

傣药石梓皮和接骨草的化学成分研究

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摘要: 采用色谱法从傣药石梓皮(1)和接骨草(2)中分别得到9个和17个化合物, 利用波谱学方法鉴定了它们的结构。从石梓皮得到: 芹菜素(1-1)、棕榈酸(1-2)、specioside 6'-O- α -D-galactopyranoside (1-3)、甾甾醇(1-4)、 β -谷甾醇(1-5)、osmanthuside J(1-6)、luteolin-4'-O- β -glucopyranoside (1-7)、苯甲酸(1-8)、酪醇(1-9)。化合物1-3、1-6、1-7为首次从石梓皮中分离得到。从接骨草得到: 熊果酸(2-1)、肉豆蔻酸(2-2)、齐墩果酸(2-3)、菝葜亭(2-4)、胡萝卜苷(2-5)、3',5-二羟基-4'-甲氧基黄酮-7-O- α -L-鼠李糖基(1 \rightarrow 6)- β -D-葡萄糖苷(2-6)、绿原酸(2-7)、麦芽糖(2-8)、槲皮素(2-9)、脑苷脂(2-10)、3 β -hydroxylup-12-en-28-oic acid (2-11)、 α , β -香树素(2-12)、烟花苷(2-13)、1H-indole-3-carboxylic acid (2-14)、木犀草素(2-15)、阿魏酸(2-16)、n-tritetracontan-5 α -ol(2-17)。其中化合物2-6、2-8、2-10、2-11、2-13、2-14、2-17均为首次从接骨草中分离得到。

关键词: 石梓皮; 接骨草; 傣药; 化学成分

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Chemical Constituents from Bark of *Gmelina arborea* and *Sambucus chinensis*

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Abstract: Nine and seventeen compounds were isolated from bark of *Gmelina arborea* and *Sambucus chinensis* respectively. Compounds from *Gmelina arborea* were identified by physicochemical data and spectral analysis as apigenin (1-1), palmitic acid (1-2), specioside 6'-O- α -D-galactopyranoside (1-3), stigmasterol (1-4), β -sitosterol (1-5), osmanthuside J (1-6), luteolin-4'-O- β -glucopyranoside (1-7), benzoic acid (1-8), tyrosol (1-9). Compounds 1-3, 1-6, 1-7 were obtained from *Gmelina arborea* for the first time. Compounds from *Sambucus chinensis* were identified as ursolic acid (2-1), teradecanoic acid (2-2), oleanolic acid (2-3), scopoletin (2-4), daucosterol (2-5), 3',5-dihydroxy-4'-methoxy flavone-7-O- α -L-rhamnosyl(1 \rightarrow 6)- β -D-glucoside (2-6), chlorogenic acid (2-7), maltose (2-8), quercetin (2-9), cerebroside (2-10), 3 β -hydroxylup-12-en-28-oic acid (2-11), α , β -amyrin (2-12), nicotiflorin (2-13), 1H-indole-3-carboxylic acid (2-14), luteolin (2-15), ferulic acid (2-16), n-tritetracontan-5 α -ol (2-17). Compounds 2-6, 2-8, 2-10, 2-11, 2-13, 2-14, 2-17 were obtained from *Sambucus chinensis* for the first time.

Key words: barks of *Gmelina arborea*; *Sambucus chinensis*; Dai Medicine; chemical constituents

傣药石梓皮为云南石梓(*Gmelina arborea* Roxb.)的树皮, 系马鞭草科(Verbenaceae)石梓属(*Gmelina*)落叶乔木, “石梓皮”为西双版纳地区习称, 树皮做药用。云南石梓又名滇石梓(云南植物志), 酸树(傣语), maisuo, 埋索。在《中华本草》中功能与主治项下记载“除风止痒, 清火解毒”。主治“唉火接”(咳嗽咽痛), “兵洞烘洞飞暖”(皮肤瘙

痒, 斑疹, 疥癣, 湿疹)^[1]。接骨草(*Sambucus chinensis* Lindl.)是忍冬科(Caprifoliaceae)接骨木属(*Sambucus*)多年生草本植物, 又名陆英, 蒴藋, 排风藤, 八棱麻, 大臭草等。《中华本草》记载: 其味甘、微苦, 性平。祛风, 利湿, 舒筋, 活血。主治风疹瘙痒, 丹毒, 疮肿。据文献^[2]报道, 接骨草含有萜类化合物、黄酮类化合物等, 具有广泛的生物活性, 如抗肝炎、镇痛、抗菌消炎等, 但目前对其抗类风湿疾病方面进行的相关研究较少。

