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南岭栲叶多酚类化学成分的分离与鉴定

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摘　要:采用 Sephadex LH-20、MCI gel CHP 20P 和 Toyopearl Butyl-650C 等柱色谱及半制备液相色谱技术,从壳斗科(Fagaceae)锥属(*Castanopsis*)植物南岭栲(*Castanopsis fordii* Hance)叶子乙醇提取物中分离得到 18 个多酚类化合物,运用波谱学方法解析鉴定为:没食子酸(**1**)、没食子酸甲酯(**2**)、没食子酸乙酯(**3**)、莽草酸-3-*O*-没食子酸酯(**4**)、3,3′-二甲基鞣花酸(**5**)、3,3′-二甲氧基鞣花酸-4′-*O*-α-D-吡喃木糖苷(**6**)、3-甲氧基-4′-鼠李糖鞣花酸(**7**)、6-*O*-没食子酰基熊果苷(**8**)、龙胆酸 5-*O*-β-D-(6′-*O*-没食子酰基)-吡喃葡萄糖(**9**)、4-hydroxy-3-methoxyphenol 1-*O*-β-D-(6′-*O*-galloyl) glucoside(**10**)、1,6-二-*O*-没食子酰基-β-D-葡萄糖苷(**11**)、gallic acid 3-*O*-β-D-(6′-*O*-galloyl)-glucopyranoside(**12**)、benzyl 6-*O*-galloyl-β-D-glucopyranoside(**13**)、2,3-di-*O*-galloyl-D-glucose(**14**)、gemin D(**15**)、特里马素(**16**)、丁香素(**17**)、viburnolide A(**18**)。所有化合物均为首次从该植物中分离得到。

关键词:南岭栲;多酚类成分;提取分离;结构鉴定

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Isolation and Identification of Polyphenols from the Leaves of *Castanopsis fordii* Hance

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Abstract: Eighteen polyphenols were isolated from the ethanol extract of the leaves of *Castanopsis fordii* Hance using Sephadex LH-20, MCI gel CHP 20P, Toyopearl Butyl-650C column chromatographies and semi-preparative HPLC. Their structures were identified by spectral analysis and were determined as gallic acid(**1**), methyl gallate(**2**), ethyl gallate(**3**), 3-*O*-galloyl-(-)-shikimic acid(**4**), 3,3′-di-*O*-methylellagic acid(**5**), 3,3′-di-*O*-methyl ellagic acid-4′-*O*-α-D-xylopyranoside(**6**), 3-*O*-methy-lellagic acid 4′-*O*-rhamnopyranoside(**7**), 6-*O*-galloylarbutin(**8**), gentisic acid 5-*O*-β-D-(6′-*O*-galloyl)-glucopyranoside(**9**), 4-hydroxy-3-methoxyphenol 1-*O*-β-D-(6′-*O*-galloyl) glucoside(**10**), 1,6-di-*O*-galloyl-β-D-glucose(**11**), 1,6-di-*O*-3-galloyl-D-glucose(**12**), benzyl 6-*O*-galloyl-D-glucopyranoside(**13**), 2,3-di-*O*-galloyl-D-glucose(**14**), gemin D(**15**), tellimagrandin(**16**), eugeniin(**17**), viburnolide A(**18**). All the compounds were isolated from this plant for the first time.

Key words: *Castanopsis fordii* Hance; polyphenols; isolation and separation; structural identification

南岭栲(*Castanopsis fargesii* Hance)又名毛锥为壳斗科(Fagaceae)锥属(*Castionpsis*)植物,是中国南亚热带和中亚热带典型的常绿阔叶林植物,在我国主要分布于长江以南各地[1],在木材生产、保持水土流失等方面具有很高的利用价值,民间常常用于止泻、慢性溃疡等疾病的治疗[1,2]。现有的研究发现锥属植物含有大量的多酚类成分且结构类型多样[3,4],具有开发成抗氧化、抑制心血管疾病、抗炎抑菌等保健品和药用的潜在价值。该植物资源丰富,但是关于其化学成分及生物活性的研究鲜有报道。因此本研究以广泛生长于中国广西桂林阳朔县的南岭栲为研究对象,对其乙醇提取物的化学成分进行研究,通过 Sephadex LH-20、MCI gel CHP 20P 和 Toyopearl Butyl-650C 等柱色谱与半制备液相色

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谱技术及波谱学方法分离鉴定了 18 个多酚类化合物,所有化合物均为首次从南岭栲中分离得到,为该植物的合理开发与可持续利用奠定了基础。

