

白花洋紫荆花的化学成分及其胰脂肪酶抑制活性研究

彭京¹, 何瑞杰¹, 谢桃结², 阳丙媛¹, 王亚凤¹, 黄永林^{1*}¹广西壮族自治区中国科学院广西植物研究所 广西植物功能物质与资源持续利用重点实验室, 桂林 541006;²柳州市园林科学研究所, 柳州 545005

摘要:为研究白花洋紫荆(*Bauhinia variegata* var. *candida*)花的化学成分,以白花洋紫荆花的乙醇提取物为对象,运用葡聚糖凝胶柱层析、MCI柱层析、半制备高效液相色谱等方法进行分离纯化,根据化合物的核磁共振波谱数据进行结构鉴定。结果从白花洋紫荆花中分离纯化得到17个化合物,包括1个葡萄糖苷类、2个苯甲酸类、2个香豆酸类、1个多环酚类、11个黄酮类,分别鉴定为 β -D-甲基葡萄糖苷(1)、对羟基苯甲酸甲酯(2)、对甲氧基苯甲酸(3)、对香豆酸(4)、对甲氧基桂皮酸(5)、pacharin(6)、柚皮素(7)、异牡荆苷(8)、山柰酚(9)、6-羟基山柰酚-3-O-葡萄糖甙(10)、山柰酚-3-O-鼠李糖苷(11)、百蕊草素(12)、kaempferol 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-lucopyranoside(13)、槲皮素(14)、3-O-甲基槲皮素(15)、quercetin-3-O- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside(16)、quercetin-3-O-(6"-O- α -L-rhamnopyranosyl)- β -D-glucoside(17)。本研究得到的化合物均为首次从该植物中分离得到。共筛选了化合物10、12、13、14、17的胰脂肪酶活性,结果显示该5个化合物对胰脂肪酶均具有一定的抑制活性。

关键词:白花洋紫荆;化学成分;结构鉴定;胰脂肪酶抑制剂

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Chemical constituents from the flowers of *Bauhinia variegata* var. *candida* and its pancreatic lipase inhibitory activity

PENG Jing¹, HE Rui-jie¹, XIE Tao-jie², YANG Bing-yuan¹, WANG Ya-feng¹, HUANG Yong-lin^{1*}¹Guangxi Key Laboratory of Plant Functional Phytochemicals and Sustainable Utilization, Guangxi Institute of Botany, Guangxi Zhuang Autonomous Region and Chinese Academy of Sciences, Guilin 541006, China;²Liuzhou Institute of Gardening, Liuzhou 545005, China

Abstract: To study the chemical constituents from the flowers of *B. variegata* var. *candida*. The constituents were isolated from the ethanol extract of flowers of *B. variegata* var. *candida* and purified by column chromatography Sephadex LH-20, MCI and semi-preparative high performance liquid chromatography. The structures of the compounds were identified by NMR spectroscopic data. A total of 17 compounds were isolated from the flowers of *B. variegata* var. *candida*, including one glucoside, two benzoic acids, two coumarins, one polycyclic phenols, eleven flavonoids, and the structures were identified as methyl β -D-glucopyranoside (1), methyl 4-hydroxybenzoate (2), 4-methoxybenzoic acid (3), *p*-coumaric acid (4), *p*-methoxy cinnamic acid (5), pacharin (6), naringenin (7), isovitexin (8), kaempferol (9), 6-hydroxykaempfero-3-O-glucoside (10), kaempferol-3-O- α -L-rhamnoside (11), kaempferol 3-O-neohesperidoside (12), kaempferol 3-O- α -L-rhamnopyranosyl-(1-2)- β -D-lucopyranoside (13), quercetin (14), 3-O-methylquercetin (15), quercetin-3-O- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside (16), quercetin-3-O-(6"-O- α -L-rhamnopyranosyl)- β -D-glucoside (17). All the compounds were obtained from the plant for the first time. Compounds 10, 12, 13, 14, 17 were screened for pancreatic lipase inhibitory activity, and the results showed that the five compounds have certain inhibitory activity on pancrelipase.

Key words: *Bauhinia variegata* var. *candida*; chemical constituents; structure identification; pancreatic lipase inhibitor

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*通信作者 Tel:86-773-3550194; E-mail: hyl@gxib. cn

