



交趾黄檀心材的黄酮类和三萜类成分

钟艳霞, 陈郊, 莫新良, 徐志防, 邱声祥, 刘新红

引用本文:

钟艳霞, 陈郊, 莫新良, 等. 交趾黄檀心材的黄酮类和三萜类成分[J]. 热带亚热带植物学报, 2021, 29(5): 573–578.

在线阅读 View online: <https://doi.org/10.11926/jtsb.4435>

您可能感兴趣的其他文章

Articles you may be interested in

木槿的化学成分研究

Chemical Constituents from the Stems of *Hibiscus syriacus*

热带亚热带植物学报. 2021, 29(3): 331–338 <https://doi.org/10.11926/jtsb.4288>

杨桃叶的化学成分研究

Chemical Constituents from the Leaves of *Averrhoa carambola*

热带亚热带植物学报. 2021, 29(1): 105–111 <https://doi.org/10.11926/jtsb.4246>

降香檀叶的非黄酮类成分研究

Non-flavonoid Constituents from the Leaves of *Dalbergia odorifera*

热带亚热带植物学报. 2019, 27(2): 213–218 <https://doi.org/10.11926/jtsb.3941>

宁前胡内生真菌*Fusarium tricinctum*固体发酵代谢产物研究

Metabolites of *Fusarium tricinctum*, An Endophytic Fungus Isolated from Ningguo *Peucedanum praeruptorum* on Solid Fermentation

热带亚热带植物学报. 2020, 28(2): 203–208 <https://doi.org/10.11926/jtsb.4135>

薏苡糠壳的化学成分及其种子萌发活性研究

Chemical Constituents of *Coix lachryma-jobi* and Their Activities on Seed Germination

热带亚热带植物学报. 2021, 29(5): 556–562 <https://doi.org/10.11926/jtsb.4361>

向下翻页, 浏览PDF全文

交趾黄檀心材的黄酮类和三萜类成分

钟艳霞^{1a}, 陈郊², 莫新良^{1a}, 徐志防³, 邱声祥³, 刘新红^{1b*}

(1. 茅台学院, a. 酿酒工程系; b. 资源环境系, 贵州 仁怀 564507; 2. 贵州茅台酒股份有限公司, 贵州 仁怀 564507; 3. 中国科学院华南植物园, 广州 510650)

摘要: 为研究交趾黄檀(*Dalbergia cochinchinensis*)的化学成分, 采用有机溶剂提取、萃取及多种色谱分离技术, 从其心材中分离得到 5 个新黄酮和 7 个其他类型成分。根据理化性质和波谱数据, 其结构分别鉴定为: 7-hydroxy-2',3',4'-trimethoxyisoflavan (1)、6,4'-dihydroxy-7-methoxyflavan (2)、R-dalbergiphenol (3)、R-4-methoxydalbergione (4)、mimosifoliol (5)、R-5-O-methylattylicin (6)、R-latifolin (7)、maackiain (8)、secundiflorol I (9)、3,9-dimethoxy-6H-benzofufo[3,2-c]chromen-6-one (10)、mucodianin C (11)、lup-(20)29-ene-2 α ,3 α -diol (12)。化合物 1、5、8~12 为首次从交趾黄檀植物中分离得到。

关键词: 交趾黄檀; 心材; 黄酮类; 新黄酮类; 三萜类

doi: 10.11926/jtsb.4435

Flavonoid and Triterpenoid Compounds from the Heartwood of *Dalbergia cochinchinensis*

ZHONG Yanxia^{1a}, CHEN Jiao², MO Xinliang^{1a}, XU Zhifang³, QIU Shengxiang³, LIU Xinhong^{1b*}

(1a. Department of Brewing Engineering; 1b. Department of Resources and Environment, Moutai Institute, Renhuai 564507, Guizhou, China; 2. Kweichow Moutai Co. Ltd, Renhuai 564507, Guizhou, China; 3. South China Botanical Garden, Chinese Academy of Sciences, Guangzhou 510650, China)

Abstract: To investigate the chemical constituents of *Dalbergia cochinchinensis*, five neoflavonoids and seven other compounds were isolated from its heartwood by various methods, such as organic solvent extraction, fractionation and chromatographic separation techniques. Based on physical and chemical properties and spectral data, their structures were identified as 7-hydroxy-2',3',4'-trimethoxyisoflavan (1), 6,4'-dihydroxy-7-methoxyflavan (2), R-dalbergiphenol (3), R-4-methoxydalbergione (4), mimosifoliol (5), R-5-O-methylattylicin (6), R-latifolin (7), maackiain (8), secundiflorol I (9), 3,9-dimethoxy-6H-benzofufo[3,2-c]chromen-6-one (10), mucodianin C (11), lup-(20)29-ene-2 α ,3 α -diol (12). Compounds 1, 5 and 8~12 were isolated from *D. cochinchinensis* for the first time.

