

苏铁的化学成分研究

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摘要:对苏铁(*Cycas revoluta*)的化学成分进行研究,采用多种色谱技术(硅胶、氧化铝和 Sephadex LH-20 等)从苏铁茎的乙酸乙酯部位分离得到 16 个化合物,其结构由 HR-ESI-MS、¹H 和 ¹³C NMR 等波谱学方法鉴定为 5,6-去氢柳杉酚(1)、cunningine A(2)、6-羟基-5,6-去氢柳杉酚(3)、6 α -羟基-7-氧代弥罗松酚(4)、ligballinol(5)、xanthoxyl(6)、callisignan A(7)、(2*R*,3*R*)-bis[(4-hydroxy-3-methoxyphenyl)methyl]-1,4-diacetate(8)、开环异落叶松脂醇(9)、二氢山萘酚(10)、4'-甲基木犀草素(11)、5-methoxypinosylvin(12)、*N*-benzoylphenyl alaninol(13)、(*E*,4*R*)-4-hydroxy-4,5,5-trimethyl-3-(3-oxobut-1-enyl)cyclohex-2-enone(14)、3-hydroxy-5 α ,6 α -epoxy- β -ionone(15)和 acuminantin(16)。以上化合物均为首次从苏铁属植物中分离得到,其中化合物 13 和 16 为首次以天然产物报道。本研究还首次发现了苏铁属植物中含有松香烷型二萜类(1~4)和芪类(12)化合物。化合物 11 具有中等的体外 α -葡萄糖苷酶抑制活性。

关键词:苏铁;化学成分;松香烷型二萜;芪类; α -葡萄糖苷酶

中图分类号:R284.2

文献标识码:A

文章编号:1001-6880(2019)1-0075-06

DOI:10.16333/j.1001-6880.2019.1.012

Chemical constituents from *Cycas revoluta*

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Abstract: Sixteen compounds were isolated from the stems of *Cycas revoluta* by various column chromatography involving silica gel, Al₂O₃, and Sephadex LH-20. Their structures were identified as 5,6-dehydrosugiol (1), cunningine A (2), 6-hydroxy-5,6-dehydrosugiol (3), 6 α -hydroxy-7-oxoferruginol (4), ligballinol (5), xanthoxyl (6), callisignan A (7), (2*R*,3*R*)-bis[(4-hydroxy-3-methoxyphenyl)methyl]-1,4-diacetate (8), secoisolariciresinol (9), dihydrokaempferol (10), 4'-methyluteolin (11), 5-methoxypinosylvin (12), *N*-benzoylphenyl alaninol (13), (*E*,4*R*)-4-hydroxy-4,5,5-trimethyl-3-(3-oxobut-1-enyl)cyclohex-2-enone (14), 3-hydroxy-5 α ,6 α -epoxy- β -ionone (15), and acuminantin (16) based on HR-ESI-MS, ¹H, and ¹³C NMR spectroscopic data. All the isolates were obtained from this genus for the first time, of which compounds 13 and 16 were firstly reported as the natural products. This is the first time to reveal abietane-type diterpenes (1-4) and stilbene (12) in this genus. Compound 11 showed moderate α -glucosidase inhibitory activity *in vitro*, with an inhibition rate of 52.51 \pm 2.63 % at the concentration of 198.00 μ g/mL.

Key words: *Cycas revoluta*; chemical constituents; abietane-type diterpenes; stilbenes; α -glucosidase

苏铁(*Cycas revoluta* Thunb.), 别名铁树, 又名凤尾铁、凤尾蕉、凤尾松等, 为苏铁科(Cycadaceae)苏铁属中分布最广泛的种^[1]。现代药理学研究表

明, 苏铁种子具有平肝、降血压等活性^[2], 其顶生枝具有利尿和止血作用, 在治疗高血压、癌症、肝脏疾病、艾滋病和糖尿病等多种疾病的药物中均有应用^[3]。前期研究表明, 苏铁中主要含有双黄酮(穗花杉双黄酮和扁柏双黄酮)、黄酮、偶氮类化合物、木脂素和甾体等成分, 其中偶氮类化合物为苏铁的

