

黄杨中的非生物碱化学成分*

林云良^{1,2}, 邱明华^{1**}, 李忠荣¹, 周琳¹, 刘剑秋²

(1 中国科学院昆明植物研究所植物化学与西部植物资源持续利用国家重点实验室, 云南 昆明 650204;

2 福建师范大学生物工程学院, 福建 福州 350000)

摘要: 从黄杨 *Buxus sinica* 地上部分分离出 10 个化合物, 通过光谱分析鉴定为: Cleomiscosin A (1), 3, 5-二羟基-4', 6, 7-三甲氧基-黄酮-3'-O-β-D-葡萄糖甙 (2), 5, 3', 4'-三羟基-3, 6, 7-三甲氧基-黄酮 (3), Cleomiscosin A-4'-O-β-D-glucopyranoside (4), 3, 5-二甲氧基苯甲酸-4-O-β-D-葡萄糖甙 (5), 4', 5-二羟基-3, 6, 7-三甲氧基-黄酮 (6), 羽扇豆烷醇 (7), (+)-Pinoresinol-O-β-D-glucopyranoside (8), β-谷甾醇 (9), 胡萝卜甙 (10)。其中化合物 1~5, 6, 8 均为首次从该属植物中分离得到。

关键词: 黄杨; 非生物碱化学成分; 分离鉴定

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Non-alkaloid Constituents of *Buxus sinica* (Buxaceae)

LIN Yun-Liang^{1,2}, QIU Ming-Hua^{1**}, LI Zhong-Rong¹, ZHOU Lin¹, LIU Jian-Qiu²

(1 State Key Laboratory of Phytochemistry and Plant Resources in West China, Chinese Academy of Science, Kunming 650204, China;

2 Fujian Normal University, Fuzhou 350000, China)

Abstract: From the aerial parts of *Buxus sinica*, ten non-alkaloid compounds were isolated and identified as cleomiscosin A (1), 3, 5-dihydroxyl-4', 6, 7-trimethyl flavone-3'-O-β-D-glucopyranoside (2), 3, 5, 3', 4'-tetrahydroxyl-3, 6, 7-trimethyl flavone (3), cleomiscosin A-4'-O-β-D-glucopyranoside (4), 3, 5-dimethoxybenzoic acid-4-O-β-D-glucopyranoside (5), 4', 5-dihydroxyl-3, 6, 7-trimethyl flavone (6), lupine (7), (+)-pinoresinol-O-β-D-glucopyranoside (8), β-sitosterol (9), and daucosterol (10). Their structures were identified by spectral evidence.

Key words: *Buxus sinica*; Non-alkaloid constituents; Flavones

黄杨 *Buxus sinica* (Rehd. et. Wils) Cheng 为黄杨科 (Buxaceae) 黄杨属 (*Buxus*) 植物, 又名青明矮、千年矮、黄头艾、万年青、黄木、锦熟黄杨。主要分布于我国南部各省、区及湖北。多分布于溪流的石罅中或岸边; 亦有栽培 (郑勉等, 1980)。黄杨作为药用植物早已记载于《本草纲目》: “叶苦平无毒”, “主治妇人难产, 入达生散中用, 又主暑日生疳; 捣烂涂之。” 本药主要有行气活血、祛湿通络、清热解毒、祛风、止血等功能 (吴征镒等, 1988)。民间用以治疗疳

疾、梅毒、风湿、皮炎、和狂犬病。黄杨木粉是民间流传治疗“心病”的有效药物 (李进喜等, 1984)。为继续该科生物活性及化学成分的研究 (邱明华, 1996), 对产于湖北神农架的黄杨地上部分进行了分析, 从中提取分离出 10 个化合物, 通过波谱分析, 分别鉴定为: Cleomiscosin A (1), 3, 5-二羟基-4', 6, 7-三甲氧基-黄酮-3'-O-β-D-葡萄糖甙 (2), 5, 3', 4'-三羟基-3, 6, 7-三甲氧基-黄酮 (3), Cleomiscosin A-4'-O-β-D-glucopyranoside (4), 3, 5-二甲氧基苯甲酸-4-O-

