·特约专稿 ·

黄盾盘菌的化学成分

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摘 要 从子囊菌亚门黄盾盘菌 (*Scutellinia ascoboloides*)发酵液中首次分离得到 8个化合物,其结构通过光谱学技术确定为:α-甜没药醇 (**1**), pelandjauic acid (**2**), geranicardic acid (**3**), (4*E*, 8*E*) - N - 2′-羟基棕榈酰 - 9 - 甲基 - 4, 8 - sphingadienine (**4**), 麦角甾 - 7, 22 - 二烯 - 3 - 酮 (**5**), 麦角甾 - 4, 6, 8(14), 22 - 四烯 - 3 - 酮 (**6**), 麦角甾 - 5, 7, 22 - 三烯 - 3β - 醇 (**7**), 麦角甾 - 7, 22 - 二烯 - 3β, 5α, 6β - 三醇 (**8**).

关键词 黄盾盘菌; 化学成分; 甜没药醇; pelandjauic acid; geranicardic acid; 神经酰胺; 麦角甾醇
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A Chemical Analysis of Ascomycete *Scutellinia ascoboloides*

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Abstract: Eight known compounds have been isolated from a culture of the ascomycete *Scutellinia ascoboloides*. Their structures have been established as (-) - (4*S*, 8*S*) - α - bisabolol (**1**), pelandjauic acid (**2**), geranicardic acid (**3**), (4*E*, 8*E*, 2*S*, 3*R*, 2′*R*) - N - 2′- hydroxyhexadecanoyl - 9 - methyl - 4, 8 - sphingadienine (**4**), ergosta - 7, 22 - dien - 3 - one (**5**), (22*E*, 24*R*) - ergosta - 4, 6, 8(14), 22 - tetraen - 3 - one (**6**), ergosta - 5, 7, 22 - trien - 3β - ol (**7**), cerevisterol (**8**) by a spectroscopic analysis. This is the first time that these compounds from this fungus have been reported.

Key words: *Scutellinia ascoboloides*; component; bisabolol; pelandjauic acid; geranicardic acid; ceramide; ergosterol

黄盾盘菌 (*Scutellinia ascoboloides*),俗称黄毛盖,属盘菌科毛盘属高等真菌,子囊盘盾状,边缘稍高起,有微细白毛,子实层下凹呈黄色,主要分布于河北和江苏[1]. 目前未见该菌化学成分的文献报道. 为了从真菌中寻找具有生物活性的次生代谢产物,我们对黄盾盘菌发酵液进行了系统的化学成分研究,从其乙酸乙酯提取物中分离得到 8个已知化合物 (结构见图 1),经波谱解析分别鉴定为:α-甜没药醇 (**1**), pelandjauic acid (**2**), geranicardic acid (**3**), (4*E*, 8*E*) - N - 2′-羟基棕榈酰 - 9 - 甲基 - 4, 8 - sphingadienine (**4**), 麦角甾 - 7, 22 - 二烯 - 3 - 酮 (**5**), 麦角甾 - 4, 6, 8(14), 22 - 四烯 - 3 - 酮 (**6**), 麦角甾 - 5, 7, 22 - 三烯 - 3β - 醇 (**7**), 麦角甾 - 7, 22 - 二烯 - 3β, 5α, 6β - 三醇 (**8**).

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1 仪器与材料

熔点由四川大学科仪厂生产的 XRC-1型显微熔点仪测定,温度计未校正;比旋光值由 Horiba SEPA-300旋光仪测定; IR由 BRUKER TENSOR 27 FT-IR型红外光谱仪测定;质谱由 VG AutoSpec-3000质谱仪测定;核磁共振由 Bruker AV-400和 DRX-500测定,其中 ^{1}H NMR在 400 MHz和 500 MHz下测定, ^{13}C NMR在 100 MHz和 125 MHz下测定;柱层析硅胶和 GF_{254} TLC预制板均为青岛海洋化工厂生产; Sephadex LH-20为瑞典 Amersham Biosciences公司产品;显色方法为荧光灯下波长 254和 365 nm处观察荧光,10%硫酸乙醇溶液和硫酸香草醛处理后加热显色及碘蒸气显色.