1 仪器与材料

核磁共振谱用 Bruker Avance 500 MHz 超导核磁共振波谱仪测定,TMS 为内标;半制备液相色谱仪(北京赛谱锐思公司);薄层色谱硅胶 GF_{254} 为 Merck 公司产品;Sephadex LH-20(25 ~ 100 μm)为 GE Healthcare Bio-Science AB 公司产品;MCI gel CHP 20P(75 ~ 150 μm)为 Mitsubishi Chemical 公司产品;Toyopearl HW-40F 为 TOSOH 公司产品;所用试剂甲醇、乙醇、乙腈等均为分析纯(AR)。

实验样品于 2014 年 8 月采自广西壮族自治区桂林市阳朔县,经广西壮族自治区中国科学院广西植物研究所吕仕洪副研究员鉴定为壳斗科锥属植物南岭栲(*Castanopsis fargesii* Hance)的树叶,凭证标本(20140821)保存于广西壮族自治区中国科学院广西植物研究所广西植物功能物质研究与利用重点实验室。

2 提取与分离

新鲜南岭栲树叶 5.0 kg,切成碎片后用 80% 乙醇室温浸提 2 次,每次 20 L,每次 5 d。提取液经减压浓缩后得无醇味水溶液,过滤后经 Sephadex LH-20 柱层析(8.5 cm × 40 cm),甲醇-水(0 ~ 100% MeOH,20% 为一梯度,每一梯度 2 L)进行梯度洗脱,得到 9 个部分分别为 Fr1(45.0 g)、Fr2(19.6 g)、Fr3(29.1 g)、Fr4(90.8 g)、Fr5(110.0 g)、Fr6(40.0 g)、Fr7(2.0 g)、Fr8(4.1 g)、Fr9(150.0 g)。Fr2 经 MCI gel CHP 20P 柱层析(4.5 cm × 25 cm),甲醇-水(0 ~ 40% MeOH,10% 为一梯度,每梯度 0.3 L)梯度洗脱得到 Fr21(8.9 g)、Fr22(7.0 g)、Fr23(1.5 g)。Fr22 经 HP20SS 柱层析(4.5 cm × 27 cm),甲醇-水(0 ~ 100% MeOH,10% 为一梯度,每梯度 0.3 L)梯度洗脱得到 Fr221(1.12 g)、Fr222(2.59 g)、Fr223(1.72 g)、Fr224(0.88 g)、Fr225(1.20 g)和 Fr226(7,52 mg)。Fr222 经 Sephadex LH-20 柱层析(2.0 cm × 21 cm),甲醇-水(0 ~ 60% MeOH,10% 为一梯度,每梯度 0.1 L)进行梯度洗脱得到 Fr2221(0.71 g)、Fr2222(0.50 g)、Fr2223(0.87 g)、Fr2224(0.08 g)。Fr2223 通过半制备液相色谱(C18,10 mm × 250 mm)制备得到化合物 **18**(10 mg)。Fr23 经甲醇、水结晶得到化合物 **6**(827 mg)。Fr4 经 MCI gel CHP 20P 柱层析(4.0 cm × 38 cm)得到 7 个部分,其中 Fr45 经甲醇、水结晶得到化合物 **5**(98 mg)。Fr41(21.3 g)经 Sephadex LH-20 柱层析(4.0 cm × 23 cm),甲醇-水(0 ~ 100% MeOH,10% 为一梯度,每梯度 0.4 L)梯度洗脱得到 Fr411(8.87 g)、Fr412(4.31 g)、Fr413(5.83 g)。Fr411 经 HP20SS 柱层析(4.5 cm × 28 cm),甲醇-水(0 ~ 100% MeOH,10% 为一梯度,每梯度 0.3 L)梯度洗脱得到 Fr4111(0.81 g)、Fr4112(1.84 g)、Fr4113(3.50 g)、Fr4114(1.83 g)。Fr4112 经 Sephadex LH-20 柱层析(2.5 cm × 21 cm),甲醇-水(0 ~ 80% MeOH,10% 为一梯度,每梯度 0.2 L)进行梯度洗脱得到化合物 **4**(8 mg)。Fr4113 经 HW-40F 柱层析(2.5 cm × 21 cm),甲醇-水(0 ~ 80% MeOH,10% 为一梯度,每梯度 0.2 L)进行梯度洗脱得到 Fr41131(98 mg)、Fr41132(0.83 g)、Fr41133(1.30 g)、Fr41134(0.17 g)、Fr41135(0.49 g)。Fr41135 通过半制备液相色谱(C18,10 mm × 250 mm)制备得化合物 **8**(48 mg)和 **10**(8 mg)。Fr412 经 ODS 柱层析(5.0 cm × 26 cm),甲醇-水(0 ~ 100% MeOH,10% 为一梯度,每梯度 0.3 L)进行梯度洗脱得到 Fr4121(0.24 g)、Fr4122(1.24 g)、Fr4123(0.53 g)、Fr4124(0.21 g)、Fr4125(1.0 g)、Fr4126(0.22 g)、Fr4127(0.12 g)、Fr4128(78 mg),其中 Fr4125 经甲醇、水结晶得到化合物 **9**(13 mg)。Fr4122 通过半制备液相色谱(C_{18},10 mm × 250 mm)制备得化合物 **1**(66 mg)和 **14**(66 mg)。Fr413 通过 HP20SS 柱层析(5.0 cm × 26 cm),甲醇-水(0 ~ 100% MeOH,10% 为一梯度,每梯度 0.2 L)进行梯度洗脱得到 Fr4131(2.11 g)、Fr4132(0.78 g)、Fr4133(0.97 g)、Fr4134(0.68 g)。Fr4131 经 Sephadex LH-20 柱层析(2.5 cm × 32 cm),乙醇-水(100 ~ 60% EtOH,10% 为一梯度,每梯度 0.15 L)进行梯度洗脱得到 Fr41311(1.03 g)、Fr41312(0.72 g)。Fr41311 通过半制备液相色谱(C_{18},10 mm × 250 mm)制备得化合物 **11**(54 mg)和 **12**(45 mg)。Fr41312 通过半制备液相色谱(C_{18},10 mm × 250 mm)制备得到化合物 **15**(52 mg)。Fr43 通过半制备液相色谱(C_{18},10 mm × 250 mm)制备得到化合物 **2**(40 mg)和 **3**(10 mg)。Fr9 经 MCI gel CHP 20P 柱层析(4.5 cm × 40 cm),甲醇-水(0 ~ 80% MeOH,10% 为一梯度,每梯度 0.4 L)进行梯度洗脱得到 Fr91(13,31.4 g)、Fr92(11.4 g)、Fr93

