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三种毒菌的化学成分研究

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摘 要:本文对三种毒菌的化学成分进行了研究。从光盖伞(*Psilocybe spp*)分离鉴定了 4个化合物,经波谱分析鉴定为:(22*E*, 24*R*)麦角甾-7, 22-二烯-3β-十八烷酸酯(**1**)、β-胡萝卜苷(**2**)、(22*E*, 24*R*)-5α, 6α-环氧麦角甾-8, 22-二烯-3β, 7α-二醇(**3**)、色氨酸(**4**);从假褐云斑鹅膏(*Amanita pseudoporphyria*)分离鉴定了 4个化合物:(22*E*, 24*R*)-3β-羟基-5α, 8α-过氧化麦角甾-6, 22-二烯(**5**)、(22*E*, 24*R*)麦角甾-7, 22-二烯-3β, 5α, 6β-三醇(**6**)、1-O-β-D-吡喃葡萄糖基-(2*S*, 3*R*, 4*E*, 8*E*, 2′*R*)-2-*N*-(2-羟基棕榈酰)-9-甲基-4, 8-脱氢鞘氨醇(**7**)、1-O-β-D-吡喃葡萄糖基-(2*S*, 3*R*, 4*E*, 8*E*, 2′*R*)-2-*N*-(2-羟基十八烷酰)-9-甲基-4, 8-脱氢鞘氨醇(**8**);大青褶伞(*Chlorophyllum molybdites*)发酵菌丝体分离鉴定了 4个化合物:**5**、**6**、(22*E*, 24*R*)-5α, 6α-环氧麦角甾-8(14), 22-二烯-3β, 7α-二醇(**9**)、(22*E*, 24*R*)麦角甾-7, 22-二烯-3β-醇(**10**)。除化合物 **9**外其它化合物均为首次从以上相应毒菌中分离得到。

关键词:光盖伞;假褐云斑鹅膏;大青褶伞;化学成分

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Chemical Constituents of Three Poisonous Mushrooms

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Abstract: Four known compounds were isolated from *Psilocybe* spp, which were identified as (22*E*, 24*R*)-octadecylergosta-7, 22-dien-3β-ol (**1**), β-daucosterol (**2**), (22*E*, 24*R*)-5α, 6α-epoxyergosta-8, 22-diene-3β, 7α-diol (**3**), tryptophan (**4**). Four known compounds were isolated from *Amanita pseudoporphyria*, which were identified as (22*E*, 24*R*)-5α, 8α-epidioxyergosta-6, 22-dien-3β-ol (**5**), (22*E*, 24*R*)-ergosta-7, 22-dien-3β, 5α, 6β-triol (**6**), (2*S*, 3*R*, 4*E*, 8*E*)-1-(*O*-β-D-glucopyranosyl)-3-hydroxy-2-[(*R*)-2′-hydroxypalmitoyl]amino-9-methyl-4, 8-octadecadiene (**7**), (2*S*, 3*R*, 4*E*, 8*E*)-1-(O-β-D-glucopyranosyl)-3-hydroxy-2-[(*R*)-2′-hydroxyoctadecanoyl]amino-9-methyl-4, 8-octadecadiene (**8**). Four known compounds were isolated from mycelium of *Chlorophyllum molybdites*, which were identified as 5, 6, (22*E*, 24*R*)-5α, 6α-epoxyergosta-8(14), 22-diene-3β, 7α-diol (**9**), (22*E*, 24*R*)-ergosta-7, 22-dien-3β-ol (**10**). This is the first time that compounds 1-8 and 10 were isolated from these titled mushrooms, respectively.