傣药痹通胶囊, 其部分临床结果表明该药对痛风性关节炎, 治愈率57.5%, 好转率35%, 总有效率

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92.5%, 无毒副作用, 为优秀的傣药制剂^[3]。石梓皮和接骨草作为傣药痹痛胶囊的配方药用植物。通过对石梓皮和接骨草化学成分的纯化与分离, 以期找到活性化合物。本研究以云南石梓皮(1)和接骨草(2)为研究对象, 对其化学成分进行研究, 分别鉴定了9个和17个化合物, 分别为: 芹菜素(1-1), 棕榈酸(1-2), specioside 6'-*O*- α -D-galactopyranoside(1-3), 豆甾醇(1-4), β -谷甾醇(1-5), osmanthuside J(1-6), luteolin-4'-*O*- β -glucopyranoside(1-7), 苯甲酸(1-8), 酪醇(1-9)。化合物1-3、1-6、1-7为首次从石梓皮中分离得到。熊果酸(2-1), 肉豆蔻酸(2-2), 齐墩果酸(2-3), 菝葜亭(2-4), 胡萝卜苷(2-5), 3', 5-二羟基-4'-甲氧基黄酮-7-*O*- α -L-鼠李糖基(1 \rightarrow 6)- β -D-葡萄糖苷(2-6), 绿原酸(2-7), 麦芽糖(2-8), 槲皮素(2-9), 脑苷脂(2-10), 3 β -hydroxylup-12-en-28-oic acid(2-11), α , β -amyrin(2-12), 烟花苷(2-13), 1H-indole-3-carboxylic acid(2-14), 木犀草素(2-15), 阿魏酸(2-16), n-tritetracontan-5 α -ol(2-17)。其中化合物2-6、2-8、2-10、2-11、2-13、2-14、2-17均为首次从接骨草中分离得到。

1 仪器与材料

Avance-600 超导核磁共振仪(TMS为内标)测定; EI-MS用Waters AutoSpecPremier P776双聚焦三扇形磁质谱仪测定; 柱层析所用硅胶(80~100目、200~300目)(青岛海洋化工厂); 薄层层析硅胶(GF-254)(青岛海洋化工厂); 大孔树脂DM-130(山东鲁抗医药股份有限公司); MCI(日本三菱化学株式会社); Sephadex LH-20(美国GE公司); RP-18(德国Merck公司); 实验所用有机溶剂为色谱纯或工业纯重蒸。

云南石梓树皮于2015年10月采于云南省西双版纳傣族自治州勐仑镇中科院西双版纳热带植物园。接骨草于2016年11月购自云南昆明中豪螺蛳湾药材市场(千草原), 云南石梓树皮和接骨草均由中国科学院西双版纳热带植物园宋启示研究员鉴定, 标本存放于中国科学院西双版纳热带植物园民族药研究组实验室。

2 提取与分离

将云南石梓树皮晾干, 粉碎, 称重得18 kg。用90%甲醇热回流提取3次(3 \times 5 h)。减压回收得甲醇浸膏3119 g。总浸膏用水搅拌溶解后, 分别用石

油醚、乙酸乙酯和正丁醇进行萃取, 得石油醚浸膏90 g, 乙酸乙酯浸膏330 g, 正丁醇浸膏1760 g。乙酸乙酯部分经硅胶柱(200~300目)分离, 以氯仿-甲醇($V_{\text{氯仿}}/V_{\text{甲醇}} = 100:0, 50:1, 20:1, 10:1, 8:1, 4:1, 1:1$)梯度洗脱, 得到A1-A7七个组分; A1经反复硅胶柱层析, MCI和Sephadex LH-20纯化, 得到化合物1-4(3 g), 1-5(2.5 g); A2经反复硅胶柱层析, MCI和Sephadex LH-20纯化, 得到化合物1-2(15 mg); A3经反复硅胶柱层析, MCI和Sephadex LH-20纯化, 得到化合物1-6(1.5 mg), 1-1(2 mg); 正丁醇部分经硅胶柱(200~300目)分离, 以氯仿-甲醇($V_{\text{氯仿}}/V_{\text{甲醇}} = 20:1, 10:1, 5:1, 2:1, 1:1, 0:1$)得到B1-B6六个组份; B2经Phenomenex RP-18 column和Sephadex LH-20凝胶柱后经过重结晶得到白色晶体, 得到化合物1-4(50 mg); B4经Phenomenex RP-18 column和Sephadex LH-20凝胶柱, 半制备HPLC[甲醇/水60:40(v/v)]得到化合物1-7(3 mg), 1-8(2 mg), 1-9(2 mg)。其中化合物1-3、1-6、1-7均为首次从石梓皮中分离得到。

