

瓦山安息香树皮中四氢呋喃型木脂素类成分

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[摘要] 目的:研究瓦山安息香树皮中木脂素类成分。方法:采用反复硅胶柱色谱和葡聚糖凝胶柱色谱的色谱方法结合波谱方法分离鉴定瓦山安息香树皮的化学成分。结果:从瓦山安息香树皮提取物的醋酸乙酯萃取部位和三氯甲烷部位中分离得到 8 个四氢呋喃型木脂素类化合物,1 个苯并呋喃型木脂素和 1 个丁烷型木脂素。根据化合物的波谱数据鉴定化合物的结构为(-)-(2*R*, 3*R*)-secoisolariciresinol (1), 2*R*, 3*S*-dihydrodehydrodiconiferyl alcohol (2), 罗汉松脂醇 (3), (±)-salicifoliol (4), (-)-epipinoresinol (5), lariciresinol-4'-monomethy ether (6), (+)-pinoresinol monomethy ether (7), piperitol (8), styraxin (9), 1*R*, 2*R*, 5*S*, 6*R*-2-(4'-hydroxy-3'-methoxyphenyl)-6-(3'', 4''-dimethoxyphenyl)-3, 7-dioxabicyclo[3. 3. 0]octane 4'-O-β-D-glucopyranoside (10)。结论:6 个化合物(1, 4, 6, 7, 8, 10)首次从安息香属植物中分离的得到。

[关键词] 瓦山安息香; 四氢呋喃型木脂素; 苯并呋喃型木脂素; 丁烷型木脂素

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Tetrahydrofuranoid Lignans from Stem Bark of *Styrax perkinsiae* ZHANG Ya-mei, ZHANG Pu-zhao*
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[Abstract] **Objective:** To study the lignans components in the stem bark of *Styrax perkinsiae*. **Method:** The chemical components in the stem bark of *S. perkinsiae* were isolated and identified by repeated chromatography on silica gel column, sephadex gel filtration chromatography and spectral methods. **Result:** Eight tetrahydrofuranoid lignans, one benzofuranoid lignan, and one dibenzyl butane lignan were isolated from EtOAc fraction and CHCl₃ fraction of the stem bark of *S. perkinsiae* and identified as following: (-) - (2*R*, 3*R*) - secoisolariciresinol (1), 2*R*, 3*S*-dihydrodehydrodiconiferyl alcohol (2), matairesinol (3), (±) -salicifoliol (4), (-) -epipinoresinol (5), lariciresinol-4'-monomethy ether (6), (+) -pinoresinol monomethy ether (7), piperitol (8), styraxin (9), 1*R*, 2*R*, 5*S*, 6*R*-2-(4'-hydroxy-3'-methoxyphenyl)-6-(3'', 4''-dimethoxyphenyl)-3, 7-dioxabicyclo [3. 3. 0] octane 4'-O-β-D-glucopyranoside (10). **Conclusion:** Six compounds (1, 4, 6, 7, 8, 10) were isolated from the plants of *Styrax* for the first time.

[Key words] *Styrax perkinsiae*; tetrahydrofuranoid lignan; benzofuranoid lignan; dibenzyl butane lignan

安息香属又名野茉莉属,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]。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]。目前从瓦山安息香种

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]。本实验对瓦山安息香树皮的化学成分进行了研究,从瓦山安息香树皮的提取物的乙酸乙酯萃取部位和三氯甲烷部位中分离得到 8 个四氢呋喃型木脂素类化合物、1 个苯并呋喃型木脂素和 1 个丁烷型木脂素,其中 6 个化合物首次从安息香属植物中

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分离的得到。

1 材料

¹H-NMR, ¹³C-NMR 均采用 Avance 600 型核磁共振仪(Bruker)测定,化学位移值(δ)用 ppm 表示,以四甲基硅烷(TMS)作为内标。质谱用 Daltonics BioTOF-Q 型质谱仪(Bruker)测定。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, Elmer 600 型制备液相(Perkin)。所有溶剂均为分析纯级别,其中,石油醚沸点为 60~90 °C。

实验用瓦山安息香(*Styrax perkinsiae*)样品于 2008 年 8 月采自云南省永德县大雪山自然保护区,植物标本(A-158)由中国科学院成都生物研究所高信芬研究员鉴定,并保存在本实验室。

