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牛蒡子化学成分的研究

秦智彬[1,3],丁林芬[1],李　兰[1],梁南熙[2],余文怡[1],徐兴梦[1],邓　亮[1*],郭亚东[1*],

[1]昆明医科大学药学院暨云南省天然药物药理重点实验室,昆明 650500;

[2]昆明市圣济药业有限公司,昆明,650118;[3] 西安市第二医院,西安. 710003

摘　要:从牛蒡子甲醇提取液中分离得到16个化合物,通过理化性质和波谱学方法鉴定出14个化合物,分别是牛蒡子苷(**1**),牛蒡苷元(**2**),罗汉松树脂酚(**3**),牛蒡酚B(**4**),异牛蒡酚A(**5**),牛蒡酚A(**6**),(+)-Diasyringaresinol(**7**),tanegool(**8**),arctignan F(**9**),牛蒡酚F(**10**),牛蒡酚C(**11**),arctignan D(**12**),arctignan E(**13**),牛蒡酚H(**14**),其中化合物**7**和**8**为首次从该种植物中分离得到。

关键词:牛蒡子;菊科;木脂素;化学成分

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Chemical Constituents of the Seed of *Arctium lappa* L.

QIN Zhi-bin [1,3], DING Lin-fen[1], LI-Lan[1], LIANG Nan-xi[2], YU Wen-yi[1],

XU Xing-meng[1], DENG Liang[1*], GUO Ya-dong[1*]

[1]*School of Pharmaceutical Science & Yunnan Key Laboratory of Pharmacology for Natural Products, Kunming Medical University, Kunming, 650500, China*; [2]*. Kunming shengji pharmaceutical Co., Ltd, Kunming, China, 650118*; [3]*. Xi'an No. 2 hospital, Xi'an, 710003, China*

Abstract: 16 compounds were isolated and purified from methanol extract of the seed of *Arctium lappa L.* Among them, 15 chemical constituents were identified by physico-chemical and spectroscopic analysis as actiin (**1**), arctigenin (**2**), matairesinol (**3**), lappaol B (**4**), isolappaol A (**5**), lappaol A (**6**), (+)-Diasyringaresinol (**7**), tanegool (**8**), arctignan F (**9**), lappaol F (**10**), lappaol C (**11**), arctignan D (**12**), arctignan E (**13**), lappaol H (**14**). Compound **7** and **8** were firstly isolated from the burdock seed.

Key words: *Arctium lappa* L.; Compositae; lignans; chemical constituents

牛蒡子为菊科植物牛蒡(*Arctium lappa* L.)的干燥成熟果实,属辛凉解表药具疏散风热、宣肺透疹、消肿解毒之功效。用于治疗风热感冒、咳痰多、咽喉肿痛、斑疹不透、风疹作痒、痈肿疮毒等症,在我国分布广泛[1]。其脂肪油营养不亚于核桃油、大豆油。牛蒡叶多作外用,有明显的消炎、解毒、镇痛作用。牛蒡根,又名东洋参,有明显的降血糖、降血脂、降血压、补肾壮阳、润肠通便和抑制癌细胞滋生、扩散及移弃水中重金属的作用,是非常理想的天然保健食品,在国内外市场上作为蔬菜均有销售,享有"蔬菜之王"的美誉[2,3]。为了解其里面的主要化学成分,我们对买自昆明菊花村药材市场的牛蒡子进行化学成分研究。通过柱层析,制备HPLC和现代波谱学技术分离鉴定了14个木脂素类化合物,分别为牛蒡子苷(**1**),牛蒡苷元(**2**),罗汉松树脂酚(**3**),牛蒡酚B(**4**),异牛蒡酚A(**5**),牛蒡酚A(**6**),(+)-Diasyringaresinol(**7**),tanegool(**8**),arctignan F(**9**),牛蒡酚F(**10**),牛蒡酚C(**11**),arctignan D(**12**),arctignan E(**13**),牛蒡酚H(**14**),其中化合物**7**和**8**为首次从该种植物中分离得到。

1　仪器与试剂

1D-NMR在Bruker AM-400、Bruker DRX-500或Bruker AM-600核磁共振仪上测定,TMS作为内标,δ为ppm,J为Hz;ESI-MS在Burker HCT或Esquire质谱仪上测定;高分辨质谱在Auto-Spec Premier P776质谱仪上测定;拌样及层析用硅胶(100-200,200~300目),均为青岛海洋化工厂生产;反相填充材料RP-18为40~60 μm,Merk公司生产;MCI填充材料为MCI-gel CHP-20P;HPLC分析仪器为

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*通讯作者　Tel:871-65922809;E-mail:yadongkmmc@163.com

Agilent 1260 型高效液相色谱仪,色谱柱为 Agilent 公司的 ZORBAX SB-C_{18} 反相柱(9.6 × 150 mm,5 μm)。凝胶为 Sephadex LH-20;显色剂非碱为 10% H_2SO_4 的乙醇溶液,喷洒后适当加热。

