

翻白叶树根的化学成分研究

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摘要: **目的** 研究翻白叶树 *Pterospermum heterophyllum* 根的化学成分。**方法** 应用多种色谱技术进行分离纯化, 根据理化性质和波谱数据鉴定化合物的结构。**结果** 从翻白叶树根 95%乙醇提取物中分离得到 12 个化合物, 分别鉴定为莨菪苷(1)、2, 6-二甲氧基-4-羟基-苯酚-1-O-β-D-吡喃葡萄糖苷(2)、3-甲氧基-4-羟基-苯酚-1-O-β-D-吡喃葡萄糖苷(3)、4-羟基-2-甲氧基-苯酚-1-O-β-D-吡喃葡萄糖苷(4)、甲基熊果苷(5)、(+)-南烛木树脂酚-3α-O-β-D-吡喃葡萄糖苷(6)、(-)-南烛木树脂酚-3α-O-β-D-吡喃葡萄糖苷(7)、(-)-南烛木树脂酚-2α-O-β-D-吡喃葡萄糖苷(8)、(-)-异落叶松树脂酚-6-O-β-D-吡喃葡萄糖苷(9)、(-)-8, 8'-二甲氧基-开环异落叶松树脂酚-1-O-β-D-吡喃葡萄糖苷(10)、(+)-3-oxo-α-ionyl-O-β-D-glucopyranoside(11)、roseoside(12)。**结论** 化合物 1~11 为首次从该属植物中分离得到。

关键词: 翻白叶树; 莨菪苷; 2, 6-二甲氧基-4-羟基-苯酚-1-O-β-D-吡喃葡萄糖苷; (-)-南烛木树脂酚-2α-O-β-D-吡喃葡萄糖苷; 甲基熊果苷

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Studies on chemical constituents from roots of *Pterospermum heterophyllum*

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Abstract: **Objective** To study the chemical constituents from the roots of *Pterospermum heterophyllum*. **Methods** The chemical constituents were isolated and purified by chromatographic techniques, and their structures were identified by physicochemical characteristics and spectroscopic analyses. **Results** Twelve compounds were isolated from the 95% EtOH extract in the roots of *P. heterophyllum* and were identified as scopolin (1), 2, 6-dimethoxy-4-hydroxyphenol-1-O-β-D-glucopyranoside (2), 3-methoxy-4-hydroxyphenol-1-O-β-D-glucopyranoside (3), 4-hydroxy-2-methoxyphenol-1-O-β-D-glucopyranoside (4), methylarbutin (5), (+)-lyoniresinol-3α-O-β-D-glucopyranoside (6), (-)-lyoniresinol-3α-O-β-D-glucopyranoside (7), (-)-lyoniresinol-2α-O-β-D-glucopyranoside (8), (-)-isolariciresinol-6-O-β-D-glucopyranoside (9), (-)-8, 8'-dimethoxy-1-O-β-D-glucopyranosyl)secoisolariciresinol (10), (+)-3-oxo-α-ionyl-O-β-D-glucopyranoside (11), and roseoside (12). **Conclusion** Compounds 1—11 are isolated from the plants in *Pterospermum* Schreber for the first time.

Key words: *Pterospermum heterophyllum* Hance; scopolin; 2, 6-dimethoxy-4-hydroxyphenol-1-O-β-D-glucopyranoside; (-)-lyoniresinol-2α-O-β-D-glucopyranoside; methylarbutin

翻白叶树 *Pterospermum heterophyllum* Hance 为梧桐科 (Sterculiaceae) 翅子树属 *Pterospermum* Schreber 植物, 以根入药, 又名半枫荷。其性温, 味甘, 具有祛风除湿、舒筋活血的功能, 主要用于治疗风湿性关节炎、腰肌劳损、半身不遂、跌打损

伤等症状^[1-2]。国内外对该属植物的化学成分研究主要分离得到三萜类、黄酮类、苯丙素类和大柱香波龙烷型苷类化合物等^[3-8]。但对翻白叶树根有效成分及其药理研究很少, 为阐明其药效物质基础, 合理开发和利用资源, 本课题组对采自广西的翻白叶树

