

## CHEMICAL CONSTITUENTS OF BASIDIOMYCETES

### *Cortinarius longipes*

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Comprising about 4200 epithets, *Cortinarius* is the most widely distributed genus in the world. Many species of this genus are known to produce biologically active natural products, and studies on the chemical constituents have led to the isolation of alkaloid [1, 2], disulfide metabolites [3], chromogenic triterpenoids [4], and cerebrosides [5–7]. As one part of our work on bioactive metabolites of higher fungi, the chemical constituents of *Cortinarius longipes* were studied for the first time, and 14 compounds were isolated and characterized.

Fruiting bodies of *Cortinarius longipes* were collected in Ailaoshan, Yunnan, P. R. China, in 2003. A voucher specimen was deposited at the herbarium of Kunming Institute of Botany, Chinese Academy of Sciences.

Fresh fruiting bodies of *Cortinarius longipes* (12 kg) were extracted with ethanol and chloroform at room temperature. The combined extract was then suspended with water and extracted four times with ethyl acetate to afford a deep brown gum (150 g), which was purified by column chromatography with silica gel to yield compounds **1–14**.

The compounds were identified using UV, IR, MS, and NMR spectral data and determined as (22*E*,24*R*)-ergosta-7,22-dien-3*β*-ol (**1**) [8], 5*α*,6*α*-epoxy-(22*E*,24*R*)-ergosta-8(14),22-diene-3*β*,7*β*-diol (**2**) [9], (22*E*,24*R*)-ergosta-7,22-dien-3*β*,5*α*,6*β*-triol (**3**) [10], 5*α*,8*α*-epidioxy-(22*E*,24*R*)-ergosta-6,22-dien-3*β*-ol (**4**) [9], russulamide (**5**) [11], armillaramide (**6**) [12], betulinic acid (**7**) [13], ursolic acid (**8**) [14], uracil (**9**) [15], thymidine (**10**) [16], uridine (**11**) [17], inosine (**12**) [18], ethyl-*β*-glucopyranoside (**13**) [19], and ethyl-*β*-*N*-acetyl-glucosaminide (**14**) [20].

**(22*E*,24*R*)-Ergosta-7,22-dien-3*β*-ol (1)**. Colorless needles, mp 159.5–161.0°C. EI-MS *m/z*: 398 [M]<sup>+</sup>, 380 [M – H<sub>2</sub>O]<sup>+</sup>, 271 [M – C<sub>9</sub>H<sub>17</sub> – 2H]<sup>+</sup>, 255 [M – C<sub>9</sub>H<sub>17</sub> – H<sub>2</sub>O]<sup>+</sup>.

**5*α*,6*α*-Epoxy-(22*E*,24*R*)-ergosta-8(14),22-diene-3*β*,7*β*-diol (2)**. White powder. EI-MS *m/z*: 428 [M]<sup>+</sup>, 410 [M – H<sub>2</sub>O]<sup>+</sup>, 395 [M – H<sub>2</sub>O – Me]<sup>+</sup>, 377 [M – 2H<sub>2</sub>O – Me]<sup>+</sup>, 285 [M – C<sub>9</sub>H<sub>17</sub> – H<sub>2</sub>O]<sup>+</sup>, 267 [M – C<sub>9</sub>H<sub>17</sub> – 2H<sub>2</sub>O]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm, J/Hz): 5.20 (2H, m, H-22, 23), 4.40 (1H, d, J = 5.6, H-7), 3.89 (1H, m, H-3), 3.11 (1H, d, J = 3.6, H-6), 1.00 (3H, s, H-19), 1.00 (3H, d, J = 6.7, H-21), 0.90 (3H, d, J = 6.8, H-28), 0.90 (3H, s, H-18), 0.84 (3H, d, J = 6.7, H-27), 0.81 (3H, d, J = 6.7, H-26). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 32.2 (C-1), 31.1 (C-2), 68.7 (C-3), 39.6 (C-4), 67.8 (C-5), 61.4 (C-6), 65.1 (C-7), 125.2 (C-8), 38.8 (C-9), 35.8 (C-10), 18.1 (C-11), 36.6 (C-12), 43.0 (C-13), 152.6 (C-14), 25.0 (C-15), 27.2 (C-16), 56.9 (C-17), 18.1 (C-18), 16.5 (C-19), 39.2 (C-20), 21.2 (C-21), 135.3 (C-22), 132.3 (C-23), 42.9 (C-24), 33.1 (C-25), 19.7 (C-26), 20.0 (C-27), 17.6 (C-28).