实验药材购自于云南昆明菊花村药材市场。由中国科学院昆明植物研究所植物园成晓研究员鉴定。

2 提取与分离

干燥牛蒡子 21 kg,粉碎后用甲醇提取三次(50 L/次),合并提取液,减压蒸馏除去有机溶剂,得到粗提物 1.4 kg,将此粗提物用 2.0 kg 100 ~ 200 目硅胶拌样,以不同比例的石油醚-丙酮系统(9∶1,8∶2,7∶3,1∶1,0∶1)进行梯度洗脱,用 TLC 进行检测,合并相同组分得到七个馏分:Ⅰ-Ⅶ。

馏分Ⅳ用丙酮结晶,得到化合物 **1**(35.4 g)。

馏分Ⅶ以聚酰胺拌样,以甲醇-水系统(45%-100%)在 MCI 柱上进行梯度洗脱,以 TLC 进行检测,合并相同组分得到Ⅶa,Ⅶb,Ⅶc,Ⅶe,Ⅶf 和Ⅶg。Ⅶa 段先以不同比例的氯仿-丙酮系统(95∶5-1∶1)进行梯度洗脱,用 TLC 进行检测,合并相同组分,然后再以甲醇-水系统(23∶87,流速 3 mL/min)进行半制备,得到化合物 **3**(181.8 mg,t_R = 12.8 min),**4**(1.5 g,t_R = 12.9 min),和 **5**(42.2 mg,t_R = 19.3 min)。Ⅶb 段经过多次柱层析得到化合物 **6**(6.1 mg)和 **7**(2.8 mg)。Ⅶc 用甲醇结晶,得到化合物 **2**(55.89 g),对其浑浊液以甲醇-水系统(43∶57,流速 3 mL/min)进行半制备,得到化合物 **10**(121.0 mg,t_R = 15.2 min)。Ⅶd 段经过多次柱层析得到化合物 **8**(57.5 mg)和 **11**(54.2 mg)。Ⅶf 段以乙腈-水系统(23∶77,流速 3 mL/min)进行半制备,得到化合物 **12**(55.1 mg)和 **13**(70.0 mg)。Ⅶg 段以甲醇-水系统(45∶55,流速 3 mL/min)进行半制备,得到化合我 **9**(4.4 mg,t_R = 13.6 min)和 **14**(26.9 mg,t_R = 19.3 min)。

3 结构鉴定

化合物 1 白色针状结晶,ESI-MS *m/z* 557 [M + Na]$^+$,结合^{13}C 和^{1}H NMR 数据推定分子式为 $C_{27}H_{34}O_{11}$,^{1}H NMR (methanol-d_4, 400 MHz):δ_H 6.82 (1H,d,*J* = 2.0 Hz,H-2),7.05 (1H,d,*J* = 8.2 Hz,H-5),6.66 (m,H-6),2.83-2.90 (1H,m,H-7a),2.83-2.90 (1H,m,H-7b),6.59-6.53 (1H,m,H-2′),6.84 (1H,d,*J* = 9.0,H-5′),6.59-6.63 (1H,d,*J* = 8.0,H-6′),2.56 ~ 2.59 (1H,m,H-7′a),2.56 ~ 2.59 (1H,m,H-7′b),2.56 ~ 2.59 (1H,m,H-8′),4.2 (1H,m,H-9′a),3.96 (1H,m,H-9′b),3.40-4.53 (6H,m,Sugar-H);^{13}C NMR (methanol-d_4,100 MHz):δ_C 134.2 (s,C-1),113.0 (d,C-2),150.6 (s,C-3),149.1 (s,C-4),117.8 (d,C-5),122.1 (d,C-6),35.4 (t,C-7),47.6 (d,C-8),181.4 (s,C-9),132.7 (s,C-1′),113.5 (d,C-2′),150.4 (s,C-3′),146.8 (s,C-4′),114.7 (d,C-5′),122.9 (d,C-6′),38.9 (t,C-7′),42.5 (t,C-8′),72.9 (t,C-9′),102.8 (d,C-1″),74.9 (d,C-2″),77.8 (d,C-3″),71.3 (d,C-4″),78.2 (d,C-5″),62.5 (t,C-6″),56.4,56.5,56.6 (OCH_3)。以上波谱数据与参考文献[4]一致,故推断该化合物为牛蒡子苷。

