bioactive secondary metabolites from *S. deltoidea*, we investigated its aerial parts, which led to the isolation of 15 known compounds. All these compounds were isolated from *S. deltoidea* for the first time.

The aerial parts of *S. deltoidea* were collected in Dafang (Guizhou province, China) in March 2006, and were authenticated by Prof. Qing-De Long, Guiyang Medical University, China. A voucher specimen was deposited in the School of Pharmacy, Guiyang Medical University.

The aerial parts of *S. deltoidea* (4.2 kg) were extracted with 95% EtOH (3 × 10 L) for 2 h each at reflux. After solvent removal under vacuum, the viscous extract was partitioned with petroleum ether, EtOAc, and *n*-BuOH. The petroleum ether fraction and EtOAc fraction were purified by column chromatography with silica gel, RP-18, and Sephadex LH-20 to yield compounds **1**–**15**.

All compounds were identified by spectroscopic methods, including NMR and mass spectrometry. The spectroscopic data of all compounds were in good agreement with the literature data. Cytotoxic activities *in vitro* were tested for these compounds.

Cynaropicrin (1), yellow oil, $C_{19}H_{22}O_6$. EIMS *m/z*: 346 $[M]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 2.96 (1H, dd, J = 8.8, H-1α), 1.74 (1H, m, H-2α), 2.18 (1H, m, H-2β), 4.53 (1H, t, J = 7.2; 7.9, H-3α), 2.84 (1H, t, J = 10.0; 9.2, H-5), 4.29 (1H, t, J = 10.0; 9.6, H-6β), 3.21 (1H, m, H-7), 5.14 (1H, s, H-8), 2.40 (1H, dd, J = 3.6; 3.2, H-9), 2.69 (1H, dd, J = 5.2, H-9), 5.65 (1H, d, J = 2.8, H-13), 6.21 (1H, d, J = 3.2, H-13), 4.93 (1H, s, H-14), 5.15 (1H, s, H-14), 5.37 (1H, s, H-15), 5.47 (1H, s, H-15), 4.36 (2H, s, H-32), 5.99 (1H, s, H-4′), 6.34 (1H, s, H-4′) [2]. ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 44.9 (C-1), 38.6 (C-2), 73.2 (C-3), 151.9 (C-4), 50.9 (C-5), 78.5 (C-6), 47.1 (C-7), 74.0 (C-8), 36.5 (C-9), 141.6 (C-10), 137.1 (C-11), 169.3 (C-12), 122.7 (C-13), 118.0 (C-14), 113.1 (C-15), 165.2 (C-1′), 139.2 (C-2″), 126.3 (C-3″), 61.4 (C-4″).

Deacylcynaropicrin (2), yellow oil, $C_{15}H_{18}O_4$. EIMS *m/z*: 262 $[M]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 2.94 (1H, m, H-1), 1.73 (2H, m, H-2), 2.18 (2H, s, H-2), 4.54 (1H, t, J = 7.6, H-3), 2.70 (1H, d, J = 5.2, H-5), 4.14 (1H, dd, J = 9.2, H-6), 2.81 (1H, m, H-7), 3.95 (1H, m, H-8), 2.30 (1H, d, J = 4.0, H-9), 2.66 (1H, d, J = 4.8, H-9), 6.23 (1H, d, J = 3.6, H-13), 6.16 (1H, d, J = 2.4, H-13), 5.11 (1H, s, H-14), 4.98 (1H, s, H-14), 5.44 (1H, s, H-15), 5.34 (1H, s, H-15) [3]. ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 45.0 (C-1), 39.0 (C-2), 71.8 (C-3), 152.3 (C-4), 51.1 (C-5), 78.9 (C-6), 50.8 (C-7), 73.5 (C-8), 41.2 (C-9), 142.6 (C-10), 138.1 (C-11), 170.1 (C-12), 123.2 (C-13), 117.0 (C-14),113.0 (C-15).

11,13β-Dihydrodesacylcynaropicrin (3), yellow oil, $C_{15}H_{20}O_4$. EIMS *m/z*: 264 $[M]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 2.90 (1H, m, H-1), 1.73 (1H, m, H-2), 4.53 (1H, t, J = 7.2; 7.6, H-3), 2.80 (1H, t, J = 9.6, H-5), 4.05 (1H, t, J = 10.0, H-6), 2.01 (1H, dd, J = 9.6, H-7), 3.75 (1H, m, H-8), 2.24 (1H, m, H-9), 2.70 (1H, d, J = 4.8, H-9), 2.58 (1H, m, H-11), 1.39 (3H, d, J = 3.6, H-13), 4.99 (1H, s, H-14), 5.07 (1H, s, H-14), 5.35 (1H, s, H-15), 5.30 (1H, s, H-15) [2]. ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 44.9 (C-1), 38.6 (C-2), 73.2 (C-3), 152.8 (C-4), 50.3 (C-5), 79.3 (C-6), 55.9 (C-7), 74.7 (C-8), 41.8 (C-9), 143.2 (C-10), 43.8 (C-11), 179.2 (C-12), 15.8 (C-13), 116.0 (C-14), 111.6 (C-15).

