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云南寻甸产臭参中化学成分研究

李小珍[1,2],晏永明[3],庄小翠[1,2],程永现[1,2,3]*

[1]中国科学院昆明植物研究所 植物化学与西部植物资源持续利用国家重点实验室,昆明 650201;
[2]云南中医学院,昆明 650500;[3] 深圳大学医学部药学院,深圳 518060

摘　要:采用色谱法从臭参中分离得到24个化合物,利用波谱学方法鉴定了它们的结构,分别鉴定为choushenglycolipid A(**1**)、(-)-(7*R*,8*S*,7′*E*)-4-hydroxy-3,5′-dimethoxy-7,4′-epoxy-8,3′-neolign-7′-ene-9,9′-diol 9′-ethyl ether(**2**)、(7*S*,8*R*)-dihydrodehydrodiconiferyl alcohol(**3**)、3-*O*-demethyldihydrodehydrodiconiferyl alcohol(**4**)、prunustosanan AI(**5**)、*threo*-guaiacylglycerol-*β*-*O*-4-lariciresinol ether(**6**)、(+)-落叶松脂素(**7**)、5′-methoxylariciresinol(**8**)、(-)-(7′*S*,8*S*,8′*R*)-4,4′-dihydroxy-3,3′,5,5′-tetramethoxy-7′,9-epoxy-lignan-9′-ol-7-one(**9**)、(7*S*,8*S*)-3-methoxy-3′,7-epoxy-8,4′-oxyneoligna-4,9-diol 9′-*O*-*β*-D-glucopyranoside(**10**)、(-)-secoisolariciresinol(**11**)、(+)-异落叶松脂素(**12**)、burselignan(**13**)、*threo*-guaiacylglycerol-*β*-*O*-4′-coniferyl ether(**14**)、4-[1-乙氧基-1-(4′-羟基-3′-甲氧基)苯基]甲基-2-(4-羟基-3-甲氧基)苯基-3-羟甲基四氢呋喃(**15**)、(-)-(7*R*,7′*R*,7″*R*,8*S*,8′*S*,8″*S*)-4′,4″-dihydroxy-3,3′,3″,5-tetramethoxy-7,9′:7′,9-diepoxy-4,8″-oxy-8,8′-sesquineolignan-7″,9″-diol(**16**)、连翘脂素-4′-*O*-*β*-D-葡萄糖苷(**17**)、retusin-8-methylether(**18**)、ladanein(**19**)、怀特酮(**20**)、3-methoxy-9-hydroxy-pterocarpan(**21**)、trichocarpin(**22**)、(*Z*)-8-*O*-*β*-D-glucopyranosyl cinnamic acid(**23**)和4-hydroxycinnamyl-*O*-*β*-D-glucopyranoside(**24**)。化合物**1**为新化合物,除化合物**7**、**11**~**13**、**23**和**24**外,其余化合物均为首次从本属中被分离得到。

关键词:寻甸;臭参;木脂素;黄酮

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Compounds from *Codonopsis pilosula* Produced in Xundian of Yunnan Province

LI Xiao-zhen[1,2], YAN Yong-ming[3], ZHUANG Xiao-cui[1,2], CHENG Yong-xian[1,2,3]*

[1]*State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650201, China*; [2]*Yunnan University of Traditional Chinese Medicine, Kunming 650500, China*; [3]*School of Pharmaceutical Sciences, Shenzhen University Health Science Center, Shenzhen 518060, China*

Abstract: Twenty four compounds were isolated from the roots of *Codonopsis pilosula* produced in Xundian of Yunnan province, which is well known as Choushen. Their structures were identified as choushenglycolipid A (**1**), (-)-(7*R*,8*S*,7′*E*)-4-hydroxy-3,5′-dimethoxy-7,4′-epoxy-8,3′-neolign-7′-ene-9,9′-diol 9′-ethyl ether (**2**), (7*S*,8*R*)-dihydrodehydrodiconiferyl alcohol (**3**), 3-*O*-demethyldihydrodehydrodiconiferyl alcohol (**4**), prunustosanan AI (**5**), *threo*-guaiacylglycerol-*β*-*O*-4-lariciresinol ether (**6**), (+)-lariciresinol (**7**), 5′-methoxylariciresinol (**8**), (-)-(7′*S*,8*S*,8′*R*)-4,4′-dihydroxy-3,3′,5,5′-tetramethoxy-7′,9-epoxy-lignan-9′-ol-7-one (**9**), (7*S*,8*S*)-3-methoxy-3′,7-epoxy-8,4′-oxyneoligna-4,9-diol 9′-*O*-*β*-D-glucopyranoside (**10**), (-)-secoisolariciresinol (**11**), (+)-isolariciresinol (**12**), burselignan (**13**), *threo*-guaiacylglycerol-*β*-*O*-4′-coniferyl ether (**14**), 4-[1-ethoxyl-1-(4-hydroxy-3-methoxy) benzyl] methyl-2-(4-hydroxy-3-methoxy) benzyl-3-hydroxymethyl-tetrahydro-furan (**15**), (-)-(7*R*,7′*R*,7″*R*,8*S*,8′*S*,8″*S*)-4′,4″-dihydroxy-3,3′,3″,5-tetramethoxy-7,9′:7′,9-diepoxy-4,8″-oxy-8,8′-sesquineolignan-7″,9″-diol (**16**), (+)-pinoresinol-4′-*O*-*β*-D-glucopyranoside (**17**), retusin-8-methylether (**18**), ladanein (**19**), wighteone (erythrinin B) (**20**), 3-methoxy-9-hydroxy-pterocarpan (**21**), trichocarpin (**22**), (*Z*)-8-*O*-*β*-D-glucopyranosylcinnamic acid (**23**) and 4-hydroxycinnamyl-*O*-*β*-D-glucopyranoside (**24**), respectively, by spectroscopic methods. Compound **1** is new and the other compounds with exception of compounds **7**, **11**-**13**, **23** and **24** were isolated from the genus *Codonopsis* for the first time.

