

高等真菌黑虎掌子实体的化学成分*

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The Chemical Constituents from Basidiocarps of *Sarcodon aspratium*

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Abstract: Fifteen known compounds, cerebroside B (1), psicofuranine (2), uridic triphosphate (3), uracil (4), adenine (5), 3 β -acetoxy-(22E, 24R)-24-methyl-5 α -cholest-7, 22-diene-5, 6 β -diol (6), (22E)-27-nor-24-methyl-5 α -cholesta-7, 22-diene-3 β , 5, 6 β -triol (7), 3 β -hydroxy-5 α , 8 α -epidioxy-24 ξ -methylcholesta-6-en (8) (22 mg), 3 β -O-glucopyranosyl-5 α , 6 β -dihydroxyergosta-7, 22-diene (9), (24S)-ergosta-4, 6, 8 (14), 22-tetraen-3-one (10), (22E, 24R)-24-methylergosta-7, 22-diene-3 β , 5 α , 6 β -triol (11), (22E, 24S)-24-methyl-5 α -cholest-7, 22-diene-3 β , 5, 6 β -triol (12), 3 β -hydroxy-5 α , 8 α -epidioxyergosta-6, 22-diene (13), 3 β -hydroxyergosta-5, 7, 22-triene (14) and D-allitol (15) were isolated from the fresh fruiting bodies of *Sarcodon aspratium* (Berk.) S. Ito, and their structures were identified by means of spectroscopy. All the compounds are reported firstly in genus *Sarcodon*.

Key words: *Sarcodon aspratium*, Cerebroside, Ergosterols, Nucleosides,

关键词: 黑虎掌; 脑苷脂; 麦角甾醇; 核苷

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黑虎掌 (*Sarcodon aspratium* (Berk.) S. Ito), 又名香茸, 是一种美味食用菌。近年来发现该属 *S. scabrosus* (Fr.) P. Karst. 中含有对神经生长因子 (NGF) 的合成具有诱导作用的生物活性二萜 (Oh 等, 1998)。作为“高等真菌生物活性代谢产物研究”的一部分, 我们对采自云南武定的样品进行了化学分析。

从黑虎掌的新鲜子实体中分得 15 个化合物。它们分别为 cerebroside B (1) (120 mg), 阿洛酮糖腺苷 (2) (12 mg), 三磷酸尿苷 (3) (7 mg), 尿嘧啶 (4) (12 mg), 腺嘌呤 (5) (8 mg), 3 β -acetoxy-(22E, 24R)-24-methyl-5 α -cholest-7, 22-diene-5, 6 β -diol (6) (12 mg), (22E)-27-nor-24-methyl-5 α -cholesta-7, 22-diene-3 β , 5, 6 β -triol (7) (8 mg), 3 β -hydroxy-5 α , 8 α -epidioxy-24 ξ -methylcholesta-6-en (8) (22 mg), 3 β -O-glucopyranosyl-5 α , 6 β -dihydroxyergosta-7, 22-diene (9) (17 mg), (24S)-ergosta-4, 6, 8 (14), 22-tetraen-3-one (10) (25 mg), (22E, 24R)-24-methylergosta-7, 22-diene-3 β , 5 α , 6 β -triol (11) (89 mg), (22E, 24S)-24-methyl-5 α -cholest-7, 22-diene-3 β , 5, 6 β

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-triol (12) (32 mg), 3 β -hydroxy-5 α , 8 α -epidioxyergosta-6, 22-diene (13) (220 mg), 3 β -hydroxyergosta-5, 7, 22-triene (14) (275 mg) 和 D-阿洛醇 (15) (107 mg)。其中化合物 1 具有细胞免疫调节功能。近年来有不少关于这类化合物抗癌、抗真菌、抗病毒和免疫调节的报道 (Natori 等, 1994); 化合物 2 具有抗癌和抗菌作用 (Annie Grouiller 等, 1984); 化合物 3 也具有消炎、抗肿瘤和加速血小板凝聚作用, 并且是一种免疫抑制剂 (Fujimoto 等, 1994)。

