

阔刺兔唇花全草的化学成分研究

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摘要: 目的 研究阔刺兔唇花 *Lagochilus platyacanthus* 的化学成分。方法 利用多种色谱方法进行分离纯化, 综合运用各种光谱方法鉴定化合物的结构。结果 从阔刺兔唇花全草 95%乙醇提取物中分离鉴定了 21 个化合物, 包括 15 个黄酮类化合物: 芹菜素-7, 4'-二甲醚 (1)、刺槐素 (2)、芹菜素 (3)、木犀草素-7, 3', 4'-三甲醚 (4)、木犀草素-7, 4'-二甲醚 (5)、香叶木素 (6)、金圣草素 (7)、槲皮素-3-O-芸香糖-7-O-葡萄糖苷 (8)、芦丁 (9)、horridin (10)、芹菜素-6, 8-二-C-葡萄糖苷 (11)、异鼠李素-3-O-芸香糖苷 (12)、异鼠李素-3-O-刺槐二糖苷 (13)、异鼠李素-3-O-葡萄糖苷 (14)、异鼠李素-3-O-芸香糖-4'-O-葡萄糖苷 (15); 3 个木脂素类化合物: 1-(4-hydroxy-3-methoxy)-phenyl-2-[4-(1, 2, 3-trihydroxypropyl)-2-methoxy]-phenoxy-1, 3-propandiol (16)、(+)-异落叶松脂醇 3- α -O- β -D-葡萄糖苷 (17)、(-)-异落叶松脂醇 3- α -O- β -D-葡萄糖苷 (18); 2 个环烯醚萜类化合物: 8-O-乙酰哈巴苷 (19)、京尼平苷酸 (20) 及 1 个苯乙醇苷类化合物: lavandulifolioside (21)。结论 21 个化合物均为首次从阔刺兔唇花植物中分离得到, 除化合物 1、3、9、19 及 20 外, 其余化合物均为首次从兔唇花属植物中分离得到。

关键词: 阔刺兔唇花; 刺槐素; 木犀草素-7, 4'-二甲醚; 香叶木素; (+)-异落叶松脂醇 3- α -O- β -D 葡萄糖苷

中图分类号: R284.1

文献标志码: A

文章编号: 0253-2670(2014)22-3224-06

DOI: 10.7501/j.issn.0253-2670.2014.22.003

Chemical constituents from whole herb of *Lagochilus platyacanthus*

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Abstract: Objective To study the chemical constituents from the whole herb of *Lagochilus platyacanthus*. **Methods** The chemical constituents were isolated and purified by various chromatographic techniques and the structures were identified by spectral analysis. **Results** Twenty-one compounds were isolated from the 95% ethanol extract of *L. platyacanthus*, including 15 flavonoids: apigenin-7, 4'-dimethyl ether (1), acacetin (2), apigenin (3), luteolin-7, 3', 4'-trimethyl ether (4), luteolin-7, 4'-dimethyl ether (5), diosmetin (6), chrysoeriol (7), quercetin-3-O-rutinoside-7-O-glucoside (8), rutin (9), horridin (10), apigenin-6, 8-di-C- β -D-glucopyranoside (11), isorhamnetin-3-O-rutinoside (12), isorhamnetin-3-O-robinobioside (13), isorhamnetin-3-O- β -D-glucoside (14), and isorhamnetin-3-O-rutinoside-4'-O-glucoside (15); three lignans: 1-(4-hydroxy-3-methoxy)-phenyl-2-[4-(1, 2, 3-trihydroxypropyl)-2-methoxy]-phenoxy-1, 3-propandiol (16), (+)-isolarisiresinol 3- α -O- β -D-glucopyranoside (17), and (-)-isolarisiresinol 3- α -O- β -D-glucopyranoside (18); two iridoids: 8-O-acetylharpagide (19) and geniposidic acid (20), and one phenylethanoid glycoside: lavandulifolioside (21). **Conclusion** All the compounds are obtained from this plant for the first time. The compounds are isolated from the plants in genus *Lagochilus* Bunge for the first time except compounds 1, 3, 9, 19, and 20.

Key words: *Lagochilus platyacanthus* Rupr.; acacetin; luteolin-7, 4'-dimethyl ether; diosmetin; (+)-isolarisiresinol 3- α -O- β -D-glucopyranoside

阔刺兔唇花 *Lagochilus platyacanthus* Rupr. 为石坡灌丛中, 俄罗斯也有分布^[1]。据报道, 兔唇花唇形科兔唇花属植物, 在我国分布于新疆, 生于碎石植物主要有二萜类、环烯醚萜类、黄酮类、香豆

收稿日期: 2014-07-23

基金项目: 上海市科学技术委员会资助项目 (09405801700)

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素类、多糖类等化学成分,具有消炎止血、镇静等药理作用^[2-3]。