Key words: *Dalbergia cochinchinensis*; Heartwood; Flavonoids; Neoflavonoid; Triterpenoid

交趾黄檀(*Dalbergia cochinchinensis*)主要产于泰国、老挝、越南、柬埔寨等东南亚地区, 其木材表面具有光泽, 木质结构均匀且细腻, 硬度大, 强度高, 具有很强的抗虫性能和耐腐蚀性能, 适于制作精美工艺品、高档红木家具、高级乐器等^[1~2]。

交趾黄檀心材在泰国有作为民间药材使用^[3], 据报道, 其主要含有二氢黄酮、异黄酮、新黄酮、二氢异黄酮、查尔酮、苯并呋喃、酚类等成分。有学者已从交趾黄檀中分离鉴定出 65 个化合物, 包括 9 个二氢黄酮、8 个异黄酮、7 个新黄酮、3 个二氢异

收稿日期: 2021-04-26 接受日期: 2021-06-08

基金项目: 贵州省教育厅青年科技人才成长项目(KY[2018]449, KY[2018]465); 贵州省特色重点实验室项目(KY[2018]003); 贵州省科技计划项目([2019]1295)资助

This work was supported by the Project for Growth of Young Talents in Guizhou Educational Committee (Grant No. KY[2018]449, KY[2018]465), the Project of Guizhou Key Laboratory (Grant No. KY[2018]003), and the Project for Science and Technology Planning in Guizhou (Grant No. KY[2019]1295).

作者简介: 钟艳霞, 女, 硕士, 讲师, 研究方向为天然产物化学。E-mail: 290827232@qq.com

* 通信作者 Corresponding author. E-mail: liuxinhong@mtxy.edu.cn

黄酮、5 个查尔酮、3 个黄烷、2 个黄酮、1 个异黄烷、6 个酚类、5 个苯甲酸及苯甲酮类、4 个苯并呋喃类、2 个甾体类、3 个萜类、1 个紫檀烷类、2 个糖苷及其苷元、1 个菲醌类、1 个氧杂蒽酮、1 个二苯乙烯类、1 个叔醇类^[4~14]。本课题组在前期研究的基础上进一步对其心材进行化学成分研究, 从中分离得到 12 个化合物。

1 材料和方法

1.1 材料

试验材料于 2011 年由老挝进口, 为佛山市家禾木家具有限公司彭庆明提供, 由中国科学院华南植物园邓云飞研究员鉴定为交趾黄檀(*Dalbergia cochinchinensis*)心材。

1.2 仪器和试剂

美国 Applied Biosystems 公司生产的 API2000 LC/MS/MS 质谱仪; 瑞士 Bruker 公司生产的 DRX-400(500)型核磁共振波谱仪, 内标为四甲基硅烷试剂, 化学位移 δ 用 ppm 表示, 偶合常数 J 用 Hz 表示。

柱色谱硅胶(100~200 和 200~300 目); 柱色谱反相硅胶 Rp-C₁₈(50 和 70 μm); 柱色谱用凝胶 Sepha-

dex LH-20 (日本三菱); 薄层硅胶层析板(烟台黄务); 反相硅胶层析板(德国 Merck); 氯仿、乙酸乙酯、甲醇、盐酸等试剂均为分析纯。

1.3 提取和分离

交趾黄檀心材 5.0 kg 用工业酒精浸提 3 次, 依次为 72、48 和 48 h, 减压浓缩后合并得到总浸膏, 再溶于适量水中得悬浊液, 倒入分液漏斗加入乙酸乙酯溶剂进行萃取, 合并 3 次萃取液再减压浓缩, 最后得到乙酸乙酯部分 250.0 g。

取乙酸乙酯部分 235.0 g, 采用硅胶(100~200 目)柱色谱进行分离, 依次以正己烷-乙酸乙酯(7:1~1:1)为洗脱剂进行梯度洗脱, 每次 1 L 收集洗脱液, 各洗脱液减压浓缩后用 TLC 板检查, 合并主点相似洗脱液, 共计得到 13 个组分 Fr-1~Fr-13。Fr-2 采用硅胶柱色谱分离, 以正己烷-乙酸乙酯(50:1~10:1)为洗脱剂进行梯度洗脱, 收集洗脱液, 合并相似组分, 共计得到 8 个亚组分 Fr-2-1~Fr-2-8。Fr-2-8 采用 ODS-C₁₈ 反相柱层析分离, 以 97% 甲醇-水为流动相, 从洗脱液中析出白色针状结晶, 即为化合物 **10** (2.5 mg) (图 1)。Fr-3 采用硅胶柱色谱分离, 以正己烷-乙酸乙酯(50:1~1:1)为洗脱剂进行梯度洗脱, 共计得到 6 个亚组分 Fr-3-1~Fr-3-6。其中 Fr-3-4 采用凝胶(甲醇)柱色谱等度洗脱得到化