Key words: Xundian; *Codonopsis pilosula*; lignans; flavones

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*通信作者 Tel:86-871-65223048;E-mail:yxcheng@mail.kib.ac.cn

臭参,俗名臭药、云南参、臭党参,是滇地知名食材,目前在云南的寻甸、宜良等地都有大量栽种,因

其根具有特殊臭味故名。食用臭参后人们普遍会出现矢气频频现象,表明臭参具有排除体内积气作用[1,2],因此秋冬季节云南产区的人们习惯将臭参作为廉价滋补品加以食用,历史已悠久。臭参为何物?长期以来莫衷一是,文献报导党参属多个植物的根均可作为臭参用,但寻甸和宜良地区栽培和应用历史悠久的臭参经洪德元院士鉴定为党参(*Codonopsis pilosula*)[3],党参是常用中药,具有健脾益肺,养血生津功效[4],通过文献检索,未见党参具有排除体内积气之作用。药材有道地之分,古有"橘生淮南则为橘,生于淮北则为枳"的描述,民间也有"一方水土养一方人"的俗语,产于云南山区高海拔地区的党参是否因环境因子的改变与北方产党参品质上有了差异或分化?此引起了作者的兴趣,希望通过系统的化学成分和药理作用研究逐步回答这一问题,也为臭参进一步研发成为系列特色保健食品和新资源食品原料提供最直接的支撑。

1 仪器与材料

Bruker Avance Ⅲ 400 MHz、Bruker Avance 600 MHz 和 Bruker Avance 800 MHz 核磁共振仪(TMS 为内标,δ 为 ppm,J 为 Hz);硅胶 GF_{254}(青岛海洋化工厂);RP-18(40 ~ 63 μm,日本 Daiso);MCI gel CHP 20P(75 ~ 150 μm,日本三菱公司产品);Sephadex LH-20(25 ~ 100 μm,Pharmacia 公司)。Agilent 1200 型 HPLC 和北京创新通恒 LC3000 型 HPLC,色谱柱为 Agilent Zorbax SB-C_{18}(250 mm × 9.4 mm,i.d.5 μm)。

臭参样品系 2015 年 11 月采集于云南省昆明市寻甸县金源乡妥托村委会老黑山村,系栽培品种,此地经年栽培的臭参此前经由中国科学院植物研究所洪德元研究员鉴定为党参(*Codonopsis pilosula*),其凭证标本(标本号:1016268)保存于中国科学院昆明植物研究所标本馆。

2 提取与分离

取干燥臭参根 13 kg,粉碎后用 80% 乙醇回流提取(78 L×3×3 h),提取液合并浓缩后得总提物,总提物用水混悬后依次用乙酸乙酯萃取 3 次,分别得乙酸乙酯萃取部分和水部分。其中乙酸乙酯部位(350 g)行 MCI gel CHP 20P 柱(甲醇/水,35% ~ 100%),梯度洗脱,得 10 个组分(C.1 ~ C.10)。其中 C.1(2.6 g)经硅胶柱层析,以石油醚/丙酮(10∶1,6∶1,3∶1,1∶1,0∶1)洗脱得 C.1.1-C.1.4。C.1.3(776 mg)经 Sephadex LH-20(MeOH)层析后,再经制备和半制备 HPLC(乙腈/水,10∶90)纯化得 24(2 mg)。C.4(14.4 g)经 Sephadex LH-20(MeOH)分离,得 C.4.1 ~ C.4.5。其中 C.4.3(3.0 g)经 RP-18 柱(甲醇/水,3∶7,4∶6,5∶5,6∶4,7∶3,8∶2,1∶0)得 C.4.3.1 ~ C.4.3.7。C.4.3.4 通过制备和半制备 HPLC(乙腈/水,25∶75)纯化得化合物 **10**(0.5 mg)。C.4.4(1.7 g)经 RP-18 柱(甲醇/水,3∶7,4∶6,5∶5,6∶4,7∶3,8∶2,1∶0)得 C.4.4.1-C.4.4.4。C.4.4.1(665 mg)经过制备薄层色谱(氯仿/甲醇,(0.05% 甲酸)20∶1)得 C.4.4.1.1-C.4.4.1.7。C.4.4.1.6 通过半制备 HPLC(甲醇/水,(0.05% 甲酸)36∶64)纯化得化合物 **13**(1.2 mg)、**14**(1.6 mg);C.4.4.1.7 通过半制备 HPLC(乙腈/水,(0.05% 甲酸)20∶80)纯化得化合物 **4**(4.2 mg)、**17**(10.2 mg)、**23**(6.7 mg)。C.4.4.2(552 mg)经过制备薄层色谱(氯仿/甲醇,(0.05% 甲酸)9∶1)得 C.4.4.2.1-C.4.4.2.5。其中 C.4.4.2.2 通过半制备 HPLC(甲醇/水,(0.05% 甲酸)45∶55)纯化得化合物 **7**(4.4 mg)、**8**(1.2 mg);C.4.4.2.3 通过半制备 HPLC(甲醇/水,(0.05% 甲酸)43∶57)纯化得化合物 **3**(29.5 mg)、**5**(0.6 mg)、**9**(1.1 mg)、**12**(6.2 mg)、**11**(24.3 mg);C.4.4.2.4 通过半制备 HPLC(甲醇/水,(0.05% 甲酸)43∶57)纯化得化合物 **6**(5.7 mg)。C.5(8.5 g)经 Sephadex LH-20(MeOH)凝胶过滤,得 C.5.1-C.5.5。其中 C.5.2(5.5 g)经 RP-18 柱(甲醇/水,11∶9,13∶7,15∶9,17∶3,19∶1,1∶0)得 C.5.2.1-C.5.2.4。C.5.2.2(2.1 g)经 Sephadex LH-20(MeOH)得 C.5.2.2.1-C.5.2.2.3。C.5.2.2.2(571 mg)经制备 HPLC(甲醇/水,40%-100%)得 C.5.2.2.2.1-C.5.2.2.2.4。其中 C.5.2.2.2.2(169 mg)分别经制备和半制备 HPLC(乙腈/水,28∶72)纯化得 **15**(0.4 mg);C.5.2.3(1.9 g)经 Sephadex LH-20(MeOH)得 C.5.2.3.1-C.5.2.3.4。C.5.2.3.2(1.6 g)经 RP-18 柱(甲醇/水,9∶11,11∶9,13∶7,15∶9,17∶3,19∶1,1∶0)得 C.5.2.3.2.1-C.5.2.3.2.8。C.5.2.3.2.2(341 mg)经半制备 HPLC(乙腈/水,(0.05% 甲酸)33∶67)纯化得化合物 **1**(1.1 mg)。C.5.3(1.3 g)经 RP-18 柱(甲醇/水,4∶6,5∶5,6∶4,7∶3,8∶2,9∶1,1∶0)得 C.5.3.1-C.5.3.6。C.5.3.3(102 mg)经过半制备 HPLC(甲醇/水,61∶39)纯化得化合物 **22**(1.1

mg)。C. 7 经过硅胶柱层析(石油醚/丙酮;10∶1,6∶1,3∶1,1∶1,0∶1)梯度洗脱得 C. 7. 1-C. 7. 6。其中,C. 7. 3(757 mg)经 Sephadex LH-20(MeOH)柱层析分离,得 C. 7. 3. 1-C. 7. 3. 3。C. 7. 3. 2(187 mg)经制备 HPLC(甲醇/水,69% ~ 100%)得 C. 7. 3. 2. 0-C. 7. 3. 2. 3。C. 7. 3. 2. 2 经半制备 HPLC(乙腈/水,43∶57)纯化得 **2**(1. 0 mg)、**18**(0. 5 mg)。C. 7. 4(478 mg)经 Sephadex LH-20(MeOH)柱层析分离得 3 个组分,C. 7. 4. 1-C. 7. 4. 4。C. 7. 4. 3(124 mg)经半制备 HPLC(乙腈/水,36∶64)纯化得 **16**(1. 2 mg)。C. 8(9. 0 g)经 Sephadex LH-20(MeOH)柱层析分离,得 C. 8. 1-C. 8. 5。其中 C. 8. 5(74 mg)经制备(乙腈/水,57∶43)后得 C. 8. 5. 1-C. 8. 5. 7。C. 8. 5. 2 通过半制备 HPLC(乙腈/水,42∶58)纯化得 **19**(1. 0 mg)、**21**(0. 5 mg);C. 8. 5. 6 通过半制备 HPLC(乙腈/水,52∶48)纯化得 **20**(2. 7 mg)。