接骨草干燥枝叶20 kg, 晒干粉碎后用90%甲醇冷浸提取3次(3 d, 3 d, 3 d), 减压回收得甲醇浸膏1450 g。总浸膏用水搅拌溶解后, 分别用石油醚、乙酸乙酯和正丁醇进行萃取, 得石油醚浸膏231 g, 乙酸乙酯浸膏28 g, 正丁醇浸膏117 g。石油醚部分(30 g)经硅胶柱(200~300目)分离, 以石油醚-丙酮($V_{\text{石油醚}}/V_{\text{丙酮}} = 100:0, 50:1, 10:1, 5:1, 1:1, 0:1$)梯度洗脱, 得到A1-A7七个组份; A2经反复硅胶柱色谱、Sephadex LH-20纯化, 得到化合物2-11(5 mg); A3经反复硅胶柱色谱、Sephadex LH-20纯化, 得到化合物2-12(6 mg); A5经反复硅胶柱色谱、Sephadex LH-20纯化, 得到化合物2-7(20 mg), 2-15(15 mg)。乙酸乙酯部分(20 g)硅胶柱(200~300目)分离, 以氯仿-甲醇($V_{\text{氯仿}}/V_{\text{甲醇}} = 100:0, 50:1, 20:1, 10:1, 5:1, 1:1, 0:1$)梯度洗脱, 得到B1-B7七个组份。B2经反复硅胶柱层析, MCI和Sephadex LH-20纯化, 得到化合物2-1(3 mg), 2-2(2 mg); B3、B4、B5经反复硅胶柱色谱、Phenomenex RP-18 column和Sephadex LH-20纯化, 得到化合物2-3(5 mg), 2-4(5 mg), 2-5(7 mg), 2-6(40 mg), 2-8(2 mg), 2-9(10 mg), 2-10(3 mg), 2-13(3 mg), 2-14(20 mg), 2-16(17 mg)。正丁醇部分上大孔树脂分段, 分别以体积分数为30%、60%、90%、100%比例的甲醇/水溶液梯度洗脱得到C1-C2四个组分; C2经

反复硅胶柱色谱、Phenomenex RP-18 column 和 Sephadex LH-20 纯化, 得到化合物 **2-17** (2 mg)。其中化合物 **2-6**、**2-8**、**2-10**、**2-11**、**2-13**、**2-14**、**2-17** 均为首次从该接骨草中分离得到。

3 结构鉴定

化合物 1-1 淡黄色粉末; 易溶于氯仿, $^1\text{H NMR}$ (CD_3OD , 600 MHz) δ : 12.96 (1H, 5-OH), 7.91 (2H, d, $J = 8.8$ Hz, H-2', 6'), 6.91 (2H, d, $J = 8.8$ Hz, H-3', 5'), 6.77 (1H, s, H-3), 6.47 (1H, d, $J = 2.0$ Hz, H-8), 6.18 (1H, d, $J = 2.0$ Hz, H-6); $^{13}\text{C NMR}$ (CD_3OD , 151 MHz) δ : 183.91 (C-4), 166.33 (C-2), 166.09 (C-7), 163.24 (C-9), 162.77 (C-4'), 159.44 (C-5), 129.46 (C-2', 6'), 123.26 (C-1'), 117.09 (C-3', 5'), 105.30 (C-10), 103.83 (C-3), 100.14 (C-6), 95.04 (C-8)。以上数据与文献^[4]报道基本一致, 因此确定化合物 **1-1** 为芹菜素。

化合物 1-2 白色粉末; 分子式为 $\text{C}_{16}\text{H}_{32}\text{O}_2$; $^1\text{H NMR}$ (CDCl_3 , 600 MHz) δ : 2.35 (2H, t, $J = 7.5$ Hz, H-2), 1.63 (2H, dt, $J = 15.0$ Hz, H-3), 0.88 (3H, t, $J = 7.0$ Hz, H-16); $^{13}\text{C NMR}$ (CDCl_3 , 151 MHz) δ : 179.5 (C-1), 34.1 (C-2), 32.2 (C-3), 29.9 ~ 29.3 (C-4 ~ C-13), 24.9 (C-14), 22.9 (C-15), 14.5 (C-16)。以上数据与文献^[5]报道基本一致, 因此确定化合物 **1-2** 为棕榈酸。

化合物 1-3 无定型粉末; $^1\text{H NMR}$ ($\text{C}_5\text{D}_5\text{N}$, 500 MHz) δ : 6.45 (1H, d, $J = 5.9$ Hz, H-3), 5.53 (1H, d, $J = 9.3$ Hz, H-1), 5.40 (1H, br d, $J = 7.3$ Hz, H-6), 5.09 (1H, dd, $J = 5.9$ Hz, H-4), 4.75 (1H, d, $J = 9.5$ Hz, H-10), 4.48 (1H, c, H-7), 2.92 (1H, c, H-5), 2.90 (1H, c, H-9); $^{13}\text{C NMR}$ ($\text{C}_5\text{D}_5\text{N}$, 126 MHz) δ : 167.72 (C-9'''), 161.71 (C-4'''), 145.34 (C-7'''), 141.57 (C-3), 130.88 (C-2''', C-6'''), 126.33 (C-1'''), 117.07 (C-3''', C-5'''), 115.72 (C-8'''), 103.39 (C-4), 100.44 (C-1''), 100.41 (C-1'), 95.01 (C-1), 79.44 (C-6), 78.70 (C-3'), 76.19 (C-5'), 75.38 (C-2'), 71.84 (C-5''), 71.36 (C-4'), 70.71 (C-2''), 70.33 (C-6'), 66.80 (C-8), 63.01 (C-6''), 60.55 (C-10), 58.52 (C-7), 43.47 (C-9), 36.92 (C-5)。以上数据与文献^[6]报道一致, 因此确定化合物 **1-3** 为 specioside-6'-O- α -D-galactopyranoside。

