

紫丁香树叶化学成分研究

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摘 要: 目的 研究紫丁香 *Syringa oblata* 树叶的化学成分。方法 采用硅胶柱色谱和高效液相色谱等对紫丁香树叶化学成分进行分离纯化, 通过理化性质及波谱数据分析鉴定结构。结果 从紫丁香叶甲醇提取物中分离得到 35 个单体化合物, 分别鉴定为齐墩果酸 (1)、乌苏酸 (2)、白桦酸 (3)、1,3-苯并间二氧杂环戊烯-5-丙醇 (4)、对羟基苯丙醇 (5)、对羟基苯乙醇 (6)、丁香苦素 D (7)、丁香苦素 E (8)、丁香苦素 F (9)、丁香苦素 A (10)、丁香苦素 C (11)、3,4-二羟基苯乙醇 (12)、丁香苦素 B (13)、syringopicrogenin B (14)、蚱蜢酮 (15)、(7*R*,8*S*)-4,9,9'-三羟基-3,3'-二甲氧基-7,8-二氢苯并呋喃-1'-丙基新木脂素 (16)、落叶松脂醇 (17)、丁香苷 (18)、3(*Z*)-己烯醇葡萄糖苷 (19)、槲皮素-3-*O*- β -D-吡喃葡萄糖苷 (20)、(8*E*)-ligstroside (21)、落叶松脂素-4-*O*- β -D-吡喃葡萄糖苷 (22)、(8*E*)-ligstroside B (23)、(8*E*)-ligstroside A (24)、红景天苷 (25)、7-脱氢马钱子苷 (26)、fliederoside B (27)、syringopicroside B (28)、木犀榄苷二甲酯 (29)、lilacoside (30)、丁香苦苷 (31)、橄榄苦苷 (32)、(+)-表松脂素-4'-*O*- β -D-葡萄糖苷 (33)、毛蕊花糖苷 (34)、(+)-落叶松脂素-4'-*O*- β -D-吡喃葡萄糖苷 (35)。结论 其中化合物 4、5、14~16、19、23、24、26、27 为首次从紫丁香中分离得到。

关键词: 紫丁香; 环烯醚萜; 木脂素; 丁香苦素; 对羟基苯丙醇; 蚱蜢酮; 7-脱氢马钱子苷

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Chemical constituents from leaf of *Syringa oblata*

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Abstract: **Objective** To study the chemical constituents from the leaf of *Syringa oblata*. **Methods** The compounds was isolated by silica gel column chromatography and HPLC, and their structure were identified by spectral data analysis. **Results** A total of 35 compounds were isolated and identified as oleanolic acid (1), ursolic acid (2), betulinic acid (3), 1,3-benzodioxole-5-propanol (4), *p*-hydroxyl benzene propyl alcohol (5), *p*-hydroxyl benzene ethel alcohol (6), syringopicrogenin D (7), syringopicrogenin E (8), syringopicrogenin F (9), syringopicrogenin A (10), syringopicrogenin C (11), 3,4-dihydroxyl benzene ethel alcohol (12), syringobittergenin B (13), syringo-picrogenin B (14), grasshopper ketone (15), (7*R*,8*S*)-4,9,9'-trihydroxyl-3,3'-dimethoxyl-7,8-dihydrobenzofuran-1'-propylneolignan (16), lariciresinol (17), syringin (18), 3(*Z*)-enol glucoside (19), quercetin-3-*O*- β -D-glucopyranoside (20), (8*E*)-ligstroside (21), epipinoresinol-4-*O*- β -D-glucopyranoside (22), (8*E*)-ligstroside B (23), (8*E*)-ligstroside A (24), salidroside (25), 7-dehydrologanin (26), fliederoside B (27), syringopicroside B (28), oleoside dimethyl ester (29), lilacoside (30), syringopicroside (31), oleuropein (32), (+)-lariciresinol-4-*O*- β -D-glucopyranoside (33), verbascoside (34), and (+)-epipinoresinol-4'-*O*- β -D-glucopyranoside (35). **Conclusion** Compounds 4, 5, 14—16, 19, 23, 24, 26, and 27 are isolated from *S. oblata* for the first time.

Key words: *Syringa oblata* Lindl.; iridoids; lignans; syringopicrogenin; *p*-hydroxyl benzene propyl alcohol; grasshopper ketone; 7-dehydrogenation of loganin

紫丁香 *Syringa oblata* Lindl. 为木犀草科 (Oleaceae) 丁香属 *Syringa* Linn. 植物, 具有清热解毒、利湿退黄等功效, 用于治疗急性痢疾、乙型肝炎、黄疸型肝炎、结膜炎等疾病^[1], 以紫丁香叶为

原料生产的炎立消胶囊、片剂用于治疗痢疾、急性黄疸型肝炎等疾病取得较好的疗效^[2]。又由于紫丁香具有耐寒、耐旱、适应性强、花絮繁茂、芳香浓郁等特点, 用作绿化及观赏植物得到广泛种植, 具

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有丰富资源, 因此研究其中化学成分, 对开发紫丁香植物资源利用具有重要意义。为进一步研究紫丁香的生物活性, 本实验在前期分别对紫丁香的树皮、树枝、花蕾、种子及其外壳化学成分进行研究^[3-7]的基础上, 对紫丁香树叶的化学成分进行了研究, 从中分离并鉴定了 35 个化合物, 其结构见图 1, 分

别为齐墩果酸 (oleanolic acid, **1**)、乌苏酸 (ursolic acid, **2**)、白桦酸 (betulinic acid, **3**)、1,3-苯并间二氧杂环戊烯-5-丙醇 (1,3-benzodioxole-5-propanol, **4**)、对羟基苯丙醇 (*p*-hydroxyl benzene propyl alcohol, **5**)、对羟基苯乙醇 (*p*-hydroxyl benzene ethyl alcohol, **6**)、丁香苦素 D (syringopicrogenin