3 结构鉴定

化合物 1 无色胶状物。UV(MeOH)λ_{max}(log ε) 208 (4. 02) nm. $[\alpha]_D^{24}$-25. 2 (c 0. 11, MeOH)通过^{13}C NMR、DEPT 谱及高分辨质谱 m/z 355. 1732 $[M+Na]^+$(calcd for $C_{16}H_{28}O_7Na$, 355. 1733)确定其分子式为 $C_{16}H_{28}O_7$,不饱和度为 3。化合物 **1** 的 ^{1}H NMR 和^{13}C NMR 谱中,在中场区显示一组典型的信号(表 1),表明一个葡萄糖残基的存在。^{1}H NMR 谱(表 1)中给出 2 质子信号(δ_H5. 89, d, J = 15. 6 Hz, H-2;δ_H7. 00, dq, J = 15. 6, 6. 9 Hz, H-3),表明结构中含有一个反式双键。^{1}H-^{1}H COSY 谱中可以看到 H-3/H-4 的相关,表明了甲基与双键相连。HMBC 谱(图 1)H-3/C-1 (($_C$168. 1)的相关,表明双键与羰基相连;H-6(/C-1 的相关表明 C-1 通过氧桥与葡萄糖的 C-6(相连。^{1}H-^{1}H COSY 谱中 H-1″/H-2″/H-3″/H-4″/H-5″/H-6″相关,表明 H-1″-H-6″自旋体系的存在。HMBC 谱中 H-1″/C-1″δ_C104. 4)相关表明上述自旋系统通过氧桥与葡萄糖的端基碳相连。最后,端基质子的偶合常数(δ_H4. 23, d, J = 7. 9 Hz, H-1′)显示苷键为 β 构型[5,6]。至此,化合物 **1** 的结构得以确定。其属于糖脂类化合物,为新化合物,将其命名为 choushenglycolipid A。

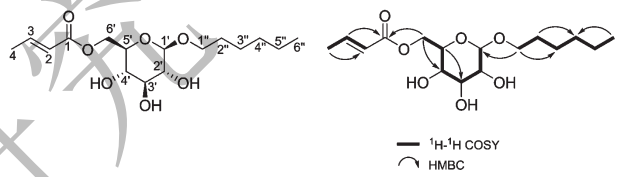

图 1 化合物 1 的关键^{1}H-^{1}H COSY 和 HMBC 相关

Fig. 1 Key ^{1}H-^{1}H COSY and HMBC correlations for **1**

表 1 化合物 1 的氢谱(600 MHz)和碳谱(150 MHz)数据(氘代甲醇)

Table 1 ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR data of compound **1** (δ in ppm, methanol-d_4)

Position	δ_H, (mult, J in Hz)	δ_C, mult	Position	δ_H, (mult, J in Hz)	δ_C, mult
1		168. 1 s	6′	4. 42 dd (11. 9, 1. 9)	64. 6 t
2	5. 89 d (15. 6)	123. 3 d		4. 24 dd (11. 9, 6. 2)	
3	7. 00 dq (15. 6, 6. 9)	146. 8 d	1″	3. 78 m	71. 1 t
4	1. 88 dd (6. 9, 1. 6)	18. 1 q		3. 54 m	
			2″	1. 60 m	30. 8 t
1′	4. 23 d (7. 9)	104. 4 d	3″	1. 34 m	26. 7 t
2′	3. 17 t-like (7. 9)	75. 3 d	4″	1. 32 overlapped	32. 8 t
3′	3. 33 m	77. 9 d	5″	1. 32 overlapped	23. 7 t
4′	3. 29 overlapped	71. 7 d	6″	0. 89 t (7. 0)	14. 4 q
5′	3. 46 m	75. 0 d			

化合物 2 淡黄色胶状物;^{1}H NMR (400 MHz, $CDCl_3$) δ: 6. 55 (5H, overlapped, H-2, H-5, H-6, H-2′, H-6′), 6. 55 (1H, d, J = 15. 8 Hz, H-7′), 6. 18 (1H, dt, J = 15. 8, 6. 2 Hz, H-8′), 5. 61 (1H, s, 4-OH), 5. 58 (1H, d, J = 5. 8 Hz, H-7), 4. 12 (2H, d, J = 6. 2 Hz, H-9′), 3. 96 (1H, m, Ha-9), 3. 93 (1H, m, Hb-9), 3. 90 (3H, s, 3-OMe), 3. 86 (3H, s, 5′-OMe), 3. 62 (1H, dd, J = 11. 9, 5. 8 Hz, H-8), 3. 55 (2H, q, J = 7. 0 Hz, H-10′), 1. 25 (3H, t, J = 7. 0 Hz, H-11′);^{13}C NMR (150 MHz, $CDCl_3$) δ: 148. 4

(C-4′),146.8 (C-3),145.9 (C-4),144.6 (C-5′),133.0 (C-1),132.4 (C-7′),131.2 (C-1′),128.1 (C-3′),124.4 (C-8′),119.6 (C-6),114.9 (C-2′),114.4 (C-5),110.5 (C-6′),108.9 (C-2),88.4 (C-7),71.5 (C-9′),65.8 (C-10′),64.1 (C-9),56.1 (3-OMe),56.1 (5′-OMe),53.7 (C-8),15.4 (C-11′)。以上数据和文献[7]对照基本一致,故确定化合物 **2** 为(-)-(7*R*,8*S*,7′*E*)-4-hydroxy-3,5′-dimethoxy-7,4′-epoxy-8,3′-neolign-7′-ene-9,9′-diol 9′-ethyl ether。