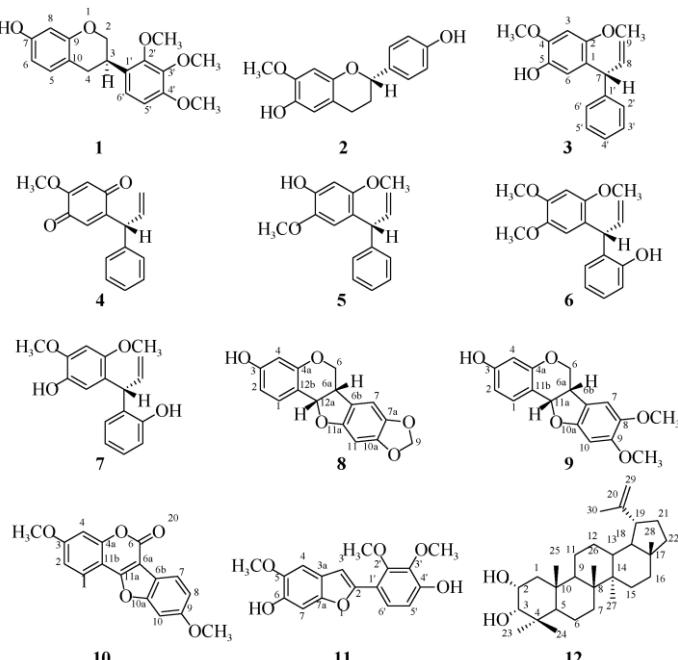


图 1 化合物 1~12 的结构

Fig. 1 Structures of compounds 1~12

合物 **3** (7.5 mg)。Fr-3-6 先后采用凝胶柱色谱(氯仿-甲醇)等度洗脱、ODS 反相柱色谱(甲醇-水)梯度洗脱, 得化合物 **4** (10.2 mg)。Fr-4 采用凝胶柱(氯仿-甲醇 1:3)色谱分离, 得到 7 个亚组分 Fr-4-1~Fr-4-7。Fr-4-3 采用正相硅胶柱色谱、Sephadex LH-20 凝胶柱色谱和制备薄层硅胶层析, 得到化合物 **5** (15.3 mg)、**6** (18.2 mg) 和 **12** (2.1 mg)。Fr-5 采用硅胶柱(氯仿-甲醇 100:1~10:1)色谱分离, 依次梯度洗脱后经过合并得亚组分 Fr-5-1~Fr-5-17。有无色结晶从 Fr-5-4 中析出来, 即为化合物 **7** (20.0 mg)。Fr-5-6 采用硅胶柱色谱分离, 经正己烷-乙酸乙酯(4:1~1:1)梯度洗脱得 13 个亚组分, Fr-5-6-10 经反复凝胶柱色谱和硅胶柱色谱分离, 得到化合物 **8** (25.5 mg)。Fr-5-6-12 采用硅胶柱色谱分离, 以正己烷-丙酮(8:1~3:1)梯度洗脱得到 56 个组分, 其中 Fr-5-6-12-6 经硅胶柱色谱分离, 以正己烷-乙酸乙酯(4:1)等度洗脱, 得到化合物 **1** (11.1 mg), Fr-5-6-12-11 经凝胶柱(甲醇)层析及薄层硅胶层析板制备得到化合物 **2** (2.5 mg) 和 **9** (3.2 mg)。Fr-7 采用硅胶柱色谱(氯仿-甲醇 500:1~50:1)和凝胶(甲醇)柱色谱分离, 有淡黄色结晶从组分 Fr-7-11-18 中析出, 即为化合物 **11** (3.8 mg)。

1.4 结构鉴定

化合物 1 无色结晶; ESI-MS *m/z*: 339 [M + Na]⁺, 655 [2M + Na]⁺, 315 [M - H]⁻, 分子式为 C₁₈H₂₀O₅; ¹H NMR (400 MHz, CDCl₃): δ 6.94 (1H, d, *J* = 8.1 Hz, H-5), 6.80 (1H, d, *J* = 8.6 Hz, H-6'), 6.66 (1H, d, *J* = 8.7 Hz, H-5'), 6.40 (1H, dd, *J* = 8.1, 2.5 Hz, H-6), 6.37 (1H, d, *J* = 2.4 Hz, H-8), 5.17 (br s, -OH), 4.28 (1H, ddd, *J* = 10.4, 3.4, 1.6 Hz, H-2a), 3.99 (1H, t, *J* = 10.3 Hz, H-2b), 3.90 (3H, s, H-2'), 3.89 (3H, s, H-3'), 3.85 (3H, s, H-4'), 3.54 (1H, m, H-3), 2.89 (2H, m, H-4); ¹³C NMR (100 MHz, CDCl₃): δ 155.1 (C-7), 155.0 (C-9), 152.6 (C-4'), 151.9 (C-2'), 142.3 (C-3'), 130.4 (C-5), 127.3 (C-1'), 121.4 (C-6'), 114.6 (C-10), 108.0 (C-6), 107.5 (C-5'), 103.2 (C-8), 70.4 (C-2), 61.3 (2'-OCH₃), 60.8 (3'-OCH₃), 56.0 (4'-OCH₃), 31.8 (C-3), 31.3 (C-4)。以上数据与文献[15]报道一致, 故鉴定为 7-hydroxy-2',3',4'-trimethoxyisoflavan。

化合物 2 无色结晶; ESI-MS *m/z*: 273 [M + H]⁺, 295 [M + Na]⁺, 567 [2M + Na]⁺, 271 [M - H]⁻, 分子式为 C₁₆H₁₆O₄; ¹H NMR [500 MHz, (CD₃)₂CO]:

