牛蒡子中一个新木脂素类化合物

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摘要: 本文对牛蒡子中的化学成分进行了研究。采用多种柱色谱方法并结合制备型 HPLC 的方法分离纯化牛蒡子中的化学成分, 进一步利用 IR、UV、CD、MS、HR-ESI-MS、1D 和 2D NMR 等技术对分离得到的化合物进行结构分析和鉴定。从牛蒡子 80%乙醇提取物中分离鉴定了 10 个化合物, 分别为: (7*R*,8*R*)-4,7,9,9'-tetrahydroxy-3,3'-dimethoxy-8-4'-oxyneolign-7'-ene-9'-*O*-*β*-*D*-glucopyranoside (**1**)、(7*R*,8*R*)-4,7,9,9'-tetrahydroxy-3,3'-dimethoxy-8-*O*-4'-neolignan-9'-*O*-*β*-*D*-glucopyranoside (**2**)、(7*R*,8*R*)-4,7,9,9'-tertahydroxy-3,3'-dimethoxy-8-4'-oxyneolignan (**3**)、(7*S*,8*R*)-dihydrodehydrodiconiferylalcohol-4-*O*-*β*-*D*-glucopyranoside (**4**)、(7*S*,8*R*,7'*R*,8'*R*)-pinoresinol-4,4'-di-*O*-*β*-*D*-glucopyranoside (**5**)、(8*S*,7'*S*,8'*R*)-4,4',9'-trihydroxy-3,3'-dimethoxy-7',9-epoxylignan-7-oxo-4'-*O*-*β*-*D*-glucopyranoside (**6**)、1-*O*-*β*-*D*-xylopyranosyl-(1→6)-*O*-*β*-*D*-glucopyranoside-2-methoxy-4-hydroxyphenol (**7**)、1-*O*-*β*-*D*-xylopyranosyl-(1→6)-*O*-*β*-*D*-glucopyranoside-3-methoxy-4-hydroxyphenol (**8**)、4-*O*-*β*-*D*-xylopyranosyl-(1→6)-*O*-*β*-*D*-glucopyranoside-4-hydroxy-3-methoxybenzylalcohol (**9**) 和 2-phenethyl *β*-primeveroside (**10**)。其中化合物 **1** 为一个新的 8-*O*-4'型木脂素, 化合物 **2**～**10** 均为首次从牛蒡子中分离得到。

关键词: 菊科; 牛蒡子; 化学成分; 提取; 分离; 木脂素

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A new neolignan from the fruits of *Arctium lappa* L.

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Abstract: In our study of the chemical constituents of the dried mature fruits of *Arctium lappa* L., ten compounds were isolated by various chromatography methods and preparative HPLC. Their structures were elucidated as (7*R*,8*R*)-4,7,9,9'-tetrahydroxy-3,3'-dimethoxy-8-4'-oxyneolign-7'-ene-9'-*O*-*β*-*D*-glucopyranoside (**1**), (7*R*,8*R*)-4,7,9,9'-tetrahydroxy-3,3'-dimethoxy-8-*O*-4'-neolignan-9'-*O*-*β*-*D*-glucopyranoside (**2**), (7*R*,8*R*)-4,7,9,9'-tertahydroxy-3,3'-dimethoxy-8-4'-oxyneolignan (**3**), (7*S*,8*R*)-dihydrodehydrodiconiferylalcohol-4-*O*-*β*-*D*-glucopyranoside (**4**), (7*S*,8*R*,7'*R*,8'*R*)-pinoresinol-4,4'-di-*O*-*β*-*D*-glucopyranoside (**5**), (8*S*,7'*S*,8'*R*)-4,4',9'-trihydroxy-3,3'-dimethoxy-7',9-epoxylignan-7-oxo-4'-*O*-*β*-*D*-glucopyranoside (**6**), 2-methoxy-4-hydroxyphenol-1-*O*-*β*-*D*-xylopyranosyl-(1→6)-*O*-*β*-*D*-glucopyranoside (**7**), 3-methoxy-4-hydroxyphenol-1-*O*-*β*-*D*-xylopyranosyl-(1→6)-*O*-*β*-*D*-glucopyranoside (**8**), 4-hydroxy-3-methoxybenzylalcohol-4-*O*-*β*-*D*-xylopyranosyl-(1→6)-*O*-*β*-*D*-

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glucopyranoside (**9**) and 2-phenethyl *β*-primeveroside (**10**) by their spectroscopic data (IR, UV, CD, MS, HR-ESI-MS, and 1D and 2D NMR) and comparison to literature data. Compound **1** is a new 8-*O*-4'-neolignan. Compounds **2**−**10** were isolated from the dried mature fruits of *Arctium lappa* L. for the first time.

