

瓦山安息香树皮的化学成分研究

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摘要: 目的 研究瓦山安息香 *Styrax perkinsiae* 树皮的化学成分。方法 采用硅胶柱色谱、大孔吸附树脂等方法进行分离纯化, 根据波谱数据并参考文献鉴定其化学成分。结果 从瓦山安息香树皮正丁醇部位分离得到 10 个木脂素类化合物, 分别鉴定为 obassioside B (1)、落叶松脂醇-4-*O*- β -*D*-葡萄糖苷 (2)、(-)-开环异落叶松脂素-4-*O*- β -*D*-吡喃葡萄糖苷 (3)、落叶松脂醇-4'-*O*- β -*D*-葡萄糖苷 (4)、lanicepside A (5)、异落叶松脂素-4-*O*- β -*D*-吡喃葡萄糖苷 (6)、(+)-落叶松醇-9- β -*D*-吡喃葡萄糖苷 (7)、isotachioside (8)、 $2R^*, 3S^*$ -dihydrodehydrodiconiferyl alcohol 4'-*O*- β -*D*-glucopyranoside (9)、松脂醇 (10)。结论 化合物 2~9 为首次从安息香属植物中分离的得到。

关键词: 安息香属; 瓦山安息香; 落叶松脂醇-4-*O*- β -*D*-葡萄糖苷; (-)-开环异落叶松脂素-4-*O*- β -*D*-吡喃葡萄糖苷; 松脂醇

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Chemical constituents from stem bark of *Styrax perkinsiae*

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Abstract: Objective To study the chemical constituents from the stem bark of *S. perkinsiae*. **Methods** The chemical constituents were separated and purified by chromatographic methods after solvent extraction and were identified by spectroscopic analyses. **Results** Ten lignans were isolated from the stem bark of *S. perkinsiae* and identified as following: obassioside B (1), lariciresinol 4-*O*- β -*D*-glucoside (2), (-)-secoisolariciresinol 4-*O*- β -*D*-glucopyranoside (3), lariciresinol 4'-*O*- β -*D*-glucoside (4), lanicepside A (5), isolariciresinol 4-*O*- β -*D*-glucopyranoside (6), (+)-lariciresinol 9-*O*- β -*D*-glucopyranoside (7), isotachioside (8), $2R^*, 3S^*$ -dihydrodehydrodiconiferyl alcohol 4'-*O*- β -*D*-glucopyranoside (9), and pinoresinol (10). **Conclusion** Eight compounds (2—9) are isolated from the plants of *Styrax* Linn. for the first time.

Key words: *Styrax* Linn.; *Styrax perkinsiae* Rhed.; lariciresinol 4-*O*- β -*D*-glucoside; (-)-secoisolariciresinol 4-*O*- β -*D*-glucopyranoside; pinoresinol

安息香属 *Styrax* Linn. 是安息香科 (Styracaceae) 的模式属, 又名野茉莉属, 乔木或灌木, 中国约有 30 种, 7 变种, 除少数种类分布至东北或西北地区外, 其余主产于长江流域以南各省区^[1]。该属植物的树脂含较多的香脂酸, 称“安息香”, 有开窍清神行气、活血、止痛的作用, 是医药上的贵重药材。目前已从安息香属植物中分离出多种类型的化学成分, 包含有木脂素、萜类和甾体等, 药理活性研究主要集中在抗基质金属蛋白酶-1、细胞毒、抗溃疡、抗氧化、抗补体、抗菌和抗真菌等活性^[2]。瓦山安息香 *Styrax perkinsiae* Rhed. 产自云南、四川^[1], 已