δ 8.58 (1H, s, 4'-OH), 7.27 (2H, d, *J* = 8.4 Hz, H-2', 6'), 7.09 (1H, s, 6-OH), 6.84 (2H, d, *J* = 8.5 Hz, H-3', 5'), 6.54 (1H, s, H-5), 6.40 (1H, s, H-8), 4.87 (1H, dd, *J* = 10.3, 2.0 Hz, H-2), 3.78 (3H, s, 7-OCH₃), 2.86 (1H, m, H-4a), 2.63 (1H, ddd, *J* = 16.2, 5.3, 2.9 Hz, H-4b), 2.10 (1H, m, H-3a), 1.96 (1H, m, H-3b); ¹³C NMR [125 MHz, (CD₃)₂CO]: δ 158.0 (C-4'), 149.2 (C-7), 147.6 (C-9), 141.2 (C-6), 134.2 (C-1'), 128.3 (C-2', 6'), 116.0 (C-3', 5'), 115.9 (C-5), 114.2 (C-10), 101.8 (C-8), 78.2 (C-2), 56.4 (7-OCH₃), 31.0 (C-3), 25.4 (C-4)。以上数据与文献[6]报道基本一致, 故鉴定为 6,4'-dihydroxy-7-methoxyflavan。

化合物 3 棕色油状固体; ESI-MS *m/z*: 269 [M - H]⁻, 271 [M + H]⁺, 293 [M + Na]⁺, 分子式为 C₁₇H₁₈O₃; ¹H NMR (400 MHz, CDCl₃): δ 7.22~7.09 (5H, m, B-ring), 6.65 (1H, s, H-6), 6.43 (1H, s, H-3), 6.18 (1H, ddd, *J* = 17.0, 10.1, 6.7 Hz, H-8), 5.11 (2H, overlapped, H-9a, -OH), 5.00 (1H, d, *J* = 6.6 Hz, H-7), 4.84 (1H, d, *J* = 17.1 Hz, H-9b), 3.81 (3H, s, -OCH₃), 3.64 (3H, s, -OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ 150.3 (C-2), 144.8 (C-4), 143.0 (C-1'), 140.2 (C-8), 139.1 (C-5), 128.3 (C-3', 5'), 127.9 (C-2', 6'), 125.7 (C-4'), 124.4 (C-1), 115.7 (C-9), 115.0 (C-6), 97.1 (C-3), 56.7 (4-OCH₃), 55.9 (2-OCH₃), 46.7 (C-7)。以上数据与文献[16]报道一致, 故鉴定为 *R*-dalbergiphenol。

化合物 4 棕黄色粉末; ESI-MS *m/z*: 255 [M + H]⁺, 277 [M + Na]⁺, 531 [2M + Na]⁺, 253 [M - H]⁻, 分子式为 C₁₆H₁₄O₃; ¹H NMR (400 MHz, CDCl₃): δ 7.34~7.16 (5H, m, B-ring), 6.49 (1H, s, H-6), 6.10 (1H, ddd, *J* = 17.0, 10.2, 6.7 Hz, H-8), 5.92 (1H, s, H-3), 5.28 (1H, d, *J* = 10.2 Hz, H-9a), 5.00 (1H, d, *J* = 17.2 Hz, H-9b), 3.81 (1H, s, -OCH₃), 4.93 (1H, d, *J* = 6.6 Hz, H-7); ¹³C NMR (100 MHz, CDCl₃): δ 186.5 (C-2), 182.6 (C-5), 158.7 (C-4), 151.2 (C-1), 139.5 (C-1'), 137.4 (C-8), 131.8 (C-4'), 129.0 (C-3', 5'), 128.8 (C-2', 6'), 127.4 (C-6), 118.4 (C-9), 108.1 (C-3), 56.5 (4-OCH₃), 47.2 (C-7)。以上数据与文献[17]报道一致, 故鉴定为 *R*-4-methoxydalbergione。

化合物 5 棕黄色油状固体; ESI-MS *m/z*: 271 [M + H]⁺, 293 [M + Na]⁺, 563 [2M + Na]⁺, 269 [M - H]⁻, 分子式为 C₁₇H₁₈O₃; ¹H NMR (400 MHz, CDCl₃): δ 7.39~7.17 (5H, m, B-ring), 6.58 (1H, s, H-6), 6.45 (1H, s, H-3), 6.31 (1H, ddd, *J* = 16.9, 10.2, 6.5 Hz,

H-8), 5.30 (1H, d, $J = 10.2$ Hz, H-9a), 5.02 (1H, d, $J = 17.2$ Hz, H-9b), 4.88 (2H, overlapped, H-7, -OH), 3.80 (3H, s, 2-OCH₃), 3.75 (3H, s, 5-OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ 148.5 (C-2), 147.6 (C-4), 142.9 (C-5), 141.5 (C-1'), 139.5 (C-8), 128.6 (C-3', 5'), 128.5 (C-2', 6'), 126.7 (C-4'), 119.7 (C-1), 116.9 (C-9), 113.3 (C-6), 101.6 (C-3), 56.5 (5-OCH₃), 55.8 (2-OCH₃), 48.9 (C-7)。以上数据与文献[18]报道一致, 故鉴定为 mimosifoliol。

