

洋金花根中苯丙素类化学成分研究

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摘要: 目的 研究洋金花 *Daturae Flos* 根中苯丙素类化学成分。方法 采用硅胶、ODS 及 HPLC 等色谱方法分离化合物, 利用 NMR、MS 波谱学方法鉴定其结构。结果 从洋金花根 70%乙醇回流提取物的正丁醇部位分离得到 19 个化合物, 分别鉴定为淫羊藿苷 E5 (1)、alangisesquin A (2)、glycopentoside F (3)、conicaoside (4)、(7*S*,8*R*)-dehydrodiconiferyl alcohol 9'-*O*- β -glucopyranoside (5)、落叶松脂醇-4'-*O*- β -D-葡萄糖苷 (6)、7*R*,8*R*-threo-4,7,9-trihydroxy-3,3'-dimethoxy-8-*O*-4'-neolignan-9'-*O*- β -D-glucopyranoside (7)、vitriol A (8)、leptolepisol D (9)、苏式-2,3-二-(4-羟基-3-甲氧基苯)-3-甲氧基丙醇 (10)、hyuganoid IIIb (11)、officinoid (12)、落叶松脂醇-9-*O*- β -D-葡萄糖苷 (13)、stroside A (14)、erythro-buddlenol B (15)、sargentoid D (16)、(+)-(7*S*,8*S*)-4-hydroxy-3,3',5'-trimethoxy-8',9'-dinor-8,4'-oxy-neolignan-7,9-diol-7'-oic acid (17)、5'-甲氧基落叶松脂醇 (18)、dehydrodiconiferyl alcohol 4-*O*- β -D-glucopyranoside (19)。结论 化合物 2~19 为首次从茄科植物中分离得到, 化合物 1 为首次从曼陀罗属植物中分离得到。

关键词: 洋金花; 白花曼陀罗; 茄科; 苯丙素类; 淫羊藿苷 E5; alangisesquin A; 落叶松脂醇-4'-*O*- β -D-葡萄糖苷; leptolepisol D; stroside A

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Phenylpropanoids from roots of *Daturae Flos*

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Abstract: **Objective** To study the phenylpropanoids from the roots of *Datura metel*. **Methods** The separations and purifications were taken by silica gel and ODS chromatogram columns as well as preparative HPLC, and the structural identification based on physicochemical property, ¹H-NMR and ¹³C-NMR as well as HR-MS data. **Results** Nineteen compounds obtained from the butanol fraction of the 70% ethanol extract of *D. metel* roots, which were identified as icaricresinol E5 (1), alangisesquin A (2), Glycopentoside F (3), conicaoside (4), (7*S*,8*R*) dehydrodiconiferyl alcohol 9'-*O*- β -glucopyranoside (5), icaricresinol-4'-*O*- β -D-glucopyranoside (6), 7*R*,8*R*-threo-4,7,9-trihydroxy-3,3'-dimethoxy-8-*O*-4'-neolignan-9'-*O*- β -D-glucopyranoside (7), vitriol A (8), leptolepisol D (9), threo-2,3-bis-(4-hydroxy-3-methoxyphenyl)-3-methoxy-propanol (10), hyuganoid IIIb (11), officinoid (12), icaricresinol-9-*O*- β -D-glucopyranoside (13), stroside A (14), erythro-buddlenol B (15), sargentoid D (16), (+)-(7*S*,8*S*)-4-hydroxy-3,3',5'-trimethoxy-8',9'-dinor-8,4'-oxyneolignan-7,9-diol-7'-oic acid (17), 5'-methoxy icaricresinol (18), and dehydrodiconiferyl alcohol 4-*O*- β -D-glucopyranoside (19). **Conclusion** Compounds 2—19 are isolated from Solanaceae family for the first time and compound 1 is firstly isolated from genus *Datura* L.

Key words: *Daturae Flos*; *Datura metel* L.; Solanaceae; phenylpropanoids; icaricresinol E5; alangisesquin A; icaricresinol-4'-*O*- β -D-glucopyranoside; leptolepisol D; stroside A

洋金花为茄科(Solanaceae)曼陀罗属 *Datura* L. 茄花、闹羊花。《中国药典》2015 年版记载其味辛, 植物白花曼陀罗 *Datura metel* L. 的干燥花, 又名风 性温, 有毒, 具有平喘止咳、解痉定痛的功效, 用

