

狭叶薰衣草中木脂素类化合物的研究

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摘要: 目的 对狭叶薰衣草 *Lavandula angustifolia* 中的木脂素类化合物进行研究。方法 运用 RP-HPLC、TLC、硅胶、凝胶、MCI-gel 树脂等方法进行分离纯化, 并根据理化性质和波谱数据鉴定化合物的结构。结果 从狭叶薰衣草中分离得到 11 个木脂素类化合物, 分别鉴定为松脂醇 (1)、丁香树脂醇 (2)、fraxiresinol-4'-O- β -D-glucopyranoside (3)、syringaresinol-4'-O- β -D-glucopyranoside (4)、8-hydroxypinoresinol-4-O- β -D-glucopyranoside (5)、rel-(2 α ,3 β)-7-O-methylcedrusin (6)、落叶松脂醇-4'-O- β -D-葡萄糖苷 (7)、(2S,3R)-2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxybenzofuran-5-(trans) propen-1-ol-3-O- β -glucoside (8)、(7S,8R)-dihydrodehydrodiconiferyl alcohol-9- β -D-glucopyranoside (9)、(7R,8R)-7,8-dihydro-9'-hydroxyl-3'-methoxyl-8-hydroxymethyl-7-(4-hydroxy-3-methoxyphenyl)-1'-benzofuranpropanol-9'-O- β -D-glucopyranoside (10)、(E)-3-((2S,3S)-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxy-2,3-dihydrobenzofuran-5-yl) allyl-2-hydroxyacetate (11)。结论 11 个化合物均首次从狭叶薰衣草中分离得到。

关键词: 狭叶薰衣草; 木脂素类; 松脂醇; 丁香树脂醇; 落叶松脂醇-4'-O- β -D-葡萄糖苷

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Study on lignans compounds from *Lavandula angustifolia*

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Abstract: Objective To investigate the lignans compounds constituents of *Lavandula angustifolia*. **Methods** The chemical constituents were isolated and purified by TLC, silica gel, MCI-gel, and RP-HPLC, and their structures were identified by analysis of spectroscopic evidences and physicochemical properties. **Results** A total of 11 constituents were isolated from *L. angustifolia* and elucidated as pinoresinol (1), syringaresinol (2), fraxiresinol-4'-O- β -D-glucopyranoside (3), syringaresinol-4'-O- β -D-glucopyranoside (4), 8-hydroxypinoresinol-4-O- β -D-glucopyranoside (5), rel-(2 α ,3 β)-7-O-methylcedrusin (6), lariciresinol-4'-O- β -D-glucoside (7), (2S,3R)-2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxybenzofuran-5-(trans) propen-1-ol-3-O- β -glucoside (8), (7S,8R)-dihydrodehydrodiconiferyl alcohol-9- β -D-glucopyranoside (9), (7R,8R)-7,8-dihydro-9'-hydroxyl-3'-methoxyl-8-hydroxymethyl-7-(4-hydroxy-3-methoxyphenyl)-1'-benzofuranpropanol-9'-O- β -D-glucopyranoside (10), and (E)-3-((2S,3S)-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxy-2,3-dihydrobenzofuran-5-yl) allyl-2-hydroxyacetate (11). **Conclusion** The 11 compounds are isolated from this plant for first time.

Key words: *Lavandula angustifolia* Mill; lignans compounds; pinoresinol; syringaresinol; ariciresinol-4'-O- β -D-glucoside

狭叶薰衣草 *Lavandula angustifolia* Mill 属于唇 洲各地, 现在世界各地都有种植。在我国, 新疆则是薰衣草之乡^[1], 薰衣草属于传统大宗芳香植物, 原产于地中海沿岸、大洋洲列岛以及欧