化合物 6 无色结晶; ESI-MS m/z : 301 [M + H]⁺, 323 [M + Na]⁺, 623 [2M + Na]⁺, 299 [M - H]⁻, 分子式为 C₁₈H₂₀O₄; ¹H NMR (400 MHz, CDCl₃): δ 7.18~7.10 (2H, m, B-ring), 6.90~6.83 (2H, m, B-ring), 6.69 (1H, s, H-6), 6.55 (1H, s, H-3), 6.34 (1H, m, H-8), 6.06 (1H, s, 2'-OH), 5.29 (1H, d, $J = 10.3$ Hz, H-9a), 5.22 (1H, d, $J = 5.6$ Hz, H-7), 5.04 (1H, d, $J = 17.2$ Hz, H-9b), 3.76 (3H, s, -OCH₃), 3.87 (3H, s, -OCH₃), 3.86 (3H, s, -OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ 150.1 (C-2), 153.8 (C-2'), 148.5 (C-4), 143.7 (C-5), 139.0 (C-8), 129.2 (C-1'), 128.3 (C-4'), 127.7 (C-6'), 121.3 (C-1), 120.6 (C-5'), 116.8 (C-9), 116.3 (C-3'), 113.2 (C-6), 97.9 (C-3), 57.0 (4-OCH₃), 56.6 (5-OCH₃), 56.1 (2-OCH₃), 40.2 (C-7)。以上数据与文献[19]报道一致, 故鉴定为 R-5-O-methylatifolin。

化合物 7 无色结晶; ESI-MS m/z : 287 [M + H]⁺, 309 [M + Na]⁺, 595 [2M + Na]⁺, 285 [M - H]⁻, 分子式为 C₁₇H₁₈O₄; ¹H NMR (400 MHz, CDCl₃): δ 7.18~7.10 (2H, m, B-ring), 6.89~6.81 (2H, m, B-ring), 6.75 (1H, s, H-6), 6.52 (1H, s, H-3), 6.32 (1H, m, H-8), 6.05 (1H, s, 2'-OH), 5.32~5.22 (2H, overlapped, H-9a, 5-OH), 5.19 (1H, d, $J = 5.8$ Hz, H-7), 5.04 (1H, dt, $J = 17.1, 1.4$ Hz, H-9b), 3.87 (3H, s, -OCH₃), 3.85 (3H, s, -OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ 153.7 (C-2'), 149.4 (C-2), 145.5 (C-4), 140.1 (C-5), 139.0 (C-8), 129.4 (C-1'), 128.4 (C-4'), 127.7 (C-6'), 122.5 (C-1), 120.6 (C-5'), 116.7 (C-9), 116.3 (C-3'), 115.2 (C-6), 97.0 (C-3), 57.1 (4-OCH₃), 56.1 (2-OCH₃), 40.0 (C-7)。以上数据与文献[19]报道一致, 故鉴定为 R-latifolin。

化合物 8 白色粉末; ESI-MS m/z : 283 [M - H]⁻, 307 [M + Na]⁺, 285 [M + H]⁺, 分子式为 C₁₆H₁₂O₅; ¹H NMR (400 MHz, CDCl₃): δ 7.36 (1H, d, $J = 8.4$ Hz, H-1), 6.72 (1H, s, H-7), 6.55 (1H, dd, $J = 8.4, 2.4$ Hz,

H-2), 6.44 (1H, s, H-11), 6.42 (1H, d, $J = 2.4$ Hz, H-4), 5.92 (1H, d, $J = 0.9$ Hz, H-9 α), 5.90 (1H, d, $J = 0.9$ Hz, H-9 β), 5.47 (1H, d, $J = 6.9$ Hz, H-12a), 5.42 (1H, s, -OH), 4.22 (1H, dd, $J = 11.0, 5.0$ Hz, H-6 α), 3.64 (1H, t, $J = 11.0$ Hz, H-6 β), 3.47 (1H, m, H-6a); ¹³C NMR (100 MHz, CDCl₃) δ : 157.1 (C-3), 156.6 (C-4a), 154.2 (C-11a), 148.1 (C-10a), 141.7 (C-7a), 132.1 (C-1), 117.9 (C-6b), 112.6 (C-12b), 109.8 (C-2), 104.7 (C-7), 103.6 (C-4), 101.3 (C-9), 93.8 (C-11), 78.5 (C-12a), 66.4 (C-6), 40.1 (C-6a)。以上数据与文献[20]报道基本一致, 故鉴定为 maackianin。

化合物 9 棕色粉末; ESI-MS m/z : 301 [M + H]⁺, 323 [M + Na]⁺, 623 [2M + Na]⁺, 299 [M - H]⁻, 分子式为 C₁₇H₁₆O₅; ¹H NMR [500 MHz, (CD₃)₂CO]: δ 8.75 (1H, s, 3-OH), 7.29 (1H, d, $J = 8.4$ Hz, H-1), 7.00 (1H, s, H-7), 6.55 (1H, dd, $J = 8.4, 2.4$ Hz, H-2), 6.48 (1H, s, H-10), 6.36 (1H, d, $J = 2.3$ Hz, H-4), 5.46 (1H, d, $J = 7.0$ Hz, H-11a), 4.26 (1H, dd, $J = 10.6, 4.5$ Hz, H-6 α), 3.75 (3H, s, 9-OCH₃), 3.74 (3H, s, 8-OCH₃), 3.56 (1H, m, H-6a), 3.63 (1H, m, H-6 β); ¹³C NMR [125 MHz, (CD₃)₂CO]: δ 159.8 (C-3), 157.8 (C-4a), 155.1 (C-10a), 151.8 (C-9), 145.0 (C-8), 133.1 (C-1), 118.7 (C-6b), 113.1 (C-11b), 111.6 (C-7), 110.6 (C-2), 104.1 (C-4), 96.9 (C-10), 79.1 (C-11a), 67.2 (C-6), 57.7 (8-OCH₃), 56.5 (9-OCH₃), 41.4 (C-6a)。以上数据与文献[21]报道一致, 故鉴定为 secundiflorol I。

