

女贞树皮的化学成分研究

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摘要:采用硅胶、Sephadex LH-20 等多种材料进行分离纯化,通过理化方法和波谱分析进行结构鉴定,从女贞树皮的醇提溶液的乙酸乙酯萃取部分中分离鉴定了 19 个化合物,分别为:尼克酰胺(1);D-阿洛醇(2);对羟基苯甲醇(3);乙酰氧基齐墩果酸(4);苯甲酸(5);北升麻宁(6);Borreriagenin(7);C-Veratroylglycol(8);methyl-2-O- β -glucopyranosylbenzoate(9);3',7-二羟基-4'-甲氧基异黄酮(10);7-羟基香豆素(11);咖啡酸甲酯(12);齐墩果酸(13);(-)-囊五脂素(14);苜蓿油脑(15);表儿茶素(16);2 α -羟基齐墩果酸(17);桦木酸(18);白桦脂醇(19)。其中,化合物 4、6、10、11、13、17、18、19 已在女贞子中得到,但上述所有化合物均首次从女贞树皮中分离得到。

关键词:女贞树皮;提取;分离;结构鉴定

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Study on Chemical Constituents of the *Ligustrum lucidum* Bark

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Abstract: 19 compounds were separated and purified from the ethyl acetate extracts in the alcohol solution of the *Ligustrum lucidum* bark silica gel and Sephadex LH-20 column chromatography. Their structures were identified as nicotinamide (1); D-allitol (2); p-hydroxybenzyl alcohol (3); Acetyloleanolic acid (4); benzoic acid (5); cimidahurinine (6); Borreriagenin (7); C-Veratroylglycol (8); methyl-2-O- β -glucopyranosylbenzoate (9); 3',7-dihydroxy-4'-methoxyisoflavone (10); umbelliferone (11); caffeic acid methyl ester (12); oleanolic acid (13); (-)-chicanine (14); dillapiol (15); L-Epicatechin (16); 2 α -hydroxy-oleanolic acid (17); betulinic acid (18); Betulin (19), all the above compounds were isolated from the bark of *Ligustrum lucidum* for the first time, and compounds (4), (6), (10), (11), (13), (17), (18), (19) had been isolated from *Ligustrum lucidum* previously.

Key words: *Ligustrum lucidum* bark; extraction; isolation; structure identification

女贞(*Ligustrum lucidum*),属于木犀科女贞属常绿乔木,别称冬青等。主要分布安徽、江浙、山东、福建等地。其果实女贞子是我国传统中药,最早见于《神农本草经》,具有扶正固、补肝益肾、平肝火、补腰膝等功效^[1]。目前,对于女贞子的化学成分研究较多,其主要含有三萜类化合物^[2]、裂环环烯醚萜类化合物^[3]、黄酮类化合物^[4]以及苯乙醇类化合物^[5]等。但未见有关女贞树皮化学成分的报道,为了进一步研究其女贞植物的化学成分,完善其药用价值,并为开发该中药的药理活性成分提供化学依据,我们对其树皮进行了提取分离。

1 仪器与材料

熔点由四川大学科学仪器厂生产的 XTC-1 型显微熔点仪测定;质谱由英国 Micromass 公司产 VG Auto-Spec-3000 质谱仪测定;¹H, ¹³C NMR 用 Bruker DRX-500 MHz 超导核磁共振仪测定, TMS 为内标;制备型 MPLC 仪器为 Büchi 公司生产(Büchifraction collector C-660, Büchi pump module C-605 and manager C-615); HPLC 为 Agilent 1100, Zorbax SB-C-18 column, 5 μ m, 4.6 \times 150 mm; Sephadex LH-20 为瑞士 Amersham Biosciences 公司生产;柱层析硅胶和 GF254TLC 预制板均为青岛海洋化工厂生产。

显色方法为 254、365 nm 荧光、10% 硫酸乙醇溶液和硫酸香草醛溶液处理后加热显色、硫酸铜丙酮显色及碘蒸气显色。

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女贞 (*Ligustrum lucidum*) 干燥树皮, 采自安徽新华学院校内, 由安徽中医学院刘金旗教授鉴定。