Key words: Asteraceae; Arctii Fructus; chemical constituent; extraction; isolation; lignan

牛蒡子 (Arctii Fructus) 为菊科 (Asteraceae) 牛蒡属 (*Arctium*) 植物牛蒡 *Arctium lappa* L.的干燥成熟果实, 我国有牛蒡属植物 2 种。牛蒡为两年生草本植物, 在全国大部分地区均有分布, 喜温暖湿润气候, 耐寒、耐热性较强, 多生于山坡、山谷、林缘、林中, 海拔 750～3 500 m 处。目前从牛蒡子中分离得到的化合物主要为木脂素类、脂肪酸以及其他类成分等[1−6]。现代研究表明, 牛蒡子中所含主要成分木脂素类化合物具有抗肿瘤、抗炎、抗病毒、改善肾脏代谢功能、降血糖等多种生理活性[7−11]。

为了进一步揭示牛蒡子的药效物质基础, 本实验利用现代色谱分离技术及光谱鉴定技术, 依据牛蒡子的传统水煎剂用法重点对牛蒡子水溶性成分进行了研究, 共从牛蒡子中分离鉴定了 10 个化合物, 其中包括 1 个新的 8-*O*-4'型木脂素和 9 个首次从牛蒡子中分离得到的单体化合物。这些化合物大多为糖苷类化合物, 包括 5 个木脂素的糖苷类化合物、3 个酚苷类化合物以及 1 个苯乙醇苷类化合物 (图 1)。

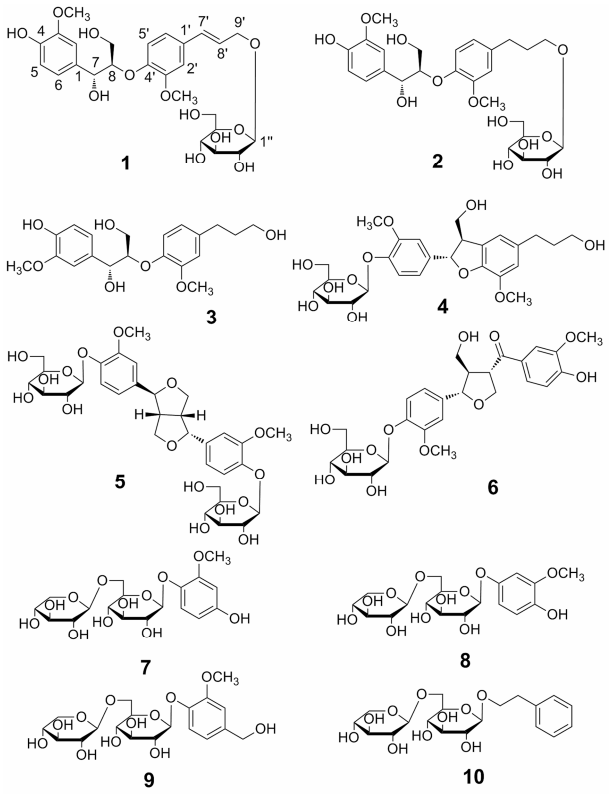

Figure 1　Structures of compounds **1**−**10**

化合物 **1**, 白色无定形粉末, UV (MeOH) λ_{max} (logε): 230 (3.99)、280 (3.68) nm; $[\alpha]_D^{25}$ −29.71 (*c* 0.1, MeOH−H_2O, 1∶1); CD (MeOH) λ_{max} ($\Delta\varepsilon$): 257 (−1.23)、302 (−0.57) nm; 高分辨质谱 HR-ESI-MS *m*/*z* 561.192 1 $[M+Na]^+$ (calcd. for $C_{26}H_{34}O_{12}Na$, 561.194 8) 提示化合物 **1** 分子式为 $C_{26}H_{34}O_{12}$。IR 显示该化合物结构中含有羟基 (3 384 cm^{-1}) 和苯环 (1 602、1 511、1 453 cm^{-1})。

化合物 **1** 的 ^{1}H NMR (500 MHz, DMSO-d_6) 谱中 (表 1), 显示有 6 个芳香质子信号 δ_H 7.05 (1H, brs, H-2)、6.67 (1H, d, *J* = 8.0 Hz, H-5)、6.75 (1H, d, *J* = 8.0

Table 1　^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) data ofcompound **1** (in DMSO-d_6, *J* in Hz)