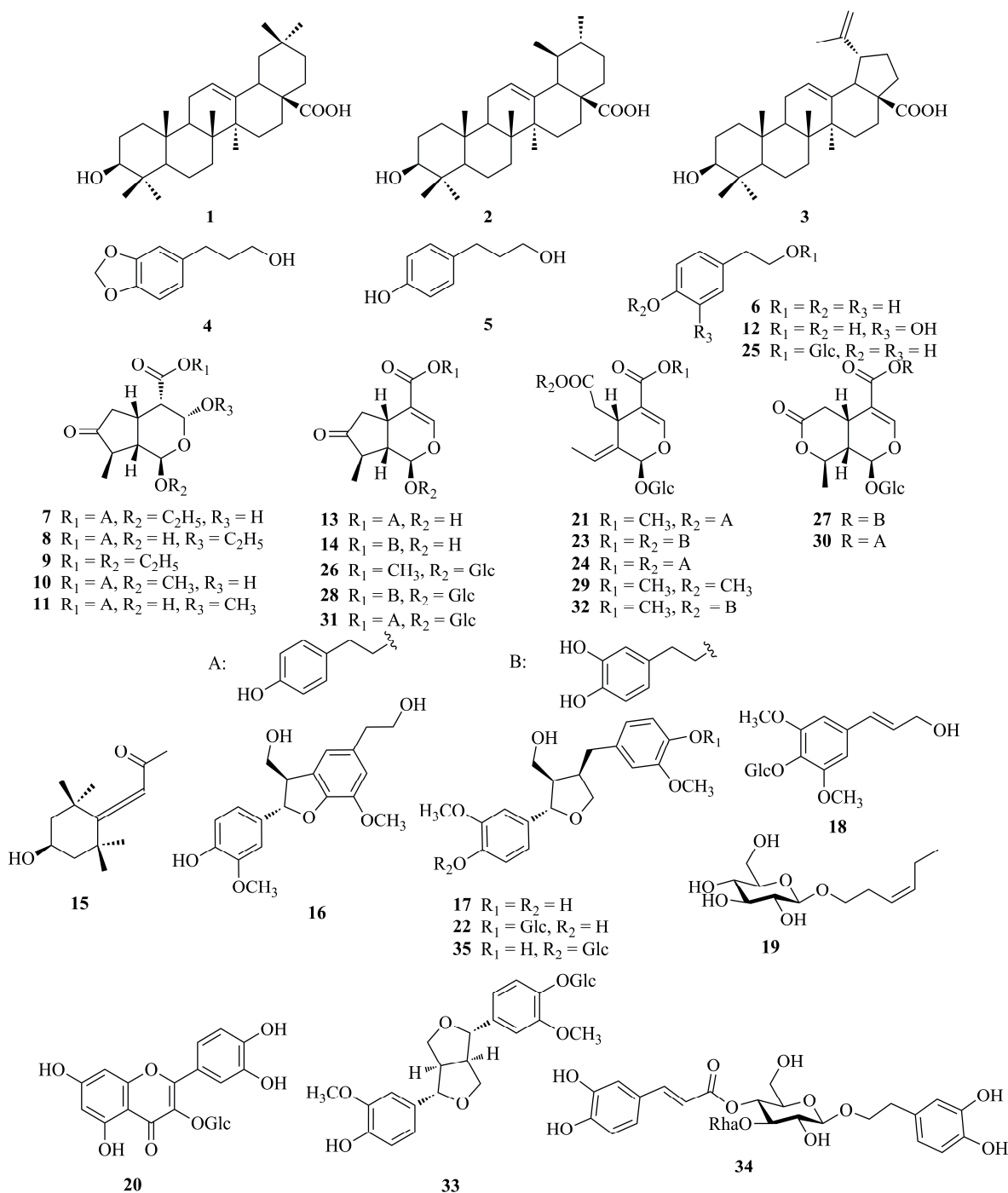


图 1 从紫丁香树叶中分得化合物的结构

Fig. 1 Structure of compounds from leaf of *S. oblata*

D, 7)、丁香苦素 E (syringopicrogenin E, 8)、丁香苦素 F (syringopicrogenin F, 9)、(syringopicrogenin A, 10)、丁香苦素 C (syringopicrogenin C, 11)、3,4-二羟基苯乙醇 (3,4-dihydroxyl benzene ethel alcohol, 12)、丁香苦素 B (syringobittergenin B, 13)、syringopicrogenin B (14)、蚱蜢酮 (grasshopper ketone, 15)、(7R,8S)-4,9,9'-三羟基-3,3'-二甲氧基-7,8-二氢苯并呋喃-1'-丙基新木脂素 [(7R,8S)-4,9,9'-trihydroxyl-3,3'-dimethoxyl-7,8-dihydrobenzofuran-1'-propylneolignan, 16]、落叶松脂醇 (lariciresinol, 17)、丁香苷 (syringin, 18)、3(Z)-己烯醇葡萄糖苷 [3(Z)-enol glucoside, 19]、槲皮素-3-O-β-D-吡喃葡萄糖苷 (quercetin-3-O-β-D-glucopyranoside, 20)、(8E)-ligstroside (21)、落叶松脂素-4-O-β-D-吡喃葡萄糖苷 (epipinoresinol-4-O-β-D-glucopyranoside, 22)、(8E)-ligstroside B (23)、(8E)-ligstroside A (24)、红景天苷 (salidroside, 25)、7-脱氢马钱子苷 (7-dehydrologanin, 26)、fliederoside B (27)、syringopicroside B (28)、木犀榄苷二甲酯 (29)、lilacoside (30)、丁香苦苷 (syrigopicroside, 31)、橄榄苦苷 (oleuropein, 32)、(+)-表松脂素-4'-O-β-D-葡萄糖苷 [(+)-lariciresinol-4'-O-β-D-glucopyranoside, 33]、毛蕊花糖苷 (verbascoside, 34)、(+)-落叶松脂素-4'-O-β-D-吡喃葡萄糖苷 [(+)-epipinoresinol-4'-O-β-D-glucopyranoside, 35]。其中化合物 4、5、14~16、19、23、24、26、27 为首次从紫丁香中分离得到。该研究结果为系统开发紫丁香树叶天然资源提供重要参考。

1 材料与仪器

X-6 显微熔点测定仪 (北京泰克仪器有限公司); Magna FTIR-750 型傅里叶变换红外光谱仪 (美国 Nicolet 公司); AM-400 型和 Bruker-600 MHz 核磁共振波谱仪 (德国 Bruker 公司); MAT-95 型质谱仪 (Thermo Finnigan 公司); AUTOPOL V 型旋光仪 (美国鲁道夫公司); 日本日立公司高效液相色谱仪: HITACHI L-7100 泵, HITACHI L-3350 示差折光检测器, GL SCIRNCES Inc. Inertsil PREP-Sil Φ250 mm×10 mm 和 Inertsil PREP-ODS Φ250 mm×10 mm 色谱柱; 柱色谱用硅胶 (200~300 目, 青岛海洋化工厂); 薄层色谱硅胶板 (烟台化工厂)。

紫丁香叶于 2012 年 8 月 10 日采于齐齐哈尔大学校园内, 放置室内阴干, 经齐齐哈尔大学植物学教授沙伟鉴定为 *Syringa oblata* Lindl. 的树叶, 标本

(SO-20120810) 收藏于齐齐哈尔大学天然产物研究室。

2 提取和分离

干燥的紫丁香叶 (6.7 kg) 每次用甲醇 30 L 室温浸泡 3 d 后滤过, 重复 3 次, 合并浸出液浓缩至小体积后用水混悬, 依次用正己烷、醋酸乙酯和正丁醇萃取, 浓缩得到正己烷萃取物 680.2 g、醋酸乙酯萃取物 440.0 g 和正丁醇萃取物 857.5 g。

取正己烷萃取物 18.0 g, 用硅胶柱色谱分离, 依次用正己烷-醋酸乙酯 (9:1、1:1)、醋酸乙酯进行洗脱, 合并相同流分浓缩得到 8 个组分 (FH₁~FH₈)。FH₅ (4.7 g) 经硅胶柱色谱分离得化合物 1 (493.7 mg)、2 (216.9 mg)、3 (19.8 mg)。

取醋酸乙酯萃取物 58.4 g, 用硅胶柱色谱分离, 依次用正己烷-醋酸乙酯 (1:1)、醋酸乙酯、醋酸乙酯-甲醇 (8:2) 和甲醇洗脱, 合并相同流分得到 12 个组分 (FE₁~FE₁₂)。FE₆ (6.1 g) 用 HPLC (PREP-Sil Φ 250 mm×10 mm 色谱柱) 分离, 得到化合物 4 (130.7 mg)、5 (939.4 mg)、6 (456.0 mg)、7 (78.6 mg)、8 (32.4 mg)、9 (69.8 mg)。FE₇ (2.1 g) 用硅胶柱色谱分离后经 HPLC (PREP-Sil Φ 250 mm×10 mm 色谱柱) 分离, 得到化合物 10 (23.1 mg)、11 (81.7 mg)、12 (30.7 mg)、13 (39.7 mg)。FE₈ (3.76 g) 用硅胶柱色谱分离后进行 HPLC (PREP-Sil Φ 250 mm×10 mm 色谱柱) 分离, 得到化合物 14 (51.7 mg)、15 (22.9 mg)、16 (67.2 mg)、17 (19.5 mg)、18 (4.7 mg)。FE₉ (12.4 g) 用硅胶柱色谱粗分离后进行 HPLC (PREP-ODS Φ 250 mm×10 mm 色谱柱) 分离, 得到化合物 19 (25.0 mg)、20 (5.5 mg)、21 (14.2 mg)。FE₁₀ (6.6 g) 用硅胶柱色谱分离后进行 HPLC (PREP-ODS Φ 250 mm×10 mm 色谱柱) 分离, 得到化合物 22 (75.0 mg)、23 (80.4 mg)、24 (21.5 mg)。

取正丁醇萃取物 29.6 g, 用硅胶柱色谱分离, 依次用醋酸乙酯-甲醇 (9:1、7:3、1:1) 混合溶剂和甲醇洗脱, 合并相同流分得到 9 个组分 (FB₁~FB₉)。FB₂ (1.0 g) 用 HPLC (PREP-ODS Φ 250 mm×10 mm 色谱柱) 分离, 得到化合物 25 (1.0 mg)、26 (17.0 mg)、27 (10.0 mg)、28 (10.4 mg)、29 (71.2 mg)、30 (12.2 mg)、31 (84.7 mg)、32 (22.5 mg)。FB₃ (3.4 g) 用硅胶柱色谱分离后进行 HPLC (PREP-ODS Φ 250 mm×10 mm 色谱柱) 分离, 得到化合物 33 (30.5 mg)、34 (4.7 mg)、35 (10.5 mg)。

3 结构鉴定

化合物 **1**: 白色粉末 (醋酸乙酯), mp 245~247 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 5.28 (1H, d, $J = 3.2$ Hz, H-12), 3.23 (1H, dd, $J = 13.6, 3.8$ Hz, H-3), 2.81 (1H, dd, $J = 11.0, 3.8$ Hz, H-18), 1.12 (3H, s, H-27), 1.00 (3H, s, H-25), 0.93 (3H, s, H-23), 0.92 (3H, s, H-26), 0.90 (3H, s, H-30), 0.77 (3H, s, H-29), 0.76 (3H, s, H-24); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 178.2 (C-28), 138.2 (C-13), 124.5 (C-12), 76.8 (C-3), 54.8 (C-5), 52.4 (C-18), 47.6 (C-17), 46.8 (C-9), 41.6 (C-14), 40.1 (C-19), 38.5 (C-8), 38.4 (C-20), 38.3 (C-4), 38.2 (C-1), 36.5 (C-10), 36.3 (C-22), 32.7 (C-7), 30.2 (C-21), 28.2 (C-23), 27.5 (C-15), 27.0 (C-2), 23.8 (C-16), 23.2 (C-29), 22.8 (C-27), 21.0 (C-30), 18.0 (C-6), 17.0 (C-11), 16.9 (C-26), 16.1 (C-25), 15.2 (C-24)。以上数据与文献报道一致^[8], 故鉴定化合物 **1** 为齐墩果酸。