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于哮喘咳嗽、脘腹冷痛、风湿痹痛、小儿慢惊以及外科麻醉^[1]。本课题组对其花、叶、种子等部位进行了系统的化学成分研究^[2-9],并已报道其具有不同的生物活性,如抗肿瘤、抗炎等^[10-12],其中洋金花活性较强,其开发成的洋金花胶囊在治疗银屑病的临床应用中取得了显著的治疗效果^[13]。但关于洋金花根各方面的研究报道却很罕见,化学成分方面甚少。为了合理开发该药用资源,明确其药效物质基础,本实验对洋金花根乙醇提取物正丁醇部位的化学成分进行了较系统的研究,得到19个苯丙素类化合物,分别鉴定为淫羊藿苷 E5 (icariside E5, **1**)、alangisesquin A(**2**)、glycopentoside F(**3**)、conicaoside(**4**)、(7*S*,8*R*)-dehydrodiconiferyl alcohol 9'-*O*- β -glucopyranoside(**5**)、落叶松脂醇-4'-*O*- β -*D*-葡萄糖苷 (iariciresinol-4'-*O*- β -*D*-glucopyranoside, **6**)、7*R*,8*R*-threo-4,7,9-trihydroxy-3,3'-dimethoxy-8-*O*-4'-neolignan-9'-*O*- β -*D*-glucopyranoside(**7**)、vitrifol A(**8**)、leptolepisol D(**9**)、苏式-2,3-二-(4-羟基-3-甲氧基苯)-3-甲氧基丙醇 [*threo*-2,3-bis-(4-hydroxy-3-methoxyphenyl)-3-methoxy-propanol, **10**]、hyuganoside IIIb(**11**)、officinalioside(**12**)、落叶松脂醇-9-*O*- β -*D*-葡萄糖苷 (iariciresinol-9-*O*- β -*D*-glucopyranoside, **13**)、stroside A(**14**)、*erythro*-buddlenol B(**15**)、sargentodoside D(**16**)、(+)-(7*S*,8*S*)-4-hydroxy-3,3',5'-trimethoxy-8',9'-dinor-8,4'-oxyneo-lignan-7,9-diol-7'-oic acid(**17**)、5'-甲氧基落叶松脂醇 (5'-methoxy iariciresinol, **18**)、dehydrodiconiferyl alcohol 4-*O*- β -*D*-glucopyranoside(**19**)。化合物**2**~**19**为首次从茄科植物中分离得到,化合物**1**为首次从曼陀罗属植物中分离得到。

1 仪器与材料

2424-2998 型分析 HPLC (美国 Waters 公司); 515-2414 型制备 HPLC (美国 Waters 公司); Sunfire C₁₈ 色谱柱 (250 mm×4.6 mm, 5 μ m, 美国 Waters 公司); Atlantis[®] prep T3 (250 mm×19 mm, 10 μ m, 美国 Waters 公司); Bruker-400 超导核磁共振光谱仪 (德国 Bruker 公司); Q-ToF-MS (ESI) 高分辨质谱 (美国 Waters 公司); 硅胶柱色谱 (200~300、80~100 目, 青岛海洋化工厂); TLC 用 Silica gel 60 F₂₅₄ (中国青岛海洋化工厂); 其他试剂均为分析纯。

原植物采收于黑龙江中医药大学药用植物园,经黑龙江中医药大学药学院药用植物教研室樊锐锋副教授鉴定为白花曼陀罗 *Datura metel* L. 的根。标本

(20150927) 保存于黑龙江中医药大学中药化学实验室。

2 提取与分离

干燥粉碎的洋金花根 50 kg, 用 1.5 倍量 70% 乙醇连续回流提取 3 次, 每次 2 h, 减压浓缩得提取物 4 kg。提取物与水混悬均匀, 依次用石油醚 (60~90 $^{\circ}$ C)、醋酸乙酯、水饱和正丁醇萃取。取正丁醇萃取物 237 g 经正相硅胶柱色谱, 二氯甲烷-甲醇系统 (50:1 $\rightarrow$ 0:1) 梯度洗脱, 得到 14 个部分, 即 Fr. I~XIV。Fr. VII (24.5 g) 经过反相 ODS 柱色谱得到 10 个流分, 其中流分 8 (2 g) 经 HPLC 分离即得化合物 **2** (5 mg); Fr. VIII (21.3 g) 经过反相 ODS 柱色谱得到 20 个流分, 其中流分 4 (2.5 g) 经 HPLC 分离得到化合物 **14** (6 mg), 依次流分 9 (3 g) 得到化合物 **6** (9 mg)、**7** (7 mg), 流分 10 (2.5 g) 得到化合物 **12** (9 mg)、**16** (6 mg), 流分 11 (4 g) 得到化合物 **3** (6 mg)、**4** (8 mg)、**17** (7 mg), 流分 12 (2 g) 得到化合物 **5** (10 mg)、**8** (7 mg); Fr. IX (18.6 g) 经过反相 ODS 柱色谱分离, 得到 12 个流分, 流分 9 即为化合物 **1** (5 mg), 其中流分 7 (2.5 g) 经 HPLC 分离得到化合物 **11** (6 mg)、**13** (7 mg), 依次流分 8 (1.5 g) 得到化合物 **9** (7 mg)、**10** (8 mg), 流分 11 (1 g) 得到化合物 **18** (5 mg)、**19** (5 mg); Fr. X (7.8 g) 经过反相 ODS 柱色谱得到 19 个流分, 流分 15 (0.5 g) 再经 HPLC 分离得到化合物 **15** (7 mg)。