在新疆,阔刺兔唇花全草作为止血药,用于治疗各种出血以及冠心病、心绞痛、溃疡、失眠、健忘等病症^[2]。然而,截至目前,仍未见有关阔刺兔唇花化学成分的相关研究报道。鉴于此,为了进一步阐明该植物的药效物质基础,首次对分布于新疆的阔刺兔唇花全草进行了系统的化学成分研究,从其95%乙醇提取物中分离鉴定了21化合物,分别鉴定为芹菜素-7,4'-二甲醚(apigenin-7,4'-dimethyl ether, **1**)、刺槐素(acacetin, **2**)、芹菜素(apigenin, **3**)、木犀草素-7,3',4'-三甲醚(luteolin-7,3',4'-trimethyl ether, **4**)、木犀草素-7,4'-二甲醚(luteolin-7,4'-dimethyl ether, **5**)、香叶木素(diosmetin, **6**)、金圣草素(chrysoeriol, **7**)、槲皮素-3-O-芸香糖-7-O-葡萄糖苷(quercetin-3-O-rutinoside-7-O-glucoside, **8**)、芦丁(rutin, **9**)、horridin(**10**)、芹菜素-6,8-二-C-葡萄糖苷(apigenin-6,8-di-C- β -D-glucopyranoside, **11**)、异鼠李素-3-O-芸香糖苷(isorhamnetin-3-O-rutinoside, **12**)、异鼠李素-3-O-刺槐二糖苷(isorhamnetin-3-O-robinobioside, **13**)、异鼠李素-3-O-葡萄糖苷(isorhamnetin-3-O- β -D-glucoside, **14**)、异鼠李素-3-O-芸香糖-4'-O-葡萄糖苷(isorhamnetin-3-O-rutinoside-4'-O-glucoside, **15**)、1-(4-hydroxy-3-methoxy)-phenyl-2-[4-(1,2,3-trihydroxypropyl)-2-methoxy]-phenoxy-1,3-propandiol(**16**)、(+)-异落叶松脂醇 3- α -O- β -D-葡萄糖苷[(+)-isolarisiresinol 3- α -O- β -D-glucopyranoside, **17**]、(-)-异落叶松脂醇 3- α -O- β -D-葡萄糖苷[(-)-isolarisiresinol 3- α -O- β -D-glucopyranoside, **18**]、8-O-乙酰哈巴苷(8-O-acetylharpagide, **19**)、京尼平苷酸(geniposidic acid, **20**)、lavandulifolioside(**21**)。除化合物**1**、**3**、**9**、**19**及**20**外,其余化合物均为首次从兔唇花属植物中分离得到。

1 仪器与材料

Bruker AV-400/600 型核磁共振仪(德国 Bruker 公司);ESI-MS 联用仪(Trace DSQ, 美国 Thermo 公司);LC3000 型制备高效液相色谱仪(北京创新通恒有限责任公司);1100/1200 型高效液相色谱仪(美国 Agilent 公司);ODS(40~60 μ m, 美国 Sepax 公司);Sephadex LH-20(瑞典 GE 公司);MCI(175~150 μ m, 日本三菱公司);柱色谱硅胶及 GF₂₅₄ 薄层色谱硅胶板均购自青岛海洋化工厂;

D-101 型大孔吸附树脂购自国药集团化学试剂有限公司。药材提取试剂为工业纯,柱色谱试剂均为分析纯,制备液相试剂为色谱纯。

阔刺兔唇花药材采自新疆吉木乃,由上海中医药大学中药研究所徐红研究员鉴定为唇形科植物阔刺兔唇花 *Lagochilus platyacanthus* Rupr., 凭证标本(20100723-020)保存于上海中医药大学中药研究所。

2 提取与分离

阔刺兔唇花全草 10.6 kg, 粉碎,用 5 倍量的 95% 乙醇溶液室温浸泡 8 次,每次 4 d, 减压浓缩得总浸膏 1.05 kg, 将总浸膏用水分散,将其依次用二氯甲烷、正丁醇萃取,浓缩萃取液分别得到二氯甲烷部位 350 g、正丁醇部位 574 g。

将二氯甲烷部位用硅胶柱色谱分离,用石油醚-醋酸乙酯(100:0 $\rightarrow$ 0:100)梯度洗脱,经薄层检测合并流分,得 11 个流分(Fr. 1~11)。将上述流分经反复硅胶柱色谱,同时结合凝胶柱色谱及高效制备液相色谱等方法,共分离得到化合物 **1** (15 mg)、**2** (150 mg)、**3** (11 mg)、**4** (12 mg)、**5** (10 mg)、**6** (3 mg) 和 **7** (12 mg)。

将正丁醇部位用大孔树脂柱色谱进行分离,依次用水及 30%、60%、95%乙醇梯度洗脱,得流分 Fr. 1~4。上述 4 个流分再用 MCI 分离,同时结合 ODS 柱色谱,凝胶柱色谱以及制备高效液相色谱等方法,共分离鉴定 14 个化合物:**8** (10 mg)、**9** (640 mg)、**10** (5 mg)、**11** (5 mg)、**12** (3 mg)、**13** (5 mg)、**14** (4 mg)、**15** (3 mg)、**16** (4 mg)、**17** (22 mg)、**18** (44 mg)、**19** (198 mg)、**20** (14 mg) 和 **21** (16 mg)。