化合物 2 白色块状结晶,ESI-MS *m/z* 371 [M + Na]$^+$,结合^{13}C 和^{1}H NMR 数据推定分子式为 $C_{26}H_{32}O_{11}$,^{1}H NMR (methanol-d_4, 400 MHz):δ_H 6.64 (1H,d,*J* = 2.0 Hz,H-2),6.82 (1H,d,*J* = 8.2 Hz,H-5),6.61 (dd,*J* = 8.0,2.0 Hz H-6),2.90 (1H,dd,*J* = 14,6.5 Hz,H-7a),2.94 (1H,dd,*J* = 14,5.0 Hz,H-7b),2.57 (t,ddd,*J* = 8.0,6.5,5.0 Hz,H-8),6.46 (1H,d,*J* = 2.0 Hz,H-2′),6.74 (1H,d,*J* = 8.0 Hz,H-5′),6.54 (1H,dd,*J* = 8.0,2.0 Hz,H-6′),2.52 (1H,dd,*J* = 13.5,5.0 Hz,H-7′a),2.64 (1H,dd,*J* = 13.5,6.0 Hz,H-7′b),2.48 (1H,m,H-8′),3.88 (1H,dd, *J* = 9.0,7.5 Hz,H-9′a),4.13 (1H,dd, *J* = 9.0,7.5 Hz,H-9′b);^{13}C NMR (methanol-d_4,100 MHz):δ_C 132.8 (s,C-1),113.8 (d,C-2),149.0 (s,C-3),146.4 (s,C-4),116.1 (d,C-5),123.0 (d,C-6),35.4 (t,C-7),47.7 (d,C-8),181.6 (s,C-9),130.7 (s,C-1′),113.8 (d,C-2′),150.4 (s,C-3′),149.1 (s,C-4′),113.0 (d,C-5′),122.0 (d,C-6′),38.9 (t,C-7′),42.4 (t,C-8′),72.9 (t,C-9′),56.3,56.3,56.4 (OCH_3)。以上波谱数据与参考文献[5]一致,故推断该化合物为牛蒡苷元。

化合物 3 白色无定型粉末,ESI-MS *m/z* 381 [M + Na]$^+$,结合^{13}C 和^{1}H NMR 数据推定分子式为 $C_{20}H_{22}O_6$,^{1}H NMR (methanol-d_4, 400 MHz):δ_H 6.61 (1H,d,*J* = 2.0 Hz,H-2),6.82 (1H,d,*J* = 8.0 Hz,H-5),6.60 (dd,*J* = 8.0 Hz H-6),2.88 (1H,dd,*J* = 14.0,7.0 Hz,H-7a),2.94 (1H,dd,*J*

=14.0,5.5 Hz,H-7b),2.56 (t,dt,J =7.0,5.5 Hz,H-8),6.41 (1H,d,J =2.0 Hz,H-2′),6.79 (1H,d,J =8.0 Hz,H-5′),6.51 (1H,dd,J =8.0,2.0 Hz,H-6′),2.53 (1H,dd,J =13.5,8.0 Hz,H-7′a),2.61 (1H,dd,J =13.5,6.5 Hz,H-7′b),2.47 (1H,m,H-8′),3.88 (1H,dd,J =9.0,7.5 Hz,H-9′a),4.15 (1H,dd,J =9.0,7.5 Hz,H-9′b);^{13}C NMR (methanol-d_4,100 MHz):δ_C 131.5 (s,C-1),113.2 (d,C-2),149.0 (s,C-3),146.3 (s,C-4),116.1 (d,C-5),123.0 (d,C-6),35.3 (t,C-7),47.7 (d,C-8),181.6 (s,C-9),130.8 (s,C-1′),113.8 (d,C-2′),149.0 (s,C-3′),146.3 (s,C-4′),113.8 (d,C-5′),122.2 (d,C-6′),38.9 (t,C-7′),42.5 (t,C-8′),72.9 (t,C-9′),56.3,56.3 (OCH_3)。以上波谱数据与参考文献[5]一致,故推断该化合物为罗汉松树脂酚。

化合物 4 无色油状,ESI-MS m/z 573 [M + Na]$^+$,结合^{13}C 和^{1}H NMR 数据推定分子式为 $C_{31}H_{34}O_9$,^{1}H NMR (methanol-d_4,400 MHz):δ_H 6.64 (1H,d,J =2.0 Hz,H-2),6.59 (d,J =2.0 Hz H-6),2.92 (1H,dd,J =14.0,6.5 Hz,H-7a),2.96 (1H,dd,J =14.0,5.5 Hz,H-7b),2.60 (t,m,H-8),6.53 (1H,d,J =2.0 Hz,H-2′),6.76 (1H,d,J =8.0 Hz,H-5′),6.58 (1H,dd,J =8.0,2.0 Hz,H-6′),2.55 (1H,H-7′),2.66 (1H,dd,J =13.0,6.0 Hz,H-7′b),2.52 (1H,m,H-8′),6.94 (1H,d,J =2.0 Hz,H-2″),6.87 (1H,d,J =8.0 Hz,H-5″),6.90 (1H,dd,J =8.0,2.0 Hz,H-6″),5.53 (1H,d,J =7.5 Hz,H-7″),3.53 (1H,dt,J =7.5,6.0 Hz,H-8″);^{13}C NMR (methanol-d_4,100 MHz):δ_C 130.1(s,C-1),112.8 (d,C-2),148.1 (s,C-3),145.3 (s,C-4),132.8 (d,C-5),118.9 (d,C-6),35.7 (t,C-7),47.8 (d,C-8),181.5 (s,C-9),132.7 (s,C-1′),113.5 (d,C-2′),150.4 (s,C-3′),149.1 (s,C-4′),113.8 (d,C-5′),122.1 (d,C-6′),38.9 (t,C-7′),42.6 (t,C-8′),72.9 (t,C-9′),134.6 (s,C-1″),110.4 (d,C-2″),149.1 (s,C-3″),147.5 (s,C-4″),116.1 (d,C-5″),119.7 (d,C-6″),89.1 (t,C-7″),55.3 (d,C-8″),64.8 (t,C-9″),56.3,56.3,56.3 (OCH_3)。以上波谱数据与参考文献[5]一致,故推断该化合物为牛蒡酚 B。