3 结构鉴定

化合物 **1**: 无色油状物。ESI-MS m/z : 523.212 9 $[M+H]^+$ 。¹H-NMR (400 MHz, CD₃OD) δ : 4.68 (1H, d, J = 7.3 Hz, H-1''), 6.91 (2H, s, H-2', 6'), 6.57 (1H, d, J = 1.8 Hz, H-2), 6.55 (1H, d, J = 8.0 Hz, H-5), 6.47 (1H, dd, J = 1.8, 8.0 Hz, H-6), 6.30 (1H, dt, J = 5.7, 15.9 Hz, H-8'), 4.23 (2H, d, J = 5.4 Hz, H-9'), 2.96 (1H, dd, J = 5.6, 13.8 Hz, H-7a), 2.71 (1H, dd, J = 9.4, 13.8 Hz, H-7b), 3.80 (3H, s, 3'-OCH₃), 3.68 (3H, s, 3-OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 133.2 (C-1), 115.7 (C-2), 148.4 (C-3), 145.4 (C-4), 113.8 (C-5), 122.6 (C-6), 39.2 (C-7), 42.8 (C-8), 66.9 (C-9), 135.4 (C-1'), 109.1 (C-2'), 153.5 (C-3'), 145.0 (C-4'), 139.0 (C-5'), 119.2 (C-6'), 131.5 (C-7'), 129.7 (C-8'), 63.7 (C-9'), 105.4 (C-1''), 76.0 (C-2''), 77.9 (C-3''), 71.3 (C-4''), 78.1 (C-5''), 62.5 (C-6''), 56.4 (3-OCH₃), 56.3 (3'-OCH₃)。以上数据与文献报道对照基本一

致^[14]，故鉴定化合物 **1** 为淫羊藿苷 E5。

化合物 **2**：白色粉末。ESI-MS m/z : 747.281 4 $[M+H]^+$ 。¹H-NMR (400 MHz, CD₃OD) δ : 4.39 (1H, d, $J = 7.7$ Hz, H-1''), 4.89 (1H, d, $J = 5.2$ Hz, H-7), 4.26 (1H, dt, $J = 3.2, 5.2$ Hz, H-8), 6.96 (1H, brs, H-2), 7.01 (1H, brs, H-6), 6.94 (1H, d, $J = 1.9$ Hz, H-2''), 6.72 (1H, d, $J = 8.1$ Hz, H-5''), 6.77 (1H, dd, $J = 1.9, 8.1$ Hz, H-6''), 6.75 (2H, s, H-2', 6'), 6.55 (1H, brd, $J = 15.8$ Hz, H-7''), 5.70 (1H, d, $J = 5.9$ Hz, H-7'), 3.79 (6H, s, 3', 5'-OCH₃), 3.81 (3H, s, 3-OCH₃), 3.89 (3H, s, 3''-OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 133.8 (C-1), 111.4 (C-2), 148.7 (C-3), 146.9 (C-4), 115.7 (C-5), 120.7 (C-6), 74.1 (C-7), 87.4 (C-8), 61.7 (C-9), 136.3 (C-1'), 104.1 (C-2'), 154.5 (C-3'), 139.3 (C-4'), 154.6 (C-5'), 104.2 (C-6'), 89.1 (C-7'), 53.3 (C-8'), 72.5 (C-9'), 132.6 (C-1''), 112.3 (C-2''), 145.6 (C-3''), 149.3 (C-4''), 129.7 (C-5''), 116.9 (C-6''), 132.6 (C-7''), 129.7 (C-8''), 62.8 (C-9''), 104.1 (C-1'''), 75.2 (C-2'''), 78.3 (C-3'''), 71.7 (C-4'''), 78.1 (C-5'''), 62.8 (C-6'''), 56.4 (3-OCH₃), 56.8 (3'-OCH₃), 56.8 (5'-OCH₃), 56.9 (3''-OCH₃)。以上数据与文献报道对照基本一致^[15]，故鉴定化合物 **2** 为 alangisesquin A。

化合物 **3**：无色油状物。ESI-MS m/z : 749.297 1 $[M+H]^+$ 。¹H-NMR (400 MHz, CD₃OD) δ : 4.31 (1H, d, $J = 7.8$ Hz, H-1''), 6.97 (1H, d, $J = 1.7$ Hz, H-2''), 6.70 (1H, d, $J = 8.0$ Hz, H-5''), 6.78 (1H, dd, $J = 1.7, 8.0$ Hz, H-6''), 6.77 (1H, d, $J = 1.7$ Hz, H-2), 6.66 (1H, d, $J = 7.9$ Hz, H-5), 6.64 (1H, dd, $J = 1.7, 7.9$ Hz, H-6), 6.68 (1H, s, H-2', 6'), 4.95 (1H, d, $J = 6.0$ Hz, H-7'); ¹³C-NMR (100 MHz, CD₃OD) δ : 133.6 (C-1), 113.4 (C-2), 149.0 (C-3), 145.7 (C-4), 116.2 (C-5), 122.2 (C-6), 33.8 (C-7), 43.8 (C-8), 73.8 (C-9), 140.8 (C-1'), 104.1 (C-2'), 154.3 (C-3'), 135.7 (C-4'), 154.3 (C-5'), 104.2 (C-6'), 84.2 (C-7'), 56.4 (C-8'), 61.5 (C-9'), 130.8 (C-1''), 113.4 (C-2''), 148.6 (C-3''), 146.8 (C-4''), 115.7 (C-5''), 122.1 (C-6''), 78.0 (C-7''), 87.4 (C-8''), 61.5 (C-9''), 104.2 (C-1'''), 75.2 (C-2'''), 78.2 (C-3'''), 71.7 (C-4'''), 78.0 (C-5'''), 62.8 (C-6'''), 56.7 (3', 5'-OCH₃), 56.4 (3, 3''-OCH₃)。以上数据与文献报道对照基本一致^[16]，故鉴定化合物 **3** 为 glycopentoside F。

