

光叶子花的化学成分研究*

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摘要:【目的】为进一步开发光叶子花的药用价值, 对光叶子花进行了化学成分研究。【方法】通过硅胶、Sephadex LH-20 凝胶及 RP-C18 反相硅胶等色谱柱分离纯化, 并运用 MS 和 NMR 等波谱学方法鉴定化合物的化学结构。【结果】从光叶子花花的工业甲醇提取物中分离得到 6 个化合物, 分别鉴定为: D-松醇 (1)、菠留醇 (2)、3-O-[6'-O-palmitoyl-β-D-glucosyl]-spinasta-7,22-diene (3)、胡萝卜苷 (4)、isorhamnetin-3-O-(6''-O-E-feruloyl)-β-D-galactopyranoside (5)、isorhamnetin-3-O-β-D-glucopyranoside (6)。【结论】光叶子花的化学成分研究较少, 本文较深入地对其花的化学成分进行了研究, 化合物 2、5 和 6 均为首次从该植物中分离得到, 在一定程度上丰富了光叶子花的化学成分研究, 有利于进一步开发其药用价值。

关键词: 光叶子花; 化学成分; 结构鉴定

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Chemical Constituents from *Bougainvillea glabra*

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Abstract: [Purpose] The study on the chemical constituents of the flower of *Bougainvillea glabra* Choisy was to exploit its medicinal value. [Method] Compounds were isolated by column chromatography of silica gel, Sephadex LH-20 and RP-C18, and their structures were identified by spectral methods (MS and NMR). [Result] Six compounds were finally isolated and identified as D-pinitol (1), α-spinaterol (2), 3-O-[6'-O-palmitoyl-β-D-glucosyl]-spinasta-7,22-diene (3), daucosterol (4), isorhamnetin-3-O-(6''-O-E-feruloyl)-β-D-galactopyranoside (5), and isorhamnetin-3-O-β-D-glucopyranoside (6), respectively. [Conclusion] There are few reports on the chemical constituents of *B. glabra*, and we extensively investigated the chemical constituents of its flower. Compounds 2, 5 and 6 were isolated from this species for the first time. To a certain extent, our study enriched the chemical constituents of *B. glabra*. This work will be conducive to the exploiting of the medicinal value of *B. glabra*.

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光叶子花 (*Bougainvillea glabra* Choisy) 为紫茉莉科叶子花属植物, 又名宝巾、簕杜鹃、小叶九重葛等, 藤状灌木, 原产南美。因苞片大, 色彩鲜艳, 且持续时间长, 极具观赏性, 光叶子花在中国南方各地被广泛应用于城市景观及园林美化。光叶子花在中国民间已经有较长的药用历史。《中药大辞典》及《昆明民间常用草药》中记载: 光叶子花“苦涩、温, 具有调和气血, 治妇女赤白带下, 月经不调”等功效^[1]。研究表明: 光叶子花不同颜色苞片的提取物都有一定的抗菌作用, 白色光叶子花尤为显著^[2]; 光叶子花提取物具有抗氧化活性^[3]; 光叶子花叶片有抗病虫害的作用^[4], 其叶片提取物还表现出抗糖尿病的特性^[5], 还可有效降低血液中胆固醇含量^[6]。目前, 对于叶子花属植物的化学成分研究还不够深入, 仅有文献报道从该属植物中发现了 D-松醇^[7]、甜菜色素^[8]、3 个黄酮类化合物^[9]、2 个三萜类化合物^[10]和一些挥发性物质^[11-12]。为了进一步开发光叶子花的药用价值, 明确其活性化学物质基础, 本研究对光叶子花花的化学成分进行了较系统的研究。

1 材料与方法

1.1 材料

光叶子花花于 2016 年 6 月采于昆明市。原植物经中国科学院西双版纳热带植物园张玉梅副研究员鉴定为 *Bougainvillea glabra* Choisy。

1.2 提取与分离

干燥的光叶子花花 350 g, 粉碎, 用 2 L 工业甲醇超声提取 3 次, 每次 30 min, 合并 3 次提取液, 减压浓缩得浸膏 40.9 g。经硅胶柱色谱, 以氯仿—甲醇 (10:1、6:1、8:2、0:1 体积比) 梯度洗脱, 得到 11 个组分。(Fr.1~Fr.11)。Fr.3 经 Sephadex LH-20 柱色谱得到 (Fr.3-1~Fr.3-7), 其中 Fr.3-4、Fr.3-5 和 Fr.3-6 经重结晶得到化合物 1 (5.5 g), Fr.3-3 经硅胶柱色谱和 Sephadex LH-20 柱色谱得到化合物 2 (200 mg) 和化合物 3 (108 mg)。Fr.4 经 Sephadex LH-20 柱色谱和重结晶得化合物 4 (312 mg)。Fr.5 经 Sephadex LH-20 柱色谱得到化合物 5 (36 mg)。Fr.6 经 Sephadex LH-20 柱色谱