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根的化学成分进行了系统研究。在对翻白叶树根乙醇提取物不同部位的抗肿瘤活性筛选中发现其95%乙醇提取物的石油醚部位对卵巢癌A2780细胞具有细胞毒活性, IC_{50} 为3.84 $\mu\text{g/mL}$; 经石油醚、醋酸乙酯萃取后剩余的水溶液经大孔吸附树脂分离, 30%乙醇洗脱部分对结肠癌HCT-8细胞、肝癌Bel-7402细胞、胃癌BGC823细胞和肺癌A549细胞具有细胞毒活性, 其 IC_{50} 分别为3.68、3.64、1.51和2.40 $\mu\text{g/mL}$ 。本实验在已有研究工作的基础上^[9], 继续对翻白叶树根具有细胞毒活性的大孔吸附树脂30%乙醇洗脱部分的化学成分进行研究, 分离得到12个化合物, 分别鉴定为莨菪苷(scopolin, 1)、2, 6-二甲氧基-4-羟基-苯酚-1- O - β -D-吡喃葡萄糖苷(2, 6-dimethoxy-4-hydroxyphenol-1- O - β -D-glucopyranoside, 2)、3-甲氧基-4-羟基-苯酚-1- O - β -D-吡喃葡萄糖苷(3-methoxy-4-hydroxyphenol-1- O - β -D-glucopyranoside, 3)、4-羟基-2-甲氧基-苯酚-1- O - β -D-吡喃葡萄糖苷(4-hydroxy-2-methoxyphenol-1- O - β -D-glucopyranoside, 4)、甲基熊果苷(methylarbutin, 5)、(+)-南烛木树脂酚-3 α - O - β -D-吡喃葡萄糖苷[(+)-lyoniresinol-3 α - O - β -D-glucopyranoside, 6]、(-)-南烛木树脂酚-3 α - O - β -D-吡喃葡萄糖苷[(-)-lyoniresinol-3 α - O - β -D-glucopyranoside, 7]、(-)-南烛木树脂酚-2 α - O - β -D-吡喃葡萄糖苷[(-)-lyoniresinol-2 α - O - β -D-glucopyranoside, 8]、(-)-异落叶松树脂酚-6- O - β -D-吡喃葡萄糖苷[(-)-isolariciresinol-6- O - β -D-glucopyranoside, 9]、(-)-8, 8'-二甲氧基-开环异落叶松树脂酚-1- O - β -D-吡喃葡萄糖苷[(-)-8, 8'-dimethoxy-1- O -(β -D-glucopyranosyl) secoisolariciresinol, 10]、(+)-3-oxo- α -ionyl- O - β -D-glucopyranoside (11)、roseoside (12)。其中化合物1~11为首次从该属植物中分离得到。

1 仪器与材料

XT5B 显微熔点测定仪(北京市科仪电光仪器厂); Jasco P-2000 Polarimeter (Perkin-Elmer 343型旋光仪); Inova 500型核磁共振仪(美国Varian公司); Agilent 1100 Series LC/MSD Trap-SL型质谱仪(美国Agilent公司); Agilent 1260型高效液相色谱仪(美国Agilent公司)。柱色谱硅胶(200~300目)及薄层色谱硅胶GF254为青岛海洋化工厂产品; HPD-100大孔吸附树脂(河北沧州宝恩化工有限公司); Grace Allsphere ODS-2 (250 mm $\times$ 10 mm, 5 μm)型ODS色谱柱; 反相硅胶色谱为Alltech产

Bulk Sorbent High Capacity C₁₈型; Sephadex LH-20(瑞典Pharmacia公司); 所用试剂及溶剂为分析纯或色谱纯。

翻白叶树根2002年采自广西, 由广西柳州林业局龙光日工程师鉴定为翻白叶树 *Pterospermum heterophyllum* Hance 的根, 标本(2002-120)保存于中国医学科学院药物研究所植物标本室。