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为中华人民共和国卫生部《药品标准》维吾尔药分册的收载品种之一^[2]。薰衣草被首载于阿维森纳著的《医典》之中^[3]，它的医用价值主要体现在具有杀菌、抗真菌、抗氧化、抗痉挛、松弛平滑肌、镇静、抗抑郁等作用，而且对烧伤和昆虫咬伤也有效，同时对高血压患者^[4]、老年痴呆者也有利^[4-5]。为进一步探究狭叶薰衣草药效物质基础，本实验采用现代分离纯化方法对狭叶薰衣草进行研究，从其地上部分90%乙醇提取物醋酸乙酯萃取部分中分离得到11个木脂素类化合物，分别鉴定为松脂醇(pinoresinol, **1**)、丁香树脂醇(syringaresinol, **2**)、fraxiresinol-4'-O- β -D-glucopyranoside (**3**)、syringaresinol-4'-O- β -D-glucopyranoside (**4**)、8-hydroxypinoresinol-4-O- β -D-glucopyranoside(**5**)、rel-(2 α ,3 β)-7-O-methylcedrusin (**6**)、落叶松脂醇-4'-O- β -D-葡萄糖苷(lariciresinol-4'-O- β -D-glucoside, **7**)、(2S,3R)-2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxy-benzofuran-5-(trans)-propen-1-ol-3-O- β -glucoside (**8**)、(7S,8R)-dihydrodehydrodiconiferyl alcohol-9- β -D-glucopyranoside (**9**)、(7R,8R)-7,8-dihydro-9'-hydroxyl-3'-methoxyl-8-hydroxymethyl-7-(4-hydroxy-3-methoxyphenyl)-1'-benzofuranpropanol 9'-O- β -D-glucopyranoside (**10**)、(E)-3-[(2S,3S)-2-(4-hydroxy-3-methoxyphenyl)-3-(hydroxymethyl)-7-methoxy-2,3-dihydrobenzofuran-5-yl] allyl-2-hydroxyacetate (**11**)。11个化合物均首次从狭叶薰衣草中分离得到。

1 仪器与材料

Agilent 1100 series 半制备高效液相色谱仪、Agilent Zorbax SB-C₁₈ 色谱柱(250 mm×9.4, 5 μ m)、Zorbax PrepHT GF 色谱柱(250 mm×21.2 mm, 7 μ m)、美国安捷伦公司; Buchi R-210 型旋转蒸发仪(瑞士步琦有限公司); DLSB-5L/25 低温冷却液循环泵(巩义市予华仪器有限责任公司); VG AUTO Spec-3000 质谱仪(英国质谱仪器公司); Bruker AM-400 核磁共振仪(瑞士布鲁克公司); 紫外光谱仪 UV-2401A(日本岛津公司); Bio-Rad FTS-185 傅里叶变换红外光谱仪(美国伯乐 Bio-Rad 公司); ZF-20D 暗箱式紫外分析仪(巩义市予华仪器有限责任公司)。柱色谱硅胶(80~100、200~300 目), GF₂₅₄ 硅胶板(100 mm×100 mm), 均为青岛海洋化工厂产品; MCI 填充材料为 MCI-gel CHP-20P(75~150 μ m, 北京慧德易科技有限公司); D-101 大孔吸附

树脂(青岛海洋化工厂); Sephadex LH-20 凝胶(美国 GE 公司); 工业级丙酮、石油醚、醋酸乙酯、乙醇、甲醇; 分析纯乙腈(国药集团化学试剂有限公司); 氘代甲醇、氘代氯仿(美国 Sigma-Aldrich 公司); 去离子水、娃哈哈纯净水等试剂。

狭叶薰衣草样品于 2013 年 10 月采自云南省玉溪市澄江县, 并由云南民族大学胡秋芬教授鉴定为狭叶薰衣草 *Lavandula angustifolia* Mill.