Position	δ_H	δ_C
1		133.4
2	7.05, brs	111.5
3		147.5
4		145.9
5	6.67, d, (8.0)	115.1
6	6.75, d, (8.0)	119.5
7	4.70, d, (4.0)	71.4
8	4.26, m	84.8
9	3.56, d, (11.0)	60.6
	3.22, overlap	
1'		131.9
2'	6.96, brs	111.5
3'		150.1
4'		147.5
5'	6.96, d, (8.0)	115.8
6'	6.87, d, (8.0)	119.9
7'	6.54, d, (15.5)	124.6
8'	6.23, dt, (15.5, 5.5)	130.1
9'	4.40, dd, (11.0, 5.5)	69.2
	4.19, overlap	
1"	4.19, d, (7.5)	102.6
2"	2.97, m	73.8
3"	3.01, m	77.1
4"	3.04, m	70.7
5"	3.14, m	76.0
6"	3.67, d, (11.5)	61.6
	3.44, dd, (11.5, 5.0)	
3-CH_3O	3.71, s	56.1
3'-CH_3O	3.78, s	55.9

Hz, H-6)、6.96 (1H, brs, H-2')、6.96 (1H, d, J = 8.0 Hz, H-5') 和 6.87 (1H, d, J = 8.0 Hz, H-6'), 表明有两个 ABX 自旋体系苯环存在。此外, 还观察到两个连氧次甲基质子信号 δ_H 4.70 (1H, J = 4.0 Hz, H-7)、4.26 (1H, m, H-8); 两个连氧亚甲基质子信号 δ_H 3.56 (1H, J = 11.0 Hz, H-9)、3.22 (1H, overlap, H-9)、4.40 (1H, dd, J = 11.0, 5.5 Hz, H-9')、4.19 (1H, overlap, H-9'); 以及两个烯烃氢信号 δ_H 6.54 (1H, d, J = 15.5 Hz, H-7')、6.23 (1H, dt, J = 15.5, 5.5, H-8'), 表明了一个丙三醇单元和一个烯丙醇单元的存在。同时还观察到两个甲氧基信号 δ_H 3.71 (3H, s)、3.78 (3H, s), 以及一个 β-葡萄糖端基质子信号 δ_H 4.19 (1H, d, J = 7.5 Hz, H-1")。在 ^{13}C NMR (表 1) 中共显示了 26 个碳信号, 除了 2 个甲氧基碳信号、6 个葡萄糖碳信号外, 剩下的 18 个碳信号可归属为一个木脂素的碳骨架[1]。

化合物 **1** 的 HMBC 谱中 (图 2), H-7 与 C-1、C-2、C-6、C-8、C-9 的相关, H-7'与 C-1'、C-2'、C-6'、C-8'、C-9'的相关, 以及 H-8 与 C-4'的相关充分说明了化合物 **1** 是一个 8-*O*-4'型木脂素。葡萄糖端基质子 H-1" 与 C-9'的相关表明葡萄糖连接在化合物 **1** 的 9'位上, 甲氧基质子信号 δ_H 3.71 (3H, s)、3.78 (3H, s) 分别与 C-3、C-3'存在着远程相关点, 因此两个甲氧基分别位于化合物 **1** 的 C-3、C-3'。

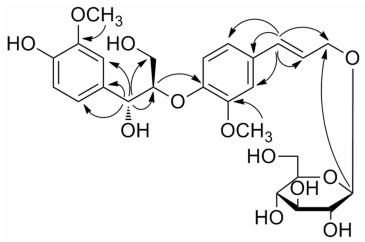

Figure 2 Key HMBC of compound **1**

通过文献调研可知, 对于 8-*O*-4'型木脂素苷类化合物, C-7 和 C-8 的绝对构型可以利用在氘代氯仿中测定苷元 H-7 的偶合常数并结合 CD 图谱进行确定[12], 而葡萄糖的绝对构型则可以通过气相色谱进行确定[13]。因此, 采用纤维素酶对化合物 **1** 进行水解[13], 并分别获得苷元 **1a** 以及单体葡萄糖。苷元 **1a** 在氘代氯仿中 H-7 的偶合常数为 7.5 Hz, 说明 C-7 和 C-8 的相对构型为苏式。结合化合物 **1** 在 CD 谱中 257 nm 处的负 Cotton 效应, 确定了该化合物绝对构型为 7*R*,8*R*。单体葡萄糖经三甲基硅烷基咪唑衍生化后进行气相色谱分析, 并与标准 *D*-型葡萄糖对比确定化合物中葡萄糖单元为 *D* 型[13]。

综上所述, 化合物 **1** 的化学结构被确定为 (7*R*,8*R*)-4,7,9,9'-tetrahydroxy-3,3'-dimethoxy-8-4'-oxyneolign-7'-ene-9'-*O*-*β*-*D*-glucopyranoside。