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** 通讯作者: Author for correspondence

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作者简介: 林云良 (1972-) 男, 助理研究员, 主要从事核磁共振谱技术研究。

β -D-葡萄糖甙 (5), 4', 5-二羟基-3, 6, 7-三甲氧基-黄酮 (6), 羽扇豆烷醇 (7), (+)-Pinoresinol-O- β -D-glucopyranoside (8), β -谷甾醇 (9), 胡萝卜甙 (10); 其中化合物 1~5, 6, 8 均为首次从该属植物中分离得到。该植物丙酮提取物中得到生物碱成分含量很少。

1 实验部分

1.1 实验仪器、材料和样品

熔点用四川大学科仪 XRC-1 显微熔点仪测定, 温度未校正。红外光谱用 Bio-Rad FTS135 红外光谱仪测定, KBr 压片。紫外光谱用日本岛津 UV-210A 型仪测定。质谱用 ESPUIRE-LC 和 VG AutoSpec 3000 型质谱仪测定。柱层析及薄层层析用硅胶为青岛海洋化工厂生产, 显色剂为 5% 硫酸溶液。 ^1H , ^{13}C NMR-DEPT 用 Bruker AV-400 和 DRX-500 超导核磁共振仪测定, CDCl_3 、 CD_3OD 、 $\text{C}_5\text{D}_5\text{N}$ 、 $\text{DMSO}-d_6$ 为溶剂。

黄杨 (*Buxus sinica*) 采自湖北神农架地区, 由中国科学院昆明植物研究所王宗玉教授鉴定。

1.2 提取和分离

将黄杨 (*Buxus sinica*) 的地上部分切成小块, 风干, 粉碎后称取 7 kg, 用相当于样品三倍体积的 70% 丙酮冷浸 3 次, 每次 24 h。提取液减压浓缩后, 用氯仿萃取 5 次, 每次用三倍于水溶液体积的溶剂, 得浸膏 106 g。粗提物氯仿部分进行反复硅胶柱层析分离, 洗脱剂: 氯仿, 氯仿: 丙酮 (9:1, 8:2, 7:3), 丙酮; 依次得到化合物 7, 9, 1, 6, 3 和 10。粗提物的水溶性部分先经 D101 大孔树脂柱层析, 洗脱液依次用水, 甲醇。将甲醇洗脱下来的部分经硅胶柱层析, 洗脱剂: 氯仿, 氯仿: 甲醇 (9:1, 8:2, 7:3), 甲醇; 依次得到化合物 8, 5, 2 和 4。

1.3 鉴定

化合物 1, 白色晶体, $\text{C}_{20}\text{H}_{18}\text{O}_8$, MW: 386; mp: 247–249°C; (–) FAB-MS m/z (%): 385 $[\text{M}-1]^-$ (100), 206 (72); IR $\nu_{\text{max}}^{\text{KBr}}$: 3460, 1710, 1610, 1575, 1520, 1500, 1440, 1420, 1370, 1300, 1280, 850, 820 和 750 cm^{-1} ; UV λ_{max} (MeOH) (log ϵ): 325 (4.25), 287 (4.10), 232 (4.40) 和 211 nm (4.47); ^1H NMR ($\text{C}_5\text{D}_5\text{N}$, 400 MHz) δ : 3.69 (3H, s, OCH_3), 3.78 (3H, s, OCH_3), 3.83–4.47 (3H, m, 8'-H, 9'-H), 5.56 (1H, d, 7-H), 6.42 (1H, d, $J=10$ Hz, 3-H), 6.71 (1H, s, 5-H), 7.27 (3H, m, 2', 5', 6'-H), 7.72 (1H, d, $J=10$ Hz, 4-H), 11.42 (1H, m, OH); ^{13}C NMR ($\text{C}_5\text{D}_5\text{N}$, 100.6 MHz) δ : 160.8s (C-2), 116.1d (C-3), 144.5d (C-4), 101.2d (C-5), 146.4s (C-6), 138.3s (C-7), 133.1s (C-8), 139.4s (C-4), 112.0s (C-10), 130.5s