得到化合物 6 (25 mg)。所有化合物的波谱检测均由中国科学院昆明植物研究所仪器共享中心完成, 其中质谱仪为三扇型双聚焦磁质谱仪, 核磁共振仪为 Bruker DRX-400 和 Bruker AV-800。化合物 1~6 的结构见图 1。

2 结构鉴定

化合物 1: 白色固体, $C_7H_{14}O_6$ 。EI-MS m/z : 194 $[M]^+$ 。 1H -NMR (D_2O , 400 MHz) δ : 3.89 (2H, overlap, H-1, H-6), 3.67 (1H, dd, $J=10.0, 2.6$ Hz, H-2), 3.61 (1H, dd, $J=10.0, 2.6$ Hz, H-5), 3.50 (1H, dd, $J=9.5, 10.0$ Hz, H-4), 3.48 (3H, s, 3-OMe), 3.19 (1H, dd, $J=10.0, 9.5$ Hz, H-3); ^{13}C -NMR (D_2O , 100 MHz) δ : 72.1 (C-1), 71.4 (C-2), 82.7 (C-3), 70.5 (C-4), 71.6 (C-5), 69.7 (C-6), 59.7 (-OCH₃)。以上数据与文献^[13]中 D-松醇 (D-pinitol) 的数据一致。

化合物 2: 白色固体, $C_{29}H_{50}O$ 。EI-MS m/z : 414 $[M]^+$ 。 1H -NMR ($CDCl_3$, 800 MHz) δ : 5.15 (1H, m, H-7), 5.02 (2H, dd, $J=15.2, 8.8$ Hz, H-22, H-23), 3.59 (1H, m, H-3), 1.03 (3H, d, $J=6.6$ Hz, H-21), 0.85 (3H, d, $J=6.6$ Hz, H-26), 0.81 (3H, t, $J=6.6$ Hz, H-29), 0.80 (3H, s, H-19), 0.80 (3H, overlap, H-27), 0.55 (3H, s, H-18); ^{13}C -NMR ($CDCl_3$, 200 MHz) δ : 37.2 (C-1), 31.5 (C-2), 71.1 (C-3), 38.0 (C-4), 40.2 (C-5), 29.6 (C-6), 117.5 (C-7), 139.6 (C-8), 49.4 (C-9), 34.2 (C-10), 21.5 (C-11), 39.5 (C-12), 43.3 (C-13), 55.1 (C-14), 23.0 (C-15), 28.5 (C-16), 55.9 (C-17), 12.0 (C-18), 13.0 (C-19), 40.8 (C-20), 21.4 (C-21), 138.2 (C-22), 129.4 (C-23), 51.2 (C-24), 31.9 (C-25), 21.1 (C-26), 19.0 (C-27), 25.4 (C-28), 12.2 (C-29)。以上数据与文献^[14]中菠留醇的数据一致。

化合物 3: 白色固体, $C_{51}H_{88}O_7$ 。EI-MS m/z : 812 $[M]^+$ 。 1H -NMR ($CDCl_3$, 800 MHz) δ : 5.35 (2H, dd, $J=15.2, 8.4$ Hz, H-22, H-23), 5.15 (1H, m, H-7), 4.39 (1H, d, $J=7.7$ Hz, H-1'), 3.56 (1H, m, H-3), 1.03 (3H, d, $J=6.6$ Hz, H-21), 0.85 (3H, d, $J=6.2$ Hz, H-26), 0.81 (3H, t, $J=6.6$ Hz, H-29), 0.81 (3H, overlap, H-27), 0.80 (3H, s, H-19), 0.55 (3H, s, H-18); ^{13}C -NMR ($CDCl_3$, 200 MHz) δ : 37.1 (C-1), 29.4 (C-2), 78.9 (C-3), 34.2 (C-4), 40.2 (C-5), 29.4 (C-6), 117.3 (C-7), 139.5 (C-8), 49.4 (C-9), 34.4 (C-10), 22.7 (C-