实验部分

JASCO P-2000 旋光仪; Nicolet 5700 傅里叶变换红外光谱仪; JASCO J-815 圆二色谱仪; Bruker 500 MHz 核磁共振仪; Agilent 6520 HPLC-Q-TOF 质谱仪; Agilent 1200 型高效液相色谱仪, 包括四元高压梯度泵、自动脱气机、二极管阵列检测器、自动进样器、柱温箱。Shimadzu 制备型高效液相色谱仪。大孔树脂 HP-20 为日本三菱化学株式会社生产, 反向硅胶 C-18 为 YMC 公司生产, 凝胶 Sephadex LH-20 为 GE 公司生产。

牛蒡子于 2011 年 11 月采于黑龙江省五常镇, 经中国医学科学院药物研究所马林教授鉴定为牛蒡 *Arctium lappa* L.的干燥成熟果实。标本 (ID-S-2434) 存放于中国医学科学院、北京协和医学院药物研究所植物标本室。

1 提取与分离

牛蒡子 (100 kg) 经 80%乙醇回流提取 (3×2 h), 得浸膏 (约 4.2 kg)。浸膏经水 (10 L) 分散后, 用乙酸乙酯萃取 (3×10 L)。所得水部位 (400 g) 进行 HP-20 大孔吸附树脂 (4.0 kg) 柱色谱, 用 H_2O (20 L)、15% EtOH (20 L)、30% EtOH (20 L)、50% EtOH (20 L)、95% EtOH (20 L) 梯度洗脱。

取 15% EtOH 洗脱部分 (40 g) 进行中压反相柱色谱, 用水−甲醇进行梯度洗脱 (0∶100～100∶0), 共得到 17 个部分 (Fr.1～Fr.17), 其中 Fr.5 再经 Sephadex LH-20 和制备型高效液色谱相分离得到化合物 **7** (18 mg)、**8** (100 mg)、**9** (27 mg)。

取 30% EtOH 洗脱部分 (86.4 g) 进行中压反相柱色谱, 用水−甲醇进行梯度洗脱 (0∶100～100∶0), 共得到 13 个部分 (Fr.1～Fr.13), 其中 Fr.8 再经 Sephadex LH-20 和制备型高效液相色谱分离得到化合物 **10** (23 mg); Fr.9 再经 Sephadex LH-20 和制备型高效液相色谱分离得到化合物 **1** (16 mg)、**2** (31 mg)、**3** (14 mg)、**5** (15 mg); Fr.10 再经 Sephadex LH-20 和制备型高效液相色谱分离得到化合物 **4** (15 mg)、**6** (19 mg)。

2 结构鉴定

化合物 **1** 白色无定形粉末, UV (MeOH) λ_{max} (logε): 230 (3.99)、280 (3.68) nm; $[\alpha]_D^{25}$ −29.71 (c 0.1,

MeOH−H_2O, 1∶1); CD (MeOH) λ_{max} ($\Delta\varepsilon$): 257 (−1.23)、302 (−0.57) nm; 高分辨质谱 HR-ESI-MS *m/z* 561.192 1 $[M+Na]^+$ (calcd. for $C_{26}H_{34}O_{12}Na$, 561.194 8) 提示化合物 **1** 分子式为 $C_{26}H_{34}O_{12}$。IR 显示该化合物结构中含有羟基 (3 384 cm^{-1}) 和苯环 (1 602、1 511、1 453 cm^{-1})。核磁数据见表 1。

化合物 **2**　白色无定形粉末。ESI-MS: *m/z* 541.2 $[M+H]^+$, $C_{26}H_{36}O_{12}$。^{1}H NMR (500 MHz, DMSO-d_6): δ_H 6.97 (1H, brs, H-2), 6.90 (1H, d, *J* = 8.5 Hz, H-5'), 6.81 (1H, brs, H-2'), 6.75 (1H, d, *J* = 8.5 Hz, H-6), 6.68 (1H, d, *J* = 8.5 Hz, H-5), 6.66 (1H, d, *J* = 8.5 Hz, H-6'), 4.70 (1H, brs, H-7), 4.16 (1H, dd, *J* = 9.5, 4.5 Hz, H-8), 4.10 (1H, d, *J* = 7.5 Hz, H-1''), 3.78 (1H, overlap, H-9'a), 3.74 (3H, s, 3-OCH_3), 3.71 (3H, s, 3'-OCH_3), 3.63 (1H, dd, *J* = 11.5, 5.5 Hz, H-6''a), 3.55 (1H, d, *J* = 11.0 Hz, H-9a), 3.43 (1H, m, H-6''b), 3.41 (1H, overlap, H-9'b), 3.21 (1H, m, H-9b), 3.10 (1H, m, H-5''), 3.04 (1H, m, H-4''), 3.01 (1H, m, H-3''), 2.93 (1H, m, H-2''), 2.56 (2H, t, *J* = 7.5 Hz, H-7'), 1.77(2H, m, H-8'); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 133.4 (C-1), 111.5 (C-2), 147.4 (C-3), 145.9 (C-4), 115.1 (C-5), 119.5 (C-6), 71.5 (C-7), 85.3 (C-8), 60.6 (C-9), 135.3 (C-1'), 113.4 (C-2'), 150.0 (C-3'), 146.8 (C-4'), 116.6 (C-5'), 120.7 (C-6'), 31.6 (C-7'), 31.7 (C-8'), 68.4 (C-9'), 103.4 (C-1''), 73.8 (C-2''), 77.1 (C-3''), 70.7 (C-4''), 76.0 (C-5''), 61.6 (C-6''), 56.1 (3-OCH_3), 55.9 (3'-OCH_3)。与文献[12]报道的化合物 (7*R*,8*R*)-7,9,9'-trihydroxy-3,3'-dimethoxy-8-*O*-4'-neolignan-9'-*O*-*β*-*D*-glucopyranoside 的波谱数据基本一致，故鉴定化合物 **2** 为 (7*R*,8*R*)-7,9,9'-trihydroxy-3,3'-dimethoxy-8-*O*-4'-neolignan-9'-*O*-*β*-*D*-glucopyranoside。

