TRITERPENE FROM *Armillaria mellea*

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In China, *Armillaria mellea* Vahl. ex Fr. is eaten as food by people and used for the treatment of dizziness, headache, neurasthenia, insomnia, numbness in limbs, and infantile convulsion [1]. Previous studies on *A. mellea* emphasized the artificially cultured mycelia, but the natural rhizomorphs have not been studied previously. We attempted to find the dominant components of the extract.

The rhizomorphs of the fungus used in this study were collected in Shanxi Province, China in September 2003. A voucher specimen (DMF-00541) has been deposited at the Department of Medicinal Fungus, Institute of Medicinal Plant Development, Chinese Academy of Medical Sciences.

Dried and minced rhizomorphs of *A. mellea* (5 kg) were extracted three times with MeOH, 3 h each time. The solvent was removed under reduced pressure to give a crude extract (100 g). The aqueous suspension of the extract was partitioned successively with light petroleum, EtOAc, and *n*-BuOH, resulting in light petroleum (17 g), ethyl acetate (11 g), and *n*-BuOH (8 g) extracts. The light petroleum-soluble fraction (17 g) was concentrated and subjected to 200–300 mesh silica gel column chromatography eluting with a gradient of light petroleum–EtOAc (from 0:1 to 1:1) to yield twelve fractions. The subfractions were then purified by successive column chromatography on 300–400 mesh silica gel using light petroleum–EtOAc and light petroleum–acetone as elution systems, which was monitored by TLC and which led to the isolation of compounds **1–5**. The structures were elucidated by ^{1}H NMR, ^{13}C NMR, HSQC, HMBC, and MS analysis. All the data were in good agreement with the literature data. All the compounds were isolated from the rhizomorphs of *A. mellea* for the first time.

3β-Hydroxyglutin-5-ene (1) [2] 5 mg, colorless needles, $C_{30}H_{50}O$, mp 210–212°C. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.83, 0.93, 0.97, 0.99, 1.02, 1.07, 1.12, 1.14 (each 3H, s, 8 × CH_3), 5.97 (1H, s, OH); 3.45 (1H, t, J = 3, H-3), 5.61 (1H, d, J = 6, H-6).

^{13}C NMR spectrum data (150 MHz, $CDCl_3$, δ): 18.1.0 (C-1), 27.9 (C-2), 76.4 (C-3), 40.9 (C-4), 141.7 (C-5), 122.1 (C-6), 23.7 (C-7), 47.5 (C-8), 34.9 (C-9), 49.8 (C-10), 33.2 (C-11), 30.4 (C-12), 37.9 (C-13), 39.4 (C-14), 34.7 (C-15), 35.1 (C-16), 30.8 (C-17), 43.2 (C-18), 35.1 (C-19), 28.3 (C-20), 32.2 (C-21), 39.0 (C-22), 29.0 (C-23), 25.5 (C-24), 16.2 (C-25), 18.4 (C-26), 19.6 (C-27), 32.4 (C-28), 32.1 (C-29), 34.6 (C-30). Mass spectrum (EI, 70 eV), *m*/*z*: 426.4 $[M]^+$.

Friedelane-2α,3β-diols (2) [3] 5 mg, needlelike crystals, $C_{30}H_{52}O_2$, mp 232–234°C. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.54 (m, H-2), 3.98 (m, H-3).

^{13}C NMR spectrum data (150 MHz, $CDCl_3$, δ): 23.9 (C-1), 71.4 (C-2), 76.5 (C-3), 43.7 (C-4), 37.792 (C-5), 41.4 (C-6), 17.5 (C-7), 52.3 (C-8), 36.5 (C-9), 53.2 (C-10), 35.5 (C-11), 30.6 (C-12), 39.7 (C-13), 38. 4 (C-14), 32.3 (C-15), 36.1 (C-16), 30.0 (C-17), 42.8 (C-18), 35.3 (C-19), 28.2 (C-20), 32.8 (C-21), 39.3 (C-22), 10.9 (C-23), 15.9 (C-24), 18.2 (C-25), 18.7 (C-26), 20.1 (C-27), 32.1 (C-28), 31. 8 (C-29), 35.0 (C-30). Mass spectrum (EI, 70 eV), *m*/*z*: 444.4 $[M]^+$, 429, 291, 273, 249, 222, 191, 181, 163, 135, 123, 109, 81, 69 (100%), 55, 41.

Friedelin (3) [4] 60 mg, colorless needles, $C_{30}H_{50}O$, mp 256–258°C. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.70, 0.81, 0.93, 0.98, 0.99, 1.03, 1.16 (each 3H, s, 7 × CH_3), 0.86 (3H, d, J = 6.8, 23-CH_3).