(9.11 g)、Fr94(17,4.0 g)、Fr95(8.37 g)、Fr96(4.85 g)、Fr97(8.76 g)、Fr98(7.65 g)。Fr92 通过半制备液相色谱(C_{18},10 mm×250 mm)制备得到化合物 **16**(98 mg)。

3　结构鉴定

化合物 1　白色无定型粉末,^{1}H NMR(acetone-d_6,500 MHz) δ:7.11(2H,s,H-2,6);^{13}C NMR(acetone-d_6,125 MHz) δ:169.2(C-7),145.6(2C,C-3,5),138.7(C-4),121.4(C-1),110.0(2C,C-2,6)。以上数据与文献[5]报道一致,故鉴定化合物 **1** 为没食子酸。

化合物 2　白色无晶状粉末,^{1}H NMR(acetone-d_6,500 MHz) δ:7.04(2H,s,H-2,6),3.74(3H,s,-OCH_3);^{13}C NMR(acetone-d_6,125 MHz) δ:168.0(C-7),145.7(2C,C-3,5),138.8(C-4),120.9(C-1),109.6(2C,C-2,6),52.1(-OCH_3)。以上数据与文献[6]报道一致,故鉴定化合物 **2** 为没食子酸甲酯。

化合物 3　白色粉末,^{1}H NMR(acetone-d_6,500 MHz) δ:7.06(2H,s,H-2,6),4.20(2H,q,J=7.1 Hz,-CH_2-),1.26(3H,t,J=7.1 Hz,-CH_3);^{13}C NMR(acetone-d_6,125 MHz) δ:166.6(C-7),145.2(2C,C-3,5),138.1(C-4),120.7(C-1),108.8(2C,C-2,6),60.3(-CH_2-),13.7(-CH_3)。以上数据与文献[7]报道一致,故鉴定化合物 **3** 为没食子酸乙酯。

化合物 4　棕色无定形粉末,^{1}H NMR(MeOD,500 MHz) δ:7.09(2H,s,H-galloyl-2,6),6.77(1H,m,H-2),5.72(1H,m,H-3),4.11(1H,dd,J=11.5,4.9 Hz,H-4),3.97(2H,dd,J=6.7,4.0 Hz,H-5),2.77(1H,d,J=18.4 Hz,H-6a),2.29(1H,dd,J=18.4,3.4 Hz,H-6b);^{13}C NMR(MeOD,125 MHz) δ:169.6(-COOH),167.8(C-galloyl-7),146.2(2C,C-galloyl-3,5),139.9(C-galloyl-4),134.6(C-2),132.8(C-1),121.3(C-galloyl-1),110.4(2C,C-galloyl-2,6),70.7(C-3),70.7(C-4),68.6(C-5),31.5(C-6)。以上数据与文献[8]报道一致,故鉴定化合物 **4** 为(-)-莽草酸-3-*O*-没食子酸酯