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Lupenone (4), white powder. EIMS *m/z*: 424 $[M]^+$, 409, 313, 245, 218, 205, 189, 175, 161, 149, 135, 121, 109, 95, 81, 69, 55. ^{1}H NMR and ^{13}C NMR [4].

Lupeol (5), colorless needles. EIMS *m/z*: 426 $[M]^+$, 411, 315, 257, 218, 207, 189, 175, 162, 149, 135, 122, 109, 95, 81, 68, 55. ^{1}H NMR and ^{13}C NMR [5].

Taraxasterone (6), colorless needles. EIMS *m/z*: 424 $[M]^+$, 409, 355, 313, 298, 245, 218, 205, 189, 175, 149, 135, 109, 95. ^{1}H NMR [6].

Taraxasterol (7), colorless needles. EIMS *m/z*: 426 $[M]^+$, 408, 357, 249, 218, 207, 204, 189, 121. ^{1}H NMR and ^{13}C NMR [7].

Taraxasterol acetate (8), colorless needles. EIMS *m/z*: 468 $[M]^+$, 453, 408, 393, 357, 339, 272, 249, 218, 203, 189, 175, 161, 135, 121, 95, 81, 67, 43, 29. ^{13}C NMR [8].

***β*-Amyrin (9)**, white powder. EIMS *m/z*: 426 $[M]^+$, 411, 257, 218, 207, 203, 189, 175, 161, 147, 135, 119, 107, 95, 81, 69. ^{1}H NMR [9].

Indolyl-3-carboxylic acid (10), yellow powder. EIMS *m/z*: 161 $[M]^+$. ^{1}H NMR (400 MHz, acetone-d_6, δ, ppm, J/Hz): 8.06 (1H, d, J = 6.8, H-4), 7.93 (1H, s, H-2), 7.43 (1H, d, J = 6.8, H-7), 7.17 (2H, m, H-5, 6). ^{13}C NMR (100 MHz, acetone-d_6, δ, ppm): 132.0 (C-2), 108.6 (C-3), 123.3 (C-4), 122.0 (C-5), 121.9 (C-6), 112.8 (C-7), 127.8 (C-8), 137.9 (C-9), 166.3 (–COOH) [10].

Rutin (11), straw yellow needles. ESIMS *m/z*: 633 $[M+Na]^+$. ^{1}H NMR and ^{13}C NMR [11].

Arachidic acid (12), white powder. EIMS *m/z*: 312 $[M]^+$, 284, 213, 129, 115, 97, 83, 73, 57. ^{1}H NMR and ^{13}C NMR [12].

Stearic acid (13), white needles. EIMS *m/z*: 284 $[M]^+$, 269, 256, 241, 227, 213, 199, 185, 171, 157, 143, 129. ^{1}H NMR [13].

Daucosterin (14), white powder. EIMS *m/z*: 576 $[M]^+$. ^{1}H NMR [14].

***β*-Sitosterol (15)**, colorless needles. EIMS *m/z*: 414 $[M]^+$, 396, 382, 303, 273, 255, 213, 175, 161, 95, 81. ^{13}C NMR [15].

Antitumor properties, studied by the sulforhodamine B (SRB) and MTT methods as described previously [16, 17], showed that cynaropicrin (**1**), deacylcynaropicrin (**2**), and 11,13*β*-dihydrodesacylcynaropicrin (**3**) had antitumor activities against human leucocythemia cell line K562 and human lung adenocarcinoma cell line A549. Their IC_{50} were 3.16 μg/mL, 7.14 μg/mL, and 77.7 μg/mL against human leucocythemia cell line K562, as well as 32.4 μg/mL, 33.0 μg/mL, and 53.0 μg/mL against human lung adenocarcinoma cell line A549, respectively. This evidence appears to indicate that cynaropicrin (**1**), deacylcynaropicrin (**2**), and 11,13*β*-dihydrodesacylcynaropicrin (**3**) may be responsible for the antitumor effect of *S. deltoidea*.

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