豆科 (Leguminosae) 羊蹄甲属 (*Bauhinia*) 植物全世界约 600 种, 遍布于世界热带地区, 我国有 40 种, 4 亚种, 11 变种, 主产南部和西南部, 因树冠雅致花大而艳丽有香气, 观赏价值很高, 而且容易培植, 常栽培于庭园、路边供观赏, 是良好的观赏植物^[1]。羊蹄甲属植物作为传统中药广泛被用来治疗糖尿病、抗菌消炎、镇痛、止血和利尿等^[2]。白花洋紫荆 (*Bauhinia variegata* var. *candida*) 是洋紫荆 (*Bauhinia variegata* L.) 的变种, 属豆科羊蹄甲属落叶乔木, 花性味是苦、涩、平, 入药可以用来治疗消化不良、风热咳嗽、肝炎, 因花开时非常美丽而稠密, 且带有香味, 民间常用来裹面粉油炸或作为青菜汤吃^[3]。但是, 目前白花洋紫荆花的化学成分及可食性药理方面的研究还未见有相报道。为了充分掌握白花洋紫荆的物质基础及为其可食性提供科学依据, 本研究对白花洋紫荆花乙醇提取物进行了系统的分离纯化, 分离鉴定的化合物以黄酮类成分为主, 文献报道此类化合物具有较好的胰脂肪酶抑制剂活性, 因此又对分离得到的化合物进行了胰脂肪酶抑制剂活性研究, 旨在为该植物的开发利用与发现新的用途提供科学依据。

1 材料与方法

1.1 仪器与材料

Bruker Avance 500 MHz 超导核磁共振波谱仪 (Bruker, 德国); LCMS-IT-TOF (日本 Shimadzu 公司); LC52 半制备液相色谱仪 (赛谱锐思, 北京); Sephadex LH-20 (25 ~ 100 μm ; GE Healthcare Bio-Science AB, Uppsala, 瑞士); MCI gel CHP 20P (75 ~ 150 μm ; Mitsubishi Chemical, Tokyo, 日本); Toyopearl HW-40F (TOSOH Co, Tokyo, 日本); GF₂₅₄ 薄层色谱硅胶 (Merck, 德国); 奥利司他 (美国 MCE); 4-甲基伞形酮油酸酯 (美国 Sigma); 猪胰脂肪酶 (美国 Sigma); 磷酸盐缓冲液 (北京 Solarbio); 所用试剂甲醇、乙醇等均为分析纯 (AR)。

实验所用白花洋紫荆花采自广西柳州市, 经柳州市园林科学研究所刘思鉴定为白花洋紫荆 (*B. variegata* var. *candida*) 的花, 凭证样品 (2020.03.18) 存放于广西植物功能物质研究与资源持续利用重点实验室。

1.2 实验方法

1.2.1 提取与分离

取新鲜白花洋紫荆花 25 kg 用纯乙醇室温浸提 3 次, 每次 7 d, 合并提取液并过滤, 减压浓缩后得到

浸膏 1183.5 g, 加水溶解后用石油醚、乙酸乙酯分别萃取 3 次, 回收乙酸乙酯溶液得到浸膏 192.6 g。乙酸乙酯浸膏 190.0 g 经 MCI gel CHP 20P 层析柱 (8 cm \times 18 cm) 分离, 甲醇-水 (0 \rightarrow 100%, 每 10% 为 1 梯度) 进行梯度洗脱, 得到 Fr: 1 ~ 7 共 7 个组份。Fr2 (34.3 g) 经 Sephadex LH-20 层析柱 (6 cm \times 30 cm) 分离, 甲醇-水 (0 \rightarrow 100%, 每 10% 为 1 梯度) 进行梯度洗脱, 得到 Fr: 2-1 ~ 2-9 共 9 个组份。Fr2-1 (3.7 g) 过 Toyopearl HW-40F 层析柱分离得到化合物 **1** (30 mg)。Fr2-7 (12.3 g) 过硅胶 (4 cm \times 30 cm) 柱层析, 石油醚: 二氯甲烷 (4: 1, 3: 2, 2: 3, 1: 4) 进行梯度洗脱, 得到化合物 **2** (13 mg)、**8** (26 mg)、**12** (30 mg)、**13** (30 mg)。Fr2-8 (7.6 g) 过 Toyopearl HW-40F (4 cm \times 30 cm) 柱层析, 甲醇-水 (0 \rightarrow 100%, 每 10% 为 1 梯度) 梯度洗脱, Fr2-8-4 及 Fr2-8-6 放置后有结晶析出, 分别得到化合物 **16** (23 mg)、**17** (28 mg)。Fr2-8-2 再经硅胶柱层析得到化合物 **11** (9 mg)。Fr3 (11.0 g) 经 Sephadex LH-20 层析柱 (4 cm \times 30 cm) 分离, 甲醇-水 (0 \rightarrow 100%, 每 10% 为 1 梯度) 进行梯度洗脱, 得到 Fr3-1 ~ 3-10 共 10 个组份。Fr3-2 (3.0 g) 经硅胶柱层析 (3 cm \times 30 cm) 分离, 经石油醚: 二氯甲烷 (8: 2, 7: 3, 5: 5) 进行梯度洗脱, 得到化合物 **3** (23 mg)、**4** (4 mg)、**5** (11 mg)、**10** (46 mg)。Fr3-5 (2.3 g) 经硅胶柱层析 (3 cm \times 25 cm) 分离, 经石油醚: 二氯甲烷 (8: 2, 7: 3, 5: 5) 进行梯度洗脱, 得到化合物 **6** (7 mg)、**14** (32 mg)、**15** (26 mg)。Fr. 3-8 (86 mg) 经半制备 HPLC (半制备柱: C₁₈, 10 mm \times 250 mm, 5 μm , YMC 公司; 流动相: 30% 乙腈等梯度洗脱; 流速: 2 mL/min; 柱温: 35 $^{\circ}\text{C}$) 分离得到化合物 **7** (t_{R} = 12.5 min, 8 mg)、**9** (t_{R} = 14.6 min, 15 mg)。

