细梗香草化学成分的分离鉴定

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［摘要］ **目的**：对细梗香草正丁醇部位进行系统的化学成分研究。**方法**：取细梗香草药材粉碎，用 70% 乙醇回流提取，减压回收溶剂得浸膏，浸膏经水溶解后，用正丁醇萃取，得到正丁醇部位，采用大孔树脂柱，中压 ODS 柱色谱，硅胶柱色谱，LH-20 型羟丙基葡聚糖凝胶（Sephadex LH-20）柱色谱和制备高效液相色谱等技术手段进行分离纯化，分离得到单体化合物，并经波谱数据分析和文献数据鉴定化合物的结构。**结果**：从细梗香草正丁醇提取物中分离得到 15 个化合物，其中 6 个皂苷类和 9 个黄酮苷类化合物，分别鉴定为细梗香草皂苷 B（**1**），细梗香草皂苷 C（**2**），kaempferol-3-*O*-*β*-*D*-xylopyranosyl（1→3）-［4-*O*-*E*-*p*-coumaroyl-*α*-*L*-rhamnopyranosyl（1→2）］［*β*-*D*-glucopyranosyl（1→6）］-*β*-*D*-galactopyranoside-7-*O*-*α*-*L*-rhamnopyranoside（**3**），kaempferol-3-*O*-｛［*β*-*D*-xylopyranosyl（1→3）-*α*-*L*-rhamnopyranosyl（1→6）］［*α*-*L*-rhamnopyranosyl（1→2）］｝-*β*-*D*-3-trans-*p*-coumaroylgalactopyranoside（**4**），细梗香草皂苷 K（**5**），3*β*-*O*-｛*α*-*L*-rhamnopyranosyl-（1→2）-*O*-*β*-*D*-glucopyranosyl-（1→4）-［*O*-*β*-*D*-glucopyranosyl-（1→2）］-*α*-*L*-arabinopyranosyl｝-16*α*-hydroxyolean-28，13*β*-olide（**6**），细梗香草皂苷 I（**7**），quercetin-3-*O*-（2″，6″-di-*O*-*α*-rhamnopyranosyl）-*β*-galactopyranoside（**8**），kaempferol-3-*O*-｛［*β*-*D*-xylopyranosyl（1→3）-*α*-*L*-rhamnopyranosyl（1→6）］［*α*-*L*-rhamnopyranosyl-（1→2）］｝-*β*-*D*-galactopyranoside（**9**），kaempferol-3-*O*-［2-glucopyranosyl（1→3）rhamnopyranosyl-6-rhamnopyranosyl］-*β*-*D*-galactopyranoside（**10**），kaempferol-3-*O*-*α*-*L*-rhamnopyranosy-（1→2）-［*α*-*L*-rhamnopyranosy-（1→6）］-*β*-*D*-galactopyranoside（**11**），capilliposide I（**12**），kaempferol-3-*O*-｛（*β*-*D*-glucopyranosyl-（1→3）-［4-*O*-（*E*-*p*-coumaroyl）］-*α*-*L*-rhamnopyranosyl-（1→6）-（*β*-*D*-galactopyranoside）｝-7-*O*-*α*-*L*-rhamnopyranoside（**13**），kaempferol-3-*O*-｛［*β*-*D*-glucopyranosyl（1→3）］-4-*O*-（*E*-*p*-coumaroyl）｝-*α*-*L*-rhamnopyranosyl（1→6）-*β*-*D*-glucopyranoside-7-*O*（4-*O*-acetyl）-*α*-*L*-rhamnopyranoside（**14**），（3*β*，20*S*，23*S*，24*R*）-3，20，23，24，25，29-hexahydroxydammaran-21-oic acid-21，23-lactone 3-*O*-*β*-*D*-glucopyranosyl-（1→6）-*β*-*D*-glucopyranoside（**15**）。**结论**：化合物 **3**，**4**，**6**，**9**，**10**，**13**～**15** 为首次在该植物中分离得到。

［关键词］ 细梗香草；正丁醇部位；化学成分；结构鉴定
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Separation Identification of Chemical Constituents of *Lysimachia capillipes*