化合物 5　浅黄色粉末,^{1}H NMR(500 MHz,DMSO-d_6) δ:7.52(2H,s,H-5,5′),4.04(6H,s,-OCH_3);^{13}C NMR(125 MHz,DMSO-d_6) δ:159.0(2C,C-7,7′),152.7(2C,C-4,4′),141.7(2C,C-2,2′),140.7(2C,C-3,3′),112.6(2C,C-6,6′),112.2(2C,C-5,5′),112.0(2C,C-1,1′),61.5(2C,C-8,8′)。以上数据与文献[9]报道一致,故鉴定化合物 **5** 为 3,3′-二甲基鞣花酸。

化合物 6　白色粉末,^{1}H NMR(500 MHz,DMSO-d_6) δ:8.57(1H,s,H-5),8.34(1H,s,H-5′),6.34(1H,d,J=3.2 Hz,H-xyl-1),6.05(1H,d,J=4.5 Hz,H-xyl-4),5.98(2H,t,J=6.4 Hz,H-xyl-5a),4.90(3H,s,3-OCH_3),4.87(3H,s,3′-OCH_3),4.65(1H,dd,J=10.3,4.5 Hz,H-xyl-5b),4.16~4.09(2H,m,H-xyl-2,3);^{13}C NMR(125 MHz,DMSO-d_6) δ:158.5(C-7′),158.4(C-7),152.8(C-4),151.2(C-4′),141.9(C-3′),141.6(C-2′),141.0(C-2),140.2(C-3),114.2(C-1′),112.8(C-6′),111.9(C-6),111.9(C-5′),111.6(C-5),111.1(C-1),101.8(C-xyl-1),76.1(C-xyl-3),73.0(C-xyl-2),69.2(C-xyl-4),65.8(C-xyl-5),61.7(3′-OCH_3),61.0(3-OCH_3)。以上数据与文献[10,11]报道一致,故鉴定化合物 **6** 为 3,3′-二甲氧基鞣花酸-4′-*O*-α-D-吡喃木糖苷。

化合物 7　淡黄色粉末,^{1}H NMR(500 MHz,DMSO-d_6) δ:7.72(1H,s,H-5),7.51(1H,s,H-5′),5.47(1H,s,H-rha-1),4.69(1H,dd,J=4.9 Hz,H-rha-2),4.04(3H,s,3-OCH_3),4.00(1H,m,H-rha-3),3.85(1H,m,H-rha-4),3.54(1H,dd,J=9.3,6.2 Hz,H-rha-5),1.13(3H,d,J=6.2 Hz,H-rha-6);^{13}C NMR(125 MHz,DMSO-d_6) δ:159.2(C-7′),159.1(C-7),153.1(C-4′),153.0(C-4),147.0(C-3′),146.9(C-2′),140.6(C-3),140.5(C-2),114.8(C-1′),113.5(C-6′),113.4(C-6),112.2(C-5′),111.9(C-5),111.9(C-1),100.6(C-rha-1),72.3(C-rha-4),70.6(C-rha-2),70.4(C-rha-3),70.3(C-rha-5),61.4(3-OCH_3)18.3(C-rha-6)。以上数据与文献[12]报道一致,故鉴定化合物 **7** 为 3-甲氧基-4′-鼠李糖鞣花酸。

化合物 8　白色粉末,^{1}H NMR(acetone-d_6,500 MHz) δ:7.14(2H,s,H-galloyl-2,6),6.90(2H,d,J=8.8 Hz,H-2′,6′),6.66(2H,d,J=8.8 Hz,H-3′,5′),4.77(1H,d,J=7.7 Hz,H-glc-1),4.57(1H,dd,J=11.8,1.4 Hz,H-glc-6a),4.33(1H,dd,J=11.8,6.9 Hz,H-glc-6b),3.75(1H,m,H-glc-5),3.58-3.43(3H,m,H-glc-2,3,4);^{13}C NMR(acetone-d_6,125 MHz) δ:167.2(C-galloyl-7),153.1(C-1′),151.6(C-4′),145.9(2C,C-galloyl-3,5),138.9(C-galloyl-4),121.0(C-galloyl-1),118.7(2C,C-galloyl-2,6),

116.3(2C,C-2′,6′),109.8(2C,C-3′,5′),102.8(C-glc-1),77.1(C-glc-3),74.6(C-glc-2),74.2(C-glc-5),71.0(C-glc-4),64.5(C-glc-6)。以上数据与文献[13,14]报道一致,故鉴定化合物**8**为6-*O*-没食子酰基熊果苷。