从瓦山安息香种子的乙醇提取物分离得到 12 个 2-芳基苯并呋喃类新木脂素, 发现这类化合物有促雌激素生成活性^[3]。为了发现具有促雌激素生成活性的化合物, 本实验对瓦山安息香树皮的化学成分进行了研究, 共获得了 10 个木脂素类成分, 分别为 obassioside B (1)、落叶松脂醇-4-*O*- β -*D*-葡萄糖苷 (lariciresinol 4-*O*- β -*D*-glucoside, 2)、(-)-开环异落叶松脂素-4-*O*- β -*D*-吡喃葡萄糖苷 [(-)-secoisolariciresinol 4-*O*- β -*D*-glucopyranoside, 3]、落叶松脂醇-4'-*O*- β -*D*-葡萄糖苷 (lariciresinol 4'-*O*- β -*D*-glucoside, 4)、lanicepside A (5), 异落叶松脂素-4-*O*- β -*D*-吡喃葡

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葡萄糖苷 (isolariciresinol 4-*O*- β -*D*-glucopyranoside, **6**)、(+)-落叶松醇-9- β -*D*-吡喃葡萄糖苷 [(+)-lariciresinol 9-*O*- β -*D*-glucopyranoside, **7**]、isotachioside (**8**)、2*R*^{*},3*S*^{*}-dihydrodehydrodiconiferyl alcohol 4-*O*- β -*D*-glucopyranoside (**9**)、松脂醇 (pinoresinol, **10**)。化合物**2**~**9**为首次从安息香属植物中分离得到。

1 仪器与材料

Bruker Avance 600 核磁共振仪, Bruker Daltonics BioTOF-Q 质谱仪, 柱色谱硅胶 (硅胶 G, 200~300 目) 和薄层色谱硅胶 GF₂₅₄ 购于青岛海洋化工厂, HPLC 为 Perkin Elmer 600 液相色谱 (Kromasil100-10-C₁₈, 250 mm×10 mm, 10 μ m)。所有溶剂均为分析纯。

实验用材料于2008年8月采自云南省永德县大雪山自然保护区, 由中国科学院成都生物研究所高信芬研究员鉴定为瓦山安息香 *Styrax perkinsiae* Rhed., 植物标本 (A-158) 保存在成都生物研究所天然产物研究中心。

2 提取与分离

瓦山安息香树皮 4.5 kg 粉碎后, 用 95%乙醇室温浸泡 4 次, 每次 5 d。减压回收乙醇, 得浸膏 803 g, 分散于水中, 依次用以石油醚、氯仿、醋酸乙酯、正丁醇萃取。减压回收溶剂得石油醚部分 62 g、氯仿部分 97 g、醋酸乙酯部分 60 g、正丁醇部分 493 g。正丁醇部分过 D101 大孔吸附树脂, 依次用水及 40%、70%、95%乙醇洗脱, 各部分质量分别为 243、111、115、4.2 g。水洗脱部分经硅胶柱色谱, 采用氯仿-甲醇梯度洗脱, 分成 3 部分 Fr. 1 (50 g)、Fr. 2 (30 g)、Fr. 3 (140 g)。Fr. 2 经反相柱色谱, 甲醇-水梯度洗脱, 分成 5 部分: Fr. 2-1 (2.2 g)、Fr. 2-2 (3.4 g)、Fr. 2-3 (10.8 g)、Fr. 2-4 (7.5 g)、Fr. 2-5 (3.0 g)。每部分各取 1 g 进行半制备色谱分离, 检测波长 254 nm, 体积流量 3 mL/min, 乙腈-水洗脱, 从 Fr. 2-1 中分得化合物 **1** (6 mg)、**2** (20 mg)、**3** (8 mg)、**4** (10 mg), 从 Fr. 2-2 中分得化合物 **5** (3 mg)、**6** (20 mg), 从 Fr. 2-3 中分得化合物 **7** (9 mg)、**8** (6 mg)、**9** (15 mg), 从 Fr. 2-5 中分得化合物 **10** (30 mg)。

3 结构鉴定

化合物 **1**: 白色无定形粉末。¹H-NMR (600 MHz, CD₃OD) δ : 7.41 (1H, d, J = 8.1 Hz, H-6'), 7.34 (1H, d, J = 1.4 Hz, H-2'), 7.17 (1H, s, H-4), 6.98 (1H, s, H-3), 6.92 (1H, s, H-6), 6.90 (1H, d, J = 8.1 Hz, H-5'), 6.00