化合物 **4**：白色无定形粉末。ESI-MS m/z : 553.223 5 $[M+H]^+$ 。¹H-NMR (400 MHz, CD₃OD) δ :

4.86 (1H, d, $J = 7.8$ Hz, H-1''), 6.78 (2H, s, H-2, 6), 6.79 (1H, d, $J = 1.8$ Hz, H-2'), 6.70 (1H, d, $J = 8.0$ Hz, H-5'), 6.63 (1H, dd, $J = 1.8, 8.0$ Hz, H-6'), 2.88 (1H, dd, $J = 5.0, 13.4$ Hz, H-7'a), 2.50 (1H, dd, $J = 11.0, 13.4$ Hz, H-7'b), 3.83 (3H, s, 3'-OCH₃), 3.89 (6H, s, 3, 5-OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 141.6 (C-1), 104.6 (C-2, 6), 154.3 (C-3, 5), 135.4 (C-4), 84.0 (C-7), 54.1 (C-8), 60.6 (C-9), 133.5 (C-1'), 113.3 (C-2'), 149.2 (C-3'), 145.9 (C-4'), 116.2 (C-5'), 122.1 (C-6'), 33.6 (C-7'), 43.8 (C-8'), 73.8 (C-9'), 105.4 (C-1''), 75.9 (C-2''), 78.3 (C-3''), 71.7 (C-4''), 78.3 (C-5''), 62.4 (C-6''), 57.0 (3, 5-OCH₃), 56.4 (3'-OCH₃)。以上数据与文献报道对照基本一致^[17]，故鉴定化合物 **4** 为 conicaoside。

化合物 **5**：浅黄色无定形粉末。ESI-MS m/z : 521.197 3 $[M+H]^+$ 。¹H-NMR (400 MHz, CD₃OD) δ : 4.36 (1H, d, $J = 7.8$ Hz, H-1''), 6.97 (1H, brs, H-6'), 6.94 (1H, brs, H-2'), 6.95 (1H, d, $J = 1.9$ Hz, H-2), 6.76 (1H, d, $J = 8.2$ Hz, H-5), 6.82 (1H, dd, $J = 1.9, 8.2$ Hz, H-6), 5.52 (1H, d, $J = 6.2$ Hz, H-7), 6.57 (1H, d, $J = 15.7$ Hz, H-7'), 6.23 (1H, dt, $J = 5.8, 15.7$ Hz, H-8'), 3.81 (3H, s, 3-OCH₃), 3.87 (3H, s, 3'-OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 134.5 (C-1), 110.6 (C-2), 149.1 (C-3), 147.6 (C-4), 116.2 (C-5), 119.8 (C-6), 89.4 (C-7), 56.8 (C-8), 64.9 (C-9), 132.3 (C-1'), 112.2 (C-2'), 145.5 (C-3'), 149.4 (C-4'), 130.4 (C-5'), 116.7 (C-6'), 134.3 (C-7'), 124.2 (C-8'), 71.0 (C-9'), 103.2 (C-1''), 75.2 (C-2''), 77.9 (C-3''), 71.6 (C-4''), 78.2 (C-5''), 62.7 (C-6''), 55.5 (3-OCH₃), 56.4 (3'-OCH₃)。以上数据与文献报道对照基本一致^[18]，故鉴定化合物 **5** 为 (7*S*,8*R*)-dehydrodiconiferyl alcohol 9'-*O*- β -glucopyranoside。

化合物 **6**：白色粉末。ESI-MS m/z : 523.272 9 $[M+H]^+$ 。¹H-NMR (400 MHz, CD₃OD) δ : 4.86 (1H, d, $J = 7.5$ Hz, H-1''), 7.01 (1H, d, $J = 1.8$ Hz, H-2'), 7.08 (1H, d, $J = 8.2$ Hz, H-5'), 6.89 (1H, dd, $J = 1.8, 8.2$ Hz, H-6'), 6.77 (1H, d, $J = 2.0$ Hz, H-2), 6.71 (1H, d, $J = 8.2$ Hz, H-5), 6.62 (1H, dd, $J = 2.0, 8.2$ Hz, H-6), 2.55 (1H, dd, $J = 11.2, 13.4$ Hz, H-7a), 2.96 (1H, dd, $J = 4.6, 13.4$ Hz, H-7b), 4.74 (1H, d, $J = 6.8$ Hz, H-7'), 3.83 (3H, s, 3-OCH₃), 3.85 (3H, s, 3'-OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 133.8 (C-1), 114.1 (C-2), 149.0 (C-3), 146.4 (C-4), 116.0 (C-5), 122.2

(C-6), 33.7 (C-7), 43.8 (C-8), 73.5 (C-9), 138.2 (C-1'), 111.8 (C-2'), 150.9 (C-3'), 147.2 (C-4'), 118.3 (C-5'), 119.6 (C-6'), 84.0 (C-7'), 54.1 (C-8'), 60.5 (C-9'), 103.0 (C-1''), 75.0 (C-2''), 78.2 (C-3''), 71.4 (C-4''), 77.9 (C-5''), 62.6 (C-6''), 56.8 (3-OCH₃), 56.7 (3'-OCH₃)。以上数据与文献报道对照基本一致^[19], 故鉴定化合物 **6** 为落叶松脂醇-4'-O-β-D-葡萄糖苷。