3 结构鉴定

化合物 **1**: 黄色针晶(二氯甲烷)。¹H-NMR (400 MHz, CDCl₃) δ : 6.60 (1H, s, H-3), 12.81 (1H, s, 5-OH), 6.38 (1H, d, J = 2.2 Hz, H-6), 6.50 (1H, d, J = 2.2 Hz, H-8), 7.86 (2H, d, J = 8.8 Hz, H-2', 6'), 7.03 (2H, d, J = 8.8 Hz, H-3', 5'), 3.91 (3H, s, -OCH₃), 3.90 (3H, s, -OCH₃); ¹³C-NMR (100 MHz, CDCl₃) δ : 164.1 (C-2), 104.3 (C-3), 182.5 (C-4), 162.6 (C-5), 98.1 (C-6), 165.5 (C-7), 92.6 (C-8), 157.7 (C-9), 105.6 (C-10), 123.6 (C-1'), 128.1 (C-2', 6'), 114.5 (C-3', 5'), 162.2 (C-4'), 55.8 (-OCH₃), 55.5 (-OCH₃)。以上数据与文献报道一致^[4], 故鉴定化合物 **1** 为芹菜素-7,4'-二甲醚。

化合物 **2**: 淡黄色粉末。¹H-NMR (400 MHz, C₅D₅N) δ : 6.92 (1H, s, H-3), 13.69 (1H, s, 5-OH), 6.74

(1H, d, $J = 2.0$ Hz, H-6), 6.80 (1H, d, $J = 2.0$ Hz, H-8), 7.92 (2H, d, $J = 8.8$ Hz, H-2', 6'), 7.05 (2H, d, $J = 8.8$ Hz, H-3', 5'), 3.72 (3H, s, 4'-OCH₃); ¹³C-NMR (100 MHz, C₅D₅N) δ : 165.3 (C-2), 103.9 (C-3), 182.1 (C-4), 162.3 (C-5), 99.4 (C-6), 163.3 (C-7), 94.2 (C-8), 157.9 (C-9), 104.4 (C-10), 123.3 (C-1'), 127.9 (C-2', 6'), 114.2 (C-3', 5'), 54.8 (4'-OCH₃)。以上数据与文献报道基本一致^[5], 故鉴定化合物 **2** 为刺槐素。

化合物 **3**: 黄色粉末。¹H-NMR (400 MHz, DMSO-*d*₆) δ : 6.78 (1H, s, H-3), 12.96 (1H, s, 5-OH), 6.17 (1H, d, $J = 2.0$ Hz, H-6), 6.47 (1H, d, $J = 2.0$ Hz, H-8), 7.92 (2H, d, $J = 8.8$ Hz, H-2', 6'), 6.91 (2H, d, $J = 8.8$ Hz, H-3', 5'); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ : 164.4 (C-2), 103.0 (C-3), 182.0 (C-4), 161.6 (C-5), 99.0 (C-6), 163.9 (C-7), 94.7 (C-8), 157.5 (C-9), 103.9 (C-10), 121.4 (C-1'), 128.7 (C-2', 6'), 116.2 (C-3', 5'), 161.4 (C-4')。以上数据与文献报道基本一致^[6], 故鉴定化合物 **3** 为芹菜素。

化合物 **4**: 淡黄色粉末。¹H-NMR (400 MHz, C₅D₅N) δ : 7.01 (1H, s, H-3), 13.59 (1H, s, 5-OH), 6.62 (1H, d, $J = 2.0$ Hz, H-6), 6.74 (1H, d, $J = 2.0$ Hz, H-8), 7.08 (1H, d, $J = 8.5$ Hz, H-5'), 7.69 (1H, dd, $J = 8.5$, 1.9 Hz, H-6'), 3.83 (3H, s, -OCH₃), 3.81 (3H, s, -OCH₃), 3.73 (3H, s, -OCH₃); ¹³C-NMR (100 MHz, C₅D₅N) δ : 164.4 (C-2), 105.0 (C-3), 182.8 (C-4), 162.7 (C-5), 98.7 (C-6), 165.9 (C-7), 93.0 (C-8), 158.2 (C-9), 106.0 (C-10), 124.0 (C-1'), 110.1 (C-2'), 153.3 (C-4'), 112.1 (C-5'), 120.7 (C-6'), 56.1 (-OCH₃), 55.9 (-OCH₃), 55.9 (-OCH₃)。以上数据与文献报道基本一致^[7], 故鉴定化合物 **4** 为木犀草素-7, 3', 4'-三甲醚。

化合物 **5**: 黄色固体。¹H-NMR (400 MHz, pyridine-*d*₅) δ : 6.98 (1H, s, H-3), 13.67 (1H, s, 5-OH), 6.75 (1H, d, $J = 2.2$ Hz, H-8), 6.61 (1H, d, $J = 2.2$ Hz, H-6), 7.65 (2H, dd, $J = 10.3$, 2.0 Hz, H-2', 6'), 7.30 (1H, d, $J = 8.2$ Hz, H-5'), 3.82 (3H, s, -OCH₃), 3.73 (3H, s, -OCH₃)。以上数据与文献报道基本一致^[8], 故鉴定化合物 **5** 为木犀草素-7, 4'-二甲醚。