收稿日期:2018-02-05

接受日期:2018-05-23

基金项目:中国科学院百人计划;云岭学者人才项目

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特征性成分^[4]。前述研究主要围绕苏铁的种子和叶展开,而苏铁茎的化学成分少有报道。为了深入揭示苏铁的化学成分,作者对苏铁茎的乙酸乙酯部位进行了系统研究,从中分离鉴定 16 个化合物,均为首次从苏铁属植物中分离得到;其中化合物 **13** 和 **16** 为首次以天然产物报道。首次发现苏铁属植物中含有松香烷型二萜类(**1~4**)和芪类(**12**)化合物。本研究进一步丰富了苏铁属植物的化学成分多样性,为苏铁资源的深入开发利用提供了一定的依据。

1 仪器、试剂与材料

岛津 LCMS-IT-TOF 质谱仪 (Shimadzu, 日本);¹H 和¹³C NMR 谱用 DRX-500 和 Avance III-600 型超导核磁共振仪 (Bruker, 德国)测定;HPLC 分离利用岛津 SIL10AP 液相色谱仪 (Shimadzu, 日本)开展,色谱柱为 Agilent XDB-C₁₈ (5 μm, 9.4 × 250 mm);MCI (CHP-20P gel)购自日本三菱化学公司;中压液相 (Dr Flash-II) 为上海利穗产品;Sephadex LH-20 购自 Pharmacia 公司;硅胶薄层色谱购自默克化工技术(上海)有限公司,柱色谱硅胶(200~300目)购自青岛海洋化工有限公司;柱色谱氧化铝(100~200目)购于上海五四化学试剂厂;分析纯乙腈和甲醇购自江苏汉邦科技有限公司;显色剂为 10% 的硫酸-乙醇溶液。

FlexStation 3 台式多功能酶标仪 (Bio-RAD 680, 美国);α-葡萄糖苷酶-麦芽糖酶(固体酵母)和生物技术级对硝基苯-α-D-吡喃葡萄糖苷 (PNPG)均购自上海源叶生物科技有限公司,分析纯磷酸氢二钠和磷酸二氢钠分别购自上海阿达玛斯试剂有限公司和成都市联合化工试剂研究所,分析纯无水碳酸钠购自西陇化工有限公司。

苏铁植物样品于 2016 年 7 月采自中国科学院昆明植物研究所昆明植物园,由中国科学院昆明植物研究所雷立公副研究员确定为苏铁 (*Cycas revoluta* Thunb.), 标本存放于中国科学院昆明植物研究所抗病毒与天然药物研究组(标本凭证号: No. 201607003)。

2 实验方法

2.1 提取与分离

新鲜苏铁茎(20 kg)粉碎后,用 90% 乙醇室温浸提 3 次,每次 48 h,合并提取液减压浓缩得到浸膏 2 kg。将总浸膏分散于水中,用乙酸乙酯萃取 3 次(10 L × 3),合并后减压浓缩,得到乙酸乙酯部位 960 g。乙酸乙酯部位经硅胶柱层析(4 kg, 20 × 85

cm), 丙酮-石油醚体系(0:1→1:0)梯度洗脱,经 TLC 检测合并,得到 7 个流分 Frs. 1~7。Fr. 3(16 g)经硅胶柱色谱层析(200 g, 5.5 × 25 cm), 丙酮-石油醚体系(5:95→100:0)梯度洗脱得到 4 个流分 Frs. 3-1~3-4。流分 Fr. 3-3(2.23 g)经硅胶柱色谱层析(30 g, 3 × 26 cm), 丙酮-石油醚体系(2:98→5:95)梯度洗脱得到 3 个流分 Frs. 3-3-1~3-3-3。Fr. 3-3-1(500 mg)经反复硅胶柱以及凝胶柱色谱层析,得到化合物 **15**(1.2 mg)和 **16**(1 mg)。Fr. 3-3-3(76 mg)经制备型 HPLC(液相条件:0~25 min, 水-乙腈 40:60, 流速:3 mL/min), 得到化合物 **1**(2 mg)、**2**(3 mg)、**3**(3 mg)和 **4**(4 mg)。Fr. 4(12 g)经 MCI 柱色谱层析,水-甲醇(90:10→0:100)梯度洗脱, TLC 检测合并相同流分得到 3 个流分 Frs. 4-1~4-3。继续对 Fr. 4-2(11 g)进行硅胶柱色谱层析(120 g, 5.2 × 24 cm), 用乙酸乙酯-石油醚体系(2:98→50:50)梯度洗脱,得到 13 个流分 Frs. 4-2-1~4-2-13。Fr. 4-2-5(190 mg)经反复硅胶柱色谱层析,分离得到化合物 **5**(7 mg)、**7**(5 mg); Fr. 4-2-8(1.6 g)经硅胶柱色谱层析(20 g, 4.5 × 26 cm), 乙酸乙酯-石油醚体系(5:95→50:50)梯度洗脱,分离得到化合物 **6**(2 mg)、**13**(2 mg)和 **14**(3 mg)。Fr. 6(140 g)经硅胶柱色谱层析(1.5 kg, 9.3 × 40 cm), 水-甲醇-氯仿体系(9:1:0.1→6:4:0.4)梯度洗脱,得到 5 个流分 Frs. 6-1~6-5。Fr. 6-2(14.2 g)经 Rp C₁₈ 柱色谱,水-甲醇(70:30→0:100)梯度洗脱,得到 3 个流分 Frs. 6-2-1~6-2-3。Fr. 6-2-2(510 mg)经反复凝胶及硅胶柱色谱层析后,经 HPLC(Agilent XDB-C₁₈, 9.4 × 250 mm, 5 μm)纯化,用乙腈-水(35:65)洗脱,分离得到化合物 **8**(6 mg)和 **9**(7 mg)。Fr. 6-2-1(7.5 g)经硅胶柱色谱层析(150 g, 4.2 × 28 cm), 得到 4 个流分 Frs. 6-2-1-1~6-2-1-4。Fr. 6-2-1-2(1.7 g)经反复硅胶及凝胶柱色谱层析,得到化合物 **11**(30 mg); Fr. 6-2-1-3(0.2 g)经 HPLC(Agilent XDB-C₁₈, 9.4 × 250 mm, 5 μm)纯化,乙腈-水(58:42)洗脱,得到化合物 **10**(2 mg)和 **12**(7 mg)。