2 提取与分离

翻白叶树干燥根8 kg, 粉碎, 用95%乙醇回流提取3次, 减压浓缩提取液, 依次用石油醚和醋酸乙酯萃取, 剩余水溶液上大孔吸附树脂柱(HPD-100型), 通过蒸馏水及30%、50%、70%、95%乙醇依次洗脱得到5个部位。取30%乙醇洗脱物100 g, 经硅胶柱色谱分离, 氯仿-甲醇梯度洗脱, 通过薄层色谱检识合并得到FA、FB、FC、FD等15个组分。FA通过Sephadex LH-20凝胶柱色谱分离, 氯仿-甲醇(4:1)洗脱, 然后通过反相HPLC制备分离, 得到化合物1(10 mg)、2(8 mg)。FC通过反相硅胶柱色谱分离, 甲醇-水梯度洗脱, 得到6个组分a~f; 组分a通过HPLC制备得到化合物3(9 mg); 组分c通过Sephadex LH-20凝胶柱色谱分离, 氯仿-甲醇(1:1)洗脱, 再通过HPLC制备得到化合物6(24 mg)、7(63 mg)、10(10 mg); 组分f通过HPLC制备色谱柱得到化合物4(6 mg)、5(6 mg)。FE通过反相柱色谱分离, 甲醇-水梯度洗脱, 得到FE1、FE2、FE3、FE4等9个组分; 组分FE2通过HPLC制备得到化合物8(5 mg)和12(25 mg); 组分FE4通过HPLC制备得到化合物9(5 mg)。组分FH通过反相柱色谱分离, 甲醇-水梯度洗脱, 得到5个组分FH1~5, 组分FH3通过制备HPLC得到化合物11(126 mg)。

3 结构鉴定

化合物1: 无色粉末。ESI-MS m/z : 377 [$M+Na$]⁺。¹H-NMR (500 MHz, CD₃OD) δ : 7.83 (1H, d, J = 9.0 Hz, H-4), 7.14 (1H, s, H-5), 7.12 (1H, s, H-8), 6.24 (1H, d, J = 9.0 Hz, H-3), 5.01 (1H, d, J = 7.5 Hz, H-1'), 3.85 (3H, s, -OCH₃), 3.84 (1H, brd, J = 12.0 Hz, H-6'a), 3.65 (1H, d, J = 12.0, 5.5 Hz, H-6'b), 3.42~3.50 (3H, m, H-2', 3', 5'), 3.35 (1H, t, J = 9.0 Hz, H-4'); ¹³C-NMR (125 MHz, CD₃OD) δ : 163.8 (C-2), 114.8 (C-3), 145.9 (C-4), 111.0 (C-5), 148.6 (C-6), 152.0 (C-7), 105.5 (C-8), 151.0 (C-9), 139.5 (C-10), 102.3 (C-1'), 75.0 (C-2'), 78.1 (C-3'), 71.5 (C-4'), 78.7

(C-5'), 62.7 (C-6'), 57.4 (6-OCH₃)。以上数据与文献报道基本一致^[10], 故鉴定化合物 **1** 为菝葜苷。

化合物 **2**: 无色粉末。ESI-MS m/z : 355 [M+Na]⁺。¹H-NMR (500 MHz, CD₃OD) δ : 6.07 (2H, s, H-3, 5), 4.61 (1H, d, J = 7.0 Hz, H-1'), 3.73 (6H, s, 2, 6-OCH₃); ¹³C-NMR (125 MHz, CD₃OD) δ : 129.9 (C-1), 155.1 (C-2), 94.8 (C-3), 156.3 (C-4), 94.8 (C-5), 155.1 (C-6), 106.5 (C-1'), 76.0 (C-2'), 78.1 (C-3'), 71.6 (C-4'), 78.6 (C-5'), 62.9 (C-6'), 57.1 (2, 6-OCH₃)。以上数据与文献报道基本一致^[11], 故鉴定化合物 **2** 为 2, 6-二甲氧基-4-羟基-苯酚-1- β -D-吡喃葡萄糖苷。