Key words: *Psilocybe* spp; *Amanita pseudoporphyria; Chlorophyllum molybdites*; chemical constituents

自然界的有毒菌种类繁多,全球估计达 1000种以上,我国的毒蘑菇(包括怀疑有毒的)多达 421种,隶属于 39科 112属[1]。我国对毒蘑菇的化学成分研究甚少,开展毒菌的化学成分研究,对开发新药和保障食用菌安全具有深远的意义。本文对三种未见化学成分报道的毒菌:光盖伞(*Psilocybe spp*),假褐云斑鹅膏(*Amanita pseudoporphyria*)和大青褶伞(*Chlorophyllum molybdites*)发酵菌丝体的化学成分进行了研究。从光盖伞分离鉴定了 4个化合物,经波谱分析鉴定为:(22*E*, 24*R*)麦角甾-7, 22-二烯-3β-十八烷酸酯(**1**)、β-胡萝卜苷(**2**)、(22*E*, 24*R*)-5α, 6α-环氧麦角甾-8, 22-二烯-3β, 7α-二醇(**3**)、色氨酸(**4**)。从假褐云斑鹅膏分离鉴定了 4个化合物:(22*E*, 24*R*)-3β-羟基-5α, 8α-过氧化麦角甾-6, 22-二烯(**5**)、(22*E*, 24*R*)麦角甾-7, 22-二烯-3β, 5α, 6β-三醇(**6**)、1-O-β-D-吡喃葡萄糖基-(2*S*, 3*R*, 4*E*, 8*E*, 2′R)-2-N-(2-羟基棕榈酰)-9-甲基-4, 8-脱氢鞘氨醇(**7**)、1-O-β-D-吡喃葡萄糖基-(2*S*, 3*R*, 4*E*, 8*E*, 2′R)-2-N-(2-羟基十八烷酰)-9-甲基-4, 8-脱氢鞘氨醇(**8**)。日本学者 Kazuko Yoshikawa曾对大青褶伞

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子实体的化学成分进行了研究,得到了 2个新甾醇类化合物 (22*E*, 24*R*)-3α-ureido-ergosta-4, 6, 8(14), 22-tetraene和 (22*E*, 24*R*)-5α, 8α-epidioxyergosta-6, 9, 22-triene-3-O-β-D-glucopyranoside[2],但其发酵菌丝体的化学成分未见报道。本文从大青褶伞发酵菌丝体分离鉴定了 4个甾醇类化合物: 5、6、(22*E*, 24*R*)-5α, 6α-环氧麦角甾-8 (14), 22-二烯-3β, 7α-二醇 (**9**)、(22*E*, 24*R*)麦角甾-7, 22-二烯-3β醇 (**10**)。除化合物 **9**外其它化合物均为首次从以上相应毒菌中分离得到。