(2H, s, -OCH₂O-), 4.25 (1H, d, J = 7.8 Hz, H-1'''), 4.03 (3H, s, 7-OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ : 156.1 (C-2), 148.3 (C-3'), 148.2 (C-4'), 144.9 (C-7), 143.1 (C-8), 140.9 (C-5), 130.8 (C-9), 124.7 (C-1'), 118.7 (C-6'), 110.1 (C-4), 108.2 (C-5'), 104.7 (C-6), 103.1 (C-2'), 101.2 (-OCH₂O-), 100.3 (C-1'''), 76.8 (C-5'''), 76.5 (C-3'''), 73.8 (C-2'''), 71.0 (C-1''), 70.3 (C-4'''), 66.5 (C-3''), 61.4 (C-6'''), 55.3 (7-OCH₃), 39.1 (C-2'')。以上波谱数据与文献报道一致^[4], 故鉴定化合物 **1** 为 obassioside B。

化合物 **2**: 白色无定形粉末。¹H-NMR (600 MHz, CD₃OD) δ : 7.09 (1H, d, J = 8.2 Hz, H-5), 6.90 (1H, s, H-2'), 6.89 (1H, s, H-2), 6.76 (3H, brs, H-6, 5', 6'), 4.85 (1H, d, J = 7.3 Hz, H-1''), 4.75 (1H, d, J = 6.8 Hz, H-7'), 3.84 (6H, s, 3, 3'-OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ : 149.5 (C-4), 147.6 (C-3'), 145.7 (C-4'), 145.0 (C-3), 135.8 (C-1), 134.3 (C-1'), 120.9 (C-6), 118.4 (C-6'), 116.9 (C-5), 114.7 (C-5'), 113.0 (C-2), 109.3 (C-2'), 101.7 (C-1''), 82.6 (C-7'), 76.8 (C-5''), 76.4 (C-3''), 73.6 (C-2''), 72.1 (C-9'), 70.0 (C-4''), 61.4 (C-6''), 59.1 (C-9'), 55.4 (3'-OCH₃), 55.1 (3-OCH₃), 52.6 (C-8'), 42.4 (C-8), 32.3 (C-7)。以上数据与文献报道一致^[5], 故鉴定化合物 **2** 为落叶松脂醇-4-*O*- β -*D*-葡萄糖苷。

化合物 **3**: 白色无定形粉末。¹H-NMR (600 MHz, CD₃OD) δ : 7.03 (1H, d, J = 8.1 Hz, H-5), 6.68 (1H, brs, H-2), 6.66 (1H, brs, H-5'), 6.65 (1H, brs, H-6), 6.61 (1H, brs, H-2'), 6.53 (1H, d, J = 8.1 Hz, H-6'), 3.75 (3H, s, 3-OCH₃), 3.74 (3H, s, 3'-OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ : 149.2 (C-3), 147.4 (C-3'), 144.8 (C-4), 144.1 (C-4'), 136.1 (C-1), 132.4 (C-1'), 121.5 (C-6), 121.3 (C-6'), 116.4 (C-5), 114.5 (C-5'), 112.9 (C-2), 112.1 (C-2'), 101.8 (C-1''), 76.8 (C-5''), 76.5 (C-3''), 73.6 (C-2''), 70.0 (C-4''), 61.2 (C-6''), 60.7 (C-9), 60.6 (C-9'), 55.2 (3-OCH₃), 55.0 (3'-OCH₃), 42.9 (C-8), 42.7 (C-8'), 34.7 (C-7), 34.7 (C-7')。以上数据与文献报道一致^[6], 故鉴定化合物 **3** 为 (-)-开环异落叶松脂素-4-*O*- β -*D*-吡喃葡萄糖苷。