2 提取与分离

干燥狭叶薰衣草地上部分 4.7 kg, 粉碎后过 40 目筛, 用 90%乙醇室温浸泡 1 个月, 超声提取 6 次(每次 120 min), 滤过, 减压浓缩, 浓缩液用醋酸乙酯萃取 5 次, 每次用量为 10 L, 合并得到浸膏 758 g。大孔吸附树脂充分吸附浸膏里的化合物, 上柱用去离子水冲洗 2~3 d, 除去部分糖和色素。然后用甲醇-水(20%、50%、70%、85%)梯度洗脱, 分成 4 个部分(A~D)。用 MCI 除色素后, 由 HPLC 紫外吸收发现木脂素类化合物主要在 B 和 C 部分。B(36 g)部分经 MCI 除色素后, 采用硅胶柱色谱, 用乙醚-醋酸乙酯进行梯度洗脱, 用色谱柱 Zorbax PrepHT GF(250 mm×21.2 mm, 7 μ m), 以 40%甲醇-水溶液为流动相, 体积流量为 8 mL/min 进行制备, 再用色谱柱 [Agilent Zorbax SB-C₁₈(250 mm×9.4 mm, 5 μ m)], 以 37%甲醇-水和 27%乙腈-水为流动相(2 种体系交替使用), 体积流量为 3 mL/min 进行半制备, 得到化合物 **1**(23.1 mg)、**2**(20.8 mg)、**3**(30.7 mg)、**4**(8.5 mg)、**7**(25.3 mg)、**8**(28.1 mg)、**11**(9.8 mg)。C(23 g)部分经 MCI 除色素后, 采用硅胶柱色谱, 乙醚-醋酸乙酯(1:20)进行洗脱, 得到 3 个组分(C1~C3)。C2、C3 用 Zorbax PrepHT GF 柱, 以 70%甲醇-水溶液为流动相, 体积流量为 8 mL/min 进行制备, 再用反相柱, 以 65%甲醇-水和 55%乙腈-水为流动相(2 种体系交替使用), 体积流量为 3 mL/min 进行半制备, 得到化合物 **10**(8.6 mg)。C1 与 C2、C3 半制备得到的大极性部分合并再采用硅胶柱色谱法进一步除杂, 先用石油醚除去部分杂质, 再用 90%甲醇-水将样品从柱子上洗脱下来。再由 HPLC, 以 65%甲醇-水和 55%乙腈-水为流动相(2 种体系交替使用), 体积流量为 3 mL/min 进行分离与纯化, 得到化合物 **5**(11.8 mg)、**6**(16.3 mg)、**9**(14.2 mg)。

3 结构鉴定

化合物 **1**: 白色针状结晶(甲醇-水), 分子式

$C_{21}H_{22}O_6$, 1H -NMR (400 MHz, $CDCl_3$) δ : 6.94 (2H, d, $J = 1.7$ Hz, H-2, 2'), 6.80 (2H, dd, $J = 8.0, 1.7$ Hz, H-6, 6'), 6.76 (2H, d, $J = 8.0$ Hz, H-5, 5'), 4.74 (2H, d, $J = 4.2$ Hz, H-7, 7'), 4.26 (2H, dd, $J = 9.2, 6.9$ Hz, H-9b, 9'b), 3.90 (6H, s, $-OCH_3$), 3.87 (2H, dd, $J = 9.2, 3.8$ Hz, H-9a, 9'a), 3.09 (2H, m, H-8, 8'); ^{13}C -NMR (100 MHz, $CDCl_3$) δ : 146.8 (s, C-3, 3'), 145.3 (s, C-4, 4'), 132.7 (s, C-1, 1'), 118.8 (d, C-6, 6'), 114.2 (d, C-5, 5'), 108.5 (d, C-2, 2'), 85.7 (d, C-7, 7'), 71.5 (t, C-9, 9'), 55.8 (q, $-OCH_3$), 54.2 (d, C-8, 8'). 以上数据与文献报道一致^[6], 故鉴定化合物 1 为松脂醇。

化合物 2: 白色棱晶 (甲醇-水), 分子式 $C_{22}H_{26}O_8$ 。 1H -NMR (400 MHz, $CDCl_3$) δ : 6.61 (4H, s, H-2, 2', 6, 6'), 5.41 (2H, brs, 4, 4'-OH), 4.76 (2H, brd, $J = 4.2$ Hz, H-7, 7'), 4.15 (2H, dd, $J = 9.0, 6.8$ Hz, H-9a, 9'a), 3.75 (12H, s, $4 \times OCH_3$), 3.65 (2H, dd, $J = 9.0, 3.8$ Hz, H-9b, 9'b), 2.94 (2H, m, H-8, 8'); ^{13}C -NMR (100 MHz, $CDCl_3$) δ : 147.2 (s, C-3, 3', 5, 5'), 134.3 (s, C-4, 4'), 132.1 (s, C-1, 1'), 102.7 (d, C-2, 2', 6, 6'), 86.1 (d, C-7, 7'), 71.7 (t, C-9, 9'), 56.4 (q, $-OCH_3$), 54.2 (d, C-8, 8'). 以上数据与文献报道一致^[7], 故鉴定化合物 2 为丁香树脂醇。