**(22*E*, 24*R*)-Ergosta-7,22-diene-3*β*,5*α*,6*β*-triol (3)**. Colorless needles, mp 224.0–227.0°C. EI-MS *m/z*: 430 [M]<sup>+</sup>, 412 [M – H<sub>2</sub>O]<sup>+</sup>, 394 [M – 2H<sub>2</sub>O]<sup>+</sup>, 379 [M – 2H<sub>2</sub>O – Me]<sup>+</sup>, 269 [M – 2H<sub>2</sub>O – C<sub>9</sub>H<sub>17</sub>]<sup>+</sup>, 251 [M – 3H<sub>2</sub>O – C<sub>9</sub>H<sub>17</sub>]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N, δ, ppm, J/Hz): 4.84 (1H, m, H-3), 4.32 (1H, br.s, H-6), 5.74 (1H, dd, J = 5.0, 2.4, H-7), 0.65 (3H, s, H-18), 1.54 (3H, s, H-19), 1.05 (3H, d, J = 6.7, H-21), 5.20 (1H, dd, J = 15.4, 7.8, H-22), 5.25 (1H, dd, J = 15.4, 7.2, H-23), 0.84 (3H, d, J = 6.7, H-26), 0.86 (3H, d, J = 6.7, H-27), 0.94 (3H, d, J = 6.8, H-28). <sup>13</sup>C NMR (100 MHz, C<sub>5</sub>D<sub>5</sub>N, δ, ppm): 32.7 (C-1), 33.9 (C-2), 68.5 (C-3), 42.0 (C-4), 76.1 (C-5), 74.3 (C-6), 120.5 (C-7), 141.6 (C-8), 43.8 (C-9), 38.1 (C-10), 22.4 (C-11), 39.9 (C-12), 43.8 (C-13), 55.3 (C-14), 23.5 (C-15), 28.5 (C-16), 56.1 (C-17), 12.5 (C-18), 18.8 (C-19), 40.9 (C-20), 20.2 (C-21), 136.2 (C-22), 132.2 (C-23), 43.1 (C-24), 33.4 (C-25), 21.4 (C-26), 19.9 (C-27), 17.9 (C-28).

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**5 $\alpha$ ,8 $\alpha$ -Epidioxy-(22*E*,24*R*)-ergosta-6,22-dien-3 $\beta$ -ol (4).** Colorless needles, mp 177.0–178.5°C. EI-MS *m/z*: 428 [M]<sup>+</sup>, 410 [M – H<sub>2</sub>O]<sup>+</sup>, 396 [M – O<sub>2</sub>]<sup>+</sup>, 363, 271, 251, 152, 107. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm, J/Hz): 3.94 (1H, m, H-3), 6.23 (1H, d, J = 8.5, H-6), 6.49 (1H, d, J = 8.5, H-7), 0.86 (3H, s, H-18), 1.20 (3H, s, H-19), 0.98 (3H, d, J = 6.6, H-21), 5.12 (1H, dd, J = 15.1, 7.5, H-22), 5.20 (1H, dd, J = 15.1, 7.5, H-23), 0.82 (3H, d, J = 3.6, H-26), 0.79 (3H, d, J = 3.4, H-27), 0.88 (3H, d, J = 6.8, H-28), 2.08–1.49 (20H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 34.7 (C-1), 30.1 (C-2), 66.5 (C-3), 37.0 (C-4), 82.1 (C-5), 135.4 (C-6), 130.7 (C-7), 79.4 (C-8), 51.1 (C-9), 37.0 (C-10), 23.4 (C-11), 39.4 (C-12), 44.6 (C-13), 51.7 (C-14), 20.6 (C-15), 28.6 (C-16), 56.2 (C-17), 12.9 (C-18), 18.1 (C-19), 39.7 (C-20), 20.9 (C-21), 135.2 (C-22), 132.3 (C-23), 42.7 (C-24), 33.1 (C-25), 20.0 (C-26), 19.6 (C-27), 17.5 (C-28).

**Russulamide (5).** White powder. EI-MS *m/z*: 683 [M]<sup>+</sup>, 665, 456, 439, 409, 384, 357, 339.

**Armillaramide (6).** White powder. Negative FAB-MS *m/z* 554 [M – H]<sup>–</sup>.

**Betulinic Acid (7).** White powder. EI-MS *m/z*: 456 [M]<sup>+</sup>, 441 [M – Me]<sup>+</sup>, 438 [M – H<sub>2</sub>O]<sup>+</sup>, 426 [M – 2Me]<sup>+</sup>, 415 [M – C<sub>3</sub>H<sub>5</sub>]<sup>+</sup>.

**Ursolic Acid (8).** White powder. EI-MS *m/z*: 456 [M]<sup>+</sup>, 438, 248, 203, 189, 133.

**Uracil (9).** White powder. EI-MS *m/z* 112 [M]<sup>+</sup>.

**Thymidine (10).** White powder. EI-MS *m/z*: 242 [M]<sup>+</sup>, 127, 117, 99, 73. <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N,  $\delta$ , ppm, J/Hz): 8.08 (1H, s, H-6), 1.88 (3H, s, H-7), 6.95 (1H, t, J = 6.7, H-1'), 2.63 (2H, m, H-2'), 5.00 (1H, m, H-3'), 4.43 (1H, m, H-4'), 4.16 (2H, m, H-5'). <sup>13</sup>C NMR (100 MHz, C<sub>5</sub>D<sub>5</sub>N,  $\delta$ , ppm): 151.9 (C-2), 164.9 (C-4), 110.5 (C-5), 136.6 (C-6), 12.7 (C-7), 85.5 (C-1'), 41.4 (C-2'), 71.5 (C-3'), 88.9 (C-4'), 62.4 (C-5').

**Uridine (11).** Colorless needles, mp 165.5–166.5°C. Negative FAB-MS *m/z* 111 [M – H – C<sub>5</sub>H<sub>9</sub>O<sub>4</sub>]<sup>–</sup>.

**Inosine (12).** Colorless needles, mp 212.0–214.0°C. Negative FAB-MS *m/z* 267 [M – H]<sup>–</sup>.

**Ethyl- $\beta$ -glucopyranoside (13).** Colorless oil. Negative FAB-MS *m/z* 207 [M – H]<sup>–</sup>.

**Ethyl- $\beta$ -*N*-acetylglucosaminide (14).** White powder. Negative FAB-MS *m/z* 248 [M – H]<sup>–</sup>.

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