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,每次时间为 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、三氯甲烷、乙酸乙酯、正丁醇萃取。减压回收溶剂得石油醚部分 62 g,三氯甲烷部分 97 g,乙酸乙酯部分 60 g,正丁醇部分 493 g。乙酸乙酯部分和三氯甲烷部分经反复硅胶、凝胶、反相柱色谱等方法分离、纯化,得到化合物 **1**(24 mg), **2**(10 mg), **3**(50 mg), **4**(5 mg), **5**(8 mg), **6**(14 mg), **7**(16 mg), **8**(12 mg), **9**(6 mg), **10**(12 mg)。

3 结构鉴定

化合物 **1** 白色无定形粉末,ESI-MS m/z 385.2 $[M + Na]^+$, 361.2 $[M - H]^-$ 。¹H-NMR (600 MHz, MeOH-*d*₄) δ : 6.66 (d, $J = 8.0$ Hz, 2H, H-5, H-5'), 6.59 (d, $J = 1.5$ Hz, 2H, H-2, H-2'), 6.55 (dd, $J = 7.9, 1.5$ Hz, 2H, H-6, H-6'), 3.74 (s, 6H, 2 \times OCH₃), 3.59 (m, 4H, H-9, 9'), 2.66 (dd, $J = 13.7, 6.0$ Hz, 2H, H_a-7, 7'), 2.56 (dd, $J = 13.7, 7.0$ Hz, 2H, H_b-7, 7'), 1.91 (m, 2H, H-8, 8'); ¹³C-NMR (150 MHz, MeOH-*d*₄) δ : 147.4 (C-3, 3'), 144.1 (C-4, 4'), 132.5 (C-1, 1'), 121.3 (C-6, 6'), 114.4 (C-5, 5'), 112.0 (C-2, 2'), 60.7 (C-9, 9'), 54.8 (2 \times OCH₃), 42.8 (C-8, 8'), 34.7 (C-7', 7'')。以上波谱数据与文献[4]报道的(-)-(2*R*, 3*R*)-secoisolariciresinol 一致,故鉴定化合物 **1** 为(-)-(2*R*, 3*R*)-secoisolariciresinol。

化合物 **2** 白色无定形粉末,ESI-MS m/z 383.5 $[M + Na]^+$, 359.2 $[M - H]^-$ 。¹H-NMR (600 MHz, MeOH-*d*₄) δ : 6.95 (d, $J = 1.7$ Hz, 1H, H-2'), 6.82

(dd, $J = 8.1, 1.7$ Hz, 1H, H-6'), 6.76 (d, $J = 8.1$ Hz, 1H, H-5'), 6.72 (s, 2H, H-4, 6), 5.49 (d, $J = 6.2$ Hz, 1H, H-2), 3.84 (s, 3H, OCH₃), 3.81 (s, 3H, OCH₃), 3.84 (m, 1H, H_a-11), 3.75 (m, H_b-11), 3.57 (t, $J = 6.5$ Hz, 2H, H-10), 3.47 (dd, $J = 11.0, 6.2$ Hz, 1H, H-3), 2.67~2.57 (m, 2H, H-8), 1.87~1.76 (m, 2H, H-9); ¹³C-NMR (150 MHz, MeOH-*d*₄) δ : 147.7 (C-3', C-4'), 146.1 (C-7a), 143.8 (C-7), 135.5 (C-1'), 133.4 (C-5), 128.5 (C-3a), 118.4 (C-6'), 116.6 (C-4), 114.8 (C-5'), 112.8 (C-6), 109.2 (C-2'), 87.6 (C-2), 63.6 (C-10), 60.9 (C-11), 55.4 (OCH₃), 55.0 (OCH₃), 54.0 (C-3), 34.4 (C-8), 31.5 (C-9)。以上波谱数据与文献[5]报道的 2*R*, 3*S*-dihydrodehydrodiconiferyl alcohol 一致,故鉴定化合物 **2** 为 2*R*, 3*S*-dihydrodehydrodiconiferyl alcohol。