2 提取与分离流程

干燥女贞树皮 (*Ligustrum lucidum*, 约 5.0 kg) 用 95% 乙醇 (5 × 10 L) 提取, 减压浓缩至无醇味, 加水悬浮, 分别用石油醚 (3 × 5 L)、乙酸乙酯 (3 × 5 L) 和正丁醇 (3 × 5 L) 依次萃取, 减压浓缩得浸膏石油醚部分 36.4 g, 乙酸乙酯部分 31.1 g 和正丁醇部分 254.5 g。乙酸乙酯部分经硅胶柱层析 (CHCl₃-MeOH 梯度洗脱: 100/0, 98/2, 95/5, 90/10, 80/20, 50/50), 得六个部分 (A-F)。

组分 B (CHCl₃-MeOH, 98:2 洗脱部分), 浓缩得深褐色的油状物, 多次硅胶柱分离 (petroleum ether-Me₂CO = 9:2 ~ 6:5, petroleum ether-EtOAc = 8:2 ~ 5:5, v/v), 最后用 Sephadex LH-20 凝胶柱纯化 (CHCl₃-MeOH = 1:1, v/v), 最终得到化合物 **1** (8.3 mg)、化合物 **4** (12.6 mg)、化合物 **11** (10.2 mg); 组分 C (CHCl₃-MeOH, 98:2 洗脱部分), 经反相硅胶柱层析分为 C1 和 C2 两个亚组分, C1 经凝胶柱 (CHCl₃-MeOH = 1:1, v/v) 纯化和硅胶层析柱 (petroleum ether-Me₂CO = 8:2 ~ 4:6, v/v) 得到化合物 **2** (12.3 mg)、化合物 **3** (11.3 mg)、化合物 **6** (9.8 mg)、化合物 **12** (8.9 mg); C2 经中压制备 (MPLC) (MeCN-H₂O, 40% ~ 100%, v/v, 1 mL/min, 5 ~ 8 Mpa) 和凝胶柱 (CHCl₃-MeOH = 1/1, v/v) 纯化分别得到化合物 **9** (14.4 mg)、化合物 **19** (11.5 mg)、化合物 **15** (15.9 mg); 将 D 部分经过硅胶柱层析 (CHCl₃-MeOH = 9:1 ~ 6:4, v/v), 利用中压制备 (MPLC) (MeCN-H₂O, 40% ~ 100%, v/v, 1 mL/min, 4-9 Mpa) 得化合物 **7** (11.8 mg)、化合物 **13** (13.9 mg) 以及化合物 **16** (14.6 mg); E 部分分别通过中压制备 (MPLC) (CH₃CN-H₂O, 40% ~ 100%, v/v, 1 mL/min, 5 ~ 8 Mpa) 和 HPLC (CH₃CN-H₂O, 20% ~ 100%, v/v) 分析、HPLC (CH₃CN-H₂O, 30% ~ 100%, v/v) 制备得到化合物 **5** (14.8 mg)、化合物 **14** (9.2 mg)、化合物 **8** (15.6 mg); F 部分合并, 通过硅胶柱 (petroleum ether-EtOAc = 6:1 ~ 1:1, v/v) 洗脱, Sephadex LH-20 凝胶柱纯化 (CHCl₃-MeOH = 1:1, v/v), 化合物 **10** (8.9 mg)、化合物 **18** (11.4 mg)、化合物 **17** (13.1 mg)。

3 化合物的理化常数和波谱数据

化合物 **1** 尼克酰胺, C₆H₆N₂O, 白色粉末。¹H

NMR (500 MHz, CD₃OD) δ: 7.55 (ddd, 1H, *J* = 8.1, 5.1, 0.9 Hz, H-5), 8.30 (ddd, 1H, *J* = 8.1, 2.0, 1.7 Hz, H-4), 8.69 (dd, 1H, *J* = 5.1, 1.5 Hz, H-6), 9.02 (brd, 1H, *J* = 1.8 Hz, H-2); ¹³C NMR (125 MHz, CD₃OD) δ: 152.9 (C-2), 131.5 (C-3), 137.4 (C-4), 125.2 (C-5), 149.6 (C-7), 169.9 (-CONH₂)。上述数据于文献相一致^[6], 确定为: nicotinamide。

化合物 **2** D-阿洛醇, C₆H₁₄O₆, 无色针晶。¹H NMR (500 MHz, D₂O) δ: 3.50 (2H, dd, *J* = 11.8, 6.0 Hz, H-1a, H-6a), 3.60 (4H, m, H-2, H-3, H-4, H-5), 3.70 (2H, dd, *J* = 11.8, 2.5 Hz, H-1b, H-6b); ¹³C NMR (125 MHz, D₂O) δ: 66.0 (t, C-1, C-6), 72.0 (d, C-2, C-5), 73.5 (d, C-3, C-4); EI-MS *m/z* (%): 182 [M]⁺。以上数据与文献值相一致^[7]。确定为: D-allitol。