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[**Abstract**] **Objective**: To systemically study the chemical constituents of *n*-butanol fraction from *Lysimachia capillipes*. **Method**: The whole plant of *L. capillipes* was crushed into power, extracted by 70% methanol, concentrated under reduced pressure, and then its *n*-butanol extract was obtained by fractional extraction. The compounds from *n*-butanol fraction were isolated and purified by macroporous resin column chromatography, medium pressure ODS, silica gel, Sephadex LH-20 and preparative HPLC. Their structures were identified on the basis of spectral analysis and comparison with literature data. **Result**: Fifteen compounds including 6 saponins and 9 flavonoid glycosides were isolated from *L. capillipes*, and were identified as ascapilliposide B (**1**) and capilliposide C (**2**), kaempferol-3-*O*-*β*-*D*-xylopyranosyl (1→3)-[4-*O*-*E*-*p*-coumaroyl-*α*-*L*-rhamnopyranosyl (1→2)] [*β*-*D*-glucopyranosyl (1→6)]-*β*-*D*-galactopyranoside-7-*O*-*α*-*L*-rhamnopyranoside (**3**), kaempferol-3-*O*-{[*β*-*D*-xylopyranosyl (1→3)-*α*-*L*-rhamnopyranosyl (1→6)] [*α*-*L*-rhamnopyranosyl (1→2)]}-*β*-*D*-3-trans-*p*-coumaroylgalactopyranoside (**4**), capilliposide K (**5**), 3*β*-*O*-{*α*-*L*-rhamnopyranosyl-(1→2)-*O*-*β*-*D*-glucopyranosyl-(1→4)-[*O*-*β*-*D*-glucopyranosyl-(1→2)]-*α*-*L*-arabinopyranosyl)}-16*α*-hydroxyolean-28, 13*β*-olide (**6**), capilliposide I (**7**), quercetin-3-*O*-(2″, 6″-di-*O*-*α*-rhamnopyranosyl)-*β*-galactopyranoside (**8**), kaempferol-3-*O*-{[*β*-*D*-xylopyranosyl (1→3)-*α*-*L*-rhamnopyranosyl (1→6)] [*α*-*L*-rhamnopyranosyl-(1→2)]}-*β*-*D*-galactopyranoside (**9**), kaempferol-3-*O*-[2-glucopyranosyl (1→3) rhamnopyranosyl-6-rhamnopyranosyl]-*β*-*D*-galactopyranoside (**10**), kaempferol-3-*O*-*α*-*L*-rhamnopyranosy-(1→2)-[*α*-*L*-rhamnopyranosy-(1→6)]-*β*-*D*-galactopyranoside (**11**), capilliposide I (**12**), kaempferol-3-*O*-{(*β*-*D*-glucopyranosyl-(1→3)-[4-*O*-(*E*-*p*-coumaroyl)]-α-*L*-rhamnopyranosyl-(1→6)-(*β*-*D*-galactopyranoside)}-7-*O*-*α*-*L*-rhamnopyranoside (**13**), kaempferol-3-*O*-{[*β*-*D*-glucopyranosyl (1→3)]-4-*O*-(*E*-*p*-coumaroyl)}-*α*-*L*-rhamnopyranosyl (1→6)-*β*-*D*-glucopyranoside-7-*O* (4-*O*-acetyl)-*α*-*L*-rhamnopyranoside (**14**), and (3*β*, 20*S*, 23*S*, 24*R*)-3, 20, 23, 24, 25, 29-hexahydroxydammaran-21-oic acid-21, 23-lactone 3-*O*-*β*-*D*-glucopyranosyl-(1→6)-*β*-*D*-gluco-pyranoside (**15**). **Conclusion**: The compounds **3**, **4**, **6**, **9**, **10**, **13**-**15** were isolated from this plant for the first time.

[**Key words**] *Lysimachia capillipes*; *n*-butanal extract; chemical constituents; structure identification

细梗香草为报春花科珍珠菜属植物细梗香草的干燥全草,别名又称作排香、香排草,在江西、福建、浙江、湖南、广东等省份均有分布。民间习称“满山香”,其药材基源复杂,但细梗香草是惟一的草本“满山香”,满山香药材现收载于《江西省中药材标准》(2014 年版),性甘,味平,归肝、胃、肾经[1-3],具有祛风、止咳、调经的功效,用于感冒咳嗽、气管炎、哮喘、月经不调、神经衰弱的治疗。以细梗香草(满山香)为原料的单味中成药“满山香片”临床用于外感风热,发热头痛,咽痛,身痛。据文献报道细梗香草药材中主要含黄酮类、皂苷类、内酯类和酸类等成分[4-8]。目前,国内外对细梗香草化学成分研究较少,本课题组主要对乙醇提取物中的正丁醇部位进行化学成分分离纯化和结构鉴定研究,为今后满山香药材及其片剂的质量标准研究提供理论及技术支持。通过分离得到 15 个化合物,并分离鉴定为细梗香草皂苷 B(**1**),细梗香草皂苷 C(**2**),kaempferol-3-*O*-*β*-*D*-xylopyranosyl(1→3)-[4-*O*-*E*-*p*-coumaroyl-*α*-*L*-rhamnopyranosyl(1→2)][*β*-*D*-glucopyranosyl(1→6)]-*β*-*D*-galactopyranoside-7-*O*-*α*-*L*-rhamnopyranoside(**3**),kaempferol-3-*O*-{[*β*-*D*-xylopyranosyl(1→3)-*α*-*L*-rhamnopyranosyl(1→6)][*α*-*L*-rhamnopyranosyl(1→2)]}-*β*-*D*-3-trans-*p*-coumaroylgalactopyranoside(**4**),细梗香草皂苷 K(**5**),3*β*-*O*-{*α*-*L*-rhamnopyranosyl-(1→2)-*O*-*β*-*D*-glucopyranosyl-(1→4)-[*O*-*β*-*D*-glucopyranosyl-(1→2)]-*α*-*L*-arabinopyranosyl)}-16*α*-hydroxyolean-28, 13*β*-olide(**6**),细梗香草皂苷 I(**7**),quercetin-3-*O*-(2″,6″-di-*O*-*α*-rhamnopyranosyl)-*β*-galactopyranoside (**8**), kaempferol-3-*O*-{[*β*-*D*-xylopyranosyl (1→3)-*α*-*L*-rhamnopyranosyl (1→6)][*α*-*L*-rhamnopyranosyl-(1→2)]}-*β*-*D*-galactopyranoside (**9**), kaempferol-3-*O*-[2-glucopyranosyl (1→3) rhamnopyranosyl-6-rhamnopyranosyl]-*β*-*D*-galactopyranoside (**10**),