化合物 **3**: 无色粉末。ESI-MS m/z : 325 [M+Na]⁺。¹H-NMR (500 MHz, CD₃OD) δ : 6.74 (1H, d, J = 2.0 Hz, H-2), 6.63 (1H, d, J = 9.0 Hz, H-5), 6.53 (1H, dd, J = 9.0, 2.0 Hz, H-6), 4.68 (1H, d, J = 7.0 Hz, H-1'), 3.84 (1H, brd, J = 12.0 Hz, H-6'a), 3.62 (1H, dd, J = 12.0, 6.0 Hz, H-6'b), 3.77 (3H, s, 3-OCH₃); ¹³C-NMR (125 MHz, CD₃OD) δ : 152.8 (C-1), 103.7 (C-2), 149.2 (C-3), 142.9 (C-4), 115.9 (C-5), 109.9 (C-6), 103.7 (C-1'), 75.0 (C-2'), 78.2 (C-3'), 71.5 (C-4'), 78.0 (C-5'), 62.6 (C-6'), 56.3 (3-OCH₃)。以上数据与文献报道基本一致^[12], 故鉴定化合物 **3** 为 3-甲氧基-4-羟基-苯酚-1- β -D-吡喃葡萄糖苷。

化合物 **4**: 无色粉末。ESI-MS m/z : 325 [M+Na]⁺。¹H-NMR (500 MHz, CD₃OD) δ : 6.96 (1H, d, J = 9.0 Hz, H-6), 6.41 (1H, d, J = 2.5 Hz, H-3), 6.24 (1H, dd, J = 9.0, 2.5 Hz, H-5), 4.60 (1H, d, J = 7.5 Hz, H-1'), 3.75 (3H, s, 2-OCH₃); ¹³C-NMR (125 MHz, CD₃OD) δ : 141.3 (C-1), 152.3 (C-2), 104.6 (C-3), 155.3 (C-4), 107.9 (C-5), 120.8 (C-6), 102.1 (C-1'), 75.4 (C-2'), 78.1 (C-3'), 71.7 (C-4'), 78.4 (C-5'), 62.9 (C-6'), 56.8 (2-OCH₃)。以上数据与文献报道基本一致^[13], 故鉴定化合物 **4** 为 4-羟基-2-甲氧基-苯酚-1- β -D-吡喃葡萄糖苷。

化合物 **5**: 无色粉末。ESI-MS m/z : 309 [M+Na]⁺。¹H-NMR (500 MHz, CD₃OD) δ : 6.99 (2H, d, J = 9.0 Hz, H-2, 6), 6.77 (2H, d, J = 9.0 Hz, H-3, 5), 4.71 (1H, d, J = 7.5 Hz, H-1'), 3.82 (1H, brd, J = 12.0 Hz, H-6'a), 3.64 (1H, dd, J = 12.0, 5.0 Hz, H-6'b), 3.69 (3H, s, 4-OCH₃); ¹³C-NMR (125 MHz, CD₃OD) δ : 153.2 (C-1), 119.2 (C-2, 6), 115.4 (C-3, 5), 156.6 (C-4), 103.5 (C-1'), 75.0 (C-2'), 78.1 (C-3'), 71.4

(C-4'), 78.0 (C-5'), 62.6 (C-6'), 56.0 (4-OCH₃)。以上数据与文献报道基本一致^[14], 故鉴定化合物 **5** 为甲基熊果苷。

化合物 **6**: 无色粉末, mp 178~179 °C。ESI-MS m/z : 605 [M+Na]⁺。[α]_D²⁰ +9.5 (c 0.04, MeOH)。¹H-NMR (500 MHz, CD₃OD) δ : 6.52 (1H, s, H-8), 6.37 (2H, s, H-2', 6'), 4.36 (1H, d, J = 6.0 Hz, H-4), 4.22 (1H, d, J = 7.5 Hz, H-1''), 3.84 (1H, dd, J = 10.0, 6.0 Hz, H-3 α), 3.81 (1H, brd, J = 11.0 Hz, H-6''a), 3.80 (3H, s, 7-OCH₃), 3.69 (6H, s, 3', 5'-OCH₃), 3.59 (2H, dd, J = 11.0, 5.0 Hz, H-6''b, 2 α), 3.48 (1H, dd, J = 11.0, 7.0 Hz, H-2 α), 3.39 (1H, dd, J = 9.5, 3.5 Hz, H-3 α), 3.28 (3H, s, 5-OCH₃), 2.66 (1H, dd, J = 15.0, 4.0 Hz, H-1a), 2.56 (1H, dd, J = 15.0, 12.0 Hz, H-1b), 2.02 (1H, m, H-3), 1.65 (1H, m, H-2); ¹³C-NMR (125 MHz, CD₃OD) δ : 34.2 (C-1), 40.9 (C-2), 47.1 (C-3), 43.1 (C-4), 147.9 (C-5), 139.7 (C-6), 148.9 (C-7), 108.1 (C-8), 130.5 (C-9), 126.7 (C-10), 134.7 (C-1'), 107.2 (C-2', 6'), 149.3 (C-3', 5'), 139.7 (C-4'), 66.5 (C-2 α), 71.7 (C-3 α), 60.4 (5-OCH₃), 57.1 (3', 5'-OCH₃), 56.9 (7-OCH₃), 105.1 (C-1''), 75.5 (C-2''), 78.5 (C-3''), 72.0 (C-4''), 78.3 (C-5''), 63.1 (C-6'')。以上数据与文献报道基本一致^[15], 故鉴定化合物 **6** 为 (+)-南烛木树脂酚-3 α -O- β -D-吡喃葡萄糖苷。