化合物 **3** 对羟基苯甲醇, C₇H₈O₂。¹H NMR (500 MHz, acetone-*d*₆) δ: 7.11 (1H, d, *J* = 8.2 Hz, H-2, H-6), 6.77 (1H, d, *J* = 8.3, H-3, H-5), 3.50 (2H, brs, H-7); ¹³C NMR (125 MHz, acetone-*d*₆) δ: 157.1 (C-1), 131.1 (C-2), 126.6 (C-3), 115.7 (C-4), 40.5 (C-5)。以上数据与文献值相一致^[8]。确定为: p-hydroxybenzyl alcohol。

化合物 **4** 乙酰氧基齐墩果酸, C₃₂H₅₀O₄, 无色晶体, mp. 260 ~ 261 °C, EMS *m/z* 498.8 [M⁺]⁺。¹H NMR (500 MHz, CDCl₃) δ: 5.32 (1H, t, *J* = 4.6 Hz, H-12), 4.53 (1H, d, *J* = 10.1 Hz, H-3), 2.86 (1H, dd, *J* = 7.7, 3.5 Hz, H-18), 2.08 (3H, s, COCH₃), 1.16 (3H, s, H-27), 0.96 (3H, s, H-25), 0.94 (3H, s, H-30), 0.93 (3H, s, H-29), 0.88 (3H, s, H-24), 0.87 (3H, s, H-23), 0.78 (3H, s, H-26); ¹³C NMR (125 MHz, CDCl₃) δ: 38.4 (t, C-1), 22.6 (t, C-2), 81.0 (d, C-3), 37.9 (t, C-4), 55.5 (s, C-5), 18.3 (t, C-6), 33.9 (t, C-7), 39.4 (d, C-8), 47.7 (d, C-9), 37.8 (s, C-10), 23.7 (t, C-11), 122.7 (d, C-12), 143.8 (s, C-13), 41.8 (s, C-14), 32.8 (t, C-15), 23.8 (t, C-16), 46.6 (s, C-17), 41.1 (d, C-18), 45.9 (t, C-19), 30.8 (s, C-20), 32.7 (t, C-21), 27.8 (t, C-22), 28.1 (q, C-23), 16.7 (q, C-24), 15.6 (q, C-25), 17.2 (q, C-26), 26.0 (q, C-27), 183.3 (s, C-28), 33.2 (t, C-29), 23.7 (q, C-30), 171.2 (-COCH₃), 21.4 (COCH₃)。以上数据于参考文献值相一致^[9], 确定为: Acetyloleanolic acid。

化合物 **5** 苯甲酸, C₇H₆O₂, 白色固体。¹H NMR

(500 MHz, CDCl₃) δ: 8.4 (1H, d, *J* = 8.3 Hz, H-2, H-6), 7.8 (1H, d, *J* = 8.5 Hz, H-3, H-5), 7.7 (1H, m, H-4); ¹³C NMR (125 MHz, CDCl₃) δ: 172.4 (s, -COOH), 133.6 (d, C-3, C-5), 129.9 (d, C-2, C-6), 131.4 (m, C-1)。以上数据与文献值相一致^[8]。确定为: benzoic acid。

化合物 6 北升麻宁, 白色粉末, mp 88 ~ 90 °C, EI-MS *m/z* 339 [M + Na]⁺。 ¹H NMR (500 MHz, D₂O) δ: 7.07 (1H, d, *J* = 1.6 Hz, H-2), 7.76 (2H, m, H-5, 6), 4.75 (1H, d, *J* = 7.8 Hz, H-1'), 3.70 (2H, t, *J* = 7.1 Hz, H-8), 2.71 (2H, t, *J* = 7.1 Hz, H-7); ¹³C NMR (125 MHz, D₂O) δ: 146.9 (C-4), 146.8 (C-3), 132.2 (C-1), 125.3 (C-6), 119.8 (C-2), 117.2 (C-5), 104.6 (C-1'), 78.5 (C-3'), 77.8 (C-5'), 75.0 (C-2'), 71.5 (C-4'), 64.4 (C-8), 62.6 (C-6'), 36.6 (C-7)。以上数据与文献值相一致^[10]。确定为: cimidarurinine。