1.2.2 胰脂肪酶抑制活性筛选

采用猪胰脂肪酶抑制剂活性筛选模型对分离得到量较多的化合物 **10**、**12**、**13**、**14**、**17** 进行活性测试, 实验方法参照相关文献^[4], 以奥利司他 (orlistat) 为阳性对照, 以 4-甲基伞形酮油酸酯 (4-MUO) 为底物。将猪胰脂肪酶溶解于 PBS 缓冲液配置成 1 mg/mL 的溶液, 离心取上清液备用。准确称取 1 mmol 4-MUO 溶解于 10 mL PBS 缓冲液配置成 0.1 mmol/mL 溶液备用。准确称取 10 mmol 样品溶解于 PBS 缓冲液并定容至 1 mL 备用。取 25 μL 不同浓度的样品与 25 μL 胰脂肪酶溶液孵育五分钟后再加入 50 μL 4-MUO 底物, 反应 20 min 后加入 100 μL 0.1

mol/mL 柠檬酸钠溶液终止反应,在 320 nm 激发波长和 450 nm 发射波长下测量吸光度,抑制率的计算公式如下。

胰脂肪酶抑制率 =

$$\left[\frac{1 - (A_{\text{样品}} - A_{\text{样品对照}})}{(A_{\text{空白}} - A_{\text{空白对照}})} \right] \times 100\%$$

式中, $A_{\text{样品}}$ 为加入样品和活性酶反应后的吸光值; $A_{\text{样品对照}}$ 为加入样品和失活酶反应后的吸光值; $A_{\text{空白}}$ 为加入活性酶和 PBS 反应后的吸光值; $A_{\text{空白对照}}$ 为加入失活酶和 PBS 反应后的吸光值,所有反应组中均有 4-MUO。

2 结果与分析

2.1 化合物结构鉴定

化合物 1 无色油状;ESI-MS: m/z 195 $[M + H]^+$, 分子式为 $C_7H_{14}O_6$; 1H NMR (500 MHz, CD_3OD) δ : 4.18 (1H, d, $J = 7.8$ Hz, H-1), 3.87 (1H, dd, $J = 12.0, 1.6$ Hz, H-6a), 3.67 (1H, dd, $J = 12.0, 5.4$ Hz, H-6b), 3.53 (3H, s, -OCH₃), 3.35 (1H, t, $J = 8.9$ Hz, H-3), 3.31 (1H, m, H-5), 3.28 (1H, m, H-4), 3.16 (1H, dd, $J = 8.9, 7.8$ Hz, H-2); ^{13}C NMR (125 MHz, CD_3OD) δ : 105.3 (C-1), 75.1 (C-2), 78.1 (C-3), 71.5 (C-4), 77.8 (C-5), 62.6 (C-6), 57.3 (-OCH₃)。以上数据与文献^[5]对照基本一致,故鉴定化合物 **1** 为 β -D-甲基葡萄糖苷。

化合物 2 白色粉末;ESI-MS: m/z 153 $[M + H]^+$, 分子式为 $C_8H_8O_3$; 1H NMR (500 MHz, CD_3OD) δ : 7.96 (2H, d, $J = 9.0$ Hz, H-2, 6), 6.97 (2H, d, $J = 9.0$ Hz, H-3, 5), 3.84 (3H, s, -OCH₃); ^{13}C NMR (125 MHz, CD_3OD) δ : 122.5 (C-1), 132.1 (C-2/6), 115.4 (C-3/5), 160.3 (C-4), 52.0 (-OCH₃), 167.3 (-COO)。以上数据与文献^[6]对照基本一致,故鉴定化合物 **2** 为对羟基苯甲酸甲酯。