化合物 5 无色油状,ESI-MS m/z 559 [M + Na]$^+$,结合^{13}C 和^{1}H NMR 数据推定分子式为 $C_{39}H_{32}O_6$,^{1}H NMR (methanol-d_4,400 MHz):δ_H 6.62 (1H,d,J =2.0 Hz,H-2),6.49 (d,J =2.0 Hz H-6),2.91 (1H,dd,J =14.0,6.5 Hz,H-7a),2.95 (1H,dd,J =14.0,5.5 Hz,H-7b),6.42 (1H,d,J =2.0 Hz,H-2′),6.80 (1H,d,J =8.0 Hz,H-5′),6.54 (1H,dd,J =8.0,2.0 Hz,H-6′),2.63 (1H,dd,J =13.0,7.0 Hz,H-7′b),3.90 (1H,dd,J =9.0,6.0 Hz,H-9′a),4.15 (1H,dd,J =9.0,6.0 Hz,H-9′b),6.92 (1H,d,J =8.0 Hz,H-2″),6.87 (1H,d,J =8.0 Hz,H-5″),6.89 (1H,dd,J =8.0,2.0 Hz,H-6″),5.53 (1H,d,J =7.0 Hz,H-7″),3.55 (1H,dt,J =7.0,6.0 Hz,H-8″);^{13}C NMR (methanol-d_4,100 MHz):δ_C 130.2(s,C-1),116.1 (d,C-2),148.1 (s,C-3),146.4 (s,C-4),134.5(d,C-5),119.7 (d,C-6),35.3 (t,C-7),47.7 (d,C-8),181.6 (s,C-9),130.7 (s,C-1′),114.2 (d,C-2′),149.1 (s,C-3′),147.5 (s,C-4′),116.1 (d,C-5′),123.1 (d,C-6′),39.0 (t,C-7′),42.5 (t,C-8′),72.9 (t,C-9′),133.4 (s,C-1″),110.5 (d,C-2″),149.0 (s,C-3″),145.4 (s,C-4″),114.0 (d,C-5″),119.7 (d,C-6″),89.0 (t,C-7″),55.3 (d,C-8″),64.7 (t,C-9″),56.3,56.4,56.6 (OCH_3)。以上波谱数据与参考文献[5]一致,故推断该化合物为异牛蒡酚 A。

化合物 6 无色油状,ESI-MS m/z 559 [M + Na]$^+$,结合^{13}C 和^{1}H NMR 数据推定分子式为 $C_{39}H_{32}O_6$,^{1}H NMR (methanol-d_4,400 MHz):δ_H 6.68 (1H,d,J =2.0 Hz,H-2),6.81 (1H,d,J =8.0 Hz H-5),6.61 (1H,dd,J =8.0,2.0 Hz H-6),2.90 (1H,dd,J =14.0,7.0 Hz,H-7a),2.97 (1H,dd,J =14.0,5.5 Hz,H-7b),2.57 (1H,ddd,J =12.0,7.0,5.0 Hz H-8),6.42 (1H,br s,H-2′),6.42 (1H,br s,H-6′),2.54 (1H,dd,J =13.5,8.0 Hz,H-7′a),2.64 (1H,dd,J =13.5,5.5 Hz,H-7′b),2.49 (1H,m,H-8′),3.90 (1H,dd,J =9.0,6.0 Hz,H-9′a),4.17 (1H,dd,J =9.0,7.0 Hz,H-9′b),6.92 (1H,d,J =2.0 Hz,H-2″),6.87 (1H,d,J =8.0 Hz,H-5″),6.89 (1H,dd,J =8.0,2.0 Hz,H-6″),5.50 (1H,d,J =7.0 Hz,H-7″),3.55 (1H,dt,J =7.0,6.0 Hz,H-8″);^{13}C NMR (methanol-d_4,100 MHz):δ_C 131.5(s,C-1),113.4 (d,C-2),148.3 (s,C-3),146.3 (s,C-4),116.2 (d,C-5),119.7 (d,C-6),35.6 (t,C-7),47.9 (d,C-8),181.6 (s,C-9),130.1 (s,C-1′),115.0 (d,C-2′),150.0 (s,C-3′),

146.3 (s,C-4′),134.8 (s,C-5′),122.3 (d,C-6′),39.0 (t,C-7′),42.8 (t,C-8′),72.9 (t,C-9′),132.7 (s,C-1″),110.4 (d,C-2″),147.5 (s,C-3″),145.4 (s,C-4″),116.2 (d,C-5″),119.1 (d,C-6″),89.1 (t,C-7″),55.4 (d,C-8″),65.0 (t,C-9″),56.3,56.8 (OCH_3)。以上波谱数据与参考文献[5]一致,故推断该化合物为牛蒡酚 A。

