

金锦香的化学成分研究

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摘要: 目的 研究金锦香 *Osbeckia chinensis* 的化学成分。方法 利用硅胶柱色谱与 Sephadex LH-20 凝胶柱色谱进行分离和纯化, 根据化合物的理化数据和波谱数据鉴定其结构。结果 从金锦香全草乙醇提取物中分离鉴定了 16 个化合物: 3-甲氧基-鞣花酸-4-*O*- β -D-吡喃葡萄糖苷 (1)、3,3'-二甲氧基-鞣花酸-4-*O*- β -D-吡喃葡萄糖苷 (2)、3,3',4'-三甲氧基-鞣花酸-4-*O*- β -D-吡喃葡萄糖苷 (3)、山柰酚-3-*O*- β -L-吡喃鼠李糖苷 (4)、槲皮素-3-*O*- β -D-吡喃半乳糖苷 (5)、槲皮素-3-*O*- β -L-吡喃鼠李糖苷 (6)、山柰酚-6-*C*- β -D-吡喃葡萄糖苷 (7)、槲皮素-3-*O*- β -L-吡喃鼠李糖苷-2"-乙酸酯 (8)、山柰酚-3-*O*- β -D-吡喃葡萄糖苷-3",6"-二-*E*-(4-羟基)-肉桂酸酯 (9)、4'-hydroxyflavone-3-*O*-(6-*O*-*trans*-*p*-coumaroyl)- β -D-glucopyranoside (10)、山柰酚-3-*O*- β -D-吡喃葡萄糖苷-6"-*E*-(4-羟基)-肉桂酸酯 (11)、3 β -hydroxy-9(11)-fernen-23-oic acid (12)、1,2-dihydroxy-9(11)-arborinen-3-one (13)、cholest-5-ene-2,3,21-triol (14)、 β -谷甾醇 (15)、胡萝卜苷 (16)。结论 除化合物 5 和 16 外, 其余化合物均为首次从该植物中分离得到。

关键词: 金锦香; 野牡丹科; 鞣花酸; 黄酮; 3-甲氧基-鞣花酸-4-*O*- β -D-吡喃葡萄糖苷

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Chemical constituents from *Osbeckia chinensis*

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Abstract: **Objective** To investigate the chemical constituents from *Osbeckia chinensis*. **Methods** The constituents were separated by column chromatography and their structures were elucidated by spectral data analyses. **Results** Sixteen compounds were isolated from *O. chinensis* and identified as 4-*O*- β -D-glucopyranosyl-3-*O*-methylelagic acid (1), 4-*O*- β -D-glucopyranosyl-3,3'-di-*O*-methylelagic acid (2), 4-*O*- β -D-glucopyranosyl-3,3',4'-tri-*O*-methylelagic acid (3), kaempferol-3-*O*- β -L-ramnopyranoside (4), quercetin-3-*O*- β -D-galactopyranoside (5), quercetin-3-*O*- β -L-rhamnopyranoside (6), kaempferol-6-*C*- β -D-glucopyranoside (7), quercetin-3-*O*- β -L-rhamnopyranosyl-2"-acetyl (8), kaempferol-3-*O*- β -D-glucopyranosyl-2",6"-bis-*O*-*E*-(4-hydroxy)-cinnamoyl (9), 4'-hydroxyflavone-3-*O*-(6-*O*-*trans*-*p*-coumaroyl)- β -D-glucopyranoside (10), kaempferol-3-*O*- β -D-glucopyranosyl-6"-*O*-*E*-(4-hydroxy)-cinnamoyl (11), 3 β -hydroxy-9(11)-fernen-23-oic acid (12), 1,2-dihydroxy-9(11)-arborinen-3-one (13), cholest-5-ene-2,3,21-triol (14), β -sitosterol (15), and daucosterol (16). **Conclusion** Except for compounds 5 and 16, all compounds are obtained from *O. chinensis* for the first time.

Key words: *Osbeckia chinensis* Linn. ex Walp; Melastomataceae; ellagic acid; flavone; 4-*O*- β -D-glucopyranosyl-3-*O*-methylelagic acid

金锦香 *Osbeckia chinensis* Linn. ex Walp 为野牡丹科金锦香属植物, 金锦香属约 100 种, 我国 12 种, 分布于西藏至台湾, 以及长江流域以南各省区^[1]。金