化合物 1-4 白色粉末; 用两种不同的溶剂系统展开, 与豆甾醇对照品色谱相应的位置上, 显相同

的紫红色斑点 (10% 硫酸加热显色), 因此确定化合物 **1-4** 为豆甾醇。

化合物 1-5 无色针晶; mp. 136 ~ 140 $^{\circ}\text{C}$, 分子式为 $\text{C}_{29}\text{H}_{50}\text{O}$ 。其 $^1\text{H-NMR}$ 图谱与 β -谷甾醇的标准图谱完全一致。同时用两种不同的溶剂系统展开, 在与对照品色谱相应的位置上, 显相同的紫红色斑点 (10% 硫酸加热显色), 因此确定化合物 **1-5** 为 β -谷甾醇。

化合物 1-6 吸湿性非晶粉末; $^1\text{H NMR}$ (CD_3OD , 500 MHz) δ : 7.07 (2H, d, $J = 8.8$ Hz, H-2, 6), 6.69 (2H, d, $J = 8.8$ Hz, H-3, 5), 5.00 (1H, d, $J = 2.6$ Hz, H-4), 4.27 (1H, d, $J = 7.7$ Hz, H-2), 2.83 (2H, t, $J = 6.6$ Hz, H-2 β); $^{13}\text{C NMR}$ (CD_3OD , 126 MHz) δ : 168.74 (C-9'), 156.73 (C-4), 152.85 (C-3'), 150.70 (C-4'), 146.88, (C-7') 131.53 (C-6), 130.96 (C-2), 130.73 (C-1), 128.71 (C-1'), 124.19 (C-6'), 116.15 (C-5'), 116.05 (C-3), 114.90 (C-8'), 112.58 (C-2'), 110.09 (ApiC-1), 104.38 (GlcC-1), 79.01 (ApiC-3), 78.48 (GlcC-3), 78.00 (ApiC-2), 76.76 (GlcC-5), 75.05 (GlcC-2), 75.03 (ApiC-4), 72.20 (C- α), 71.67 (GlcC-4), 68.61 (GlcC-6), 67.54 (ApiC-5), 56.44 (C-10'), 36.39 (C- β)。以上数据与文献^[7]报道基本一致, 因此确定化合物 **1-6** 为 osmanthuside J。

化合物 1-7 黄色粉末; 微溶于水、甲醇、乙醇, $^1\text{H NMR}$ (CD_3OD , 800 MHz) δ : 7.46 (1H, dd, $J_5', 6' = 8.4$ Hz, $J_2', 5' = 2.4$ Hz, H-6'), 7.45 (1H, d, $J = 2.4$ Hz, H-2'), 7.32 (1H, d, $J = 8.4$ Hz, H-5'), 6.62 (1H, s, H-3), 6.43 (1H, d, $J = 2.1$ Hz, H-8), 6.22 (1H, d, $J = 2.1$ Hz, H-6), 4.95 (1H, d, $J = 7.5$ Hz, H-1''), 3.91 (1H, dd, H-6b''), 3.72 (1H, dd, H-6a''), 3.55 (1H, t, H-2''), 3.50 (2H, obs, H-3'', H-5''), 3.40 (1H, t, H-4''); $^{13}\text{C NMR}$ (CD_3OD , 201 MHz) δ : 183.88 (C-4), 166.31 (C-2), 165.60 (C-7), 163.13 (C-5), 159.44 (C-9), 150.02 (C-4'), 148.55 (C-3'), 127.14 (C-1'), 119.94 (C-6'), 117.91 (C-5'), 114.88 (C-2'), 105.36 (C-10), 105.01 (C-3), 103.06 (C-1''), 100.34 (C-6), 95.18 (C-8), 78.38 (C-5''), 77.48 (C-3''), 74.72 (C-2''), 71.25 (C-4''), 62.35 (C-6'')。以上数据与文献^[8]报道基本一致, 因此确定化合物 **1-7** 为 luteolin-4'-O- β -glucopyranoside。

化合物 1-8 白色粉末; $^1\text{H NMR}$ (CD_3OD , 600 MHz) δ : 8.02 (2H, m, H-2, 6), 7.57 (1H, m, H-4),

7.45(2H, m, H-3, 5); ^{13}C NMR (CD_3OD , 151 MHz) δ : 169.99 (C-7), 134.01 (C-4), 132.05 (C-1), 130.65 (C-2, 6), 129.46 (C-3, 5)。以上数据与文献^[9]报道基本一致,因此确定化合物**1-8**为苯甲酸。

化合物 1-9 白色结晶; ^1H NMR (CD_3OD , 800 MHz) δ : 7.06(2H, d, $J = 8.6$ Hz, H-4, 8), 6.74(2H, d, $J = 8.6$ Hz, H-5, 7), 3.67(2H, t, $J = 7.0$ Hz, H-1), 2.74(2H, t, $J = 7.0$ Hz, H-2); ^{13}C NMR (CD_3OD , 201 MHz) δ : 156.77 (C-1), 131.00 (C-4), 130.86 (C-3, 5), 116.11 (C-2, 6), 64.60 (C-2'), 39.42 (C-1')。以上数据与文献^[10]报道基本一致,因此确定化合物**1-9**为酪醇。