与 *S. cabrosus* 不同, 黑虎掌没有苦味, 也许正因此而没有从中发现前述的活性二萜。但值得注意的是, 黑虎掌所含有的脑苷脂, 核苷, 及多羟基甾角甾醇类化合物最初都是从海洋生物中得到的。高等真菌与海洋生物在进化上究竟有何种联系是一个值得进一步探讨的课题。

实验部分

MS 用 VG Autospec-3000 型测定, NMR 用 Bruker AM-400 超导核磁仪测定, IR 用 KBr 片法由 Bio-Rad FTS-135 红外分光光度仪测定; UV 由 Shimadzu 的 UV-210A 紫外分光光度仪测定, 旋光由 JASCO-20 旋光仪测定, 熔点由显微熔点仪测定 (温度计未校正)。

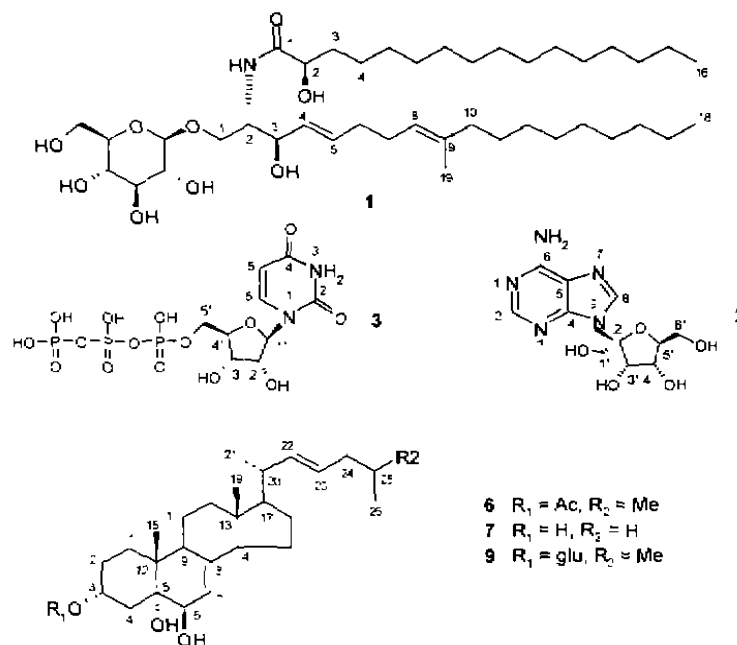
黑虎掌子实体采自云南武定, 由昆明植物所分类室王向华助研鉴定。

将新鲜的黑虎掌子实体 (6.2kg) 分别用 95% 的乙醇, 氯仿-甲醇 1:1 提取 3 次。浓缩合并提取液后, 将浓缩物 (48 g) 分别用氯仿-水, 乙酸乙酯-水分配, 然后用柱层析和制备薄层层析的方法对氯仿部分和乙酸乙酯部分进行分离。少数极性较大的化合物使用了 RP-18 柱层析方法纯化。共得到 15 个化合物。其中, 化合物 4, 5, 8, 11-15 是高等真菌子实体中常见的物质, 通过与标准品进行薄层对照以及与文献中光谱数据进行对比而鉴定。