化合物9 白色粉末,^{1}H NMR(DMSO-d_6,500 MHz)δ:7.38(1H,d,J=3.1 Hz,H-2),7.13(1H,dd,J=9.0,3.1 Hz,H-6),6.98(2H,s,H-galloyl-2,6),6.68(1H,d,J=9.0 Hz,H-5),4.76(1H,d,J=7.8 Hz,H-glc-1),4.23-4.19(2H,m,H-glc-2,6b),3.67(1H,m,H-glc-5),3.37(1H,m,H-glc-6a),3.31-3.26(2H,m,H-glc-3,4);^{13}C NMR(DMSO-d_6,500 MHz)δ:172.6(-COOH),167.4(C-galloyl-7),157.1(C-4),150.3(C-3),146.3(2C,C-galloyl-3,5),139.6(C-galloyl-4),125.5(C-2),120.5(C-galloyl-1),118.7(C-6),118.3(C-5),115.1(C-1),110.0(2C,C-galloyl-2,6),102.2(C-glc-1),76.9(C-glc-3),74.69(C-glc-5),74.1(C-glc-2),71.0(C-glc-4),64.7(C-glc-6)。以上数据与文献[15]报道一致,故鉴定化合物**9**为龙胆酸5-*O*-β-D-(6′-*O*-没食子酰基)-吡喃葡萄糖苷。

化合物10 白色粉末,^{1}H NMR(acetone-d_6,500 MHz)δ:7.11(2H,s,H-galloyl-2,6),6.94(1H,d,J=8.8 Hz,H-5),6.44(1H,d,J=2.7 Hz,H-2),6.23(1H,dd,J=8.8,2.7 Hz,H-6),4.75(1H,d,J=7.7 Hz,H-glc-1),4.55(1H,dd,J=11.7,1.9 Hz,H-glc-6a),4.33(1H,dd,J=11.7,6.9 Hz,H-glc-6b),3.75(1H,m,H-glc-5),3.72(3H,s,-OCH_3),3.58-3.54(1H,t,J=8.9 Hz,H-glc-4),3.52-3.47(2H,m,H-glc-2,3);^{13}C NMR(acetone-d_6,125 MHz)δ:167.1(C-galloyl-7),153.6(C-4′),150.3(C-3′),145.8(2C,C-galloyl-3,5),140.3(C-1′),138.9(C-galloyl-4),120.8(C-galloyl-1),118.1(C-5′),109.8(2C,C-galloyl-2,6),107.2(C-2′),102.7(C-6′),101.3(C-glc-1),76.6(C-glc-3),74.5(C-glc-2),73.9(C-glc-5),70.8(C-glc-4),64.4(C-glc-6),56.1(-OCH_3)。以上数据与文献[13]报道一致,故鉴定化合物**10**为4-hydroxy-3-methoxyphenol 1-*O*-β-D-(6′-*O*-galloyl)glucoside。

化合物11 浅黄色粉末,^{1}H NMR(500 MHz,MeOD)δ:7.13(2H,s,H-galloyl-2′,6′),7.08(2H,s,galloyl-2,6),5.69(1H,d,J=7.3 Hz,H-glc-1),4.55(1H,dd,J=12.0,1.7 Hz,H-glc-6a),4.41(1H,dd,J=12.0,5.0 Hz,H-glc-6b),3.72(1H,m,H-glc-5),3.58-3.48(3H,m,H-glc-2,3,4);^{13}C NMR(125 MHz,MeOD)δ:168.3(C-galloyl-7),167.0(C-galloyl-7′),146.5(2C,C-galloyl-3′,5′),146.4(2C,C-galloyl-3,5),140.4(C-galloyl-4′),139.8(C-galloyl-4),121.3(C-galloyl-1),120.6(C-galloyl-1′),110.6(2C,C-galloyl-2,6),110.2(2C,C-galloyl-2′,6′),95.9(C-glc-1),78.0(C-glc-3),76.4(C-galloyl-5),74.1(C-galloyl-2),71.2(C-glc-4),64.4(C-glc-6)。以上数据与文献[16]报道一致,故鉴定化合物**11**为1,6-二-*O*-没食子酸-β-D-葡萄糖苷。

化合物12 浅黄色粉末,^{1}H NMR(500 MHz,MeOD)δ:7.46(1H,d,J=1.9 Hz,H-galloyl-2′),7.28(1H,d,J=1.9 Hz,H-galloyl-6′),7.17(2H,s,H-galloyl-2,6),4.90(1H,d,J=8.0 Hz,H-glc-1),4.66(1H,dd,J=12.0,1.4 Hz,H-glc-6a),4.35(1H,dd,J=12.1,5.9 Hz,H-glc-6b),3.80(1H,m,H-glc-5),3.58-3.47(3H,m,H-glc-2,3,4);^{13}C NMR(125 MHz,MeOD)δ:170.6(C-galloyl-7),168.4(C-galloyl-7′),146.9(C-galloyl-3),146.7(C-galloyl-5),146.4(2C,C-galloyl-3′,5′),141.3(C-galloyl-4),139.8(C-galloyl-4′),122.4(C-galloyl-1),121.2(C-galloyll-1′),113.6(C-galloyl-2),111.4(C-galloyl-6),110.3(2C,C-galloyl-2′,6′),104.1(C-glc-1),77.2(C-glc-3),76.0(C-galloyl-5),74.7(C-glc-2),71.4(C-glc-4),65.0(C-glc-6)。以上数据与文献[17,18]报道一致,故鉴定化合物**12**为gallic acid 3-*O*-β-D-(6′-*O*-galloyl)-glucopyranoside。

