热带亚热带植物学报　2017, 25(6): 610 ~ 616
Journal of Tropical and Subtropical Botany

大叶桃花心木根的化学成分研究

米承能[1,2], 梅文莉[1], 李薇[1], 王军[1], 蔡彩虹[1], 李绍鹏[2], 戴好富[1*]
(1. 中国热带农业科学院热带生物技术研究所，农业部热带作物生物学与遗传资源利用重点实验室，海口 571101；2. 海南大学热带农林学院，海口 570228)

摘要：为了解大叶桃花心木(*Swietenia macrophylla* King)的化学成分，从其根的乙醇提取物中共分离得到 13 个化合物，经理化性质和波谱分析，分别鉴定为 1,5-dihydroxyxanthone (**1**)、1,6-dihydroxy-5-methoxyxanthone (**2**)、euxanthone (**3**)、1,2-dimethoxyxanthone (**4**)、(+)儿茶素 (**5**)、(+) sesamin (**6**)、*bis*-(2-ethylhexyl)phthalate (**7**)、3-oxotirucalla-7,24-dien-21-oic acid (**8**)、(20*S*)-3β-acetoxy-24-methylenedam-maran-20-ol (**9**)、cycloeucalenol (**10**)、β-谷甾醇 (**11**)、7-deacetoxy-7-oxogedunin (**12**)和 7-deacetoxy-7α-hydroxygedunin (**13**)，其中化合物 **1**~**4**、**6~10** 和 **13** 为首次从桃花心木属植物中分离得到，且化合物 **4** 对乙酰胆碱酯酶具有一定的抑制活性。

关键词：大叶桃花心木；化学成分；呫酮；柠檬苦素；乙酰胆碱酯酶抑制活性
doi: 10.11926/jtsb.3754

Chemical Constituents from the Roots of *Swietenia macrophylla* King

MI Cheng-neng[1,2], MEI Wen-li[1], LI Wei[1], WANG Jun[1], CAI Cai-hong[1], LI Shao-peng[2], DAI Hao-fu[1*]
(1. *Key Laboratory of Biology and Genetic Resources of Tropical Crops, Ministry of Agriculture, Institute of Tropical Bioscience and Biotechnology, Academy of Tropical Agricultural Sciences*, Haikou 571101, China; 2. *Institute of Tropical Agriculture and Forestry, Hainan University*, Haikou 570228, China)

Abstract: In order to understand the chemical constituents of *Swietenia macrophylla* King, thirteen compounds were isolated from its roots. On the basis of spectral data, they were identified as 1,5-dihydroxyxanthone (**1**), 1,6-dihydroxy-5-methoxyxanthone **(2)**, euxanthone (**3**), 1,2-dimethoxyxanthone (**4**), (+) catechin (**5**), (+) sesamin (**6**), *bis*-(2-ethylhexyl) phthalate (**7**), 3-oxotirucalla-7,24-dien-21-oic acid (**8**), (20*S*)-3β-acetoxy-24-methylenedam-maran-20-ol (**9**), cycloeucalenol (**10**), β-sitosterol (**11**), 7-deacetoxy-7-oxogedunin (**12**) and 7-deacetoxy-7α-hydroxygedunin (**13**). Among them, compounds **1**−**4**, **6**−**10** and **13** were isolated from the genus *Swietenia* for the first time. Moreover, compound **4** exhibited inhibitory activity against acetylcholinesterase.

Key words: *Swietenia macrophylla*; Chemical constituent; Xanthone; Limonoid; Anti-acetylcholinesterase activity

大叶桃花心木(*Swietenia macrophylla* King)为楝科(Meliaceae)桃花心木属植物，原产于拉丁美洲，广泛分布于整个美洲的热带地区，特别是中美洲、墨西哥和玻利维亚[1]。现已在全球的热带地区广泛栽培，在我国海南、广东、广西、福建、云南、台湾等地也有种植[2]，主要用于绿化造林[3]。其种子在马来西亚及印度尼西亚等地被用来治疗糖尿病、高血压、疟疾等疾病以及缓解疼痛[1,4]。近年来，为了寻找大叶桃花心木中的生物活性成分，对其地上部分的化学成分及生物活性进行了较为系统的研

收稿日期: 2017−04−21　　**接受日期**：2017−06−19
基金项目：海南省重点研发计划项目(社会发展)(ZDYF2016140)；中国热带农业科学院基本科研业务费专项基金(17CXTD-15)；海南自然科学基金创新研究团队项目(2017CXTD020)资助
This work was supported by the Key Research Project for Social Development in Hainan Province (Grant No. ZDYF2016140), the National Nonprofit Institute Research Grant of CATAS-ITBB (Grant No. 17CXTD-15), and the Natural Science Foundation of Hainan (Grant No. 2017CXTD020).
作者简介：米承能(1988~)，男，研究生，从事天然产物化学研究。E-mail: 1034594309@qq.com
* 通信作者 Corresponding author. E-mail: daihaofu@itbb.org.cn

究，分离的化学成分以结构复杂多变，氧化程度高的柠檬苦素类化合物为主，这类化合物具有抗氧化[5]、拒食[6–8]、细胞毒[9–10]、抗病毒[11]等多种活性。然而，对大叶桃花心木根的化学成分研究目前还未见报道，本研究从大叶桃花心木根的乙醇提取物的乙酸乙酯部分分离鉴定了 13 个化合物，并检测了化合物对乙酰胆碱酯酶活性的抑制作用，为大叶桃花心木的开发利用提供科学依据。