化合物 7 无色油状,ESI-MS *m/z* 441 [M + Na]$^+$,结合^{13}C 和^{1}H NMR 数据推定分子式为 $C_{22}H_{26}O_8$,^{1}H NMR ($CDCl_3$,600 MHz):δ_H 3.18 (2H, m,H-1 , H-5),3.57 (2H,dd,*J* =9.6,3.6 Hz,H-4b,H-8b) , 3.73 (2H,dd,*J* =9.6,6.8 Hz,H-4a,H-8a),4.90 (2H,d,*J* =4.3 Hz,H-2 ,H-6),3.91 (12H,s,4-OCH_3),6.61 (4H,s,H-2′,H-6′,H-2″ ,H-6″);^{13}C NMR (150MHz,$CDCl_3$) δ:30.8 (d,C-1 , C-5),56.9 (OCH_3),72.9 (t,C-4 , C-8),87.8 (d, C-2 , C-6), 104.5 (d, C-2′, C-6′, C-2″,, C-6″), 133.2 (s,C-1′ , C-1″),134.9 (s,C-4′ , C-4″),and 149.5 (s,C-3′,C-5′,C-3″ ,C-5″。以上波谱数据与参考文献[6]一致,故推断该化合物为(+)-Diasyringaresinol。

化合物 8 无色油状,ESI-MS *m/z* 399 [M + Na]$^+$,结合^{13}C 和^{1}H NMR 数据推定分子式为 $C_{20}H_{24}O_7$,^{1}H NMR (methanol-d_4,400 MHz):δ_H 7.14 (1H,d,*J* =7.9 Hz,H-5),7.10 (1H,d,*J* =7.9 Hz, H-5′),7.08 (1H,br s,H-2),6.99 (1H,br s,H-20), 6.97 (1H,d,*J* =7.9 Hz,H-6),6.76 (1H,d,*J* = 7.9 Hz,H-6′),4.89 (1H,d,*J* =6.8 Hz,H-1′),4.66 (1H,d,*J* =7.5 Hz,H-7),4.57 (1H,d,*J* =8.1 Hz, H-7′),4.27 (1H,dd,*J* =9.0 Hz,4.5 Hz,H-9′ b), 3.90 (1H,dd,J =9.0,7.5 Hz,H-9′ a),3.88 (3H, s,-OCH_3),3.85 (3H,s,3-OCH_3),3.79 (1H,dd,*J* =11.1,4.5 Hz,H-9a),3.69 (1H,dd,*J* =11.0,6.4 Hz,H-9b),2.63 (1H,m,H-8′),2.28 (1H,m,H-8);^{13}C NMR (100 MHz,methanol-d_4) δ:149.1 (s, C-3),149.0 (s,C-3′),147.4 (s,C-4),147.3 (C-4′),136.2 (s,C-1),134.0 (s,C-1′),120.8 (d,C-2′),120.7 (d,C-6),116.0(d,C-5),116.0 (d,C-5′),111.3 (C-2′),111.1 (d,C-2),85.8 (d,C-7), 77.6 (d,C-7′),71.2 (t,C-9),63.3 (t,C-9′),52.9 (d,C-8),56.4,56.3,56.0 (3-OCH_3)。以上波谱数据与参考文献[7]一致,故推断该化合物为 tanegool。

化合物 9 无色油状,ESI-MS *m/z* 753[M + Na]$^+$,结合^{13}C 和^{1}H NMR 数据推定分子式为 $C_{40}H_{42}O_{13}$,^{1}H NMR (methanol-d_4,600 MHz):δ_H 6.58 (1H,d,*J* =2.0 Hz,H-2),6.55 (1H,d,*J* =2.0 Hz, H-6),2.79 (1H,dd,*J* =14.0,7.0 Hz,H-7a),2.85 (1H,dd,*J* =14.0,5.0 Hz,H-7b),2.43 (1H,m,H-8),6.38 (1H,d,*J* =2.0 Hz,H-2′),6.40 (1H,d,*J* =2.0 Hz,H-6′),2.35 (1H,dd,*J* =13.0,8.0 Hz, H-7′a),2.48 (1H,dd,*J* =13.0,8.0 Hz,H-7′b), 2.43 (1H,m,H-8′),3.72 (1H,dd,*J* =9.0,8.0 Hz, H-9′a),3.95 (1H,dd,*J* =9.0,7.0 Hz,H-9′b), 6.92 (1H,d,*J* =2.0 Hz,H-2″),6.87 (1H,d,*J* = 8.0 Hz,H-5″),6.90 (1H,dd,*J* =8.0,2.0 Hz,H-6″),5.48 (1H,d,*J* =7.0 Hz,H-7″),3.59 (1H,dt,*J* =7.0,6.0 Hz,H-8″),7.56 (1H,d,*J* =2.0 Hz,H-2‴),6.80 (1H,d,*J* =8.0 Hz,H-5‴),7.55 (1H, dd,*J* =8.0,2.0 Hz,H-6‴),5.18 (1H,dd,*J* =8.0, 5.0 Hz,H-8‴);^{13}C NMR (methanol-d_4,150 MHz): δ_C 132.5(s,C-1),114.9 (d,C-2),149.4 (s,C-3), 147.6 (s,C-4),134.9 (s,C-5),119.9 (d,C-6), 34.9 (t,C-7),48.0 (d,C-8),181.8 (s,C-9),130.3 (s,C-1′),115.9 (d,C-2′),149.2 (s,C-3′),143.5 (s,C-4′),129.8 (s,C-5′),124.6 (d,C-6′),39.0 (t,C-7′),42.8 (t,C-8′),72.8 (t,C-9′),131.3 (s, C-1″),112.0 (d,C-2″),148.9 (s,C-3″),145.3 (s, C-4″),116.2 (d,C-5″),121.2 (d,C-6″),89.4 (t,C-7″),55.5 (d, C-8″),65.2 (t, C-9″),129.7 (s, C-1‴),110.4 (d,C-2‴),148.2 (s,C-3‴),153.2 (s, C-4‴),119.3 (d, C-5‴),124.8 (d, C-6‴),199.9 (s,C-7‴),48.0 (d,C-8‴),64.0 (t,C-9‴),56.4, 56.5,56.5,56.8 (OCH_3)。以上波谱数据与参考文献[8]一致,故推断该化合物为 arctignan F。