2.2 α-葡萄糖苷酶抑制活性

按文献报道的 96 孔板筛选方法^[5-7], 对部分化合物进行体外 α-葡萄糖苷酶抑制活性筛选, 计算各化合物的抑制率, 并利用 GraphPad Prism 5 软件计算 IC₅₀ 值。

3 结果与讨论

3.1 结构鉴定

化合物 **1** 白色粉末; mp. 280~282 °C; ¹H

NMR (CDCl₃, 600 MHz) δ : 8.00 (1H, s, H-6), 6.85 (1H, s, H-14), 6.45 (1H, s, H-11), 3.50 (1H, m, H-15), 1.50 (3H, s, H-20), 1.26 (6H, d, $J = 6.8$ Hz, H-17, H-18), 1.25 (3H, s, H-16), 1.16 (3H, s, H-19); ¹³C NMR (CDCl₃, 150 MHz) δ : 37.7 (C-1), 18.6 (C-2), 40.3 (C-3), 37.4 (C-4), 172.9 (C-5), 124.9 (C-6), 185.2 (C-7), 123.9 (C-8), 153.9 (C-9), 41.0 (C-10), 124.5 (C-11), 157.2 (C-12), 133.4 (C-13), 111.0 (C-14), 26.9 (C-15), 22.5 (C-16), 22.3 (C-17), 32.6 (C-18), 32.9 (C-19), 29.1 (C-20); HRESIMS: m/z 297.1851 ([M-H]⁻, *calcd.* for C₂₀H₂₆O₂, 297.1860), 以上数据与文献^[8]报道一致, 故鉴定为 5,6-去氢柳杉酚 (5,6-dehydrosugiol)。

化合物 2 白色粉末; mp. 246 ~ 248 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 7.83 (1H, s, H-14), 6.63 (1H, s, H-11), 3.30 (1H, m, H-15), 2.74 (H, m, H-2), 2.47 (1H, m, H-2), 2.13 (2H, t, $J = 6.1$ Hz, H-1), 1.96 (2H, t, $J = 6.4$ Hz, H-3), 1.59 (3H, s, H-20), 1.41 (3H, s, H-19), 1.31 (3H, s, H-18), 1.20 (6H, d, $J = 5.9$ Hz, H-16, H-17); ¹³C NMR (CDCl₃, 150 MHz) δ : 37.6 (C-1), 33.7 (C-2), 217.2 (C-3), 47.8 (C-4), 53.9 (C-5), 72.1 (C-6), 198.3 (C-7), 121.1 (C-8), 153.1 (C-9), 38.1 (C-10), 112.0 (C-11), 160.2 (C-12), 134.9 (C-13), 121.1 (C-14), 27.0 (C-15), 22.5 (C-16), 22.4 (C-17), 29.9 (C-18), 20.1 (C-19), 24.7 (C-20); HRESIMS: m/z 329.1755 ([M-H]⁻, *calcd.* for C₂₀H₂₆O₄, 329.1758), 以上数据与文献^[9]报道一致, 故鉴定为 cunningine A。