化合物 10 白色针状结晶; ESI-MS m/z : 297 [M + H]⁺, 319 [M + Na]⁺, 615 [2M + Na]⁺, 295 [M - H]⁻, 分子式为 C₁₇H₁₂O₅; ¹H NMR (400 MHz, CDCl₃): δ 7.96 (1H, d, $J = 8.6$ Hz, H-1), 7.89 (1H, d, $J = 8.4$ Hz, H-7), 7.18 (1H, d, $J = 1.8$ Hz, H-10), 7.05 (1H, dd, $J = 8.4, 2.0$ Hz, H-8), 6.99 (2H, m, H-2, 4), 3.92 (3H, s, -OCH₃), 3.91 (3H, s, -OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ 162.6 (C-3), 160.1 (C-11a), 159.2 (C-9), 158.5 (C-6), 156.5 (C-10a), 155.1 (C-4a), 122.4 (C-7), 121.6 (C-1), 116.6 (C-6b), 113.2 (C-2), 113.0 (C-8), 106.1 (C-11b), 103.5 (C-6a), 101.4 (C-4), 96.8 (C-10), 55.9 (-OCH₃), 55.8 (-OCH₃)。以上数据与文献[22]报道一致, 故鉴定为 3,9-dimethoxy-6H-benzofufo[3,2-c]chromen-6-one。

化合物 11 黄色粉末; ESI-MS m/z : 317 [M + H]⁺, 339 [M + Na]⁺, 655 [2M + Na]⁺, 315 [M - H]⁻, 分子式为 C₁₇H₁₆O₆; ¹H NMR (400 MHz, DMSO-*d*₆):

δ 7.24 (1H, d, J = 8.8 Hz, H-6'), 7.04 (1H, s, H-4), 6.99 (1H, s, H-3), 6.93 (1H, s, H-7), 6.73 (1H, d, J = 8.8 Hz, H-5'), 3.78 (3H, s, 5-OCH₃), 3.81 (3H, s, 2'-OCH₃), 3.80 (3H, s, 3'-OCH₃); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 148.6 (C-2'), 150.4 (C-4'), 148.2 (C-2), 145.2 (C-7a), 145.0 (C-5), 144.6 (C-6), 139.7 (C-3'), 120.5 (C-3a), 117.2 (C-1'), 115.4 (C-6'), 107.2 (C-5'), 103.8 (C-3), 102.6 (C-4), 97.7 (C-7), 58.9 (3'-OCH₃), 56.0 (2'-OCH₃), 55.8 (5-OCH₃)。以上数据与文献[23]报道一致, 故鉴定为 mucodianin C。

化合物 12 白色粉末; ESI-MS *m/z*: 441 [M - H]⁻, 465 [M + Na]⁺, 907 [2M + Na]⁺, 分子式为 C₃₀H₅₀O₂; ¹H NMR (400 MHz, CDCl₃): δ 4.57 (1H, s, H-29b), 4.69 (1H, d, J = 2.0 Hz, H-29a), 3.98 (1H, ddd, J = 14.7, 7.1, 4.1 Hz, H-2), 3.42 (1H, s, H-3), 2.38 (1H, td, J = 11.0, 5.8 Hz, H-19), 2.04 (1H, d, J = 2.8 Hz, H-21), 1.69 (3H, s, H-30), 1.02 (3H, s, H-26), 1.00 (3H, s, H-27), 0.95 (3H, s, H-24), 0.88 (3H, s, H-25), 0.84 (3H, s, H-23), 0.78 (3H, s, H-28); ¹³C NMR (100 MHz, CDCl₃): δ 150.9 (C-20), 109.4 (C-29), 79.0 (C-3), 66.7 (C-2), 50.1 (C-9), 48.3 (C-5), 48.2 (C-18), 48.0 (C-19), 43.0 (C-14), 42.9 (C-17), 42.1 (C-1), 41.0 (C-8), 40.0 (C-22), 38.6 (C-10), 38.3 (C-4), 38.0 (C-13), 35.6 (C-16), 34.0 (C-7), 29.8 (C-21), 28.5 (C-23), 27.4 (C-15), 25.0 (C-12), 21.6 (C-24), 20.9 (C-11), 19.3 (C-30), 18.0 (C-6, 28), 17.1 (C-25), 16.0 (C-26), 14.6 (C-27)。以上数据与文献[24-25]报道基本一致, 故鉴定为 lup-(20)29-ene-2 α ,3 α -diol。