kaempferol-3-*O*-α-*L*-rhamnopyranosy-(1→2)-[α-*L*-rhamnopyranosy-(1→6)]-β-*D*-galactopyranoside (**11**), capilliposide I (**12**), kaempferol-3-*O*-{(β-*D*-glucopyranosyl-(1→3)-[4-*O*-(*E*-*p*-coumaroyl)]-α-*L*-rhamnopyranosyl-(1→6)-(β-*D*-galactopyranoside)}-7-*O*-α-*L*-rhamnopyranoside (**13**), kaempferol-3-*O*-{[β-*D*-glucopyranosyl(1→3)]-4-*O*-(*E*-*p*-coumaroyl)}-α-*L*-rhamnopyranosyl (1→6)-β-*D*-glucopyranoside-7-*O*(4-*O*-acetyl)-α-*L*-rhamnopyranoside (**14**), (3β,20*S*,23*S*,24*R*)-3,20,23,24,25,29-hexahydroxydammaran-21-oic acid-21,23-lactone 3-*O*-β-*D*-glucopyranosyl-(1→6)-β-*D*-gluco-pyranoside (**15**)。其中化合物 **3**,**4**,**6**,**9**,**10**,**13**~**15** 为首次在该植物中分离得到。

1 材料

1260 型 HPLC,1200 型制备液相,1260 型 ELSD(美国 Aglient 科技有限公司);2010 系列 HPLC(日本岛津公司);Sepacore 型中压制备液相色谱仪(瑞士步琪);TLC Visualzer 型薄层成像系统(瑞士卡玛公司);C_{18} 反相填料(日本 YMC 公司);硅胶 G 预制板(青岛海洋化工,20 cm×10 cm);LH-20 型羟丙基葡聚糖凝胶(Sephadex LH-20,美国 GE 公司);AB-8 型大孔树脂(东鸿化工有限公司);其他试剂均为分析纯。

细梗香草药材由课题组前往江西省吉安市永丰县石马镇济民村、上升村、北坑村采集,经江西中医药大学刘勇教授鉴定为报春花科珍珠菜属植物细梗香草(*Lysimachia capillipes*)的干燥全草。标本保存在江西省药品检验检测研究院标本馆。

2 提取分离

取干燥的细梗香草全草药材 4 kg,打粉,用 70% 的乙醇回流提取 2 次,每次 2 h,滤过,取续滤液合并转移至旋转蒸发仪内,减压浓缩至无醇味,得浸膏约 3 L,取药液 1.2 L 用纯净水稀释至 3 L,用水饱和正丁醇按照(1∶1)萃取,萃取 4 次,减压浓缩成浸膏。取正丁醇萃取所得药材浸膏用纯净水溶解稀释至 2 L,离心(3 000 r·min^{-1},10 min),取上清液上 AB-8 大孔树脂柱分别用水,40% 乙醇,70% 乙醇,95% 乙醇洗脱合并得 Fr. 1 ~ Fr. 4 共 4 个馏分;馏分 Fr. 3(50.98 g)过中压 C_{18} 反相色谱柱甲醇-水(70∶30)反复洗脱得 Fr. 3. 1 ~ Fr. 3. 4 共 4 个馏分,Fr. 3. 1 经硅胶柱色谱三氯甲烷-甲醇梯度洗脱,Sephadex LH-20 柱色谱及制备液相得到化合物 **1**(300.67 mg),**3**(5.33 mg),**4**(5.82 mg)和 **5**(7.18 mg),Fr. 3. 2 经硅胶柱色谱三氯甲烷-甲醇梯度洗脱,Sephadex LH-20 柱色谱及制备液相得到化合物 **2**(150.37 mg);馏分 Fr. 2(11.74 g)过中压 C_{18} 反相柱甲醇-水(38∶62,40∶60,45∶55,100∶0)4 个梯度反复洗脱得 Fr. 2. 1 ~ Fr. 2. 5 共 5 个馏分,Fr. 2. 1 经硅胶柱色谱三氯甲烷-甲醇梯度洗脱,Sephadex LH-20 柱色谱及制备液相得到化合物 **6**(7.48 mg),**7**(10.01 mg),**8**(4.83 mg),**9**(24.33 mg),**10**(7.63 mg),**11**(14.36 mg),**12**(31.01 mg),**13**(57.62 mg),**14**(8.46 mg)和 **15**(6.79 mg)。

3 结构鉴定

化合物 1　白色粉末(甲醇),ESI-MS *m/z* 1 176.7[M]$^-$,^{1}H-NMR(600 MHz,C_5D_5N)δ:5.69(1H,d,*J* = 6.0 Hz),5.27(1H,d,*J* = 6.0 Hz),5.01(1H,d,*J* = 6.0 Hz),4.81(1H,d,*J* = 6.0 Hz);^{13}C-NMR(150 MHz,C_5D_5N)δ:39.49(C-1),26.91(C-2),89.35(C-3),40.07(C-4),55.98(C-5),18.28(C-6),34.62(C-7),43(C-8),50.63(C-9),37.11(C-10),19.58(C-11),33.58(C-12),87.91(C-13),44.25(C-14),37.11(C-15),70.15(C-16),51.85(C-17),47.65(C-18),38.59(C-19),33.65(C-20),42.01(C-21),72.96(C-22),28.37(C-23),16.96(C-24),16.71(C-25),18.95(C-26),19.99(C-27),98.16(C-28),33.69(C-29),25.97(C-30);Ara:105.04(C-1),79.98(C-2),73.66(C-3),78.56(C-4),64.62(C-5);Glc-1:105.17(C-1),76.57(C-2),78.15(C-3),72.17(C-4),78.33(C-5),63.35(C-6);Glc-2:104.55(C-1),85.75(C-2),77.88(C-3),71.4(C-4),78.68(C-5),62.63(C-6);Xly:108.02(C-1),76.46(C-2),77.88(C-3),71.05(C-4),67.81(C-5);173.39(C-a),35.26(C-b),25.46(C-c),31.71(C-d),22.83(C-e),14.32(C-f)。上述数据与文献[3]中基本一致,故鉴定化合物为细梗香草皂苷 B。