化合物 **6**: 淡黄色粉末。¹H-NMR (400 MHz, DMSO-*d*₆) δ : 12.98 (1H, s, 5-OH), 6.20 (1H, s, H-6), 10.82 (1H, s, 7-OH), 6.52 (1H, s, H-8), 7.57 (2H, d, $J = 5.8$ Hz, H-2', 6'), 9.97 (1H, s, 3'-OH), 6.93 (2H, s, H-3, 5'), 3.90 (3H, s, -OCH₃); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ : 164.3 (C-2), 103.4 (C-3), 182.0 (C-4),

161.6 (C-5), 99.0 (C-6), 163.8 (C-7), 94.2 (C-8), 157.5 (C-9), 110.4 (C-10), 121.7 (C-1'), 110.4 (C-2'), 150.9 (C-3'), 148.2 (C-4'), 116.0 (C-5'), 120.5 (C-6'), 56.1 (-OCH₃)。以上数据与文献报道基本一致^[9], 故鉴定化合物 **6** 为香叶木素。

化合物 **7**: 类白色粉末。¹H-NMR (400 MHz, DMSO-*d*₆) δ : 12.96 (1H, s, 5-OH), 6.48 (1H, d, $J = 1.7$ Hz, H-6), 6.17 (1H, d, $J = 1.8$ Hz, H-8), 7.54 (2H, d, $J = 6.4$ Hz, H-6', 2'), 6.91 (2H, s, H-3, 5'), 3.88 (3H, s, -OCH₃); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ : 164.8 (C-2), 103.7 (C-3), 181.9 (C-4), 161.6 (C-5), 99.1 (C-6), 163.8 (C-7), 94.3 (C-8), 157.6 (C-9), 103.3 (C-10), 121.7 (C-1'), 110.3 (C-2'), 151.0 (C-3'), 148.2 (C-4'), 116.0 (C-5'), 120.5 (C-6'), 56.1 (-OCH₃)。以上数据与文献报道基本一致^[10], 故鉴定化合物 **7** 为金圣草素。

化合物 **8**: 黄色粉末。¹H-NMR (400 MHz, DMSO-*d*₆) δ : 12.60 (1H, s, 5-OH), 6.43 (1H, d, $J = 2.0$ Hz, H-6), 6.71 (1H, d, $J = 2.0$ Hz, H-8), 7.53 (2H, m, H-2', 6'), 6.84 (1H, d, $J = 8.1$ Hz, H-5'), 5.37 (1H, d, $J = 7.2$ Hz, H-1''), 4.38 (1H, m, H-1'''), 5.06 (1H, d, $J = 7.3$ Hz, H-1'''), 0.98 (3H, d, $J = 6.2$ Hz, -CH₃); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ : 156.2 (C-2), 133.7 (C-3), 177.7 (C-4), 161.1 (C-5), 99.5 (C-6), 163.0 (C-7), 94.7 (C-8), 156.2 (C-9), 105.8 (C-10), 121.2 (C-1'), 115.4 (C-2'), 144.9 (C-3'), 148.8 (C-4'), 116.6 (C-5'), 121.8 (C-6'); 3-O-Glc: 101.2 (C-1''), 73.3 (C-2''), 76.6 (C-3''), 69.7 (C-4''), 74.2 (C-5''), 67.2 (C-6''); Rha: 100.0 (C-1'''), 70.2 (C-2'''), 70.5 (C-3'''), 70.7 (C-4'''), 17.9 (C-6'''); 7-O-Glc: 100.9 (C-1'''), 72.0 (C-2'''), 76.2 (C-3'''), 68.4 (C-4'''), 77.3 (C-5'''), 60.8 (C-6''')。以上数据与文献报道基本一致^[11], 故鉴定化合物 **8** 为槲皮素-3-O-芸香糖-7-O-葡萄糖苷。

化合物 **9**: 黄色粉末。¹H-NMR (600 MHz, DMSO-*d*₆) δ : 12.59 (1H, s, 5-OH), 10.81 (1H, s, -OH), 9.64 (1H, s, -OH), 9.16 (1H, s, -OH), 6.18 (1H, s, H-6), 6.37 (1H, s, H-8), 7.52 (2H, d, $J = 9.1$ Hz, H-2', 6'), 6.83 (1H, d, $J = 8.2$ Hz, H-5'), 5.33 (1H, d, $J = 7.0$ Hz, H-1''), 5.26 (1H, d, $J = 3.4$ Hz, H-1'''), 0.98 (3H, d, $J = 6.2$ Hz, H-6'''); ¹³C-NMR (150 MHz, DMSO-*d*₆) δ : 156.9 (C-2), 133.8 (C-3), 177.8 (C-4), 161.7 (C-5), 99.1 (C-6), 164.5 (C-7), 94.0 (C-8), 157.1 (C-9), 104.4 (C-10), 121.6 (C-1'), 115.7 (C-2'), 145.2 (C-3'), 148.9 (C-4'), 116.7 (C-5'), 122.0 (C-6'); 3-O-Glc: 101.2