化合物 3 淡黄色胶状物;^{1}H NMR (400 MHz, methanol-d_4) δ:6.92 (1H,d, J = 1.6 Hz,H-2),6.79 (1H,dd, J = 8.0,1.6 Hz,H-6),6.73 (1H,d, J = 8.0 Hz,H-5),6.69 (2H,overlapped,H-2′,H-6′),5.46 (1H,d, J = 6.3 Hz,H-7),3.81 (3H,s,5′-OMe),3.77 (3H,s,3-OMe),3.72 (2H,overlapped,H-9),3.54 (2H,t, J = 6.4 Hz,H-9′),3.44 (1H,dd, J = 11.0,6.3 Hz,H-8),2.58 (2H,t, J = 7.5 Hz,H-7′),1.78 (2H,m,H-8′);^{13}C NMR (150 MHz, methanol-d_4) δ:149.0 (C-3),147.4 (C-4),147.4 (C-4′),145.1 (C-5′),136.9 (C-1′),134.7 (C-1),129.8 (C-3′),119.7 (C-6),117.9 (C-2′),116.1 (C-5),114.0 (C-6′),110.5 (C-2),89.0 (C-7),64.9 (C-9),62.2 (C-9′),56.7 (5′-OMe),56.3 (3-OMe),55.3 (C-8),35.8 (C-8′),32.9 (C-7′)。以上数据和文献[8]对照基本一致,故确定化合物 **3** 为(7*S*,8*R*)-dihydrodehydrodiconiferyl alcohol。

化合物 4 淡黄色胶状物;^{1}H NMR (400 MHz, methanol-d_4) δ:6.96 (1H,d, J = 1.6 Hz,H-2),6.82 (1H,dd, J = 8.1,1.6 Hz,H-6),6.74 (1H,d, J = 8.1 Hz,H-5),6.59 (1H,br s,H-2′),6.55 (1H,br s,H-6′),5.47 (1H,d, J = 6.1 Hz,H-7),3.79 (3H,s,5′-OMe),3.73 (2H,overlapped,H-9),3.53 (2H,t, J = 6.1 Hz,H-9′),3.42 (1H,dd, J = 12.4,6.1 Hz,H-8),2.54 (2H,t, J = 7.5 Hz,H-7′),1.77 (2H,m,H-8′);^{13}C NMR (150 MHz,methanol-d_4) δ:149.0 (C-3),147.3 (C-4),146.5 (C-4′),141.8 (C-5′),136.7 (C-1′),135.1 (C-1),129.8 (C-3′),119.6 (C-6),117.0 (C-2′),116.7 (C-5),116.1 (C-6′),110.5 (C-2),88.7 (C-7),65.1 (C-9),62.3 (C-9′),56.4 (5′-OMe),55.7 (C-8),35.8 (C-8′),32.7 (C-7′)。以上数据和文献[9]对照基本一致,故确定化合物 **4** 为 3-*O*-demethyldihydrodehydrodiconiferyl alcohol。

化合物 5 淡黄色胶状物;^{1}H NMR (400 MHz, $CDCl_3$) δ:7.54 (1H,s,H-2′),7.53 (1H,s,H-6′),6.90 (3H,overlapped,H-2,H-5,H-6),5.67 (1H,d, J = 7.0 Hz,H-7),4.02 (4H,overlapped,H-9,H-9′),3.95 (3H,s,5′-OMe),3.87 (3H,s,3-OMe),3.69 (1H,dd, J = 12.2,6.0 Hz,H-8),3.20 (2H,m,H-8′);^{13}C NMR (150 MHz,$CDCl_3$) δ:199.0 (C-7′),153.4 (C-4′),148.0 (C-3),146.1 (C-4),144.7 (C-5′),132.2 (C-1),131.4 (C-3′),128.3 (C-1′),119.6 (C-2′),118.3 (C-6),114.6 (C-5),112.3 (C-6′),108.8 (C-2),89.4 (C-7),64.1 (C-9),58.5 (C-9′),56.3 (5′-OMe),56.2 (3-OMe),53.0 (C-8),40.1 (C-8′)。以上数据和文献[10]对照基本一致,故确定化合物 **5** 为 prunustosanan AI。

化合物 6 淡黄色胶状物;^{1}H NMR (400 MHz, methanol-d_4) δ:6.98 (1H,d, J = 2.0 Hz,H-2″),6.89 (1H,d, J = 1.6 Hz,H-2′),6.75-6.81 (5H,m,H-2,H-5,H-6′,H-5″,H-6″),6.70 (1H,d, J = 8.1 Hz,H-5′),6.65 (1H,dd, J = 8.1,1.5 Hz,H-6),4.79 (1H,d, J = 5.9 Hz,H-7″),4.70 (1H,d, J = 6.9 Hz,H-7′),4.30 (1H,m,H-8″),3.95 (1H,dd, J = 8.3,6.4 Hz,Ha-9),3.82 (3H,s,3′-OMe),3.83 (1H,overlapped,Ha-9″),3.79 (1H,overlapped,Ha-9′),3.77 (3H,s,3″-OMe),3.77 (1H,m,Hb-9″),3.76 (3H,s,3-OMe),3.72 (1H,dd, J = 8.2,5.8 Hz,Hb-9),3.61 (1H,dd, J = 11.0,6.4 Hz,Hb-9′),2.91 (1H,dd, J = 12.5,4.6 Hz,Ha-7),2.69 (1H,m,H-8),2.48 (1H,dd, J = 12.5,11.5 Hz,Hb-7),2.35 (1H,m,H-8′);^{13}C NMR (150 MHz,methanol-d_4) δ:151.8 (C-3),149.0 (C-3′),148.7 (C-3″),147.5 (C-4),147.0 (C-4″),146.9 (C-4′),136.5 (C-1),135.7 (C-1′),134.1 (C-1″),122.2 (C-6),121.1 (C-6″),119.8 (C-6′),119.3 (C-5′),116.0 (C-5),115.6 (C-5″),114.2 (C-2),111.8 (C-2″),110.6 (C-2′),86.4 (C-8″),84.0 (C-7′),74.1 (C-7″),73.4 (C-9),62.3 (C-9″),60.4 (C-9′),56.5 (3-OMe),56.4 (3″-OMe),56.3 (3′-OMe),54.0 (C-8′),43.8 (C-8),33.7 (C-7)。以上数据和文献[11]对照基本一致,故确定化合物 **6** 为 *threo*-guaiacylglycerol-β-*O*-4-lariciresinol ether。

化合物 7 淡黄色胶状物;^{1}H NMR (400 MHz, methanol-d_4) δ:6.89 (1H,d, J = 2.0 Hz,H-2),6.78

(1H,d, J = 1.9 Hz,H-2′),6.74 (2H,overlapped,H-5,H-6),6.70 (1H,d,J = 8.0 Hz,H-5′),6.63 (2H,dd,J = 8.0,1.9 Hz,H-6′),4.73 (1H,d, J = 6.9 Hz,H-7),3.96 (1H,dd, J = 8.1,6.6 Hz,Hb-9′),3.82 (3H,s,3′-OMe),3.81 (3H,s,3-OMe),3.81 (1H,overlapped,Hb-9),3.70 (1H,dd, J = 8.1,6.0 Hz,Ha-9′),3.61 (1H,dd, J = 10.9,6.1 Hz,Ha-9),2.91 (1H,dd, J = 13.4,4.6 Hz,Hb-7′),2.72 (1H,m,H-8′),2.47 (1H,dd, J = 13.4,11.7 Hz,Ha-7′),2.36 (1H,m,H-8);^{13}C NMR (150 MHz,methanol-d_4) δ:149.0 (C-3,C-3′),147.0 (C-4),145.8 (C-4′),135.8 (C-1),133.5 (C-1′),122.2 (C-6′),119.8 (C-6),116.2 (C-5′),116.0 (C-5),113.4 (C-2′),110.6 (C-2),84.0 (C-7),73.5 (C-9′),60.4 (C-9),56.4 (3-OMe),56.4 (3′-OMe),54.0 (C-8),43.9 (C-8′),33.6 (C-7′)。以上数据和文献[12]对照基本一致,故确定化合物 **7** 为(+)-落叶松脂素。