化合物 2　白色粉末(甲醇),ESI-MS *m/z* 1 161.8[M-H]$^-$,^{1}H-NMR(600 MHz,C_5D_5N)δ:5.50(1H,d,*J* = 7.2 Hz),5.24(1H,d,*J* = 6.0 Hz),4.93(1H,d,*J* = 7.2 Hz),4.81(1H,d,*J* = 6.0 Hz);^{13}C-NMR(150 MHz,C_5D_5N)δ:40.13(C-1),26.55(C-2),89.37(C-3),42.07(C-4),56.05(C-5),19.03(C-6),34.7(C-7),44.33(C-8),50.7(C-9),38.7(C-10),20.07(C-11),33.77(C-12),88(C-13),44.55(C-14),37.25(C-15),70.25(C-16),51.88(C-17),47.75(C-18),39.55(C-19),33.77(C-20),43.09(C-21),72.93(C-22),28.46(C-23),18.35(C-24),17.05(C-25),19.65(C-26),21.28(C-27),98.24(C-28),33.73(C-29),26.03(C-30);

Ara: 105.08 (C-1), 80.12 (C-2), 73.66 (C-3), 78.97 (C-4), 64.59 (C-5); Glc-1: 105.32 (C-1), 76.67 (C-2), 78.01 (C-3), 72.23 (C-4), 78.65 (C-5), 63.41 (C-6); Glc-2: 104.58 (C-1), 85.88 (C-2), 78.38 (C-3), 71.49 (C-4), 78.24 (C-5), 62.72 (C-6); Xyl: 108.13 (C-1), 76.56 (C-2), 78.97 (C-3), 71.11 (C-4), 67.9 (C-5); 172.64 (C-a), 26.98 (C-b), 44.88 (C-c), 22.84 (C-d), 22.75 (C-e)。上述数据与文献[9]中基本一致,故鉴定化合物为细梗香草皂苷 C。

化合物 **3** 淡黄色粉末(甲醇),ESI-MS *m/z* 1 181 $[M+H]^+$,^{1}H-NMR (600 MHz, MeOD) δ: 8.10 (1H, d, J = 9.0 Hz), 7.68 (1H, d, J = 8.4 Hz), 7.51 (1H, d, J = 8.4 Hz), 6.93 (1H, d, J = 9.0 Hz), 6.78 (1H, d, J = 9.0 Hz), 6.36 (1H, d, J = 2.4 Hz), 6.34 (1H, d, J = 1.8 Hz), 6.17 (1H, d, J = 1.8 Hz), 5.76 (1H, d, J = 12.6 Hz), 5.61 (1H, d, J = 7.8 Hz), 4.64 (1H, d, J = 1.2 Hz), 4.29 (1H, d, J = 7.8 Hz), 4.26 (1H, d, J = 7.8 Hz); ^{13}C-NMR (150 MHz, MeOD) δ: 158.61 (C-2), 134.26 (C-3), 179.6 (C-4), 162.97 (C-5), 100.85 (C-6), 163.01 (C-7), 95.39 (C-8), 158.32 (C-9), 105.43 (C-10), 123.07 (C-1′), 132.2 (C-2′, 6′), 116.76 (C-3′, 5′), 160.12 (C-4′); Gal: 100.9 (C-1), 77.61 (C-2), 75.16 (C-3), 70.97 (C-4), 75.72 (C-5), 69.8 (C-6); Rha-1: 102.18 (C-1), 72.34 (C-2), 78.94 (C-3), 73.36 (C-4), 68.78 (C-5), 17.52 (C-6); Xyl: 100.85 (C-1), 71.93 (C-2), 72.41 (C-3), 73.36 (C-4), 71.17 (C-5), 17.87 (C-6); Glc: 105.13 (C-1), 74.08 (C-2), 77.52 (C-3), 71.17 (C-4), 67.96 (C-5); Rha-2: 102.53 (C-1), 74.87 (C-2), 77.28 (C-3), 71.93 (C-4), 77.52 (C-5), 62.13 (C-6); 167.52 (C-a), 115.79 (C-b), 132.2 (C-c), 127.64 (C-d), 145.91 (C-e), 116.25 (C-f), 161.35 (C-g) 为香豆酸上质子信号。上述数据与文献[10]中基本一致,故鉴定化合物为 kaempferol-3-*O*-β-*D*-xylopyranosyl (1→3)-[4-*O*-*E*-*p*-coumaroyl-α-*L*-rhamnopyranosyl (1→2)] [β-*D*-glucopyranosyl (1→6)]-β-*D*-galactopyranoside-7-*O*-α-*L*-rhamnopyranoside。