化合物 7 Borreriagenin, C₁₀H₁₄O₅, 白色粉末。 ¹H NMR (500 MHz, acetone-*d*₆) δ: 3.86 (1H, m, H-1a), 3.79 (1H, m, H-1b), 3.92 (1H, m, H-3a), 3.88 (1H, m, H-3b), 2.99 (1H, m, H-4), 3.36 (1H, m, H-5), 5.43 (1H, d, *J* = 7.7 Hz, H-6), 5.85 (1H, br s, H-7), 2.99 (1H, m, H-9), 4.73 (1H, m, H-10a), 4.21 (1H, m, H-10b); ¹³C NMR (125 MHz, acetone-*d*₆) δ: 60.9 (t, C-1), 62.9 (t, C-3), 45.8 (d, C-4), 44.1 (d, C-5), 88.4 (d, C-6), 125.2 (d, C-7), 153.5 (s, C-8), 48.5 (d, C-9), 60.6 (t, C-10), 181.1 (s, C-11); EI-MS *m/z* (%): 214 [M]⁺ (1), 166 (50), 136 (100)。以上数据与文献值相一致^[11]。确定为: Borreriagenin。

化合物 8 C-Veratroylglycol, C₁₀H₁₂O₅, 黄色固体。 ¹H NMR (500 MHz, CD₃OD) δ: 3.73 (1H, dd, *J* = 5.3 Hz, 11.8 Hz, H-3a), 3.86 (1H, dd, *J* = 4.1, 11.6 Hz, H-3b), 3.91 (3H, s, OCH₃), 5.12 (1H, dd, *J* = 3.8, 5.2 Hz, H-2), 6.86 (1H, d, *J* = 8.3 Hz, H-5'), 7.56 (1H, brs, H-2'), 7.58 (1H, dd, *J* = 2.1, 8.6 Hz, H-6'); ¹³C NMR (125 MHz, CD₃OD) δ: 56.6 (3'-OCH₃), 66.4 (C-4), 75.6 (C-2), 112.7 (C-2'), 116.2 (C-5'), 125.4 (C-1', C-6'), 149.6 (C-3'), 154.7 (C-4'), 199.7 (C-1)。以上数据与文献值相一致^[12]。确定为: C-Veratroylglycol。

化合物 9 methyl-2-*O*-β-glucopyranosylbenzoate, C₁₄H₁₈O₈, 褐色针状晶体, ESI-MS *m/z*: [M + Na]⁺。 ¹H NMR (500 MHz, CD₃OD) δ: 7.79 (1H, t, *J* = 1.1, 7.6,

8.0 Hz, H-7), 7.56 (1H, t, *J* = 7.1, 7.6 Hz, H-6), 7.42 (1H, d, *J* = 8.6 Hz, H-4), 7.15 (1H, t, *J* = 7.6, 15.1 Hz, H-5), 4.91 (1H, d, *J* = 7.6 Hz, H-1'), 3.94 (1H, m, H-6'), 3.92 (3H, s, 1-OMe), 3.75 (1H, m, H-6'), 3.55 (1H, m, H-2'), 3.53 (1H, m, H-3'), 3.51 (1H, m, H-4'), 3.45 (1H, m, H-5'); ¹³C NMR (125 MHz, CD₃OD) δ: 168.7 (C-1), 158.9 (C-3), 135.3 (C-5), 132.2 (C-7), 123.8 (C-6), 122.5 (C-2), 119.2 (C-4), 104.2 (C-1'), 78.6 (C-5'), 77.7 (C-3'), 75.1 (C-2'), 71.4 (C-4'), 62.7 (C-6'), 53.0 (1-OMe)。以上数据与参考文献相一致^[13]。确定为: methyl-2-*O*-β-glucopyranosylbenzoate。

