·化学·

小蜡树的酚苷及苯乙醇苷类成分

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［摘要］ **目的**：系统研究小蜡树 *Fraxinux sieboldiana* 枝乙醇提取物的化学成分。**方法**：运用正相和反相硅胶、大孔吸附树脂、凝胶、反相高效液相等色谱方法进行分离；应用包括一维和二维 NMR 等波谱方法鉴定化合物的结构。**结果**：从小蜡树枝的乙醇提取物水相部位分离得到 4 个酚苷和 12 个苯乙醇苷类成分，分别鉴定为：2,6-二甲氧基-对苯二酚-4-*O*-*β*-*D*-吡喃葡萄糖苷（**1**），2,6-二甲氧基-对苯二酚-1-*O*-*β*-*D*-吡喃葡萄糖苷（**2**），4-羟基-3-甲氧基苯基 *β*-*D*-吡喃葡萄糖苷（**3**），4-羟基-3-甲氧基苯基 *β*-*D*-吡喃木糖基（1→6）-*O*-*β*-*D*-吡喃葡萄糖苷（**4**），osmanthuside H（**5**），2-（4-羟基苯基）乙基 *β*-*D*-吡喃葡萄糖苷（**6**），2-（3,4-二羟基苯基）乙基 *β*-*D*-吡喃葡萄糖苷（**7**），2-羟基-4-（2-羟基乙基）-苯基 *β*-*D*-吡喃葡萄糖苷（**8**），4-（2-羟基乙基）-2-甲氧基苯基 *β*-*D*-吡喃葡萄糖苷（**9**），calceolarioside B（**10**），calceolarioside A（**11**），ferruginoside A（**12**），isolugrandoside（**13**），类叶升麻苷（**14**），chiritotoside C（**15**）和 plantasisoside（**16**）。**结论**：化合物 **1** ~ **4**，**9**，**12**，**13** 和 **16** 为首次从该属植物中分离得到。

［关键词］ 小蜡树；化学成分；酚苷；苯乙醇苷

小蜡树 *Fraxinux sieboldiana*，又称庐山梣，其茎皮在我国江西当地和日本作为中药秦皮使用，具有利尿、止咳平喘、治疗风湿关节炎的作用[1]。为了从该植物中获得可供新药先导物筛选发现的结构多样性天然产物，作者对采自江西庐山的小蜡树枝化学成分进行了系统的研究。前文对其乙醇提取物中得到的 9 个新化合物结构以及香豆素类成分及其生物活性进行了详细报道[2-3]，本文报道 4 个酚苷（**1** ~ **4**）和 12 个苯乙醇苷类成分（**5** ~ **16**）的结构鉴定。其中，化合物 **1** ~ **4**，**9**，**12**，**13** 和 **16** 为首次从该属植物中发现。

1 材料

Inova 500 核磁共振仪，Micromass Autospec-Ultima ETOF 质谱仪。Waters 600 高效液相色谱仪（Alltech 公司 Econosphere C_{18} 制备柱，250 mm × 22 mm × 10 μm，Waters 2478 型检测器）。中压液相色谱仪（Búchi Gradient Former B-687，Rp C18，43 ~ 60 μ，Pharmacia 公司）。闪式快速分离系统（Sq 16x，combi Flash，Rp C_{18}，40 ~ 60 μ，Micron Silicag Gel，Isco 公司）。Sephadex LH-20 为 Pharmacia 公司产品。RA 型大孔树脂为北京化工七厂产品。柱色谱硅胶（200-300 目）和薄层色谱硅胶 GF254（60 型）均为青岛海洋化工厂生产。

小蜡树药材于 2004 年 8 月采自江西省庐山，由中国医学科学院药物研究所马林副教授鉴定为小蜡树 *F. sieboldiana* 的枝及枝皮，标本现存于中国医学科学院药物研究所植物标本库，标本号为 No. ZH02272。

2 提取分离

药材的提取和初步分离过程见文献[3]。C 部分经正相硅胶柱色谱分离，氯仿-甲醇（90∶10 ~ 0∶100）梯度洗脱，得到 5 个亚组分（C_1 ~ C_5）。C_1 亚组分经 Sephadex LH-20 柱色谱纯化（甲醇），再经反相 HPLC 制备纯化（甲醇-水 25∶75）得到化合物 **1**（15.7 mg），**2**（12.2 mg），**3**（9.1 mg）。C_2 亚组分经反相 HPLC 制备纯化（甲醇-水 25∶75）得到化合物 **6**（62.9 mg），**7**（45.3 mg）和 **8**（16.2 mg）。C_3 亚组分经 Sephadex LH-20 柱色谱（甲醇-水 70∶30）和反相 HPLC 制备（甲醇-水 20∶80）反复纯化，得到化合物 **4**（205.8 mg）和 **5**（11.5 mg）。