化合物 **4** 淡黄色粉末(甲醇),ESI-MS *m/z* 1 019 $[M+H]^+$,^{1}H-NMR (600 MHz, MeOD) δ: 6.15 (1H, d, J = 2.4 Hz), 6.34 (1H, d, J = 2.4 Hz), 8.07 (1H, d, J = 2.4 Hz), 6.83 (1H, d, J = 6.0 Hz), 5.73 (1H, d, J = 7.8 Hz), 5.02 (1H, d, J = 1.2 Hz), 4.61 (1H, d, J = 3.0 Hz), 4.23 (1H, d, J = 7.8 Hz); ^{13}C-NMR (150 MHz, MeOD) δ: 158.61 (C-2), 134.28 (C-3), 179.32 (C-4), 162.47 (C-5), 100.7 (C-6), 165.48 (C-7), 95.36 (C-8), 158.34 (C-9), 105.17 (C-10), 123.05 (C-1′), 132.21 (C-2′, 6′), 116.25 (C-3′, 5′), 161.35 (C-4′), 上述数据与文献[11]中基本一致,故鉴定化合物为 kaempferol-3-*O*-{[β-*D*-xylopyranosyl (1→3)-α-*L*-rhamnopyranosyl (1→6)] [α-*L*-rhamnopyranosyl (1→2)]}-β-*D*-3-trans-*p*-coumaroylgalactopyranoside。

化合物 **5** 白色粉末(甲醇),ESI-MS *m/z* 1 223.8 $[M-H]^-$,^{1}H-NMR (600 MHz, C_5D_5N) δ: 5.34 (1H, br t, H-12), 5.50 (1H, d, J = 6.0 Hz), 5.20 (1H, d, J = 6.0 Hz), 5.00 (1H, d, J = 6.0 Hz), 4.91 (1H, d, J = 12.0 Hz), 4.78 (1H, d, J = 6.0 Hz); ^{13}C-NMR (150 MHz, C_5D_5N) δ: 39.15 (C-1), 26.71 (C-2), 89.25 (C-3), 39.9 (C-4), 56.08 (C-5), 18.72 (C-6), 33.29 (C-7), 40.37 (C-8), 47.3 (C-9), 37.1 (C-10), 24.14 (C-11), 123.17 (C-12), 144.66 (C-13), 42.31 (C-14), 34.77 (C-15), 69.52 (C-16), 45.51 (C-17), 42.62 (C-18), 47.64 (C-19), 32.14 (C-20), 44.95 (C-21), 86.72 (C-22), 28.35 (C-23), 17.06 (C-24), 15.96 (C-25), 17.1 (C-26), 27.76 (C-27), 69.52 (C-28), 33.95 (C-29), 25.65 (C-30); Ara: 105.1 (C-1), 79.9 (C-2), 73.68 (C-3), 79.12 (C-4), 63.32 (C-5); Glc-1: 105 (C-1), 75.99 (C-2), 78.51 (C-3), 71.87 (C-4), 78.65 (C-5), 62.91 (C-6); Glc-2: 104.55 (C-1), 85.71 (C-2), 76.54 (C-3), 70.36 (C-4), 78.3 (C-5), 62.59 (C-6); Xyl: 107.99 (C-1), 75.96 (C-2), 78.11 (C-3), 71.36 (C-4), 67.78 (C-5); Glc-3: 107.18 (C-1), 76.36 (C-2), 77.8 (C-3), 71.87 (C-4), 78.65 (C-5), 62.59 (C-6)。上述数据与文献[12]中基本一致,故鉴定化合物为细梗香草皂苷 K。

化合物 **6** 白色粉末(甲醇),ESI-MS *m/z* 1 059 $[M-H]^-$,^{1}H-NMR (600 MHz, C_5D_5N) δ: 5.51 (1H, d, J = 6.0 Hz), 5.28 (1H, d, J = 6.0 Hz), 4.94 (1H, d, J = 12.0 Hz), 4.81 (1H, d, J = 6.0 Hz); ^{13}C-NMR (150 MHz, C_5D_5N) δ: 40.08 (C-1), 25.82 (C-2), 89.22 (C-3), 39.42 (C-4), 55.88 (C-5), 16.99 (C-6), 34.34 (C-7), 42.66 (C-8), 50.11 (C-9), 37.34 (C-10), 19.84 (C-11), 34.34 (C-12), 92.43 (C-13), 43.38 (C-14), 38.05 (C-15), 71.64 (C-16), 45.38 (C-17), 51.74 (C-18), 38.71 (C-19), 31.74 (C-20), 37.15 (C-21), 28.42 (C-22), 16.6 (C-23), 26.91 (C-24), 16.29 (C-25), 18.39 (C-26), 21.18 (C-27),

177.9(C-28),33.34(C-29),23.31(C-30);Glc-1:105.09(C-1),85.87(C-2),78(C-3),71.12(C-4),78.66(C-5),64.63(C-6);Glc-2:105.39(C-1),76.67(C-2),78.24(C-3),71.5(C-4),78.79(C-5),63.4(C-6);Xly:108.12(C-1),76.55(C-2),77.49(C-3),71.12(C-4),67.9(C-5);Ara:104.56(C-1),80.18(C-2),72.25(C-3),78.39(C-4),64.6(C-5)。上述数据与文献[13]中基本一致,故鉴定化合物为3β-*O*-{α-*L*-rhamnopyranosyl-(1→2)-*O*-β-*D*-glucopyranosyl-(1→4)-[*O*-β-*D*-glucopyranosyl-(1→2)]-α-*L*-arabinopyranosyl}-16α-hydroxyolean-28,13β-olide。