化合物 3: 黄色无定形粉末, 分子式 $C_{27}H_{34}O_{12}$ 。 1H -NMR (500 MHz, CD_3OD) δ : 6.76 (1H, s, H-2), 6.76 (1H, s, H-6), 4.73 (1H, s, H-7), 3.92 (1H, d, $J = 9.2$ Hz, H-9a), 4.12 (1H, d, $J = 9.3$ Hz, H-9b), 7.17 (1H, d, $J = 1.7$ Hz, H-2'), 7.18 (1H, dd, $J = 8.7, 1.7$ Hz, H-5'), 7.01 (1H, d, $J = 8.7$ Hz, H-6'), 4.95 (1H, d, $J = 5.8$ Hz, H-7'), 3.08 (1H, m, H-8'), 3.83 (1H, dd, $J = 8.7, 6.6$ Hz, H-9'a), 4.53 (1H, t, $J = 8.7$ Hz, H-9'b), 4.93 (1H, d, $J = 7.5$ Hz, H-1''), 3.54 (1H, dd, $J = 9.5, 7.5$ Hz, H-2''), 3.52 (1H, t, $J = 9.5$ Hz, H-3''), 3.43 (1H, t, $J = 9.5$ Hz, H-4''), 3.42 (1H, m, H-5''), 3.73 (1H, dd, $J = 12.1, 4.5$ Hz, H-6''), 3.91 (1H, dd, $J = 12.1, 3.5$ Hz, H-6''), 3.92 (3H, s, 3-OMe), 3.92 (3H, s, 5-OMe), 3.94 (3H, s, 3'-OMe); ^{13}C -NMR (125 MHz, CD_3OD) δ : 128.2 (C-1), 106.3 (C-2), 149.1 (C-3), 136.8 (C-4), 149.2 (C-5), 106.4 (C-6), 89.5 (C-7), 92.7 (C-8), 76.3 (C-9), 137.3 (C-1'), 111.7 (C-2'), 151.1 (C-3'), 147.6 (C-4'), 117.9 (C-5'), 120.5 (C-6'), 87.2 (C-7'), 62.5 (C-8'), 72.4 (C-9'), 102.7 (C-1''), 75.2 (C-2''), 78.2 (C-3''), 71.4 (C-4''), 78.4 (C-5''), 62.5 (C-6''), 56.7 (3-OMe), 56.7 (5-OMe), 56.5 (3'-OMe)。

以上数据与文献报道基本一致^[8], 故鉴定化合物 3 为 fraxiresinol-4'-O- β -D-glucopyranoside。

化合物 4: 黄色无定形粉末, 分子式 $C_{27}H_{34}O_{12}$ 。 1H -NMR (500 MHz, CD_3OD) δ : 6.76 (1H, s, H-2), 6.76 (1H, s, H-6), 4.73 (1H, s, H-7), 3.08 (1H, m, H-8), 3.92 (1H, d, $J = 9.2$ Hz, H-9a), 4.30 (1H, d, $J = 9.3$ Hz, H-9b), 7.17 (1H, d, $J = 1.7$ Hz, H-2'), 7.01 (1H, d, $J = 8.7$ Hz, H-6'), 4.95 (1H, d, $J = 5.8$ Hz, H-7'), 3.08 (1H, m, H-8'), 3.83 (1H, dd, $J = 8.7, 6.6$ Hz, H-9'a), 4.53 (1H, t, $J = 8.7$ Hz, H-9'b), 4.93 (1H, d, $J = 7.5$ Hz, H-1''), 3.54 (1H, dd, $J = 9.5, 7.5$ Hz, H-2''), 3.52 (1H, t, $J = 9.5$ Hz, H-3''), 3.43 (1H, t, $J = 9.5$ Hz, H-4''), 3.42 (1H, m, H-5''), 3.73 (1H, dd, $J = 12.1, 4.5$ Hz, H-6''), 3.91 (1H, dd, $J = 12.1, 3.5$ Hz, H-6''), 3.92 (3H, s, 3-OMe), 3.92 (3H, s, 5-OMe), 3.94 (3H, s, 3'-OMe), 3.95 (3H, s, 5'-OMe); ^{13}C -NMR (125 MHz, CD_3OD) δ : 128.2 (C-1), 106.3 (C-2), 149.1 (C-3), 136.8 (C-4), 149.2 (C-5), 106.4 (C-6), 89.5 (C-7), 55.5 (C-8), 76.3 (C-9), 137.3 (C-1'), 105.3 (C-2'), 151.1 (C-3'), 147.6 (C-4'), 117.9 (C-5'), 104.3 (C-6'), 87.2 (C-7'), 62.5 (C-8'), 72.4 (C-9'), 102.7 (C-1''), 75.2 (C-2''), 78.2 (C-3''), 71.4 (C-4''), 78.4 (C-5''), 62.5 (C-6''), 56.7 (3-OMe), 56.7 (5-OMe), 54.8 (3'-OMe), 54.8 (5'-OMe)。以上数据与文献报道基本一致^[9], 故鉴定化合物 4 为 syringaresinol-4'-O- β -D-glucopyranoside。