1 材料和方法

1.1 材料

试验材料于 2014 年 4 月采集于海南省海口市中国热带农业科学院，经中国热带农业科学院热带生物技术研究所刘寿柏博士鉴定为楝科桃花心木属植物大叶桃花心木(*Swietenia macrophylla* King)，凭证标本(DYTHXM201404)存放于中国热带农业科学院热带生物技术研究所。

1.2 仪器和试剂

薄层层析硅胶和柱色谱硅胶(200~300 目)为青岛海洋化工厂产品，Sephadex LH-20 为 Merck 公司产品，ODS (20~45 μm)为 Fuji 公司产品；MS 谱采用 Autospec-3000 质谱仪测定；NMR 采用 Brucker AV-500 型超导核磁仪测定，以 TMS 为内标；旋光仪为 Rudolph Research Analytical 生产的 Rudolph Autopol III polarimeter 型旋光仪；乙酰胆碱酯酶、SHENGCHAN 碘化硫代乙酰胆碱、二硫代二硝基苯甲酸(DNTB)和他克林均购自 Sigma 公司；酶标仪采用美国宝特公司 ELX-800 酶标仪，超净工作台为上海博讯实业有限公司医疗设备厂产品。

1.3 提取和分离

大叶桃花心木根(干重 57.0 kg)用 95%乙醇室温浸提 3 次，每次 7 d，合并提取液减压浓缩，得乙醇提取物(8.0 kg)。将提取物分散于水中成悬浊液，依次用石油醚和乙酸乙酯萃取 3 次，减压浓缩，分别得石油醚萃取物(231.4 g)和乙酸乙酯萃取物(3931.0 g)。乙酸乙酯萃取物经硅胶柱色谱(200~300 目)，以氯仿-甲醇(10∶1)洗脱，收集得到 Fr.1 (573.0 g)。Fr.1 经减压硅胶柱层析(硅胶 H)，以石油醚-乙酸乙酯(0∶1~5∶1)和氯仿-甲醇(1∶0~0∶1)梯度洗脱，TLC 检测合并，共收集得到 17 个流份(Fr.1-1~Fr.1-17)。Fr.1-3 (18.3 g)反复经 Sephadex LH-20 和正相硅胶柱色谱，得到化合物 **7** (30.0 mg)和 **9** (18.7 mg)；Fr.1-4 (21.5 g)结晶析出化合物 **10** (30.0 mg)和 **11** (30.0 mg)； Fr.1-8 (19.5 g)经加压 ODS 柱层析，以甲醇-水(3∶7~1∶0)梯度洗脱，再反复经 Sephadex LH-20 和正相硅胶柱色谱分离得到化合物 **1** (6.1 mg)、**2** (2.2 mg)、**3** (13.1 mg)、**4** (5.4 mg)、**6** (3.4 mg)和 **8** (28.8 mg)；Fr.1-10 (153.8 g)经反复加压硅胶柱层色谱、Sephadex LH-20 柱色谱及加压 ODS 柱色谱，得到化合物 **12** (30.0 mg)和 **13** (30.0 mg)；Fr.1-17 (25.0 g)经反复 Sephadex LH-20 和硅胶柱色谱分离，重结晶得到化合物 **5** (30.0 mg)。

1.4 结构鉴定

化合物 1　黄色针状结晶(丙酮); ESI-MS *m/z*: 251 $[M + Na]^+$; $C_{13}H_8O_4$; ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.58 (1H, s, 1-OH), 7.72 (1H, dd, *J* = 8.3, 8.3 Hz, H-3), 7.58 (1H, dd, *J* = 1.6, 8.0 Hz, H-8), 7.34 (1H, dd, *J* = 1.6, 8.0 Hz, H-6), 7.28 (1H, dd, *J* = 8.0, 8.0 Hz, H-7), 7.08 (1H, d, *J* = 8.3 Hz, H-4), 6.80 (1H, d, *J* = 8.3 Hz, H-2); ^{13}C NMR (125 MHz, DMSO-d_6): δ 161.2 (C-1), 110.3 (C-2), 137.8 (C-3), 107.7 (C-4), 155.9 (C-4a), 146.6 (C-5), 121.4 (C-6), 124.7 (C-7), 115.0 (C-8), 121.2 (C-8a), 182.4 (C-9), 108.4 (C-9a), 145.5 (C-10a)。上述数据与文献[12]报道一致，故鉴定为 1,5-Dihydroxyxanthone。

化合物 2　黄色针状结晶(丙酮); ESI-MS *m/z*: 281 $[M + Na]^+$; $C_{14}H_{10}O_5$; ^{1}H NMR (500 MHz, acetone-d_6): δ 12.86 (1H, s, 1-OH), 7.88 (1H, d, *J* = 8.8 Hz, H-8), 7.69 (1H, dd, *J* = 8.3, 8.3 Hz, H-3), 7.07 (H, d, *J* = 8.3 Hz, H-4), 7.01 (H, d, *J* = 8.8 Hz, H-7), 6.78 (1H, d, *J* = 8.3 Hz, H-2), 4.02 (3H, s, 5-OMe); ^{13}C NMR (125 MHz, acetone-d_6): δ 162.9 (C-1), 111.2 (C-2), 137.5 (C-3), 107.8 (C-4), 157.1 (C-4a), 135.6 (C-5), 157.7 (C-6), 114.8 (C-7), 122.3 (C-8), 111.2 (C-8a), 182.3 (C-9), 109.0 (C-9a), 151.9 (C-10a), 61.8 (5-OMe)。上述数据与文献[13]报道一致，故鉴定为 1,6-Dihydroxy-5-methoxyxanthone。