化合物**7** 白色粉末(甲醇),(+)ESI-MS *m/z* 1 091.7[M+Na]$^+$,(−)ESI-MS *m/z* 1 067.7[M−H]$^-$,^{1}H-NMR(600 MHz,C_5D_5N)δ:5.82(1H,d,*J*=7.8 Hz),5.19(1H,d,*J*=7.8 Hz),4.94(1H,d,*J*=6.0 Hz);^{13}C-NMR(150 MHz,C_5D_5N)δ:38.781(C-1),26.35(C-2),88.34(C-3),39.36(C-4),55.18(C-5),18.24(C-6),32.83(C-7),42.0(C-8),49.48(C-9),36.48(C-10),30.95(C-11),33.49(C-12),91.82(C-13),42.12(C-14),32.96(C-15),68.29(C-16),51.66(C-17),50.41(C-18),37.31(C-19),32.46(C-20),44.57(C-21),74.3(C-22),27.77(C-23),16.26(C-24),15.84(C-25),17.52(C-26),19.12(C-27),176.59(C-28),32.96(C-29),25.02(C-30);167.41(COO),128.24(C-b),137.46(C-c),20.62(C-d),15.97(C-e)为当归酰氧基上质子信号,Ara:104.65(C-1),80.96(C-2),73.23(C-3),68.09(C-4),64.63(C-5);Glc-1:105.86(C-1),75.5(C-2),77.98(C-3),71.32(C-4),77.98(C-5),62.32(C-6);Glc-2:103.7(C-1),75.9(C-2),76.24(C-3),71.32(C-4),77.98(C-5),64.83(C-6)。上述数据与文献[14]中基本一致,故鉴定化合物为细梗香草皂苷Ⅰ。

化合物**8** 淡黄色粉末(甲醇),FAB-MS *m/z* 755[M−H]$^-$,301[M−H−$C_{18}H_{30}O_{13}$]$^-$,^{1}H-NMR(600 MHz,MeOD)δ:6.18(1H,d,*J*=1.8 Hz),6.36(1H,d,*J*=1.8 Hz),7.70(1H,d,*J*=1.8 Hz),6.88(1H,d,*J*=8.4 Hz),7.57(1H,dd,*J*=1.8,2.4 Hz)5.67(1H,d,*J*=7.8 Hz),5.22(1H,br s,H-1),4.55(1H,br s,H-1′);^{13}C-NMR(150 MHz,MeOD)δ:158.37(C-2),134.5(C-3),179.28(C-4),163.12(C-5),99.87(C-6),166.15(C-7),94.69(C-8),158.39(C-9),105.74(C-10),123.31(C-1′),117.32(C-2′),145.86(C-3′),149.63(C-4′),116.13(C-5′),123.01(C-6′);Glc:101.04(C-1),77.44(C-2),75.76(C-3),70.85(C-4),75.27(C-5),66.97(C-6);Rha-1:102.58(C-1),72.42(C-2),72.27(C-3),74.06(C-4),69.84(C-5),17.4(C-6);Rha-2:101.85(C-1),72.09(C-2),72.32(C-3),73.88(C-4),69.71(C-5),17.97(C-6)。上述数据与文献[15]中基本一致,故鉴定化合物为 quercetin-3-*O*-(2″,6″-di-*O*-α-rhamnopyranosyl)-β-galactopyranoside。

化合物**9** 淡黄色粉末(甲醇),ESI-MS *m/z* 873[M+H]$^+$,^{1}H-NMR(600 MHz,MeOD)δ:6.18(1H,d,*J*=1.8 Hz),6.37(1H,d,*J*=1.8 Hz),8.07(1H,d,*J*=8.4 Hz),6.90(1H,d,*J*=9.0 Hz),5.58(1H,d,*J*=7.8 Hz),5.23(1H,d,*J*=1.8 Hz),4.57(1H,d,*J*=1.8 Hz),4.39(1H,d,*J*=7.8 Hz);^{13}C-NMR(150 MHz,MeOD)δ:158.49(C-2),134.45(C-3),179.36(C-4),163.09(C-5),100.13(C-6),166.5(C-7),94.46(C-8),158.58(C-9),105.66(C-10),123.06(C-1′),132.23(C-2′,6′),116.18(C-3′,5′),161.29(C-4′);Glc:100.99(C-1),77.58(C-2),75.69(C-3),70.77(C-4),75.39(C-5),67.41(C-6);Rha-1:102.59(C-1),72.43(C-2),72.35(C-3),74.08(C-4),69.84(C-5),17.54(C-6);Rha-2:101.69(C-1),71.31(C-2),82.97(C-3),72.6(C-4),69.43(C-5),18.04(C-6);Xyl:105.66(C-1),75.16(C-2),77.44(C-3),70.86(C-4),67.41(C-5)。上述数据与文献[16]中基本一致,故鉴定化合物为 kaempferol-3-*O*-{[β-*D*-xylopyranosyl(1→3)-α-*L*-rhamnopyranosyl(1→6)][α-*L*-rhamnopyranosyl-(1→2)]}-β-*D*-galactopyranoside。