化合物 **7**: 无色粉末。ESI-MS m/z : 605 [M+Na]⁺。[α]_D²⁰ -46.4 (c 0.07, MeOH)。¹H-NMR (500 MHz, CD₃OD) δ : 6.52 (1H, s, H-8), 6.35 (2H, s, H-2', H-6'), 4.16 (1H, d, J = 6.5 Hz, H-4), 4.07 (1H, d, J = 8.0 Hz, H-1''), 3.80 (1H, overlapped, H-3 α), 3.79 (3H, s, 7-OCH₃), 3.78 (1H, brd, J = 12.0 Hz, H-6''a), 3.69 (6H, s, 3', 5'-OCH₃), 3.62 (1H, dd, J = 12.0, 5.5 Hz, H-6''b), 3.52~3.56 (3H, m, H-2 α , 3 α), 3.26 (3H, s, 5-OCH₃), 2.61 (2H, m, H-1), 2.07 (1H, m, H-3), 1.62 (1H, m, H-2); ¹³C-NMR (125 MHz, CD₃OD) δ : 34.1 (C-1), 41.5 (C-2), 46.9 (C-3), 43.5 (C-4), 147.8 (C-5), 139.8 (C-6), 149.0 (C-7), 108.0 (C-8), 130.5 (C-9), 126.5 (C-10), 134.9 (C-1'), 107.3 (C-2', 6'), 149.3 (C-3', 5'), 139.2 (C-4'), 66.5 (C-2 α), 71.8 (C-3 α), 60.4 (5-OCH₃), 57.2 (3', 5'-OCH₃), 56.9 (7-OCH₃), 104.6 (C-1''), 75.4 (C-2''), 78.5 (C-3''), 72.2 (C-4''), 78.3 (C-5''), 63.0 (C-6'')。以上数据与文献报道基本一致^[15], 故鉴定化合物 **7** 为 (-)-南烛木树脂酚-3 α -O- β -D-吡喃葡萄糖苷。

化合物 **8**: 无色粉末。ESI-MS m/z : 605 $[M+Na]^+$ 。 $[\alpha]_D^{20}$ -56.7 (c 0.03, MeOH)。 1H -NMR (500 MHz, CD_3OD) δ : 6.52 (1H, s, H-8), 6.33 (2H, s, H-2', H-6'), 4.24 (1H, brd, J = 6.0 Hz, H-4), 4.20 (1H, d, J = 8.0 Hz, H-1''), 3.88 (1H, dd, J = 10.0, 6.0 Hz, H-2 α), 3.80 (3H, s, 7-OCH₃), 3.78 (1H, brd, J = 12.0 Hz, H-6''a), 3.68 (6H, s, 3', 5'-OCH₃), 3.60 (1H, dd, J = 12.0, 5.0 Hz, H-6''b), 3.52 (1H, m, H-2 α), 3.48 (2H, m, H-3 α), 3.26 (3H, s, 5-OCH₃), 3.20~3.29 (3H, m, H-3'', 4'', 5''), 3.11 (1H, t, J = 8.0 Hz, H-2''), 2.73 (1H, brd, J = 14.0 Hz, H-1a), 2.52 (1H, dd, J = 12.0, 14.0 Hz, H-1b), 1.83 (1H, m, H-3), 1.78 (1H, m, H-2); ^{13}C -NMR (125 MHz, CD_3OD) δ : 34.4 (C-1), 38.5 (C-2), 50.4 (C-3), 43.1 (C-4), 148.0 (C-5), 139.9 (C-6), 148.9 (C-7), 108.0 (C-8), 130.3 (C-9), 126.8 (C-10), 134.8 (C-1'), 107.2 (C-2', 6'), 149.3 (C-3', 5'), 139.2 (C-4'), 75.2 (C-3 α), 63.5 (C-2 α), 104.9 (C-1''), 60.2 (5-OCH₃), 56.8 (7-OCH₃), 57.1 (3', 5'-OCH₃), 75.4 (C-2''), 78.4 (C-3''), 72.0 (C-4''), 78.3 (C-5''), 63.1 (C-6'')。以上数据与文献报道基本一致^[15], 故鉴定化合物 **8** 为 (-)-南烛木树脂酚-2 α -O- β -D-吡喃葡萄糖苷。