化合物 3　黄色针状结晶(丙酮); ESI-MS *m/z*: 251 $[M + Na]^+$; $C_{13}H_8O_4$; ^{1}H NMR (500 MHz, acetone-d_6): δ 12.71 (1H, s, 1-OH), 9.10 (1H, s, 7-OH), 7.69 (1H, dd, *J* = 8.2, 8.2 Hz, H-3), 7.59 (1H, d, *J* = 3.0 Hz, H-8), 7.52 (1H, d, *J* = 9.0 Hz, H-5), 7.42 (1H,

dd, *J* = 3.0, 9.0 Hz, H-6), 6.99 (1H, d, *J* = 8.2 Hz, H-4), 6.76 (1H, d, *J* = 8.2 Hz, H-2); ^{13}C NMR (125 MHz, acetone-d_6): δ 162.7 (C-1), 110.5 (C-2), 137.8 (C-3), 107.8 (C-4), 157.3 (C-4a), 120.2 (C-5), 126.2 (C-6), 155.0 (C-7), 109.1 (C-8), 121.8 (C-8a), 183.0 (C-9), 109.1 (C-9a), 151.0 (C-10a)。上述数据与文献[14]报道一致，故鉴定为 Euxanthone。

化合物 4 黄色针状结晶(丙酮); ESI-MS *m/z*: 279 [M + Na]$^+$; $C_{15}H_{12}O_4$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (1H, dd, *J* = 8.0, 1.5 Hz, H-8), 7.67 (1H, dd, *J* = 8.0, 8.0 Hz, H-6), 7.41 (1H, d, *J* = 8.0 Hz, H-5), 7.36 (1H, d, *J* = 9.2 Hz, H-3), 7.34 (1H, dd, *J* = 8.0, 8.0 Hz, H-7), 7.24 (1H, d, *J* = 9.2 Hz, H-4), 4.02 (3H, s, 1-OMe), 3.94 (3H, s, 2-OMe); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.0 (C-1), 149.3 (C-2), 120.4 (C-3), 113.3 (C-4), 151.5 (C-4a), 117.5 (C-5), 134.6 (C-6), 123.8 (C-7), 126.9 (C-8), 122.3 (C-8a), 176.8 (C-9), 117.3 (C-9a), 155.5 (C-10a), 61.8 (1-OMe), 57.3 (2-OMe)。上述数据与文献[15]报道一致，故鉴定为 1,2-Dimethoxyxanthone。

化合物 5 白色针状结晶(氯仿-甲醇); $[\alpha]_D^{25}$ + 0.80 ° (*c* 1, MeOH), ESI-MS *m/z*: 313 [M + Na]$^+$; $C_{15}H_{14}O_6$; ^{1}H NMR (500 MHz, acetone-d_6): δ 6.89 (1H, d, *J* = 1.9 Hz, H-2′), 6.79 (1H, m, H-6′), 6.75 (1H, m, H-5′), 6.02 (1H, d, *J* = 2.3 Hz, H-8), 5.87 (1H, d, *J* = 2.3 Hz, H-6), 4.56 (1H, d, *J* = 7.9 Hz, H-2), 3.99 (1H, m, H-3), 2.91 (1H, dd, *J* = 5.4, 16.1 Hz, H-4a), 2.54 (1H, dd, *J* = 8.5, 16.1 Hz, H-4b); ^{13}C NMR (125 MHz, acetone-d_6): δ 82.6 (C-2), 68.3 (C-3), 28.8 (C-4), 157.2 (C-5), 96.1 (C-6), 157.7 (C-7), 95.4 (C-8), 156.8 (C-9), 100.6 (C-10), 132.1 (C-1′), 115.2 (C-2′), 145.7 (C-3′), 145.6 (C-4′), 115.7 (C-5′), 120.0 (C-6′)。上述数据与文献[16]报道一致，故鉴定为(+)儿茶素。

化合物 6 黄色油状物; $[\alpha]_D^{25}$ +62.8 ° (*c* 1, $CHCl_3$), ESI-MS *m/z*: 377 [M + Na]$^+$; $C_{20}H_{18}O_6$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.85 (2H, s, H-2′, H-2″), 6.80 (2H, d, *J* = 8.1 Hz, H-6′, H-6″), 6.78 (2H, d, *J* = 8.1 Hz, H-5′, H-5″), 5.95 (4H, s, 2×OCH_2O), 4.71 (2H, d, *J* = 3.6 Hz, H-2, H-6), 4.23 (2H, dd, *J* = 6.6, 8.8 Hz, H-4a, H-8a), 3.87 (2H, dd, *J* = 2.8, 8.8 Hz, H-4b, H-8b), 3.05 (2H, s, H-1, H-5); ^{13}C NMR (125 MHz, $CDCl_3$): δ 54.5 (C-1, C-5), 85.9 (C-2, C-6), 71.9 (C-4, C-8), 135.2 (C-1′, C-1″), 106.6 (C-2′, C-2″), 148.1 (C-3′, C-3″), 147.3 (C-4′, C-4″), 108.3 (C-5′, C-5″), 119.5 (C-6′, C-6″), 101.2 (OCH_2O)。上述数据与文献[17]报道一致，故鉴定为(+) Sesamin。