Cerebroside B (1) $C_{41}H_{77}NO_9$, 白色无定形粉末, mp 144-149 $^{\circ}C$; $[\alpha]_D^{27} + 5.2^{\circ}$ (c 0.0025, MeOH); IR $_{max}^{KBr}$ cm^{-1} : 3380 (OH), 2960, 1650, 720; EI-MS m/z : 297 (15), 111 (27), 57 (100); FAB $^{-}$ -MS m/z 727 [M] $^{+}$ (100), 564 [M-1-162] $^{+}$ (20); HRFAB $^{-}$ -MS m/z 726.5561 [M-1] $^{+}$ (calcd. 727.5594); 1H NMR (CD_3OD , 400 MHz): 8.63 (1H, m, H-1a), 3.99 (1H, dd, J=10.7, 5.4, H-1b), 4.16 (1H, m, H-2), 4.16 (1H, m, H-3), 5.47 (1H, m, H-4), 5.47 (1H, m, H-5), 1.94 (2H, m, H-6), 1.94 (2H, m, H-7), 5.32 (1H, m, H-8), 1.82 (2H, m, H-10), 1.24 (2H, m, H-11), 1.14 (12H, br.s, H-12-H-17), 0.78 (3H, t, J=6.9, H-18), 1.45 (3H, t, J=6.6, H-19), 4.15 (1H, m, H-2'), 1.41 (1H, m, H-3'), 1.25 (22H, br.s, H-4'-H-14'), 1.25 (2H, br.s, H-15'), 0.76 (3H, t, J=6.9, H-16'), 4.98 (1H, d, J=7.6, H-1''), 3.31 (1H, m, H-2''), 3.63 (1H, m, H-3''), 3.63 (1H, m, H-4''), 3.16 (1H, m, H-5''), 3.86 (1H, dd, J=11.8, 5.6, H-6a''), 3.91 (1H, br.d, J=11.8, H-6b''), 7.38 (1H, d, J=8.7, NH); ^{13}C NMR (CD_3OD , 100 MHz), 868.6 (t, C-1), 53.2 (d, C-2), 71.8 (d, C-3), 130.2 (d, C-4), 131.3 (d, C-5), 38.4 (t, C-6), 30.6 (t, C-7), 122.4 (d, C-8), 134.5 (s, C-9), 31.5 (t, C-10), 27.3 (t, C-11), 28.2-27.1 (各 t, C-12-C-15), 30.4 (t, C-16), 21.8 (t, C-17), 13.1 (q, C-18), 15.2 (q, C-19), 174.3 (s, C-1'), 71.1 (d, C-2'), 34.2 (t, C-3'), 28.2-27.4 (各 t, C-4'-C-13'), 27.1 (t, C-14'), 27.1 (t, C-15'), 13.3 (q, C-16'), 104.2 (d, C-1''), 73.6 (d, C-2''), 77.2 (d, C-3''), 70.5 (d, C-4''), 77.4 (d, C-5''), 61.6 (t, C-6'')。 (Higuchi 等, 1994)

阿洛酮糖腺苷 (2) $C_{11}H_{15}N_5O_5$, 无色针晶, mp 186 $^{\circ}C$; $[\alpha]_D^{27} - 39.6^{\circ}$ (c 0.0030, H_2O); IR $_{max}^{KBr}$ cm^{-1} : 3380, 3210, 1640, 1280; UV $_{max}^{MeOH}$ nm (log ϵ) 261, 200; EI-MS m/z 297 [M] $^{+}$ (12), 266 [M-CH $_2$ OH] $^{+}$ (28), 135 (100); FAB $^{-}$ -MS m/z 296 [M-1] $^{+}$ (100); 1H NMR (D_2O , 400 MHz): 8.22 (1H, s, H-2), 8.38 (1H, s, H-8), 4.33 (2H, m, H-1'), 5.05 (1H, m, H-3'), 4.50 (1H, m, H-4'), 4.22 (1H, m, H-5'), 3.75 (2H, m, H-6''), 7.20 (2H, s, NH $_2$); ^{13}C NMR (D_2O , 100 MHz): 153.3 (d, C-2),

149.7 (s, C-4), 121.5 (s, C-5), 157.7 (s, C-6), 140.6 (d, C-8), 63.1 (t, C-1), 90.9 (d, C-2'), 75.5 (d, C-3'), 72.4 (d, C-4'), 87.8 (d, C-5'), 64.9 (t, C-6')。 (Annie 等, 1984)