化合物 **9**: 淡黄色粉末。ESI-MS m/z : 545 $[M+Na]^+$ 。 $[\alpha]_D^{20}$ -37.1 (c 0.03, MeOH)。 1H -NMR (500 MHz, CD_3OD) δ : 6.70 (1H, d, J = 8.0 Hz, H-5'), 6.69 (1H, s, H-8), 6.63 (1H, brs, H-2'), 6.58 (1H, brd, J = 8.0 Hz, H-6'), 6.36 (1H, s, H-5), 4.56 (1H, d, J = 7.0 Hz, H-1''), 3.77 (3H, s, 7-OCH₃), 3.74 (3H, s, 3'-OCH₃), 2.91 (1H, brd, J = 9.5 Hz, H-4), 2.77 (2H, brd, J = 8.0 Hz, H-1), 1.97 (1H, m, H-3), 1.75 (1H, m, H-2); ^{13}C -NMR (125 MHz, CD_3OD) δ : 33.9 (C-1), 40.1 (C-2), 48.4 (C-3), 47.8 (C-4), 118.8 (C-5), 148.8 (C-6), 149.4 (C-7), 116.4 (C-8), 134.7 (C-9), 138.4 (C-10), 132.3 (C-1'), 113.5 (C-2'), 146.4 (C-3'), 146.1 (C-4'), 114.0 (C-5'), 123.6 (C-6'), 66.0 (C-2 α), 61.6 (C-3 α), 57.0 (3'-OCH₃), 56.7 (7-OCH₃), 102.5 (C-1''), 74.8 (C-2''), 77.9 (C-3''), 70.6 (C-4''), 78.1 (C-5''), 62.3 (C-6'')。以上数据与文献报道基本一致^[16], 故鉴定化合物 **9** 为 (-)-异落叶松树脂醇-6-O- β -D-吡喃葡萄糖苷。

化合物 **10**: 无色粉末。 $[\alpha]_D^{20}$ -67.8 (c 0.03, MeOH)。ESI-MS m/z : 607 $[M+Na]^+$ 。 1H -NMR (500 MHz, CD_3OD) δ : 6.28 (2H, s, H-5, 9), 6.25 (2H, s,

H-5', 9'), 4.19 (1H, d, J = 8.0 Hz, H-1''), 4.05 (1H, dd, J = 10.0, 6.0 Hz, H-1a), 3.80 (1H, dd, J = 12.0, 2.0 Hz, H-6''a), 3.69 (12H, s, 6, 8, 6', 8'-OCH₃), 3.65 (1H, dd, J = 11.0, 7.0 Hz, H-1'a), 3.62 (1H, dd, J = 12.0, 5.0 Hz, H-6''b), 3.50 (1H, dd, J = 11.0, 7.0 Hz, H-1'b), 3.40 (1H, dd, J = 10.0, 7.0 Hz, H-1b), 2.68 (1H, dd, J = 14.0, 6.5 Hz, H-3a), 2.60 (1H, dd, J = 14.0, 6.5 Hz, H-3'a), 2.52 (1H, dd, J = 14.0, 9.0 Hz, H-3'b), 2.49 (1H, dd, J = 14.0, 9.0 Hz, H-3b), 1.86 (1H, m, H-2'), 2.02 (1H, m, H-2); ^{13}C -NMR (125 MHz, CD_3OD) δ : 71.4 (C-1), 41.6 (C-2), 37.0 (C-3), 134.6 (C-4, 4'), 107.6 (C-5, 9), 149.2 (C-6, 8), 133.4 (C-7), 63.0 (C-1'), 44.1 (C-2'), 36.6 (C-3'), 107.5 (C-5', 9'), 147.9 (C-6', 8'), 133.6 (C-7'), 56.9 (6, 8-OCH₃), 56.9 (6', 8'-OCH₃), 105.1 (C-1''), 75.6 (C-2''), 78.6 (C-3''), 72.1 (C-4''), 78.3 (C-5''), 63.2 (C-6'')。以上数据与文献报道基本一致^[17], 故鉴定化合物 **10** 为 (-)-8, 8'-二甲氧基-1-O-(β -D-吡喃葡萄糖基)开环异落叶松树脂酚。