化合物 **7**: 白色无定形粉末。ESI-MS m/z : 541.223 5 [M+H]⁺。¹H-NMR (400 MHz, CD₃OD) δ : 4.24 (1H, d, J = 7.8 Hz, H-1''), 6.84 (1H, d, J = 1.8 Hz, H-2'), 6.96 (1H, d, J = 8.2 Hz, H-5'), 6.86 (1H, dd, J = 1.8, 8.2 Hz, H-6'), 2.66 (2H, t, J = 7.5 Hz, H-7'), 3.86 (3H, s, 3'-OCH₃), 3.81 (3H, s, 3-OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 133.8 (C-1), 111.4 (C-2), 148.8 (C-3), 147.6 (C-4), 115.9 (C-5), 122.3 (C-6), 74.2 (C-7), 87.8 (C-8), 61.9 (C-9), 137.2 (C-1'), 114.4 (C-2'), 151.7 (C-3'), 147.1 (C-4'), 119.8 (C-5'), 122.1 (C-6'), 32.7 (C-7'), 33.7 (C-8'), 69.9 (C-9'), 104.5 (C-1''), 75.2 (C-2''), 77.9 (C-3''), 71.7 (C-4''), 78.2 (C-5''), 62.8 (C-6''), 56.6 (3-OCH₃), 56.4 (3'-OCH₃)。以上数据与文献报道对照基本一致^[20], 故鉴定化合物 **7** 为 7*R*,8*R*-threo-4,7,9-trihydroxy-3,3'-dimethoxy-8-O-4'-neolignan-9'-O-β-D-glucopyranoside。

化合物 **8**: 黄色油状物。ESI-MS m/z : 539.223 1 [M+H]⁺。¹H-NMR (400 MHz, CD₃OD) δ : 7.06 (1H, brs, H-2'), 6.71 (1H, brs, H-6'), 6.99 (1H, d, J = 1.8 Hz, H-2), 6.75 (1H, d, J = 8.1 Hz, H-5), 6.85 (1H, dd, J = 1.8, 8.1 Hz, H-6), 6.79 (1H, brs, H-2''), 6.93 (1H, brs, H-6''), 5.58 (2H, d, J = 6.6 Hz, H-7, 7'), 3.82 (3H, s, 3-OCH₃), 3.84 (3H, s, 3'-OCH₃), 3.87 (3H, s, 3''-OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 132.8 (C-1), 109.3 (C-2), 147.6 (C-3), 146.0 (C-4), 114.5 (C-5), 118.3 (C-6), 87.7 (C-7), 54.9 (C-8), 62.4 (C-9), 135.4 (C-1'), 110.6 (C-2'), 143.9 (C-3'), 147.6 (C-4'), 128.7 (C-5'), 114.6 (C-6'), 88.0 (C-7'), 54.9 (C-8'), 62.4 (C-9'), 135.4 (C-1''), 112.6 (C-2''), 143.7 (C-3''), 145.9 (C-4''), 128.2 (C-5''), 116.7 (C-6''), 34.3 (C-7''), 31.4 (C-8''), 60.7 (C-9''), 55.2 (3-OCH₃), 55.2 (3'-OCH₃), 55.9 (3''-OCH₃)。以上数据与文献报道对照基本一致^[21], 故鉴定化合物 **8** 为 vitrifol A。

化合物 **9**: 黄色无定形粉末。ESI-MS m/z : 517.202 4 [M+H]⁺。¹H-NMR (400 MHz, CD₃OD) δ : 4.95 (1H, d, J = 5.3 Hz, H-7'), 3.68 (3H, s, 3-OCH₃),

3.78 (3H, s, 3'-OCH₃), 3.81 (3H, s, 3''-OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 134.2 (C-1), 111.8 (C-2), 148.7 (C-3), 147.0 (C-4), 118.4 (C-5), 120.8 (C-6), 75.1 (C-7), 86.1 (C-8), 62.2 (C-9), 139.4 (C-1'), 120.2 (C-2'), 151.4 (C-3'), 148.3 (C-4'), 115.9 (C-5'), 112.4 (C-6'), 74.0 (C-7'), 56.6 (C-8'), 64.4 (C-9'), 132.0 (C-1''), 115.7 (C-2''), 148.4 (C-3''), 146.2 (C-4''), 114.6 (C-5''), 123.2 (C-6''), 56.4 (3-OCH₃), 56.4 (3'-OCH₃), 56.4 (3''-OCH₃)。以上数据与文献报道对照基本一致^[22], 故鉴定化合物 **9** 为 leptolepisol D。