三磷酸尿苷 (3) $\text{C}_9\text{H}_{15}\text{N}_2\text{O}_{13}\text{P}_3$, 无色晶体, $mp\ 140^\circ\text{C}$ [$\alpha_D^{27} - 68^\circ$ ($c\ 0.0036, \text{H}_2\text{O}$); $\text{IR}_{\text{max}}^{\text{KBr}}\ \text{cm}^{-1}$: 3650, 3560, 3460, 1770, 1710; $\text{UV}_{\text{max}}^{\text{MeOH}}$ ($\log\epsilon$) 265, 254; EI-MS m/z 484 [$\text{M}]^+$ (8), 403 [$\text{M} - (\text{HO})_2\text{OP}]^+$ (40), 243 (100); FAB⁻-MS m/z 483 [$\text{M}-1]^+$ (100); $^1\text{H NMR}$ (D_2O , 400 MHz): 5.28 (1H, d, $J=7.6$, H-5), 7.12 (1H, d, $J=7.6$, H-6), 4.28 (1H, s, H-1'), 3.96 (1H, m, H-2'), 4.02 (1H, dd, $J=3.2, 2.8$, H-3'), 3.85 (1H, dd, $J=9.8, 2.8$, H-4'), 3.38-3.31 (2H, m, H-5'); $^{13}\text{C NMR}$ (D_2O , 100 MHz): 153.2 (s, C-2), 168.6 (s, C-4), 113.2 (d, C-5), 135.4 (d, C-6), 90.4 (d, C-1'), 72.8 (d, C-2'), 76.3 (d, C-3'), 84.2 (d, C-4'), 68.4 (t, C-5')。 (Wong 等, 1983)

3 β -acetoxo-(22E, 24R)-24-methyl-5 α -cholest-7, 22-diene-5, 6 β -diol (6) $\text{C}_{30}\text{H}_{48}\text{O}_4$, 无色针晶, $mp\ 118-122^\circ\text{C}$; $\text{IR}_{\text{max}}^{\text{KBr}}\ \text{cm}^{-1}$: 3440, 1730, 1648; EI-MS m/z 472 [$\text{M}]^+$ (52), 454 [$\text{M} - \text{H}_2\text{O}]^+$ (25), 436 [$\text{M} - 2\text{H}_2\text{O}]^+$ (16), 59 (100); HR-EIMS m/z 472.3435 (calcd. 472.355); $^1\text{H NMR}$ (CDCl_3 , 400 MHz): 85.32 (1H, dd, $J=4.9, 2.2\ \text{Hz}$, H-7), 5.20 (2H, m, H-23, 22), 5.10 (1H, m, H-3), 3.56 (1H, br.s, H-6), 2.08 (1H, dd, $J=11.25, 9.35\ \text{Hz}$, ax-4H), 2.04 (3H, s, Ac), 1.72 (1H, dd, $J=11.25, 2.68\ \text{Hz}$, eq-4H), 1.12 (3H, s, H-19), 1.04 (3H, d, $J=6.4\ \text{Hz}$, H-21), 0.92 (3H, d, $J=6.6\ \text{Hz}$, H-28), 0.61 (3H, s, H-18); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): 32.9 (t, C-1), 30.2 (t, C-2), 72.3 (d, C-3), 38.6 (t, C-4), 75.8 (d, C-5), 73.8 (d, C-6), 116.8 (s, C-7), 141.4 (s, C-8), 43.5 (d, C-9), 38.0 (s, C-10), 21.8 (t, C-11), 39.5 (t, C-12), 43.6 (s, C-13), 54.6 (d, C-14), 22.9 (t, C-15), 29.7 (t, C-16), 56.1 (d, C-17), 12.3 (q, C-18), 18.8 (q, C-19), 40.9 (d, C-20), 21.1 (q, C-21), 135.4 (d, C-22), 132.3 (d, C-23), 42.8 (d, C-24), 30.8 (d, C-25), 20.2 (q, C-26), 19.8 (q, C-27), 17.7 (q, C-28), 170.6/21.2 (s/q, Ac)。 (Hirokazu 等, 1988)