化合物 10 3',7-二羟基-4'-甲氧基异黄酮, 白色无定型粉末, 分子式 C₁₆H₁₂O₅, ESI-MS *m/z* 285 [M + H]⁺。 ¹H NMR (500 MHz, pyridine-*d*₅) δ: 8.23 (1H, s, H-2), 8.50 (1H, d, *J* = 8.6 Hz, H-5), 7.38 (1H, dd, *J* = 8.6, 2.1 Hz, H-6), 7.16 (1H, d, *J* = 2.1 Hz, H-8), 7.61 (1H, d, *J* = 2.0 Hz, H-2'), 7.33 (1H, d, *J* = 8.1 Hz, H-2'), 7.26 (1H, dd, *J* = 8.6, 2.0 Hz, H-6'), 3.82 (3H, s, OCH₃)。 ¹³C NMR (125 MHz, pyridine-*d*₅) δ: 152.8 (d, C-2), 124.2 (s, C-3), 175.8 (s, C-4), 128.3 (d, C-5), 116.0 (d, C-7), 164.2 (s, C-10), 125.1 (s, C-1'), 116.5 (d, C-2'), 148.5 (s, C-3'), 146.7 (s, C-4'), 114.1 (d, C-5'), 122.6 (d, C-6'), 56.0 (q, OCH₃)。以上数据与参与文献相一致^[14]。确定为: 3',7-dihydroxy-4'-Methoxyisoflavone。

化合物 11 7-羟基香豆素, 针状晶体, C₉H₆O₃。 ESI-MS *m/z*: 163 [M + H]⁺。 ¹H NMR (500 MHz, pyridine-*d*₅) δ: 7.71 (1H, d, *J* = 9.6 Hz, H-1), 6.27 (1H, d, *J* = 9.6 Hz, H-2), 7.01 (1H, d, *J* = 2.1 Hz, H-6), 7.11 (1H, t, *J* = 9.1, 2.0 Hz, H-8), 7.41 (1H, d, *J* = 9.6 Hz, H-9); ¹³C NMR (125 MHz, pyridine-*d*₅) δ: 144.2 (d, C-1), 113.9 (d, C-2), 161.2 (s, C-3), 156.6 (d, C-5), 103.9 (d, C-2), 161.2 (s, C-3), 156.6 (d, C-5), 103.2 (s, C-6), 162.9 (d, C-7), 111.9 (d, C-8), 129.8 (s, C-9), 111.8 (s, C-10)。以上数据与参考文献相一致^[14]。确定为: umbelliferone。

化合物 12 咖啡酸甲酯, 无色颗粒晶体, mp. 161 ~ 163 °C, 分子式为 C₁₀H₁₀O₄。 ¹H NMR (500 MHz, CD₃OD) δ: 7.57 (1H, d, *J* = 16.0 Hz, H-7), 7.04 (1H, d, *J* = 1.9 Hz, H-2), 6.94 (1H, dd, *J* = 8.3, 1.9 Hz, H-7), 6.78 (1H, d, *J* = 8.3 Hz, H-5), 6.29 (1H, d, *J* = 16.0 Hz, H-8), 3.75 (3H, s, OCH₃); ¹³C

NMR (125 MHz, CD₃OD) δ : 127.7 (s, C-1), 114.9 (d, C-2), 146.9 (s, C-3), 149.7 (s, C-4), 115.2 (d, C-5), 123.0 (d, C-6), 147.0 (d, C-7), 116.6 (d, C-8), 169.9 (s, C-9), 52.1 (q, OCH₃)。以上数据与参考文献相一致^[15], 确定为: caffeic acid methyl ester。

化合物 13 齐墩果酸, C₃₀H₄₈O₃, 白色粉末, EI-MS m/z : 456。¹H NMR (500 MHz, CDCl₃) δ : 0.60 (3H, s), 0.62 (3H, s), 0.72 (3H, s), 0.72 (3H, s), 0.75 (3H, s), 0.80 (3H, s), 0.97 (3H, s), 2.65 (1H, m, H-18), 3.02 (1H, m, H-3), 5.09 (1H, brs, H-12); ¹³C NMR (125 MHz, CDCl₃) δ : 38.3 (C-1), 26.5 (C-2), 78.4 (C-3), 38.5 (C-4), 55.1 (C-5), 18.1 (C-6), 32.5 (C-7), 39.1 (C-8), 47.5 (C-9), 36.8 (C-10), 22.8 (C-11), 122.1 (C-12), 143.7 (C-13), 41.1 (C-14), 27.4 (C-15), 23.1 (C-16), 46.1 (C-17), 41.1 (C-18), 45.8 (C-19), 30.3 (C-20), 33.5 (C-21), 32.3 (C-22), 27.7 (C-23), 15.0 (C-24), 15.3 (C-25), 16.5 (C-26), 25.6 (C-27), 32.7 (C-29), 23.2 (C-30)。以上数据于文献报道相一致^[16], 确定为: oleanolic acid。