^{13}C NMR spectrum data (125 MHz, $CDCl_3$, δ): 22.3 (C-1), 41.5 (C-2), 212.89 (C-3), 58.2 (C-4), 42.1 (C-5), 41.3 (C-6), 18.2 (C-7), 53.1 (C-8), 37.5 (C-9), 59.5 (C-10), 35.6 (C-11), 30.5 (C-12), 39.7 (C-13), 38.3 (C-14), 32.2 (C-15), 36.0 (C-16), 30.0 (C-17), 42.8 (C-18), 35.3 (C-19), 28.1 (C-20), 32.4 (C-21), 39.2 (C-22), 6.7 (C-23), 14.6 (C-24), 17.9 (C-25), 20.2 (C-26), 18.6 (C-27), 32.1 (C-28), 35.0 (C-29), 31.7 (C-30). Mass spectrum (EI, 70 eV), *m*/*z*: 426 $[M]^+$.

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3α-Hydroxyfriedel-2-one (4) [5, 6] 15 mg, colorless needles, $C_{30}H_{50}O_2$, mp 252–254°C. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.89, 0.93, 0.98, 0.99, 1.01, 1.03, 1.04, 1.15 (each 3H, s, 7 × CH_3), 1.06 (3H, d, J = 6.6), 3.81 (1H, d, J = 11.4, H-3), 3.53 (1H, d, J = 3, OH), 2.52 (1H, dd, J = 13.8, 3, H-1β), 2.40 (1H, dd, J = 13.8, 13.2, H-1α), 1.85 (1H, dt, J = 13.2, 3, H-4).

^{13}C NMR spectrum data (150 MHz, $CDCl_3$, δ): 35.0 (C-1), 211.9 (C-2), 77.0 (C-3), 54.5 (C-4), 39.6 (C-5), 40.6 (C-6), 17.8 (C-7), 53.1 (C-8), 37.6 (C-9), 60.4 (C-10), 35.9 (C-11), 30.3 (C-12), 39.2 (C-13), 38.1 (C-14), 32.7 (C-15), 36.1 (C-16), 29.9 (C-17), 42.7 (C-18), 35.3 (C-19), 28.1 (C-20), 32.3 (C-21), 38.9 (C-22), 10.8 (C-23), 14.1 (C-24), 17.5 (C-25), 20.1 (C-26), 18.5 (C-27), 32.0 (C-28), 35.0 (C-29), 31.7 (C-30). Mass spectrum (EI, 70 eV), *m*/*z*: 442 $[M]^+$.

3-Hydroxyfriedel-3-en-2-one (5) [4, 6] 2 mg, colorless needles, $C_{30}H_{48}O_2$, mp 268–270°C. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.93, 0.94, 0.98, 0.99, 1.04, 1.09, 1.18 (each 3H, s, 7 × CH_3), 0.91 (3H, d, J = 7.8), 2.52 (1H, dd, J = 17.4, 3.6, H-1β), 2.42 (1H, dd, J = 17.4, 14.4, H-1α), 5.97 (1H, s, OH).

^{13}C NMR spectrum data (150 MHz, $CDCl_3$, δ): 34.7 (C-1), 195.0 (C-2), 142.5 (C-3), 140.7 (C-4), 39.7 (C-5), 38.2 (C-6), 17.6 (C-7), 52.6 (C-8), 35.9 (C-9), 55.7 (C-10), 35.2 (C-11), 30.2 (C-12), 39.2 (C-13), 39.5 (C-14), 28.9 (C-15), 38.4 (C-16), 30.0 (C-17), 42.7 (C-18), 28.1 (C-19), 39.2 (C-20), 29.6 (C-21), 35.9 (C-22), 10.3 (C-23), 14.0 (C-24), 17.9 (C-25), 20.0 (C-26), 18.8 (C-27), 32.1 (C-28), 34.9 (C-29), 31.7 (C-30). Mass spectrum (EI, 70 eV), *m*/*z*: 440.2 $[M]^+$.

REFERENCES

1. J. S. Yang, Y. W. Chen, X. Z. Feng, D. Q. Yu, and X. T. Liang, *Planta Med.*, **50**, 288 (1984).
2. A. G. Gonzalez, E. A. Ferro, and A. G. Ravelo, *Phytochemistry*, **26**, 2785 (1987).
3. A. Patra and S. K. Chaudhuri, *Magn. Reson. Chem*., **25**, 95 (1987).
4. S. L. Mao, S. M. Sang, A. N. Lao, and Z. L. Chen, *Chin. Trad. Herb. Drugs,* **31**, 729 (2000).
5. L. B. Qu, X. L. Chen, J. S. Lu, J. W. Yuan, Y. F. Zhao, *Chem. Nat. Comp.,* **41**, 565 (2005).
6. S. K. Talapatra, D. K. Pradhan, and B. Talapatra, *Indian J. Chem.*, **16B**, 361 (1978).