化合物 7 无色油状; ESI-MS *m/z*: 413 [M + Na]$^+$; $C_{24}H_{38}O_4$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (2H, dd, *J* = 3.4, 5.6 Hz, H-2), 7.52 (2H, dd, *J* = 3.4, 5.6 Hz, H-3), 4.21 (4H, dd, *J* = 6.0, 10.9 Hz, H-6), 1.68 (2H, t, *J* = 6.2 Hz, H-7), 1.29~1.46 (16H, m, H-8, H-9, H-10, H-12), 0.87~0.93 (12H, m, H-11, H-13); ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.6 (C-1), 128.9 (C-2), 131.0 (C-3), 167.9 (C-4), 68.2 (C-6), 38.8 (C-7), 30.5 (C-8), 29.0 (C-9), 23.1 (C-10), 14.2 (C-11), 23.8 (C-12), 11.1 (C-13)。上述数据与文献[18]报道一致，故鉴定为 *bis*-(2-Ethylhexyl) phthalate。

化合物 8 白色结晶(氯仿); $[\alpha]_D^{25}$ +7.8 ° (*c* 1, $CHCl_3$), ESI-MS *m/z*: 477 [M + Na]$^+$; $C_{30}H_{46}O_3$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.31 (1H, m, H-7), 5.08 (1H, t, *J* = 6.8 Hz, H-24), 2.73 (1H, dt, *J* = 5.3, 14.4 Hz, H-2a), 2.26 (1H, m, H-2b), 2.26 (1H, m, H-9), 2.26 (1H, m, H-20), 2.07 (2H, m, H-6), 2.05 (1H, m, H-17), 1.98 (2H, m, H-23), 1.94 (1H, m, H-1a), 1.73 (1H, m, H-5), 1.67 (3H, s, H-27), 1.58 (3H, s, H-26), 1.51 (2H, m, H-11), 1.45 (1H, m, H-1b), 1.12 (3H, s, H-29), 1.04 (3H, s, H-28), 1.00 (3H, s, H-30), 0.98 (3H, s, H-19), 0.88 (3H, s, H-18); ^{13}C NMR (125 MHz, $CDCl_3$): δ 38.7 (C-1), 35.0 (C-2), 217.0 (C-3), 48.0 (C-4), 52.5 (C-5), 24.5 (C-6), 118.4 (C-7), 145.6 (C-8), 48.3 (C-9), 35.2 (C-10), 18.0 (C-11), 30.2 (C-12), 43.5 (C-13), 51.1 (C-14), 33.6 (C-15), 27.3 (C-16), 49.9 (C-17), 21.8 (C-18), 12.9 (C-19), 47.5 (C-20), 182.2 (C-21), 32.4 (C-22), 26.1 (C-23), 123.7 (C-24), 132.4 (C-25), 17.8 (C-26), 25.8 (C-27), 24.7 (C-28), 21.7 (C-29), 27.5 (C-30)。上述数据与文献报道[19]一致, 故鉴定为 3-Oxotirucalla-7,24-dien-21-oic acid。

化合物 9 白色粉末; ESI-MS *m/z*: 523 [M + Na]$^+$; $C_{33}H_{57}O_3$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.73 (1H, s, H-24a), 4.64 (1H, d, *J* = 1.0 Hz, H-24b), 4.47 (1H, dd, *J* = 10.7, 5.6 Hz, H-3), 2.26 (1H, m, H-25), 2.10 (1H, m, H-23a), 2.08 (1H, m, H-23b), 2.03 (3H, s, CH_3COO), 1.83 (1H, m, H-16a), 1.74 (1H, m, H-17), 1.73 (1H, m, H-12a), 1.68 (1H, m, H-1a), 1.62 (1H, m, H-2a), 1.61 (1H, m, H-2b), 1.60 (1H, m, H-13), 1.58 (1H, m, H-22a), 1.57 (1H, m, H-22b), 1.54 (1H, m,

H-7a), 1.52 (1H, m, H-12b), 1.51 (1H, m, H-6a), 1.46 (1H, m, H-11a), 1.45 (1H, m, H-6b), 1.42 (1H, m, H-15a), 1.34 (1H, m, H-9), 1.27 (1H, m, H-7b), 1.26 (1H, m, H-11b), 1.25 (1H, m, H-16b), 1.13 (3H, m, H-21), 1.08 (1H, m, H-15b), 1.06 (1H, m, H-1b), 1.03 (3H, d, *J* = 6.8 Hz, H-26), 1.03 (3H, d, *J* = 6.8 Hz, H-27), 0.96 (3H, s, H-30), 0.87 (3H, s, H-18), 0.86 (3H, s, H-19), 0.84 (3H, s, H-28), 0.84 (3H, s, H-29), 0.82 (1H, m, H-5); ^{13}C NMR (125 MHz, $CDCl_3$): δ 38.8 (C-1), 23.9 (C-2), 80.7 (C-3), 38.1 (C-4), 56.1 (C-5), 18.3 (C-6), 35.3 (C-7), 40.5 (C-8), 50.6 (C-9), 37.2 (C-10), 21.2 (C-11), 25.3 (C-12), 42.3 (C-13), 50.2 (C-14), 31.2 (C-15), 27.6 (C-16), 49.7 (C-17), 16.7 (C-18), 16.5 (C-19), 75.8 (C-20), 25.5 (C-21), 40.7 (C-22), 28.2 (C-23), 156.6 (C-24), 106.3 (C-24), 34.1 (C-25), 22.0 (C-26), 22.1 (C-27), 28.1 (C-28), 16.7 (C-29), 15.7 (C-30), 173.9 (O<u>C</u>OCH$_3$), 21.2 (<u>C</u>H$_3$COO)。以上数据与文献[20]报道一致，故鉴定为(20*S*)-3β-Acetoxy-24-methylenedam-maran-20-ol。