化合物**10** 淡黄色粉末(甲醇),ESI-MS *m/z* 903[M+H]$^+$,^{1}H-NMR(600 MHz,MeOD)δ:6.20(1H,d,*J*=1.8 Hz),6.40(1H,d,*J*=1.8 Hz),8.07(1H,d,*J*=9.0 Hz),6.90(1H,d,*J*=8.4 Hz),5.59(1H,d,*J*=7.8 Hz),4.48(1H,d,*J*=7.8 Hz),5.11(1H,d,*J*=3.6 Hz),4.39(1H,d,*J*=7.8 Hz);^{13}C-NMR(150 MHz,MeOD)δ:158.71(C-2),134.5(C-3),179.43(C-4),163.14(C-5),99.81(C-6),165.57(C-7),94.73(C-8),158.42(C-9),105.93(C-10),123.01(C-1′),132.24(C-2′,6′),116.17(C-3′,5′),161.29(C-4′);Glc-1:101(C-1),77.6(C-2),75.68(C-3),70.85(C-4),75.37(C-5),67.37(C-6);Rha-1:102.58(C-1),72.34(C-2),71.32(C-3),74.06(C-4),69.44(C-5),18.04(C-6);Rha-2:101.68(C-1),72.42(C-2),82.95(C-3),

72.6(C-4),70.74(C-5),17.52(C-6);Glc-2:105.66(C-1),75.15(C-2),77.45(C-3),69.83(C-4),77.59(C-5),62.05(C-6)。上述数据与文献[17]中基本一致,故鉴定化合物为 kaempferol-3-*O*-[2-glucopyranosyl(1→3)rhamnopyranosyl-6-rhamnopyranosyl]-*β*-*D*-galactopyranoside。

化合物 **11** 淡黄色粉末(甲醇),FAB-MS *m/z* 739[M−H]$^-$,285[M−H−$C_{18}H_{30}O_{13}$]$^-$,^{1}H-NMR(600 MHz,MeOD)*δ*:6.20(1H,d,*J*=2.4 Hz),6.40(1H,d,*J*=2.4 Hz),8.07(1H,d,*J*=9.0 Hz),6.90(1H,d,*J*=9.0 Hz),5.62(1H,d,*J*=7.8 Hz),5.23(1H,d,*J*=1.8 Hz),4.53(1H,d,*J*=1.8 Hz);^{13}C-NMR(150 MHz,MeOD)*δ*:158.67(C-2),134.45(C-3),179.4(C-4),163.14(C-5),99.75(C-6),165.61(C-7),94.65(C-8),158.41(C-9),105.88(C-10),123.03(C-1′),132.21(C-2′,6′),116.17(C-3′,5′),161.28(C-4′);Gal:100.85(C-1),77.55(C-2),75.71(C-3),70.7(C-4),75.29(C-5),67.12(C-6);Rha-1:102.48(C-1),72.42(C-2),72.34(C-3),74.07(C-4),69.83(C-5),17.53(C-6);Rha-1:101.83(C-1),72.08(C-2),72.28(C-3),73.87(C-4),69.69(C-5),17.95(C-6)。上述数据与文献[18]中基本一致,故鉴定化合物为 kaempferol-3-*O*-*α*-*L*-rhamnopyranosy-(1→2)-[*α*-*L*-rhamnopyranosy-(1→6)]-*β*-*D*-galactopyranoside。

化合物 **12** 淡黄色粉末(甲醇),FAB-MS *m/z* 1 049[M+H]$^+$,^{1}H-NMR(600 MHz,MeOD)*δ*:6.21(1H,d,*J*=2.4 Hz),6.38(1H,d,*J*=2.4 Hz),8.10(1H,d,*J*=9.0 Hz),6.94(1H,d,*J*=9.0 Hz),5.67(1H,d,*J*=7.2 Hz),5.25(1H,d,*J*=1.2 Hz),4.64(1H,d,*J*=1.2 Hz),4.29(1H,d,*J*=7.8 Hz);^{13}C-NMR(150 MHz,MeOD)*δ*:157.28(C-2),133.01(C-3),178.09(C-4),161.75(C-5),98.48(C-6),164.35(C-7),93.35(C-8),157.03(C-9),104.42(C-10),121.63(C-1′),130.87(C-2′,6′),114.84(C-3′,5′),159.92(C-4′);Gal:99.45(C-1),75.91(C-2),74.32(C-3),69.54(C-4),73.45(C-5),66.56(C-6);Rha-1:101.13(C-1),70.94(C-2),71(C-3),72.34(C-4),68.42(C-5),16.09(C-6);Rha-2:100.55(C-1),70.52(C-2),76.11(C-3),72.66(C-4),66.1(C-5),16.4(C-6);Glc:104.06(C-1),73.74(C-2),76.17(C-3),69.8(C-4),77.71(C-5),60.78(C-6);167.55(C-a),113.87(C-b),129.91(C-c),125.87(C-d),145.55(C-e),115.4(C-f),159.9(C-g)为香豆酸上质子信号。上述数据与文献[19]中基本一致,故鉴定化合物为 capilliposide I。