30% 乙醇洗脱部分用反相中压液相色谱分离，

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0～100%甲醇梯度洗脱,一共得到 F～J 5 个洗脱部分。G 部分经正相硅胶柱色谱分离,氯仿-甲醇(100∶0～50∶50)梯度洗脱,得到 3 个亚组分(G_1～G_3)。G_1亚组分经反相 HPLC 制备纯化(甲醇-水 30∶70)得到化合物 **9**(10.1 mg)。G_2亚组分经 Sephadex LH-20 柱色谱反复纯化(甲醇),再经反相 HPLC 制备纯化(甲醇-水 30∶70)得到化合物 **10**(215.8 mg),**11**(22.5 mg),**12**(13.0 mg),**13**(11.0 mg),**14**(16.8 mg)和 **15**(11.6 mg)。I 部分经正相硅胶柱色谱分离,氯仿-甲醇(100∶0～50∶50)梯度洗脱,得到 3 个亚组分(I_1～I_3)。I_2亚组分经反相 HPLC 制备纯化(甲醇-水 30∶70)得到化合物 **16**(4.0 mg)。

3 结构鉴定

化合物 **1** 白色粉末;ESI-MS *m/z* 355 [M + Na]$^+$, 371 [M + K]$^+$;^{1}H-NMR (DMSO-d_6, 500 MHz) δ:6.30 (2H, s, H-3,5), 4.60 (1H, d, J = 8.0 Hz, H-1′), 3.20 (1H, dd, J = 8.0, 8.5 Hz, H-2′), 3.24 (1H, dd, J = 8.5, 8.5 Hz, H-3′), 3.09 (1H, dd, J = 9.0, 8.5 Hz, H-4′), 3.35 (1H, m, H-5′), 3.70 (1H, dd, J = 11.5, 2.0 Hz, H-6a′), 3.39 (1H, dd, J = 11.5, 5.0 Hz, H-6b′), 3.65 (6H, 2 × OMe), 7.76 (1H, s, OH-1)。^{13}C-NMR (DMSO-d_6, 125 MHz) δ: 130.4 (C-1), 148.1 (C-2,6), 95.0 (C-3,5), 150.3 (C-4), 101.6 (C-1′), 73.3 (C-2′), 76.8 (C-3′), 70.1 (C-4′), 77.2 (C-5′), 60.9 (C-6′), 55.8 (2 × OMe)。以上数据与文献报道 2,6-二甲氧基-对苯二酚-4-*O*-*β*-*D*-吡喃葡萄糖苷(2,6-dimethoxy-*p*-hydroquinone- 4-*O*-*β*-*D*-glucopyranoside)的数据一致[4]。

化合物 **2** 白色粉末;ESI-MS *m/z* 355 [M + Na]$^+$, 371 [M + K]$^+$; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ:6.05 (2H, s, H-3,5), 4.63 (1H, d, J = 7.5 Hz, H-1′), 3.19 (1H, dd, J = 7.5, 8.5 Hz, H-2′), 3.16 (1H, dd, J = 8.5, 8.5 Hz, H-3′), 3.10 (1H, dd, J = 9.0, 8.5 Hz, H-4′), 3.00 (1H, m, H-5′), 3.59 (1H, dd, J = 11.5, 2.0 Hz, H-6a′), 3.41 (1H, dd, J = 11.5, 5.0 Hz, H-6b′), 3.67 (6H, 2 × OMe), 9.19 (1H, s, OH-4)。^{13}C-NMR (DMSO-d_6, 125 MHz) δ: 127.5 (C-1), 153.1 (C-2,6), 93.8 (C-3,5), 153.8 (C-4), 103.4 (C-1′), 74.1 (C-2′), 76.4 (C-3′), 70.0 (C-4′), 76.9 (C-5′), 61.0 (C-6′), 56.1 (2 × OMe)。以上数据与文献报道 2,6-二甲氧基-对苯二酚-1-*O*-*β*-*D*-吡喃葡萄糖苷(2,6-dimethoxy-p-hydroquinone-1-*O*-*β*-*D*-glucopyranoside)的数据一致[5]。