化合物 **3** 白色无定形粉末,ESI-MS m/z 383.2 $[M + Na]^+$, 359.0 $[M - H]^-$ 。¹H-NMR (600 MHz, MeOH-*d*₄) δ : 6.70 (d, $J = 8.0$ Hz, 1H, H-5), 6.68 (d, $J = 8.0$ Hz, 1H, H-5'), 6.67 (d, $J = 1.7$ Hz, 1H, H-2), 6.58 (dd, $J = 8.0, 1.7$ Hz, 1H, H-6), 6.56 (d, $J = 1.7$ Hz, 1H, H-2'), 6.51 (dd, $J = 8.0, 1.7$ Hz, 1H, H-6'), 4.18~4.14 (m, 1H, H-9'), 3.96~3.89 (m, 2H, H-9'), 3.79 (s, 3H, 3'-OCH₃), 3.78 (s, 3H, 3-OCH₃), 2.88 (m, 2H, H-7), 2.66 (m, 1H, H-7'), 2.53 (m, 1H, H-8), 2.49 (m, 1H, H-8'); ¹³C-NMR (150 MHz, MeOH-*d*₄) δ : 180.3 (C-9), 147.7 (C-3, 3'), 145.0 (C-4), 144.8 (C-4'), 130.1 (C-1'), 129.4 (C-1), 121.7 (C-6), 120.9 (C-6'), 114.8 (C-5'), 114.7 (C-5), 112.6 (C-2), 111.9 (C-2'), 71.5 (C-9'), 55.0 (3-OCH₃), 54.9 (3'-OCH₃), 46.4 (C-8), 41.1 (C-8'), 37.5 (C-7'), 34.0 (C-7)。以上波谱数据与文献[6]报道的 matairesionol 一致,故鉴定化合物 **3** 为 matairesionol。

化合物 **4** 白色无定形粉末,ESI-MS m/z 349.1 $[M - H]^-$ 。¹H-NMR (600 MHz, MeOH-*d*₄) δ : 6.95 (d, $J = 1.5$ Hz, 1H, H-2), 6.83~6.74 (m, 2H, H-5, 6), 4.64 (d, $J = 6.5$ Hz, 1H, H-7), 4.51 (dd, $J = 9.6, 6.9$ Hz, 1H, H-9ax), 4.33 (m, 1H, H-9eq), 4.32~4.23 (m, 1H, H-9'eq), 4.11~4.04 (m, 1H, H-9'ax), 3.85 (s, 3H, OMe), 3.52 (td, $J = 8.8, 3.3$ Hz, 1H, H-8'), 3.23~3.11 (m,

1H, H-8); ¹³C-NMR (150 MHz, MeOH-*d*₄) δ: 179.7 (C-7'), 147.8 (C-3), 146.3 (C-4), 130.9 (C-1), 118.8 (C-6), 114.8 (C-5), 109.7 (C-2), 86.4 (C-7), 70.5 (C-9), 69.5 (C-9'), 55.1 (OMe), 48.1 (C-8), 46.2 (C-8')。以上波谱数据与文献[7]报道的(±)-salicifoliol一致,故鉴定化合物4为(±)-salicifoliol。

化合物5 白色无定形粉末,ESI-MS *m/z* 381.2 [M + Na]⁺, 357.2 [M - H]⁻。¹H-NMR (600 MHz, DMSO-*d*₆) δ: 6.97 (d, *J* = 1.6 Hz, 1H, H-2), 6.94 (d, *J* = 1.6 Hz, 1H, H-2'), 6.85 ~ 6.71 (m, 4H, H-5, 6, 5', 6'), 4.42 (d, *J* = 6.9 Hz, 1H, H-7), 4.10 (d, *J* = 9.3 Hz, 1H, H-7'), 3.86 (s, 3H, OCH₃), 3.85 (s, 3H, OCH₃), 3.78 (t, *J* = 8.7 Hz, 1H, H-9a), 3.47 ~ 3.34 (m, 1H, H-9'a), 2.94 (dd, *J* = 15.4, 6.9 Hz, 1H, H-8')。¹³C-NMR (150 MHz, DMSO-*d*₆) δ: 147.8 (C-3), 147.5 (C-3'), 146.0 (C-4), 145.3 (C-4'), 132.5 (C-1), 130.0 (C-1'), 118.8 (C-6), 118.0 (C-6'), 114.7 (C-5), 114.6 (C-5'), 109.6 (C-2), 109.2 (C-2'), 88.1 (C-7), 82.2 (C-7'), 70.6 (C-9), 69.2 (C-9'), 55.0 (OCH₃), 54.2 (C-8), 49.9 (C-8')。以上波谱数据与文献[8]报道的(-)-epipinoresinol一致,故鉴定化合物5为(-)-epipinoresinol。