化合物 5: 白色无定形粉末, 分子式为 $C_{26}H_{32}O_{12}$ 。 1H -NMR (400 MHz, CD_3OD) δ : 7.11 (1H, s, H-2), 7.15 (1H, d, $J = 7.9$ Hz, H-5), 6.95 (1H, d, $J = 7.9$ Hz, H-6), 4.71 (1H, s, H-7), 4.06 (1H, d, $J = 9.3$ Hz, H-9a), 3.87 (1H, overlapped, H-9b), 3.85 (3H, s, 3- OCH_3), 7.05 (1H, brs, H-2'), 6.79 (1H, d, $J = 7.9$ Hz, H-5'), 6.87 (1H, brd, $J = 7.9$ Hz, H-6'), 4.83 (1H, d, $J = 5.5$ Hz, H-7'), 3.03 (1H, dd, $J = 13.3, 5.9$ Hz, H-8'), 3.76 (1H, dd, $J = 8.9, 6.3$ Hz, H-9'a), 4.46 (1H, t, $J = 8.6$ Hz, H-9'b), 3.86 (3H, s, 3'- OCH_3), 4.88 (1H, d, $J = 7.0$ Hz, H-1''), 4.21 (1H, d, $J = 7.8$ Hz, H-1''), 4.16 (1H, m, H-2''), 3.22 (1H, m, H-3''), 3.22 (1H, m, H-4''), 3.26 (1H, m, H-5''), 3.61 (2H, m, H-6''); ^{13}C -NMR (100 MHz, CD_3OD) δ : 132.7 (C-1), 113.4 (C-2), 150.3 (C-3), 149.1 (C-4), 117.2 (C-5), 121.2 (C-6), 88.7 (C-7), 92.8 (C-8), 76.1 (C-9), 56.8 (3- OCH_3), 133.7 (C-1'), 111.2 (C-2'), 147.6 (C-3'),

147.4 (C-4'), 116.2 (C-5'), 120.5 (C-6'), 87.7 (C-7'), 62.2 (C-8'), 72.1 (C-9'), 56.5 (3'-OCH₃), 102.7 (C-1''), 74.7 (C-2''), 77.8 (C-3''), 71.3 (C-4''), 78.1 (C-5''), 62.5 (C-6''). 以上数据与文献报道基本一致^[10-11], 故鉴定化合物 **5** 为 8-羟基松脂醇-4-O-β-D-吡喃葡萄糖苷。