化合物 **3** 白色粉末;ESI-MS *m/z* 325 [M + Na]$^+$; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ:6.67 (1H, d, J = 2.5 Hz, H-2), 6.63 (1H, d, J = 9.0 Hz, H-5), 6.44 (1H, dd, J = 9.0, 2.5 Hz, H-6), 4.65 (1H, d, J = 7.5 Hz, H-1′), 3.19 (1H, dd, J = 7.5, 8.5 Hz, H-2′), 3.24 (1H, dd, J = 8.5, 8.5 Hz, H-3′), 3.17 (1H, dd, J = 9.0, 8.5 Hz, H-4′), 3.23 (1H, m, H-5′), 3.65 (1H, dd, J = 11.5, 2.0 Hz, H-6a′), 3.42 (1H, dd, J = 11.5, 5.0 Hz, H-6b′), 3.72 (3H, OMe), 8.50 (1H, s, OH-4)。^{13}C-NMR (DMSO-d_6, 125 MHz) δ: 150.7 (C-1), 101.7 (C-2), 147.8 (C-3), 141.3 (C-4), 115.2 (C-5), 107.9 (C-6), 102.5 (C-1′), 73.3 (C-2′), 77.1 (C-3′), 69.9 (C-4′), 76.7 (C-5′), 60.8 (C-6′), 55.5 (OMe)。以上数据与文献报道 4-羟基-3-甲氧基苯基 *β*-*D*-吡喃葡萄糖苷(4-hydroxy-3-methoxyphenyl-*β*-*D*-glucopyranoside)的数据一致[6]。

化合物 **4** 白色粉末;ESI-MS *m/z* 457 [M + Na]$^+$, 473 [M + K]$^+$; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ:6.61 (1H, d, J = 2.5 Hz, H-2), 6.64 (1H, d, J = 8.5 Hz, H-5), 6.49 (1H, dd, J = 8.5, 2.5 Hz, H-6), 4.63 (1H, d, J = 8.0 Hz, H-1′), 4.15 (1H, d, J = 7.5 Hz, H-1″), 3.72 (3H, OMe), 8.48 (1H, s, OH-4)。^{13}C-NMR (DMSO-d_6, 125 MHz) δ: 150.7 (C-1), 102.3 (C-2), 147.8 (C-3), 141.3 (C-4), 115.4 (C-5), 107.9 (C-6), 101.6 (C-1′), 73.3 (C-2′), 76.5 (C-3′), 69.9 (C-4′), 76.6 (C-5′), 68.6 (C-6′), 104.1 (C-1″), 73.2 (C-2″), 75.7 (C-3″), 69.6 (C-4″), 65.6 (C-5″), 55.5 (OMe)。以上数据与文献报道 4-羟基-3-甲氧基苯基 *β*-*D*-吡喃木糖基(1→6)-*O*-*β*-*D*-吡喃葡萄糖苷[4-hydroxy-3-methoxyphenyl *β*-*D*-xylopyranosyl(1→6)-*O*-*β*-*D*-glucopyranoside]的数据一致[6]。

化合物 **5** 无色透明胶状物;ESI-MS *m/z* 455 [M + Na]$^+$, 471 [M + K]$^+$, 431 [M − H]$^-$; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ:7.03 (2H, d, J = 8.0 Hz, H-2,6), 6.65 (2H, d, J = 8.0 Hz, H-3,5), 2.72 (2H, t, J = 7.0 Hz, H_2-7), 3.82 (1H, m, H-8a), 3.56 (1H, m, H-8b), 4.16 (1H, d, J = 7.5 Hz, H-1′), 2.93 (1H, dd, J = 8.5, 8.0 Hz, H-2′), 3.11 (1H, dd, J =