化合物 3 白色粉末; mp. 170 ~ 172 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 7.88 (1H, s, H-14), 6.80 (1H, s, H-11), 3.28 (1H, m, H-15), 2.38 (2H, t, $J = 3.5$ Hz, H-3), 1.97 (1H, m, H-2), 1.97 (1H, d, $J = 7.1$ Hz, H-5), 1.74 (1H, t, $J = 5.9$ Hz, H-2), 1.71 (1H, t, $J = 7.4$ Hz, H-1), 1.49 (3H, s, H-20), 1.47 (1H, t, $J = 6.5$ Hz, H-1), 1.44 (6H, s, H-18, H-19), 1.21 (6H, d, $J = 7.9$ Hz, H-16, H-17); ¹³C NMR (CDCl₃, 150 MHz) δ : 35.7 (C-1), 18.7 (C-2), 39.1 (C-3), 34.8 (C-4), 142.1 (C-5), 145.5 (C-6), 181.4 (C-7), 121.0 (C-8), 156.5 (C-9), 41.6 (C-10), 112.0 (C-11), 161.5 (C-12), 136.0 (C-13), 125.9 (C-14), 28.2 (C-15), 22.9 (C-16), 23.0 (C-17), 28.8 (C-18), 28.1 (C-19), 37.1 (C-20);

HRESIMS: m/z 313.1798 ([M-H]⁻, *calcd.* for C₂₀H₂₆O₃, 313.1809), 以上数据与文献^[10]报道一致, 故鉴定为 6-羟基-5,6-去氢柳杉酚 (6-hydroxy-5,6-dehydrosugiol)。

化合物 4 白色胶状物; ¹H NMR (CDCl₃, 600 MHz) δ : 7.82 (1H, s, H-14), 6.76 (1H, s, H-11), 4.63 (1H, s, -OH), 4.54 (1H, d, $J = 12.5$ Hz, H-6), 3.22 (1H, m, H-15), 2.26 (1H, d, $J = 12.6$ Hz, H-5), 1.82 (2H, m, H-3), 1.62 (2H, m, H-2), 1.32 (5H, m, H-1, H-16), 1.21 (12H, m, Me-17, 18, 19, 20); ¹³C NMR (CDCl₃, 150 MHz) δ : 20.1 (C-1), 40.4 (C-2), 44.5 (C-3), 40.0 (C-4), 57.3 (C-5), 75.0 (C-6), 201.2 (C-7), 122.3 (C-8), 157.9 (C-9), 35.3 (C-10), 110.4 (C-11), 162.7 (C-12), 135.3 (C-13), 127.5 (C-14), 28.0 (C-15), 22.9 (C-16), 22.9 (C-17), 22.4 (C-18), 36.8 (C-19), 25.4 (C-20); HRESIMS: m/z 315.1945 ([M-H]⁻, *calcd.* for C₂₀H₂₈O₃, 315.1966), 以上数据与文献^[11]报道一致, 故鉴定为 6 α -羟基-7-氧代弥罗松酚 (6 α -hydroxy-7-oxoferruginol)。

化合物 5 白色粉末; mp. 145 ~ 147 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 7.19 (4H, d, $J = 8.6$ Hz, H-2, H-2', H-6, H-6'), 6.76 (4H, d, $J = 8.6$ Hz, H-3, H-3', H-5, H-5'), 4.68 (2H, d, $J = 4.1$ Hz, H-7, H-7'), 4.19 (2H, m, H-9, H-9'), 3.80 (2H, m, H-9, H-9'), 3.11 (2H, m, H-8, H-8'); ¹³C NMR (CDCl₃, 150 MHz) δ : 133.0 (C-1, C-1'), 116.2 (C-3, C-3', C-5, C-5'), 158.2 (C-4, C-4'), 128.7 (C-2, C-2', C-6, C-6'), 87.4 (C-7, C-7'), 55.3 (C-8, C-8'), 72.5 (C-9, C-9'); HRESIMS: m/z 299.1301 ([M+H]⁺, *calcd.* for C₁₈H₁₈O₄, 299.1278), 以上数据与文献^[12]报道一致, 故鉴定为 ligballinol。