(C-1''), 74.5 (C-2''), 76.9 (C-3''), 70.4 (C-4''), 76.4 (C-5''), 67.5 (C-6''); 6-O-Rha: 101.6 (C-1'''), 70.8 (C-2'''), 71.0 (C-3'''), 72.3 (C-4'''), 68.7 (C-5'''), 18.2 (C-6'''). 以上数据与文献报道基本一致^[12], 故鉴定化合物 **9** 为芦丁。

化合物 **10**: 黄色粉末。¹H-NMR (400 MHz, DMSO-*d*₆) δ : 12.67 (1H, s, 5-OH), 6.18 (1H, d, J = 1.9 Hz, H-6), 6.37 (1H, d, J = 2.0 Hz, H-8), 7.49 (1H, d, J = 2.1 Hz, H-2'), 6.83 (1H, d, J = 8.4 Hz, H-5'), 7.54 (1H, dd, J = 8.4, 2.1 Hz, H-6'), 5.53 (1H, d, J = 7.7 Hz, H-1''), 4.34 (1H, s, H-2''), 0.80 (3H, d, J = 6.2 Hz, H-6''), 5.07 (1H, s, H-1'''), 0.97 (3H, d, J = 6.2 Hz, H-6'''); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ : 156.6 (C-2), 132.9 (C-3), 177.4 (C-4), 161.4 (C-5), 98.9 (C-6), 164.3 (C-7), 93.8 (C-8), 156.9 (C-9), 104.2 (C-10), 121.8 (C-1'), 115.3 (C-2'), 145.0 (C-3'), 148.5 (C-4'), 116.3 (C-5'), 121.4 (C-6'); 3-O-Rha: 100.7 (C-1''), 77.3 (C-2''), 68.5 (C-3''), 71.9 (C-4''), 70.7 (C-5''), 17.9 (C-6''); 2-O-Rha: 101.0 (C-1'''), 70.6 (C-2'''), 70.8 (C-3'''), 72.0 (C-4'''), 67.3 (C-5'''), 17.4 (C-6'''). 以上数据与文献报道基本一致^[13], 故鉴定化合物 **10** 为 horridin。

化合物 **11**: 黄色粉末。¹H-NMR (400 MHz, DMSO-*d*₆) δ : 6.83 (1H, s, H-3), 13.72 (1H, s, 5-OH), 9.37 (1H, s, 7-OH), 8.04 (2H, d, J = 8.7 Hz, H-2', 6'), 6.90 (2H, d, J = 8.7 Hz, H-3', 5'), 10.38 (1H, s, 4'-OH), 4.76 (1H, d, J = 10.0 Hz, H-1''), 3.27 (3H, m, H-3'', 4'', 5''), 3.50 (2H, m, H-6''a, 6''b), 3.70 (1H, m, H-6''b), 5.01 (1H, d, J = 4.6 Hz, H-1'''), 3.89 (1H, t, J = 9.2 Hz, H-2'''), 3.39 (3H, m, H-3''', 4''', 5'''), 3.76 (1H, m, H-6'''b); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ : 164.6 (C-2), 104.3 (C-3), 182.8 (C-4), 159.1 (C-5), 108.0 (C-6), 161.7 (C-7), 105.8 (C-8), 155.5 (C-9), 103.1 (C-10), 122.0 (C-1'), 129.5, 129.2 (C-2', 6'), 116.5, 116.3 (C-3', 5'), 161.7 (C-4'); 6-C-Glc: 73.8 (C-1''), 72.4 (C-2''), 79.3 (C-3''), 71.0 (C-4''), 82.4 (C-5''), 61.7 (C-6''); 8-C-Glc: 74.5 (C-1'''), 71.4 (C-2'''), 78.3 (C-3'''), 69.5 (C-4'''), 81.4 (C-5'''), 60.3 (C-6'''). 以上数据与文献报道基本一致^[14], 故鉴定化合物 **11** 为芹菜素-6, 8-二-C-葡萄糖苷。

化合物 **12**: 黄色粉末。¹H-NMR (400 MHz, DMSO-*d*₆) δ : 12.56 (1H, s, 5-OH), 6.17 (1H, d, J = 1.9 Hz, H-6), 6.39 (1H, d, J = 1.9 Hz, H-8), 7.86 (1H, d,

J = 2.0 Hz, H-2'), 6.91 (1H, d, J = 8.4 Hz, H-5'), 7.51 (1H, dd, J = 8.4, 2.0 Hz, H-6'), 5.43 (1H, d, J = 7.4 Hz, H-1''), 0.98 (3H, d, J = 6.2 Hz, H-6'''), 3.84 (3H, s, -OCH₃); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ : 157.0 (C-2), 133.4 (C-3), 177.6 (C-4), 161.6 (C-5), 99.5 (C-6), 94.4 (C-8), 156.7 (C-9), 104.1 (C-10), 121.5 (C-1'), 113.7 (C-2'), 147.4 (C-3'), 149.9 (C-4'), 115.7 (C-5'), 122.7 (C-6'); 3-O-Glc: 101.8 (C-1''), 74.8 (C-2''), 76.9 (C-3''), 70.5 (C-4''), 76.4 (C-5''), 67.3 (C-6''); 6-O-Rha: 101.4 (C-1'''), 70.8 (C-2'''), 71.0 (C-3'''), 72.3 (C-4'''), 68.8 (C-5'''), 18.2 (C-6'''), 56.1 (-OCH₃)。以上数据与文献报道基本一致^[15], 故鉴定化合物 **12** 为异鼠李素-3-O-芸香糖苷。