化合物 **6**: 白色无定形粉末, 分子式为 C₂₀H₂₂O₆, UV λ(EtOH): 228, 283, 288 nm; IR ν_{max}^{KBr} (cm⁻¹): 3 408, 1 608, 1 520, 1 502。HR-FAB-MS *m/z*: 486.188 5 [M+H]⁺ (计算值 486.188 1)。¹H-NMR (400 MHz, CD₃OD) δ: 5.48 (1H, d, *J* = 6.3 Hz, H-2), 3.48 (1H, dt, *J* = 6.2, 6.3 Hz, H-3), 3.82 (1H, m, H-3a), 3.75 (1H, m, H-3'a), 6.73 (1H, s, H-4), 2.63 (2H, t, *J* = 7.7 Hz, H-5a), 1.82 (2H, tt, *J* = 6.5, 7.7 Hz, H-5b), 3.59 (2H, t, *J* = 6.5 Hz, H-5c), 6.73 (1H, s, H-6), 6.96 (1H, d, *J* = 1.8 Hz, H-2'), 6.77 (1H, d, *J* = 8.1 Hz, H-5'), 6.83 (1H, dd, *J* = 1.8, 8.2 Hz, H-6'), 3.86 (3H, s, 7-OMe), 3.82 (3H, s, 3'-OMe); ¹³C-NMR (100 MHz, CD₃OD) δ: 89.2 (C-2), 55.8 (C-3), 65.2 (C-3a/a'), 118.2 (C-4), 130.2 (C-4a), 137.2 (C-5), 33.1 (C-5a), 35.8 (C-5b), 62.5 (C-5c), 114.2 (C-6), 145.6 (C-7), 147.8 (C-7a), 135.1 (C-1'), 110.8 (C-2'), 149.3 (C-3'), 147.7 (C-4'), 116.2 (C-5'), 119.8 (C-6'), 56.8 (7-OMe), 56.6 (3'-OMe)。以上数据与文献报道基本一致^[12-14], 故鉴定化合物 **6** 为 *rel*-(2α,3β)-7-O-methylcedrusin。

化合物 **7**: 白色粉末, 分子式 C₂₆H₃₀O₁₁。 ¹H-NMR (400 MHz, CD₃OD) δ: 6.78 (1H, d, *J* = 2.0 Hz, H-2), 6.72 (1H, d, *J* = 7.6 Hz, H-5), 6.62 (1H, dd, *J* = 7.6, 2.0 Hz, H-6), 2.48 (1H, dd, *J* = 11.6, 13.6 Hz, H-7a), 2.92 (1H, dd, *J* = 13.6, 4.8 Hz, H-7b), 2.72 (1H, m, H-8), 3.98 (1H, dd, *J* = 8.4, 6.4 Hz, H-9a), 3.73 (1H, m, H-9b), 6.99 (1H, d, *J* = 2.0 Hz, H-2'), 7.13 (1H, d, *J* = 8.4 Hz, H-5'), 6.88 (1H, dd, *J* = 8.4, 2.0 Hz, H-6'), 4.85 (1H, d, *J* = 6.8 Hz, H-7'), 2.35 (1H, m, H-8'), 3.81 (1H, m, H-9'), 4.88 (1H, d, *J* = 7.6 Hz, H-1''), 3.89 (1H, m, H-2''), 3.29 (1H, m, H-3''), 3.27 (1H, m, H-4''), 3.31 (1H, m, H-5''), 3.67 (2H, m, H-6''), 3.82 (3H, s, 3-OMe), 3.86 (3H, s, 3'-OMe); ¹³C-NMR (100 MHz, CD₃OD) δ: 133.7 (C-1), 113.7 (C-2), 149.2 (C-3), 145.7 (C-4), 116.4 (C-5), 122.3 (C-6), 33.7 (C-7), 43.9 (C-8), 73.8 (C-9), 139.8 (C-1'), 111.7 (C-2'), 151.1 (C-3'), 147.6 (C-4'), 118.3 (C-5'),

119.5 (C-6'), 83.7 (C-7'), 54.2 (C-8'), 60.7 (C-9'), 103.3 (C-1''), 75.2 (C-2''), 78.2 (C-3''), 71.6 (C-4''), 77.8 (C-5''), 62.7 (C-6''), 56.7 (3-OMe), 56.7 (3'-OMe)。以上数据与文献报道一致^[15-16], 故鉴定化合物 **7** 为落叶松脂醇-4'-O-β-D-葡萄糖苷。