(C-1'), 112.9d (C-2'), 148.6s (C-3'), 148.6s (C-4'), 114.0d (C-5'), 121.1d (C-6'), 79.8d (C-7'), 77.3d (C-8'), 60.7t (C-9'), 56.3q (6- OCH_3), 55.9q (3'- OCH_3)。 (Anil *et al.*, 1980)

化合物 2, 黄色晶体, $\text{C}_{24}\text{H}_{26}\text{O}_{13}$, MW: 522; mp 407–409°C; (–) FAB-MS m/z (%): 521 $[\text{M}-\text{H}]^-$ (100), 359 $[\text{M}-\text{H}-162]^-$ (26); UV λ_{max} (MeOH): 339, 280 nm; IR $\nu_{\text{max}}^{\text{KBr}}$: 3350, 1650, 1600, 1100 cm^{-1} ; ^1H NMR ($\text{C}_5\text{D}_5\text{N}$, 400 MHz) δ : 3.89 (3H, s, 3- OMe), 3.90 (3H, s, 6- OMe), 3.99 (3H, s, 7- OMe), 6.69 (1H, s, H-8), 7.69 (1H, d, H-5'), 7.71 (1H, d, H-2'), 13.2 (1H, s, 5-OH), 4.56 (1H, m, 6''-OH), 5.00 (1H, d, H-1'), 5.04 (1H, brs, 4''-OH), 5.09 (1H, brs, 3''-OH), 5.24 (1H, brs, 2''-OH); ^{13}C NMR ($\text{C}_5\text{D}_5\text{N}$, 100.6 MHz) δ : 152.6s (C-2), 139.2s (C-3), 179.2s (C-4), 150.1s (C-5), 132.8s (C-6), 159.5s (C-7), 91.3d (C-8), 156.1s (C-9), 106.9s (C-10), 126.6s (C-1'), 117.4d (C-2'), 148.9s (C-3'), 149.3s (C-4'), 117.4d (C-5'), 120.9s (C-6'), 60.6q (6- OCH_3), 60.0q (7- OCH_3), 56.5q (4'- OCH_3); 3'-O-Glc: 103.1d (C-1''), 74.8d (C-2''), 78.5d (C-3''), 71.2 (C-4''), 79.2d (C-5''), 62.3t (C-6'')。 (Bruce *et al.*, 1977)

化合物 3, 黄色晶体, $\text{C}_{18}\text{H}_{16}\text{O}_8$, MW: 360; mp 213–214°C; EI-MS m/z (%): 359 $[\text{M}-1]^+$ (40), 345 $[\text{M}-\text{Me}]^+$ (55), 343 $[\text{M}-\text{OH}]^+$ (10), 342 $[\text{M}-\text{H}_2\text{O}]^+$ (10), 341 $[\text{M}-\text{H}_3\text{O}]^+$ (20), 332 $[\text{M}-\text{CO}]^+$ (2), 331 $[\text{M}-\text{CHO}]^+$ (7), 329 $[\text{M}-\text{MeO}]^+$ (8), 317 $[\text{M}-\text{MeCO}]^+$ (12), 314 $[\text{M}-\text{CH}_2\text{O}_2]^+$ (5); ^1H NMR (CDCl_3 , 400 MHz) δ : 3.73 (3H, s, 3- OMe), 3.79 (3H, s, 6- OMe), 3.91 (3H, s, 3- OMe), 12.22 (1H, s, 5-OH), 7.59 (1H, d, H-2'), 7.47 (1H, dd, H-6'), 6.83 (1H, d, H-5'), 6.53 (1H, H-8); ^{13}C NMR (CDCl_3 , 100.6 MHz) δ : 151.7s (C-2), 137.6s (C-3), 178.1s (C-4), 151.6s (C-5), 131.6s (C-6), 158.5s (C-7), 91.2d (C-8), 155.9s (C-9), 105.5s (C-10), 120.7s (C-1'), 115.5d (C-2'), 145.2s (C-3'), 148.7s (C-4'), 115.6d (C-5'), 120.5s (C-6'), 59.5q (3- OCH_3), 59.9q (6- OCH_3), 56.4q (7- OCH_3)。 (Atta-ur-Rahman *et al.*, 1988)