化合物 **4**: 白色无定形粉末。¹H-NMR (600 MHz, CD₃OD) δ : 7.13 (1H, d, J = 8.3 Hz, H-5'), 6.98 (1H, d, J = 1.7 Hz, H-2'), 6.87 (1H, dd, J = 8.3, 1.7 Hz, H-6'), 6.78 (1H, d, J = 1.7 Hz, H-2), 6.71 (1H, d, J = 8.3 Hz, H-5), 6.64 (1H, dd, J = 8.3, 1.7 Hz, H-6), 4.88 (1H, d,

$J = 7.3$ Hz, H-1''), 3.85 (3H, s, 3'-OCH₃), 3.82 (3H, s, 3-OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ : 149.5 (C-3'), 147.6 (C-3), 145.9 (C-4'), 144.5 (C-4), 138.2 (C-1'), 132.1 (C-1), 120.8 (C-6), 118.2 (C-6'), 116.6 (C-5'), 114.8 (C-5), 112.1 (C-2), 110.0 (C-2'), 101.6 (C-1''), 82.4 (C-7'), 76.8 (C-5''), 76.5 (C-3''), 73.5 (C-2''), 72.3 (C-9), 70.0 (C-4''), 61.1 (C-6''), 59.1 (C-9'), 55.4 (3'-OCH₃), 55.0 (3-OCH₃), 52.7 (C-8'), 42.4 (C-8), 32.2 (C-7)。以上数据与文献报道一致^[5], 故鉴定化合物 **4** 为落叶松脂醇-4'-O- β -D-葡萄糖苷。

化合物 **5**: 白色无定形粉末。¹H-NMR (600 MHz, CD₃OD) δ : 7.15 (1H, d, $J = 8.3$ Hz, H-5'), 7.08 (1H, d, $J = 1.8$ Hz, H-2'), 6.96 (2H, brs, H-2', 6'), 6.79 (1H, dd, $J = 8.3, 1.8$ Hz, H-6'), 6.77 (1H, d, $J = 8.0$ Hz, H-5), 4.89 (1H, d, $J = 7.4$ Hz, H-1'') 3.88 (3H, s, 3'-OCH₃), 3.85 (3H, s, 3-OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ : 149.4 (C-3'), 147.8 (C-3), 146.2 (C-4'), 146.1 (C-4), 138.2 (C-1'), 132.5 (C-1), 119.4 (C-6'), 119.3 (C-6), 116.2 (C-5'), 114.7 (C-5), 110.9 (C-2'), 109.9 (C-2), 101.4 (C-1''), 84.4 (C-7), 76.8 (C-5''), 76.4 (C-3''), 75.9 (C-7'), 73.5 (C-2''), 70.0 (C-4''), 69.7 (C-9'), 61.9 (C-9), 61.1 (C-6''), 55.4 (3'-OCH₃), 55.1 (3-OCH₃), 54.4 (C-8), 51.3 (C-8')。以上数据与文献报道一致^[7], 故鉴定化合物 **5** 为 lanicepside A。

化合物 **6**: 白色无定形粉末。¹H-NMR (600 MHz, CD₃OD) δ : 6.76 (1H, d, $J = 8.0$ Hz, H-5'), 6.74 (1H, s, H-2), 6.69 (1H, d, $J = 1.8$ Hz, H-2'), 6.63 (1H, dd, $J = 8.0, 1.8$ Hz, H-6'), 6.42 (1H, s, H-6), 4.61 (1H, d, $J = 7.3$ Hz, H-1''), 3.82 (3H, s, 3'-OCH₃), 3.78 (3H, s, 3-OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ : 147.7 (C-3), 147.2 (C-4), 144.8 (C-3'), 144.4 (C-4'), 136.7 (C-1), 133.1 (C-1'), 130.7 (C-6), 121.9 (C-6'), 117.2 (C-5), 114.7 (C-2), 112.4 (C-5'), 111.9 (C-2'), 100.9 (C-1''), 76.4 (C-5''), 76.2 (C-3''), 73.2 (C-2''), 69.0 (C-4''), 64.4 (C-9), 60.7 (C-6''), 60.0 (C-9'), 55.4 (3'-OCH₃), 55.0 (3-OCH₃), 46.8 (C-8'), 46.2 (C-7'), 38.4 (C-8), 32.2 (C-7)。以上数据与文献报道一致^[8], 故鉴定化合物 **6** 为异落叶松脂素-4-O- β -D-吡喃葡萄糖苷。