化合物 10　白色结晶(氯仿); $[\alpha]_D^{25}$ +47.4 °(*c* 1, $CHCl_3$), EI-MS *m/z*: 449 $[M + Na]^+$; $C_{30}H_{50}O$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.71 (1H, br s, H-30a), 4.66 (1H, br s, H-30b), 3.21 (1H, ddd, *J* = 4.7, 9.1, 10.9 Hz, H-3), 1.03 (3H, d, *J* = 6.9 Hz, H-27), 1.01 (3H, d, *J* = 6.9 Hz, H-26), 0.97 (3H, d, *J* = 6.2 Hz, H-29), 0.96 (3H, s, H-18), 0.89 (3H, d, *J* = 6.3 Hz, H-21), 0.88 (3H, s, H-28), 0.38 (1H, d, *J* = 4.0 Hz, H-19a), 0.14 (1H, d, *J* = 4.0 Hz, H-19b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 30.9 (C-1), 34.9 (C-2), 76.7 (C-3), 44.7 (C-4), 43.5 (C-5), 24.8 (C-6), 25.3 (C-7), 47.0 (C-8), 23.7 (C-9), 29.6 (C-10), 27.1 (C-11), 33.0 (C-12), 45.5 (C-13), 49.0 (C-14), 35.5 (C-15), 28.2 (C-16), 52.3 (C-17), 17.9 (C-18), 27.4 (C-19), 36.3 (C-20), 18.5 (C-21), 35.1 (C-22), 31.4 (C-23), 157.0 (C-24), 33.9 (C-25), 22.1 (C-26), 22.0 (C-27), 19.3 (C-28), 14.5 (C-29), 106.1 (C-30)。上述数据与文献[21]报道一致，故鉴定此化合物为 Cycloeucalenol。

化合物 11　白色针状结晶(氯仿)，与 β-谷甾醇标准品进行 TLC 比较，3 个系统展开，R_f 值一致，故鉴定为 β-谷甾醇。

化合物 12　无色片状结晶(氯仿); $[\alpha]_D^{25}$ +11.8 °(*c* 1, $CHCl_3$), ESI-MS *m/z*: 461 $[M + Na]^+$; $C_{26}H_{30}O_6$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (1H, s, H-21), 7.36 (1H, t, *J* = 1.3 Hz, H-23), 7.08 (1H, d, *J* = 10.2 Hz, H-1), 6.33 (1H, d, *J* = 1.3 Hz, H-22), 5.89 (1H, d, *J* = 10.2 Hz, H-2), 5.44 (1H, s, H-17), 3.83 (1H, s, H-15), 2.90 (1H, t, *J* = 14.4 Hz, H-6a), 2.38 (1H, dd, *J* = 3.2, 14.6 Hz, H-6b), 2.18 (1H, d, *J* = 10.9 Hz, H-9), 2.15 (1H, dd, *J* = 3.2, 14.4 Hz, H-5), 1.98 (1H, m, H-11a), 1.91 (3H, s, H-30), 1.84 (1H, m, H-12b), 1.77 (1H, m, H-11b), 1.45 (1H, m, H-12a), 1.33 (3H, m, H-19), 1.12 (3H, s, H-28), 1.11 (3H, s, H-18), 1.10 (3H, s, H-29); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.1 (C-1), 126.4 (C-2), 203.4 (C-3), 45.3 (C-4), 54.6 (C-5), 36.8 (C-6), 208.3 (C-7), 53.5 (C-8), 47.6 (C-9), 39.6 (C-10), 17.2 (C-11), 32.2 (C-12), 37.8 (C-13), 65.7 (C-14), 53.6 (C-15), 167.0 (C-16), 78.1 (C-17), 21.0 (C-18), 19.9 (C-19), 120.2 (C-20), 141.1 (C-21), 109.9 (C-22), 143.2 (C-23), 27.0 (C-28), 20.7 (C-29), 17.4 (C-30)。上述数据与文献[22]报道一致，故鉴定为 7-Deacetoxy-7-oxogedunin。