化合物 2-1 白色针状结晶; ^1H NMR (CD_3OD , 600 MHz) δ : 5.23 (1H, t, $J = 3.5$ Hz, H-12), 3.15 (1H, dd, $J = 11.6, 4.5$ Hz, H-3), 1.09 (3H, s, H-27), 0.97 (9H, overlapped, H-23, 24, 29), 0.89 (3H, d, $J = 6.4$ Hz, H-30), 0.85 (3H, s, H-25), 0.77 (3H, s, H-26); ^{13}C NMR (CD_3OD , 151 MHz) δ : 181.35 (C-28), 139.66 (C-13), 126.88 (C-12), 79.65 (C-3), 56.74 (C-5), 54.38 (C-18), 43.25 (C-9, 17), 40.78 (C-14), 40.43 (C-8), 39.99 (C-4), 39.84 (C-19), 38.11 (C-1), 34.34 (C-22), 31.78 (C-7), 29.22 (C-21), 28.76 (C-10), 27.90 (C-15, 23), 25.33 (C-2), 24.36 (C-16), 24.08 (C-11), 21.57 (C-30), 19.48 (C-6), 17.82 (C-26), 17.65 (C-29), 16.38 (C-24), 16.02 (C-25)。以上数据与文献^[11]报道一致,因此确定化合物**2-1**为熊果酸。

化合物 2-2 白色结晶性粉末; 分子式为 $\text{C}_{14}\text{H}_{28}\text{O}_2$ 。 ^1H NMR (CDCl_3 , 600 MHz) δ : 0.88 (3H, t, $J = 7.1$ Hz, 14Me), 1.62 (H, m, $\beta\text{-CH}_2$), 2.35 (2H, t, $J = 7.5$ Hz, $\alpha\text{-CH}_2$); ^{13}C NMR (CDCl_3 , 151 MHz) δ : 177.91 (C-1), 33.79 (C-2), 24.86 (C-3), 29.22 (C-4), 29.39 (C-5), 29.86 (C-6), 29.74 (C-7), 29.59 (C-8), 31.39 (C-9), 29.52 (C-10), 29.52 (C-11), 32.08 (C-12), 22.85 (C-13), 14.28 (C-14)。以上数据与文献^[12]报道一致,因此确定化合物**2-2**为肉豆蔻酸。

化合物 2-3 白色针状结晶; ^1H NMR (CDCl_3 , 500 MHz) δ : 5.24 (1H, s, H-12), 3.15 (1H, dd, $J = 11.4, 4.5$ Hz, H-3), 2.85 (1H, dd, $J = 13.7, 3.6$ Hz, H-18), 1.16 (3H, s, H-27), 0.97 (3H, s, H-23), 0.94 (6H, s, H-24, 29), 0.91 (3H, s, H-30), 0.82 (3H, s, H-25), 0.78 (3H, s, H-26); ^{13}C NMR

(CDCl_3 , 126 MHz) δ : 183.53 (C-28), 143.74 (C-13), 122.76 (C-12), 79.16 (C-3), 55.33 (C-5), 47.75 (C-9), 46.65 (C-17), 46.00 (C-19), 41.71 (C-14), 41.08 (C-18), 39.39 (C-8), 38.89 (C-4), 38.51 (C-1), 37.22 (C-10), 33.92 (C-21), 33.21 (C-29), 32.72 (C-7), 32.57 (C-22), 30.82 (C-20), 28.23 (C-23), 27.81 (C-15), 27.22 (C-2), 26.04 (C-27), 23.72 (C-30), 23.53 (C-16), 23.03 (C-11), 18.42 (C-6), 17.28 (C-26), 15.68 (C-24), 15.46 (C-25)。以上数据与文献^[13]报道基本一致,因此确定化合物**2-3**为齐墩果酸。

化合物 2-4 无色针状结晶; 分子式为 $\text{C}_{10}\text{H}_8\text{O}_4$ 。 ^1H NMR ($\text{C}_3\text{D}_6\text{O}$, 500 MHz) δ : 8.81 (1H, s, 7-OH), 7.85 (1H, d, $J = 9.6$ Hz, H-4), 7.20 (1H, s, H-5), 6.79 (1H, s, H-8), 6.18 (1H, d, $J = 9.6$ Hz, H-3), 3.90 (3H, s, 6-OCH₃); ^{13}C NMR ($\text{C}_3\text{D}_6\text{O}$, 126 MHz) δ : 151.89 (C-7), 151.22 (C-9), 146.02 (C-6), 144.73 (C-4), 113.41 (C-3), 110.01 (C-5), 103.79 (C-8), 56.77 (6-OCH₃)。以上数据与文献^[14]报道一致,因此确定化合物**2-4**为莨菪亭(scopoletin)。

化合物 2-5 白色粉末(吡啶); mp. 283 ~ 284 °C, 分子式为 $\text{C}_{35}\text{H}_{60}\text{O}_6$, 其 ^1H NMR 和 ^{13}C NMR 图谱与胡萝卜苷的标准图谱完全一致, TLC 上斑点位置及显色与胡萝卜苷标准品的相同, 且与标准品混合熔点不下降, 因此确定化合物**2-5**为胡萝卜苷(daucosterol)。