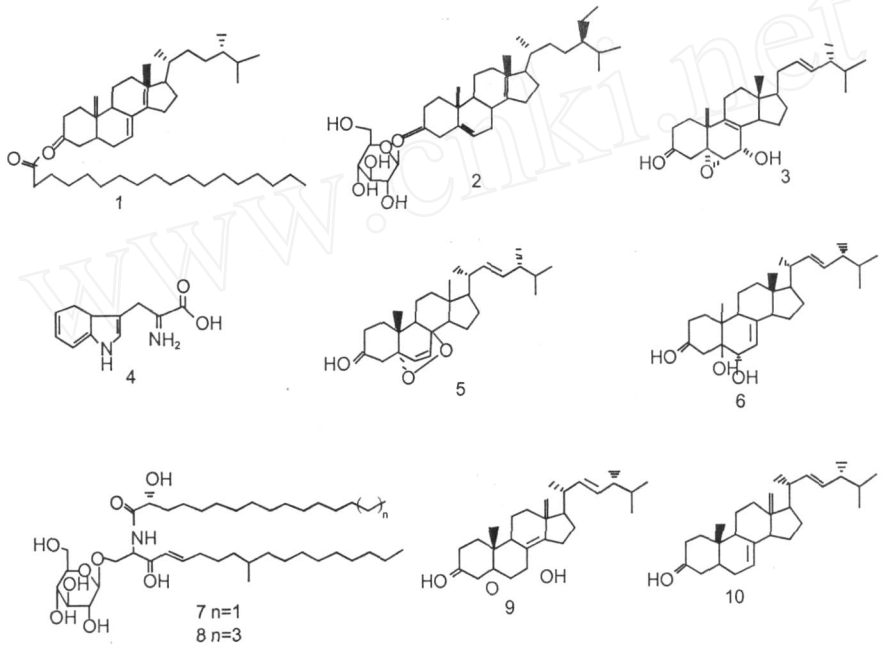

图 1 化合物 1～10的结构

Fig. 1 Structures of compounds **1-10**

1 实验部分

1.1 仪器与材料

VG Auto Spec-3000型质谱仪 (美国 Beckman公司); Bruker AM-400和 DRX-500核磁共振仪 (瑞士 Bruker公司), TMS为内标;柱色谱硅胶 (200～300目)和硅胶 H及薄层色谱硅胶 GF254 (青岛海洋化工厂); Sephadex LH-20 (Pharmacia公司); Agilent 1100高效液相色谱仪 (美国 Agilent公司)。所用试剂为工业级,经重蒸后使用。

光盖伞子实体 2003年 6月采集于湖南望城,标本鉴定人为湖南师范大学生命科学学院张平博士,标本保存在湖南师范大学生命科学学院真菌室。

假褐云斑鹅膏 2005年采集于湖南郴州临武,由湖南师范大学生命科学学院陈作红鉴定,标本保存在湖南师范大学生命科学学院真菌室。

大青褶伞发酵菌丝体由本研究室发酵。

1.2 提取和分离

光盖伞子实体 450 g,相继用 $CHCl_3$-MeOH (1∶1)和 MeOH分别提取 3次,合并提取液,真空浓缩得浸膏 (30 g)。将总浸膏加水混悬,用乙酸乙酯、正丁醇相继萃取,得到乙酸乙酯浸膏 (18 g)、正丁醇浸膏 (12 g)。将乙酸乙酯部分用 200～300目的硅胶柱层析分离,以石油醚-丙酮进行梯度洗脱,经薄层层析追踪检测,分为 A-F组分。组分 A经减压硅胶柱层析 (硅胶 H),以石油醚-乙酸乙酯 (19∶1)溶剂洗脱,分离得到化合物 **1** (23 mg);组分 C经硅胶柱层析,以石油醚-丙酮 (6∶1)溶剂洗脱,分离得到化合物 **3** (15 mg);组分 D经硅胶柱层析,以氯仿-甲醇 (9∶1)溶剂洗脱,分离得到化合物 **2** (30 mg)。正丁醇部分经反相 C-18柱层析,以甲醇-水系统梯度洗脱,分离得到化合物 **4** (120 mg)。

假褐云斑鹅膏 300 g相继用 MeOH和 MeOH-H_2O (1∶1)分别提取 3次,得总浸膏 (45 g)。按照与光盖伞相类似的分离纯化方法,经硅胶、凝胶以及 HPLC等柱层析,分离得化合物 **5** (320 mg)、**6** (210 mg)、**7** (10 mg)、**8** (8 mg)。

大青褶伞发酵菌丝体 250 g(由本研究室发酵)

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的提取方法和分离方法同光盖伞的子实体,得乙酸乙酯部分(20 g)。按照与光盖伞相类似的分离纯化方法,经反复使用硅胶、凝胶等柱层析方法,得到化合物 **5**(110 mg)、**6**(85 mg)、**9**(10 mg)、**10**(45 mg)。