化合物13 白色无定型粉末,^{1}H NMR(acetone-d_6,500 MHz)δ:7.34(2H,d,J=8.0 Hz,H-2,6),7.27(2H,dd,J=8.0,7.1 Hz,H-3,5),7.22(1H,d,J=7.1 Hz,H-4),7.14(2H,s,H-galloyl-2,6),4.80(1H,d,J=12.0 Hz,H-7a),4.60(1H,d,J=12.0 Hz,H-7b),4.57(1H,dd,J=11.8,2.1 Hz,H-glc-6a),4.41(1H,d,J=7.8 Hz,H-glc-1),4.35(1H,dd,J=11.8,6.2 Hz,H-glc-6b),3.59(1H,dd,J=10.5,6.2 Hz,H-glc-5),3.48-3.43(2H,m,H-glc-2,3),3.30(1H,m,H-glc-4);^{13}C NMR(acetone-d_6,125 MHz)δ:167.3(C-galloyl-7),145.9(2C,C-galloyl-3,5),139.0(C-1),138.5(C-galloyl-4),128.9(2C,C-3,5),128.7(2C,C-2,6),128.2(C-4),121.3(C-galloyl-1),109.8(2C,C-galloyl-2,6),102.7(C-glc-1),77.4(C-7),74.8(C-glc-3),74.4(C-glc-2),

71.1(C-glc-4),70.9(C-glc-5),64.5(C-glc-6)。以上数据与文献[19]报道一致,故鉴定化合物 **13** 为 benzyl 6-*O*-galloyl-β-D-glucopyranoside。

化合物 14 棕黄色粉末,^{1}H NMR(acetone-d_6,500 MHz) δ:7.07,7.04(each 2H,s,α-H-galloyl-2,6),7.02,7.01(each 2H,s,β-H-galloyl-2,6),5.74(1H,t,*J*=9.7 Hz,α-H-glc-3),5.46(1H,d,*J*=3.4 Hz,α-H-glc-1),5.39(1H,t,*J*=9.7 Hz,β-H-glc-3),5.06(1H,dd,*J*=9.7,8.1 Hz,β-H-glc-2),4.95(1H,d,*J*=8.1 Hz,β-H-glc-1),4.90(1H,dd,*J*=9.7,3.4 Hz,α-H-glc-2),4.02(1H,m,α-H-glc-5),3.92-3.82(6H,m,α-H-glc-4,6a,6b,β-H-glc-4,6a,6b),3.57(1H,ddd,*J*=14.3,7.2,4.6 Hz,β-H-glc-5);^{13}C NMR(acetone-d_6,125 MHz) δ:167.4,166.7(each 1C,α-C-galloyl-7),166.9,166.4(each 1C,β-C-galloyl-7),145.8(4C,α-C-galloyl-3,5),145.7(4C,β-C-galloyl-3,5),139.1,138.9(each 1C,α-C-galloyl-4),139.0,138.8(each 1C,β-C-galloyl-4),121.1,120.4(each 1C,α-C-galloyl-1),120.9,120.8(each 1C,β-C-galloyl-1),109.9(4C,α-C-galloyl-2,6),109.8(4C,β-C-galloyl-2,6),95.7(β-C-glc-1),90.6(α-C-glc-1),77.3(β-C-glc-5),76.5(β-C-glc-3),74.1(β-C-glc-2),73.7(α-C-glc-3),73.3(α-C-glc-2),72.5(α-C-glc-5),69.4(β-C-glc-4),69.2(α-C-glc-4),61.9(β-C-glc-6),61.8(α-C-glc-6)。以上数据与文献[20]报道一致,故鉴定化合物 **14** 为 2,3-di-*O*-galloyl-D-glucose。