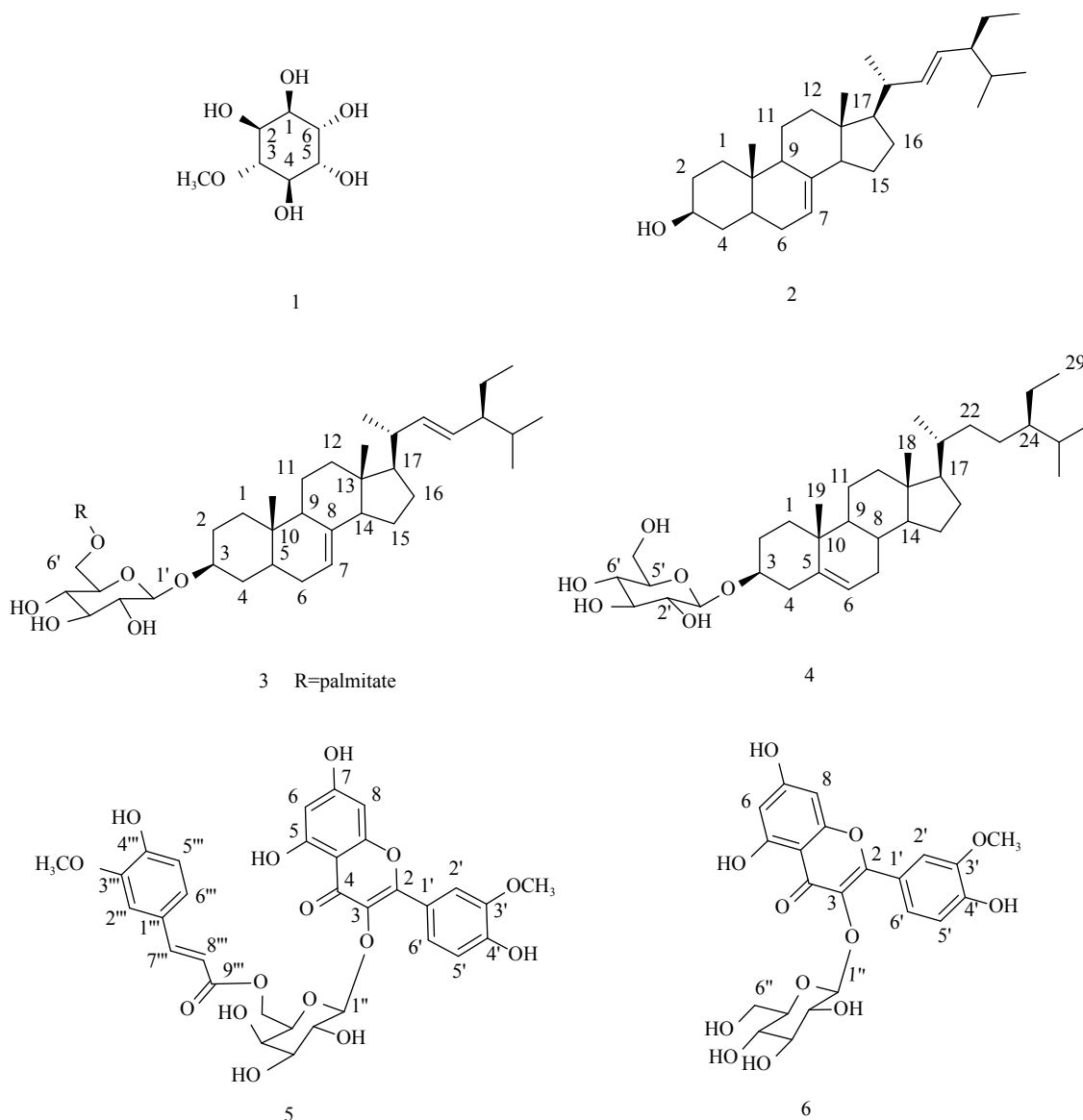


图1 化合物1~6结构

Fig. 1 Chemical structures of compounds 1-6

11), 39.4 (C-12), 43.3 (C-13), 55.1 (C-14), 23.0 (C-15), 29.2 (C-16), 55.9 (C-17), 12.0 (C-18), 12.9 (C-19), 40.8 (C-20), 21.1 (C-21), 138.1 (C-22), 129.5 (C-23), 51.2 (C-24), 31.9 (C-25), 21.4 (C-26), 19.0 (C-27), 25.4 (C-28), 12.2 (C-29), 101.1 (C-1'), 73.9 (C-2'), 75.9 (C-3'), 70.0 (C-4'), 73.6 (C-5'), 63.2 (C-6'), 174.7 (C-1''), 34.3~22.7 (C-2''~C-16''), 14.1 (C-17''). 以上数据与文献^[15]中 3-O-[6'-O-palmitoyl]- β -D-glucosyl]-spinasta-7,22-diene 的数据一致。

化合物 4: 白色粉末, 与 daucosterol 标准品对照, 经 TLC 检测, 其 R_f 值在 3 种不同溶剂体系中一致且显色相同, 故确定为 daucosterol。