化合物 4, 白色粉末, $\text{C}_{26}\text{H}_{40}\text{O}_{13}$, MW: 548; mp 411–413°C; (–) FAB-MS m/z (%): 547 $[\text{M}-\text{H}]^-$, 385 $[\text{M}-\text{H}-162]^-$ (100); IR $\nu_{\text{max}}^{\text{KBr}}$: 3460, 1710, 1610, 1575, 1520, 1500, 1440, 1420, 1370, 1300, 1280, 1230, 1195, 1155, 1130, 1100, 1080, 1050, 1030, 990, 940, 850, 820, 750 cm^{-1} ; ^1H NMR ($\text{C}_5\text{D}_5\text{N}$, 400 MHz) δ : 3.67 (3H, s, OMe), 3.80 (3H, s, OMe), 5.51 (1H, d, 7'-H), 6.41

(1H, d, 3-H), 6.72 (1H, s, 5-H), 7.72 (1H, d, 4-H); ^{13}C NMR ($\text{C}_5\text{D}_5\text{N}$, 100.6 MHz) δ : 160.8s (C-2), 116.2d (C-3), 144.5d (C-4), 101.1d (C-5), 146.4s (C-6), 138.5s (C-7), 133.1s (C-8), 139.4s (C-4), 111.9s (C-10), 127.6s (C-1'), 112.3d (C-2'), 149.1s

(C-3'), 148.9s (C-4'), 116.6d (C-5'), 121.7d (C-6'), 80.0d (C-7'), 77.6d (C-8'), 60.8t (C-9'), 56.2q (6-OCH₃), 55.9q (3'-OCH₃); 4'-O-Glc: 102.2d (C-1''), 74.8d (C-2''), 78.5d (C-3''), 71.2 (C-4''), 78.9d (C-5''), 62.3t (C-6''). (Munehisa *et al.*, 1984)