化合物 **8**: 淡黄色无定形粉末, 分子式为 C₂₆H₃₂O₁₁。 ¹H-NMR (400 MHz, CD₃OD) δ: 6.97 (1H, d, *J* = 1.7 Hz, H-2), 6.77 (1H, d, *J* = 8.3 Hz, H-5), 6.86 (1H, dd, *J* = 8.3, 1.7 Hz, H-6), 5.62 (1H, d, *J* = 5.9 Hz, H-7), 3.67 (1H, m, H-8), 3.87 (2H, dd, *J* = 20.0, 1.2 Hz, H-9), 7.02 (1H, s, H-2'), 6.95 (1H, s, H-6'), 6.53 (1H, d, *J* = 15.6 Hz, H-7'), 6.22 (1H, dt, *J* = 15.6, 5.9 Hz, H-8'), 4.18 (2H, d, *J* = 5.9 Hz, H-9'), 4.26 (1H, d, *J* = 7.8 Hz, H-1''), 4.21 (1H, m, H-2''), 3.29 (1H, m, H-3''), 3.27 (1H, m, H-4''), 3.31 (1H, m, H-5''), 3.67 (2H, m, H-6''), 3.87 (3H, s, 3-OMe), 3.82 (3H, s, 3'-OMe); ¹³C-NMR (100 MHz, CD₃OD) δ: 130.7 (C-1), 121.1 (C-2), 147.8 (C-3), 149.6 (C-4), 116.7 (C-5), 111.3 (C-6), 89.9 (C-7), 53.6 (C-8), 72.8 (C-9), 133.1 (C-1'), 112.7 (C-2'), 145.8 (C-3'), 149.6 (C-4'), 134.9 (C-5'), 117.5 (C-6'), 132.5 (C-7'), 128.1 (C-8'), 63.1 (C-9'), 104.1 (C-1''), 75.2 (C-2''), 78.2 (C-3''), 71.6 (C-4''), 78.6 (C-5''), 63.2 (C-6''), 57.8 (3-OMe), 57.5 (3'-OMe)。以上数据与文献报道基本一致^[17-18], 故鉴定化合物 **8** 为 (2*S*,3*R*)-2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxy-benzofuran-5-(*trans*)-propen-1-ol-3-O-β-glucoside。

化合物 **9**: 淡黄色无定形粉末, 分子式为 C₂₆H₃₄O₁₁。 ¹H-NMR (500 MHz, CD₃OD) δ: 6.88 (1H, d, *J* = 1.5 Hz, H-2), 6.67 (1H, d, *J* = 8.3 Hz, H-5), 6.68 (1H, dd, *J* = 8.3, 1.5 Hz, H-6), 5.49 (1H, d, *J* = 6.4 Hz, H-7), 3.47 (1H, m, H-8), 4.01 (2H, dd, *J* = 20.0, 1.2 Hz, H-9), 6.63 (1H, s, H-2'), 6.65 (1H, s, H-6'), 2.53 (2H, t, *J* = 7.6 Hz, H-7'), 1.91 (2H, m, H-8'), 3.57 (1H, m, H-9'), 3.22 (1H, m, H-9'), 4.26 (1H, d, *J* = 7.8 Hz, H-1''), 4.21 (1H, m, H-2''), 3.27 (1H, m, H-3''), 3.27 (1H, m, H-4''), 3.31 (1H, m, H-5''), 3.67 (2H, m, H-6''), 3.83 (3H, s, 3-OMe), 3.86 (3H, s, 3'-OMe); ¹³C-NMR (125 MHz, CD₃OD) δ: 136.8 (C-1), 110.5 (C-2), 149.2 (C-3), 147.6 (C-4), 116.2 (C-5), 119.8 (C-6), 89.3 (C-7), 52.6 (C-8), 72.2 (C-9), 129.7 (C-1'), 114.2 (C-2'), 145.2 (C-3'), 147.6 (C-4'), 134.7 (C-5'), 118.1 (C-6'), 32.7 (C-7'), 35.7 (C-8'), 62.3 (C-9'),

104.3 (C-1''), 75.2 (C-2''), 78.2 (C-3''), 72.6 (C-4''), 77.6 (C-5''), 62.7 (C-6''), 56.8 (3-OMe), 56.3 (3'-OMe)。以上数据与文献报道基本一致^[19-20], 故鉴定化合物 **9** 为 (7*S*,8*R*)-dihydrodehydrodiconiferyl alcohol-9-β-*D*-glucopyranoside。