化合物 **2**: 白色粉末 (醋酸乙酯), mp 283~287 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 5.28 (1H, d, $J = 3.6$ Hz, H-12), 3.21 (1H, dd, $J = 7.8, 4.4$ Hz, H-3), 2.18 (1H, d, $J = 11.6$ Hz, H-18), 1.34 (3H, s, H-27), 1.08 (3H, s, H-25), 0.98 (3H, s, H-23), 0.95 (3H, s, H-26), 0.92 (3H, d, $J = 6.4$ Hz, H-30), 0.85 (3H, d, $J = 6.8$ Hz, H-29), 0.78 (3H, s, H-24); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 179.9 (C-28), 138.8 (C-13), 125.7 (C-12), 79.2 (C-3), 56.1 (C-5), 53.5 (C-18), 48.3 (C-17), 48.2 (C-9), 42.6 (C-14), 41.2 (C-8), 39.7 (C-19), 39.5 (C-1), 39.1 (C-20), 39.0 (C-4), 38.3 (C-22), 37.6 (C-10), 34.1 (C-7), 32.1 (C-21), 29.2 (C-23), 29.0 (C-15), 28.3 (C-2), 26.2 (C-16), 24.2 (C-27), 23.8 (C-11), 21.5 (C-30), 18.0 (C-6), 17.7 (C-29), 17.7 (C-26), 16.7 (C-25), 15.8 (C-25)。以上数据与文献报道一致^[9], 故鉴定化合物 **2** 为乌苏酸。

化合物 **3**: 白色粉末 (醋酸乙酯), mp 283~285 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 4.70 (1H, brs, H-29a), 4.62 (1H, brs, H-29b), 3.21 (1H, dd, $J = 10.8, 4.8$ Hz, H-3), 2.98 (1H, m, H-19), 1.69 (3H, s, H-30), 0.96 (3H, s, H-27), 0.95 (3H, s, H-26), 0.93 (3H, s, H-23), 0.82 (3H, s, H-25), 0.78 (3H, s, H-24); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 179.8 (C-28), 150.0 (C-20), 109.8 (C-29), 78.8 (C-3), 56.1 (C-17), 55.6 (C-5), 50.7 (C-9), 49.5 (C-19), 46.7 (C-18), 42.6 (C-14), 40.8 (C-8), 38.8 (C-4), 38.5 (C-1), 38.2

(C-13), 37.0 (C-10), 36.8 (C-22), 34.5 (C-7), 32.3 (C-16), 30.8 (C-15), 29.8 (C-21), 27.9 (C-23), 27.6 (C-2), 25.6 (C-12), 21.0 (C-11), 19.8 (C-30), 18.4 (C-6), 16.2 (C-26), 15.8 (C-25), 15.4 (C-24), 14.8 (C-27)。以上数据与文献报道一致^[9], 故鉴定化合物 **3** 为白桦酸。

化合物 **4**: 淡黄色蜡状物。 $^1\text{H-NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ : 6.78 (1H, d, $J = 7.6$ Hz, H-5), 6.65 (1H, d, $J = 1.2$ Hz, H-2), 6.56 (1H, dd, $J = 7.6, 1.2$ Hz, H-6), 5.95 (2H, s, H-1'), 4.54 (1H, t, 9-OH), 3.37 (2H, m, H-9), 2.50 (2H, t, $J = 6.4$ Hz, H-7), 1.67 (2H, m, H-8); $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO}-d_6$) δ : 147.4 (C-3), 145.4 (C-4), 135.7 (C-1), 122.2 (C-6), 109.6 (C-2), 108.3 (C-1'), 60.6 (C-9), 43.0 (C-8), 34.3 (C-7)。以上数据与有机化合物光谱数据库标准图谱对照一致, 鉴定化合物 **4** 为 1,3-苯并间二氧杂环戊烯-5-丙醇。

化合物 **5**: 白色粉末 (醋酸乙酯), mp 165~167 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 9.13 (1H, s, Ar-OH), 6.98 (2H, d, $J = 8.4$ Hz, H-2, 6), 6.65 (2H, d, $J = 8.4$ Hz, H-3, 4), 3.51 (2H, t, $J = 6.4$ Hz, H-3'), 2.80 (2H, t, $J = 6.4$ Hz, H-1'), 1.87 (2H, m, H-2'); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 153.4 (C-4), 143.5 (C-1), 135.7 (C-1), 127.8 (C-2, 6), 114.6 (C-3, 5), 62.1 (C-3'), 42.5 (C-2'), 11.1 (C-1')。以上数据与文献报道一致^[10], 故鉴定化合物 **5** 为对羟基苯丙醇。

化合物 **6**: 淡黄色晶体 (醋酸乙酯), mp 83~84 °C; $^1\text{H-NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ : 9.10 (1H, s, Ar-OH), 6.97 (2H, d, $J = 8.4$ Hz, H-3, 5), 6.65 (2H, d, $J = 8.4$ Hz, H-2, 6), 4.55 (1H, t, $J = 4.8$ Hz, 8-OH), 3.51 (2H, dd, $J = 7.2, 4.8$ Hz, H-8), 2.57 (2H, t, $J = 7.2$ Hz, H-7)。以上数据与文献报道一致^[3], 故鉴定化合物 **6** 为对羟基苯乙醇。

化合物 **7**: 白色无定形粉末 (甲醇), mp 150~153 °C; $[\alpha]_D^{20} -63.4^\circ$ (c 0.36, MeOH); $^1\text{H-NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ : 9.32 (1H, s, Ar-OH), 7.03 (2H, d, $J = 8.0$ Hz, H-2', 6'), 6.68 (2H, d, $J = 8.0$ Hz, H-3', 5'), 5.18 (1H, s, H-1), 5.07 (1H, d, $J = 8.8$ Hz, H-3), 4.21 (2H, t, $J = 6.4$ Hz, H- α), 3.70 (1H, dq, $J = 18.4, 7.2$ Hz, H-1''), 3.40 (1H, dq, $J = 18.4, 7.2$ Hz, H-1''), 2.77 (2H, t, $J = 6.4$ Hz, H- β), 2.67 (1H, m, H-5), 2.31 (1H, dd, $J = 18.6, 8.0$ Hz, H-6a), 2.13 (2H, m, H-4, 8), 1.95 (1H, d, $J = 18.6$ Hz, H-6b), 1.86 (1H, dd, $J = 12.2, 6.4$ Hz, H-9), 1.08 (3H, t, $J = 7.2$ Hz, H-2''), 0.98 (3H, d,

$J = 6.8$ Hz, H-10); $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ : 217.4 (C-7), 172.1 (C-11), 155.8 (C-4'), 129.9 (C-2', 6'), 128.1 (C-1'), 115.2 (C-3', 5'), 94.5 (C-3), 92.1 (C-1), 65.4 (C- α), 63.7 (C-1''), 49.2 (C-4), 46.2 (C-8), 42.6 (C-9), 42.1 (C-6), 33.6 (C- β), 32.4 (C-5), 15.1 (C-2''), 13.0 (C-10)。以上数据与文献报道一致^[11], 故鉴定化合物 7 为丁香苦素 D。

化合物 8: 白色无定形粉末 (甲醇), mp 148~151 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{20} +136.8^{\circ}$ (c 0.41, MeOH); $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ : 9.32 (1H, s, Ar-OH), 7.03 (2H, d, $J = 8.4$ Hz, H-2', 6'), 6.68 (2H, d, $J = 8.4$ Hz, H-3', 5'), 5.05 (1H, d, $J = 8.8$ Hz, H-3), 4.89 (1H, s, H-1), 4.19 (2H, t, $J = 6.4$ Hz, H- α), 3.77 (1H, dq, $J = 7.2$, 18.4 Hz, H-1''), 3.52 (1H, dq, $J = 7.2$, 18.4 Hz, H-1'''), 2.76 (2H, t, $J = 6.4$ Hz, H- β), 2.60 (1H, m, H-5), 2.32 (1H, dd, $J = 7.6$, 18.6 Hz, H-6a), 2.11 (2H, m, H-4, 8), 1.95 (1H, d, $J = 18.6$ Hz, H-6b), 1.89 (1H, dd, $J = 6.8$, 12.8 Hz, H-9), 1.18 (3H, t, $J = 6.8$ Hz, H-2''), 1.0 (3H, d, $J = 6.8$ Hz, H-10); $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ : 217.0 (C-7), 172.0 (C-11), 155.6 (C-4'), 129.7 (C-2', 6'), 127.8 (C-1'), 115.0 (C-3', 5'), 97.5 (C-1), 88.4 (C-3), 65.1 (C- α), 62.1 (C-1''), 50.4 (C-4), 44.7 (C-8), 42.6 (C-9), 42.1 (C-6), 33.5 (C- β), 32.6 (C-5), 14.9 (C-2''), 12.7 (C-10)。以上数据与文献报道一致^[11], 故鉴定化合物 8 为丁香苦素 E。

化合物 9: 淡黄色粉末 (醋酸乙酯), mp 146~148 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{24} -47.0^{\circ}$ (c 0.25, MeOH); $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ : 7.03 (2H, d, $J = 8.4$ Hz, H-2', 6'), 6.68 (2H, d, $J = 8.4$ Hz, H-3', 5'), 5.04 (1H, d, $J = 8.8$ Hz, H-3), 4.89 (1H, s, H-1), 4.19 (2H, t, $J = 6.4$ Hz, H- α), 3.81 (1H, dq, $J = 9.6$, 6.8 Hz, H-1'''), 3.77 (1H, dq, $J = 9.6$, 6.8 Hz, H-1''), 3.55 (1H, m, H-1'''), 3.52 (1H, m, H-1''), 2.76 (2H, t, $J = 6.8$ Hz, H- β), 2.60 (1H, m, H-5), 2.32 (1H, dd, $J = 18.8$, 7.6 Hz, H-6a), 2.11 (2H, m, H-4, 8), 1.89 (2H, m, H-6b, 9), 1.20 (3H, t, $J = 6.8$ Hz, H-2'''), 1.18 (3H, t, $J = 6.8$ Hz, H-2''), 1.0 (3H, d, $J = 6.8$ Hz, H-10); $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ : 217.1 (C-7), 171.9 (C-11), 155.6 (C-4'), 129.7 (C-2', 6'), 127.8 (C-1'), 115.1 (C-3', 5'), 97.5 (C-1), 98.1 (C-3), 65.1 (C- α), 63.2 (C-1'''), 62.1 (C-1''), 50.4 (C-4), 44.7 (C-8), 42.2 (C-9), 42.1 (C-6), 33.5 (C- β), 32.6 (C-5), 15.8 (C-2'''), 14.9 (C-2''), 12.7 (C-10)。以上数据与文献报道一致^[12], 故鉴定化合