化合物 **13**: 黄色粉末。¹H-NMR (400 MHz, DMSO-*d*₆) δ : 12.59 (1H, s, 5-OH), 6.19 (1H, d, J = 2.0 Hz, H-6), 6.41 (1H, d, J = 2.0 Hz, H-8), 8.01 (1H, d, J = 2.0 Hz, H-2'), 6.90 (1H, d, J = 8.4 Hz, H-5'), 7.51 (1H, dd, J = 8.4, 2.0 Hz, H-6'), 5.45 (1H, d, J = 7.7 Hz, H-1''), 1.06 (3H, d, J = 6.2 Hz, H-6'''), 3.86 (3H, s, -OCH₃); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ : 156.7 (C-2), 133.5 (C-3), 177.7 (C-4), 161.6 (C-5), 99.3 (C-6), 94.3 (C-8), 156.9 (C-9), 104.2 (C-10), 121.5 (C-1'), 113.9 (C-2'), 147.4 (C-3'), 149.9 (C-4'), 115.6 (C-5'), 122.4 (C-6'); 3-O-Gal: 102.3 (C-1''), 71.6 (C-2''), 73.4 (C-3''), 68.9 (C-4''), 74.0 (C-5''), 65.6 (C-6''); 6-O-Rha: 100.5 (C-1'''), 70.9 (C-2'''), 71.1 (C-3'''), 72.3 (C-4'''), 68.4 (C-5'''), 18.3 (C-6'''), 56.4 (-OCH₃)。以上数据与文献报道基本一致^[16], 故鉴定化合物 **13** 为异鼠李素-3-O-刺槐二糖苷。

化合物 **14**: 黄色粉末。¹H-NMR (600 MHz, DMSO-*d*₆) δ : 12.56 (1H, s, 5-OH), 6.11 (1H, s, H-6), 6.32 (1H, s, H-8), 7.93 (1H, d, J = 2.0 Hz, H-2'), 6.90 (1H, d, J = 8.4 Hz, H-5'), 7.46 (1H, dd, J = 8.4, 2.0 Hz, H-6'), 5.55 (1H, d, J = 7.3 Hz, H-1''), 3.83 (3H, s, -OCH₃); ¹³C-NMR (150 MHz, DMSO-*d*₆) δ : 155.7 (C-2), 132.8 (C-3), 176.9 (C-4), 161.1 (C-5), 99.5 (C-6), 94.0 (C-8), 156.6 (C-9), 103.0 (C-10), 121.1 (C-1'), 113.4 (C-2'), 149.5 (C-3'), 146.9 (C-4'), 115.2 (C-5'), 121.9 (C-6'); 3-O-Glc: 100.9 (C-1''), 74.4 (C-2''), 76.4 (C-3''), 69.8 (C-4''), 77.4 (C-5''), 60.6 (C-6''), 55.6 (-OCH₃)。以上数据与文献报道基本一致^[17], 故鉴定化合物 **14** 为异鼠李素-3-O-葡萄糖苷。

化合物 **15**: 黄色粉末。¹H-NMR (400 MHz,

DMSO- d_6) δ : 6.45 (1H, d, J = 2.0 Hz, H-6), 6.80 (1H, d, J = 2.0 Hz, H-8), 8.02 (1H, d, J = 2.0 Hz, H-2'), 7.55 (1H, dd, J = 8.4, 2.0 Hz, H-6'), 6.92 (1H, d, J = 8.5 Hz, H-5'), 5.49 (1H, d, J = 7.7 Hz, H-1''), 5.08 (1H, d, J = 7.3 Hz, H-1'''), 4.43 (1H, m, H-1'''), 3.87 (3H, s, -OCH₃), 1.06 (3H, d, J = 6.2 Hz, -CH₃); ¹³C-NMR (100 MHz, DMSO- d_6) δ : 157.4 (C-2), 133.8 (C-3), 178.0 (C-4), 161.3 (C-5), 99.8 (C-6), 163.4 (C-7), 95.1 (C-8), 156.5 (C-9), 106.1 (C-10), 121.2 (C-1'), 113.9 (C-2'), 150.3 (C-3'), 147.5 (C-4'), 115.7 (C-5'), 122.6 (C-6'); Glc1: 100.3 (C-1''), 77.7 (C-2''), 76.9 (C-3''), 71.6 (C-4''), 74.1 (C-5''), 65.7 (C-6''); Rha: 102.2 (C-1'''), 70.9 (C-2'''), 72.3 (C-3'''), 73.4 (C-4'''), 68.7 (C-5'''), 18.4 (C-6'''); Glc2: 100.5 (C-1'''), 70.0 (C-2'''), 71.1 (C-3'''), 73.6 (C-4'''), 68.5 (C-5'''), 61.1 (C-6'''), 56.4 (-OCH₃)。以上数据与文献报道基本一致^[18], 故鉴定化合物 **15** 为异鼠李素-3-O-芸香糖-4'-O-葡萄糖苷。