黄盾盘菌于 2005年 7月份采集于云南哀牢山,由昆明植物所藏穆研究员鉴定,标本存于昆明植物研究所标本馆.对该菌种采用斜面转摇瓶液体培养的方法进行发酵培养.培养规模: 300 mL ×60瓶;培养基组成:每升灭菌水含去皮土豆 200 g,葡萄糖 20 g,盐酸硫胺 10 mg, KH_2PO_4 3 g, $MgSO_4$ 1.5 g,灭菌前用柠檬酸 0.1 g调 pH至 6.5;在恒温 25 ℃、摇速 150 r/min条件下培养发酵 30 d

2 提取与分离

黄盾盘菌发酵液 (18 L)用乙酸乙酯萃取 3次,合并减压蒸干得 2.8 g粗提物,经硅胶柱层析,以氯仿-甲醇梯度洗脱得 7个馏份 (Fr.A-Fr.G). Fr.B(氯仿-甲醇 98∶2洗脱部分)经 Sephadex LH-20柱层析,以氯仿-甲醇 (1∶1)洗脱得 3个亚组份 Fr B1～Fr B3, Fr B1经硅胶柱层析,以石油醚-乙酸乙酯 (10∶1)洗脱得到化合物 **5** (5.1 mg); Fr B2经过重结晶得到化合物 **6** (12 mg); Fr B3经进一步的硅胶柱层析,以纯氯仿洗脱得到化合物 **2**和 **3**的混合物 (12 mg); Fr C(氯仿-甲醇 95∶5洗脱部分)经硅胶柱层析,以石油醚-丙酮 (10∶1)洗脱得 2个亚组份,其中 Fr C1再经硅胶柱层析,以纯氯仿洗脱得到化合物 **1** (7.1 mg), Fr C2经重结晶得到化合物 **7** (4.1 mg). Fr D(氯仿-甲醇 90∶10洗脱部分)经硅胶柱层析,以氯仿-丙酮 (15∶1)洗脱得 2个亚组份, Fr D1再经硅胶柱层析,以石油醚-丙酮 (5∶1)洗脱得到化合物 **4** (7.0 mg), Fr D2经 Sephadex LH-20柱层析,以氯仿-甲醇 (1∶1)洗脱得化合物 **8** (18.0 mg).

3 化学结构及鉴定

3.1 化合物 1 α-甜没药醇[2], $C_{15}H_{26}O$, 油状物; EI-MS *m/z*(%): 222 $[M]^+$ (1), 204 $[M-H_2O]^+$ (5), 149 (30), 108 (100); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H: 5.37 (1H, br s, H-2), 1.61 (3H, s, H-7), 1.10 (3H, s, H-10), 2.06 (2H, m, H-11), 5.12 (1H, t, 6.0, H-12), 1.68 (3H, s, H-14), 1.64 (3H, s, H-15); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C: 134.1 (s, C-1), 120.5 (d, C-2), 26.9 (t, C-3), 43.0 (d, C-4), 23.2 (t, C-5), 31.0 (t, C-6), 23.3 (q, C-7), 74.3 (t, C-8), 40.1 (t, C-9), 23.3 (t, C-10), 22.0 (t, C-11), 124.6 (d, C-12), 131.7 (s, C-13), 25.7 (q, C-14), 17.7 (q, C-15).

3.2 化合物 2 Pelandjauic acid, $C_{24}H_{36}O_3$, 油状物; FABMS (neg.) *m/z* 371 $[M-H]^-$, 743 $[2M-H]^-$; ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H: 6.78 (1H, d, 7.5, H-4), 7.38 (1H, dd, 7.5, 8.0, H-5), 6.87 (1H, d, 8.0, H-6), 2.99 (2H, t, 7.5, H-8), 1.61 (2H, m, H-9), 1.26-1.36 (14H, H-10～13 and H-21～23), 2.04 (4H, m, H-14/20), 2.77 (2H, m, H-17), 5.30-5.40 (4H, m, H-15/16/18/19), 0.88 (3H, s, H-24); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C: 176.2 (s, C-1), 110.3 (s, C-2), 163.6 (s, C-3), 115.9 (d, C-4), 135.4 (d, C-5), 122.8 (d, C-6), 147.8 (s, C-7), 36.5 (t, C-8), 31.5 (t, C-9), 29.2-29.7 (t, C-10～13 and C-21), 27.2 (t, C-14), 130.1 (d, C-15), 128.0 (d, C-16), 25.6 (t, C-17), 127.9 (d, C-18), 130.2 (d, C-19), 27.2 (t, C-20), 31.9 (t, C-22), 22.6 (t, C-23), 14.7 (q, C-24).