化合物 14 (-)-囊五脂素, C₂₀H₂₂O₅, 无色粉末。EI-MS m/z (%) 342 [M]⁺ (25), 192 (100), 175 (15), 135 (10); ¹H NMR (500 MHz, CDCl₃) δ : 6.76~6.93 (6H, m, Ar-H), 4.61 (1H, d, J = 9.2 Hz, H-7), 5.40 (1H, d, J = 4.2 Hz, H-7'), 2.41~2.46 (2H, m, H-8, 8'), 0.98 (3H, d, J = 6.4 Hz, H-9), 0.59 (3H, d, J = 6.9 Hz, H-9'), 5.95 (2H, s, -OCH₂O-), 5.57 (1H, s, 4'-OH), 3.90 (3H, s, 3'-OH); ¹³C NMR (CDCl₃, 125 MHz) δ : 134.9 (C-1), 106.5 (C-2), 147.5 (C-3), 146.6 (C-4), 107.9 (C-5), 119.5 (C-6), 85.7 (C-7), 47.4 (C-8), 11.8 (C-9), 134.7 (C-1'), 108.4 (C-2'), 145.1 (C-3'), 146.3 (C-4'), 114.0 (C-5'), 119.0 (C-6'), 84.7 (C-7'), 43.4 (C-8'), 9.5 (C-9'), 100.8 (-OCH₂O-), 55.9 (-OCH₃); 以上数据与参考文献相一致^[17], 确定为: (-)-chicanine。

化合物 15 蒺藜油脑, C₁₂H₁₄O₄, EI-MS m/z (%) 222 [M]⁺ (100), 207 (26), 177 (35), 149 (55), 77 (25), 69 (42)。¹H NMR (500 MHz, CDCl₃) δ : 6.33 (1H, s, H-6), 5.88 (1H, m, H-8), 5.85 (2H, s, -OCH₂O-), 5.00 (2H, m, H-3'), 3.99 (3H, s, -OCH₃), 3.74 (3H, s, -OCH₃), 3.28 (2H, d, J = 6.5 Hz, H-1'); ¹³C NMR (125 MHz, CDCl₃) δ : 126.0 (C-1), 135.9 (C-2), 137.6 (C-3), 144.6 (C-4),

144.2 (C-5), 102.7 (C-6), 33.9 (C-1'), 137.4 (C-2'), 115.5 (C-3'), 101.1 (-OCH₂O-), 61.2 (-OCH₃), 59.9 (-OCH₃)。以上数据与参考文献相一致^[18], 确定为: dillapiol。

化合物 16 表儿茶素, C₁₅H₁₄O₆, EI-MS m/z (%) 290 [M]⁺ (33), 152 (49), 139 (100), 123 (27)。¹H NMR (500 MHz, CD₃OD) δ : 6.97 (1H, d, J = 1.5 Hz, H-2'), 6.80 (1H, d, J = 8.2, 1.8 Hz, H-6'), 6.75 (1H, d, J = 8.2 Hz, H-5'), 5.94 (1H, d, J = 2.2 Hz, H-6), 5.91 (1H, d, J = 2.2 Hz, H-8), 4.80 (1H, br s, H-2), 4.11 (1H, dd, J = 14.3, 7.1 Hz, H-3), 2.87 (1H, dd, J = 16.7, 4.6 Hz, H-4), 2.85 (1H, dd, J = 14.3, 7.1 Hz, H-4); ¹³C NMR (CD₃OD, 125 MHz) δ : 79.8 (C-2), 67.5 (C-3), 29.2 (C-4), 100.1 (C-4a), 157.6 (C-5), 95.9 (C-6), 157.3 (C-7), 96.4 (C-8), 157.9 (C-8a), 132.3 (C-1'), 115.3 (C-2'), 145.7 (C-3'), 145.9 (C-4'), 115.8 (C-5'), 119.4 (C-6')。以上数据与参考文献相一致^[19], 确定为: L-Epicatechin。