化合物 2-6 白色粉末; 熔点 272 ~ 273 °C, 分子式为 $\text{C}_{28}\text{H}_{34}\text{O}_{15}$ 。 ^1H NMR ($\text{C}_5\text{D}_5\text{NO}$, 500 MHz) δ : 5.49 (H, dd, $J = 12.8, 3.0$ Hz), 2.85 (H, dd, $J = 17.1, 3.0$ Hz), 3.21 (H, dd, $J = 17.1, 12.8$ Hz), 6.69 (H, d, $J = 2.1$ Hz), 6.60 (H, d, $J = 2.1$ Hz), 7.51 (H, d, $J = 1.9$ Hz), 6.97 (H, d, $J = 8.3$ Hz), 7.11 (H, dd, $J = 8.3, 1.9$ Hz), 3.72 (3H, s), 12.48 (H, s), 10.50 (H, br, s), 5.62 (H, d, $J = 7.4$ Hz), 1.56 (3H, d, $J = 5.6$ Hz); ^{13}C NMR ($\text{C}_5\text{D}_5\text{NO}$, 126 MHz) δ : 197.48 (C-4), 166.81 (C-7), 164.87 (C-5), 163.87 (C-9), 149.49 (C-3'), 148.81 (C-4'), 132.53 (C-1'), 118.45 (C-6'), 115.70 (C-2'), 112.67 (C-5'), 104.66 (C-10), 102.84 (RhaC-1), 101.92 (GlcC-1), 98.09 (C-8), 96.81 (C-6), 79.80 (C-2), 78.83 (GlcC-5), 77.92 (GlcC-3), 74.97 (GlcC-2), 74.47 (RhaC-4), 73.17 (RhaC-3), 72.50 (RhaC-2), 71.66 (GlcC-4), 70.21 (RhaC-5), 67.74 (GlcC-6), 56.25

(4'-OCH₃), 45.53 (C-3), 18.99 (RhaC-6)。以上数据与文献^[15]报道一致,因此确定化合物 **2-6** 为 3', 5-二羟基-4'-甲氧基黄酮-7-O- α -L-鼠李糖基(1 \rightarrow 6)- β -D-葡萄糖苷。

化合物 2-7 白色粉末; ¹H NMR (600 MHz, CD₃OD) δ : 7.56 (1H, d, J = 15.9 Hz, H-7'), 7.05 (1H, d, J = 1.9 Hz, H-2'), 6.95 (1H, dd, J = 8.2, 1.9 Hz, H-6'), 6.78 (1H, d, J = 8.2 Hz, H-5'), 6.26 (1H, d, J = 15.9 Hz, H-8'), 5.33 (1H, td, J = 9.0, 4.4 Hz, H-3), 4.16 (1H, m, H-5), 3.73 (1H, dd, J = 8.4, 3.1 Hz, H-4), 2.21 (2H, ddd, J = 17.0, 13.6, 2.5 Hz, H-2), 2.06 (2H, ddd, J = 14.1, 9.0, 6.7 Hz, H-6); ¹³C NMR (150 MHz, CD₃OD) δ : 177.1 (C-7), 168.6 (C-1'), 149.5 (C-6'), 147.1 (C-3'), 146.8 (C-7'), 127.8 (C-4'), 123.0 (C-9'), 116.5 (C-8'), 115.3 (C-2'), 115.2 (C-5'), 76.2 (C-1), 73.5 (C-3), 72.0 (C-4), 71.3 (C-5), 38.8 (C-6), 38.2 (C-2)。以上数据与文献^[16]报道一致,因此确定化合物 **2-7** 为绿原酸。

化合物 2-8 无色针晶;分子式为 C₁₂H₂₂O₁₁。¹H NMR (CD₃OD, 800 MHz) δ : 5.09 (1H, d, J = 3.4 Hz, H-1), 4.46 (1H, d, J = 7.8 Hz, H-1'); ¹³C NMR (CD₃OD, 201 MHz) δ : 98.13 (C-1'), 93.90 (C-1), 78.03 (C-5), 77.96 (C-4), 76.22 (C-3), 74.81 (C-3'), 73.78 (C-2'), 72.94 (C-2), 71.79 (C-5'), 71.66 (C-4'), 62.81 (C-6), 62.70 (C-6')。以上数据与文献^[17]报道一致,因此确定化合物 **2-8** 为麦芽糖 (maltose)。

化合物 2-9 黄色粉末; ¹H NMR (500 MHz, CD₃OD) δ : 7.73 (1H, d, J = 2.0 Hz, H-2'), 7.64 (1H, dd, J = 8.4 Hz, 2.0 Hz, H-6'), 6.88 (1H, d, J = 8.8 Hz, H-5'), 6.38 (1H, d, J = 1.6 Hz, H-8), 6.17 (1H, d, J = 2.0 Hz, H-6); ¹³C NMR (125 MHz, CD₃OD) δ : 177.25 (C-4), 165.55 (C-7), 162.50 (C-5), 158.20 (C-9), 148.77 (C-2), 147.95 (C-4'), 146.23 (C-3'), 137.24 (C-3), 124.12 (C-1'), 121.65 (C-6'), 116.25 (C-2'), 116.00 (C-5'), 104.51 (C-10), 99.22 (C-6), 94.40 (C-8)。以上数据与文献^[18]报道一致,因此确定化合物 **2-9** 为槲皮素。