化合物6 白色无定形粉末,ESI-MS *m/z* 387.2 [M + Na]⁺, 373.1 [M - H]⁻。¹H-NMR (600 MHz, MeOH-*d*₄) δ: 6.94 (d, *J* = 1.7 Hz, 1H, H-2), 6.91 (d, *J* = 8.3 Hz, 1H, H-5), 6.87 (dd, *J* = 8.3, 1.7 Hz, 1H, H-6), 6.79 (d, *J* = 1.7 Hz, 1H, H-2'), 6.71 (d, *J* = 8.0 Hz, 1H, H-5'), 6.64 (dd, *J* = 8.3, 1.7 Hz, 1H, H-6'), 3.83 (s, 3H, OCH₃), 3.82 (s, 3H, OCH₃), 3.81 (s, 3H, OCH₃); ¹³C-NMR (150 MHz, MeOH-*d*₄) δ: 149.1 (C-3), 148.5 (C-3'), 147.6 (C-4), 144.5 (C-4'), 135.9 (C-1), 132.1 (C-1'), 120.8 (C-6), 118.2 (C-6'), 114.8 (C-5), 112.1 (C-5'), 111.5 (C-2), 109.6 (C-2'), 82.5 (C-7'), 72.2 (C-9), 59.1 (C-9'), 55.2 (OCH₃), 55.1 (OCH₃), 55.0 (OCH₃), 52.7, 42.6 (C-8), 32.3 (C-8')。以上波谱数据与文献[9]报道的lariciresinol-4'-monomethy ether一致,故鉴定化合物6为lariciresinol-4'-monomethy ether。

化合物7 白色无定形粉末,ESI-MS *m/z* 395.2 [M + Na]⁺, 371.2 [M - H]⁻。¹H-NMR (600 MHz,

MeOH-*d*₄) δ: 6.98 (s, 1H, H-2'), 6.95 (d, *J* = 1.7 Hz, 1H, H-2), 6.92 (m, 2H, H-5', 6'), 6.81 (dd, *J* = 8.2, 1.7 Hz, 1H, H-5), 6.77 (d, *J* = 8.1 Hz, 1H, H-5), 4.74 (d, *J* = 4.3 Hz, 1H, H-7), 4.71 (d, *J* = 4.3 Hz, 1H, H-7'), 4.28 ~ 4.18 (m, 2H, H-9), 3.85 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃), 3.81 (s, 3H, OCH₃), 3.14 (s, 2H, H-9'); ¹³C-NMR (150 MHz, MeOH-*d*₄) δ: 149.3 (C-3'), 148.8 (C-4'), 147.8 (C-3), 146.0 (C-4), 133.9 (C-1'), 132.4 (C-1), 118.7 (C-6), 118.4 (C-6'), 114.7 (C-5), 111.6 (C-5'), 109.8 (C-2), 109.6 (C-2'), 86.1 (C-7), 85.9 (C-7'), 71.3 (C-9), 71.2 (C-9'), 55.1 (OCH₃), 55.1 (OCH₃), 55.0 (OCH₃), 54.0 (C-8), 54.0 (C-8')。以上波谱数据与文献[10]报道的(+)-pinoresinol monomethy ether一致,故鉴定化合物7为(+)-pinoresinol monomethy ether。