化合物 3 白色粉末;ESI-MS: m/z 153 $[M + H]^+$, 分子式为 $C_8H_8O_3$; 1H NMR (500 MHz, CD_3OD) δ : 7.97 (2H, d, $J = 8.6$ Hz, H-2, 6), 6.98 (2H, d, $J = 8.6$ Hz, H-3, 5), 3.86 (3H, s, -OCH₃); ^{13}C NMR (125 MHz, CD_3OD) δ : 169.8 (-COO), 165.0 (C-4), 132.8 (C-2/6), 124.0 (C-1), 114.7 (C-3/5), 56.0 (-OCH₃)。以上数据与文献^[7]对照基本一致,故鉴定化合物 **3** 为对甲氧基苯甲酸。

化合物 4 白色粉末;ESI-MS: m/z 165 $[M + H]^+$, 分子式为 $C_9H_8O_3$; 1H NMR (500 MHz, CD_3OD) δ : 7.60 (1H, d, $J = 15.5$ Hz, H-7), 7.44 (2H, d, $J = 8.5$ Hz, H-3, 5), 6.81 (2H, d, $J = 8.5$ Hz, H-2, 6),

6.28 (1H, d, $J = 15.5$ Hz, H-8); ^{13}C NMR (125 MHz, CD_3OD) δ : 127.2 (C-1), 131.1 (C-2/6), 116.8 (C-3/5), 161.1 (C-4), 146.8 (C-7), 115.7 (C-8), 171.0 (-COO)。以上数据与文献^[8]对照基本一致,故鉴定化合物 **4** 为对香豆酸。

化合物 5 白色无晶形粉末;ESI-MS: m/z 179 $[M + H]^+$, 分子式为 $C_{10}H_{10}O_3$; 1H NMR (500 MHz, CD_3OD) δ : 7.62 (1H, d, $J = 15.9$ Hz, H-7), 7.54 (2H, d, $J = 8.7$ Hz, H-2, 6), 6.94 (2H, d, $J = 8.7$ Hz, H-3, 5), 6.32 (1H, d, $J = 15.9$ Hz, H-8), 3.83 (3H, s, OCH₃); ^{13}C NMR (125 MHz, CD_3OD) δ : 128.4 (C-1), 130.1 (C-2/6), 115.4 (C-3/5), 163.9 (C-4), 146.2 (C-7), 116.6 (C-8), 170.8 (-COO), 55.9 (-OCH₃)。以上数据与文献^[9]对照基本一致,故鉴定化合物 **5** 为对甲氧基桂皮酸。

化合物 6 无针形粉末;ESI-MS: m/z 271 $[M + H]^+$, 分子式为 $C_{16}H_{14}O_4$; 1H NMR (500 MHz, CD_3OD) δ : 7.07 (1H, t, $J = 8.1$ Hz, H-10), 6.93 (1H, d, $J = 11.6$ Hz, H-5), 6.89 (1H, d, $J = 8.1$ Hz, H-9), 6.62 (1H, d, $J = 11.6$ Hz, H-6), 6.58 (1H, dd, $J = 8.2, 1.1$ Hz, H-8), 6.21 (1H, s, H-4), 3.74 (3H, s, -OCH₃), 2.07 (3H, s, -CH₃); ^{13}C NMR (125 MHz, CD_3OD) δ : 148.1 (C-1), 115.0 (C-2), 156.0 (C-3), 112.5 (C-4), 129.5 (C-4a), 130.6 (C-5), 129.8 (C-6), 119.9 (C-6a), 156.5 (C-7), 101.8 (C-8), 125.3 (C-9), 113.4 (C-10), 160.7 (C-10a), 140.3 (C-11a), 56.1 (-OCH₃), 8.7 (-CH₃)。以上数据与文献^[10]对照基本一致,故鉴定化合物 **6** 为 pacharin。

化合物 7 黄色粉末;ESI-MS: m/z 273 $[M + H]^+$, 分子式为 $C_{15}H_{12}O_5$; 1H NMR (500 MHz, CD_3OD) δ : 7.30 (2H, d, $J = 8.5$ Hz, H-2', 6'), 6.82 (2H, d, $J = 8.5$ Hz, H-3', 5'), 5.89 (1H, d, $J = 2.0$ Hz, H-8), 5.88 (1H, d, $J = 2.0$ Hz, H-6), 5.30 (1H, dd, $J = 13.0, 3.0$ Hz, H-2), 3.10 (1H, d, $J = 17.1, 13.0$ Hz, H-3a), 2.68 (1H, d, $J = 17.1, 3.0$ Hz, H-3b); ^{13}C NMR (125 MHz, CD_3OD) δ : 80.4 (C-2), 43.9 (C-3), 197.8 (C-4), 165.4 (C-5), 97.1 (C-6), 168.3 (C-7), 96.2 (C-8), 164.9 (C-9), 103.3 (C-10), 131.1 (C-1'), 129.0 (C-2'/6'), 116.3 (C-3'/5'), 158.9 (C-4')。以上数据与文献^[11]对照基本一致,故鉴定化合物 **7** 为柚皮素。