化合物 **10**: 无色无定形粉末, UV $\lambda_{\text{max}}^{\text{MeOH}}$ (nm): 206 (4.76), 281 (3.82), IR $\nu_{\text{max}}^{\text{KBr}}$ (cm⁻¹): 3 422, 2 935, 2 880, 1 608, 1 518, 1 499。HR-FAB-MS *m/z*: 521.203 9 [M-H]⁻ (计算值 521.203 9), 分子式 C₂₆H₃₃O₁₁。 ¹H-NMR (500 MHz, CD₃OD) δ : 6.77 (1H, d, *J* = 8.2 Hz, H-5), 6.82 (1H, d, *J* = 8.5 Hz, H-6), 6.92 (1H, d, *J* = 1.6 Hz, H-2), 6.73 (1H, s, H-2'), 6.76 (1H, s, H-6'), 3.78 (3H, s, 3-OMe), 3.83 (3H, s, 3'-OMe), 5.47 (1H, d, *J* = 6.3 Hz, H-7), 3.46 (1H, m, H-8), 3.75 (1H, m, H-9a), 3.81 (1H, m, H-9b), 2.66 (2H, brt, *J* = 7.4 Hz, H-7'), 1.87 (2H, m, H-8'), 3.52 (1H, m, H-9'a), 3.93 (1H, m, H-9'b); ¹³C-NMR (125 MHz, CD₃OD) δ : 134.7 (s, C-1), 110.7 (d, C-2), 149.1 (s, C-3), 147.5 (s, C-4), 116.2 (d, C-5), 119.8 (d, C-6), 88.8 (d, C-7), 55.2 (d, C-8), 65.1 (t, C-9), 136.7 (s, C-1'), 114.3 (d, C-2'), 145.2 (s, C-3'), 147.5 (s, C-4'), 129.8 (s, C-5'), 118.1 (d, C-6'), 32.8 (t, C-7'), 32.8 (t, C-8'), 70.1 (t, C-9'), 104.6 (d, C-1''), 75.2 (d, C-2''), 78.3 (d, C-3''), 71.7 (d, C-4''), 77.7 (d, C-5''), 56.5 (3-OMe), 56.7 (3'-OMe)。以上数据与文献报道基本一致^[21-22], 故鉴定化合物 **10** 为 (7*R*,8*R*)-7,8-dihydro-9'-hydroxyl-3'-methoxyl-8-hydroxymethyl-7-(4-hydroxy-3-methoxyphenyl)-1'-benzofuranpropanol-9'-*O*-β-*D*-glucopyranoside。

化合物 **11**: 无色无定形粉末, 分子式 C₂₆H₃₂O₁₁。 ¹H-NMR (500 MHz, CD₃OD) δ : 6.77 (1H, d, *J* = 8.2 Hz, H-5), 6.82 (1H, d, *J* = 8.5 Hz, H-6), 6.92 (1H, d, *J* = 1.6 Hz, H-2), 6.73 (1H, s, H-2'), 6.76 (1H, s, H-6'), 3.78 (3H, s, 3-OMe), 3.83 (3H, s, 3'-OMe), 5.47 (1H, d, *J* = 6.3 Hz, H-7), 3.46 (1H, m, H-8), 3.75 (1H, m, H-9a), 3.81 (1H, m, H-9b), 6.57 (1H, d, *J* = 15.8 Hz, H-7'), 6.22 (1H, dt, *J* = 15.8, 5.9 Hz, H-8'), 3.52 (1H, m, H-9'a), 3.93 (1H, m, H-9'b); ¹³C-NMR (125 MHz, CD₃OD) δ : 134.7 (s, C-1), 110.7 (d, C-2), 149.1 (s, C-3), 147.5 (s, C-4), 116.2 (d, C-5), 119.8 (d, C-6), 88.8 (d, C-7), 55.2 (d, C-8), 65.1 (t, C-9), 136.7 (s, C-1'), 114.3 (d, C-2'), 145.2 (s, C-3'), 147.5 (s, C-4'), 129.8 (s, C-5'), 118.1 (d, C-6'), 132.4 (d, C-7'), 130.1

(d, C-8'), 64.9 (t, C-9'), 104.6 (d, C-1''), 75.2 (d, C-2''), 78.3 (d, C-3''), 71.7 (d, C-4''), 77.7 (d, C-5''), 56.5 (3-OMe), 56.7 (3'-OMe)。以上数据与文献报道基本一致^[21-22], 故鉴定化合物 **11** 为 (*E*)-3-[(2*S*,3*S*)-2-(4-hydroxy-3-methoxyphenyl)-3-(hydroxymethyl)-7-methoxy-2,3-dihydrobenzofuran-5-yl] allyl 2-hydroxyacetate。

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