9.0,8.5 Hz,H-3′),2.98 (1H,dd,*J* = 9.0,8.5 Hz,H-4′),3.23 (1H,m,H-5′),3.83 (1H,dd,*J* = 11.5,3.0 Hz,H-6a′),3.40 (1H,dd,*J* = 11.5,7.0 Hz,H-6b′),4.84 (1H,d,*J* = 3.0 Hz,H-1″),3.74 (1H,d,*J* = 3.0 Hz,H-2″),3.83 (1H,d,*J* = 9.5 Hz,H-4a″),3.57 (1H,d,*J* = 9.5 Hz,H-4b″),3.32 (2H,d,*J* = 5.0 Hz,H-5″),9.12 (1H,s,OH-4),4.45 ~ 5.03 (6H,6 × OH);^{13}C-NMR (DMSO-d_6,125 MHz) *δ*:128.6 (C-1),129.7 (C-2,6),115.0 (C-3,5),155.7 (C-4),34.8 (C-7),69.9 (C-8),102.8 (C-1′),73.3 (C-2′),76.6 (C-3′),70.2 (C-4′),75.5 (C-5′),67.7 (C-6′),109.2 (C-1″),75.8 (C-2″),78.8 (C-3″),73.2 (C-4″),63.1 (C-5″)。以上数据与文献报道 osmanthuside H 的数据一致[7]。

化合物 **6** 无色透明胶状物;ESI-MS *m/z* 323 [M + Na]$^+$;NMR 数据与文献报道 2-(4-羟基苯基)乙基 *β-D*-吡喃葡萄糖苷[2-(4-hydroxyphenyl) ethyl *β-D*-glucopyranoside]的数据一致[8]。

化合物 **7** 棕色胶状物;ESI-MS *m/z* 339 [M + Na]$^+$;^{1}H-NMR (DMSO-d_6,500 MHz) *δ*:6.60 (1H,br s,H-2),6.61 (1H,d,*J* = 8.0 Hz,H-5),6.46 (1H,dd,*J* = 8.0,2.5 Hz,H-6),2.65 (2H,t,*J* = 7.0 Hz,H_2-7),3.85 (1H,m,H-8a),3.53 (1H,m,H-8b),4.15 (1H,d,*J* = 7.5 Hz,H-1′),2.95 (1H,dd,*J* = 8.5,8.0 Hz,H-2′),3.14 (1H,dd,*J* = 8.5,8.5 Hz,H-3′),3.03 (1H,dd,*J* = 9.0,8.5 Hz,H-4′),3.07 (1H,m,H-5′),3.65 (1H,dd,*J* = 11.5,2.0 Hz,H-6a′),3.43 (1H,dd,*J* = 11.5,6.0 Hz,H-6b′);^{13}C-NMR (DMSO-d_6,125 MHz) *δ*:129.3 (C-1),115.5 (C-2),145.0 (C-3),143.5 (C-4),116.3 (C-5),119.5 (C-6),35.1 (C-7),70.0 (C-8),102.9 (C-1′),73.5 (C-2′),76.9 (C-3′),70.1 (C-4′),76.8 (C-5′),61.1 (C-6′)。以上数据与文献报道 2-(3,4-二羟基苯基)乙基 *β-D*-吡喃葡萄糖苷[2-(3,4-dihydroxyphenyl)ethyl *β-D*-glucopyranoside]的数据一致[9]。

化合物 **8** 棕色胶状物;ESI-MS *m/z* 339[M + Na]$^+$,355[M + K]$^+$;NMR (DMSO-d_6,500 MHz)数据与文献报道 2-羟基-4-(2-羟基乙基)-苯基 *β-D*-吡喃葡萄糖苷[2-hydroxy-4-(2-hydroxyethyl)-phenyl *β-D*-glucopyranoside]的数据一致[10]。

化合物 **9** 棕色胶状物;ESI-MS *m/z* 355 [M + Na]$^+$;^{1}H-NMR (MeOH-d_4,500 MHz) *δ*:6.83 (1H,d,*J* = 2.0 Hz,H-2),7.02 (1H,d,*J* = 8.0 Hz,H-5),6.70 (1H,dd,*J* = 8.0,2.0 Hz,H-6),2.71 (2H,t,*J* = 7.0 Hz,H_2-7),3.67 (2H,*J* = 7.0 Hz,H_2-8),4.76 (1H,d,*J* = 7.0 Hz,H-1′),3.42 (1H,dd,*J* = 8.5,8.0 Hz,H-2′),3.41 (1H,dd,*J* = 9.0,8.5 Hz,H-3′),3.29 (1H,dd,*J* = 9.0,8.5 Hz,H-4′),3.30 (1H,m,H-5′),3.81 (1H,dd,*J* = 12.5,2.5 Hz,H-6a′),3.63 (1H,dd,*J* = 12.5,5.0 Hz,H-6b′),3.80 (3H,s,OMe);^{13}C-NMR (MeOH-d_4,125 MHz) *δ*:135.5 (C-1),114.6 (C-2),150.8 (C-3),146.4 (C-4),118.3 (C-5),122.5 (C-6),39.8 (C-7),64.3 (C-8),103.1 (C-1′),75.0 (C-2′),78.2 (C-3′),71.4 (C-4′),77.9 (C-5′),62.5 (C-6′),56.7 (OMe)。以上数据与文献报道 4-(2-羟基乙基)-2-甲氧基苯基 *β-D*-吡喃葡萄糖苷[4-(2-hydroxyethyl)-2-methoxyphenyl *β-D*-glucopyranoside]的数据一致[11]。