化合物 10 无色油状,ESI-MS *m/z* 737[M + Na]$^+$,结合^{13}C 和^{1}H NMR 数据推定分子式为 $C_{40}H_{42}O_{12}$,^{1}H NMR (methanol-d_4,400 MHz):δ_H 6.62 (1H,d,*J* =2.0 Hz,H-2),6.50 (1H,d,*J* =2.0 Hz, H-6),2.84 (1H,dd,*J* =14.0,7.5 Hz,H-7a),2.98 (1H,dd,*J* =14.0,5.5 Hz,H-7b),2.55 (1H,m,H-8),6.44 (1H,d,*J* =2.0 Hz,H-2′),6.55 (1H,d,*J* =2.0 Hz,H-6′),2.51 (1H,m,H-8′),3.89 (1H, dd,*J* =9.5,6.0 Hz,H-9′a),4.20 (1H,dd,*J* =9.5, 7.0 Hz,H-9′b),6.91 (1H,d,*J* =2.0 Hz,H-2″), 6.83 (1H,d,*J* =8.0 Hz,H-5″),6.85 (1H,dd,*J* = 8.0,2.0 Hz,H-6″),5.44 (1H,d,*J* =7.0 Hz,H-7″),

3.55 (1H,dt,J =7.0,6.0 Hz,H-8″),6.93 (1H,d,J =2.0 Hz,H-2‴),6.84 (1H,d,J =8.0 Hz,H-5‴′),6.85 (1H,dd,J =8.0,2.0 Hz,H-6‴),5.46 (1H,d,J =7.0Hz,H-7‴),3.55 (1H,dt,J =7.0,6.0 Hz,H-8″);^{13}C NMR (methanol-d_4,100 MHz):δ_C 130.0(s,C-1),113.8 (d,C-2),147.3 (s,C-3),145.1 (s,C-4),132.5 (s,C-5),114.4 (d,C-6),35.7 (t,C-7),47.6 (d,C-8),181.4 (s,C-9),130.1 (s,C-1′),115.6 (d,C-2′),147.3 (s,C-3′),145.1 (s,C-4′),133.1 (s,C-5′),115.8 (d,C-6′),39.1 (t,C-7′),42.4 (t,C-8′),72.9 (t,C-9′),134.1 (s,C-1″),110.3 (d,C-2″),147.8 (s,C-3″),147.9 (s,C-4″),118.0 (d,C-5″),119.8 (d,C-6″),89.0 (t,C-7″),54.8 (d,C-8″),64.3 (t,C-9″),134.1 (s,C-1‴),110.4 (d,C-2‴),148.9 (s,C-3‴),134.2 (s,C-4‴),118.6 (d,C-5‴),119.7(d,C-6‴),89.0 (t,C-7‴),54.8 (d,C-8‴),64.5 (t,C-9‴),56.1,56.1,56.3,56.4 (OCH_3)。以上波谱数据与参考文献[8]一致,故推断该化合物为 lappaol F。