化合物 **10**: 黄色油状物。ESI-MS m/z : 335.144 5 [M+H]⁺。¹H-NMR (400 MHz, CD₃OD) δ : 6.63 (1H, d, J = 1.8 Hz, H-2), 6.70 (1H, d, J = 8.0 Hz, H-5), 6.59 (1H, dd, J = 1.8, 8.0 Hz, H-6), 6.61 (1H, d, J = 1.8 Hz, H-2'), 6.67 (1H, d, J = 1.8 Hz, H-5'), 6.54 (1H, dd, J = 1.8, 8.0 Hz, H-6'), 4.30 (1H, d, J = 8.4 Hz, H-7), 4.04 (1H, dd, J = 5.8, 10.8 Hz, H-9a), 3.88 (1H, dd, J = 7.0, 10.8 Hz, H-9b), 3.20 (3H, s, 7-OCH₃), 3.70 (3H, s, 3'-OCH₃), 3.74 (3H, s, 3-OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 132.7 (C-1), 115.7 (C-2), 148.5 (C-3), 146.9 (C-4), 114.4 (C-5), 122.7 (C-6), 87.4 (C-7), 56.1 (C-8), 65.0 (C-9), 132.3 (C-1'), 115.6 (C-2'), 148.4 (C-3'), 146.2 (C-4'), 112.4 (C-5'), 121.6 (C-6'), 56.8 (3-OCH₃), 56.3 (3'-OCH₃), 56.3 (7-OCH₃)。以上数据与文献报道对照基本一致^[23], 故鉴定化合物 **10** 为 苏式-2,3-二-(4-羟基-3-甲氧基苯)-3-甲氧基丙醇。

化合物 **11**: 白色粉末。ESI-MS m/z : 539.207 9 [M+H]⁺。¹H-NMR (400 MHz, CD₃OD) δ : 4.36 (1H, d, J = 7.8 Hz, H-1''), 7.02 (1H, d, J = 1.9 Hz, H-2), 6.75 (1H, d, J = 8.3 Hz, H-5), 6.85 (1H, dd, J = 1.9, 8.3 Hz, H-6), 7.07 (1H, d, J = 1.8 Hz, H-2'), 6.99 (1H, d, J = 8.4 Hz, H-5'), 6.92 (1H, dd, J = 1.8, 8.4 Hz, H-6'), 6.61 (1H, d, J = 15.9 Hz, H-7'), 6.26 (1H, dt, J = 15.9, 6.4 Hz, H-8'), 3.81 (3H, s, 3-OCH₃), 3.87 (3H, s, 3'-OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 133.8 (C-1), 111.8 (C-2), 148.9 (C-3), 147.2 (C-4), 115.9 (C-5), 120.8 (C-6), 74.0 (C-7), 87.0 (C-8), 61.9 (C-9), 132.9 (C-1'), 111.4 (C-2'), 151.8 (C-3'), 149.5 (C-4'), 118.8 (C-5'), 121.0 (C-6'), 133.6 (C-7'), 125.3 (C-8'), 70.9 (C-9'), 103.3 (C-1''), 75.2 (C-2''), 78.0 (C-3''), 71.7 (C-4''), 78.2 (C-5''), 62.8 (C-6''), 56.4 (3-OCH₃), 56.6 (3'-OCH₃)。以上数据与文献报道对照基本一致^[24], 故鉴定化合物 **11**

为 hyuganoside IIIb。

化合物 **12**: 白色无定形粉末。ESI-MS m/z : 597.213 3 $[M+H]^+$ 。 $^1\text{H-NMR}$ (400 MHz, CD_3OD) δ : 4.66 (1H, d, $J = 7.9$ Hz, H-1''), 5.14 (1H, d, $J = 7.5$ Hz, H-7'), 7.42 (2H, s, H-2, 6), 6.98 (2H, brs, H-2', 6'), 3.80 (6H, s, 3', 5'-OCH₃), 3.87 (6H, s, 3, 5-OCH₃); $^{13}\text{C-NMR}$ (100 MHz, CD_3OD) δ : 133.8 (C-1), 107.8 (C-2, 6), 154.3 (C-3, 5), 140.6 (C-4), 200.5 (C-7), 50.6 (C-8), 71.2 (C-9), 132.9 (C-1'), 105.1 (C-2', 6'), 149.2 (C-3', 5'), 137.2 (C-4'), 85.4 (C-7'), 55.6 (C-8'), 61.6 (C-9'), 104.4 (C-1''), 75.7 (C-2''), 78.4 (C-3''), 71.3 (C-4''), 78.2 (C-5''), 62.5 (C-6''), 57.2 (3, 5-OCH₃), 56.8 (3', 5'-OCH₃)。以上数据与文献报道对照基本一致^[23], 故鉴定化合物 **12** 为 officinalioside。

化合物 **13**: 白色粉末。ESI-MS m/z : 523.212 9 $[M+H]^+$ 。 $^1\text{H-NMR}$ (400 MHz, CD_3OD) δ : 4.29 (1H, d, $J = 7.8$ Hz, H-1''), 6.93 (1H, d, $J = 1.7$ Hz, H-2), 6.75 (1H, d, $J = 8.2$ Hz, H-5), 6.79 (1H, dd, $J = 1.7$, 8.2 Hz, H-6), 6.81 (1H, d, $J = 2.0$ Hz, H-2'), 6.71 (1H, d, $J = 8.0$ Hz, H-5'), 6.65 (1H, dd, $J = 2.0$, 8.0 Hz, H-6'), 3.83 (3H, s, 3-OCH₃), 3.82 (3H, s, 3'-OCH₃); $^{13}\text{C-NMR}$ (100 MHz, CD_3OD) δ : 135.7 (C-1), 110.8 (C-2), 149.0 (C-3), 147.1 (C-4), 116.0 (C-5), 119.9 (C-6), 84.2 (C-7), 51.7 (C-8), 68.5 (C-9), 133.8 (C-1'), 113.5 (C-2'), 149.0 (C-3'), 145.8 (C-4'), 116.2 (C-5'), 122.2 (C-6'), 33.7 (C-7'), 44.1 (C-8'), 73.7 (C-9'), 104.6 (C-1''), 75.2 (C-2''), 78.1 (C-3''), 71.7 (C-4''), 78.3 (C-5''), 62.9 (C-6''), 56.4 (3-OCH₃), 56.4 (3'-OCH₃)。以上数据与文献报道对照基本一致^[26], 故鉴定化合物 **13** 为落叶松脂醇-9-*O*- β -*D*-葡萄糖苷。