物 9 为丁香苦素 F。

化合物 10: 白色针状结晶 (醋酸乙酯), mp 150~152 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{20} +263.4^{\circ}$ (c 0.50, MeOH); $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ : 9.21 (1H, s, 4'-OH), 7.02 (2H, d, $J = 8.4$ Hz, H-2', 6'), 6.67 (2H, d, $J = 8.4$ Hz, H-3', 5'), 5.01 (1H, d, $J = 6.8$ Hz, H-3), 4.79 (1H, s, H-1), 4.19 (1H, m, H- α), 3.37 (3H, s, 1-OCH₃), 2.75 (1H, m, H- β), 2.67 (1H, m, H-5), 2.30 (1H, dd, $J = 10.8$, 7.6 Hz, H-6), 2.10 (2H, m, H-4, 8), 1.90 (1H, m, H-9), 0.99 (3H, d, $J = 6.8$ Hz, H-10); $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ : 217.1 (C-7), 172.0 (C-11), 155.9 (C-4'), 129.8 (C-2', 6'), 127.7 (C-1'), 115.1 (C-3', 5'), 99.0 (C-1), 88.3 (C-3), 65.1 (C- α), 54.3 (3-OCH₃), 50.4 (C-4), 44.6 (C-8), 42.2 (C-9), 42.1 (C-6), 33.5 (C- β), 32.6 (C-5), 12.7 (C-10)。以上结果文献报道一致^[4], 鉴定为丁香苦素 A。

化合物 11: 白色针晶 (醋酸乙酯), mp 156~159 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{24} -43.0^{\circ}$ (c 0.25, MeOH); $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ : 9.19 (1H, s, 4'-OH), 7.01 (2H, d, $J = 8.8$ Hz, H-2', 6'), 6.66 (2H, d, $J = 8.4$ Hz, H-3', 5'), 5.18 (1H, d, $J = 4.4$ Hz, H-1), 4.96 (1H, s, H-3), 4.19 (2H, m, H- α), 3.27 (3H, s, 3-OCH₃), 2.75 (2H, t, $J = 6.4$ Hz, H- β), 2.64 (1H, m, H-5), 2.30 (1H, dd, $J = 10.8$, 7.6 Hz, H-6), 2.16 (1H, m, H-8), 2.13 (1H, m, H-4), 1.94 (1H, dd, $J = 12.2$, 8.8 Hz, H-9), 0.99 (3H, d, $J = 6.8$ Hz, H-10); $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ : 217.3 (C-7), 171.8 (C-11), 155.9 (C-4'), 129.7 (C-2', 6'), 127.7 (C-1'), 115.1 (C-3', 5'), 92.0 (C-1), 98.0 (C-3), 65.1 (C- α), 54.3 (C-3-OCH₃), 50.4 (C-4), 44.6 (C-8), 42.2 (C-9), 42.1 (C-6), 33.5 (C- β), 32.6 (C-5), 12.7 (C-10)。以上数据与文献报道一致^[6], 故鉴定化合物 11 为丁香苦素 C。

化合物 12: 浅黄色蜡状物; $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ : 8.70 (1H, s, 4-OH), 8.55 (1H, s, 3-OH), 6.69 (1H, d, $J = 8.0$ Hz, H-5), 6.69 (1H, d, $J = 2.0$ Hz, H-2), 6.45 (1H, dd, $J = 8.0$, 2.0 Hz, H-6), 4.55 (1H, t, $J = 4.8$ Hz, α -OH), 3.51 (2H, m, H- α), 2.53 (2H, t, $J = 7.2$ Hz, H- β)。以上数据与文献报道一致^[3], 故鉴定化合物 12 为 3,4-二羟基苯乙醇。

化合物 13: 白色无定形固体 (醋酸乙酯), $[\alpha]_{\text{D}}^{24} +157.0^{\circ}$ (c 0.83, MeOH); $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ : 9.21 (1H, s, 4'-OH), 7.52 (1H, s, H-3), 7.40 (1H, s, 1-OH), 7.03 (2H, d, $J = 8.4$ Hz, H-2', 6'),

6.67 (2H, d, $J = 8.4$ Hz, H-3', 5'), 5.43 (1H, t, $J = 4.8$ Hz, H-1), 4.19 (2H, m, H- α), 3.05 (1H, ddd, $J = 10.0$, 10.0, 7.1 Hz, H-5), 2.79 (2H, t, $J = 6.8$ Hz, H- β), 2.58 (1H, dq, $J = 13.9$, 6.8, 6.4 Hz, H-8), 2.49 (1H, m, H-9), 2.38 (1H, dd, $J = 12.8$, 10.0 Hz, H-6a), 2.02 (1H, dd, $J = 12.8$, 10.0 Hz, H-6b), 1.02 (3H, d, $J = 6.8$ Hz, H-10); $^{13}\text{C-NMR}$ (100 MHz, DMSO- d_6) δ : 217.3 (C-7), 166.2 (C-11), 155.8 (C-4'), 151.3 (C-3), 129.8 (C-2', 6'), 128.2 (C-1'), 115.2 (C-3', 5'), 109.6 (C-4), 92.0 (C-1), 64.5 (C- α), 45.6 (C-8), 41.8 (C-6), 39.1 (C-9), 33.7 (C- β), 27.2 (C-5), 8.8 (C-10)。以上结果与文献报道一致^[4], 故鉴定化合物 **13** 为丁香苦素 B。

化合物 **14**: 淡黄色粉末 (醋酸乙酯), mp 136~138 °C; $[\alpha]_D^{24}$ -65.2° (c 0.64, CHCl₃); $^1\text{H-NMR}$ (400 MHz, DMSO- d_6) δ : 8.76 (1H, s, 3'-OH), 8.67 (1H, s, 4'-OH), 7.43 (1H, s, 1-OH), 7.42 (1H, s, H-3), 6.66 (1H, d, $J = 8.4$ Hz, H-5'), 6.61 (1H, dd, $J = 8.4$, 1.8 Hz, H-6'), 6.47 (1H, d, $J = 1.8$ Hz, H-2'), 5.43 (1H, s, H-1), 4.19 (2H, m, H- α), 3.05 (1H, ddd, $J = 11.3$, 10.4, 7.1 Hz, H-5), 2.79 (2H, t, $J = 6.8$ Hz, H- β), 2.73 (1H, dq, $J = 13.9$, 6.8, 6.4 Hz, H-8), 2.49 (1H, m, H-9), 2.38 (1H, dd, $J = 12.8$, 10.0 Hz, H-6a), 2.02 (1H, dd, $J = 12.8$, 10.0 Hz, H-6b), 1.02 (3H, d, $J = 6.8$ Hz, H-10); $^{13}\text{C-NMR}$ (100 MHz, DMSO- d_6) δ : 211.2 (C-7), 165.5 (C-11), 152.9 (C-3), 145.5 (C-3'), 144.1 (C-4'), 129.3 (C-1'), 119.9 (C-2'), 116.6 (C-6'), 115.9 (C-5'), 108.8 (C-4), 93.2 (C-1), 65.0 (C- α), 34.3 (C-8), 42.6 (C-6), 40.2 (C-9), 34.3 (C- β), 27.5 (C-5), 14.1 (C-10)。以上数据与文献报道一致^[13], 故鉴定化合物 **14** 为 syringopicrogenin B。

化合物 **15**: 无色脂状物; $^1\text{H-NMR}$ (400 MHz, DMSO- d_6) δ : 5.75 (1H, s, H-8), 4.04 (1H, m, H-3), 2.10 (3H, s, H-13), 2.03 (1H, dd, $J = 12.8$, 2.0 Hz, H-4a), 1.80 (1H, dd, $J = 12.5$, 2.0 Hz, H-2b), 1.31 (3H, s, H-11), 1.26 (3H, s, H-12), 1.19 (1H, dd, $J = 12.8$, 2.0 Hz, H-4b), 1.16 (1H, dd, $J = 12.5$, 2.0 Hz, H-2a), 1.05 (3H, s, H-10); $^{13}\text{C-NMR}$ (100 MHz, DMSO- d_6) δ : 209.6 (C-7), 198.3 (C-9), 119.2 (C-6), 100.0 (C-8), 71.0 (C-5), 62.5 (C-3), 50.0 (C-2), 49.7 (C-4), 36.0 (C-1), 32.1 (C-10), 30.8 (C-12), 29.2 (C-11), 26.6 (C-13)。以上数据与文献报道一致^[14], 故鉴定化合物 **15** 为蚱蜢酮。