化合物 **10** 黄色胶状物。ESI-MS *m/z* 501 [M + Na]$^+$;^{1}H-NMR (DMSO-d_6,500 MHz) *δ*:6.60 (1H,d,*J* = 1.5 Hz,H-2),6.57 (1H,d,*J* = 8.0 Hz,H-5),6.45 (1H,dd,*J* = 8.0,1.5 Hz,H-6),2.65 (2H,t,*J* = 7.0 Hz,H_2-7),3.79 (1H,m,H-8a),3.58 (1H,m,H-8b),4.23 (1H,d,*J* = 8.0 Hz,H-1′),2.99 (1H,dd,*J* = 8.5,8.0 Hz,H-2′),3.13 (1H,dd,*J* = 9.5,9.0 Hz,H-3′),3.17 (1H,dd,*J* = 9.0,8.5 Hz,H-4′),3.40 (1H,m,H-5′),4.39 (1H,br d,*J* = 11.5 Hz,H-6a′),4.15 (1H,dd,*J* = 11.5,6.0 Hz,H-6b′),7.04 (1H,d,*J* = 1.5 Hz,H-2″),6.74 (1H,d,*J* = 8.0 Hz,H-5″),6.96 (1H,dd,*J* = 8.0,1.5 Hz,H-6″),7.46 (1H,d,*J* = 16.0 Hz,H-7″),6.27 (1H,d,*J* = 16.0 Hz,H-8″);^{13}C-NMR (DMSO-d_6,125 MHz) *δ*:129.2 (C-1),115.8 (C-2),145.0 (C-3),143.5 (C-4),116.3 (C-5),119.5 (C-6),35.2 (C-7),70.2 (C-8),103.0 (C-1′),73.4 (C-2′),76.5 (C-3′),70.1 (C-4′),73.8 (C-5′),63.6 (C-6′),125.5 (C-1″),113.8 (C-2″),145.6 (C-3″),148.5 (C-4″),115.5 (C-5″),121.4 (C-6″),145.3 (C-7″),114.9 (C-8″),166.6 (C-9″)。以上数据与文献报道 calceolarioside B 的数据一致[12]。

化合物 **11** 黄色胶状物。ESI-MS *m/z* 501 [M + Na]$^+$;^{1}H-NMR (DMSO-d_6,500 MHz) *δ*:6.61 (1H,br s,H-2),6.62 (1H,d,*J* = 8.0 Hz,H-5),6.48

(1H,br d,J=8.0 Hz,H-6),2.65(2H,t,J=7.0 Hz,H_2-7),3.88 (1H,m,H-8a),3.58 (1H,m,H-8b),4.27 (1H,d,J=8.0 Hz,H-1′),3.08 (1H,dd,J=8.5,8.5 Hz,H-2′),3.44 (1H,dd,J=9.5,9.0 Hz,H-3′),4.63 (1H,dd,J=9.0,9.5 Hz,H-4′),3.40 (1H,m,H-5′),3.39 (1H,br d,J=11.5 Hz,H-6a′),3.32 (1H,dd,J=11.5,6.5 Hz,H-6b′),7.04 (1H,br s ,H-2″),6.75 (1H,d,J=8.0 Hz,H-5″),6.99 (1H,br d,J=8.0 Hz,H-6″),7.46 (1H,d,J=16.0 Hz,H-7″),6.23 (1H,d,J=16.0 Hz,H-8″);^{13}C-NMR (DMSO-d_6,125 MHz) δ: 129.1 (C-1),115.8 (C-2),145.0 (C-3),143.6 (C-4),116.3 (C-5),119.5 (C-6),35.1 (C-7),70.2 (C-8),102.8 (C-1′),73.6 (C-2′),74.7 (C-3′),71.3 (C-4′),74.1 (C-5′),60.9 (C-6′),125.4 (C-1″),113.9 (C-2″),145.8 (C-3″),148.6 (C-4″),115.5 (C-5″),121.3 (C-6″),145.4 (C-7″),114.9 (C-8″),165.9 (C-9″)。以上数据与文献报道 calceolarioside A 的数据一致[12]。