2 结果和讨论

从交趾黄檀心材中分离鉴定得到 12 个化合物, 分别为: 7-hydroxy-2',3',4'-trimethoxyisoflavan (**1**), 6,4'-dihydroxy-7-methoxyflavan (**2**), *R*-dalbergiphenol (**3**), *R*-4-methoxydalbergione (**4**), mimosifoliol (**5**), *R*-5-O-methylattyfolin (**6**), *R*-latifolin (**7**), maackian (**8**), secundiflorol I (**9**), 3,9-dimethoxy-6H-benzofufo [3,2-c] chromen-6-one (**10**), mucodianin C (**11**) 和 lup-(20)29-ene-2 α ,3 α -diol (**12**)。化合物 **1**、**5**、**8~12** 为首次从交趾黄檀心材中分离得到。

在抗骨质疏松试验中, 化合物 **3** 能显著提高骨细胞的矿化能力, 显著上调 BMP-2 和 RunX2 的 mRNA 水平, 并能显著提高骨钙素和 I 型胶原的

mRNA 表达水平^[26]。化合物 **4**、**6** 和 **7** 能显著抑制 5 α -还原酶活性, 并能竞争性抑制二氢睾酮与受体的形成, 从而有望治疗雄激素活性过高所致的疾病, 包括多毛症、痤疮、前列腺肥大、前列腺癌等^[5]。化合物 **4** 对 β -葡萄糖醛酸苷酶和 NO 生成均表现出不错的抑制效果, 提示其具有较强的抗炎活性。此外, 有报道指出, 化合物 **4** 还具有抗肿瘤、抗过敏、抗菌及疟原虫抑制活性^[27]。化合物 **5** 在 DNA 链断裂试验中显示出较弱的活性^[18]。本课题从交趾黄檀中分离得到的这 5 个已知新黄酮类成分, 特征性明显, 生物活性多样, 将为进一步发掘该属植物中潜在的新药资源提供参考价值。

参考文献

- [1] LIN G W. The kind of main wood that national standard mahogany included [J]. For Ecol, 2010(3): 24. doi: 10.13552/j.cnki.lyyst.2010.03.016.
- [2] WU P Y, ZHANG Y B, ZHANG J W. A new rosewood species: *Dalbergia cochinchinensis* [J]. Fujian Sci Technol Trop Crops, 2016, 41(4): 51–54. doi: 10.3969/j.issn.1006-2327.2016.04.016.
吴培衍, 张荣标, 张金文. 红木树种新贵——交趾黄檀 [J]. 福建热作科技, 2016, 41(4): 51–54. doi: 10.3969/j.issn.1006-2327.2016.04.016
- [3] PALASUWAN A, SOOGARUN S, LERTLUM T, et al. Inhibition of heinz body induction in an *in vitro* model and total antioxidant activity of medicinal thai plants [J]. Asian Pac J Cancer Prev, 2005, 6(4): 458–463.
- [4] DONNELLY D M X, NANGLE B J, PRENDERGAST J P, et al. *Dalbergia* species: V. Isolation of R-5-O-methylattyfolin from *Dalbergia cochinchinensis* Pierre. [J]. Phytochemistry, 1968, 7(4): 647–649. doi: 10.1016/S0031-9422(00)88241-2.
- [5] KUROYANAGI M, UENO A, HIRAYAMA Y, et al. Anti-androgen active constituents from *Dalbergia cochinchinensis* Pierre [J]. Nat Med (Tokyo, Jpn), 1996, 50(6): 408–412.
- [6] PATHAK V, SHIROTA O, SEKITA S, et al. Antiandrogenic phenolic constituents from *Dalbergia cochinchinensis* [J]. Phytochemistry, 1997, 46(7): 1219–1223. doi: 10.1016/S0031-9422(97)80015-5.
- [7] SVASTI J, SRISOMSAP C, TECHASAKUL S, et al. Dalcochinin-8'-O- β -D-glucoside and its β -glucosidase enzyme from *Dalbergia cochinchinensis* [J]. Phytochemistry, 1999, 50(5): 739–743. doi: 10.1016/S0031-9422(98)00552-4.