化合物 **16**: 浅黄色无定形固体; $^1\text{H-NMR}$ (400 MHz, CDCl₃) δ : 6.94 (1H, d, $J = 6.0$ Hz, H-2), 6.91 (1H, dd, $J = 8.0$, 2.0 Hz, H-6), 6.90 (1H, d, $J = 8.0$ Hz, H-5), 6.89 (1H, s, H-6'), 6.68 (1H, s, H-2'), 5.54 (1H, d, $J = 6.4$ Hz, H-7), 3.87 (1H, dd, $J = 8.4$, 6.8 Hz, H-9a), 3.82 (3H, s, 3-OCH₃), 3.80 (3H, s, 3'-OCH₃), 3.76 (1H, m, H-9b), 3.56 (2H, m, H-9'), 3.52 (1H, m, H-8), 2.68 (1H, t, $J = 6.5$ Hz, H-7'), 1.89 (1H, m, H-8'); $^{13}\text{C-NMR}$ (100 MHz, CDCl₃) δ : 148.0 (C-4), 146.8 (C-4'), 146.0 (C-3), 143.8 (C-3'), 135.5 (C-5'), 133.0 (C-1), 129.5 (C-1'), 119.0 (C-6'), 116.9 (C-6), 115.8 (C-5), 112.9 (C-2'), 110.8 (C-2), 87.3 (C-7), 64.5 (C-9), 60.7 (C-9'), 56.1 (3-OCH₃), 56.1 (3'-OCH₃), 53.8 (C-8), 35.2 (C-8'), 32.0 (C-7')。以上数据与文献报道一致^[15], 故鉴定化合物 **16** 为 (7*R*,8*S*)-4,9,9'-三羟基-3,3'-二甲氧基-7,8-二氢苯并呋喃-1'-丙基新木脂素。

化合物 **17**: 白色粉末 (醋酸乙酯), mp 155~157 °C; $^1\text{H-NMR}$ (400 MHz, DMSO- d_6) δ : 8.81 (1H, s, 4-OH), 8.70 (1H, s, 4'-OH), 6.81 (1H, s, H-2), 6.74 (2H, d, $J = 8.0$ Hz, H-5, 5'), 6.70 (1H, d, $J = 8.0$ Hz, H-6), 6.68 (1H, d, $J = 8.0$ Hz, H-6'), 6.67 (1H, s, H-2'), 4.65 (1H, d, $J = 6.4$ Hz, H-7), 4.07 (1H, dd, $J = 8.4$, 6.8 Hz, H-9'a), 3.92 (1H, m, H-9a), 3.98 (3H, s, 3-OCH₃), 3.88 (3H, s, 3'-OCH₃), 3.84 (1H, dd, $J = 8.4$, 6.8 Hz, H-9'b), 3.79 (1H, m, H-9b), 2.92 (1H, dd, $J = 13.6$, 4.2 Hz, H-7'a), 2.74 (1H, m, H-8'), 2.56 (1H, dd, $J = 13.6$, 4.2 Hz, H-7'b), 2.42 (1H, m, H-8); $^{13}\text{C-NMR}$ (100 MHz, DMSO- d_6) δ : 147.9 (C-4), 147.8 (C-4'), 146.0 (C-3), 145.0 (C-3'), 135.2 (C-1), 132.2 (C-1'), 121.1 (C-6'), 118.6 (C-6), 115.8 (C-5'), 115.5 (C-5), 110.4 (C-2'), 104.1 (C-2), 82.2 (C-7), 72.3 (C-9'), 59.1 (C-9), 56.0 (3-OCH₃), 56.0 (3'-OCH₃), 52.9 (C-8), 42.4 (C-8'), 32.6 (C-7')。以上数据与文献报道一致^[7], 故鉴定化合物 **17** 为落叶松脂醇。

化合物 **18**: 白色粉末 (甲醇), $^1\text{H-NMR}$ (400 MHz, DMSO- d_6) δ : 6.73 (2H, s, H-2, H-6), 6.47 (1H, d, $J = 15.6$ Hz, H-7), 6.35 (1H, dt, $J = 15.6$, 6.4 Hz, H-8), 4.90 (1H, d, $J = 6.0$ Hz, Glc-H-1), 4.10 (2H, m, H-9), 3.77 (6H, s, 2, 6-OCH₃), 3.60 (1H, m, Glc-H-6a), 3.38 (1H, m, Glc-H-6b), 3.02~3.18 (4H, m, Glc-H-2~5); $^{13}\text{C-NMR}$ (100 MHz, DMSO- d_6) δ : 152.7 (C-2, 6), 133.8 (C-1), 132.6 (C-4), 130.2 (C-8),

128.4 (C-7), 104.5 (C-3, 5), 102.5 (Glc-C-1), 77.2 (Glc-C-3), 76.5 (Glc-C-5), 74.2 (Glc-C-2), 69.9 (Glc-C-4), 61.4 (C-9), 60.9 (Glc-C-6)。以上数据与文献报道一致^[16], 故鉴定化合物 **18** 为丁香苷。

化合物 **19**: 无色脂状物, $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 5.44 (1H, m, H-4), 5.33 (1H, m, H-3), 4.34 (1H, d, $J = 7.1$ Hz, H-1'), 3.85 (2H, m, H-1), 3.83 (1H, m, H-6'), 3.60 (1H, m, H-4'), 3.58 (1H, m, H-6), 3.54 (1H, m, H-5'), 3.42 (1H, t, $J = 7.1$ Hz, H-2'), 3.31 (1H, d, $J = 7.8$ Hz, H-3'), 2.37 (2H, d, $J = 6.3$ Hz, H-2), 2.04 (2H, m, H-5), 0.96 (3H, t, $J = 7.6$ Hz, H-6); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 134.1 (C-4), 124.1 (C-3), 102.8 (C-1'), 76.3 (C-3'), 75.6 (C-5'), 73.3 (C-2'), 69.3 (C-1), 69.8 (C-4'), 61.3 (C-6'), 27.7 (C-2), 20.7 (C-5), 14.3 (C-6)。以上数据与文献报道一致^[17], 故鉴定化合物 **19** 为 3(Z)-己烯醇葡萄糖苷。

化合物 **20**: 黄色粉末 (甲醇), mp 240~242 °C; $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ : 12.67 (1H, s, 5-OH), 7.68 (1H, dd, $J = 8.0, 1.8$ Hz, H-6'), 7.66 (1H, d, $J = 1.8$ Hz, H-2'), 6.84 (1H, d, $J = 8.0$ Hz, H-5'), 6.39 (1H, d, $J = 2.0$ Hz, H-8), 6.18 (1H, d, $J = 2.0$ Hz, H-6), 5.40 (1H, d, $J = 6.0$ Hz, Glc-H-1), 3.68 (1H, m, Glc-H-6a), 3.54 (1H, m, Glc-H-6b), 3.30 (1H, m, Glc-H-4), 3.24 (1H, m, Glc-H-5), 3.13 (2H, m, Glc-2, 3); $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ : 177.4 (C-4), 167.0 (C-7), 161.8 (C-5), 156.7 (C-9), 156.3 (C-2), 149.5 (C-4'), 145.0 (C-3'), 133.0 (C-3), 121.8 (C-1'), 120.9 (C-6'), 115.8 (C-5'), 115.2 (C-2'), 103.8 (C-10), 101.3 (Glc-C-1), 99.4 (C-6), 94.0 (C-8), 77.6 (Glc-C-3), 76.9 (Glc-C-5), 74.6 (Glc-C-2), 70.0 (Glc-C-4), 61.1 (Glc-C-6)。以上数据与文献报道一致^[18], 故鉴定化合物 **20** 为槲皮素-3-*O*- β -D-吡喃葡萄糖苷。

化合物 **21**: 黄色粉末 (甲醇), mp 96~98 °C; $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ : 9.22 (1H, s, 4'-OH), 7.52 (1H, s, H-3), 7.03 (2H, d, $J = 6.8$ Hz, H-2', 6'), 6.68 (2H, d, $J = 8.4$ Hz, H-3', 5'), 5.96 (1H, q, $J = 7.0$ Hz, H-8), 5.87 (1H, s, H-1), 4.65 (1H, d, $J = 7.2$ Hz, H-Glc-1), 4.19 (2H, m, H- α), 3.82 (1H, dd, $J = 11.8, 6.7$ Hz, H-5), 3.68 (1H, m, Glc-H-6a), 3.67 (3H, s, 11-OCH₃), 3.34 (1H, m, Glc-H-6b), 3.23 (1H, m, Glc-H-5), 3.21 (1H, m, Glc-H-4), 3.19 (1H, m, Glc-H-3), 3.09 (1H, m, Glc-H-2), 2.79 (2H, t, $J = 6.8$

Hz, H- β), 2.66 (1H, dd, $J = 14.5, 6.7$ Hz, H-6a), 2.42 (1H, dd, $J = 14.5, 6.7$ Hz, H-6b), 1.62 (3H, d, $J = 7.0$ Hz, H-10); $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ : 171.2 (C-7), 166.7 (C-11), 156.3 (C-4'), 153.9 (C-3), 130.3 (C-9), 129.6 (C-2', 6'), 128.3 (C-1'), 123.5 (C-8), 115.6 (C-3', 5'), 108.1 (C-4), 99.4 (Glc-C-1), 93.4 (C-1), 77.8 (Glc-C-3), 77.0 (Glc-C-2), 70.4 (C- α), 65.5 (Glc-C-4), 63.6 (Glc-C-5), 61.6 (Glc-C-6), 39.9 (C-6), 33.9 (C- β), 30.6 (C-5), 13.4 (C-10)。以上数据与文献报道一致^[6], 故鉴定化合物 **21** 为 (8*E*)-ligstroside。