化合物 6 白色粉末; mp. 34 ~ 36 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 6.77 ~ 6.89 (6H, m, Ar-H), 5.95 (2H, s, H-10), 5.59 (1H, brs, -OH), 4.72 (2H, d, $J = 3.2$ Hz, H-7, H-7'), 4.23 (2H, m, H-9, H-9'), 3.88 (3H, s, H-10'), 3.86 (2H, m, H-9, H-9'), 3.08 (2H, m, H-8, H-8'); ¹³C NMR (CDCl₃, 150 MHz) δ : 132.9 (C-1), 108.2 (C-2), 146.7 (C-3), 145.2 (C-4), 114.2 (C-5), 118.9 (C-6), 85.9 (C-7), 54.1 (C-8), 71.7 (C-9), 101.1 (C-10), 135.1 (C-1'), 106.5 (C-2'), 147.9 (C-3'), 147.1 (C-4'), 108.5 (C-5'), 119.3 (C-6'), 85.8 (C-7'), 54.3 (C-8'), 71.6 (C-9'), 55.9 (C-10', -OMe); HRES-

IMS; m/z 355. 1178 ($[M-H]^-$, *calcd.* for $C_{20}H_{20}O_6$, 355. 1187), 以上数据与文献^[13]报道一致, 故鉴定为 xanthoxylol。

化合物 7 黄色油状物; 1H NMR ($CDCl_3$, 600 MHz) δ : 6. 96 (1H, s, H-3'), 6. 91 (1H, s, H-5'), 6. 85 (1H, m, H-6), 6. 82 (1H, m, H-5), 6. 75 (1H, s, H-2), 6. 69 ~ 6. 77 (2H, brs, H-10', H-11, -OH), 6. 25 (1H, d, $J = 18.0$ Hz, H-7'), 6. 05 (1H, dq, $J = 18.0, 6.6$ Hz, H-8'), 5. 08 (1H, d, $J = 9.5$ Hz, H-7), 3. 85 (3H, s, H-10), 3. 45 (1H, m, H-8), 1. 85 (3H, d, $J = 6.6$ Hz, H-9'), 1. 43 (3H, d, $J = 6.0$ Hz, H-9); ^{13}C NMR ($CDCl_3$, 150 MHz) δ : 133. 0 (C-1), 108. 7 (C-2), 146. 8 (C-3), 145. 9 (C-4), 114. 2 (C-5), 119. 9 (C-6), 93. 9, (C-7), 45. 9 (C-8), 17. 3 (C-9), 55. 9 (C-10), 145. 7 (C-1'), 130. 6 (C-2'), 112. 8 (C-3'), 130. 5 (C-4'), 112. 8 (C-5'), 132. 5 (C-6'), 130. 7 (C-7'), 123. 5 (C-8'), 18. 3 (C-9'); HRESIMS; m/z 313. 1445 ($[M+H]^+$, *calcd.* for $C_{19}H_{20}O_4$, 313. 1434), 以上数据与文献^[14]报道一致, 故鉴定为 callisignan A。

化合物 8 黄色油状物; mp. 103 ~ 105 °C; 1H NMR ($CDCl_3$, 600 MHz) δ : 6. 79 (2H, d, $J = 6.0$ Hz, H-5, H-5'), 6. 54 (2H, dd, $J = 6.0, 1.2$ Hz, H-6, H-6'), 6. 45 (2H, d, $J = 1.2$ Hz, H-2, H-2'), 5. 54 (2H, brs, H-4, H-4', -OH), 4. 19 (2H, dd, $J = 8.4, 4.8$ Hz, H-9, H-9'), 4. 02 (2H, d, $J = 8.4, 4.2$ Hz, H-9, H-9'), 3. 78 (6H, s, H-12, H-12', -OMe), 2. 61 (4H, d, $J = 5.4$ Hz, H-7, H-7'), 2. 07 (2H, m, H-8, H-8'), 2. 06 (6H, s, H-11, H-11'); ^{13}C NMR ($CDCl_3$, 150 MHz) δ : 131. 5 (C-1, C-1'), 121. 7 (C-2, C-2'), 114. 1 (C-3, C-3'), 143. 9 (C-4, C-4'), 146. 4 (C-5, C-5'), 111. 1 (C-6, C-6'), 35. 1 (C-7, C-7'), 39. 6 (C-8, C-8'), 64. 4 (C-9, C-9'), 171. 0 (C-10, 10'), 21. 0 (C-11, C-11'), 55. 7 (C-12, C-12'); HRESIMS: m/z 445. 1871 ($[M-H]^-$, *calcd.* for $C_{24}H_{30}O_8$, 445. 1868), 以上数据与文献^[15]报道一致, 故鉴定为 (2*R*, 3*R*)-bis[(4-hydroxy-3-methoxyphenyl)methyl]-1,4-diacetate。