化合物 **3**　白色无定形粉末。ESI-MS: *m/z* 379.1 $[M+H]^+$, $C_{20}H_{26}O_7$。^{1}H NMR (500 MHz, DMSO-d_6): δ_H 6.96 (1H, brs, H-2), 6.90 (1H, d, *J* = 8.0 Hz, H-5), 6.78 (1H, brs, H-2'), 6.75 (1H, d, *J* = 8.0 Hz, H-5'), 6.66 (1H, d, *J* = 8.0 Hz, H-6), 6.63 (1H, d, *J* = 8.0 Hz, H-6'), 4.70 (1H, brs, H-7), 4.15 (1H, dd, *J* = 9.5, 4.5 Hz, H-8), 3.74 (3H, s, 3-OCH_3), 3.71 (3H, s, 3'-OCH_3), 3.55 (1H, m, H-9a), 3.39 (2H, overlap, H-9'), 3.23 (1H, overlap, H-9b), 2.51 (2H, overlap, H-7'), 1.67(2H, m, H-8'); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 133.4 (C-1), 111.5 (C-2), 147.4 (C-3), 145.9 (C-4), 115.2 (C-5), 119.5 (C-6), 71.5 (C-7), 85.4 (C-8), 60.6 (C-9), 135.7 (C-1'), 113.3 (C-2'), 150.0 (C-3'), 146.8 (C-4'), 116.7 (C-5'), 120.6 (C-6'), 31.7 (C-7'), 34.9 (C-8'), 60.5 (C-9'), 56.1 (3-OCH_3), 55.9 (3'-OCH_3)。与文献[14]报道的化合物 (7*R*,8*R*)-7,9,9'-trihydroxy-3,3'-dimethoxy-8-*O*-4'-neolignan 的波谱数据基本一致，故鉴定化合物 **3** 为 (7*R*,8*R*)-7,9,9'-trihydroxy-3,3'-dimethoxy-8-*O*-4'-neolignan。

化合物 **4**　白色无定形粉末。ESI-MS:*m/z* 523.2 $[M+H]^+$, $C_{26}H_{34}O_{11}$。^{1}H NMR (500 MHz, DMSO-d_6): δ_H 7.05 (1H, d, *J* = 8.5 Hz, H-5), 6.95 (1H, d, *J* = 2.0 Hz, H-2), 6.83 (1H, dd, *J* = 8.5, 2.0 Hz, H-6), 6.68 (2H, brs, H-2', H-6'), 4.96 (1H, d, *J* = 5.5 Hz, H-7), 4.87 (1H, d, *J* = 7.5 Hz, H-1''), 3.77 (3H, s, 3-OCH_3), 3.74 (3H, s, 3'-OCH_3), 3.69 (1H, overlap, H-6''a), 3.64 (1H, overlap, H-8), 3.59 (1H, overlap, H-9'a), 3.41 (3H, overlap, H-9'b, H-9), 3.41 (1H, m, H-6''b), 3.27 (2H, m, H-3'', H-5''), 3.23 (1H, m, H-2''), 3.15 (1H, m, H-4''), 2.52 (1H, overlap, H-7'), 1.68 (1H, m, H-8'); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 136.0 (C-1), 110.9 (C-2), 146.6 (C-3), 146.0 (C-4), 115.8 (C-5), 118.3 (C-6), 87.0 (C-7), 54.0 (C-8), 63.6 (C-9), 135.6 (C-1'), 113.0 (C-2'), 143.8 (C-3'), 149.4 (C-4'), 129.3 (C-5'), 116.9 (C-6'), 32.0 (C-7'), 35.2 (C-8'), 60.7 (C-9'), 100.5 (C-1''), 73.7 (C-2''), 77.5 (C-3''), 70.1 (C-4''), 77.3 (C-5''), 61.1 (C-6''), 56.2 (3-OCH_3), 56.2 (3'-OCH_3)。与文献[15]报道的化合物 (7*S*,8*R*)-dihydrodehydrodiconiferylalcohol-4-*O*-*β*-*D*-glucopyranoside 的波谱数据基本一致，故鉴定化合物 **4** 为 (7*S*,8*R*)-dihydrodehydrodiconiferylalcohol-4-*O*-*β*-*D*-glucopyranoside。