化合物 8 黄色粉末;ESI-MS: m/z 433 $[M + H]^+$, 分子式为 $C_{21}H_{20}O_{11}$; 1H NMR (500 MHz, DM-

$SO-d_6$) δ : 8.02 (2H, d, $J = 8.7$ Hz, H-2', 6'), 6.89 (2H, d, $J = 8.7$ Hz, H-3', 5'), 6.76 (1H, s, H-8), 6.27 (1H, s, H-3), 4.68 (1H, d, $J = 9.2$ Hz, H-1''), 3.83 (1H, t, $J = 9.2$ Hz, H-2''), 3.76 (1H, d, $J = 10.8$ Hz, H-6a''), 3.39 ~ 3.24 (4H, m, H-3'', 4'', 5'', 6b''); ^{13}C NMR (125 MHz, DMSO- d_6) δ : 163.9 (C-2), 102.8 (C-3), 182.3 (C-4), 156.7 (C-5), 108.1 (C-6), 163.8 (C-7), 94.1 (C-8), 161.3 (C-9), 104.0 (C-10), 121.2 (C-1'), 128.4 (C-2'/6'), 116.1 (C-3'/5'), 160.0 (C-4'), 78.9 (C-1''), 73.6 (C-2''), 71.3 (C-3''), 70.7 (C-4''), 81.2 (C-5''), 61.6 (C-6'')。以上数据与文献^[12]对照基本一致,故鉴定化合物 **8** 为异牡荆苷。

化合物 9 黄色粉末;ESI-MS: m/z 285 [M + H]⁺, 分子式为 C₁₅H₁₀O₆; 1H NMR (500 MHz, CD₃OD) δ : 8.03 (2H, d, $J = 8.9$ Hz, H-2', 6'), 6.88 (2H, d, $J = 8.9$ Hz, H-3', 5'), 6.34 (1H, d, $J = 2.1$ Hz, H-8), 6.15 (1H, d, $J = 2.1$ Hz, H-6); ^{13}C NMR (125 MHz, CD₃OD) δ : 148.0 (C-2), 137.0 (C-3), 177.3 (C-4), 162.4 (C-5), 99.3 (C-6), 165.5 (C-7), 94.5 (C-8), 158.2 (C-9), 104.5 (C-10), 123.7 (C-1'), 130.6 (C-2'/6'), 116.3 (C-3'/5'), 160.5 (C-4')。以上数据与文献^[13]对照基本一致,故鉴定化合物 **9** 为山柰酚。

化合物 10 黄色粉末;ESI-MS: m/z 465 [M + H]⁺, 分子式为 C₂₁H₂₀O₁₂; 1H NMR (500 MHz, CD₃OD) δ : 8.05 (2H, d, $J = 8.9$ Hz, H-2', 6'), 6.89 (2H, d, $J = 8.9$ Hz, H-3', 5'), 6.39 (1H, s, H-8), 5.23 (H, d, $J = 7.4$ Hz, H-1''), 3.69 (1H, dd, $J = 11.9, 2.4$ Hz, H-6a), 3.53 (1H, dd, $J = 11.9, 5.5$ Hz, H-6b), 3.45 (1H, t, $J = 9.1$ Hz, H-3''), 3.42 (1H, t, $J = 9.1$ Hz, H-4''), 3.34 (1H, m, H-2''), 3.21 (1H, m, H-5''); ^{13}C NMR (CD₃OD, 125 MHz) δ : 158.5 (C-2), 135.5 (C-3), 179.5 (C-4), 163.0 (C-5), 100.0 (C-6), 166.3 (C-7), 94.8 (C-8), 159.1 (C-9), 105.7 (C-10), 122.8 (C-1'), 132.3 (C-2'/6'), 116.1 (C-3'/5'), 161.5 (C-4'), 104.2 (C-1''), 75.7 (C-2''), 78.4 (C-3''), 71.4 (C-4''), 78.1 (C-5''), 62.7 (C-6'')。以上数据与文献^[14]对照基本一致,故鉴定化合物 **10** 为 6-羟基山柰酚 3-O-葡萄糖甙。

化合物 11 黄色粉末;ESI-MS: m/z 431 [M - H]⁻, 分子式为 C₂₁H₂₀O₁₀; 1H NMR (500 MHz, CD₃OD) δ : 7.74 (2H, d, $J = 8.7$ Hz, H-2', 6'), 6.91