锦香作为民间草药, 全草入药具有清热解毒、收敛止血的功效, 可治痢疾、腹泻及蛇咬伤^[1]。目前, 关于金锦香中化学成分的研究主要报道了少数具有抗

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氧化作用的黄酮类化合物^[2-4]。为深入研究金锦香的化学成分, 本实验采用各种色谱分离方法从金锦香全草的乙醇提取物中分离鉴定了 16 个化合物: 3-甲氧基-鞣花酸-4- O - β - D -吡喃葡萄糖苷 (4- O - β - D -glucopyranosyl-3- O -methylellagic acid, **1**)、3, 3'-二甲氧基-鞣花酸-4- O - β - D -吡喃葡萄糖苷 (4- O - β - D -glucopyranosyl-3, 3'-di- O -methylellagic acid, **2**)、3, 3', 4'-三甲氧基-鞣花酸-4- O - β - D -吡喃葡萄糖苷 (4- O - β - D -glucopyranosyl-3, 3', 4'-tri- O -methylellagic acid, **3**)、山柰酚-3- O - β - L -吡喃鼠李糖苷 (kaempferol-3- O - β - L -rhamnopyranoside, **4**)、槲皮素-3- O - β - D -吡喃半乳糖苷 (quercetin-3- O - β - D -galactopyranoside, **5**)、槲皮素-3- O - β - L -吡喃鼠李糖苷 (quercetin-3- O - β - L -rhamnopyranoside, **6**)、山柰酚-6- C - β - D -吡喃葡萄糖苷 (kaempferol-6- C - β - D -glucopyranoside, **7**)、槲皮素-3- O - β - L -吡喃鼠李糖苷-2"-乙酸酯 (quercetin-3- O - β - L -rhamnopyranosyl-2"-acetyl, **8**)、山柰酚-3- O - β - D -吡喃葡萄糖苷-3", 6"-二- E -(4-羟基)-肉桂酸酯 (kaempferol-3- O - β - D -glucopyranosyl-2", 6"-bis- O - E -(4-hydroxy)-cinnamoyl, **9**)、4'-hydroxyflavone-3- O -(6- O - $trans$ - p -coumaroyl)- β - D -glucopyranoside (**10**)、山柰酚-3- O - β - D -吡喃葡萄糖苷-6"- E -(4-羟基)-肉桂酸酯 (kaempferol-3- O - β - D -glucopyranosyl-6"- O - E -(4-hydroxy)-cinnamoyl, **11**)、3 β -hydroxy-9(11)-fernen-23-oic acid (**12**)、1, 2-dihydroxy-9(11)-arborinen-3-one (**13**)、cholest-5-ene-2, 3, 21-triol (**14**)、 β -谷甾醇 (β -sitosterol, **15**)、胡萝卜苷 (daucosterol, **16**)。除化合物 **5** 和 **16** 外, 其余化合物均为首次从该植物中分离得到。

1 仪器与材料

质谱用 VG Autospec—3000 型质谱仪测定。核磁共振谱用 Bruker AM—400 和 DRX—500 核磁共振光谱仪测定, 以 TMS 为内标; 柱色谱硅胶 (200~300 目) 和薄层色谱硅胶 GF₂₅₄ 均为青岛美高集团有限公司生产; Sephadex LH—20 为 Pharmacia 公司产品。薄层色谱板通过喷洒 5%~10% 硫酸-乙醇溶液加热观察其斑点。金锦香样品采自江西省乐安县公溪镇, 由中国科学院昆明植物研究所李嵘博士鉴定为野牡丹科金锦香属植物金锦香 *Osbeckia chinensis* Linn. ex Walp, 标本 (编号为 XYZ-2006-04) 存放于中国科学院昆明植物研究所植物化学与西部资源持续利用国家重点实验室。

2 提取和分离

金锦香的干燥全草 5.0 kg, 粉碎后用 95% 乙醇回流提取 3 次, 每次 3 h, 滤液合并浓缩成浸膏用水混悬, 后用醋酸乙酯、正丁醇萃取, 萃取液浓缩至浸膏, 得醋酸乙酯部分 150 g, 正丁醇部分 90 g。取醋酸乙酯部分 130 g, 经硅胶柱色谱 (氯仿-甲醇-水 12:3:0.2) 划为 4 段: Fr₁ (30 g)、Fr₂ (30 g)、Fr₃ (30 g)、Fr₄ (40 g)。Fr₁ (30 g) 经硅胶柱反复色谱 (石油醚-丙酮 20:1, 12:1, 8:1, 5:1) 得化合物 **12** (6 mg)、**15** (200 mg)。Fr₂ (30 g) 经硅胶柱色谱 (氯仿-甲醇 9:1) 洗脱, 再经 Sephadex LH-20 (氯仿-甲醇 1:1) 分离得到化合物 **13** (5 mg) 和 **14** (5 mg)。Fr₃ (30 g) 经硅胶柱色谱 (氯仿-甲醇-水 12:3:0.1) 洗脱得到两个流份, Fr₃₋₁ 经 Sephadex LH-20 柱色谱 (氯仿-甲醇 1:1) 分离得到化合物 **10** (5 mg) 和 **9** (15 mg); Fr₃₋₂ 用半制备 HPLC (流动相为 23% 乙腈水) 分离得到化合物 **8** (10 mg)。Fr₄ (40 g) 经硅胶柱色谱 (氯仿-甲醇-水 10:3:0.3) 洗脱后, 再经 Sephadex LH-20 柱色谱 (甲醇) 得化合物 **4** (5 mg)、**5** (9 mg) 和 **6** (5 mg)。取正丁醇部分 55 g, 经硅胶柱色谱 (氯仿-甲醇-水 7:3:0.5) 划为 2 段: Fr₅ (30 g) 和 Fr₆ (20 g)。Fr₅ (30 g) 经硅胶柱色谱 (氯仿-甲醇-水 10:3:0.3) 洗脱, 再经 Sephadex LH-20 (甲醇) 得化合物 **1** (4 mg)、**2** (5 mg)、**3** (5 mg) 和 **11** (7 mg)。Fr₆ (20 g) 经硅胶柱色谱 (氯仿-甲醇-水 7:4:0.5) 洗脱后, 再经 Sephadex LH-20 柱色谱 (甲醇) 洗脱, 得化合物 **16** (100 mg) 和 **7** (10 mg)。