2 结构鉴定

化合物 1 $C_{46}H_{80}O_2$,无色油状,易溶于氯仿。EIMS *m/z*: 664 $[M]^+$, 382 $[M-C_{18}H_{36}O_2]$; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.73 (1H, m, H-7), 0.55 (3H, s, C-18), 0.81 (3H, s, C-19), 1.04 (3H, d, *J* = 6.5 Hz, H-21), 5.26～5.17 (2H, overlapped, m, H-22, 23), 0.86 (3H, d, *J* = 7.4 Hz, H-26), 0.90 (3H, d, *J* = 7.4 Hz, H-27), 0.94 (3H, d, *J* = 6.6 Hz, H-28), 0.84 (3H, s, C-18′); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 36.8 (t, C-1), 33.8 (t, C-2), 76.2 (d, C-3), 32.0 (t, C-4), 40.5 (d, C-5), 29.5 (t, C-6), 117.3 (d, C-7), 139.5 (s, C-8), 49.3 (d, C-9), 32.5 (s, C-10), 21.8 (t, C-11), 39.8 (t, C-12), 43.8 (s, C-13), 55.0 (d, C-14), 22.7 (t, C-15), 27.5 (t, C-16), 55.9 (d, C-17), 12.1 (q, C-18), 13.0 (q, C-19), 40.1 (d, C-20), 21.1 (q, C-21), 135.7 (d, C-22), 131.9 (d, C-23), 42.8 (d, C-24), 34.8 (d, C-25), 19.6 (q, C-26), 19.9 (q, C-27), 17.6 (q, C-28), 173.5 (s, C-1′), 32.0 (t, C-2′), 25.1 (t, C-3′), 29.7～29.1 (t, C-4′～17′), 14.1 (q, C-18′)。以上波谱数据与文献[3]报道一致,化合物鉴定为(22*E*, 24*R*)麦角甾-7, 22-二烯-3β-十八烷酸酯。

化合物 2 $C_{35}H_{60}O_6$,白色粉末,难溶于氯仿和甲醇。与标准品对照,确定为β-胡萝卜苷。

化合物 3 $C_{28}H_{44}O_3$,无色结晶(甲醇),易溶于氯仿,mp. 172～173 ℃。EIMS *m/z*: 428 $[M]^+$, 410 $[M-H_2O]$; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.93 (3H, m, H-3), 3.14 (H, br s, H-6), 4.39 (H, br s, H-7), 0.63 (3H, s, C-18), 1.27 (3H, s, H-19), 1.02 (3H, d, *J* = 6.4 Hz, C-21), 5.26～5.13 (overlapped, H-22, 23), 0.84 (3H, d, *J* = 6.6 Hz, H-26), 0.82 (3H, d, *J* = 6.0 Hz, H-27), 0.92 (3H, d, *J* = 5.8 Hz, H-28); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 30.8 (t, C-1), 29.1 (t, C-2), 68.5 (d, C-3), 38.9 (t, C-4), 63.2 (s, C-5), 60.1 (d, C-6), 66.9 (d, C-7), 137.0 (s, C-8), 126.4 (s, C-9), 37.8 (s, C-10), 23.0 (t, C-11), 36.1 (t, C-12), 41.8 (s, C-13), 51.1 (d, C-14), 22.8 (t, C-15), 30.8 (t, C-16), 54.3 (d, C-17), 11.5 (q, C-18), 23.6 (q, C-19), 40.5 (d, C-20), 20.9 (q, C-21), 135.4 (d, C-22), 132.1 (d, C-23), 42.8 (d, C-24), 33.1 (d, C-25), 19.6 (q, C-26), 19.6 (q, C-27), 17.6 (q, C-28)。以上波谱数据与文献[4]报道的一致,化合物鉴定为(22*E*, 24*R*)-5α, 6α-环氧麦角甾-8, 22-二烯-3β, 7α-二醇。