(2H, d, $J = 8.7$ Hz, H-3', 5'), 6.32 (1H, d, $J = 2.1$ Hz, H-8), 6.16 (1H, d, $J = 2.1$ Hz, H-6), 5.37 (1H, d, $J = 1.7$ Hz, H-1''), 4.24 (1H, dd, $J = 3.7, 1.7$ Hz, H-2''), 3.73 (1H, dd, $J = 9.0, 3.7$ Hz, H-3''), 3.34 (2H, m, H-4'', 5''), 0.92 (3H, d, $J = 5.6$ Hz, H-6''); ^{13}C NMR (125 MHz, CD₃OD) δ : 158.4 (C-2), 136.1 (C-3), 179.5 (C-4), 163.0 (C-5), 99.8 (C-6), 165.6 (C-7), 94.8 (C-8), 159.2 (C-9), 105.8 (C-10), 122.5 (C-1'), 131.7 (C-2'/6'), 116.5 (C-3'/5'), 161.4 (C-4'), 103.4 (C-1''), 71.9 (C-2''), 73.2 (C-3''), 72.0 (C-4''), 72.1 (C-5''), 17.6 (C-6'')。以上数据与文献^[15]对照基本一致,故鉴定化合物 **11** 为山柰酚-3-O-鼠李糖苷。

化合物 12 黄色粉末;ESI-MS: m/z 595 [M + H]⁺, 分子式为 C₂₇H₃₀O₁₅; 1H NMR (500 MHz, (CD₃)₂CO) δ : 8.09 (2H, d, $J = 8.8$ Hz, H-2', 6'), 6.94 (2H, d, $J = 8.8$ Hz, H-3', 5'), 6.48 (1H, br s, H-8), 6.24 (1H, br s, H-6), 5.12 (1H, d, $J = 7.8$ Hz, H-1''), 4.53 (1H, br s, H-1'''), 3.81 ~ 3.32 (10H, m, H-2'', 3'', 4'', 5'', 6a'', 6b'', 2''', 3''', 4''', 5'''), 1.08 (3H, d, $J = 6.5$ Hz, H-6'''); ^{13}C NMR (125 MHz, (CD₃)₂CO) δ : 157.7 (C-2), 134.9 (C-3), 178.9 (C-4), 162.1 (C-5), 99.4 (C-6), 165.5 (C-7), 94.7 (C-8), 158.8 (C-9), 104.9 (C-10), 121.8 (C-1'), 131.9 (C-2'/6'), 115.9 (C-3'/5'), 160.8 (C-4'), 104.2 (C-1''), 71.1 (C-2''), 77.3 (C-3''), 70.3 (C-4''), 76.6 (C-5''), 67.8 (C-6''), 101.7 (C-1'''), 74.3 (C-2'''), 71.7 (C-3'''), 74.9 (C-4'''), 68.9 (C-5'''), 17.8 (C-6''')。以上数据与文献^[16]对照基本一致,故鉴定化合物 **12** 为百蕊草素。

化合物 13 黄色粉末;ESI-MS: m/z 465 [M + H]⁺, 分子式为 C₂₇H₃₀O₁₅; 1H NMR (500 MHz, (CD₃)₂CO) δ : 8.10 (2H, d, $J = 8.8$ Hz, H-2', 6'), 6.93 (2H, d, $J = 8.8$ Hz, H-3', 5'), 6.48 (1H, br s, H-8), 6.24 (1H, br s, H-6), 5.04 (1H, d, $J = 7.8$ Hz, H-1''), 4.52 (1H, br s, H-1'''), 3.81 ~ 3.32 (10H, m, H-2'', 3'', 4'', 5'', 6a'', 6b'', 2''', 3''', 4''', 5'''), 1.10 (3H, d, $J = 6.5$ Hz, H-6'''); ^{13}C NMR (125 MHz, (CD₃)₂CO) δ : 157.7 (C-2), 135.0 (C-3), 178.9 (C-4), 162.1 (C-5), 99.4 (C-6), 165.4 (C-7), 94.7 (C-8), 158.6 (C-9), 104.9 (C-10), 121.8 (C-1'), 131.9 (C-2'/6'), 115.8 (C-3'/5'), 160.9 (C-4'), 104.7 (C-1''), 71.2 (C-2''), 77.4 (C-3''), 70.3 (C-4''), 76.8 (C-5''), 66.4

(C-6''), 100.9 (C-1'''), 73.8 (C-2'''), 72.5 (C-3'''), 74.3 (C-4'''), 68.8 (C-5'''), 17.7 (C-6'''). 以上数据与文献^[17]对照基本一致,故鉴定化合物 **13** 为 kaempferol 3-*O*- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-lucopyranoside。