化合物 **16**: 淡黄色粉末。¹H-NMR (400 MHz, CD₃OD) δ : 7.01 (1H, d, J = 1.6 Hz, H-2), 6.70 (1H, d, J = 8.1 Hz, H-5), 6.81 (2H, m, H-6, 6'), 4.81 (1H, d, J = 5.8 Hz, H-7), 4.33 (1H, m, H-8), 7.00 (1H, d, J = 1.5 Hz, H-2'), 6.87 (1H, d, J = 8.2 Hz, H-5'), 4.53 (1H, d, J = 5.9 Hz, H-7'), 3.46 (1H, dd, J = 11.2, 4.0 Hz, H-9'), 3.80 (6H, s, -OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 134.2 (C-1), 111.8 (C-2), 148.7 (C-3), 148.6 (C-4), 118.7 (C-5), 121.0 (C-6), 74.1 (C-7), 86.3 (C-8), 62.2 (C-9), 137.7 (C-1'), 112.3 (C-2'), 151.7 (C-3'), 147.0 (C-4'), 115.7 (C-5'), 120.5 (C-6'), 75.1 (C-7'), 77.4 (C-8'), 64.2 (C-9'), 56.5 (-OCH₃), 56.3 (-OCH₃)。上述数据与文献报道基本一致^[19], 故鉴定化合物 **16** 为 1-(4-hydroxy-3-methoxy)-phenyl-2-[4-(1, 2, 3-trihydroxypropyl)-2-methoxy]-phenoxy-1, 3-propandiol。

化合物 **17**: 淡黄色粉末。¹H-NMR (400 MHz, CD₃OD) δ : 6.20 (1H, s, H-2), 6.65 (2H, m, H-5, 6'), 6.80 (1H, d, J = 1.8 Hz, H-2'), 6.76 (1H, d, J = 8.0 Hz, H-5'), 4.13 (1H, d, J = 7.8 Hz, H-1''), 3.83 (3H, s, -OCH₃), 3.82 (3H, s, -OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 129.0 (C-1), 112.3 (C-2), 147.1 (C-3), 145.8 (C-4), 117.3 (C-5), 134.3 (C-6), 33.8 (C-7), 39.4 (C-8), 65.1 (C-9), 138.6 (C-1'), 114.2 (C-2'), 148.8 (C-3'), 145.1 (C-4'), 116.0 (C-5'), 123.0 (C-6'), 47.8

(C-7'), 45.8 (C-8'), 69.4 (C-9'), 105.1 (C-1''), 75.1 (C-2''), 77.8 (C-3''), 71.6 (C-4''), 77.9 (C-5''), 62.7 (C-6''), 56.4 (-OCH₃), 56.3 (-OCH₃)。以上数据与文献报道基本一致^[20], 故鉴定化合物 **17** 为 (+)-异落叶松脂醇 3 α -O- β -D-葡萄糖苷。

化合物 **18**: 淡黄色粉末。¹H-NMR (400 MHz, CD₃OD) δ : 6.20 (1H, s, H-2), 6.66 (2H, m, H-5, 6'), 2.90 (1H, dd, J = 16.0, 9.8 Hz, H-7a), 2.74 (1H, dd, J = 16.5, 3.4 Hz, H-7b), 1.97 (2H, m, H-8, 8'), 6.70 (1H, d, J = 1.6 Hz, H-2'), 6.76 (1H, d, J = 8.0 Hz, H-5'), 4.05 (1H, d, J = 7.8 Hz, H-1''), 3.82 (3H, s, -OCH₃), 3.80 (3H, s, -OCH₃); ¹³C-NMR (100 MHz, CD₃OD) δ : 129.2 (C-1), 112.3 (C-2), 147.2 (C-3), 146.0 (C-4), 117.4 (C-5), 133.7 (C-6), 33.6 (C-7), 41.1 (C-8), 65.5 (C-9), 138.7 (C-1'), 113.9 (C-2'), 149.0 (C-3'), 145.2 (C-4'), 116.0 (C-5'), 123.4 (C-6'), 45.2 (C-8'), 70.7 (C-9'), 103.7 (C-1''), 75.0 (C-2''), 77.8 (C-3''), 71.4 (C-4''), 78.2 (C-5''), 62.4 (C-6''), 56.5 (-OCH₃), 56.4 (-OCH₃)。以上数据与文献报道基本一致^[21], 故鉴定化合物 **18** 为 (-)-异落叶松脂醇 3- α -O- β -D-葡萄糖苷。