化合物 13　白色粉末; $[\alpha]_D^{25}$ +60.4 °(*c* 1, $CHCl_3$), ESI-MS *m/z*: 463 $[M + Na]^+$; $C_{26}H_{32}O_6$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (1H, s, H-21), 7.39 (1H, m, H-23), 7.09 (1H, d, *J* = 10.2 Hz, H-1), 6.33 (1H, s, H-22), 5.83 (1H, d, *J* = 10.2 Hz, H-2), 5.58 (1H, s, H-17), 3.90 (1H, s, H-15), 3.56 (1H, s, H-7), 2.51 (1H, m, H-9), 2.47 (1H, m, H-5), 1.99 (1H, m, H-11a), 1.96 (1H, m, H-6a), 1.79 (1H, m, H-11b), 1.71 (1H, m, H-12a), 1.67 (1H, m, H-6b), 1.54 (1H, m, H-12b), 1.24 (3H, s, H-18), 1.21 (3H, s, H-19), 1.14 (3H, s, H-28), 1.08 (3H, s, H-29), 1.07 (3H, s, H-20); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0 (C-1), 125.9 (C-2), 204.7 (C-3), 44.3 (C-4), 44.7 (C-5), 27.4 (C-6), 69.8 (C-7), 43.8 (C-8), 38.1 (C-9), 40.3 (C-10), 15.2 (C-11), 26.5 (C-12), 38.4 (C-13), 70.2 (C-14), 58.0 (C-15), 168.4 (C-16), 78.6 (C-17), 17.9 (C-18), 20.1 (C-19), 120.8 (C-20), 141.3 (C-21), 110.1 (C-22), 143.1 (C-23), 27.4 (C-28), 21.6 (C-29), 18.8 (C-30)。上述数据与文献[23]报道一致，故鉴定为 7-Deacetoxy-7α-hydroxygedunin。

1.5 乙酰胆碱酯酶抑制活性测定

根据米承能等[24]的方法测定化合物的抗乙酰

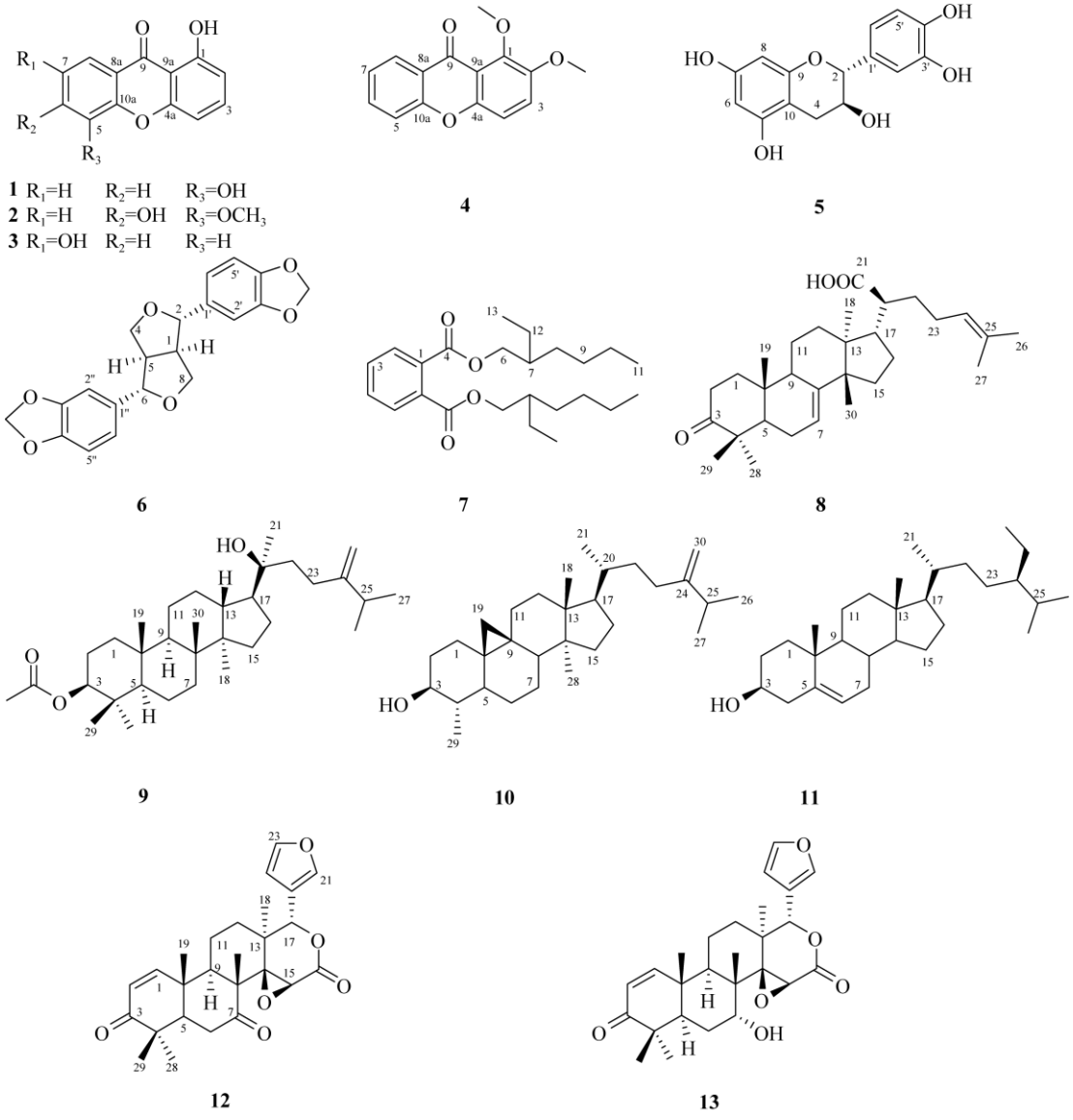

图 1 化合物 **1**~**13** 结构图

Fig. 1 Structures of compounds **1**−**13**

胆碱酯酶活性。待测样品用 DMSO 进行溶解，取 110 μL 磷酸缓冲液 (pH 8.0)、10 μL 待测样品 (50 μg mL^{-1})和 40 μL 乙酰胆碱酯酶(0.02 μg mL^{-1}) 于 96 孔板中，温育 20 min (30℃)，加入 DTNB (2.48 mg mL^{-1})和碘化硫代乙酰胆碱(1.81 mg mL^{-1}) 等体积混合液 20 μL，反应体系总体积 200 μL，30 min 后在酶标仪上于 405 nm 处进行检测。阳性对照为他克林，反应终浓度为 0.08 μg mL^{-1}，阴性对照为 DMSO，终浓度为 0.1%，3 次重复。化合物对乙酰胆碱酯酶的抑制率 =[(*E*−*S*)/*E*] ×100%，式中 *E* 为阴性对照平均吸光值，*S* 为待测样品的平均吸光值。结果表明，化合物 **4** 对乙酰胆碱酯酶有抑制活性，抑制率为 12.58%，阳性对照为 42.61%。