化合物 11 无色油状,ESI-MS m/z 577[M + Na]$^+$,结合^{13}C 和^{1}H NMR 数据推定分子式为 $C_{30}H_{34}O_{10}$,^{1}H NMR (methanol-d_4,600 MHz):δ_H 6.65 (1H,d,J =2.0 Hz,H-2),6.81 (1H,d,J =8.0 Hz H-5),6.58 (1H,dd,J =8.0,2.0 Hz H-6),2.87 (1H,dd,J =14.0,7.0 Hz,H-7a),2.94 (1H,dd,J =14.0,5.5 Hz,H-7b),2.50 (1H,ddd,J =8.5,7.0,5.5 Hz H-8),6.33 (1H,d,J =2.0 Hz,H-2′),6.36 (1H,d,J =2.0 Hz,H-6′),2.56 (1H,dd,J =13.5,5.0 Hz,H-7′b),2.39 (1H,m,H-8′),3.87 (1H,dd,J =9.5,6.5 Hz,H-9′a),4.01 (1H,dd,J =9.5,7.5 Hz,H-9′b),6.81 (1H,d,J =2.0 Hz,H-2″),6.81 (1H,d,J =8.0 Hz,H-5″),6.76 (1H,dd,J =8.0,2.0 Hz,H-6″),5.11 (1H,d,J =7.0 Hz,H-7″),3.42 (1H,dt,J =7.0,6.0 Hz,H-8″);^{13}C NMR (methanol-d_4,150 MHz):δ_C 131.0(s,C-1),114.0 (d,C-2),148.6 (s,C-3),146.7 (s,C-4),116.2 (d,C-5),123.2 (d,C-6),35.6 (t,C-7),47.6 (d,C-8),181.9 (s,C-9),127.2 (s,C-1′),111.2 (d,C-2′),149.2 (s,C-3′),144.7 (s,C-4′),130.4 (s,C-5′),123.2 (d,C-6′),39.0 (t,C-7′),43.0 (t,C-8′),73.0 (t,C-9′),136.3 (s,C-1″),111.3 (d,C-2″),149.1(s,C-3″),146.5 (s,C-4″),115.6 (d,C-5″),120.4 (d,C-6″),74.9 (d,C-7″),50.0 (d,C-8″),63.3 (t,C-9″),56.3,56.3,56.4 (OCH_3)。以上波谱数据与参考文献[5]一致,推断该化合物为 lappaol C。

化合物 12 无色油状,ESI-MS m/z 755[M + Na]$^+$,结合^{13}C 和^{1}H NMR 数据推定分子式为 $C_{40}H_{44}O_{13}$,^{1}H NMR (methanol-d_4,400 MHz):δ_H 6.65 (1H,d,J =2.0 Hz,H-2),6.530 (1H,d,J =2.0 Hz,H-6),2.85 (1H,dd,J =14.0,7.0 Hz,H-7a),2.99 (1H,dd,J =14.0,5.0 Hz,H-7b),6.40 (1H,d,J =2.0 Hz,H-2′),6.51 (1H,d,J =2.0 Hz,H-6′),4.11 (1H,dd,J =9.0,7.0 Hz,H-9′b),6.93 (1H,d,J =2.0 Hz,H-2″),6.86 (1H,d,J =8.0 Hz,H-5″),6.87 (1H,dd,J =8.0,2.0 Hz,H-6″),5.44 (1H,d,J =7.0 Hz,H-7″),3.54 (1H,dt,J =7.0,6.0 Hz,H-8″),6.84 (1H,d,J =2.0 Hz,H-2‴),6.81 (1H,d,J =8.0 Hz,H-5‴′),6.78 (1H,dd,J =8.0,2.0 Hz,H-6‴),5.11 (1H,d,J =7.0Hz,H-7‴),3.43 (1H,dt,J =7.0,6.0 Hz,H-8″);^{13}C NMR (methanol-d_4,100 MHz):δ_C 129.6(s,C-1),111.0 (d,C-2),147.5 (s,C-3),145.3 (s,C-4),134.6 (s,C-5),118.7 (d,C-6),35.0 (t,C-7),47.6 (d,C-8),181.8 (s,C-9),126.7 (s,C-1′),115.6 (d,C-2′),146.4 (s,C-3′),148.5 (s,C-4′),136.3 (s,C-5′),120.0 (d,C-6′),39.0 (t,C-7′),41.4 (t,C-8′),73.0 (t,C-9′),130.2 (s,C-1″),110.4 (d,C-2″),149.1 (s,C-3″),147.5 (s,C-4″),114.7(d,C-5″),119.8 (d,C-6″),89.1 (t,C-7″),56.9 (d,C-8″),64.9 (t,C-9″),133.3 (s,C-1‴),110.4 (d,C-2‴),148.4 (s,C-3‴),147.5 (s,C-4‴),120.0 (d,C-5‴),116.1(d,C-6‴),74.6 (d,C-7‴),55.3 (d,C-8‴),62.8 (t,C-9‴),56.2,56.3,56.5,56.3 (OCH_3)。以上波谱数据与参考文献[5]一致,故推断该化合物为 arctignan D。

化合物 13 无色油状,ESI-MS m/z 755[M + Na]$^+$,结合^{13}C 和^{1}H NMR 数据推定分子式为 $C_{40}H_{44}O_{13}$,^{1}H NMR (methanol-d_4,400 MHz):δ_H 6.65 (1H,d,J =2.0 Hz,H-2),6.530 (1H,d,J =2.0 Hz,H-6),2.89 (1H,dd,J =14.0,7.0 Hz,H-7a),2.89 (1H,dd,J =14.0,5.0 Hz,H-7b),2.53 (1H,m,H-8),6.46 (1H,d,J =2.0 Hz,H-2′),6.51 (1H,d,J =2.0 Hz,H-6′),2.51 (1H,m,H-7′a),2.53 (1H,dd,J =14.0,6.5 Hz,H-7′b),2.44 (1H,m,H-8′b),4.10 (1H,dd,J =9.0,7.5 Hz,H-9′b),