3.3 化合物 3 Geranicardic acid, $C_{24}H_{38}O_3$, 油状物; FABMS (neg) *m/z* 373 $[M-H]^-$, 745 $[2M-H]^-$; ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H: 6.78 (1H, d, 7.5, H-4), 7.38 (1H, dd, 7.5, 8.0, H-5), 6.87 (1H, d, 8.0, H-6), 2.99 (2H, t, 7.5, H-8), 1.61 (m, 2H, H-9), 1.26-1.36 (14H, H-10～13 and H-21～23), 2.04 (m, 4H, H-14/17), 5.30-5.40 (m, 4H, H-15/16), 0.88 (s, H-24); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C: 176.2 (s, C-1), 110.3 (s, C-2), 163.6 (s, C-3), 115.9 (d, C-4), 135.4 (d, C-5), 122.8 (d, C-6), 147.8 (s, C-7), 36.5 (t, C-8), 31.5 (t, C-9), 29.2-29.7 (t, C-10～13 and C-18～21), 27.2 (t, C-14/17), 129.8 (d, C-15), 129.9 (d, C-16), 31.9 (t, C-22), 22.6 (t, C

- 23), 14.7 (q, C - 24).

3.4 化合物 4 (4*E*, 8*E*) - N - 2′-羟基棕榈酰 - 9 - 甲基 - 4,8 - sphingadienine[3], $C_{35}H_{67}NO_4$, 白色无定型粉末; FABMS (neg) *m/z* 564 $[M-H]^-$; ^{1}H NNR (CD_3COCD_3, 500 MHz) δ_H: 0.87 (6H, t, 7.0, H - 18/16′), 1.20 - 1.45 (40H, m), 1.58 (3H, s, H - 19), 1.74 (1H, m, H - 3′), 1.95 (2H. t, 7.5, H - 10), 2.00 (1H, m, H - 3′), 2.08 (4H, m, H - 6/7), 3.63 (1H, m), 3.82 (2H, m), 4.00 (2H, m), 4.15 (1H, m), 4.39 (1H, d, 5), 4.74 (1H, d, 5.5), 5.15 (1H, m), 5.54 (1H, dd, 15.5, 6.5, H - 4), 5.69 (1H, m, H - 5), 7.32 (1H, d, 7.5, NH); ^{13}C NMR (CD_3COCD_3, 125 MHz) δ_C: 14.3, 16.1, 23.3, 28.4, 28.3, 29.3 - 29.8, 32.6, 33.4, 35.7, 40.4, 56.1, 62.4, 72.6, 73.6, 124.5, 131.7, 132.5, 136.2, 175.1.

3.5 化合物 5 麦角甾 - 7,22 - 二烯 - 3 - 酮[4], $C_{28}H_{40}O$, 无色针晶 (石油醚 - 丙酮); EI - MS m/z (%): 396 $[M]^+$ (5), 381 (2), 353 (3), 298 (13), 271 (30), 69 (87), 244 (16), 229 (25), 213 (16); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 0.57 (3H, s, H - 18), 0.82 (3H, d, 6.5, H - 26), 0.83 (3H, d, 6.5, H - 27), 0.91 (3H, d, 6.8, H - 28), 1.01 (3H, s, H - 19), 1.02 (3H, d, 6.6, H - 21), 5.16 (1H, dd, 15.3, 7.6, H - 22), 5.17 (1H, m, H - 7), 5.22 (1H, dd, 15.3, 7.1, H - 23); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C: 38.7 (t, C - 1), 38.1 (t, C - 2), 212.0 (s, C - 3), 44.2 (t, C - 4), 42.8 (d, C - 5), 30.0 (t, C - 6), 117.0 (d, C - 7), 139.5 (s, C - 8), 48.8 (d, C - 9), 34.4 (s, C - 10), 21.7 (t, C - 11), 39.3 (t, C - 12), 43.2 (s, C - 13), 55.0 (d, C - 14), 22.9 (t, C - 15), 28.1 (t, C - 16), 55.9 (d, C - 17), 12.1 (q, C - 18), 12.4 (q, C - 19), 40.5 (d, C - 20), 21.1 (q, C - 21), 135.6 (d, C - 22), 131.9 (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).