2 结果和讨论

本研究采取多种色谱技术，从大叶桃花心木根中分离得到了 13 个化合物，包括呫酮、黄酮、木脂素、三萜、柠檬苦素、甾体以及邻苯二甲酸衍生物等 7 类化合物，分别为 1,5-dihydroxyxanthone (**1**)、1,6-dihydroxy-5-methoxyxanthone (**2**)、euxanthone (**3**)、1,2-dimethoxyxanthone (**4**)、(+)儿茶素 (**5**)、(+) sesamin (**6**)、*bis*-(2-ethylhexyl)phthalate (**7**)、3-oxotirucalla-7,24-dien-21-oic acid (**8**)、(20*S*)-3β-acetoxy-

24-methylenedam-maran-20-ol (**9**)、cycloeucalenol (**10**)、β-谷甾醇 (**11**)、7-deacetoxy-7-oxogedunin (**12**) 和 7-deacetoxy-7α-hydroxygedunin (**13**)，其中化合物 **1**~**4**、**6**~**10** 和 **13** 为首次从桃花心木属植物中分离得到。乙酰胆碱酯酶抑制活性测试表明，化合物 **4** 有一定的乙酰胆碱酯酶抑制活性。同时，据报道化合物 **6** 对真菌 *Cladosporium cladosporioides* 有抑制活性[17]，化合物 **8** 对 MCF-7 癌细胞[16]和 HIV-1 蛋白酶[25]有抑制作用，化合物 **10** 对芳香酶有抑制作用[26]，化合物 **12** 对 *Spodoptera littoralis* 的 3 龄幼虫有拒食活性[27]，对 Hep-G2 有细胞毒活性[9]。本研究结果丰富了大叶桃花心木的化学成分，为进一步开发利用提供了科学依据。

参考文献

[1] GOH B H, KADIR A H. *In vitro* cytotoxic potential of *Swietenia macrophylla* King seeds against human carcinoma cell lines [J]. J Med Plants Res, 2011, 5(8): 1395–1404.

[2] LIU J S, ZHU L L, WANG G K, et al. Studies on chemical constituents from the fruit of *Swietenia macrophylla* [J]. Chin Med Mat, 2016, 39(7): 1530–1535. doi: 10.13863/j.issn1001−4454.2016.07.020.
刘劲松, 朱莉莉, 王国凯, 等. 向天果化学成分研究 [J]. 中药材, 2016, 39(7): 1530–1535. doi: 10.13863/j.issn1001−4454.2016.07.020.

[3] XIE G G, HUANG S M. The resources of Meliaceae plants in Hainan Island and their exploitation [J]. Trop Geogr, 1991, 11(4): 313–319.
谢国干, 黄世满. 海南岛楝科植物资源及其开发利用 [J]. 热带地理, 1991, 11(4): 313–319.

[4] MAITI A, DEWANJEE S, KUNDU M, et al. Protective effect of methanol extract of *Swietenia macrophylla* seeds on oxidative states associated with streptozotocin induced diabetic rats [J]. Nat Prod Sci, 2007, 13(4): 295–299. doi: 10.1201/9781420012347.ch7.

[5] CHEN J J, HUANG S S, LIAO C H, et al. A new phragmalin-type limonoid and anti-inflammatory constituents from the fruits of *Swietenia macrophylla* [J]. Food Chem, 2010, 120(2): 379–384. doi: 10.1016/j.foodchem.2009.09.093.

[6] MOOTOO B S, ALI A, MOTILAL R, et al. Limonoids from *Swietenia macrophylla* and *S. Aubrevilleana* [J]. J Nat Prod, 1999, 62(11): 1514–1517. doi: 10.1021/np990199x.

[7] FOWLES R, MOOTOO B, RAMSEWAK R, et al. Identification of new limonoids from *Swietenia* and their biological activity against insects [J]. Pest Manag Sci, 2010, 66(12): 1298–1303. doi: 10.1002/ps.2013.

[8] SAAD M M G, IWAGAWA T, OKAMURA H, et al. Three new mexicanolides from the stem bark of *Swietenia mahogani* JACQ [J]. Heterocycles, 2004, 63(2): 389–399. doi: 10.3987/COM-03-9932.

[9] PUDHOM K, SOMMIT D, NUCLEAR P, et al. Protoxylocarpins F-H, protolimonoids from seed kernels of *Xylocarpus granatum* [J]. J Nat Prod, 2009, 72(12): 2188–2191. doi: 10.1021/np900640u.

[10] CHENG Y B, CHIEN Y T, LEE J C, et al. Limonoids from the seeds of *Swietenia macrophylla* with inhibitory activity against dengue virus 2 [J]. J Nat Prod, 2014, 77(11): 2367–2374. doi: 10.1021/np5002829.