化合物 **11**: 无色粉末。 $[\alpha]_D^{20}$ +179.9 (c 0.10, MeOH)。ESI-MS m/z : 393 $[M+Na]^+$ 。 1H -NMR (500 MHz, CD_3OD) δ : 5.89 (1H, s, H-2), 5.43 (1H, dd, J = 15.0, 6.0 Hz, H-8), 5.66 (1H, dd, J = 15.0, 9.0 Hz, H-7), 4.36 (1H, d, J = 8.0 Hz, H-1'), 4.41 (1H, t, J = 6.0 Hz, H-9), 3.83 (1H, brd, J = 10.5 Hz, H-6'a), 3.67 (1H, dd, J = 12.0, 6.0 Hz, H-6'b), 2.69 (1H, d, J = 9.0 Hz, H-6), 2.44 (1H, d, J = 16.5 Hz, H-4a), 2.06 (1H, d, J = 16.5 Hz, H-4b), 1.95 (3H, s, H-13), 1.30 (3H, d, J = 6.0 Hz, H-10), 1.04 (3H, s, H-11), 1.02 (3H, s, H-12); ^{13}C -NMR (125 MHz, CD_3OD) δ : 166.2 (C-1), 138.5 (C-2), 202.3 (C-3), 48.6 (C-4), 37.4 (C-5), 57.1 (C-6), 126.4 (C-7), 129.1 (C-8), 77.3 (C-9), 21.3 (C-10), 27.9 (C-11), 28.3 (C-12), 24.1 (C-13), 102.7 (C-1'), 75.6 (C-2'), 78.4 (C-3'), 71.8 (C-4'), 78.3 (C-5'), 63.0 (C-6')。以上数据与文献报道基本一致^[18], 故鉴定化合物 **11** 为 (+)-3-oxo- α -ionyl-O- β -D-glucopyranoside。

化合物 **12**: 无色粉末。ESI-MS m/z : 409 $[M+Na]^+$ 。 1H -NMR (500 MHz, CD_3OD) δ : 5.81 (1H, d, J = 16.0 Hz, H-7), 5.80 (1H, m, H-8), 5.80 (1H, s, H-2), 4.36 (1H, m, H-9), 4.28 (1H, d, J = 8.0 Hz, H-1'), 3.79 (1H, dd, J = 12.0 Hz, H-6'a), 3.56 (1H, dd, J = 12.0, 5.0 Hz, H-6'b), 2.46 (1H, d, J = 17.0 Hz, H-4a), 2.09 (1H, d, J = 17.0 Hz, H-4b), 1.86 (3H, s, H-13), 1.26

(3H, d, $J = 6.5$ Hz, H-10), 0.98 (6H, s, H-11, 12); ^{13}C -NMR (125 MHz, CD_3OD) δ : 167.6 (C-1), 127.5 (C-2), 201.5 (C-3), 51.0 (C-4), 42.7 (C-5), 80.3 (C-6), 131.8 (C-7), 135.6 (C-8), 77.6 (C-9), 21.5 (C-10), 25.0 (C-11), 23.7 (C-12), 19.8 (C-13), 103.0 (C-1'), 71.9 (C-2'), 78.3 (C-3'), 75.5 (C-4'), 78.4 (C-5'), 63.1 (C-6')。以上数据与文献报道基本一致^[7,18], 故鉴定该化合物为 roseoside。

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