化合物 **14**: 黄色油状物。ESI-MS m/z : 481.166 0 $[M+H]^+$ 。 $^1\text{H-NMR}$ (400 MHz, CD_3OD) δ : 4.99 (1H, d, $J = 7.4$ Hz, H-1''), 7.59 (1H, d, $J = 2.0$ Hz, H-2), 7.15 (1H, d, $J = 8.6$ Hz, H-5), 7.66 (1H, dd, $J = 2.0$, 8.6 Hz, H-6), 6.87 (1H, d, $J = 1.4$ Hz, H-2'), 6.69 (1H, d, $J = 8.6$ Hz, H-5'), 6.73 (1H, dd, $J = 1.4$, 8.6 Hz, H-6'), 4.76 (1H, dd, $J = 5.2$, 8.7 Hz, H-8), 4.25 (1H, dd, $J = 8.8$, 10.7 Hz, H-9a), 3.70 (1H, dd, $J = 5.2$, 10.7 Hz, H-9b), 3.81 (3H, s, 3'-OCH₃), 3.85 (3H, s, 3-OCH₃); $^{13}\text{C-NMR}$ (100 MHz, CD_3OD) δ : 132.8 (C-1), 113.1 (C-2), 150.5 (C-3), 152.2 (C-4), 116.2 (C-5), 124.5 (C-6), 199.6 (C-7), 56.6 (C-8), 65.4 (C-9), 129.6 (C-1'), 112.8 (C-2'), 149.4 (C-3'), 147.1

(C-4'), 116.6 (C-5'), 122.2 (C-6'), 101.8 (C-1''), 74.7 (C-2''), 78.3 (C-3''), 71.2 (C-4''), 77.8 (C-5''), 62.4 (C-6''), 56.6 (3-OCH₃), 56.4 (3'-OCH₃)。以上数据与文献报道对照基本一致^[27], 故鉴定化合物 **14** 为 stroside A。

化合物 **15**: 白色粉末。ESI-MS m/z : 585.228 6 $[M+H]^+$ 。 $^1\text{H-NMR}$ (400 MHz, CD_3OD) δ : 7.04 (1H, brs, H-2), 7.02 (1H, brs, H-6), 6.96 (2H, brs, H-2', 6'), 6.94 (1H, d, $J = 1.8$ Hz, H-2''), 6.72 (1H, d, $J = 8.1$ Hz, H-5''), 6.77 (1H, dd, $J = 1.8$, 8.1 Hz, H-6''), 6.56 (1H, d, $J = 15.8$ Hz, H-7), 6.18 (1H, dt, $J = 6.3$, 15.8 Hz, H-8), 3.89 (3H, s, H-3), 3.86 (3H, s, H-3'), 3.79 (3H, s, H-5'), 3.74 (3H, s, H-3''); $^{13}\text{C-NMR}$ (100 MHz, CD_3OD) δ : 132.5 (C-1), 112.4 (C-2), 145.6 (C-3), 149.3 (C-4), 129.7 (C-5), 116.9 (C-6), 132.5 (C-7), 129.7 (C-8), 62.8 (C-9), 136.3 (C-1'), 104.1 (C-2', 6'), 154.6 (C-3', 5'), 139.4 (C-4'), 87.4 (C-7'), 56.4 (C-8'), 64.3 (C-9'), 133.8 (C-1''), 111.4 (C-2''), 148.7 (C-3''), 146.9 (C-4''), 115.7 (C-5''), 120.7 (C-6''), 74.1 (C-7''), 87.3 (C-8''), 61.7 (C-9''), 56.6 (3-OCH₃), 56.7 (3', 5'-OCH₃), 56.3 (3''-OCH₃)。以上数据与文献报道对照基本一致^[24], 故鉴定化合物 **15** 为 erythro-buddlenol B。