(22E)-27-nor-24-methyl-5(-cholesta-7, 22-diene-3 β , 5, 6 β -triol (7) $C_{27}H_{44}O_3$, 无色针晶, mp 233-235°C; IR $_{max}^{KBr}$ cm^{-1} : 3460, 1660, 1456, 1380; EI-MS, m/z 416 [M] $^+$ (18), 383 [$M-H_2O-CH_3$] $^+$ (25), 380 (55), 365 [$M-2H_2O-CH_3$] $^+$ (100); HR-EIMS m/z 416.3175 (calcd. 416.3288); 1H NMR ($CDCl_3$, 400 MHz): δ 5.35 (1H, bd, $J=4.8$ Hz, H-7), 5.16 (2H, m, H-22, 23), 2.02, 1.90 (H-20, 24的各H信号发生重叠), 1.08 (3H, s, H-19), 1.01 (3H, d, $J=6.6$ Hz, H-21), 0.93 (3H, d, $J=6.6$ Hz, H-28), 0.85 (3H, t, $J=7.2$ Hz, H-26); ^{13}C NMR ($CDCl_3$, 100 MHz): 33.1 (t, C-1), 30.9 (t, C-2), 67.7 (d, C-3), 42.9 (t, C-4), 76.7 (d, C-5), 73.8 (d, C-6), 117.6 (s, C-7), 141.6 (s, C-8), 43.6 (d, C-9), 38.1 (s, C-10), 22.1 (t, C-11), 39.6 (t, C-12), 43.6 (s, C-13), 54.6 (d, C-14), 22.9 (t, C-15), 29.7 (t, C-16), 56.1 (d, C-17), 12.3 (q, C-18), 18.8 (q, C-19), 40.9 (d, C-20), 21.1 (q, C-21), 135.4 (d, C-22), 132.3 (d, C-23), 43.2 (d, C-24), 30.2 (d, C-25), 19.3 (q, C-26), 17.5 (q, C-27)。 (Vincenzo等, 1987)

3 β -O-glucopyranosyl-5 α , 6 β -dihydroxyergosta-7, 22-diene (9) $C_{34}H_{56}O_8$, 白色无定形粉末; $[\alpha]_D^{25}$ -25.9° (c 0.0025, MeOH); IR $_{max}^{KBr}$ cm^{-1} : 3400, 1628, 1378, 1022; EI-MS m/z 574 [$M-H_2O$] $^+$ (18), 556 (25), 412 [$M-H_2O-Glc$] $^+$ (55), 394 (23), 69 (100); FAB $^-$ -MS m/z 591 [$M-1$] $^+$; 1H NMR ($CDCl_3$, 400 MHz): 4.18 (1H, m, H-3), 2.30 (2H, m, H-2), 2.05 (1H, dd, $J=11.25, 9.22$ Hz, ax-4H), 1.62 (1H, dd, $J=11.25, 2.2$ Hz, eq-4H), 1.05 (3H, s, H-19), 1.01 (3H, d, $J=6.8$ Hz, H-21), 0.56 (3H, s, H-18), 4.99 (1H, d, $J=7.8$, H-1*), 4.50 (1H, dd, $J=11.7, 4.9$, Ha-6*), 4.41 (1H, dd, $J=11.7, 2.0$ Hz, Hb-6*), 4.32 (1H, m, H-4*), 4.21 (1H, dd, $J=8.8, 8.8$ Hz, H-3*), 4.08 (1H, dd, $J=8.8, 7.8$ Hz, H-2*), 3.75 (1H, dd, $J=9.3, 4.9$ Hz, H-5*)。 ^{13}C NMR与文献 (Yoshihisa等, 1991) 相符。

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