化合物 4 $C_{11}H_{12}N_2O$,白色结晶(甲醇),易溶于水,mp. 280～282 ℃。FAB$^+$-MS *m/z*: 205 $[M+1]^+$; ^{1}H NMR (500 MHz, D_2O) δ: 7.14 (H, s, H-2), 7.57 (H, d, *J* = 8.0 Hz, H-4), 7.11 (H, t, *J* = 7.8 Hz, H-5), 7.03 (H, t, *J* = 7.8 Hz, H-6), 7.37 (H, d, J = 8.2 Hz, H-7), 3.31 (H, dd, *J* = 15.4, 4.7 Hz, Ha-10), 3.13 (H, dd, *J* = 15.3, 8.1 Hz, Hb-10), 3.86 (H, m, H-11); ^{13}C NMR (100 MHz, D_2O) δ: 125.3 (d, C-2), 107.8 (s, C-3), 118.8 (d, C-4), 119.8 (d, C-5), 122.5 (d, C-6), 112.3 (d, C-7), 136.7 (s, C-8), 127.0 (s, C-9), 26.8 (t, C-10), 55.4 (d, C-11), 175.0 (C-12)。以上波谱数据与文献[5]报道的一致,化合物鉴定为色氨酸。

化合物 5 $C_{28}H_{44}O_3$,无色结晶(甲醇),易溶于氯仿。与标准品对照,确定为(22*E*, 24*R*)-3β羟基-5α, 8α过氧化麦角甾-6, 22-二烯。

化合物 6 $C_{28}H_{46}O_3$,无色结晶(甲醇),易溶于氯仿。与标准品对照,确定为(22*E*, 24*R*)麦角甾-7, 22-二烯-3β, 5α, 6β-三醇。

化合物 7 $C_{41}H_{77}NO_9$,无定形粉末,难溶于氯仿和甲醇。FAB$^-$-MS *m/z*: 726 $[M-1]^-$。^{1}H NMR (500 MHz, C_5D_5N) δ: 4.73 (2H, m, overlapped, H-2, 3), 5.97 (2H, m, overlapped, H-4, 5), 5.25 (br. s, H-8), 4.56 (m, H-2′), 4.88 (1H, d, *J* = 7.7 Hz, H-1″), 1.62 (3H, s, H-19); ^{13}C NMR (125 MHz, C_5D_5N) δ: 70.2 (t, C-1), 54.6 (d, C-2), 72.4 (d, C-3), 132.4 (d, C-4), 132.0 (d, C-5), 33.1 (t, C-6), 32.2 (t, C-7), 124.2 (d, C-8), 135.9 (s, C-9), 40.1 (t, C-10), 28.4 (t, C-11), 29.7～30.1 (t, C-12～15), 28.3 (t, C-16), 23.0 (t, C-17), 14.4 (q, C-18), 16.2 (q, 19-CH_3), 175.8 (s, C-1′), 72.6 (d, C-2′), 35.7 (t, C-3′), 29.7～30.1 (t, C-4′～13′), 28.3 (t, C-14′), 23.0 (t, C-15′), 14.4 (q, C-16′), 105.7 (d, C-1‴), 75.1 (d, C-2″), 78.5 (d, C-3‴), 71.6 (d, C-4‴), 78.6 (d, C-5‴), 62.7 (t, C-6‴)。以上波谱数据与文献[6]报道的一致,化合物鉴定为1-O-β-D-吡喃葡萄糖基-(2*S*, 3*R*, 4*E*, 8*E*, 2′*R*)-2-N-(2′羟基棕榈酰)-9-甲基-

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4, 8脱氢鞘氨醇。

化合物 8 $C_{43}H_{81}NO_9$,无定形粉末,难溶于氯仿和甲醇。FAB$^-$MS *m/z*: 754 [M-1]$^-$。^{13}C NMR (100 MHz, CD_3OD) δ: 69.7 (t, C-1), 54.5 (d, C-2), 72.8 (d, C-3), 134.6 (d, C-4), 131.1 (d, C-5), 33.8 (t, C-6), 33.1 (t, C-7), 124.8 (d, C-8), 136.7 (s, C-9), 40.8 (t, C-10), 28.7 (t, C-11), 30.4～30.8 (t, C-12～15), 29.1 (t, C-16), 23.7 (t, C-17), 14.5 (q, C-18), 16.2 (q, 19-CH_3), 177.1 (s, C-1′), 73.0 (d, C-2′), 35.8 (t, C-3′), 30.4～30.8 (t, C-4′～15′), 29.1 (t, C-16′), 23.7 (t, C-17′), 14.5 (q, C-18′), 104.6 (d, C-1″), 74.9 (d, C-2″), 77.9 (d, C-3″), 71.5 (d, C-4″), 77.8 (d, C-5″), 62.7 (t, C-6″)。以上波谱数据与文献[6]报道的一致,化合物鉴定为 1-*O*-β-D-吡喃葡萄糖基-(2*S*, 3*R*, 4*E*, 8*E*, 2′*R*)-2-N-(2′羟基十八烷酰)-9-甲基-4, 8脱氢鞘氨醇。