化合物 **7**: 白色无定形粉末。¹H-NMR (600 MHz, CD₃OD) δ : 6.93 (1H, d, $J = 1.5$ Hz, H-2'), 6.80 (1H, dd, $J = 8.0, 1.5$ Hz, H-6), 6.79 (1H, d, $J = 1.5$ Hz, H-2), 6.75 (1H, d, $J = 8.0$ Hz, H-5), 6.71 (1H, d, $J = 8.0$ Hz, H-5'), 6.65 (1H, dd, $J = 8.0, 1.5$ Hz, H-6'),

4.29 (1H, d, $J = 7.8$ Hz, H-1''), 3.84 (3H, s, 3'-OCH₃), 3.83 (3H, s, 3-OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ : 147.6 (C-3), 147.6 (C-3'), 145.7 (C-4'), 144.4 (C-4), 134.3 (C-1'), 132.4 (C-1), 120.8 (C-6), 118.5 (C-6'), 114.8 (C-5'), 114.6 (C-5), 112.1 (C-2), 109.4 (C-2'), 103.2 (C-1''), 82.8 (C-7'), 76.9 (C-5''), 76.6 (C-3''), 73.8 (C-2''), 72.3 (C-9), 70.3 (C-4''), 67.1 (C-9'), 61.5 (C-6''), 55.1 (3, 3'-OCH₃), 50.3 (C-8'), 42.6 (C-8), 32.3 (C-7)。以上波谱数据与文献报道一致^[9], 故鉴定化合物 **7** 为 (+)-落叶松醇-9- β -D-吡喃葡萄糖苷。

化合物 **8**: 白色无定形粉末。¹H-NMR (600 MHz, CD₃OD) δ : 7.01 (1H, d, $J = 8.7$ Hz, H-6), 6.46 (1H, d, $J = 2.7$ Hz, H-3), 6.29 (1H, dd, $J = 8.7, 2.7$ Hz, H-5), 4.69 (1H, d, $J = 7.6$ Hz, H-1'), 3.80 (3H, s, 2-OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ : 153.6 (C-4), 150.7 (C-2), 139.6 (C-1), 119.2 (C-6), 106.3 (C-5), 103.0 (C-1'), 100.5 (C-3), 76.7 (C-5'), 76.5 (C-3'), 73.8 (C-2'), 70.0 (C-4'), 61.2 (C-6'), 55.2 (-OCH₃)。以上数据与文献报道一致^[10], 故鉴定化合物 **8** 为 isotachioside。

化合物 **9**: 白色无定形粉末。¹H-NMR (600 MHz, CD₃OD) δ : 7.14 (1H, d, $J = 8.4$ Hz, H-5'), 7.03 (1H, d, $J = 1.7$ Hz, H-2'), 6.93 (1H, dd, $J = 8.4, 1.7$ Hz, H-6'), 6.73 (1H, s, $J = 1.7$ Hz, H-6), 6.71 (1H, s, $J = 1.7$ Hz, H-4), 5.55 (1H, d, $J = 5.8$ Hz, H-2), 4.88 (1H, d, $J = 7.3$ Hz, H-1'''), 3.86 (3H, s, 7-OCH₃), 3.82 (3H, s, 3'-OCH₃); ¹³C-NMR (150 MHz, CD₃OD) δ : 149.9 (C-3'), 146.2 (C-4), 146.1 (C-8), 143.9 (C-7), 137.0 (C-1'), 135.7 (C-5), 128.2 (C-9), 118.0 (C-2'), 116.8 (C-5'), 116.6 (C-4'), 112.9 (C-6), 109.9 (C-2'), 101.4 (C-1'''), 87.0 (C-2), 76.8 (C-5'''), 76.5 (C-3'''), 73.5 (C-2'''), 70.0 (C-4'''), 63.7 (C-10), 61.1 (C-6'''), 60.8 (C-3''), 55.4 (7-OCH₃), 55.3 (3'-OCH₃), 54.3 (C-3), 34.4 (C-2''), 31.5 (C-1'')。以上数据与文献报道一致^[11], 故鉴定化合物 **9** 为 2R*,3S*-dihydrodehydro-diconiferyl alcohol 4'-O- β -D-glucopyranoside。