化合物 17 2 α -羟基齐墩果酸, 白色粉末, C₃₀H₄₈O₄。¹H NMR (500 MHz, CDCl₃) δ : 0.80 (3H, s), 0.81 (3H, s), 0.91 (3H, s), 0.95 (3H, s), 1.01 (3H, s), 1.02 (3H, s), 1.16 (3H, s), 2.86 (1H, m, H-18), 3.00 (1H, d, J = 9.8 Hz, H-3), 3.62 (1H, m, H-2), 5.26 (1H, br s, H-12); ¹³C NMR (125 MHz, CDCl₃) δ : 48.2 (C-1), 69.7 (C-2), 84.6 (C-3), 40.9 (C-4), 56.8 (C-5), 19.7 (C-6), 33.9 (C-7), 40.6 (C-8), 49.1 (C-9), 39.4 (C-10), 24.2 (C-11), 123.6 (C-12), 145.6 (C-13), 43.4 (C-14), 29.0 (C-15), 24.9 (C-16), 47.8 (C-17), 42.9 (C-18), 47.5 (C-19), 31.7 (C-20), 34.8 (C-21), 34.0 (C-22), 29.4 (C-23), 17.9 (C-24), 17.3 (C-25), 17.5 (C-26), 26.7 (C-27), 33.9 (C-29), 23.9 (C-30)。以上数据于文献报道相一致^[16], 确定为: 2 α -hydroxy-oleanolic acid。

化合物 18 桦木酸, C₃₀H₄₈O₃, mp. 289~291 °C, EMS m/z 456.8 [M⁺]₂。¹H NMR (500 MHz, CDCl₃) δ : 12.2 (1H, brs, -COOH), 4.71, 4.59 (2H, m, H-29), 1.66 (3H, s, H-30), 0.94 (3H, s, H-27), 0.89 (3H, s, H-26), 0.86 (3H, s, H-25), 0.79 (3H, s, H-24), 0.67 (3H, s, H-23); ¹³C NMR (125 MHz, CDCl₃) δ : 38.6 (t, C-1), 27.6 (t, C-2), 80.0 (d, C-3), 38.8 (t, C-4), 55.8 (s, C-5), 18.5 (t, C-6), 34.2 (t, C-7), 40.4 (d, C-8), 50.3 (d, C-9), 38.0 (s, C-

10), 20.7 (t, C-11), 25.5 (t, C-12), 37.9 (d, C-13), 42.7 (s, C-14), 30.4 (t, C-15), 32.0 (t, C-16), 56.0 (s, C-17), 49.9 (d, C-18), 48.6 (d, C-19), 150.6 (s, C-20), 29.5 (t, C-21), 37.1 (t, C-22), 28.5 (q, C-23), 16.0 (q, C-24), 16.1 (q, C-25), 16.3 (q, C-26), 14.7 (q, C-27), 177.8 (s, C-28), 110.2 (t, C-29), 19.2 (q, C-30)。以上数据与参考文献相一致^[20], 确定为: betulinic acid。

化合物 19 白桦脂醇, $C_{30}H_{50}O_2$, mp. 260 ~ 263 °C。¹H NMR (500 MHz, $CDCl_3$) δ : 4.71, 4.61 (2H, brs, H-29), 3.83 (1H, d, $J = 10.7$ Hz, H-28), 3.41 (1H, d, $J = 10.6$ Hz, H-28), 3.36 (1H, d, $J = 10.6$ Hz, H-3), 1.70 (3H, s, H-30), 1.03 (3H, s, H-27), 0.99 (3H, s, H-26), 0.96 (3H, s, H-25), 0.84 (3H, s, H-24), 0.76 (3H, s, H-23); ¹³C NMR (125 MHz, $CDCl_3$) δ : 38.9 (t, C-1), 27.6 (t, C-2), 79.4 (d, C-3), 39.1 (t, C-4), 55.6 (d, C-5), 18.5 (t, C-6), 34.5 (t, C-7), 41.2 (s, C-8), 50.6 (d, C-9), 37.3 (s, C-10), 21.1 (t, C-11), 24.5 (t, C-12), 37.6 (d, C-13), 43.1 (s, C-14), 27.3 (t, C-15), 29.5 (t, C-16), 48.0 (s, C-18), 48.1 (d, C-18), 49.0 (s, C-19), 150.7 (s, C-20), 30.2 (t, C-21), 34.1 (t, C-22), 28.5 (q, C-23), 15.4 (s, C-24), 16.3 (q, C-25), 16.4 (q, C-26), 15.0 (q, C-27), 60.8 (s, C-28), 109.8 (t, C-29), 19.6 (q, C-30)。以上数据与参考文献相一致^[21], 确定为: Betulin。