3.6 化合物 6 麦角甾 - 4,6,8(14),22 - 四烯 - 3 - 酮[5], $C_{28}H_{40}O$, 黄色针晶 (石油醚 - 丙酮); m.p. 112.5～114 ℃; EI - MS m/z (%): 392 $[M]^+$ (15), 377 (3), 349 (4), 268 (100), 253 (30), 214 (26), 173 (23), 69 (47); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 0.78 (3H, d, 6.6, H - 26), 0.82 (3H, d, 6.8, H - 27), 0.90 (3H, d, 6.8, H - 28), 0.93 (3H, s, H - 18), 0.97 (3H, m, H - 19), 1.03 (3H, d, 6.6, H - 21), 1.21 - 2.53 (18H, m, steroid necleus), 5.18 (1H, dd, 15.2, 7.2, H - 22), 5.24 (1H, dd, 15.2, 7.2, H - 23), 5.70 (1H, s, H - 4), 6.00 (1H, d, 9.4, H - 6), 6.58 (1H, d, 9.4, H - 7); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 34.1 (t, C - 1), 19.0 (t, C - 2), 199.3 (s, C - 3), 123.0 (d, C - 4), 164.2 (s, C - 5), 124.5 (d, C - 6), 133.9 (d, C - 7), 124.3 (s, C - 8), 44.0 (d, C - 9), 36.8 (s, C - 10), 25.4 (t, C - 11), 34.2 (t, C - 12), 44.0 (s, C - 13), 156.0 (s, C - 14), 35.7 (t, C - 15), 27.7 (t, C - 16), 55.8 (d, C - 17), 16.7 (q, C - 18), 18.9 (q, C - 19), 39.2 (d, C - 20), 21.2 (q, C - 21), 135.0 (d, C - 22), 132.6 (d, C - 23), 42.9 (d, C - 24), 33.1 (d, C - 25), 19.7 (q, C - 26), 20.0 (q, C - 27), 17.6 (q, C - 28).

3.7 化合物 7 麦角甾 - 5,7,22 - 三烯 - 3β - 醇[6], $C_{28}H_{44}O$, 无色针晶 (石油醚 - 丙酮); m.p. 152～154 ℃; $[\alpha]_D^{24}$ = - 129 ° (c = 0.22, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 3412, 2875, 2821, 1655, 1610, 1460, 1385, 1374, 985, 970, 835, 805 cm^{-1}; EI - MS m/z (%): 396 $[M]^+$ (55), 363 (61), 337 (40), 271 (17), 253 (48), 211 (37), 197 (28), 185 (23), 171 (30), 157 (55), 143 (57), 131 (27), 119 (30), 91 (28), 81 (27), 69 (100), 55 (56). ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 0.61 (3H, s, H - 18), 0.82 (3H, d, 6.9, H - 26), 0.84 (3H, d, 6.9, H - 27), 0.92 (3H, d, 6.9, H - 28), 0.95 (3H, s, H - 19), 1.03 (3H, d, 6.8, H - 21), 3.60 (1H, m, H - 3), 5.14 - 5.26 (2H, m, H - 22/23), 5.38 (1H, m, H - 7), 5.58 (1H, m, H - 6); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 38.4 (t, C - 1), 32.1 (t, C - 2), 70.5 (d, C - 3), 40.9 (t, C - 4), 139.8 (s, C - 5), 119.6 (d, C - 6), 116.4 (d, C - 7), 141.3 (s, C - 8), 46.4 (d, C - 9), 37.1 (s, C - 10), 21.2 (t, C - 11), 39.2 (t, C - 12), 42.9 (s, C - 13), 54.6 (d, C - 14), 23.0 (t, C - 15), 28.3 (t, C - 16), 55.9 (d, C - 17), 12.1 (q, C - 18), 16.3 (q, C - 19), 40.4 (d, C - 20), 21.2 (q, C - 21), 135.6 (d, C - 22), 132.1 (d, C - 23), 42.8 (d, C - 24), 33.1 (d, C - 25), 19.9 (q, C - 26), 19.7 (q, C - 27), 17.6 (q, C - 28).