化合物 **22**: 黄色无定形粉末; $^1\text{H-NMR}$ (600 MHz, $\text{DMSO-}d_6$) δ : 8.80 (1H, brs, 3'-OH), 6.99 (1H, d, $J = 8.4$ Hz, H-5'), 6.82 (2H, s, H-2, 2'), 6.71 (1H, d, $J = 8.4$ Hz, H-5), 6.68 (2H, m, H-6, 6'), 4.85 (1H, d, $J = 7.4$ Hz, Glc-1), 4.67 (1H, d, $J = 6.9$ Hz, H-7), 3.86 (1H, m, H-9a), 3.76 (3H, s, 3-OCH₃), 3.75 (3H, s, 3'-OCH₃), 3.72 (2H, m, Glc-H-6), 3.71 (1H, m, H-9'a), 3.67 (1H, m, H-9'b), 3.64 (1H, m, H-9b), 3.40~3.67 (4H, m, Glc-H-2~5), 2.59 (1H, m, H-8); $^{13}\text{C-NMR}$ (150 MHz, $\text{DMSO-}d_6$) δ : 148.3 (C-3), 147.5 (C-3'), 145.6 (C-4), 143.1 (C-4'), 137.1 (C-1), 131.8 (C-1'), 120.2 (C-6'), 117.6 (C-6), 116.5 (C-5'), 114.3 (C-5), 111.6 (C-2'), 109.6 (C-2), 100.5 (Glc-C-1), 81.4 (C-7), 78.0 (Glc-C-5), 77.5 (Glc-C-3), 77.2 (Glc-C-2), 73.9 (Glc-C-4), 73.1 (C-9'), 62.5 (Glc-C-6), 60.9 (C-9), 52.6 (C-8), 41.9 (C-8'), 31.3 (C-7')。以上数据与文献报道一致^[19], 故鉴定化合物 **22** 为落叶松脂素-4-*O*- β -D-吡喃葡萄糖苷。

化合物 **23**: 淡黄色粉末 (甲醇), mp 169~171 °C; $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ : 7.52 (1H, s, H-3), 6.65 (2H, s, H-2', 2''), 6.63 (2H, d, $J = 8.4$ Hz, H-6', 6''), 6.54 (2H, d, $J = 8.4$ Hz, H-5', 5''), 5.96 (1H, q, $J = 7.0$ Hz, H-8), 5.87 (1H, s, H-1), 4.49 (1H, d, $J = 7.6$ Hz, Glc-H-1), 4.16 (2H, m, H- α), 4.13 (2H, m, H- α'), 3.86 (1H, dd, $J = 11.8, 6.7$ Hz, H-5), 3.67 (1H, m, Glc-H-6a), 3.32 (1H, m, Glc-H-6b), 3.23 (1H, m, Glc-H-5), 3.21 (1H, m, Glc-H-4), 3.19 (1H, m, Glc-H-3), 3.09 (1H, m, Glc-H-2), 2.79 (2H, t, $J = 6.8$ Hz, H- β), 2.77 (2H, t, $J = 6.8$ Hz, H- β), 2.71 (2H, t, $J = 6.8$ Hz, H- β'), 2.66 (1H, dd, $J = 14.5, 6.7$ Hz, H-6a), 2.42 (1H, dd, $J = 14.5, 6.7$ Hz, H-6b), 1.64 (3H, d, $J = 7.0$ Hz, H-10); $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ : 171.1 (C-11), 166.4 (C-7), 153.9 (C-3), 135.8 (C-3'), 135.3

(C-3''), 134.3 (C-4'), 133.5 (C-4''), 130.0 (C-2''), 129.8 (C-2'), 129.6 (C-9), 128.8 (C-4), 128.7 (C-1''), 128.2 (C-1'), 123.5 (C-8), 115.2 (C-5''), 115.1 (C-5'), 113.4 (C-6'), 113.0 (C-6''), 99.5 (C-1), 98.8 (Glc-C-1), 77.7 (Glc-C-2), 76.7 (Glc-C-5), 73.5 (Glc-C-3), 71.0 (Glc-C-4), 70.0 (C- α), 68.5 (C- α'), 62.5 (Glc-C-6), 49.1 (C-6), 33.7 (C- β), 32.2 (C- β'), 30.6 (C-5), 13.1 (C-10)。以上数据与文献报道一致^[20], 故鉴定化合物 **23** 为 (8*E*)-ligstroside B。

化合物 **24**: 淡黄色粉末 (甲醇), mp 165~167 °C; ¹H-NMR (400 MHz, DMSO-*d*₆) δ : 7.45 (1H, s, H-3), 7.03 (2H, d, J = 8.2 Hz, H-2'', 6''), 7.02 (2H, d, J = 8.4 Hz, H-2', 6'), 6.68 (2H, d, J = 8.2 Hz, H-3'', 5''), 6.65 (2H, d, J = 8.4 Hz, H-3', 5'), 5.96 (1H, q, J = 7.0 Hz, H-8), 5.91 (1H, s, H-1), 4.80 (1H, d, J = 7.6 Hz, Glc-H-1), 4.19 (2H, m, H- α'), 4.16 (2H, m, H- α), 3.87 (1H, dd, J = 11.8, 6.7 Hz, H-5), 3.67 (1H, m, Glc-H-6a), 3.32 (1H, m, Glc-H-6b), 3.21 (1H, m, Glc-H-5), 3.21 (1H, m, Glc-H-4), 3.19 (1H, m, Glc-H-3), 3.08 (1H, m, Glc-H-2), 2.73 (2H, t, J = 6.6 Hz, H- β), 2.67 (2H, t, J = 6.4 Hz, H- β'), 2.66 (1H, dd, J = 14.5, 6.7 Hz, H-6a), 2.42 (1H, dd, J = 14.5, 6.7 Hz, H-6b), 1.66 (3H, d, J = 7.0 Hz, H-10); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ : 170.7 (C-11), 166.2 (C-7), 155.3 (C-4'), 154.8 (C-4''), 153.4 (C-3), 129.7 (C-2', 6'), 129.1 (C-9), 128.7 (C-1'), 128.5 (C-2'', 6''), 127.7 (C-4), 127.3 (C-1''), 98.8 (Glc-C-1), 92.9 (C-1), 73.1 (Glc-C-2), 72.7 (Glc-C-5), 71.0 (Glc-C-4), 70.0 (C-3), 69.9 (C- α), 68.7 (C- α'), 60.9 (Glc-C-6), 49.1 (C-6), 34.8 (C- β), 33.5 (C- β'), 30.0 (C-5), 13.0 (C-10)。以上数据与文献报道一致^[20], 故鉴定化合物 **24** 为 (8*E*)-ligstroside A。

化合物 **25**: 淡黄色粉末, ¹H-NMR (400 MHz, DMSO-*d*₆) δ : 9.17 (1H, s, 4-OH), 7.03 (2H, d, J = 8.4 Hz, H-2, 6), 6.66 (2H, d, J = 8.4 Hz, H-3, 5), 4.15 (1H, d, J = 7.8 Hz, H-1'), 3.87 (1H, m, H-6'a), 3.66 (1H, m, H-6'b), 3.56 (1H, m, H-2'), 3.43 (1H, m, H-3'), 3.12 (1H, m, H-4'), 3.06 (2H, m, H- α), 2.94 (1H, m, H-5'), 2.73 (2H, m, H- β); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ : 156.3 (C-4), 132.4 (C-1), 131.2 (C-3, 5), 116.8 (C-2, 6), 104.4 (C-1'), 79.9 (C-2'), 76.1 (C-3'), 73.7 (C-5'), 71.8 (C-4'), 70.6 (C- α), 62.3 (C-6'), 31.5 (C- β)。以上数据与文献报道一致^[21], 故鉴定化合物 **25** 为红景天苷。

化合物 **26**: 白色粉末 (甲醇), mp 183~186 °C; ¹H-NMR (600 MHz, DMSO-*d*₆) δ : 7.57 (1H, s, H-3), 5.38 (1H, d, J = 7.8 Hz, H-1), 5.01 (1H, d, J = 7.8 Hz, Glc-H-1), 3.66 (1H, m, Glc-H-6a), 3.60 (3H, s, -OCH₃), 3.40 (1H, m, Glc-H-6b), 3.10 (4H, m, H-5, Glc-H-3, 4, 5), 3.03 (1H, m, Glc-H-2), 2.95 (1H, m, H-9), 2.63 (1H, m, H-8), 2.52 (1H, ddd, J = 12.0, 7.2, 5.4 Hz, H-6a), 2.05 (1H, ddd, J = 12.0, 7.2, 5.4 Hz, H-6b), 1.41 (3H, d, J = 6.6 Hz, H-10); ¹³C-NMR (150 MHz, DMSO-*d*₆) δ : 218.0 (C-7), 172.0 (C-11), 153.4 (C-3), 108.1 (C-4), 99.6 (Glc-C-1'), 95.1 (C-1), 77.7 (Glc-C-5'), 77.0 (Glc-C-3'), 73.9 (Glc-C-2'), 73.6 (Glc-C-4'), 61.8 (Glc-C-6'), 51.7 (C-9), 40.3 (C-6), 39.5 (C-8), 33.9 (C-5), 21.6 (C-10)。以上数据与文献报道一致^[22], 故鉴定化合物 **26** 为 7-脱氢马钱子苷。