化合物 2-10 白色无定形粉末;分子式为 C₄₈H₉₁NO₉。¹H NMR (CD₃OD, 800 MHz) δ : 4.69 (dd, J = 10.3, 5.7 Hz), 5.48 (t, J = 4.1 Hz), 0.86 (3H, t, J = 6.9 Hz), 8.34 (d, J = 8.2 Hz), 6.85 (d, J = 4.3

Hz), 0.86 (3H, t, J = 6.9 Hz), 7.61 (d, J = 4.8 Hz), 4.91 (d, J = 7.7 Hz), 4.50 (d, J = 11.7 Hz); ¹³C NMR (CD₃OD, 201 MHz) δ : 177.21 (C-1'), 132.01 (C-5), 131.20 (C-4), 130.66 (C-8), 129.95 (C-9), 104.73 (C-1''), 77.99 (C-3''), 77.91 (C-5''), 75.00 (C-2''), 73.10 (C-3), 72.86 (C-2'), 71.52 (C-4''), 69.69 (C-1), 62.68 (C-6''), 54.60 (C-2), 35.89 (C-3'), 33.68 (C-4' ~ 23'), 33.34 (C-6), 33.10 (C-12 ~ 17), 30.85 (C-12 ~ 17), 30.85 (C-4' ~ 23'), 30.80 (C-4' ~ 23'), 30.51 (C-12 ~ 17), 30.31 (C-12 ~ 17), 30.31 (C-4' ~ 23'), 28.28 (C-7), 27.88 (C-10), 26.17 (C-11), 23.76 (C-12 ~ 17), 23.76 (C-4' ~ 23'), 14.45 (C-18), 14.45 (C-24')。以上数据与文献^[19]报道一致,因此确定化合物 **2-10** 为脑苷脂。

化合物 2-11 白色固体;分子式为 C₃₀H₄₈O₃。¹H NMR (CDCl₃, 500 MHz) δ : 5.48 (1H, t, J = 3.2 Hz, H-12), 3.46 (1H, m, H-3), 1.22, 1.05, 1.02, 1.00, 0.88, 0.76, 0.66 (each 3H, s, CH₃ \times 7); ¹³C NMR (CDCl₃, 126 MHz) δ : 180.71 (C-28), 138.23 (C-13), 125.62 (C-12), 79.03 (C-3), 55.29 (C-5), 52.86 (C-18), 47.89 (C-17), 47.63 (C-9), 42.14 (C-14), 39.54 (C-8), 39.16 (C-19), 38.95 (C-20), 38.79 (C-4), 38.69 (C-1), 37.03 (C-10), 36.87 (C-22), 33.10 (C-7), 30.75 (C-21), 28.16 (C-15), 28.10 (C-23), 27.07 (C-2), 24.28 (C-16), 23.61 (C-11), 23.36 (C-27), 21.27 (C-29), 18.39 (C-6), 17.09 (C-30), 16.99 (C-26), 15.69 (C-24), 15.52 (C-25)。以上数据与文献^[20]报道一致,因此确定化合物 **2-11** 为 3 β -hydroxylup-12-en-28-oic acid。

化合物 2-12 白色粉末; ¹H NMR (CDCl₃, 500 MHz) δ : 5.19 (1H, t, J = 3.57 Hz, H-12), 5.14 (1H, t, J = 3.57 Hz, H-13), 3.24 (2H, m, H-3); ¹³C NMR (CDCl₃, 126 MHz) δ : 145.35, 139.73, 124.55, 121.86, 79.18, 59.19, 55.30, 47.77, 47.36, 46.96, 42.21, 41.85, 41.67, 41.46, 39.93, 39.75, 38.92, 37.28, 34.87, 33.49, 32.78, 32.64, 31.40, 29.81, 28.87, 28.55, 28.24, 27.37, 27.07, 26.75, 26.29, 26.14, 23.67, 23.51, 23.41, 22.85, 21.56, 18.50, 17.62, 16.94, 15.74。以上数据与文献^[21]报道一致,因此确定化合物 **2-12** 为混合物 α , β -amyrin。

化合物 2-13 黄色粉末; ¹H NMR (CD₃OD, 600 MHz) δ : 6.20 (1H, d, J = 2.0 Hz, H-6), 6.39 (1H, d, J = 2.0 Hz, H-8), 8.06 (2H, dd, J = 2.0, 6.8 Hz, H-