化合物 8 无色透明胶状物;^{1}H NMR (400 MHz,$CDCl_3$) δ:6.84 (1H,d, J = 8.5 Hz,H-5),6.69 (2H,overlapped,H-2,H-6),6.57 (2H,s,H-2′,H-6′),5.49 (1H,s,4-OH),5.46 (1H,s,4′-OH),4.80 (1H,d, J = 6.4 Hz,H-7′),4.06 (1H,dd, J = 8.5,6.7 Hz,Ha-9),3.94 (1H,m,Ha-9′),3.89 (6H,s,3′-OMe,5′-OMe),3.87 (3H,s,3-OMe),3.80 (1H,dd, J = 11.2,6.9 Hz,Hb-9′),3.77 (1H,dd, J = 8.5,5.7 Hz,Hb-9),2.91 (1H,dd, J = 13.4,5.2 Hz,Ha-7),2.72 (1H,m,H-8),2.55 (1H,dd, J = 13.4,10.7 Hz,Hb-7),2.41 (1H,m,H-8′);^{13}C NMR (150 MHz,$CDCl_3$) δ:147.2 (C-3′,C-5′),146.7 (C-3),144.2 (C-4),134.2 (C-4′),134.1 (C-1′),132.4 (C-1),121.3 (C-6),114.6 (C-5),111.3 (C-2),102.6 (C-2′,C-6′),83.2 (C-7′),73.1 (C-9),61.2 (C-9′),56.5 (3′-OMe,5′-OMe),56.1 (3-OMe),52.7 (C-8′),42.5 (C-8),33.5 (C-7)。以上数据和文献[13]对照基本一致,故确定化合物 **8** 为5′-methoxylariciresinol。

化合物 9 淡黄色固体;^{1}H NMR (400 MHz,$CDCl_3$) δ:7.31 (2H,s,H-2,H-6),6.68 (2H,s,H-2′,H-6′),6.00 (1H,s,4-OH),5.51 (1H,s,4′-OH),4.68 (1H,d, J = 8.9 Hz,H-7′),4.30 (1H,m,H-8),4.21 (2H,m,H-9),3.98 (6H,s,3-OMe,5-OMe),3.92 (6H,s,3′-OMe,5′-OMe),3.81 (1H,m,Ha-9′),3.72 (1H,dd, J = 10.6,5.3 Hz,Hb-9′),2.89 (1H,m,H-8′);^{13}C NMR (150 MHz,$CDCl_3$) δ:197.9 (C-7),147.3 (C-3,C-5),147.1 (C-3′,C-5′),140.3 (C-4),134.7 (C-4′),131.6 (C-1′),128.3 (C-1),106.1 (C-2,C-6),103.6 (C-2′,C-6′),84.2 (C-7′),70.9 (C-9),61.5 (C-9′),56.7 (3-OMe,5-OMe),56.5 (3′-OMe,5′-OMe),52.6 (C-8′),49.6 (C-8)。以上数据和文献[14]对照基本一致,故确定化合物 **9** 为(-)-(7′S,8S,8′R)-4,4′-dihydroxy-3,3′,5,5′-tetramethoxy-7′,9-epoxy-lignan-9′-ol-7-one。

化合物 10 淡黄色胶状物;^{1}H NMR (800 MHz,methanol-d_4) δ:6.98 (1H,d,J = 1.8 Hz,H-2),6.88 (1H,dd,J = 8.1,1.8 Hz,H-6),6.84 (1H,d,J = 8.3 Hz,H-5′),6.82 (1H,d,J = 8.1 Hz,H-5),6.76 (1H,d,J = 1.8 Hz,H-2′),6.71 (1H,dd,J = 8.3,1.8 Hz,H-6′),4.87 (1H,overlapped,H-7),4.24 (1H,d,J = 7.8 Hz,H-1″),4.00 (1H,m,H-8),3.89 (1H,dt,J = 9.6,6.5 Hz,Ha-9′),3.86 (3H,s,3-OMe),3.84 (1H,m,Ha-6″),3.66 (2H,overlapped,Hb-6″,H-9),3.53 (1H,dt,J = 9.6,6.5 Hz,Hb-9′),3.45 (1H,dd,J = 12.2,4.6 Hz,H-9),3.33 (1H,m,H-3″),3.29 (1H,m,H-4″),3.24 (1H,m,H-5″),3.18 (1H,m,H-2″),2.61 (2H,t,J = 7.6 Hz,H-7′),1.87 (2H,m,H-8′);^{13}C NMR (200 MHz,methanol-d_4) δ:149.2 (C-3),148.3 (C-4),145.0 (C-3′),143.0 (C-4′),136.5 (C-1′),129.7 (C-1),122.5 (C-6′),121.7 (C-6),117.8 (C-2′),117.7 (C-5′),116.3 (C-5),112.0 (C-2),104.4 (C-1″),79.8 (C-8),78.1 (C-3″),77.9 (C-5″),77.7 (C-7),75.1 (C-2″),71.6 (C-4″),70.0 (C-9′),62.7 (C-6″),62.2 (C-9),56.5 (3-OMe),32.7 (C-8′),32.4 (C-7′)。以上数据和文献[15]对照基本一致,故确定化合物 **10** 为(7S,8S)-3-methoxy-3′,7-epoxy-8,4′-oxyneoligna-4,9-diol 9′-O-β-D-glucopyranoside。

化合物 11 淡黄色胶状物;^{1}H NMR (400 MHz,methanol-d_4) δ:6.65 (2H,br d, J = 8.0 Hz,H-5′,H-5″),6.57 (2H,br s,H-2′,H-2″),6.53 (2H,br d, J = 8.0 Hz,H-6′,H-6″),3.71 (6H,s,3′-OMe,3″-OMe),3.57 (4H,m,H-1,H-4),2.66 (2H,dd, J = 13.8,7.0 Hz,Hb-7′,Hb-7″),2.54 (2H,dd, J = 13.8,7.0 Hz,Ha-7′,Ha-7″),1.90 (2H,m,H-2,H-