化合物 **27**: 浅黄色粉末, ¹H-NMR (400 MHz, DMSO-*d*₆) δ : 8.68 (2H, brs, 3', 4'-OH), 7.52 (1H, s, H-3), 6.63 (1H, d, J = 8.4 Hz, H-5'), 6.62 (1H, d, J = 2.0 Hz, H-2'), 6.49 (1H, dd, J = 8.4, 2.0 Hz, H-6'), 5.40 (1H, d, J = 8.0 Hz, H-1), 4.55 (1H, d, J = 7.8 Hz, Glc-H-1'), 4.34 (1H, dq, J = 6.4, 7.2, 12.4 Hz, H-8), 4.16 (2H, m, H- α), 3.09~3.23 (6H, m, Glc-H-2~6), 3.04 (1H, ddd, J = 11.8, 9.6, 6.8 Hz, H-5), 3.01 (1H, m, H-9), 2.73 (2H, t, J = 6.8 Hz, H- β), 2.62 (1H, dd, J = 7.2, 10.4 Hz, H-6a), 2.05 (1H, dd, J = 7.2, 10.4 Hz, H-6b), 1.41 (3H, d, J = 7.8 Hz, H-10); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ : 172.1 (C-7), 166.1 (C-11), 153.3 (C-3), 145.6 (C-3'), 144.2 (C-4'), 129.1 (C-1'), 120.1 (C-6'), 116.6 (C-5'), 116.0 (C-2'), 108.2 (C-4), 99.7 (Glc-C-1), 95.3 (C-1), 77.8 (Glc-C-2), 73.9 (Glc-C-4), 73.6 (Glc-C-3), 70.6 (C-9), 77.0 (Glc-C-5), 65.3 (C- α), 61.8 (Glc-C-6), 40.5 (C-9), 34.3 (C-6), 33.9 (C- β), 27.2 (C-5), 21.7 (C-10)。以上数据与文献报道一致^[23], 故鉴定化合物 **27** 为 fliederose B。

化合物 **28**: 淡黄色粉末 (甲醇), mp 143~145 °C; $[\alpha]_D^{20}$ +81.1° (*c* 0.32, CHCl₃); ¹H-NMR (600 MHz, DMSO-*d*₆) δ : 8.75 (2H, brs, 3', 4'-OH), 7.41 (1H, s, H-3), 6.64 (1H, dd, J = 8.4, 1.8 Hz, H-6'), 6.63 (1H, d, J = 1.8 Hz, H-2'), 6.47 (1H, d, J = 8.4 Hz, H-5'), 5.57 (1H, s, H-1), 4.50 (1H, d, J = 7.8 Hz, Glc-H-1), 4.16 (2H, m, H- α), 3.67 (1H, dd, J = 11.2, 6.0 Hz, Glc-H-6a), 3.45 (1H, dd, J = 11.2, 6.0 Hz, Glc-H-6b), 3.21 (1H, m, Glc-H-4), 3.20 (1H, m, Glc-H-3), 3.19

(1H, m, Glc-H-5), 3.08 (1H, m, Glc-H-2), 3.00 (1H, ddd, $J = 16.8, 11.2, 5.4$ Hz, H-5), 2.72 (2H, t, $J = 6.6$ Hz, H- β), 2.50 (1H, m, H-8), 2.47 (1H, m, H-9), 2.32 (1H, m, H-6a), 1.96 (1H, m, H-6b), 1.08 (3H, d, $J = 7.8$ Hz, H-10); ^{13}C -NMR (150 MHz, DMSO- d_6) δ : 218.2 (C-7), 166.8 (C-11), 152.1 (C-3), 145.9 (C-3'), 144.4 (C-4'), 129.3 (C-2'), 128.2 (C-1'), 116.3 (C-5'), 112.5 (C-6'), 110.0 (C-4), 99.3 (Glc-C-1), 93.8 (C-1), 77.8 (Glc-C-2), 76.7 (Glc-C-5), 73.7 (Glc-C-4), 71.0 (Glc-C-3), 65.5 (C- α), 61.5 (Glc-C-6), 45.0 (C-8), 42.3 (C-6), 39.3 (C-9), 34.2 (C- β), 27.3 (C-5), 14.0 (C-10)。以上数据与文献报道一致^[6], 故鉴定化合物 **28** 为 syringopicroside B。

化合物 **29**: 白色粉末 (甲醇), mp 181~186 °C; ^1H -NMR (600 MHz, DMSO- d_6) δ : 7.52 (1H, s, H-3), 5.99 (1H, q, $J = 6.6$ Hz, H-8), 5.17 (1H, s, H-1), 4.82 (1H, d, $J = 7.8$ Hz, Glc-H-1), 3.86 (1H, m, Glc-H-6a), 3.65 (1H, m, Glc-H-6), 3.64 (3H, s, 11-OCH₃), 3.59 (3H, s, 7-OCH₃), 3.42 (1H, m, H-5), 3.17 (2H, m, Glc-H-3, 5), 3.08 (2H, m, Glc-H-2, 4), 2.67 (1H, m, H-6a), 2.49 (1H, m, H-6b), 1.67 (3H, d, $J = 6.6$ Hz, H-10); ^{13}C -NMR (150 MHz, DMSO- d_6) δ : 175.7 (C-7), 168.3 (C-11), 153.2 (C-3), 127.7 (C-9), 123.0 (C-8), 108.2 (C-4), 99.6 (Glc-C-1), 95.7 (C-1), 77.7 (Glc-C-4), 77.0 (Glc-C-3), 74.9 (Glc-C-2), 71.6 (Glc-C-4), 62.8 (Glc-C-6), 55.6 (11-OCH₃), 52.4 (7-OCH₃), 40.3 (C-6), 32.5 (C-5), 12.7 (C-10)。以上数据与文献报道一致^[24], 故鉴定化合物 **29** 为木犀榄苷二甲酯。

化合物 **30**: 浅黄色粉末, ^1H -NMR (600 MHz, DMSO- d_6) δ : 9.21 (1H, s, 4'-OH), 7.52 (1H, s, H-3), 6.62 (2H, d, $J = 8.4$ Hz, H-2', 6'), 6.49 (2H, d, $J = 8.4$ Hz, H-3', 5'), 4.55 (1H, d, $J = 7.8$ Hz, Glc-H-1), 4.36 (1H, m, H-8), 4.20 (2H, m, H- α), 3.09~3.23 (6H, m, Glc-H-2~6), 3.04 (1H, m, H-5), 3.01 (1H, m, H-10), 2.78 (1H, dd, $J = 10.4, 7.8$ Hz, H-6a), 2.78 (2H, t, $J = 6.8$ Hz, H- β), 2.42 (1H, dd, $J = 10.4, 7.8$ Hz, H-6b), 2.06 (1H, m, H-9), 1.41 (3H, d, $J = 6.6$ Hz, H-10); ^{13}C -NMR (150 MHz, DMSO- d_6) δ : 172.0 (C-7), 166.0 (C-11), 156.2 (C-3), 153.3 (C-4'), 130.2 (C-1'), 115.6 (C-3', 5'), 108.2 (C-2', 6'), 108.1 (C-4), 99.6 (Glc-C-1), 95.2 (C-1), 77.7 (Glc-C-5), 77.0 (Glc-C-3), 73.9 (Glc-C-4), 70.6 (Glc-C-2), 70.5 (C-8), 65.3 (C- α), 61.8 (Glc-C-6), 40.4 (C-9), 34.0 (C-6), 33.9 (C- β), 27.2

(C-5), 21.6 (C-10)。以上数据与文献报道一致^[25], 故鉴定化合物 **30** 为 lilacosside。

化合物 **31**: 淡黄色粉末 (甲醇), mp 110~112 °C; ^1H -NMR (600 MHz, DMSO- d_6) δ : 9.23 (1H, s, 4-OH), 7.39 (1H, s, 1-OH), 7.04 (2H, d, $J = 8.4$ Hz, H-2', 6'), 6.68 (2H, d, $J = 8.4$ Hz, H-3', 5'), 5.54 (1H, s, H-3), 5.03 (1H, s, H-1), 4.49 (1H, t, $J = 7.8$ Hz, Glc-H-1), 4.16 (2H, m, H- α), 3.67 (1H, m, Glc-H-6a), 3.45 (1H, m, Glc-H-6b), 3.21 (1H, m, Glc-H-4), 3.20 (1H, m, Glc-H-3), 3.19 (1H, m, Glc-H-5), 3.08 (1H, m, Glc-H-2), 2.90 (1H, m, H-5), 2.78 (2H, t, $J = 6.6$ Hz, H- β), 2.30 (1H, m, H-6a), 2.50 (1H, m, H-8), 2.47 (1H, m, H-9), 1.96 (1H, m, H-6b), 1.05 (3H, d, $J = 7.8$ Hz, H-10); ^{13}C -NMR (150 MHz, DMSO- d_6) δ : 218.1 (C-7), 166.5 (C-11), 156.3 (C-3), 144.4 (C-4'), 130.2 (C-2', 6'), 128.4 (C-1'), 115.6 (C-3', 5'), 109.7 (C-4), 99.1 (Glc-C-1), 93.8 (C-1), 77.8 (Glc-C-2), 77.1 (Glc-C-5), 73.5 (Glc-C-4), 70.4 (Glc-C-3), 65.1 (Glc-C-6), 61.5 (C- α), 44.6 (C-8), 42.5 (C-6), 39.5 (C-9), 34.0 (C- β), 26.9 (C-5), 13.6 (C-10)。以上数据与文献报道一致^[4], 故鉴定化合物 **31** 为丁香苦苣。