6.83 (1H,d,J =2.0 Hz,H-2″),6.80 (1H,d,J = 8.0 Hz,H-5″),6.80 (1H,dd,J =8.0,2.0 Hz,H-6″),5.11 (1H,d,J =7.0 Hz,H-7″),3.43 (1H,dt,J =7.0,6.0 Hz,H-8″),6.92 (1H,d,J =2.0 Hz,H-2‴),6.86 (1H,d,J =8.0 Hz,H-5‴),6.86 (1H,dd,J = 8.0,2.0 Hz,H-6‴),5.41 (1H,d,J = 7.0Hz,H-7‴),3.53 (1H,dt,J =7.0,6.0 Hz,H-8″);^{13}C NMR (methanol-d_4,100 MHz):δ_C 127.1(s,C-1),115,5 (d,C-2),146.5 (s,C-3),144.6 (s,C-4),136.2 (s,C-5),120.2 (d,C-6),35.6 (t,C-7),47.6 (d,C-8),181.7 (s,C-9),130.0 (s,C-1′),111.3 (d,C-2′),147.5 (s,C-3′),145.3 (s,C-4′),134.7 (s,C-5′),119.0 (d,C-6′),38.8 (t,C-7′),43.0 (t,C-8′),72.8 (t,C-9′),132.9 (s,C-1″),110.3 (d,C-2″),149.2 (s,C-3″),148.1 (s,C-4″),114.9(d,C-5″),119.7 (d,C-6″),74.7 (d,C-7″),56.8 (d,C-8″),63.2 (t,C-9″),130.3(s,C-1‴),111.1 (d,C-2‴),149.0 (s,C-3‴),148.5 (s,C-4‴),116.1 (d,C-5‴),124.5 (d,C-6‴),89.1 (t,C-7‴),55.4 (d,C-8‴),65.0 (t,C-9‴),56.2,56.3,56.4,56.4 (OCH_3)。以上波谱数据与参考文献[5]一致,故推断该化合物为 arctignan E。

化合物 14 无色油状,ESI-MS m/z 773[M + Na]$^+$,结合^{13}C 和^{1}H NMR 数据推定分子式为 $C_{40}H_{46}O_{14}$,^{1}H NMR (methanol-d_4,400 MHz):δ_H 6.65 (1H,d,J =2.0 Hz,H-2),6.530 (1H,d,J =2.0 Hz,H-6),2.89 (1H,dd,J =14.0,7.0 Hz,H-7a),2.89 (1H,dd,J =14.0,5.0 Hz,H-7b),2.53 (1H,m,H-8),6.46 (1H,d,J =2.0 Hz,H-2′),6.51 (1H,d,J =2.0 Hz,H-6′),2.51 (1H,m,H-7′a),2.53 (1H,dd,J =14.0,6.5 Hz,H-7′b),2.44 (1H,m,H-8′b),4.10 (1H,dd,J =9.0,7.5 Hz,H-9′b),6.83 (1H,d,J =2.0 Hz,H-2″),6.80 (1H,d,J = 8.0 Hz,H-5″),6.80 (1H,dd,J =8.0,2.0 Hz,H-6″),5.11 (1H,d,J =7.0 Hz,H-7″),3.43 (1H,dt,J =7.0,6.0 Hz,H-8″),6.84 (1H,d,J =2.0 Hz,H-2‴),6.81 (1H,d,J =8.0 Hz,H-5‴),6.78 (1H,dd,J =8.0,2.0 Hz,H-6‴),5.11 (1H,d,J = 7.0Hz,H-7‴),3.43 (1H,dt,J =7.0,6.0 Hz,H-8″);^{13}C NMR (methanol-d_4,100 MHz):δ_C 127.1(s,C-1),115,5 (d,C-2),146.5 (s,C-3),144.6 (s,C-4),136.2 (s,C-5),120.2 (d,C-6),35.6 (t,C-7),47.6 (d,C-8),181.7 (s,C-9),130.0 (s,C-1′),111.3 (d,C-2′),147.5 (s,C-3′),145.3 (s,C-4′),134.7 (s,C-5′),119.0 (d,C-6′),38.8 (t,C-7′),43.0 (t,C-8′),72.8 (t,C-9′),132.9 (s,C-1″),110.3 (d,C-2″),149.2 (s,C-3″),148.1 (s,C-4″),114.9(d,C-5″),119.7 (d,C-6″),74.7 (d,C-7″),56.8 (d,C-8″),63.2 (t,C-9″),133.3 (s,C-1‴),110.4 (d,C-2‴),148.4 (s,C-3‴),147.5 (s,C-4‴),120.0 (d,C-5‴),116.1(d,C-6‴),74.6 (d,C-7‴),55.3 (d,C-8‴),62.8 (t,C-9‴),56.2,56.3,56.5,56.3 (OCH_3)。以上波谱数据与参考文献[9]一致,故推断该化合物为 lappaol H。

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