COMPONENTS OF THE SCLEROTIA OF *Polyporus umbellatus*

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Polyporus umbellatus, a fungus that belongs to Polyporaceae, Basidiomycetes, is widely distributed in many provinces of China. Its dried sclerotium has been used as a diuretic in Chinese medicine for centuries [1]. We report here nine compounds (**1**–**9**) from the petroleum ether and dichloromethane extracts of the sclerotia of *P. umbellatus*.

The sclerotia of *P. umbellatus* (39.2 kg) were collected in Luonan county, northwest China's Shaanxi province in August 2004. A voucher specimen (No. ZL20040819) is deposited in the Herbarium of the Institute of Medicinal Plant Development, Chinese Academy of Medical Sciences & Peking Union Medical College.

The air dried sclerotia were extracted with hot 95% ethanol (400 L×3). After removal of the solvent under reduced pressure at 50°C, the residue (580 g) was suspended in water and extracted with petroleum ether, dichloromethane, ethyl acetate, and *n*-butanol successively.

The petroleum ether extract was column chromatographed on silica gel (100–200 mesh) using a petroleum ether-ethyl acetate mixture with increasing polarity to yield 36 fractions from which six compounds (compounds **1**–**6**) were isolated and purified on a Sephadex LH-20 column.

The dichloromethane extract was subjected to repeated column chromatography with a mixture of chloroform and methanol by gradient elution, leading to compounds **7**–**9**.

The structures of these compounds were confirmed by ^{1}H NMR, ^{13}C NMR, and MS, and all these data were in good agreement with the respective literature data.

Compound **1**, $C_{28}H_{44}O$, colorless needles, mp 165–167°C; the melting point was not depressed when mixed with the standard one. ^{1}H NMR data (600 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.63 (3H, s, H-18), 0.82 (3H, d, J = 6.5, H-26), 0.84 (3H, d, J = 6.4, H-27), 0.92 (3H, d, J = 6.6, H-28), 0.95 (3H, s, H-19), 1.04 (3H, d, J = 6.6, H-21), 3.64 (1H, m, H-3), 5.19 (1H, dd, J = 15.2, 7.6, H-22), 5.22 (1H, dd, J = 15.2, 7.0, H-23), 5.39 (1H, m, H-6), 5.58 (1H, m, H-7). Characterized as ergosterol [2].

Compound **2**, $C_{30}H_{50}O$, white needles, mp 264–265°C, ^{1}H NMR data (600 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.73 (3H, s, 24-CH_3), 0.87 (3H, s, 25-CH_3), 0.88 (3H, d, J = 6.8, 23-CH_3), 0.95 (3H, s, 30-CH_3), 1.00 (3H, s, 29-CH_3), 1.01 (3H, s, 24-CH_3), 1.05 (3H, s, 27-CH_3), 1.18 (3H, s, 28-CH_3). ^{13}C NMR data (150 MHz, $CDCl_3$, δ, ppm): 6.8 (23-C), 14.7 (24-C), 17.9 (25-C), 18.2 (7-C), 18.7 (27-C), 20.3 (26-C), 22.3 (1-C), 28.2 (20-C), 30.0 (17-C), 30.5 (12-C), 31.8 (29-C), 32.1 (28-C), 32.4 (21-C), 32.8 (15-C), 35.0 (30-C), 35.3 (19-C), 35.6 (11-C), 36.0 (16-C), 37.4 (9-C), 38.3 (14-C), 39.3 (22-C), 39.7 (13-C), 41.3 (6-C), 41.5 (2-C), 42.1 (5-C), 42.8 (18-C), 53.1 (8-C), 58.2 (4-C), 59.5 (10-C), 213.2 (3-C). Characterized as friedelin [3].

Compound **3**, $C_{16}H_{12}O_5$, yellow needles, mp 203–204°C, ^{1}H NMR data (600 MHz, $CDCl_3$, δ, ppm, J/Hz): 2.45 (3H, s, Ar-CH_3), 3.94 (3H, s, OCH_3), 6.69 (1H, d, J = 3.0, H-2), 7.08 (1H, d, J = 0.6, H-7), 7.37 (1H, d, J = 3.0, H-4), 7.63 (1H, d, J = 1.2, H-5), 12.11 (1H, s, ArOH), 12.31 (1H, s, ArOH). Characterized as physcion [4].