化合物 9 白色粉末; mp. 108 ~ 110 °C; 1H NMR (CD_3OD , 600 MHz) δ : 6. 65 (2H, d, $J = 8.0$ Hz, H-5, H-5'), 6. 57 (2H, d, $J = 1.2$ Hz, H-2, H-2'), 6. 54 (2H, dd, $J = 8.0$ Hz, 1. 2 Hz, H-6, H-6'), 3. 80 (6H, s, H-10, H-10', -OMe), 3. 57 - 3. 30

(4H, m, H-9, H-9'), 2. 64 (2H, d, $J = 6.8$ Hz, H-7, H-7'), 2. 53 (2H, d, $J = 7.8$ Hz, H-7, H-7'), 1. 90 (2H, m, H-8, H-8'); ^{13}C NMR (CD_3OD , 150 MHz) δ : 133. 9 (C-1, C-1'), 113. 3 (C-2, C-2'), 148. 8 (C-3, C-3'), 145. 5 (C-4, C-4'), 115. 8 (C-5, C-5'), 122. 7 (C-6, C-6'), 36. 0 (C-7, C-7'), 44. 1 (C-8, C-8'), 62. 1 (C-9, C-9'), 56. 2 (C-10, C-10'); HRESIMS: m/z 361. 1648 ($[M-H]^-$, *calcd.* for $C_{20}H_{26}O_6$, 361. 1657), 以上数据与文献^[16]报道一致, 故鉴定为开环异落叶松脂醇 (secoisolariciresinol)。

化合物 10 黄色粉末; mp. 200 ~ 202 °C; 1H NMR (CD_3OD , 500 MHz) δ : 7. 35 (2H, d, $J = 8.5$ Hz, H-2', H-6'), 6. 82 (2H, d, $J = 8.5$ Hz, H-3', H-5'), 5. 86 (2H, s, H-6, H-8), 4. 94 (1H, d, $J = 11.4$ Hz, H-2), 4. 52 (1H, d, $J = 11.4$ Hz, H-3); ^{13}C NMR (CD_3OD , 125 MHz) δ : 84. 9 (C-2), 73. 6 (C-3), 198. 3 (C-4), 101. 8 (C-4a), 164. 5 (C-5), 96. 4 (C-6), 169. 1 (C-7), 97. 2 (C-8), 164. 7 (C-8a), 129. 3 (C-1'), 116. 2 (C-3', C-5'), 159. 2 (C-4'), 130. 4 (C-2', C-6'); HRESIMS: m/z 287. 0559 ($[M-H]^-$, *calcd.* for $C_{15}H_{12}O_6$, 287. 0561), 以上数据与文献^[17]报道一致, 故鉴定为二氢山柰酚 (dihydrokaempferol)。

化合物 11 黄色粉末; mp. 210 ~ 212 °C; 1H NMR (CD_3OD , 600 MHz) δ : 7. 38 (1H, d, $J = 8.5$ Hz, H-6'), 7. 35 (1H, s, H-6), 7. 06 (1H, d, $J = 8.5$ Hz, H-5'), 6. 58 (1H, s, H-2'), 6. 44 (1H, s, H-3), 6. 20 (1H, s, H-8), 4. 58 (3H, brs, H-3', H-5, H-7, -OH), 3. 93 (3H, s, H-7', -OMe); ^{13}C NMR ($MeOD$, 150 MHz) δ : 163. 2 (C-2), 104. 5 (C-3), 183. 9 (C-4), 105. 4 (C-4a), 166. 2 (C-5), 100. 2 (C-6), 166. 0 (C-7), 95. 0 (C-8), 159. 4 (C-8a), 125. 0 (C-1'), 113. 9 (C-2'), 148. 2 (C-3'), 152. 7 (C-4'), 112. 7 (C-5'), 120. 0 (C-6'), 56. 5 (-OMe); HRESIMS: m/z 301. 0739 ($[M+H]^+$, *calcd.* for $C_{16}H_{12}O_6$, 301. 0707), 以上数据与文献^[18]报道一致, 故鉴定为 4'-甲基木犀草素 (4'-methyluteolin)。