化合物 **5**　白色无定形粉末。ESI-MS: *m/z* 683.2 $[M+H]^+$, $C_{32}H_{42}O_{16}$。^{1}H NMR (500 MHz, DMSO-d_6): δ_H 7.04 (1H, d, *J* = 8.5 Hz, H-5), 7.03 (1H, d, *J* = 8.5 Hz, H-5'), 6.95 (2H, brs, H-2, H-2'), 6.83 (1H, d, *J* = 8.5 Hz, H-6), 6.82 (1H, d, *J* = 8.5 Hz, H-6'), 4.88 (1H, d, *J* = 7.5 Hz, H-1''), 4.86 (1H, d, *J* = 7.5 Hz, H-1'''), 4.79 (1H, d, *J* = 6.0 Hz, H-7), 4.37 (1H, d, *J* = 6.5 Hz, H-7'), 4.09 (1H, d, *J* = 9.0 Hz, H-9'a), 3.76 (6H, s, 3-OCH_3, 3'-OCH_3), 3.69 (2H, overlap, H-6''a, H-6'''a), 3.41 (5H, overlap, H-9, H-9'b, H-6''b, H-6'''b), 3.27 (4H, m, H-3'', H-5'', H-3''', H-5'''), 3.23 (2H, m, H-2'', H-2'''), 3.15 (2H, m, H-4'', H-4'''), 3.09 (1H, t, *J* = 3.5 Hz, H-8), 2.83 (1H, dd, *J* = 14.5, 6.0 Hz, H-8'); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 135.7 (C-1), 110.8 (C-2), 149.4 (C-3), 146.4 (C-4), 115.6 (C-5), 119.1 (C-6), 87.1 (C-7), 54.5 (C-8), 70.8 (C-9), 132.8 (C-1'), 110.5 (C-2'), 149.0 (C-3'), 145.9 (C-4'), 115.3 (C-5'), 118.1 (C-6'), 81.6 (C-7'), 49.7 (C-8'), 69.3 (C-9'), 100.6 (C-1''), 73.7 (C-2''), 77.5 (C-3''), 70.1 (C-4''), 77.3 (C-5''), 61.1 (C-6''), 100.6 (C-1''), 73.7 (C-2''), 77.5 (C-3''), 70.1 (C-4''), 77.3 (C-5''), 61.1 (C-6''), 56.1 (3-OCH_3), 56.1 (3'-OCH_3)。与文献[16]报道的化合物 (7*S*,8*R*,7'*R*,8'*R*)-pinoresinol-4,4'-di-*O*-*β*-*D*-glucopyranoside 的波谱数据基本一致，故鉴定化合物 **5** 为 (7*S*,8*R*,7'*R*,8'*R*)-pinoresinol-4,4'-di-*O*-*β*-*D*-glucopyranoside。