[11] WU S F, LIN C K, CHUANG Y S, et al. Anti-hepatitis C virus activity of 3-hydroxy caruilignan C from *Swietenia macrophylla* stems [J]. J Viral Hepatitis, 2012, 19(5): 364–370. doi: 10.1111/j.1365-2893.2011.01558.x.

[12] IINUMA M, TOSA H, TANAKA T, et al. Two xanthones from root bark of *Calophyllum inophyllum* [J]. Phytochemistry, 1994, 35(2): 527–532. doi: 10.1016/S0031-9422(00)94795-2.

[13] WU Y. Chemical constituents and bioactivity of *Calophyllum inophyllum*, *Calophyllum membranceum* and *Myculium* of *Ganoderma lucidum* [D]. Beijing: Chinese Academy of Medical Sciences & Union Medical College, 2004: 41–42.
毋艳. 红厚壳、薄叶红厚壳和泰山赤灵芝菌丝体化学成分及生物活性研究 [D]. 北京: 中国协和医科大学, 2004: 41–42.

[14] CHEN Y P, LIU L, ZHOU Y H, et al. Chemical constituents from *Sappan lignum* [J]. J Chin Pharm Sic, 2008, 17(1): 82–86.
陈玉平, 刘蕾, 周雨虹, 等. 苏木的化学成分研究 [J]. 中国药学, 2008, 17(1): 82–86.

[15] MOREL C, SÉRAPHIN D, OGER J M, et al. New xanthones from *Calophyllum caledonicum* [J]. J Nat Prod, 2000, 63(11): 1471–1474. doi: 10.1021/np000215m.

[16] LI S P. Study on chemical constituents from the roots of *Rosa laevigata* Michex. [D]. Hefei: Anhui University, 2013: 1–46.
李石平. 金樱子根的化学成分研究 [D]. 合肥: 安徽大学, 2013: 1–46.

[17] JAYASINGHE L, KUMARIHAMY B M M, JAYARATHNA K H R N, et al. Antifungal constituents of the stem bark of *Bridelia retusa* [J]. Phytochemistry, 2003, 62(4): 637–641. doi: 10.1016/S0031-9422(02)00623-4.

[18] LU X H, ZHANG X J, LIANG H, et al. Chemical constituents of *Angelica sinensis* [J]. J Chin Pharm Sic, 2004, 13(1): 1–3.
路新华, 张金娟, 梁鸿, 等. 当归化学成分的研究 [J]. 中国药学, 2004, 13(1): 1–3.

[19] AL-ZIKRI P N H, TAHER M, SUSANTI D, et al. Cytotoxic tirucallane triterpenes from the stem of *Luvunga scandens* [J]. Rev Brasil Farmacogn, 2014, 24(5): 561–564. doi: 10.1016/j.bjp.2014.

10.003.

[20] NDLEBE V J, CROUCH N R, MULHOLLAND D A. Triterpenoids from the African tree *Phyllanthus polyanthus* [J]. Phytochem Lett, 2008, 1(1): 11–17. doi: 10.1016/j.phytol.2007.12.002.

[21] ZHU W M, SHEN Y M, HONG X, et al. Triterpenoids from the Dai medicinal plant *Winchia calophylla* [J]. Acta Bot Sin, 2002, 44(3): 354–358. doi: 10.3321/j.issn:1672−9072.2002.03.018.
朱伟明, 沈月毛, 洪鑫, 等. 傣族药用植物盆架树中的三萜 [J]. 植物学报, 2002, 44(3): 354–358. doi: 10.3321/j.issn:1672−9072.2002.03.018.

[22] KADOTA S, MARPAUNG L, KIKUCHI T, et al. Constituents of the seeds of *Swietenia mahagoni* JACQ: I. Isolation, structures, and ^{1}H- and ^{13}C-nuclear magnetic resonance signal assignments of new tetranortriterpenoids related to swietenine and swietenolide [J]. Chem Pharm Bull, 1990, 38(3): 639–651. doi: 10.1248/cpb.38.639.

[23] MITSUI K, SAITO H, YAMAMURA R, et al. Hydroxylated gedunin derivatives from *Cedrela sinensis* [J]. J Nat Prod, 2006, 69(9): 1310–1314. doi: 10.1021/np068021f.

[24] MI C N, MEI W L, ZUO W J, et al. Chemical constituents from *Amoora tetrapetala* [J]. Nat Prod Res Dev, 2015, 27(4): 562–566.
米承能, 梅文莉, 左文健, 等. 四瓣崖摩化学成分研究 [J]. 天然产物研究与开发, 2015, 27(4): 562–566.

[25] MA C M, NAKAMURA N, HATTORI M, et al. Inhibitory effects on HIV-1 Protease of constituents from the wood of *Xanthoceras sorbifolia* [J]. J Nat Prod, 2000, 63(2): 238–242. doi: 10.1021/np9902441.

[26] LI Y H, YANG Y F, LI K, et al. 5 Alpha-reductase and aromatase inhibitory constituents from *Brassica rapa* L. pollen [J]. Chem Pharm Bull, 2009, 57(4): 401–404. doi: 10.1248/cpb.57.401.

[27] ABDELGALEIL S A M, DOE M, NAKATANI M. Rings B, D-seco limonoid antifeedants from *Swietenia mahogani* [J]. Phytochemistry, 2013, 96: 312–317. doi: j.phytochem.2013.08.006.