化合物 **12** 棕色胶状物。ESI-MS m/z 663 $[M+Na]^+$;^{1}H-NMR (DMSO-d_6,500 MHz) δ: 6.54 (1H,br s,H-2),6.53 (1H,br d,J=8.0 Hz,H-5),6.40 (1H,br d,J=8.0 Hz,H-6),2.56 (2H,t,J=7.0 Hz,H_2-7),3.79 (1H,m,H-8a),3.54 (1H,m,H-8b),4.47 (1H,d,J=8.0 Hz,H-1′),4.23 (1H,d,J=7.5 Hz,H-1″),7.06 (1H,br d ,H-2‴),6.76 (1H,d,J=8.0 Hz,H-5‴),7.00 (1H,br d,J=8.0 Hz,H-6‴),7.47 (1H,d,J=16.0 Hz,H-7‴),6.26 (1H,d,J=16.0 Hz,H-8‴);^{13}C-NMR (DMSO-d_6,125 MHz) δ: 129.2 (C-1),115.8 (C-2),144.9 (C-3),143.5 (C-4),116.3 (C-5),119.6 (C-6),35.0 (C-7),69.8 (C-8),100.1 (C-1′),74.2 (C-2′),75.7 (C-3′),70.1 (C-4′),73.4 (C-5′),68.3 (C-6′),103.4 (C-1″),73.5 (C-2″),76.9 (C-3″),70.0 (C-4″),76.7 (C-5″),61.0 (C-6″),125.6 (C-1‴),114.2 (C-2‴),145.6 (C-3‴),148.4 (C-4‴),115.4 (C-5‴),121.3 (C-6‴),145.1 (C-7‴),114.9 (C-8‴),165.7 (C-9‴)。以上数据与文献报道 ferruginoside A 的数据一致[13]。

化合物 **13** 棕色胶状物。ESI-MS m/z 663 $[M+Na]^+$;^{1}H-NMR (DMSO-d_6,500 MHz) δ: 6.62 (1H,br s,H-2),6.61 (1H,br d,J=8.0 Hz,H-5),6.48 (1H,br d,J=8.0 Hz,H-6),2.67 (2H,t,J=7.0 Hz,H_2-7),3.86 (1H,m,H-8a),3.54 (1H,m,H-8b),4.33 (1H,d,J=8.0 Hz,H-1′),4.22 (1H,d,J=7.5 Hz,H-1″),7.04 (1H,br d ,H-2‴),6.74 (1H,d,J=8.0 Hz,H-5‴),6.99 (1H,br d,J=8.0 Hz,H-6‴),7.45 (1H,d,J=16.0 Hz,H-7‴),6.25 (1H,d,J=16.0 Hz,H-8‴);^{13}C-NMR (DMSO-d_6,125 MHz) δ: 129.2 (C-1),115.8 (C-2),144.8 (C-3),143.6 (C-4),116.4 (C-5),119.5 (C-6),35.0 (C-7),70.1 (C-8),102.5 (C-1′),71.4 (C-2′),77.5 (C-3′),67.9 (C-4′),75.3 (C-5′),68.1 (C-6′),103.4 (C-1″),73.5 (C-2″),76.9 (C-3″),70.0 (C-4″),76.7 (C-5″),61.0 (C-6″),125.5 (C-1‴),114.6 (C-2‴),145.7 (C-3‴),148.5 (C-4‴),115.5 (C-5‴),121.1 (C-6‴),145.0 (C-7‴),114.8 (C-8‴),166.1 (C-9‴)。以上数据与文献报道 isolugrandoside 的数据一致[14]。

化合物 **14** 棕色胶状物。ESI-MS m/z 663 $[M+Na]^+$;NMR(DMSO-d_6)数据与文献报道类叶升麻苷(acteoside)的数据一致[15]。

化合物 **15** 黄色胶状物。ESI-MS m/z 663 $[M+Na]^+$,679 $[M+K]^+$;NMR (DMSO-d_6)数据与文献报道 chiritotoside C 的数据一致[12]。