化合物 **16**: 无色无定形固体。ESI-MS m/z : 525.228 6 $[M+H]^+$ 。 $^1\text{H-NMR}$ (400 MHz, CD_3OD) δ : 4.83 (1H, d, $J = 7.6$ Hz, H-1''), 6.59 (1H, d, $J = 1.8$ Hz, H-2'), 6.65 (1H, d, $J = 8.0$ Hz, H-5'), 6.53 (1H, dd, $J = 1.8$, 8.0 Hz, H-6'), 6.68 (1H, d, $J = 1.8$ Hz, H-4), 7.01 (1H, d, $J = 8.2$ Hz, H-1), 6.64 (1H, dd, $J = 8.2$, 1.8 Hz, H-10), 3.74 (3H, s, 3'-OCH₃), 3.75 (3H, s, 4'-OCH₃); $^{13}\text{C-NMR}$ (100 MHz, CD_3OD) δ : 117.7 (C-1), 146.1 (C-2), 145.5 (C-3), 114.3 (C-4), 36.1 (C-5), 44.2 (C-6), 62.1 (C-6a), 44.0 (C-7), 62.0 (C-7a), 36.1 (C-8), 137.4 (C-9), 122.8 (C-10), 133.8 (C-1'), 113.4 (C-2'), 150.5 (C-3'), 148.8 (C-4'), 115.8 (C-5'), 122.7 (C-6'), 103.1 (C-1''), 75.1 (C-2''), 77.8 (C-3''), 71.4 (C-4''), 78.2 (C-5''), 62.5 (C-6''), 56.5 (3'-OCH₃), 56.3 (4'-OCH₃)。以上数据与文献报道对照基本一致^[28], 故鉴定化合物 **16** 为 sargentodoside D。

化合物 **17**: 黄色粉末。ESI-MS m/z : 394.129 2 $[M+H]^+$ 。 $^1\text{H-NMR}$ (400 MHz, CD_3OD) δ : 6.98 (1H, d, $J = 1.7$ Hz, H-2), 6.69 (1H, d, $J = 8.0$ Hz, H-5), 6.78 (1H, dd, $J = 1.7$, 8.0 Hz, H-6), 4.95 (1H, d, $J = 7.0$ Hz,

H-7), 3.82 (3H, s, 3-OCH₃), 3.81 (6H, s, 3', 5'-OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 133.5 (C-1), 111.9 (C-2), 148.7 (C-3), 147.1 (C-4), 115.9 (C-5), 121.0 (C-6), 74.6 (C-7), 89.3 (C-8), 61.9 (C-9), 123.3 (C-1'), 108.2 (C-2'), 153.7 (C-3'), 139.4 (C-4'), 153.9 (C-5'), 108.2 (C-6'), 156.8 (C-7'), 56.4 (3-OCH₃), 56.7 (3', 5'-OCH₃)。以上数据与文献报道对照基本一致^[29], 故鉴定化合物 **17** 为 (+)-(7*S*,8*S*)-4-hydroxy-3,3',5'-trimethoxy-8',9'-dinor-8,4'-oxyneolignan-7,9-diol-7'-oic acid。

化合物 **18**: 无定形固体。ESI-MS m/z : 391.170 7 [M+H]⁺。 ¹H-NMR (400 MHz, CD₃OD) δ : 6.79 (1H, d, J = 1.8 Hz, H-2), 6.76 (1H, d, J = 8.0 Hz, H-5), 6.64 (1H, dd, J = 1.8, 8.0 Hz, H-6), 6.63 (2H, s, H-2', 6'), 2.90 (1H, dd, J = 4.8, 13.4 Hz, H-7b), 2.50 (1H, dd, J = 11.2, 13.4 Hz, H-7a), 3.80 (3H, s, 3-OCH₃), 3.82 (6H, s, 3', 5'-OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 132.0 (C-1), 111.9 (C-2), 147.6 (C-3), 144.4 (C-4), 115.9 (C-5), 120.6 (C-6), 32.2 (C-7), 42.3 (C-8), 72.3 (C-9), 135.9 (C-1'), 102.5 (C-2', 6'), 148.9 (C-3', 5'), 134.2 (C-4'), 82.6 (C-7'), 52.6 (C-8'), 59.1 (C-9'), 55.1 (3-OCH₃), 54.9 (3', 5'-OCH₃)。以上数据与文献报道对照基本一致^[30], 故鉴定化合物 **18** 为 5'-甲氧基落叶松脂醇。

化合物 **19**: 白色粉末。ESI-MS m/z : 519.218 0 [M+H]⁺。 ¹H-NMR (400 MHz, CD₃OD) δ : 4.36 (1H, d, J = 7.7 Hz, H-1''), 6.99 (1H, d, J = 1.8 Hz, H-2), 7.10 (1H, d, J = 8.4 Hz, H-5), 6.89 (1H, dd, J = 1.8, 8.4 Hz, H-6), 7.06 (2H, brs, H-2', 6'), 6.53 (1H, d, J = 15.8 Hz, H-7'), 6.24 (1H, dt, J = 5.8, 15.8 Hz, H-8'), 5.60 (1H, d, J = 6.6 Hz, H-7), 3.90 (3H, s, 3'-OCH₃), 3.83 (3H, s, 3-OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 135.9 (C-1), 109.3 (C-2), 148.9 (C-3), 146.1 (C-4), 116.0 (C-5), 118.3 (C-6), 88.0 (C-7), 54.9 (C-8), 62.9 (C-9), 132.0 (C-1'), 114.7 (C-2'), 144.0 (C-3'), 147.5 (C-4'), 128.7 (C-5'), 110.8 (C-6'), 130.5 (C-7'), 126.1 (C-8'), 60.1 (C-9'), 101.3 (C-1''), 73.4 (C-2''), 76.7 (C-3''), 69.9 (C-4''), 76.4 (C-5''), 61.0 (C-6''), 55.1 (3-OCH₃), 55.1 (3'-OCH₃)。以上数据与文献报道对照基本一致^[31], 故鉴定化合物 **19** 为 dehydroconiferyl alcohol 4-*O*- β -D-glucopyranoside。

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