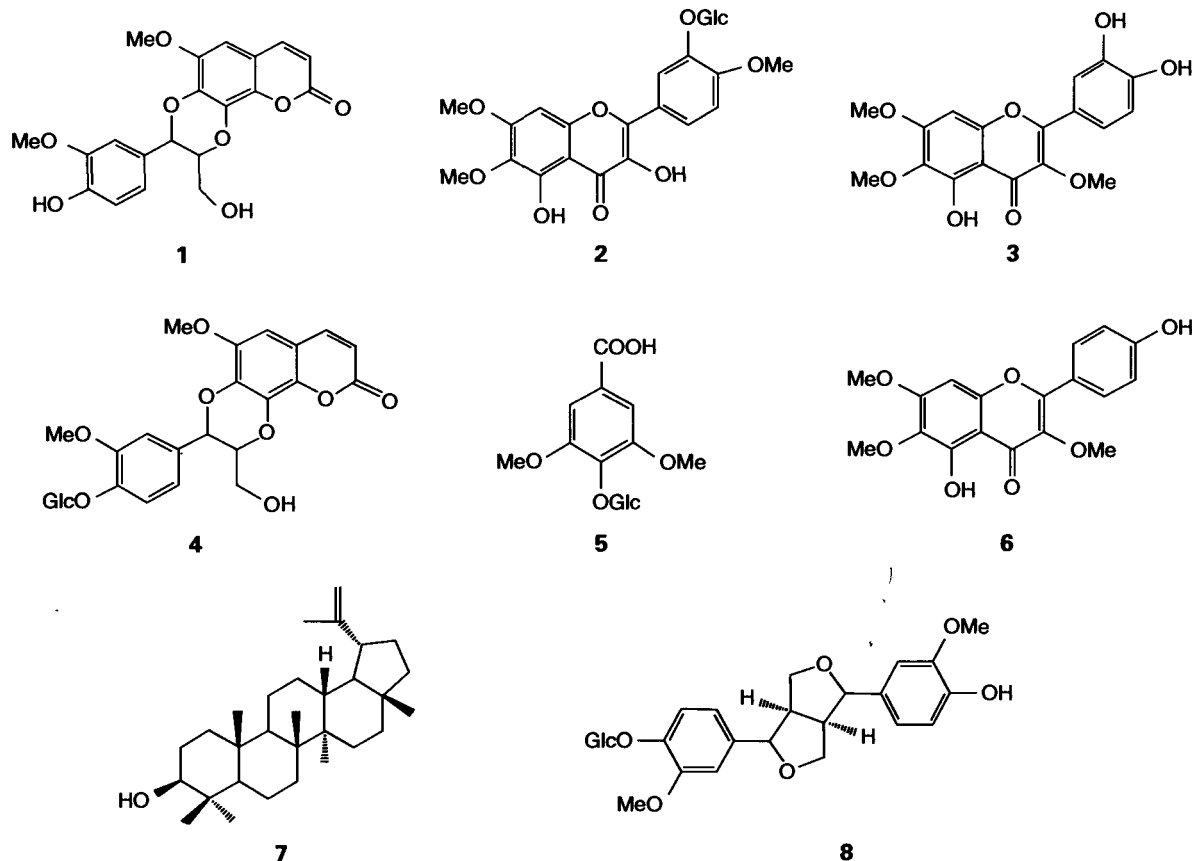


图 1 化合物 1~8 的化学结构

Fig. 1 Chemical structures of compounds 1-8

化合物 5, 白色晶体, $\text{C}_{15}\text{H}_{20}\text{O}_{10}$, MW: 360; mp 206-207°C; (-) FAB-MS m/z (%): 359 [M-H]⁻ (25), 198 [M-H-162]⁻ (100); IR $\nu_{\text{max}}^{\text{KBr}}$: 3550, 3150, 1695, 1600, 1510 cm^{-1} ; ^1H NMR ($\text{C}_5\text{D}_5\text{N}$, 400 MHz) δ : 7.20 (2H, s, H-2, 6), 6.02 (1H, d, H-1), 3.75 (6H, d, OMe); ^{13}C NMR ($\text{C}_5\text{D}_5\text{N}$, 100.6 MHz) δ : 127.7s (C-1), 108.6d (C-2), 153.4s (C-3), 139.7s (C-4), 153.4s (C-5), 104.2d (C-6), 168.7s (C-7), 104.2d (C-1'), 76.0d (C-2'), 79.0d (C-3'), 71.6d (C-4'), 78.5d (C-5'), 62.6t (C-6'), 56.5q (3-OCH₃), 56.5q (5-OCH₃). (Yue JM *et al.*, 1994)

化合物 6, 浅黄色针状晶体, $\text{C}_{18}\text{H}_{16}\text{O}_7$, MW: 344; mp 222°C; EI-MS m/z (%): 329 (56), 327 (6), 326

(10), 325 (24), 316 (2), 315 (8), 313 (5), 301 (16), 298 (7); IR $\nu_{\text{max}}^{\text{KBr}}$: 3360, 1658, 1560, 1500, 1450, 1360, 1092, 1066, 1010, 994, 876, 829 cm^{-1} ; ^1H NMR (CD_3OD , 400 MHz) δ : 7.97 ($J=9.0$, H-2'), 6.95 ($J=9.0$, H-3'), 6.95 ($J=9.0$, H-5'), 6.90 (H-8); ^{13}C NMR (CD_3OD , 100.6 MHz) δ : 149.7s (C-2), 135.6s (C-3), 179.9s (C-4), 151.6s (C-5), 131.6s (C-6), 159.6s (C-7), 90.3d (C-8), 155.6s (C-9), 105.5s (C-10), 121.6s (C-1'), 130.2d (C-2'), 115.5s (C-3'), 158.6s (C-4'), 115.5d (C-5'), 130.2s (C-6'), 60.7q (3-OCH₃), 59.9q (6-OCH₃), 56.1q (7-OCH₃). (Rodriguez *et al.*, 1972)