化合物 **6** 白色无定形粉末。ESI-MS: *m/z* 537.1 $[M+H]^+$, $C_{26}H_{32}O_{12}$。^{1}H NMR (500 MHz, DMSO-d_6): δ_H 7.55 (1H, d, *J* = 8.0 Hz, H-6), 7.50 (1H, brs, H-2), 7.05 (1H, d, *J* = 8.0 Hz, H-6'), 6.98 (1H, brs, H-2'), 6.88 (1H, d, *J* = 8.0 Hz, H-5), 6.86 (1H, d, *J* = 8.0 Hz, H-5'), 4.88 (1H, d, *J* = 7.5 Hz, H-1"), 4.58 (1H, d, *J* = 8.0 Hz, H-7'), 4.12 (1H, overlap, H-8'), 4.11 (1H, overlap, H-9a), 3.99 (1H, m, H-9b), 3.82 (3H, s, 3-OCH_3), 3.76 (3H, s, 3'-OCH_3), 3.65 (1H, d, *J* = 11.5 Hz, H-6"a), 3.49 (2H, m, H-9'), 3.44 (1H, overlap, H-6"b), 3.25 (2H, m, H-3", H-5"), 3.23 (1H, m, H-2"), 3.15 (1H, m, H-4"), 2.54 (1H, m, H-8); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 128.5 (C-1), 112.1 (C-2), 148.1 (C-3), 152.5 (C-4), 123.8 (C-5), 119.2 (C-6), 197.9 (C-7), 53.6 (C-8), 70.6 (C-9), 136.0 (C-1'), 111.3 (C-2'), 146.4 (C-3'), 149.2 (C-4'), 115.5 (C-5'), 115.5 (C-6'), 83.2 (C-7'), 49.2 (C-8'), 60.3 (C-9'), 100.5 (C-1"), 73.7 (C-2"), 77.5 (C-3"), 70.2 (C-4"), 77.4 (C-5"), 61.1 (C-6"), 56.1 (3-OCH_3), 56.1 (3'-OCH_3)。与文献[17]报道的化合物 (8*S*,7'*S*,8'*R*)-4,4',9'-trihydroxy-3,3'-dimethoxy-7',9-epoxylignan-7-oxo-4'-*O*-*β*-*D*-glucopyranoside 的波谱数据基本一致, 故鉴定化合物 **6** 为 (8*S*,7'*S*,8'*R*)-4,4',9'-trihydroxy-3,3'-dimethoxy-7',9-epoxylignan-7-oxo-4'-*O*-*β*-*D*-glucopyranoside。

化合物 **7** 白色无定形粉末。ESI-MS: *m/z* 435.1 $[M+H]^+$, $C_{18}H_{26}O_{12}$。^{1}H NMR (500 MHz, DMSO-d_6): δ_H 6.92 (1H, d, *J* = 8.5 Hz, H-6), 6.37 (1H, *J* = 2.0 Hz, H-3), 6.23 (1H, dd, *J* = 8.5, 2.0 Hz, H-5), 4.63 (1H, d, *J* = 7.5 Hz, H-1'), 4.15 (1H, d, *J* = 7.5 Hz, H-1"), 3.89 (1H, d, *J* = 11.5 Hz, H-6'a), 3.68 (3H, s, 2-OCH_3), 3.65 (1H, dd, *J* = 11.5, 5.5 Hz, H-5"a), 3.55 (1H, dd, *J* = 11.5, 7.0 Hz, H-6'b), 3.39 (1H, overlap, H-5'), 3.25 (1H, m, H-4'), 3.20 (1H, m, H-3'), 3.13 (1H, m, H-2"), 3.12 (1H, m, H-4"), 3.06 (1H, t, *J* = 8.0 Hz, H-3"), 2.95 (1H, overlap, H-2'), 2.95 (1H, t, *J* = 11.5 Hz, H-5"b); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C139.9 (C-1), 150.3 (C-2), 101.3 (C-3), 153.2 (C-4), 106.7 (C-5), 117.8 (C-6), 101.9 (C-1'), 73.8 (C-2'), 77.2 (C-3'), 70.2 (C-4'), 76.3 (C-5'), 68.8 (C-6'), 104.4 (C-1"), 73.9 (C-2"), 77.0 (C-3"), 70.1 (C-4"), 66.1 (C-5"), 56.0 (2-OCH_3)。与文献[18]报道的化合物 2-methoxy-4-hydroxyphenol-1-*O*-*β*-*D*-xylopyranosyl-(1→6)-*O*-*β*-*D*-glucopyranoside 的波谱数据基本一致, 故鉴定化合物 **7** 为 2-methoxy-4-hydroxyphenol-1-*O*-*β*-*D*-xylopyranosyl-(1→6)-*O*-*β*-*D*-glucopyranoside。

化合物 **8** 白色无定形粉末。ESI-MS: *m/z* 435.1 $[M+H]^+$, $C_{18}H_{26}O_{12}$。^{1}H NMR (500 MHz, DMSO-d_6): δ_H 6.64 (1H, d, *J* = 8.5 Hz, H-5), 6.61 (1H, d, *J* = 2.0 Hz, H-2), 6.48 (1H, dd, *J* = 8.5, 2.0 Hz, H-6), 4.63 (1H, d, *J* = 7.5 Hz, H-1'), 4.15 (1H, d, *J* = 7.5 Hz, H-1"), 3.89 (1H, d, *J* = 11.5 Hz, H-6'a), 3.72 (3H, s, 3-OCH_3), 3.65 (1H, dd, *J* = 11.5, 5.5 Hz, H-5"a), 3.55 (1H, dd, *J* = 11.5, 7.0 Hz, H-6'b), 3.45 (1H, overlap, H-5'), 3.25 (1H, m, H-4'), 3.20 (1H, m, H-3'), 3.13 (1H, m, H-2"), 3.12 (1H, m, H-4"), 3.06 (1H, t, *J* = 8.0 Hz, H-3"), 2.96 (1H, t, *J* = 11.5 Hz, H-5"b), 2.95 (1H, overlap, H-2'); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 151.2 (C-1), 104.6 (C-2), 148.3 (C-3), 141.8 (C-4), 115.8 (C-5), 108.4 (C-6), 102.0 (C-1'), 73.7 (C-2'), 77.1 (C-3'), 70.3 (C-4'), 76.2 (C-5'), 69.1 (C-6'), 102.7 (C-1"), 73.9 (C-2"), 77.0 (C-3"), 70.1 (C-4"), 66.2 (C-5"), 56.0 (3-OCH_3)。与文献[19]报道的化合物 3-methoxy-4-hydroxyphenol-1-*O*-*β*-*D*-xylopyranosyl-(1→6)-*O*-*β*-*D*-glucopyranoside 的波谱数据基本一致, 故鉴定化合物 **8** 为 3-methoxy-4-hydroxyphenol-1-*O*-*β*-*D*-xylopyranosyl-(1→6)-*O*-*β*-*D*-glucopyranoside。