Compound **4**, $C_{15}H_{10}O_4$, yellow needles, mp 198–199°C, ^{1}H NMR data (600 MHz, $CDCl_3$, δ, ppm, J/Hz): 2.47 (3H, s, Ar-CH_3), 7.11 (1H, d, J=0.6, H-2), 7.29 (1H, dd, J = 7.2, 1.2, H-7), 7.66 (1H, d, J = 7.8, H-4), 7.68 (1H, t, J = 7.8 and 7.8, H-6), 7.82 (1H, dd, J = 7.8 and 1.2, H-5), 12.01 (1H, s, ArOH), 12.12 (1H, s, ArOH). Characterized as chrysophanol [4].

Compound **5**, $C_{28}H_{44}O$, colorless lamellar crystals, mp 186–187°C, ^{1}H NMR data (600 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.58 (3H, s, 18-CH_3), 0.82 (3H, d, J = 6.6, 27-CH_3), 0.84 (3H, d, J = 6.6, 26-CH_3), 0.92 (3H, d, J = 6.6, 28-CH_3), 1.02 (3H, s, 19-CH_3), 1.03 (3H, s, 21-CH_3), 5.19 (3H, m, H-7, 22, 23). ^{13}C NMR data (150 MHz, $CDCl_3$, δ, ppm): 12.1 (18-C), 12.4 (19-C), 17.6 (28-C), 19.6 (27-C), 19.9 (26-C), 21.1 (21-C), 21.7 (11-C), 22.9 (15-C), 28.1 (16-C), 30.1 (6-C), 33.1 (25-C), 34.4 (10-C),

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38.1 (2-C), 38.8 (1-C), 39.3 (12-C), 40.5 (20-C), 42.8 (24-C), 42.9 (5-C), 43.3 (13-C), 44.2 (4-C), 48.9 (9-C), 55.0 (14-C), 55.9 (17-C), 117.0 (7-C), 132.0 (23-C), 135.6 (22-C), 139.5 (8-C), 211.9 (3-C). Characterized as ergosta-7,22-diene-3-one [5].

Compound **6**, $C_{28}H_{46}O_3$, white powder, ^{1}H NMR data (600 MHz, C_5D_5N, δ, ppm, J/Hz): 0.66 (3H, s, 18-CH_3), 0.81 (3H, d, J = 6.6, 27-CH_3), 0.86 (3H, d, J = 6.6, 26-CH_3), 0.94 (3H, d, J = 6.6, 28-CH_3), 1.06 (3H, d, J = 6.6, 21-CH_3), 4.31 (1H, br s, 6-H), 4.82 (1H, m, H-3), 5.16 (1H, m, H-7), 5.18 (1H, dd, J = 15.6, 7.8, H-22), 5.25 (1H, dd, J = 15.6, 7.8, H-23). ^{13}C NMR data (150 MHz, C_5D_5N, δ, ppm): 12.5 (18-C), 17.8 (28-C), 18.8 (19-C), 19.8 (27-C), 20.1 (26-C), 21.4 (21-C), 22.4 (15-C), 23.5 (11-C), 28.5 (16-C), 32.7 (2-C), 33.3 (25-C), 33.8 (1-C), 38.1 (10-C), 39.9 (12-C), 40.9 (20-C), 42.0 (4-C), 43.1 (24-C), 43.8 (9-C), 43.8 (13-C), 55.2 (14-C), 56.1 (17-C), 67.6 (3-C), 74.3 (6-C), 76.1 (5-C), 120.5 (7-C), 132.0 (23-C), 136.2 (22-C), 141.5 (8-C). Mass spectrum (EI, 70 eV), *m/z*: 430 $[M]^+$. Characterized as ergosta-7,22-diene-3,5,6-triol [6].