化合物 7, 白色晶体, $\text{C}_{30}\text{H}_{50}\text{O}$, MW: 426; mp: 215

-216°C; $[\alpha]_D^{26}$ (c 0.56, CHCl₃); EI-MS m/z (%): 426 [M⁺] (7), 315 (5), 234 (9), 219 (18), 203 (49), 175 (42), 109 (100), 83 (53), 71 (39), 67 (20); ¹H NMR (CDCl₃, 400 MHz) δ : 4.66 (1H, brs, H-29), 4.54 (1H, brs, H-29), 3.14 (1H, dd, H-3), 2.34 (1H, m, H-9), 1.63 (3H, s, CH₃-30), 1.34 (1H, m, H-18), 1.23 (1H, d, H-9), 1.63 (3H, s, CH₃-30), 1.00 (3H, s, CH₃-26), 0.94 (3H, s, CH₃-23), 0.92 (3H, s, CH₃-27), 0.80 (3H, s, CH₃-25), 0.76 (3H, s, CH₃-28), 0.73 (3H, s, CH₃-24); ¹³C NMR (CDCl₃, 100.6 MHz) δ : 38.7t (C-1), 27.4t (C-2), 79.0d (C-3), 38.9s (C-4), 55.3d (C-5), 18.3t (C-6), 34.3t (C-7), 40.8s (C-8), 50.4d (C-9), 37.2s (C-10), 20.9t (C-11), 25.2t (C-12), 38.1d (C-13), 42.8s (C-14), 27.4t (C-15), 35.6t (C-16), 43.0s (C-17), 48.3d (C-18), 48.0d (C-19), 151.0s (C-20), 29.9t (C-21), 40.0t (C-22), 28.0q (C-23), 15.4q (C-24), 16.1q (C-25), 16.0q (C-26), 14.6q (C-27), 18.0q (C-28), 109.3t (C-29), 19.3q (C-30). (Reynolds *et al.*, 1986)

化合物 8, 白色粉末, C₂₆H₃₂O₁₁, MW: 520; mp 110-113°C; (-) FAB-MS m/z (%): 519 [M-1]⁻ (90), 357 [M-1-162]⁻ (100); IR ν_{max}^{KBr} : 3400, 3000, 1600, 1510 cm⁻¹; ¹H NMR (CD₃OD, 400 MHz) δ : 4.59 (1H, d, J = 4.8 Hz, H-7), 4.64 (1H, d, J = 4.8 Hz, H-7'), 3.01 (2H, m, H-8 和 H-8'), 3.58 (2H, m, H-9ax 和 H-9'ax), 4.59 (2H, m, H-9eq 和 H-9'eq); ¹³C NMR (CD₃OD, 100.6 MHz) δ : 137.4s (C-1), 111.5s (C-2), 150.8s (C-3), 147.4s (C-4), 117.9d (C-5), 120.0s (C-6), 87.4d (C-7), 55.4d (C-8), 76.2t (C-9), 133.7s (C-1'), 110.9d (C-2'), 149.0s (C-3'), 147.2s (C-4'), 116.0d (C-5'), 119.7d (C-6'), 87.0d (C-7'), 55.2d (C-8'), 76.2t (C-9'), 56.7q (3-OCH₃), 56.4q (3'-OCH₃); Glc: 102.7d (C-1''), 74.8d (C-2''), 77.7d (C-3''), 71.2 (C-4''), 78.1d (C-5''), 62.3t (C-6''). (Masataka *et al.*, 1991)

化合物 9, 白色晶体, C₂₉H₃₀O; mp 136-137°C. IR 与 UV 数值与标准品一致, 混合熔点不下降, 鉴定为 β -谷甾醇。

化合物 10, 白色粉末, C₃₅H₅₀O₆; mp 283-286°C. IR 与 UV 数值与标准品一致, 混合熔点不下降, 鉴定为胡萝卜甙。

1.4 生物活性

经云南省天然药理毒理重点实验室做抗 PAF 活性筛选, 发现化合物 2 对 PAF 诱导的兔血小板聚集有一定的抑制作用, 其结果为血小板聚集率% (47.9 $\pm$ 6.9), 抑制率% (23.7 $\pm$ 5.8)。

致谢 昆明医学院云南省天然药理毒理重点实验室李玲教授帮助测定抗 PAF 活性筛选。

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