3.8 化合物 8 麦角甾 - 7,22 - 二烯 - 3β,5α,6β - 三醇[7], $C_{28}H_{46}O_3$, 白色无定型粉末; m.p. 253～255 ℃; EI - MS *m/z* (%): 430 $[M]^+$, 412 [M -

$H_2O]^+$ (35), 394 $[M-2H_2O]^+$ (37), 379 (65), 376 $[M-3H_2O]^+$ (15), 269 (33), 251 (62), 69 (100); ^{1}H NMR (C_5D_5N, 400 MHz) δ_H: 0.54 (3H, s, H-18), 0.84 (3H, d, 6.7, H-26), 0.85 (3H, d, 6.7, H-27), 0.94 (3H, d, 6.4 Hz, H-28), 1.07 (3H, d, 6.4, H-21), 1.53 (3H, s, H-19), 4.32 (1H, br. d, 4.8, H-6), 4.84 (1H, m, H-3), 5.16 (1H, dd, 15.3, 8.3 H-22), 5.24 (1H, dd, 15.3, 7.4, H-23), 5.74 (1H, m, H-7); ^{13}C NMR (C_5D_5N, 100 MHz) δ_C: 32.6 (t, C-1), 33.8 (t, C-2), 67.6 (d, C-3), 42.0 (t, C-4), 76.1 (s, C-5), 74.3 (d, C-6), 120.4 (d, C-7), 141.6 (s, C-8), 43.8 (d, C-9), 38.1 (s, C-10), 22.4 (t, C-11), 40.1 (t, C-12), 43.9 (s, C-13), 55.2 (d, C-14), 23.5 (t, C-15), 28.2 (t, C-16), 56.5 (d, C-17), 12.3 (q, C-18), 18.8 (q, C-19), 40.4 (d, C-20), 21.3 (q, C-21), 135.2 (d, C-22), 132.5 (d, C-23), 42.8 (d, C-24), 33.1 (d, C-25), 19.9 (q, C-26), 20.1 (q, C-27), 17.6 (q, C-28).

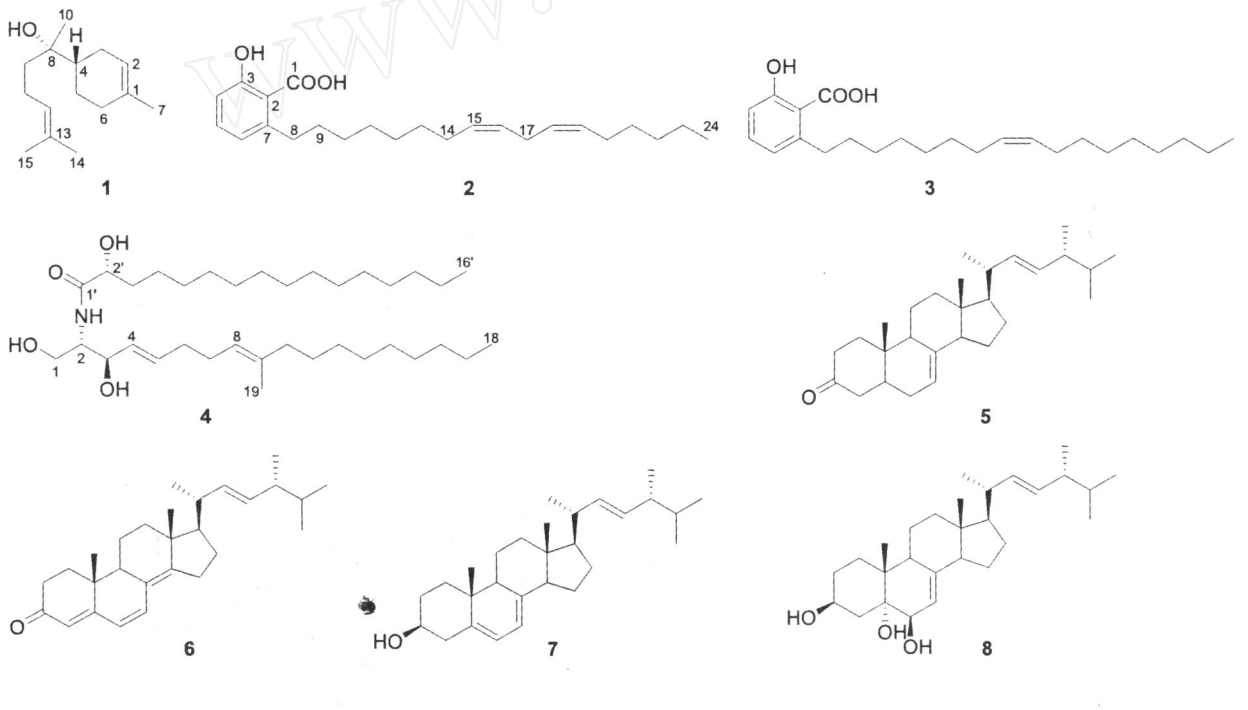

图1　化合物1~8的结构

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