化合物 15 浅黄色粉末,^{1}H NMR(500 MHz,acetone-d_6) δ:7.01(2H,s,α-H-galloyl-2,6),7.00(2H,s,β-H-galloyl-2,6),6.59(1H,s,β-H-HHDP-6),6.58(1H,s,α-H-HHDP-6),6.44(1H,s,α-H-HHDP-6′),6.43(1H,s,β-H-HHDP-6′),5.44(1H,t,*J*=9.8 Hz,α-H-glc-3),5.27(1H,d,*J*=9.7 Hz,β-H-glc-3),5.24(1H,d,*J*=3.6 Hz,α-H-glc-1),5.20-5.13(2H,m,α-H-glc-6a,β-H-glc-6a),4.96-4.85(2H,m,α-H-glc-4,β-H-glc-4),4.72(1H,d,*J*=7.8 Hz,β-H-glc-1),4.51(1H,dd,*J*=10.1,6.6 Hz,α-H-glc-5),4.20(1H,m,β-H-glc-5),3.80(1H,m,α-H-glc-2),3.74(1H,m,β-H-glc-6b),3.72(1H,m,α-H-glc-6b),3.58(1H,m,β-H-glc-2);^{13}C NMR(125 MHz,acetone-d_6) δ:168.7(α-C-galloyl-7),168.6(β-C-galloyl-7),168.0(α-C-HHDP-7),167.9(α-C-HHDP-7′),167.5(β-C-HHDP-7),167.4(β-C-HHDP-7′),145.6(4C,α-C-galloyl-4,5,β-C-galloyl-4,5),145.0(2C,α-C-HHDP-3,β-C-HHDP-3),144.9(2C,α-C-HHDP-3′,β-C-HHDP-3′),144.3(2C,α-C-HHDP-5,β-C-HHDP-5),144.2(2C,α-C-HHDP-5′,β-C-HHDP-5′),138.9(α-C-galloyl-4),138.8(β-C-galloyl-4),136.3(α-C-HHDP-4),136.2(α-C-HHDP-4′),136.1(β-C-HHDP-4),136.0(β-C-HHDP-4′),126.1(α-C-galloyl-1),126.0(β-C-galloyl-1),125.7(2C,α-C-HHDP-1,1′),120.8(β-C-HHDP-1),120.7(β-C-HHDP-1′),115.7(2C,α-C-HHDP-2,β-C-HHDP-2),115.6(2C,α-C-HHDP-2′,β-C-HHDP-2′),110.0(2C,α-C-galloyl-2,6),109.9(2C,β-C-galloyl-2,6),107.8(2C,α-C-HHDP-6,β-C-HHDP-6),107.6(2C,α-C-HHDP-6′,β-C-HHDP-6′),98.3(β-C-glc-1),93.5(α-C-glc-1),75.9(β-C-glc-5),74.3(β-C-glc-3),74.0(β-C-glc-2),71.5(α-C-glc-3),71.4(α-C-glc-2),71.2(α-C-glc-5),71.1(β-C-glc-4),66.9(α-C-glc-4),63.7(β-C-glc-6),63.6(α-C-glc-6)。以上数据与文献[21]报道一致,故鉴定化合物 **15** 为 gemin D。

化合物 16 浅棕色粉末,^{1}H NMR(acetone-d_6,500 MHz) δ:7.05,6.98(each,2H,s,α-H-galloyl-2,6),7.04,6.94(each,2H,s,β-H-galloyl-2,6),6.64(1H,s,β-H-HHDP-6),6.63(1H,s,α-H-HHDP-6),6.48(1H,s,α-H-HHDP-6′),6.46(1H,s,β-H-HHDP-6′),5.85(1H,t,*J*=10.0 Hz,α-H-glc-3),5.58(1H,t,*J*=10.0 Hz,β-H-galloyl-3),5.54(1H,d,*J*=3.7 Hz,α-H-glc-1),5.30-5.22(3H,m,α-H-glc-6a,β-H-glc-2,6a),5.12(1H,t,*J*=10.0 Hz,α-H-glc-4),5.11(1H,t,*J*=10.0 Hz,β-H-glc-4),5.09(1H,d,*J*=7.8 Hz,β-H-glc-1),5.07(1H,dd,*J*=10.0,3.7 Hz,α-H-glc-2),4.65(1H,dd,*J*=10.0,6.3 Hz,α-H-glc-5),4.25(1H,dd,*J*=10.0,3.7 Hz,β-H-glc-5),3.85(1H,d,*J*=13.0 Hz,β-H-glc-6b),3.78(1H,d,*J*=13.0,1.2 Hz,α-H-glc-6b);^{13}C NMR(acetone-d_6,125 MHz) δ:167.7,167.1(each 1C,α-C-galloyl-7),167.6,167.0(each 1C,β-C-galloyl-7),166.3(α-C-HHDP-7),166.0(β-C-HHDP-7),165.6(α-C-HHDP-7′),165.3(β-C-HHDP-7′),145.2,145.0(each 2C,α-C-galloyl-3,5),145.1,144.9(each 2C,β-C-galloyl-3,5),144.5(2C,α,β-C-HHDP-3),144.4(2C,α,β-C-HHDP-5′),144.3(2C,α,β-C-HHDP-5),143.8(2C,α,β-C-HHDP-3′),138.8,