化合物 12 白色粉末; mp. 122 ~ 124 °C; 1H NMR ($CDCl_3$, 600 MHz) δ : 7. 50 (2H, s, H-2, H-6), 7. 35 (2H, d, $J = 7.4$ Hz, H-2', H-6'), 7. 26 (1H, m, H-4'), 7. 07 (1H, d, $J = 16.4$ Hz, H-7), 6. 99 (1H, d, $J = 16.4$ Hz, H-8), 6. 62 (2H, m, H-3', H-5'), 6. 34 (1H, s, H-4), 4. 86 (1H, brs, H-5, -OH), 3. 82 (3H, s, H-9, -OMe); ^{13}C NMR ($CDCl_3$, 150 MHz) δ : 137. 0 (C-1), 126. 6 (C-2), 129. 7 (C-3), 126. 6 (C-

4), 128.7 (C-5), 126.6 (C-6), 128.7 (C-7), 129.8 (C-8), 139.7 (C-1'), 105.0 (C-2'), 156.8 (C-3'), 101.0 (C-4'), 161.1 (C-5'), 105.9 (C-6'), 55.6 (C-9, -OMe); HRESIMS: m/z 227. 1045 ($[M + H]^+$, *calcd.* for $C_{15}H_{14}O_2$, 227. 1067), 以上数据与文献^[19]报道一致, 故鉴定为 5-methoxypinosylvin。

化合物 13 白色粉末; mp. 174 ~ 176 °C; 1H NMR (CD_3OD , 600 MHz) δ : 7.15 ~ 7.72 (10H, m, Ar-H), 4.34 (1H, m, H-1'), 3.83 (2H, m, H-9'), 3.01 (1H, d, $J = 8.5$ Hz, H-N), 2.85 (2H, dd, $J = 12.8, 8.3$ Hz, H-2'); ^{13}C NMR (CD_3OD , 125 MHz) δ : 170.5 (C-1), 136.1 (C-2), 128.4 (C-3, C-7), 132.7 (C-5), 129.5 (C-4, C-6), 55.1 (C-1'), 38.1 (C-2'), 140.1 (C-3'), 129.6 (C-4', C-8'), 127.5 (C-6'), 130.5 (C-5', C-7'), 64.4 (C-9'); HRESIMS: m/z 256. 1368 ($[M + H]^+$, *calcd.* for $C_{16}H_{17}NO_2$, 256. 1332), 以上数据与文献^[20]报道一致, 故鉴定为 *N*-benzoylphenyl alaninol。

化合物 14 白色胶状物; 1H NMR (CD_3OD , 600 MHz) δ : 6.99 (1H, d, $J = 15.8$ Hz, H-1'), 6.43 (1H, d, $J = 15.8$ Hz, H-2'), 5.93 (1H, s, H-2), 2.60 (2H, s, H-6), 1.89 (3H, s, H-7), 1.05 (3H, s, H-8), 1.01 (3H, s, H-9); ^{13}C NMR (CD_3OD , 150 MHz) δ : 200.9 (C-1), 128.2 (C-2), 164.8 (C-3), 80.1 (C-4), 42.8 (C-5), 50.7 (C-6), 19.3 (C-7), 23.7 (C-8), 24.9 (C-9), 148.5 (C-1'), 131.9 (C-2'), 200.6 (C-3'), 27.8 (C-4'); HRESIMS: m/z 223. 1307 ($[M + H]^+$, *calcd.* for $C_{13}H_{18}O_3$, 223. 1329), 以上数据与文献^[21]报道一致, 故鉴定为 (*E*, 4*R*)-4-hydroxy-4, 5, 5-trimethyl-3-(3-oxobut-1-enyl)cyclohex-2-enone。

化合物 15 白色胶状物; 1H NMR (CD_3OD , 600 MHz) δ : 7.16 (1H, d, $J = 15.7$ Hz, H-1'), 6.17 (1H, d, $J = 15.7$ Hz, H-2'), 3.75 (1H, m, H-4), 2.28 (3H, s, H-4'), 1.86 (3H, s, H-7), 1.65 (1H, dd, $J = 14.3, 9.2$ Hz, H-3), 1.58 (1H, dd, $J = 14.3, 3, 1.8$ Hz, H-3), 1.26 (2H, d, $J = 10.9$ Hz, H-5), 1.20 (3H, s, H-8), 0.94 (3H, s, H-9); ^{13}C NMR (CD_3OD , 150 MHz) δ : 71.0 (C-1), 70.0 (C-2), 41.5 (C-3), 67.4 (C-4), 47.8 (C-5), 36.3 (C-6), 20.2 (C-7), 27.6 (C-8), 25.3 (C-9), 145.6 (C-1'), 133.9 (C-2'), 200.4 (C-3'), 29.9 (C-4'); HRESIMS: m/z 225. 1481 ($[M + H]^+$, *calcd.* for C_{13}