化合物 14 淡黄色粉末;ESI-MS: m/z 303 [M + H]⁺, 分子式为 C₁₅H₁₀O₇; ¹H NMR (500 MHz, CD₃OD) δ : 7.72 (1H, d, J = 2.2 Hz, H-2'), 7.63 (1H, dd, J = 8.5, 2.2 Hz, H-6'), 6.88 (1H, d, J = 8.5 Hz, H-5'), 6.39 (1H, d, J = 2.1 Hz, H-8), 6.18 (1H, d, J = 2.1 Hz, H-6); ¹³C NMR (125 MHz, CD₃OD) δ : 158.2 (C-2), 137.2 (C-3), 177.3 (C-4), 148.8 (C-5), 99.3 (C-6), 165.7 (C-7), 94.5 (C-8), 162.4 (C-9), 104.5 (C-10), 124.2 (C-1'), 116.0 (C-2'), 148.0 (C-3'), 146.2 (C-4'), 116.3 (C-5'), 121.7 (C-6')。以上数据与文献^[18]对照基本一致,故鉴定化合物 **14** 为槲皮素。

化合物 15 黄色粉末;ESI-MS: m/z 317 [M + H]⁺, 分子式为 C₁₆H₁₂O₇; ¹H NMR (500 MHz, CD₃OD) δ : 7.61 (1H, d, J = 2.1 Hz, H-2'), 7.49 (1H, dd, J = 8.5, 2.1 Hz, H-6'), 6.88 (1H, d, J = 8.5 Hz, H-5'), 6.30 (1H, d, J = 2.0 Hz, H-8), 6.15 (1H, d, J = 2.0 Hz, H-6), 3.76 (3H, s, 3-OCH₃); ¹³C NMR (125 MHz, CD₃OD) δ : 158.3 (C-2), 139.5 (C-3), 179.9 (C-4), 157.9 (C-5), 99.7 (C-6), 165.8 (C-7), 94.7 (C-8), 163.0 (C-9), 105.8 (C-10), 122.9 (C-1'), 116.4 (C-2'), 146.4 (C-3'), 149.9 (C-4'), 116.5 (C-5'), 122.3 (C-6'), 60.5 (3-OCH₃)。以上数据与文献^[19]对照基本一致,故鉴定化合物 **15** 为 3-*O*-甲基槲皮素。

化合物 16 黄色粉末;ESI-MS: m/z 611 [M + H]⁺, 分子式为 C₂₇H₃₀O₁₆; ¹H NMR (500 MHz, (CD₃)₂CO) δ : 7.89 (1H, d, J = 2.2 Hz, H-2'), 7.57 (1H, dd, J = 8.7, 2.2 Hz, H-6'), 6.86 (1H, d, J = 8.7 Hz, H-5'), 6.37 (1H, d, J = 2.0 Hz, H-8), 6.17 (1H, d, J = 2.0 Hz, H-6), 5.07 (1H, d, J = 7.6 Hz, H-1''), 4.54 (1H, br s, H-1'''), 3.81 ~ 3.26 (10H, m, H-2''、3''、4''、5''、6a''、6b''、2'''、3'''、4'''、5'''), 1.20 (3H, d, J = 6.5 Hz, H-6'''); ¹³C NMR (125 MHz, (CD₃)₂CO) δ : 158.9 (C-2), 135.8 (C-3), 179.4 (C-4), 162.7 (C-5), 100.0 (C-6), 166.0 (C-7), 94.6 (C-8), 158.3 (C-9), 105.6 (C-10), 123.0 (C-1'), 117.8 (C-2'), 149.9 (C-3'), 145.6 (C-4'), 116.1 (C-5'), 122.8 (C-6'),

105.5 (C-1''), 72.6 (C-2''), 78.1 (C-3''), 70.1 (C-4''), 75.2 (C-5''), 68.5 (C-6''), 101.8 (C-1'''), 73.8 (C-2'''), 73.1 (C-3'''), 75.1 (C-4'''), 70.2 (C-5'''), 17.9 (C-6'''). 以上数据与文献^[20]对照基本一致,故鉴定化合物 **16** 为 quercetin-3-*O*- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside。

化合物 17 黄色粉末;ESI-MS: m/z 611 [M + H]⁺, 分子式为 C₂₇H₃₀O₁₆; ¹H NMR (500 MHz, (CD₃)₂CO) δ : 7.67 (1H, d, J = 2.2 Hz, H-2'), 7.61 (1H, dd, J = 8.7, 2.2 Hz, H-6'), 6.87 (1H, d, J = 8.7 Hz, H-5'), 6.37 (1H, d, J = 2.0 Hz, H-8), 6.18 (1H, d, J = 2.0 Hz, H-6), 5.10 (1H, d, J = 7.6 Hz, H-1''), 4.53 (1H, br s, H-1'''), 3.82 ~ 3.27 (10H, m, H-2''、3''、4''、5''、6a''、6b''、2'''、3'''、4'''、5'''), 1.12 (3H, d, J = 6.5 Hz, H-6'''); ¹³C NMR (125 MHz, (CD₃)₂CO) δ : 159.3 (C-2), 135.6 (C-3), 179.3 (C-4), 162.8 (C-5), 100.0 (C-6), 165.9 (C-7), 94.6 (C-8), 158.4 (C-9), 104.6 (C-10), 123.5 (C-1'), 117.7 (C-2'), 149.7 (C-3'), 145.7 (C-4'), 116.1 (C-5'), 123.1 (C-6'), 104.5 (C-1''), 72.0 (C-2''), 77.1 (C-3''), 71.4 (C-4''), 75.7 (C-5''), 67.4 (C-6''), 102.3 (C-1'''), 72.2 (C-2'''), 72.1 (C-3'''), 73.9 (C-4'''), 69.7 (C-5'''), 17.9 (C-6'''). 以上数据与文献^[21]对照基本一致,故鉴定化合物 **17** 为 quercetin-3-*O*-(6''-*O*- α -L-rhamnopyranosyl)- β -D-glucoside。