化合物 9 $C_{28}H_{44}O_3$,白色粉末,易溶于氯仿, mp. 124～125 ℃。EIMS *m/z*: 410 [M-H_2O]$^+$, 377 [M-2H_2O-Me]$^+$; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.61 (3H, s, H-18), 1.17 (3H, s, H-19), 1.05 (3H, d, *J* = 6.4 Hz, H-21), 0.87 (3H, overlapped, H-26), 0.85 (3H, overlaped, H-27), 0.95 (3H, d, *J* = 6.7 Hz, H-28); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 32.2 (t, C-1), 31.0 (t, C-2), 68.5 (d, C-3), 39.2 (t, C-4), 65.6 (s, C-5), 62.3 (d, C-6), 63.9 (d, C-7), 125.1 (s, C-8), 38.7 (d, C-9), 33.0 (s, C-10), 19.0 (t, C-11), 36.5 (t, C-12), 41.5 (s, C-13), 152.6 (s, C-14), 24.9 (t, C-15), 27.2 (t, C-16), 56.8 (d, C-17), 17.6 (q, C-18), 16.5 (q, C-19), 39.5 (d, C-20), 21.2 (q, C-21), 135.2 (d, C-22), 132.2 (d, C-23), 40.8 (d, C-24), 33.0 (d, C-25), 19.6 (q, C-26), 19.6 (q, C-27), 17.6 (q, C-28)。上述数据与文献[4]报道一致,故鉴定该化合物为 (22*E*, 24*R*)-5α, 6α-环氧麦角甾-8 (14), 22-二烯-3β, 7α-二醇。

化合物 10 $C_{28}H_{46}O$,无色结晶 (甲醇),易溶于氯仿, mp. 159～161 ℃。EIMS *m/z*: 398 [M]$^+$; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.36 (1H, m, H-3), 0.58 (3H, s, H-18), 0.87 (3H, s, H-19), 0.83 (3H, d, *J* = 8.4 Hz, H-21), 5.22 (2H, overlapped, H-22, 23), 1.05 (3H, d, *J* = 6.5 Hz, H-26), 0.95 (3H, d, *J* = 6.5 Hz, H-27), 0.87 (3H, d, *J* = 7.22 Hz, H-28); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 37.1 (t, C-1), 31.4 (t, C-2), 71.0 (d, C-3), 37.9 (t, C-4), 40.2 (d, C-5), 29.6 (t, C-6), 117.4 (d, C-7), 139.0 (s, C-8), 49.4 (d, C-9), 33.9 (s, C-10), 21.5 (t, C-11), 39.4 (t, C-12), 43.2 (s, C-13), 55.1 (d, C-14), 22.9 (t, C-15), 28.1 (t, C-16), 55.9 (d, C-17), 12.1 (q, C-18), 13.0 (q, C-19), 40.5 (d, C-20), 21.1 (q, C-21), 135.7 (d, C-22), 131.8 (d, C-23), 42.8 (d, C-24), 33.1 (d, C-25), 19.6 (q, C-26), 19.9 (q, C-27), 17.6 (q, C-28)。上述数据与文献[7]报道一致,故鉴定该化合物为 (22*E*, 24*R*) 麦角甾-7, 22-二烯-3β-醇。

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