2',6'), 6.89 (2H, dd, $J = 2.0, 6.8$ Hz, H-3', 5'), 5.13 (1H, d, $J = 7.6$ Hz, H-1''), 3.26-3.48 (5H, m, H-2'' ~ 5'' and H-6b''), 3.81 (1H, d, $J = 10.0$ Hz, H-6a''), 4.52 (1H, d, $J = 1.6$ Hz, H-1'''), 3.64 (1H, dd, $J = 1.6, 3.2$ Hz, H-2'''), 3.53 (1H, dd, $J = 3.8, 9.4$ Hz, H-3'''), 3.26-3.48 (2H, m, H-4''', 5'''), 1.13 (3H, d, $J = 6.0$ Hz, H-6'''); ^{13}C NMR (CD₃OD, 151 MHz) δ : 179.63 (C-4), 163.60 (C-5), 163.23 (C-7), 161.60 (C-4'), 159.25 (C-9), 158.56 (C-2), 136.20 (C-3), 132.17 (C-2'), 131.91 (C-6'), 122.62 (C-1'), 116.54 (C-5'), 116.15 (C-3'), 105.90 (C-10), 103.50 (C-1''), 99.91 (C-6), 99.84 (C-1'''), 94.76 (C-8), 78.22 (C-5''), 77.52 (C-3''), 75.30 (C-2''), 73.17 (C-4'''), 72.11 (C-3'''), 72.05 (C-2'''), 71.92 (C-4''), 70.97 (C-5'''), 63.47 (C-6''), 17.65 (C-6'''). 以上数据与文献^[22]报道一致,因此确定化合物 **2-13** 为烟花苷。

化合物 2-14 无色粉末; ^1H NMR (CD₃OD, 600 MHz) δ : 8.07 (1H, m, H-7), 7.94 (1H, s, H-2), 7.43 (1H, m, H-5), 7.20 (1H, m, H-6), 7.10 (1H, m, H-8); ^{13}C NMR (CD₃OD, 151 MHz) δ : 169.24 (C-9), 138.17 (C-4), 133.38 (C-3), 127.57 (C-7), 123.58 (C-1), 122.33 (C-6), 121.97 (C-5), 112.88 (C-8), 108.74 (C-2)。以上数据与文献^[23]报道一致,因此确定化合物 **2-14** 为 1H-indole-3-carboxylic acid。

化合物 2-15 黄色无定型粉末; 分子式为 C₁₅H₁₀O₆。 ^1H NMR (500 MHz, DMSO-*d*₆) δ : 12.95 (1H, s, 5-OH), 10.80 (1H, s, 7-OH), 9.87 (1H, s, 4'-OH), 9.36 (1H, s, 3'-OH), 7.41 (1H, d, $J = 2.0$ Hz, H-6'), 7.38 (1H, d, $J = 2.0$ Hz, H-2'), 6.87 (1H, d, $J = 8.2$ Hz, H-5'), 6.64 (1H, s, H-3), 6.42 (1H, d, $J = 1.7$ Hz, H-8), 6.17 (1H, d, $J = 1.7$ Hz, H-6); ^{13}C NMR (125 MHz, DMSO-*d*₆) δ : 180.79 (C-4), 164.45 (C-2), 163.53 (C-7), 161.36 (C-5), 157.57 (C-9), 152.58 (C-4'), 146.62 (C-3'), 119.27 (C-1'), 119.01 (C-6'), 115.75 (C-5'), 111.95 (C-2'), 102.05 (C-10), 101.53 (C-3), 99.76 (C-6), 94.42 (C-8)。以上数据与文献^[24]报道一致,因此确定化合物 **2-15** 为木犀草素。

化合物 2-16 白色粉末; ^1H NMR (600 MHz, CD₃OD) δ : 7.59 (1H, d, $J = 15.9$ Hz, H-3), 7.17 (1H, d, $J = 1.8$ Hz, H-5), 7.06 (1H, dd, $J = 8.2, 1.8$ Hz, H-9), 6.81 (1H, d, $J = 8.2$ Hz, H-8), 6.31 (1H,

d, $J = 15.9$ Hz, H-2), 3.89 (3H, s, H-10); ^{13}C NMR (150 MHz, CD₃OD) δ : 170.98 (C-1), 150.57 (C-7), 149.35 (C-6), 146.86 (C-3), 127.77 (C-4), 123.95 (C-2), 116.44 (C-5), 115.88 (C-8), 111.63 (C-9), 56.40 (C-10)。以上数据与文献^[25]报道一致,因此确定化合物 **2-16** 为阿魏酸。

化合物 2-17 淡黄色粉末; 分子式为 C₄₃H₈₈O。 ^1H NMR (CDCl₃, 600 MHz) δ : 3.48 (brm, $J = 6.5$ Hz, 1H, H-5 β), 1.58 (brs, 2H, CH₂), 1.32 (brs, 4H, 2 \times CH₂), 1.29 (brs, 6H, 3 \times CH₂), 1.25 (brs, 72H, 36 \times CH₂), 0.89 (t, $J = 5.5$ Hz, 3H, Me-1), 0.86 (t, $J = 6.0$ Hz, 3H, Me-43); ^{13}C NMR (CDCl₃, 151 MHz) δ : 77.24 (CH-5), 33.39 (CH₂), 33.39 (CH₃-43), 32.08 (CH₂), 29.87 (33 \times CH₂), 29.78 (CH₂), 29.75 (CH₂), 29.52 (CH₂), 23.06 (CH₂), 22.85 (CH₂), 16.98 (CH₃-1)。以上数据与文献^[26]报道一致,因此确定化合物 **2-17** 为 n-tritetracontan-5 α -ol。

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