化合物 **1** ~ **17** 的结构见图 1。

2.2 胰脂肪酶抑制活性筛选结果

按“1.2.2”项方法平行测定三次取平均值,结果显示阳性药奥利司他的 IC₅₀ = 0.021 mmol/L,对从白花洋紫荆花中分离得到的 5 个化合物的猪胰脂肪酶抑制活性进行了筛选,结果未显示较强的抑制活性,其中化合物 **13** 的 IC₅₀ 为 0.96 mmol/L,其他化合物的 IC₅₀ 值均大于 1.89 mmol/L 与阳性药相差 100 倍以上,结果如表 1 所示。

3 结论

从白花洋紫荆花分离得到的 17 个化合物主成分为黄酮类成分,且多数被报道具有一定的生物活性,主要集中在抗氧化、抗炎、保护心血管和调节血糖等,如葡萄糖苷类化合物 β -D-甲基葡萄糖苷(**1**)对戊巴比妥钠诱发的实验性心衰猫具有加强心肌收缩力,改善心肌顺应性和左室舒缩功能,增加心排量,升高动脉血压的作用^[22]。对香豆酸(**4**)具有抗氧化、抗炎、免疫调节、抗肿瘤、抗血小板聚集、保护

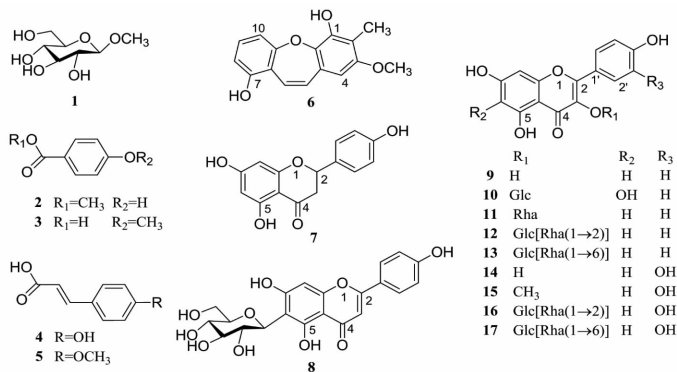


图1 化合物1-17的结构

Fig. 1 Structures of compounds 1-17

表1 不同化合物抑制胰脂肪酶活性的 IC₅₀ ($\bar{x} \pm s, n=3$)Table 1 IC₅₀ values of different compounds inhibiting pancreatic lipase activity ($\bar{x} \pm s, n=3$)

化合物 Compound	IC ₅₀ (mmol/L)
10	1.98 ± 0.05
12	2.10 ± 0.04
13	0.96 ± 0.06
14	2.16 ± 0.07
17	1.89 ± 0.03
奥利司他 Orlistat	0.017 ± 0.08

心血管、预防和改善糖尿病及神经保护作用^[23]。黄酮类化合物柚皮素(7)、山柰酚(9)、槲皮素(14)、3-O-甲基槲皮素(15)、quercetin-3-O- α -L-rhamnopyranosyl-(1→6)- β -D-glucopyranoside(16)具有广泛的药理活性,如抗氧化、抗炎、抗肿瘤、抗感染、心血管保护和血糖调节等药理活性^[24-27]。山柰酚-3-O-鼠李糖苷(11)具有较好的抗幽门螺杆菌活性,并能降低氨苄西林对幽门螺杆菌的MIC^[28],为民间用白花洋紫荆花入药提供了理论依据。胰脂肪酶主要是参与脂质的分解代谢,促进甘油三酯、胆固醇、磷脂等在十二指肠中消化,使得膳食脂肪被充分地消化和吸收,从而治疗肥胖等代谢性疾病^[29],对分离得到量较多的化合物10、12、13、14、17的猪胰脂肪酶抑制活性进行了筛选,结果显示具有一定抑制活性,但与阳性药奥利司他比较抑制活性较弱,但白花洋紫荆花中含有较多的黄酮类成分,在作为抗氧化、预防衰老等保健品开发方面具有较大的潜在价值。

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