138.3(each 1C,α-C-galloyl-4),138.2(2C,β-C-galloyl-4),135.8(α-C-HHDP-4′),135.7(β-C-HHDP-4′),135.6(2C,α,β-C-HHDP-4),125.6,125.0(each 1C,α-C-galloyl-1),125.5,125.0(each 1C,β-C-galloyl-1),120.0(β-C-HHDP-1),119.8(α-C-HHDP-1),119.7(α-C-HHDP-1′),119.6(β-C-HHDP-1′),115.2(2C,α,β-C-HHDP-2),115.1(α-C-HHDP-2′),115.1(β-C-HHDP-2′),109.3(4C,α-C-galloyl-2,6),109.2(4C,β-C-galloyl-2,6),107.2(2C,α,β-C-HHDP-6),107.0(2C,α,β-C-HHDP-6′),95.8(β-C-glc-1),90.4(α-C-glc-1),73.4(β-C-glc-2),73.1(β-C-glc-3),72.3(α-C-glc-2),71.2(β-C-glc-4),70.6(α-C-glc-4),70.3(β-C-glc-5),70.2(α-C-glc-3),66.1(α-C-glc-5),62.8(2C,α,β-C-glc-6)。以上数据与文献[22,23]报道一致,故鉴定化合物 **16** 为特里马素。

化合物 17 淡褐色无定形粉末,^{1}H NMR(acetone-d_6,500 MHz) δ:7.14,7.03,7.00(each 2H,s,H-galloyl-2,6),6.68(1H,s,H-HHDP-6),6.49(1H,s,H-HHDP-6′),6.23(1H,d,J = 8.3 Hz,H-glc-1),5.87(1H,t,J = 10 Hz,H-glc-3),5.62(1H,m,H-glc-2),5.39(1H,dd,J = 13.4,6.5 Hz,H-glc-6a),5.24(1H,t,J = 10.0 Hz,H-glc-4),4.58(1H,m,J = 10.0,6.5 Hz,H-glc-5),3.91(1H,d,J = 13.4 Hz,H-glc-6b);^{13}C NMR(acetone-d_6,125 MHz) δ:168.0,167.6,166.2(each 1C,C-galloyl-7),165.5(C-HHDP-7′),165.0(C-HHDP-7),146.1,145.9,145.8(each 2C,C-galloyl-3,5),145.2(C-HHDP-3′),145.2(C-HHDP-3),144.5(C-HHDP-5′),144.4(C-HHDP-5),139.8,139.3,139.1(each 1C,C-galloyl-4),136.5(C-HHDP-4′),136.5(C-HHDP-4),126.5(C-HHDP-2′),125.8(C-HHDP-2),120.5,120.4,119.8(each 1C,C-galloyl-1),115.7(C-HHDP-1′),115.6(C-HHDP-1),110.3,110.2,110.1(each 2C,C-galloyl-2,6),108.2(C-HHDP-6′),107.8(C-HHDP-6),93.6(C-glc-1),73.1(C-glc-3),73.0(C-glc-2),71.7(C-glc-5),70.7(C-glc-4),63.0(C-glc-6)。以上数据与文献[24,25]报道一致,故鉴定化合物 **17** 为丁香素。

化合物 18 棕色无定形粉末,^{1}H NMR(DMSO-d_6,500 MHz) δ:7.16(2H,d,J = 8.6 Hz,H-14,18),6.76(2H,d,J = 8.6 Hz,H-15,17),4.80(1H,dd,J = 12.4,9.2 Hz,H-4),4.69(1H,d,J = 7.6 Hz,H-glc-1),4.31(1H,dd,J = 9.2,7.0 Hz,H-11a),4.21(1H,td,J = 6.5,3.3 Hz,H-12),3.97(1H,m,H-11b),3.93(1H,s,H-8),3.81-3.56(2H,s,H-glc-6),3.30~3.17(3H,m,H-glc-2,3,4),3.06(1H,m,H-glc-5),3.04(1H,m,H-3a),2.91(1H,dd,J = 17.5,9.1 Hz,H-3b);^{13}C NMR(DMSO-d_6,125 MHz) δ:174.1(C-2),170.8(C-6),157.6(C-16),129.9(2C,C-14,18),122.8(C-13),115.5(2C,C-15,17),107.20(C-9),96.1(C-glc-1),89.0(C-5),88.1(C-8),77.0(C-glc-3),76.7(C-glc-5),75.0(C-11),73.4(C-12),73.1(C-glc-2),69.2(C-glc-4),59.8(C-glc-6),42.9(C-4),32.4(C-3)。以上数据与文献[26]报道一致,故鉴定化合物 **18** 为 viburnolide A。

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