- [8] SHIROTA O, PATHAK V, SEKITA S, et al. Phenolic constituents from *Dalbergia cochinchinensis* [J]. *J Nat Prod*, 2003, 66(8): 1128–1131. doi: 10.1021/np0300683.
- [9] AREE T, TIP-PYANG S, SEESUKPHRONRARAK S, et al. 2-(5,7-Dihydroxy-4-oxo-4H-chromen-3-yl)-5-methoxy-1,4-benzoquinone iso-flavonequinone) [J]. *Acta Crystallogr Sect E: Struct Rep Online*, 2003, E59(3): o363–o365. doi: 10.1107/S1600536803003684.
- [10] AREE T, TIP-PYANG S, PARAMAPOJN S, et al. 3,9-Dimethoxy-6a,11a-dihydro-6H-benzo [4,5]furo [3,2-c]chromene-4,10-diol monohydrate [J]. *Acta Crystallogr Sect E: Struct Rep Online*, 2003, E59(3): o381–o383. doi: 10.1107/S1600536803004227.
- [11] LIU R H, WEN X C, LI Y Y, et al. Chemical constituents from *Dalbergia cochinchinensis* [J]. *J. Chin Med Mat*, 2015, 38(9): 1868–1871. doi: 10.13863/j.issn1001-4454.2015.09.017.
刘荣华, 温新潮, 李于益, 等. 交趾黄檀化学成分研究 [J]. 中药材, 2015, 38(9): 1868–1871. doi: 10.13863/j.issn1001-4454.2015.09.017.
- [12] LIU R H, WEN X C, ZHANG P Z, et al. Chemical constituents of isoflavonoids from *Dalbergia cochinchinensis* [J]. *Chin Trad Herb Drugs*, 2015, 46(19): 2851–2855. doi: 10.7501/j.issn.0253-2670.2015.19.006.
刘荣华, 温新潮, 张普照, 等. 交趾黄檀异黄酮类化学成分研究 [J]. 中草药, 2015, 46(19): 2851–2855. doi: 10.7501/j.issn.0253-2670.2015.19.006.
- [13] LIU R H, WEN X C, SHAO F, et al. Flavonoids from heartwood of *Dalbergia cochinchinensis* [J]. *Chin Herb Med*, 2016, 8(1): 89–93. doi: 10.1016/S1674-6384(16)60014-X.
- [14] LIU R H, LI Y Y, SHAO F, et al. A new chalcone from the heartwood of *Dalbergia cochinchinensis* [J]. *Chem Nat Compd*, 2016, 52(3): 405–408. doi: 10.1007/s10600-016-1659-7.
- [15] EL-SEBAKHY N A, ASAAD A M, ABDALLAH R M, et al. Antibacterial isoflavans from *Astragalus species* [J]. *Phytochemistry*, 1994, 36(6): 1387–1389. doi: 10.1016/S0031-9422(00)89728-9.
- [16] MUANGNOICHAROEN N, FRAHM A W. Neoflavanoids of *Dalbergia parviflora* [J]. *Phytochemistry*, 1982, 21(3): 767–772. doi: 10.1016/0031-9422(82)83184-1.
- [17] KHAN W N, LODHI M A, ALI I, et al. New natural urease inhibitors from *Ranunculus repens* [J]. *J Enzyme Inhib Med Chem*, 2006, 21(1): 17–19. doi: 10.1080/14756360500319210.
- [18] FULLAS F, KORNBERG L J, WANI M C, et al. Two new aromatic constituents from the rootwood of *Aeschynomene mimosifolia* [J]. *J Nat Prod*, 1996, 59(2): 190–192. doi: 10.1021/np960052v.
- [19] SEKINE N, ASHITANI T, MURAYAMA T, et al. Bioactivity of latifolin and its derivatives against termites and fungi [J]. *J Agric Food Chem*, 2009, 57(13): 5707–5712. doi: 10.1021/jf900719p.
- [20] PARK J A, JA KIM H, JIN C, et al. A new pterocarpan, (−)-maackiain sulfate, from the roots of *Sophora subprostrata* [J]. *Arch Pharm Res*, 2003, 26(12): 1009–1013. doi: 10.1007/BF02994750.
- [21] TIAN F, MC LAUGHLIN J L. Bioactive flavonoids from the black locust tree, *Robinia pseudoacacia* [J]. *Pharm Biol*, 2000, 38(3): 229–234. doi: 10.1076/1388-0209(200007)3831-SFT229.
- [22] TANG L N, PANG Y L, YAN Q, et al. Synthesis of coumestan derivatives via FeCl_3 -mediated oxidative ring closure of 4-gydroxy coumarins [J]. *J Org Chem*, 2011, 76(8): 2744–2752. doi: 10.1021/jo2000644.
- [23] GONG T, WANG D X, YANG Y, et al. A novel 3-arylcoumarin and three new 2-arylbenzofurans from *Mucuna birdwoodiana* [J]. *Chem Pharm Bull*, 2010, 58(2): 254–256. doi: 10.1248/cpb.58.254.
- [24] KUMAR N, SESHADEVI T R. Triterpenoids of *Pterocarpus santalinus*: constitution of a new lupene diol [J]. *Phytochemistry*, 1975, 14(2): 521–523. doi: 10.1016/0031-9422(75)85121-1.
- [25] PAN Z H, WANG Y Y, LI M M, et al. Terpenoids from *Salvia trijuga* [J]. *J Nat Prod*, 2010, 73(6): 1146–1150. doi: 10.1021/np100250w.
- [26] KUMAR P, KUSHWAHA P, KHEDGIKAR V, et al. Neoflavanoids as potential osteogenic agents from *Dalbergia sissoo* heartwood [J]. *Bioorg Med Chem Lett*, 2014, 24(12): 2664–2668. doi: 10.1016/j.bmcl.2014.04.056.
- [27] LIU R H, LIN S, ZHANG P Z, et al. Neoflavanoids and their pharmacological activities in *Dalbergia genus* [J]. *China J Chin Mat Med*, 2017, 42(24): 4707–4715. doi: 10.19540/j.cnki.cjemm.20170928.013.
刘荣华, 林帅, 张普照, 等. 黄檀属植物新黄酮类化学成分与药理活性研究进展 [J]. 中国中药杂志, 2017, 42(24): 4707–4715. doi: 10.19540/j.cnki.cjemm.20170928.013.