化合物 **32**: 淡黄色固体 (醋酸乙酯), mp 105~107 °C; ^1H -NMR (400 MHz, DMSO- d_6) δ : 7.51 (1H, s, H-3), 6.70 (1H, d, $J = 7.6$ Hz, H-5'), 6.65 (1H, d, $J = 2.4$ Hz, H-2'), 6.54 (1H, d, $J = 7.6, 2.4$ Hz, H-6'), 6.06 (1H, q, $J = 7.2$ Hz, H-8), 6.01 (1H, s, H-1), 4.82 (1H, d, $J = 7.8$ Hz, Glc-H-1), 4.40 (1H, dt, $J = 10.7, 7.0$ Hz, Ha- α), 4.22 (1H, dt, $J = 10.7, 7.0$ Hz, Hb- α), 3.98 (1H, dd, $J = 9.0, 4.8$ Hz, H-5), 3.68 (1H, m, Glc-H-6a), 3.67 (3H, s, -OCH₃), 3.34 (1H, m, Glc-H-6b), 3.21 (1H, m, Glc-H-4), 3.20 (1H, m, Glc-H-3), 3.19 (1H, m, Glc-H-5), 3.08 (1H, m, Glc-H-2), 2.75 (2H, t, $J = 7.0$ Hz, H- β), 2.61 (1H, dd, $J = 6.7, 14.5$ Hz, H-6a), 2.45 (1H, dd, $J = 6.7, 14.5$ Hz, H-6b), 1.69 (3H, d, $J = 7.2$ Hz, H-10); ^{13}C -NMR (100 MHz, DMSO- d_6) δ : 171.4 (C-11), 166.8 (C-7), 153.7 (C-3), 146.3 (C-4'), 144.5 (C-3'), 129.0 (C-9), 129.0 (C-4), 123.8 (C-8), 120.9 (C-1'), 116.8 (C-6'), 115.2 (C-5'), 108.3 (C-2'), 99.6 (Glc-C-1), 93.3 (C-1), 77.8 (Glc-C-2), 76.7 (Glc-C-5), 73.7 (Glc-C-4), 71.0 (Glc-C-3), 65.5 (C- α), 61.5 (Glc-C-6), 51.8 (11-OCH₃), 49.1 (C-6), 34.2 (C- β), 30.6 (C-5), 13.1 (C-10)。以上数据与文献报道一致^[3], 故鉴定化合物 **32** 为橄榄苦苣。

化合物 **33**: 黄色粉末, $[\alpha]_D^{20} -31.8^\circ$ (c 0.35, MeOH); $^1\text{H-NMR}$ (600 MHz, DMSO- d_6) δ : 7.05 (1H, d, $J = 8.4$ Hz, H-5), 6.95 (1H, d, $J = 1.8$ Hz, H-2), 6.89 (1H, d, $J = 1.8$ Hz, H-2'), 6.86 (1H, dd, $J = 1.8, 8.4$ Hz, H-6), 6.76 (1H, dd, $J = 1.8, 8.0$ Hz, H-6'), 6.74 (1H, d, $J = 8.0$ Hz, H-5'), 4.87 (1H, d, $J = 7.8$ Hz, H-7), 4.66 (1H, d, $J = 7.8$ Hz, H-7'), 4.60 (1H, d, $J = 7.8$ Hz, Glc-H-1), 4.13 (2H, m, H-9), 3.76 (3H, s, OCH₃), 3.74 (3H, s, OCH₃), 3.46 (2H, m, H-9'), 3.21~3.67 (6H, m, Glc-H-2~6), 3.03 (2H, m, H-8, 8'); $^{13}\text{C-NMR}$ (150 MHz, DMSO- d_6) δ : 149.6 (C-3), 148.0 (C-3'), 146.2 (C-4), 145.9 (C-4'), 135.9 (C-1), 132.4 (C-1'), 119.4 (C-6'), 118.7 (C-6), 115.4 (C-5), 114.3 (C-5'), 111.0 (C-2), 110.4 (C-2'), 100.4 (C-1''), 86.4 (C-7), 86.0 (C-7'), 76.3 (C-5''), 75.6 (C-3''), 73.8 (C-2''), 71.5 (C-9), 70.3 (C-9''), 69.3 (C-4''), 60.3 (C-6''), 55.3 (3-OCH₃), 54.5 (3'-OCH₃), 52.5 (C-8), 51.4 (C-8'). 以上数据与文献报道一致^[26], 故鉴定化合物 **33** 为 (+)-表松脂素-4'-O- β -D-葡萄糖苷。

化合物 **34**: 褐色粉末, $^1\text{H-NMR}$ (600 MHz, DMSO- d_6) δ : 7.46 (1H, d, $J = 16.0$ Hz, H-7'), 7.02 (1H, d, $J = 1.8$ Hz, H-2'), 6.98 (1H, dd, $J = 8.4, 1.8$ Hz, H-6'), 6.75 (1H, d, $J = 8.4$ Hz, H-5'), 6.64 (1H, d, $J = 1.8$ Hz, H-2), 6.62 (1H, d, $J = 8.4$ Hz, H-5), 6.48 (1H, dd, $J = 8.4, 1.8$ Hz, H-6), 6.18 (1H, d, $J = 16.0$ Hz, H-8'), 5.02 (1H, d, $J = 1.8$ Hz, Rha-H-1), 4.36 (1H, d, $J = 7.4$ Hz, Glc-H-1), 3.90 (2H, m, H-8), 3.67 (1H, dd, $J = 6.0, 1.8$ Hz, Glc-H-6a), 3.45 (1H, dd, $J = 6.0, 1.8$ Hz, Glc-H-6b), 3.21~3.08 (4H, m, Glc-H-2~5), 3.21~3.08 (4H, m, Rha-H-2~5), 2.74 (2H, m, H-7), 0.96 (3H, d, $J = 6.0$ Hz, Rha-H-6); $^{13}\text{C-NMR}$ (150 MHz, DMSO- d_6) δ : 166.1 (C-9'), 149.2 (C-4'), 146.1 (C-7'), 146.0 (C-3'), 145.4 (C-3), 144.0 (C-4'), 129.5 (C-1), 125.8 (C-1'), 121.9 (C-6'), 120.0 (C-6), 116.7 (C-2), 116.6 (C-5'), 116.2 (C-5), 115.9 (C-2'), 113.9 (C-8'), 102.7 (Glc-C-1), 101.6 (Rha-C-1), 79.5 (Glc-C-3), 74.9 (Glc-C-5), 72.1 (Glc-C-2), 71.0 (Rha-C-4), 70.8 (Rha-C-2), 70.7 (C-8), 69.6 (Rha-C-3), 69.2 (Glc-C-4), 67.2 (Rha-C-5), 61.2 (Glc-C-6), 35.4 (C-7), 18.6 (Rha-C-6)。以上数据与文献报道一致^[27], 故鉴定化合物 **34** 为毛蕊花糖苷。

化合物 **35**: 浅黄色粉末 (甲醇), mp 243~246 $^\circ\text{C}$; $[\alpha]_D^{20} -23.0^\circ$ (c 0.42, MeOH); $^1\text{H-NMR}$ (600 MHz,

DMSO- d_6) δ : 7.02 (1H, d, $J = 8.4$ Hz, H-5'), 6.88 (1H, dd, $J = 8.4, 2.0$ Hz, H-6'), 6.78 (1H, d, $J = 2.0$ Hz, H-2'), 6.74 (1H, dd, $J = 8.4, 2.0$ Hz, H-6), 6.67 (1H, d, $J = 8.4$ Hz, H-5), 6.57 (1H, d, $J = 2.0$ Hz, H-2), 4.87 (1H, d, $J = 7.2$ Hz, Glc-H-1), 4.72 (1H, d, $J = 6.0$ Hz, H-7), 3.86 (1H, m, H-9a), 3.71 (1H, m, H-9'a), 3.67 (1H, m, H-9'b), 3.64 (1H, m, H-9b), 3.40~3.72 (6H, m, Glc-H-2~6), 2.81 (1H, dd, $J = 13.2, 4.8$ Hz, H-7'a), 2.72 (1H, m, H-8'), 2.57 (1H, dd, $J = 13.2, 4.8$ Hz, H-7'b), 2.37 (1H, m, H-8), 3.74 (6H, s, 3, 3'-OCH₃); $^{13}\text{C-NMR}$ (150 MHz, DMSO- d_6) δ : 149.5 (C-3'), 147.3 (C-3), 145.6 (C-4), 144.1 (C-4'), 135.8 (C-1'), 134.1 (C-1), 120.2 (C-6'), 117.6 (C-6), 116.5 (C-5'), 114.3 (C-5), 112.6 (C-2'), 108.6 (C-2), 103.5 (Glc-C-1), 83.2 (C-7), 78.4 (Glc-C-3), 78.1 (Glc-C-5), 75.2 (Glc-C-2), 71.7 (Glc-C-4), 62.5 (Glc-C-6), 58.5 (C-9, 9'), 54.3 (3-OCH₃), 54.2 (3'-OCH₃), 52.2 (C-8), 42.8 (C-8')。以上数据与文献报道一致^[26], 故鉴定化合物 **35** 为 (+)-落叶松脂素-4'-O- β -D-吡喃葡萄糖苷。

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