3);^{13}C NMR (150 MHz, methanol-d_4) δ:148.8 (C-3′, C-3″), 145.4 (C-4′, C-4″), 133.9 (C-1′, C-1″), 122.7 (C-6′, C-6″), 115.7 (C-5′, C-5″), 113.3 (C-2′, C-2″), 62.1 (C-4), 56.1 (3′-OMe, 3″-OMe), 44.0 (C-2, C-3), 36.0 (C-7′, C-7″)。以上数据和文献[12]对照基本一致,故确定化合物 **11** 为(-)-secoisolariciresinol。

化合物 12 淡黄色胶状物;^{1}H NMR (400 MHz, methanol-d_4) δ:6.72 (1H, d, J = 8.0 Hz, H-5), 6.65 (1H, d, J = 1.8 Hz, H-2), 6.64 (1H, s, H-2′), 6.59 (1H, dd, J = 8.0, 1.8 Hz, H-6), 6.16 (1H, s, H-5′), 3.79 (3H, s, 3′-OMe), 3.79 (1H, overlapped, H-7), 3.75 (3H, s, 3-OMe), 3.65 (3H, m, Ha-9, H-9′), 3.37 (1H, dd, J = 11.0, 3.9 Hz, Hb-9), 2.76 (2H, d, J = 7.7 Hz, H-7′), 1.97 (1H, m, H-8′), 1.72 (1H, m, H-8);^{13}C NMR (150 MHz, methanol-d_4) δ:149.0 (C-3), 147.2 (C-3′), 145.9 (C-4), 145.2 (C-4′), 138.7 (C-1), 134.1 (C-6′), 129.0 (C-1′), 123.2 (C-6), 117.3 (C-5′), 116.0 (C-5), 113.8 (C-2), 112.4 (C-2′), 65.9 (C-9′), 62.2 (C-9), 56.4 (3′-OMe), 56.3 (3-OMe), 48.0 (C-7), 48.0 (C-8), 39.9 (C-8′), 33.6 (C-7′)。以上数据和文献[16]对照基本一致,故确定化合 **12** 为(+)-异落叶松脂素。

化合物 13 黄色胶状物;^{1}H NMR (400 MHz, $CDCl_3$) δ:6.77 (1H, d, J = 8.0 Hz, , H-5), 6.62 (1H, br s, H-2), 6.54 (1H, br s, H-2′), 6.53 (1H, dd, J = 8.0, 1.8 Hz, H-6), 6.45 (1H, s, H-5′), 5.48 (1H, s, 4-OH), 5.36 (1H, s, 4′-OH), 4.10 (1H, d, J = 4.6 Hz, H-7), 3.87 (3H, s, 3′-OMe), 3.76 (3H, s, 3-OMe), 3.77-3.91 (2H, m, H-9′), 3.67 (1H, dd, J = 11.1, 4.6 Hz, Ha-9), 3.53 (1H, dd, J = 11.1, 6.3 Hz, Hb-9), 2.87 (1H, dd, J = 16.7, 5.1 Hz, Ha-7′), 2.76 (1H, dd, J = 16.7, 10.7 Hz, Hb-7′), 2.13 (2H, overlapped, H-8, H-8′);^{13}C NMR (150 MHz, $CDCl_3$) δ:146.2 (C-3), 145.5 (C-3′), 144.4 (C-4), 144.0 (C-4′), 135.3 (C-1), 131.8 (C-6′), 127.4 (C-1′), 122.6 (C-6), 115.3 (C-5′), 114.1 (C-5), 112.4 (C-2), 110.2 (C-2′), 65.7 (C-9′), 65.4 (C-9), 56.1 (3-OMe), 56.0 (3′-OMe), 47.9 (C-7), 43.7 (C-8), 35.1 (C-8′), 32.8 (C-7′)。以上数据和文献[16]对照基本一致,故确定化合物 **13** 为 burselignan。

化合物 14 无色透明胶状物;^{1}H NMR (400 MHz, methanol-d_4) δ:7.05 (1H, d, J = 1.6 Hz, H-2′), 7.04 (1H, d, J = 1.6 Hz, H-2), 6.98 (1H, d, J = 8.3 Hz, H-5′), 6.89 (1H, dd, J = 8.3, 1.6 Hz, H-6′), 6.84 (1H, dd, J = 8.1, 1.6 Hz, H-6), 6.74 (1H, d, J = 8.1 Hz, H-5), 6.52 (1H, d, J = 8.1 Hz, H-7′), 6.24 (1H, dt, J = 15.8, 5.7 Hz, H-8′), 4.87 (1H, overlapped, H-7), 4.28 (1H, m, H-8), 4.19 (2H, br d, J = 5.7 Hz, H-9′), 3.86 (3H, s, 3-OMe), 3.80 (3H, s, 3′-OMe), 3.72 (1H, dd, J = 11.9, 4.0 Hz, Ha-9), 3.46 (1H, dd, J = 11.9, 5.4 Hz, Hb-9);^{13}C NMR (150 MHz, methanol-d_4) δ:151.7 (C-3′), 149.2 (C-4′), 148.8 (C-3), 147.2 (C-4), 133.7 (C-1), 133.1 (C-1′), 131.4 (C-7′), 128.6 (C-8′), 120.8 (C-6), 120.7 (C-6′), 118.7 (C-5′), 115.8 (C-5), 111.7 (C-2′), 111.2 (C-2), 87.0 (C-8), 74.0 (C-7), 63.7 (C-9′), 61.9 (C-9), 56.5 (3-OMe), 56.3 (3′-OMe)。以上数据和文献[17]对照基本一致,故确定化合物 **14** 为 *threo*-guaiacylglycerol-β-*O*-4′-coniferyl ether。

化合物 15 淡黄色胶状物;^{1}H NMR (600 MHz, $CDCl_3$) δ:6.87 (1H, d, J = 8.0 Hz, H-5′), 6.85 (1H, d, J = 8.0 Hz, H-5″), 6.80 (1H, br d, J = 1.8 Hz, H-2′), 6.76 (1H, br dd, J = 8.0, 1.8 Hz, H-6′), 6.75 (1H, br dd, J = 8.0, 1.8 Hz, H-6″), 6.74 (1H, br d, J = 1.8 Hz, H-2″), 5.60 (1H, s, 3′-OH), 5.56 (1H, s, 3″-OH), 4.46 (1H, d, J = 8.0 Hz, H-2), 4.17 (1H, d, J = 7.9 Hz, H-7), 4.13 (1H, dd, J = 9.2, 5.1 Hz, Ha-5), 4.03 (1H, dd, J = 8.9, 8.0 Hz, Hb-5), 3.86 (3H, s, 3′-OMe), 3.85 (3H, s, 3″-OMe), 3.40 (1H, m, Ha-8), 3.32 (1H, m, Hb-8), 3.32 (2H, m, H-6), 2.57 (1H, m, H-4), 1.99 (1H, m, H-3), 1.17 (1H, t, J = 6.8 Hz, H-9);^{13}C NMR (150 MHz, $CDCl_3$) δ:146.9 (C-3′), 146.7 (C-3″), 145.6 (C-4′), 145.3 (C-4″), 133.7 (C-1″), 131.6 (C-1′), 121.2 (C-6′), 119.5 (C-6″), 114.2 (C-5′), 114.2 (C-5″), 109.7 (C-2′), 108.8 (C-2″), 84.1 (C-2), 83.2 (C-7), 70.8 (C-5), 64.3 (C-8), 63.2 (C-6), 56.1 (3′-OMe), 56.0 (3″-OMe), 51.8 (C-3), 50.1 (C-4), 15.3 (C-9)。以上数据和文献[18]对照基本一致,故确定化合物 **15** 为 4-[1-乙氧基-1-(4′-羟基-3′-甲氧基)苯基]甲基-2-(4-羟基-3-甲氧基)苯基-3-羟甲基四氢呋喃。