化合物 **10**: 白色无定形粉末。¹H-NMR (600 MHz, CD₃OD) δ : 6.94 (2H, d, $J = 1.6$ Hz, H-2, 2'), 6.80 (2H, dd, $J = 8.1, 1.6$ Hz, H-6, 6'), 6.76 (2H, d, $J = 8.1$ Hz, H-5, 5'), 4.70 (2H, d, $J = 3.9$ Hz, H-7, 7'), 3.82 (2H, m, H-9, 9'), 3.86 (6H, s, 3, 3'-OCH₃), 3.12 (2H, brs, H-8, 8'); ¹³C-NMR (150 MHz, CD₃OD) δ : 147.7 (C-3, 3'), 145.9 (C-4, 4'), 132.4 (C-1, 1'), 118.7 (C-6,

6'), 114.7 (C-5, 5'), 109.6 (C-2, 2'), 86.1 (C-7, 7'), 71.2 (C-9, 9'), 55.1 (-OCH₃), 54.0 (C-8, 8')。以上数据与文献报道一致^[12], 故鉴定化合物 **10** 为松脂醇。

参考文献

- [1] 中国科学院中国植物志编辑委员会. 中国植物志 [M]. 北京: 科学出版社, 1987.
- [2] 王 峰, 鄢琼芳, 华会明. 安息香属植物化学成分及药理作用研究进展 [J]. 广东药学院学报, 2009, 25(5): 541-545.
- [3] Li Q L, Li B G, Qi H Y, *et al.* Four new benzofurans from seeds of *Styrax perkinsiae* [J]. *Plant Med*, 2005, 71(9): 847-851.
- [4] Kinshita T, Haga Y, Narimatsu S. New nor-neolignan glycosides from *Styrax obassia* (Styracaceae) [J]. *Heterocycles*, 2005, 65(6): 1471-1480.
- [5] Sugiyama M, Kikuchi M. Characterization of lariciresinol glucosides from *Osmanthus asiaticus* [J]. *Heterocycles*, 1993, 36(1): 117-121.
- [6] Yuan Z, Tezuka Y, Fan W, *et al.* Constituents of the underground parts of *Glehnia littoralis* [J]. *Chem Pharm Bull*, 2002, 50(1): 73-77.
- [7] Zhou Z W, Yin S, Wang X N, *et al.* Two new lignan glycosides from *Saussurea laniceps* [J]. *Helv Chim Acta*, 2007, 90(5): 951-956.
- [8] Jiang Z H, Tanaka T, Sakamoto M, *et al.* Studies on a medicinal parasitic plant: lignans from the stems of *Cynomorium songaricum* [J]. *Chem Pharm Bull*, 2001, 49(8): 1036-1038.
- [9] Greca M D, Molinaro A, Monaco P, *et al.* Two new lignan glucosides from *Arum italicum* [J]. *Heterocycles*, 1993, 36(9): 2081-2086.
- [10] Inoshiri S, Sasaki M, Kohda H, *et al.* Aromatic glycosides from *Berchemia racemosa* [J]. *Phytochemistry*, 1987, 26(10): 2811-2814.
- [11] Matsuda N, Sato H, Yaoita Y, *et al.* Isolation and absolute structures of the neolignan glycosides with the enantiometric aglycones from the leavers of *Viburnum awabuki* K. Koch [J]. *Chem Pharm Bull*, 1996, 44(5): 1122-1131.
- [12] Liu L H, Pu J X, Zhao J F, *et al.* A new lignan from *Boschniakia himalaica* [J]. *Chin Chem Lett*, 2004, 15(1): 43-45.