化合物 5: 黄色固体, $C_{32}H_{30}O_{15}$ 。EI-MS m/z : 654 $[M]^+$ 。 1H -NMR ($C_5D_5N_5$, 800 MHz) δ : 7.76 (1H, d, $J=2.0$ Hz, H-2'), 7.52 (1H, dd, $J=8.4, 2.0$ Hz, H-6'), 7.34 (1H, d, $J=15.8$ Hz, H-7'''), 7.20 (1H, d, $J=1.2$ Hz, H-2'''), 6.89 (1H, d, $J=8.4$ Hz, H-5'), 6.88 (1H, dd, $J=8.1, 1.2$ Hz, H-6'''), 6.75 (1H, d, $J=8.1$ Hz, H-5'''), 6.22 (1H, d, $J=15.8$ Hz, H-8'''), 6.19 (1H, d, $J=2.0$ Hz, H-8), 6.11 (1H, d, $J=2.0$ Hz, H-6), 5.52 (1H, d, $J=7.8$ Hz, H-1'), 3.88 (3H, s, 3'-OMe), 3.76 (3H, s, 3'''-OMe); ^{13}C -NMR ($C_5D_5N_5$, 200 MHz) δ : 157.5 (C-2), 134.7 (C-3), 178.7 (C-4), 162.8 (C-5), 99.8 (C-6), 165.9 (C-7), 94.6 (C-8), 157.5 (C-9), 105.2 (C-10), 122.1 (C-1'), 114.5 (C-2'), 148.2 (C-

3'), 151.1 (C-4'), 116.2 (C-5'), 122.9 (C-6'), 104.0 (C-1''), 69.8 (C-2''), 74.7 (C-3''), 69.8 (C-4''), 74.7 (C-5''), 64.1 (C-6''), 126.4 (C-1'''), 111.2 (C-2'''), 148.2 (C-3'''), 150.2 (C-4'''), 116.2 (C-5'''), 123.8 (C-6'''), 145.7 (C-7'''), 114.5 (C-8'''), 167.2 (C-9'''), 56.5 (3'-OCH₃), 55.9 (3'''-OCH₃)。以上数据与文献^[16]中 isorhamnetin-3-O-(6'''-O-E-feruloyl)- β -D-galactopyranoside 的数据一致。

化合物 6: C₂₄H₂₂O₁₂。EI-MS m/z : 502 [M]⁺。¹H-NMR (C₅D₅N₅, 800 MHz) δ : 7.83 (1H, s, H-2'), 7.49 (1H, d, $J=8.0$, H-6'), 6.82 (1H, d, $J=8.0$, H-5'), 6.31 (1H, brs, H-8), 6.11 (1H, brs, H-6), 5.31 (1H, d, $J=6.8$, H-1''), 3.87 (3H, s, 3'-OMe); ¹³C-NMR (C₅D₅N₅, 200 MHz) δ : 157.6 (C-2), 134.7 (C-3), 178.8 (C-4), 162.9 (C-5), 99.9 (C-6), 166.0 (C-7), 94.6 (C-8), 157.3 (C-9), 105.3 (C-10), 123.1 (C-1'), 116.2 (C-2'), 151.2 (C-3'), 148.0 (C-4'), 114.6 (C-5'), 123.9 (C-6'), 103.4 (C-1''), 76.3 (C-2''), 78.5 (C-3''), 71.4 (C-4''), 78.5 (C-5''), 62.2 (C-6''), 56.6 (-OCH₃)。以上数据与文献^[17]中 isorhamnetin-3-O- β -D-glucopyranoside 的数据一致。

3 讨论

光叶子花是中国南方地区广泛栽培的园林园艺植物,民间也将其作为调经活血草药使用,但目前针对光叶子花的化学成分研究非常少,本研究组前期对光叶子花枝叶的化学成分做了较系统的研究,文献中对于光叶子花花的研究也均集中于其红色素类成分。本研究则较系统地从其花的甲醇提取物中分离得鉴定了 6 个化合物,这在一定程度上丰富了光叶子花的化学成分研究。此外,我们从 350 g 光叶子花中分离得到 5.5 g D-松醇,得率达到 1.57%,表明 D-松醇是光叶子花花的主要化学成分。据文献报道, D-松醇具有降血糖^[18-19]、抗肿瘤^[20-21]、免疫调节^[22-23]等多种生物活性,也可作为植物杀菌剂^[24],具有较大的潜在药用开发价值。由于 D-松醇的水溶性较好,甲醇溶解度不高,如采用甲醇和水的混合溶剂来提取,可能会提取得更完全,得率更高。因此,光叶子花的花可作为 D-松醇的资源植物开展进一步研究,以深入发掘其药用价值并为植物资源的可持续利用提供试验依据。

本研究由于采样量较少而未对光叶子花的花

进行更深入的纯化分离,仅从中分离得到 6 个化合物。除去已知的 D-松醇有很好的生物活性以外,未发现其他生物活性很好的单体化合物。因此,为了进一步开发和利用光叶子花这一园林绿化植物的丰富资源,有必要进一步对其花的化学成分与活性进行更系统深入的研究。

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