Compound **7**, $C_{28}H_{46}O_6$, colorless needles, mp 261–262°C, ^{1}H NMR data (600 MHz, C_5D_5N, δ, ppm, J/Hz): 0.74 (3H, d, J = 6.6, 28-CH_3), 0.85 (3H, d, J = 6.6, 27-CH_3), 0.87 (3H, d, J = 7.2, 26-CH_3), 1.08 (3H, s, 19-CH_3), 1.23 (3H, s, 18-CH_3), 1.43 (1H, septet, J = 6.6, H-25), 1.57 (3H, s, 21-CH_3), 2.93 (1H, t, J = 9.0, H-17), 3.60 (1H, br t, J = 8.4, H-9), 3.92 (1H, dd, J = 9.6 and 4.8, H-22), 4.17 (1H, br d, H-2), 4.23 (1H, br s, H-3), 6.27 (1H, d, J = 2.4, H-7). ^{13}C NMR data (150 MHz, C_5D_5N, δ, ppm): 15.7 (27-C), 16.0 (26-C), 17.9 (18-C), 21.1 (11-C), 21.4 (28-C), 21.4 (21-C), 21.5 (12-C), 24.5 (19-C), 29.5 (25-C), 31.7 (16-C), 32.1 (15-C), 32.5 (4-C), 34.5 (9-C), 36.1 (24-C), 37.3 (23-C), 38.0 (1-C), 38.7 (10-C), 48.1 (13-C), 49.9 (17-C), 51.4 (5-C), 68.1 (3-C), 68.1 (2-C), 74.5 (22-C), 76.8 (20-C), 84.1 (14-C), 121.1 (7-C), 166.2 (8-C), 203.5 (6-C). Mass spectrum (EI, 70 eV), *m/z*: 442 $[M\text{-}2H_2O]^+$. Characterized as polyporusterone A [7].

Compound **8**, $C_{28}H_{44}O_6$, colorless needles, mp 250–251°C, ^{1}H NMR data (600 MHz, C_5D_5N, δ, ppm, J/Hz): 1.01 (3H, d, J = 6.6, 27-CH_3), 1.03 (3H, d, J = 6.6, 26-CH_3), 1.07 (3H, s, 19-CH_3), 1.22 (3H, s, 18-CH_3), 1.59 (3H, s, 21-CH_3), 2.41 (1H, septet, J = 6.6, H-25), 2.61 (2H, m, H-23), 2.95 (1H, t, J = 9.0, H-17), 4.04 (1H, dd, J = 9.0 and 4.2, H-22), 4.19 (1H, br d, H-2), 4.24 (1H, br s, H-3), 4.85 (1H, br s, H-28b), 4.95 (1H, br s, H-28a), 6.26 (1H, d, J = 2.4, H-7). ^{13}C NMR data (150 MHz, C_5D_5N, δ, ppm): 17.9 (18-C), 21.2 (11-C), 21.5 (21-C), 21.6 (12-C), 21.9 (27-C), 22.1 (26-C), 24.5 (19-C), 31.8 (16-C), 32.1 (15-C), 32.5 (4-C), 33.7 (25-C), 34.5 (9-C), 38.0 (1-C), 38.4 (23-C), 38.8 (10-C), 48.2 (13-C), 50.0 (17-C), 51.5 (5-C), 68.1 (3-C), 68.2 (2-C), 75.4 (22-C), 76.8 (20-C), 84.2 (14-C), 108.7 (28-C), 121.7 (7-C), 154.4 (24-C), 166.2 (8-C), 203.7 (6-C). Mass spectrum (EI, 70 eV), m/z: 440 $[M\text{–}2H_2O]^+$. Characterized as polyporusterone B [7].

Compound **9**, $C_{42}H_{85}NO_5$, white powder, ^{1}H NMR data (600 MHz, C_5D_5N, δ, ppm, J/Hz): 0.87 (6H, m, 18-CH_3 and 24-CH_3), 1.71 (1H, m, H-6a), 1.93 (1H, m, H-6b), 1.94 (1H, m, H-5), 2.04 (1H, m, H-3′a), 2.22 (1H, m, H-3′b), 2.24 (1H, m, H-5), 4.28 (1H, m, H-4), 4.35 (1H, dd, J = 6.0 and 5.4, H-3), 4.42 (1H, dd, J = 10.8 and 5.4, H-1a), 4.51 (1H, dd, J = 10.8 and 5.4, H-1b), 4.62 (1H, dd, J = 7.8 and 3.6, H-2′), 5.11 (1H, ddd, J = 9.0, 4.8 and 4.8, H-2), 8.57 (1H, s, J = 9.0, NH). ^{13}C NMR data (150 Mhz, C_5D_5N, δ, ppm): 14.3 (C-18, C-24′), 22.9 (C-17), 26.6 (C-6), 34.2 (C-5), 35.7 (C-3′), 53.0 (C-2), 62.1 (C-1), 72.4 (C-2′), 73.0 (C-4), 76.8 (C-3), 175.2 (C-1′). Mass spectrum (EI, 70 eV), *m/z:* 665 $[M\text{–}H_2O]^+$. Characterized as N-(2′-hydroxytetracosanoyl) -1,3,4-trihydroxy-2-octadecanone [8].

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