化合物 **9** 白色无定形粉末。ESI-MS: *m/z* 449.1 $[M+H]^+$, $C_{19}H_{28}O_{12}$。^{1}H NMR (500 MHz, DMSO-d_6): δ_H 7.08 (1H, d, *J* = 8.5 Hz, H-5), 6.94 (1H, d, *J* = 2.0 Hz, H-2), 6.81 (1H, dd, *J* = 8.5, 2.0 Hz, H-6), 4.84 (1H, d, *J* = 7.5 Hz, H-1'), 4.42 (2H, d, *J* = 5.5 Hz, H-7), 4.15 (1H, d, *J* = 7.5 Hz, H-1"), 3.97 (1H, d, *J* = 11.5 Hz, H-6'a), 3.72 (3H, s, 3-OCH_3), 3.64 (1H, dd, *J* = 11.5, 5.5 Hz, H-5"a), 3.56 (1H, dd, *J* = 11.5, 7.0 Hz, H-6'b), 3.47 (1H, m, H-5'), 3.25 (1H, overlap, H-2'), 3.25 (1H, m, H-3'), 3.25 (1H, overlap, H-4"), 3.16 (1H, m, H-4'), 3.05 (1H, ddd, *J* = 13.5, 9.0, 5.0 Hz, H-3"), 2.94 (1H, m, H-2"), 2.89 (1H, t, *J* = 11.5 Hz, H-5"b); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 136.5 (C-1), 111.5 (C-2), 149.0 (C-3), 145.5 (C-4), 115.9 (C-5), 119.2 (C-6), 63.3 (C-7), 100.7 (C-1'), 73.7 (C-2'), 77.2 (C-3'), 70.0 (C-4'), 76.4 (C-5'), 68.6 (C-6'), 104.4 (C-1"), 73.9 (C-2"), 76.9 (C-3"), 70.0 (C-4"), 66.0 (C-5"), 56.0 (3-OCH_3)。与文献[20]报道的化合物 4-hydroxy-3-methoxybenzylalcohol-4-*O*-*β*-*D*-xylopyranosyl-(1→6)-*O*-*β*-*D*-glucopyranoside 的波谱数据基本一致, 故鉴定化合物 **9** 为 4-hydroxy-3-methoxybenzylalcohol-4-*O*-*β*-*D*-xylopyranosyl-(1→6)-*O*-*β*-*D*-glucopyranoside。

化合物 **10** 白色无定形粉末。ESI-MS: *m/z* 417.1 $[M+H]^+$, $C_{19}H_{28}O_{10}$。^{1}H NMR (500 MHz, DMSO-d_6): δ_H 7.16～7.26 (5H, m, H-2～H-6), 4.19 (1H, d, *J* = 7.5 Hz, H-1'), 4.18 (1H, d, *J* = 7.5 Hz, H-1"), 3.92 (1H, d, *J* = 11.5 Hz, H-6'a), 3.67 (2H, overlap, H-8a, H-5"a), 3.53 (1H, dd, *J* = 11.5, 7.0 Hz, H-6'b), 3.27 (1H, overlap, H-8b), 3.13 (1H, m, H-4'), 3.13 (1H, overlap, H-5'), 3.10 (1H, m, H-3'), 3.08 (2H, m, H-2", H-4"), 3.01 (1H, t, *J* = 8.0 Hz, H-3"), 2.97 (1H, t, *J* = 11.5 Hz, H-5"b),

2.94 (1H, overlap, H-2'), 2.85 (2H, t, J = 7.5 Hz, H-7)。与文献[21]报道的化合物 2-phenethyl β-primeveroside 的波谱数据基本一致，故鉴定化合物 **10** 为 2-phenethyl β-primeveroside。

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