参考文献

- Yang J, Wei CX. Overview in studies on *Ligustrum*. *Northwest Pharm J* (西北药学杂志), 2005, 20: 278-280.
- Cheng XF, He MF, Zhang Y, et al. Studies on constituents of fructus *Ligustrum lucidum*. *J Chin Pharm Univ* (中国药科大学学报), 2000, 31: 169-170.
- He ZD, But PPH, Chan TW, et al. Antioxidative glucosides from the fruits of *Ligustrum lucidum*. *Chem Pharm Bull*, 2001, 49: 780-784.
- Zhang XH, Shi LF. Studies on chemical constituents of *Fructus Ligustri lucidum*. *Acad J Second Mil Med Univ* (第二军医大学学报), 2004, 25: 333-334.
- Shi LF, Wang P, Chen HS, et al. Studies on water-soluble constituents from the fruits of *Ligustrum lucidum* Ait. *Acta Pharm Sin* (药学学报), 1995, 30: 935-938.
- Yuan JZ, Wu LJ, Chen YJ, et al. Isolation, identification of the chemical constituents from *Smilax glabra* Roxb. *Chin J Med Chem* (中国药物化学杂志), 2004, 14: 291-293.
- Gao JM, Dong ZJ, Liu JK. Constituents of the basidiomycetes *russula cyanoxantha*. *Acta Bot Yunnan* (云南植物学报), 2000, 22: 85-89.
- Wang F. 绿盖粉孢牛肝菌等 10 种高等真菌的化学成分. Kunming: Kunming Institute of Botany, Chinese Academy of Sciences, 2009.
- Guo FJ, Lin S, Li YC. Isolation and identification of triterpenoids from *Schefflera arboricola*. *Chin Pharm J* (中国药物化学杂志), 2005, 15: 294-296.
- Huang XJ, Yin ZQ, Ye WC, et al. Chemical constituents from fruits of *Ligustrum lucidum*. *Chin J Chin Mater Med* (中国中药化学), 2010, 35: 861-864.
- Wei XY, Xie HH, Ge XJ. Iridoids from *Dunnia sinensis*. *Phytochemistry*, 2000, 53: 837-840.
- Baderschneider B, Winterhalter P. Isolation and characterization of novel benzoates, cinnamates, flavonoids, and lignans from *Riesling Wine* and screening for antioxidant activity. *J Agric Food Chem*, 2001, 49: 2788-2798.
- Huang YZ, Zhang S, Huang S, et al. Chemical constituents of the plant *Micromelum falcatum* (Lour.) Tan. *Nat Prod Res Dev*, 2012, 24: 1161-1164.
- Zhu CC, Deng GH, Lin CZ. Chemical Constituents of *Picrasma quassioides* (D. Don) Benn. *Nat Prod Res Dev* (天然产物研究与开发), 2012, 24: 476-478.
- Xu XY, Li SZ, Song QS. Chemical constituents of the bark of *Anthocephalus chinensis*. *Nat Prod Res Dev* (天然产物研究与开发), 2011, 23: 393-398.
- Liu P, Duan HQ, Pan Q, et al. Triterpenes from herb of *Potentilla chinensis*. *Chin J Chin Mater Med* (中国中药杂志), 2006, 31: 1875-1879.
- Sadhu SK, Okuyama E, Fujimoto H, et al. Separation of *Leucas aspera*, a medicinal plant of Bangladesh, guided by prostaglandin inhibitory and antioxidant activities. *Chem Pharm Bull*, 2003, 51: 595-598.
- Benevides, Paulo JC, Sartorelli, et al. Phenylpropanoids and neolignans from *Piper regnellii*. *Phytochemistry*, 1999, 52: 339-343.
- Zhang NL. Chemical Investigation on *Albizia mollis*, *Foeniculum vulgare* and *Ardisia crispa* (毛叶合欢, 小茴香和百两金的化学成分研究). Kunming: Kunming Institute of Botany, Chinese Academy of Sciences, 2009.
- Xue HO, Yang HT, Wang HQ, et al. Study on triterpenes from *Ligularia xanthotricha*. *Chin J Chin Mater Med* (中国中药杂志), 2008, 33: 272-275.
- Wang B, Yang LY, Li GQ, et al. Antitumor triterpenes from *Scorzonera ongolica* Maxim. *Chin Pharm J* (中国药物化学杂志), 2010, 45: 727-732.