$H_{20}O_3$, 225. 1485), 以上数据与文献^[22]报道一致, 故鉴定为 3-hydroxy-5 α , 6 α -epoxy- β -ionone。

化合物 16 白色胶状物; 1H NMR (CD_3OD , 600 MHz) δ : 6.63 - 6.84 (6H, m, Ar-H), 5.92 (2H, s, H-10), 4.74 (1H, d, $J = 6.6$ Hz, H-7), 3.95 (2H, d, $J = 6.5$ Hz, H-9'), 3.84 (3H, s, H-10', -OMe), 3.70 (1H, dd, $J = 14.3, 6.0$ Hz, H-9), 3.62 (1H, dd, $J = 11.0, 4.4$ Hz, H-9), 2.48 (1H, m, H-8'), 2.31 (1H, m, H-8); ^{13}C NMR (CD_3OD , 150 MHz) δ : 138.7 (C-1), 107.4 (C-2), 149.4 (C-3), 148.6 (C-4), 109.0 (C-5), 120.1 (C-6), 84.1 (C-7), 54.4 (C-8), 60.5 (C-9), 102.5 (C-10), 133.6 (C-1'), 113.5 (C-2'), 149.2 (C-3'), 146.0 (C-4'), 116.3 (C-5'), 122.3 (C-6'), 33.7 (C-7'), 44.0 (C-8'), 73.7 (C-9'), 56.5 (C-10', -OMe); HRESIMS: m/z 357. 1331 ($[M - H]^-$, *calcd.* for $C_{20}H_{22}O_6$, 357. 1344), 以上数据和文献^[23]报道一致, 故鉴定为 acuminantin。

3.2 α -葡萄糖苷酶抑制活性

按 2.2 项方法, 对化合物 **1**、**2**、**6**、**7**、**10**、**11** 和 **12** 进行了体外 α -葡萄糖苷酶抑制活性测试, 测试结果见表 1。

表 1 7 个化合物对 α -葡萄糖苷酶的抑制作用 ($n = 3, \bar{x} \pm SD_s$)

Table 1 The inhibition rates of the tested compounds on α -glucosidase ($n = 3, \bar{x} \pm SD_s$)

化合物 Compounds	浓度 Concentration ($\mu g/mL$)	抑制率 Inhibition rates (%)
1	200.00	-1.57 \pm 0.43
	100.00	3.01 \pm 0.22
2	200.00	0.22 \pm 0.03
	100.00	1.36 \pm 0.43
6	200.00	-5.54 \pm 1.06
	100.00	-2.65 \pm 0.62
7	204.00	4.37 \pm 0.87
	102.00	2.05 \pm 0.74
10	196.00	-0.52 \pm 0.03
	98.00	1.46 \pm 0.03
11	198.00	52.51 \pm 2.63
	99.00	18.75 \pm 1.32
12	196.00	4.14 \pm 1.04
	98.00	3.14 \pm 2.14

注: 阿卡波糖为阳性对照, IC_{50} 值为 25.6 nM。

Note: Acarbose was the positive control, IC_{50} : 25.6 nM.

4 结论

本文从苏铁中分离鉴定了 16 个化合物, 均为首

次从苏铁属植物中分离得到,其中化合物 **13** 和 **16** 为首次以天然产物报道。研究还首次发现了苏铁属植物中含有松香烷型二萜类 (**1~4**) 和芪类 (**12**) 化合物。化合物 **11** 具有中等的体外抑制 α -葡萄糖苷酶活性,在浓度为 198.00 $\mu\text{g}/\text{mL}$ 时,抑制率为 $52.51 \pm 2.63\%$;浓度为 99.00 $\mu\text{g}/\text{mL}$ 时,抑制率为 $18.75 \pm 1.32\%$ 。本文首次揭示了苏铁中抑制 α -葡萄糖苷酶的活性成分,为苏铁资源进一步开发利用奠定了基础。

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