化合物 **13** 淡黄色粉末(甲醇),ESI-MS *m/z* 1 047[M−H]$^-$,^{1}H-NMR(600 MHz,MeOD)*δ*:6.49(1H,d,*J*=1.8 Hz),6.71(1H,d,*J*=1.8 Hz),8.14(1H,d,*J*=8.4 Hz),6.84(1H,d,*J*=9.0 Hz),5.10(1H,d,*J*=6.6 Hz),4.59(1H,d,*J*=1.2 Hz),5.69(1H,d,*J*=7.8 Hz),4.31(1H,d,*J*=7.8 Hz),6.94(1H,d,*J*=8.4 Hz),7.50(1H,d,*J*=8.4 Hz),7.62(1H,d,*J*=16.2 Hz),6.34(1H,d,*J*=15.6 Hz),查阅文献[22]推测可能含有香豆酸结构;^{13}C-NMR(150 MHz,MeOD)*δ*:159.62(C-2),134.83(C-3),179.5(C-4),161.6(C-5),100.86(C-6),162.48(C-7),99.9(C-8),157.34(C-9),108.78(C-10),122.76(C-1′),132.46(C-2′,6′),116.82(C-3′,5′),161.29(C-4′);Gal:104.15(C-1),75.7(C-2),74.05(C-3),69.84(C-4),77.37(C-5),68.43(C-6);Rha-1:102.53(C-1),72.35(C-2),78.84(C-3),73.84(C-4),67.96(C-5),17.51(C-6);Glc:105.32(C-1),75.44(C-2),77.59(C-3),71.03(C-4),77.47(C-5),62.16(C-6);Rha-2:102.06(C-1),71.91(C-2),72.35(C-3),74.86(C-4),71.1(C-5),17.85(C-6);168.91(C-a),116.3(C-b),131.33(C-c),127.25(C-d),146.98(C-e),115.26(C-f),162.48(C-g)为香豆酸上质子信号。上述数据与文献[20-21]中基本一致,故鉴定化合物为 kaempferol-3-*O*-{(*β*-*D*-glucopyranosyl-(1→3)-[4-*O*-(*E*-*p*-coumaroyl)]-α-*L*-rhamnopyranosyl-(1→6)-(*β*-*D*-galactopyranoside)}-7-*O*-*α*-*L*-rhamnopyranoside。

化合物 **14** 淡黄色粉末(甲醇),HR ESI-TOF-MS *m/z* 1 659.439 8(计算值 $C_{76}H_{84}O_{40}Na$,1 659.443 7)[M+Na]$^+$,^{1}H-NMR(600 MHz,MeOD)*δ*:8.55(1H,d,*J*=8.4 Hz),7.54(1H,d,*J*=8.4 Hz),7.47(1H,d,*J*=9.0 Hz),7.63(1H,d,*J*=9.0 Hz),7.62(1H,d,*J*=16.2 Hz),6.33(1H,d,*J*=15.6 Hz),查阅文献[22]推测可能含有香豆酸结构;^{13}C-NMR(150 MHz,MeOD)*δ*:159.05(C-2),133.88(C-3),178.72(C-4),161.48(C-5),100.98(C-6),162.59(C-7),96.78(C-8),157.41(C-9),107.91(C-10),122.98(C-1′),131.9(C-2′,6′),116.24(C-3′,5′),162.62(C-4′);Glc-1:103.21(C-1),75.13(C-2),78.13(C-3),77.23(C-4),71(C-5),67.98(C-6);Rha-1:100.97(C-1),71.37(C-2),71.86(C-3),73.65(C-4),71.37(C-5),17.83(C-6);Rha-2:102(C-1),69.88(C-2),79.29(C-3),72.41(C-4),67.98(C-5),17.46(C-6);Glc-2:

105.46(C-1),77.49(C-2),77.54(C-3),72.26(C-4),74.92(C-5),62.1(C-6);167.14(C-a),116.87(C-b),147.2(C-e),126.56(C-d),131.37(C-c),117.28(C-f),159.09(C-g)为香豆酸上质子信号。上述数据与文献[22]中基本一致,故鉴定化合物为kaempferol-3-*O*-{[β-*D*-glucopyranosyl(1→3)]-4-*O*-(*E*-*p*-coumaroyl)}-α-*L*-rhamnopyranosyl(1→6)-β-*D*-glucopyranoside-7-*O*(4-*O*-acetyl)-α-*L*-rhamnopyranoside。

化合物 **15** 白色粉末,HR ESI-TOF-MS *m/z* 869.450 8(计算值 869.450 5)[M+Na]$^+$,^{1}H-NMR(600 MHz,C_5D_5N)δ:5.48(1H,d,*J*=7.2 Hz),5.25(1H,d,*J*=9.0 Hz);^{13}C-NMR(150 MHz,C_5D_5N)δ:39.57(C-1),27.01(C-2),89.39(C-3),43.12(C-4),56.08(C-5),19.06(C-6),34.72(C-7),40.16(C-8),51.9(C-9),37.28(C-10),22.77(C-11),28.48(C-12),44.36(C-13),50.73(C-14),33.79(C-15),26.06(C-16),44.58(C-17),16.82(C-18),17.08(C-19),80.15(C-20),178.99(C-21),33.76(C-22),78.82(C-23),78.04(C-24),72.26(C-25),27(C-26),27.03(C-27),22.86(C-28),63.44(C-29),20.09(C-30);Glc-1:108.16(C-1),76.59(C-2),78.27(C-3),71.52(C-4),78.68(C-5),70.27(C-6);Glc-2:105.36(C-1),76.7(C-2),78.41(C-3),71.14(C-4),78.9(C-5),62.75(C-6)。上述数据与文献[23]中基本一致,故鉴定化合物为(3β,20*S*,23*S*,24*R*)-3,20,23,24,25,29-hexahydroxydammaran-21-oic acid-21,23-lactone 3-*O*-β-*D*-glucopyranosyl-(1→6)-β-*D*-gluco-pyranoside。

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