化合物8 白色无定形粉末,ESI-MS *m/z* 371.1 [M - H]⁻。¹H-NMR (600 MHz, CDCl₃) δ: 6.89 ~ 6.77 (m, 6H), 5.95 (s, 2H, -OCH₂O-), 4.72 (br s, 2H, H-7, 7'), 4.24 (m, 2H, H-9a, 9'a), 3.91 (s, 3H, OCH₃), 3.89 ~ 3.83 (m, 2H, H-9b, 9'b), 3.07 (m, 2H, H-8, 8'); ¹³C-NMR (150 MHz, CDCl₃) δ: 148.0 (C-4), 147.1 (C-3), 146.7 (C-3'), 145.3 (C-4'), 135.1 (C-1), 132.9 (C-1'), 119.3 (C-6), 119.0 (C-6'), 114.3 (C-5'), 108.6 (C-2'), 108.2 (C-5), 106.5 (C-2), 101.1 (-OCH₂O-), 85.8 (C-9, 9'), 71.7 (C-7, C-7'), 56.0 (-OCH₃), 54.4 (C-8), 54.2 (C-8')。以上波谱数据与文献[11]报道的piperitol一致,故鉴定化合物8为piperitol。

化合物9 白色无定形粉末,ESI-MS *m/z* 393.2 [M + Na]⁺, 369.1 [M - H]⁻。¹H-NMR (600 MHz, CDCl₃) δ: 6.96 ~ 6.71 (m, 6H), 5.98 (s, 2H, -OCH₂O-), 5.33 (d, *J* = 3.6 Hz, 1H, H-7'), 5.29 (d, *J* = 3.6 Hz, 1H, H-7), 4.33 (dd, *J* = 9.2, 7.0 Hz, 1H, H-9'b), 4.02 (dd, *J* = 9.4, 4.7 Hz, 1H, H-9'a), 3.91 (s, 3H, -OCH₃), 3.45 (dd, *J* = 9.1, 3.6 Hz, 1H, H-8), 3.21 (m, 1H, H-8'); ¹³C-NMR (150 MHz, CDCl₃) δ: 176.8 (C-9), 148.5 (C-3), 148.1 (C-3'), 146.7 (C-4'), 145.3 (C-4), 133.1 (C-1), 132.2 (C-1'), 119.0 (C-6'), 118.0 (C-6), 114.4 (C-5), 108.5 (C-2), 108.1 (C-5'), 105.7 (C-2'), 101.4 (-OCH₂O-), 84.5 (C-7'),

83.4 (C-7), 72.7 (C-9'), 56.0 (-OCH₃), 53.2 (C-8), 49.9 (C-8')。以上波谱数据与文献[12]报道的 styroxin 一致,故鉴定化合物 **9** 为 styroxin。

化合物 **10** 白色无定形粉末, ESI-MS *m/z* 557.3 [M + Na]⁺。¹H-NMR (600 MHz, MeOH-*d*₄) δ: 7.14 (d, *J* = 8.3 Hz, 1H, H-5'), 7.03 (s, 1H, H-2), 6.98 (s, 1H, H-2'), 6.92 (br s, 3H, H-5, 6, 6'), 4.88 (d, *J* = 7.4 Hz, 1H, H-1''), 3.87 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃), 3.81 (s, 3H, OCH₃); ¹³C-NMR (150 MHz, MeOH-*d*₄) δ: 149.6 (C-3), 149.3 (C-4'), 148.9 (C-3'), 146.1 (C-4), 136.1 (C-1), 133.9 (C-1'), 118.4 (C-6', 6), 116.7 (C-5'), 111.6 (C-5), 110.3 (C-2), 109.8 (C-2'), 101.5 (C-1''), 85.9 (C-7'), 85.7 (C-7), 76.8 (C-5''), 76.5 (C-3''), 73.5 (C-2''), 71.4 (C-9, 9'), 70.0 (C-4''), 61.1 (C-6''), 55.4 (OCH₃), 55.1 (OCH₃), 55.1 (OCH₃), 54.1 (C-8), 54.0 (C-8')。以上波谱数据与文献[13]报道的 1*R*, 2*R*, 5*S*, 6*R*-2-(4'-hydroxy-3'-methoxyphenyl)-6-(3'', 4''-dimethoxyphenyl)-3, 7-dioxabicyclo[3. 3. 0]octane 4'-*O*-β-*D*-glucopyranoside 一致,故鉴定化合物 **10** 为 1*R*, 2*R*, 5*S*, 6*R*-2-(4'-hydroxy-3'-methoxyphenyl)-6-(3'', 4''-dimethoxyphenyl)-3, 7-dioxabicyclo[3. 3. 0]octane 4'-*O*-β-*D*-glucopyranoside。

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