化合物 **16** 黄色胶状物。ESI-MS m/z 475 $[M-H]^-$;^{1}H-NMR (MeOH-d_4,500 MHz) δ: 6.85 (1H,d,J=2.0 Hz,H-2),6.73 (1H,d,J=8.0 Hz,H-5),6.70 (1H,dd,J=8.0,2.0 Hz,H-6),4.56 (1H,dd,J=11.0,3.0 Hz,H-7),3.95 (1H,dd,J=13.5,3.0 Hz,H-8a),3.64 (1H,dd,J=13.5,11.0 Hz,H-8b),4.46 (1H,d,J=8.0 Hz,H-1′),3.20 (1H,dd,J=10.0,8.0 Hz,H-2′),3.62 (1H,dd,J=10.0,10.0 Hz,H-3′),3.46 (1H,dd,J=10.0,10.0 Hz,H-4′),3.73 (1H,m,H-5′),4.55 (1H,dd,J=12.0,2.0 Hz,H-6a′),4.34 (1H,dd,J=12.0,6.0 Hz,H-6b′),7.05 (1H,d,J=2.0 Hz,H-2″),6.78 (1H,d,J=8.0 Hz,H-5″),6.95 (1H,dd,J=8.0,2.0 Hz,H-6″),7.58 (1H,d,J=16.0 Hz,H-7″),6.30 (1H,d,J=16.0 Hz,H-8″);^{13}C-NMR (MeOH-d_4,125 MHz) δ: 129.9(C-1),114.7 (C-2),146.5 (C-3),146.3 (C-4),116.5 (C-5),119.4 (C-6),78.8 (C-7),72.8 (C-8),99.5 (C-1′),80.9 (C-2′),75.0 (C-3′),72.0 (C-4′),77.2 (C-5′),64.5 (C-6′),127.7 (C-1″),115.0 (C-2″),146.8

(C-3″), 149.6 (C-4″), 116.1 (C-5″), 123.1 (C-6″), 147.3 (C-7″), 115.0 (C-8″), 169.0 (C-9″)。以上数据与文献报道 plantasisoside 的数据一致,并通过 DEPT,HSQC 和 HMBC 谱对其数据进行了准确的归属[16]。

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Phenolic and phenylethanoidal glycosides from branch of Fraxinus sieboldiana

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[**Abstract**] **Objective**: To investigate chemical constituents from an ethanolic extract of the branch of *Fraxinus sieboldiana* (Oleaceae). **Method**: The constituents were isolated and purified by a combination of various chromatographic techniques including silica gel, macroporous adsorbent resin, Sephadex LH-20, and preparative HPLC. Structures of the isolates were elucidated by spectroscopic methods including 1D and 2D NMR and MS techniques. **Result**: Four phenolic and twelve phenylethanoidal glycosides were obtained and their structures were identified as 2,6-dimethoxy-*p*-hydroquinone-4-*O*-*β*-*D*-glucopyranoside (**1**), 2,6-dimethoxy-*p*- hydroquinone-1-*O*-*β*-*D*-glucopyranoside (**2**), 4-hydroxy-3-methoxyphenyl *β*-*D*-glucopyranoside (**3**), 4-hydroxy-3-methoxyphenyl *β*-*D*-xylopyranosyl (1→6)-*O*-*β*-*D*-glucopyranoside (**4**), osmanthuside H (**5**), 2-(4-hydroxyphenyl) ethyl *β*-*D*-glucopyranoside (**6**), 2-(3, 4-dihydroxyphenyl) ethyl *β*-*D*-glucopyranoside (**7**), 2-hydroxy-4-(2-hydroxyethyl)-phenyl *β*-*D*-glucopyranoside (**8**), 4-(2-hydroxyethyl)-2-methoxyphenyl *β*-*D*-glucopyranoside (**9**), calceolarioside B (**10**), calceolarioside A (**11**), ferruginoside A (**12**), isolugrandoside (**13**), acteoside (**14**), chiritotoside C (**15**), and plantasisoside (**16**). **Conclusion**: Compounds **1**-**4**,**9**,**12**, **13** and **16** were obtained from the genus *Fraxinus* for the first time.

[**Key words**] *Fraxinus sieboldiana*; chemical constituents; phenolic glycosides; phenylethanoid glycosides

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