化合物 16 白色固体;^{1}H NMR (400 MHz, methanol-d_4) δ: 6.98 (1H, d, J = 1.5 Hz, H-2′), 6.95 (1H, d, J = 1.5 Hz, H-2″), 6.81 ~ 6.85 (2H, overlapped, H-5′, H-5″), 6.73 ~ 6.78 (2H, overlapped, H-6′, H-6″), 6.69 (2H, s, H-2, H-6), 4.97 (1H, overlapped, H-7″), 4.76 (1H, d, J = 4.3 Hz, H-7′), 4.71 (1H, d, J = 4.3 Hz, H-7), 4.27 (2H, m, Ha-9, Ha-9′), 4.09 (1H, m, H-8″), 3.88 (2H, overlapped, Hb-9, Hb-9′), 3.87 (6H, s, 3-OMe, 5-OMe), 3.86 (6H, s, 3′-OMe, 5′-OMe), 3.82 (6H, s, 3″-OMe, 5″-OMe), 3.76 (1H, dd, J = 12.1, 3.6 Hz, Ha-9″), 3.35 (1H, m, Hb-9″), 3.13 (2H, m, H-8, H-8′); ^{13}C NMR (150 MHz, methanol-d_4) δ: 154.3 (C-3, C-5), 149.1 (C-3″), 148.7 (C-3′), 147.4 (C-4′), 147.1 (C-4″), 139.1 (C-1), 136.6 (C-4), 133.7 (C-1′), 133.5 (C-1″), 120.8 (C-6′), 120.1 (C-6″), 116.1 (C-5′), 115.8 (C-5″), 111.6 (C-2′), 111.0 (C-2″), 104.2 (C-2, C-6), 88.8 (C-8″), 87.5 (C-7), 87.2 (C-7′), 74.4 (C-7″), 72.9 (C-9), 72.7 (C-9′), 61.8 (C-9″), 56.7 (3-OMe, 5-OMe), 56.4 (3′-OMe, 5′-OMe), 56.3 (3″-OMe, 5″-OMe), 55.8 (C-8′), 55.3 (C-8)。以上数据和文献[19]对照基本一致,故确定化合物 **16** 为(-)-(7*R*, 7′*R*, 7″*R*, 8*S*, 8′*S*, 8″*S*)-4′, 4″-dihydroxy-3, 3′, 3″, 5-tetramethoxy-7, 9′: 7′, 9-diepoxy-4, 8″-oxy-8, 8′-sesquineolignan-7″, 9″-diol。

化合物 17 黄色胶状物;^{1}H NMR (400 MHz, methanol-d_4) δ: 7.13 (1H, d, J = 8.3 Hz, H-5″), 7.01 (1H, d, J = 1.3 Hz, H-2″), 6.90 ~ 6.93 (2H, overlapped, H-6′, H-6″), 6.75 ~ 6.79 (2H, overlapped, H-2′, H-5′), 4.86 (1H, overlapped, H-1‴), 4.74 (1H, d, J = 3.5 Hz, H-6), 4.69 (1H, d, J = 4.1 Hz, H-2), 4.22 (2H, m, H-4), 3.85 (3H, s, 3″-OMe), 3.83 (3H, s, 3′-OMe), 3.67 (1H, m, Ha-8), 3.38 (1H, overlapped, Hb-8), 3.10 (2H, overlapped, H-1, H-5); ^{13}C NMR (150 MHz, methanol-d_4) δ: 150.9 (C-3″), 149.1 (C-3′), 147.5 (C-4″), 147.3 (C-4′), 137.4 (C-1″), 133.7 (C-1′), 120.1 (C-6′), 119.8 (C-6″), 117.9 (C-5″), 116.1 (C-5′), 111.6 (C-2″), 111.0 (C-2′), 102.8 (C-1‴), 87.5 (C-2), 87.1 (C-6), 78.2 (C-5‴), 77.8 (C-3‴), 74.9 (C-2‴), 72.7 (C-4), 71.3 (C-4‴), 62.5 (C-6‴), 56.7 (3″-OMe), 56.4 (3′-OMe), 55.5 (C-1), 55.3 (C-5)。以上数据和文献[19]对照基本一致,故确定化合物 **17** 为连翘脂素-4′-*O*-*β*-D-葡萄糖苷。

化合物 18 淡黄色固体;^{1}H NMR (800 MHz, $CDCl_3$) δ: 7.98 (1H, d, J = 8.8 Hz, H-5), 7.97 (1H, s, H-2), 7.50 (2H, d, J = 8.8 Hz, H-2′, H-6′), 7.05 (1H, J = 8.8 Hz, H-6), 6.98 (2H, d, J = 8.8 Hz, H-3′, H-5′), 4.09 (3H, s, 8-OMe), 3.85 (3H, s, 4′-OMe); ^{13}C NMR (200 MHz, $CDCl_3$) δ: 175.9 (C-4), 159.8 (C-4′), 153.1 (C-7), 151.5 (C-2), 150.1 (C-9), 134.0 (C-8), 130.3 (C-2′, C-6′), 125.0 (C-3), 124.1 (C-1′), 122.4 (C-5), 119.2 (C-10), 114.2 (C-3′, C-5′), 113.9 (C-6), 62.1 (8-OMe), 55.5 (4′-OMe)。以上数据和文献[20]对照基本一致,故确定化合物 **18** 为 retusin-8-methylether。

化合物 19 黄色固体;^{1}H NMR (800 MHz, $CDCl_3$) δ: 12.60 (1H, s, 5-OH), 7.85 (2H, d, J = 7.9 Hz, H-2′, H-6′), 7.02 (2H, d, J = 7.9 Hz, H-3′, H-5′), 6.60 (2H, overlapped, H-3, H-8), 4.01 (3H, s, OMe), 3.90 (3H, s, OMe); ^{13}C NMR (200 MHz, $CDCl_3$) δ: 182.8 (C-4), 164.4 (C-2), 162.7 (C-4′), 152.9 (C-7), 150.8 (C-5), 145.8 (C-9), 129.7 (C-6), 128.2 (C-2′, C-6′), 123.9 (C-1′), 114.7 (C-3′, C-5′), 106.0 (C-10), 104.2 (C-3), 90.6 (C-8), 56.6 (OMe), 55.7 (OMe)。以上数据和文献[21]对照基本一致,故确定化合物 **19** 为 ladanein。