化合物 **19**: 白色粉末。¹H-NMR (400 MHz, CD₃OD) δ : 6.09 (1H, s, H-1), 6.40 (1H, d, J = 6.4 Hz, H-3), 4.93 (1H, dd, J = 6.4, 1.5 Hz, H-4), 3.72 (2H, m, H-6, 6'a), 1.97 (1H, dd, J = 15.2, 4.5 Hz, H-7a), 2.19 (1H, d, J = 15.2 Hz, H-7b), 2.87 (1H, s, H-9), 1.48 (3H, s, H-10), 2.04 (3H, s, -COCH₃), 4.60 (1H, d, J = 7.9 Hz, H-1'), 3.22 (1H, t, J = 8.0 Hz, H-2'), 3.39 (1H, m, H-5'), 3.89 (1H, dd, J = 12.0, 1.4 Hz, H-6'b); ¹³C-NMR (100 MHz, CD₃OD) δ : 94.4 (C-1), 143.8 (C-3), 106.8 (C-4), 73.2 (C-5), 78.1 (C-6), 45.9 (C-7), 88.5 (C-8), 55.4 (C-9), 22.4 (C-10), 22.1 (-COCH₃), 173.2 (-COCH₃), 99.8 (C-1'), 74.4 (C-2'), 77.6 (C-3'), 71.6 (C-4'), 77.6 (C-5'), 62.8 (C-6')。以上数据与文献报道基本一致^[22], 故鉴定化合物 **19** 为 8-O-乙酰哈巴苷。

化合物 **20**: 无色簇状结晶(甲醇)。¹H-NMR (400 MHz, D₂O) δ : 5.20 (1H, d, J = 6.6 Hz, H-1), 7.47 (1H, s, H-3), 3.10 (1H, q, J = 7.4 Hz, H-5), 2.05 (1H, brd, J = 16.6 Hz, H-6a), 2.71 (1H, brdd, J = 16.3, 8.1 Hz, H-6b), 5.76 (1H, brs, H-7), 2.76 (1H, brt, J = 7.1 Hz, H-9), 4.13 (1H, brd, J = 14.2 Hz, H-10a), 4.15 (1H, brd, J = 14.1 Hz, H-10b), 4.72 (1H, d, J = 8.1 Hz, H-1'), 3.32 (3H, m, H-2', 3', 4'), 3.40 (1H, m, H-5'),

3.60 (1H, dd, $J = 12.3, 5.0$ Hz, H-6'a), 3.78 (1H, dd, $J = 12.2, 1.6$ Hz, H-6'b); ^{13}C -NMR (100 MHz, D_2O) δ : 98.8 (C-1), 152.9 (C-3), 111.5 (C-4), 34.1 (C-5), 37.9 (C-6), 129.1 (C-7), 141.2 (C-8), 45.7 (C-9), 59.7 (C-10), 171.3 (C-11), 97.0 (C-1'), 72.7 (C-2'), 76.2 (C-3'), 69.4 (C-4'), 75.6 (C-5'), 60.5 (C-6')。上述数据与文献报道基本一致^[23], 故鉴定化合物 **20** 为京尼平昔酸。

化合物 **21**: 黄色粉末。 ^1H -NMR (400 MHz, CD_3OD) δ : 6.70 (2H, m, H-2, 5), 6.58 (1H, dd, $J = 8.0, 1.7$ Hz, H-6), 6.28 (1H, d, $J = 15.9$ Hz, H- α'), 2.81 (2H, t, $J = 6.8$ Hz, H- β), 7.61 (1H, d, $J = 15.9$ Hz, H- β'), 4.39 (1H, d, $J = 7.9$ Hz, H-1'), 4.94 (1H, t, $J = 9.3$ Hz, H-4'), 3.86 (1H, dd, $J = 12.5, 2.4$ Hz, H-6'b), 5.50 (1H, s, H-1''), 1.07 (3H, d, $J = 6.2$ Hz, H-6''), 4.32 (1H, d, $J = 7.2$ Hz, H-1'''), 7.07 (1H, d, $J = 1.6$ Hz, H-2'''), 7.78 (1H, d, $J = 8.2$ Hz, H-5'''), 6.97 (1H, dd, $J = 8.2, 1.6$ Hz, H-6'''); ^{13}C -NMR (100 MHz, CD_3OD) δ : 131.5 (C-1), 116.5 (C-2), 146.2 (C-3), 144.7 (C-4), 117.1 (C-5), 121.3 (C-6), 71.9 (C- α), 36.6 (C- β), 104.2 (C-1'), 82.4 (C-3'), 70.4 (C-4'), 76.0 (C-5'), 62.4 (C-6'), 102.0 (C-1''), 82.9 (C-2''), 72.3 (C-3''), 74.2 (C-4''), 70.5 (C-5''), 18.4 (C-6''), 107.5 (C-1'''), 72.8 (C-2'''), 74.4 (C-3'''), 69.9 (C-4'''), 67.3 (C-5'''), 127.8 (C-1'''), 114.7 (C-2'''), 146.9 (C-3'''), 149.8 (C-4'''), 116.3 (C-5'''), 123.2 (C-6'''), 168.3 (C-CO)。以上数据与文献报道基本一致^[24], 故鉴定化合物 **21** 为 lavandulifolioside。

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