化合物 20 黄色固体;^{1}H NMR (400 MHz, methanol-d_4) δ: 8.00 (1H, s, H-2), 7.35 (2H, d, J = 7.4 Hz, H-2′, H-6′), 6.83 (2H, d, J = 7.4 Hz, H-3′, H-5′), 6.34 (1H, s, H-8), 5.23 (1H, t, J = 5.2 Hz, H-2″), 3.30 (2H, overlapped, H-1″), 1.77 (3H, s, H-5″), 1.65 (3H, s, H-4″); ^{13}C NMR (150 MHz, methanol-d_4) δ: 182.1 (C-4), 164.6 (C-7), 160.5 (C-5), 158.7 (C-4′), 157.7 (C-9), 154.4 (C-2), 132.0 (C-3″), 131.4 (C-2′, C-6′), 124.5 (C-3), 123.6 (C-1′), 123.6 (C-2″), 116.2 (C-3′, C-5′), 113.3 (C-6), 105.9 (C-10), 94.1 (C-8), 26.0 (C-4″), 22.3 (C-1″), 17.9 (C-5″)。以上数据和文献[22]对照基本一致,故确定化合物 **20** 为怀特酮。

化合物 21 黄色胶状物;^{1}H NMR (800 MHz, $CDCl_3$) δ: 7.39 (1H, d, J = 8.4 Hz, H-1), 7.13 (1H, d, J = 8.7 Hz, H-7), 6.55 (1H, dd, J = 8.4,

2.4 Hz, H-2), 6.46 (1H, overlapped, H-4), 6.45 (1H, overlapped, H-8), 6.42 (1H, d, J = 2.4 Hz, H-10), 5.49 (1H, d, J = 6.8 Hz, H-11a), 4.96 (1H, s, 9-OH), 4.24 (1H, dd, J = 11.2, 5.1 Hz, Ha-6), 3.77 (3H, s, 3-OMe), 3.62 (1H, t-like, J = 11.2 Hz, Hb-6), 3.53 (1H, m, H-6a); ^{13}C NMR (200 MHz, $CDCl_3$) δ: 161.3 (C-10a), 160.8 (C-3), 157.1 (C-9), 156.8 (C-5), 132.4 (C-1), 124.9 (C-7), 119.2 (C-7a), 112.8 (C-11), 109.9 (C-2), 106.5 (C-8), 103.8 (C-4), 97.1 (C-10), 78.7 (C-11a), 66.7 (C-6), 55.7 (3-OMe), 39.6 (C-6a)。以上数据和文献[23,24]对照基本一致,故确定化合物 **21** 为 3-methoxy-9-hydroxy-pterocarpan。

化合物 22 淡黄色胶状物; ^{1}H NMR (400 MHz, methanol-d_4) δ: 7.61 (1H, d, J = 3.1 Hz, H-6), 7.48 (2H, d, J = 7.3 Hz, H-2′, H-6′), 7.41 (2H, d, J = 7.3 Hz, H-3′, H-5′), 7.37 (1H, t, J = 7.3 Hz, H-4′), 7.32 (1H, dd, J = 9.1, 3.1 Hz, H-4), 6.89 (1H, d, J = 9.1 Hz, H-3), 5.41 (1H, d, J = 12.3 Hz, Ha-7′), 5.38 (1H, d, J = 12.3 Hz, Hb-7′), 4.74 (1H, d, J = 6.5 Hz, H-1″), 3.79 (1H, dd, J = 12.1, 2.3 Hz, Ha-6″), 3.68 (1H, dd, J = 12.1, 4.9 Hz, Hb-6″), 3.31-3.40 (4H, m, H-2′, H-3′, H-4′, H-5′); ^{13}C NMR (150 MHz, methanol-d_4) δ: 170.7 (C-7), 158.4 (C-5), 151.5 (C-2), 137.0 (C-1′), 129.7 (C-2′), 129.7 (C-6′), 129.5 (C-4′), 129.4 (C-3′), 129.4 (C-5′), 127.3 (C-4), 119.2 (C-3), 118.6 (C-6), 113.4 (C-1), 103.7 (C-1″), 78.1 (C-5″), 77.9 (C-3″), 74.9 (C-2″), 71.1 (C-4″), 68.2 (C-7′), 62.3 (C-6″)。以上数据和文献[25]对照基本一致,故确定化合物 **22** 为 trichocarpin。

化合物 23 黄色胶状物; ^{1}H NMR (400 MHz, methanol-d_4) δ: 7.87 (2H, d, J = 7.5 Hz, H-2, H-6), 7.35 (2H, d, J = 7.5 Hz, H-3, H-5), 7.32 (1H, t, J = 7.5 Hz, H-4), 7.04 (1H, s, H-7), 5.20 (1H, d, J = 7.6 Hz, H-1′), 3.22 ~ 3.82 (6H, m, H-2′, H-3′, H-4′, H-5′, H-6′); ^{13}C NMR (150 MHz, methanol-d_4) δ: 168.1 (C-9), 143.8 (C-8), 134.8 (C-1), 131.6 (C-2, C-6), 129.8 (C-4), 129.3 (C-3, C-5), 125.0 (C-7), 102.9 (C-1′), 78.5 (C-5′), 78.1 (C-2′), 75.7 (C-3′), 71.3 (C-4′), 62.5 (C-6′)。以上数据和文献[26,27]对照基本一致,故确定化合物 **23** 为(*Z*)-8-*O*-β-D-glucopyranosylcinnamic acid。

化合物 24 淡黄色固体; ^{1}H NMR (400 MHz, methanol-d_4) δ: 7.18 (2H, d, J = 8.5 Hz, H-2, H-6), 6.67 (2H, d, J = 8.5 Hz, H-3, H-5), 6.50 (1H, d, J = 15.9 Hz, H-7), 6.10 (1H, dt, J = 15.9, 6.4 Hz, H-8), 4.42 (1H, dd, J = 12.3, 6.4 Hz, Ha-9), 4.30 (1H, d, J = 7.8 Hz, H-1′), 4.20 (1H, dd, J = 12.3, 6.4 Hz, Hb-9), 3.10-3.83 (6H, m, H-2′, H-3′, H-4′, H-5′, H-6′); ^{13}C NMR (100 MHz, methanol-d_4, 100 MHz) δ: 158.4 (C-4), 134.1 (C-7), 129.7 (C-1), 128.8 (C-2, C-6), 123.3 (C-8), 116.3 (C-3, C-5), 103.0 (C-1′), 78.0 (C-5′), 77.8 (C-3′), 75.0 (C-2′), 71.6 (C-4′), 71.1 (C-9), 62.7 (C-6′)。以上数据和文献[28]对照基本一致,故确定化合物 **24** 为 4-hydroxycinnamyl-*O*-β-D-glucopyranoside。

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