3 结构鉴定

化合物 **1**: 白色无定型粉末, C₂₁H₁₈O₁₃。ESI-MS m/z : 477 [M-H]⁻。¹H-NMR (C₅D₅N, 400 MHz) δ : 8.46 (1H, s, H-5'), 7.76 (1H, s, H-5), 5.91 (1H, d, J = 7.9 Hz, H-1"), 4.19 (3H, s, -OCH₃); ¹³C-NMR (C₅D₅N, 100 MHz) δ : 158.9 (C-7), 158.3 (C-7'), 153.2 (C-4'), 151.4 (C-4), 143.0 (C-3), 142.3 (C-2), 139.1 (C-2'), 132.4 (C-3'), 116.2 (C-1), 114.3 (C-6), 114.0 (C-1'), 113.7 (C-5), 112.0 (C-6'), 104.9 (C-5'), 103.1 (C-1"), 79.3 (C-3"), 78.6 (C-5"), 74.9 (C-2"), 71.2 (C-4"), 62.4 (C-6"), 62.0 (-OCH₃)。与文献对照^[4-6], 鉴定化合物 **1** 为 3-甲氧基-鞣花酸-4-吡喃葡萄糖苷。

化合物 **2**: 白色无定型粉末, C₂₂H₂₀O₁₃。ESI-MS m/z : 491 [M-H]⁻。¹H-NMR (C₅D₅N, 400 MHz) δ : 8.49 (1H, s, H-5'), 8.07 (1H, s, H-5), 5.96 (1H, d, J = 7.8 Hz, H-1"), 4.28, 4.20 (6H, s, 2 $\times$ OCH₃); ¹³C-NMR

(C₅D₅N, 100 MHz) δ : 158.8 (C-7), 158.1 (C-7'), 153.4 (C-4'), 151.3 (C-4), 142.8 (C-3), 142.1 (C-2), 139.5 (C-2'), 132.7 (C-3'), 116.1 (C-1), 114.1 (C-6), 114.2 (C-1'), 113.6 (C-5), 112.0 (C-6'), 104.7 (C-5'), 103.0 (C-1''), 79.1 (C-3''), 78.5 (C-5''), 74.7 (C-2''), 71.0 (C-4''), 62.5 (C-6''), 62.0 (3-OCH₃), 61.6 (3'-OCH₃)。与文献对照^[4-6], 鉴定化合物 **2** 为 3, 3'-二甲氧基-鞣花酸-4-吡喃葡萄糖苷。

化合物 **3**: 白色无定型粉末, C₂₃H₂₂O₁₃。FAB-MS m/z : 505 [M-H]⁻。¹H-NMR (C₅D₅N, 400 MHz) δ : 8.47 (1H, s, H-5'), 7.82 (1H, s, H-5), 5.94 (1H, d, J = 7.8 Hz, H-1''), 4.26, 4.15 (6H, s, 3, 3'-2×OCH₃), 3.84 (3H, s, 4'-OCH₃); ¹³C-NMR (C₅D₅N, 100 MHz) δ : 159.1 (C-7), 158.8 (C-7'), 155.1 (C-4'), 153.1 (C-4), 142.9 (C-3), 142.1 (C-2), 142.0 (C-2', 3'), 114.2 (C-1), 113.6 (C-6), 113.4 (C-1'), 113.3 (C-5), 112.0 (C-6'), 111.5 (C-5), 108.2 (C-5'), 103.0 (C-1''), 79.2 (C-2''), 78.6 (C-3''), 74.9 (C-4''), 71.1 (C-5''), 62.4 (C-6''), 62.0 (3-OCH₃), 61.6 (3'-OCH₃), 56.7 (4'-OCH₃)。与文献对照^[4-6], 鉴定化合物 **3** 为 3, 3', 4'-三甲氧基-鞣花酸-4-吡喃葡萄糖苷。

化合物 **4**: 黄色无定型粉末, C₂₁H₂₀O₁₀。FAB-MS m/z : 431 [M-H]⁻。¹H-NMR (CD₃OD, 400 MHz) δ : 7.28 (2H, d, J = 8.4 Hz, H-2', 6'), 6.92 (2H, d, J = 8.4 Hz, H-3', 5'), 6.26 (1H, d, J = 2.0 Hz, H-8), 6.17 (1H, d, J = 2.0 Hz, H-6), 6.10 (1H, d, J = 8.2 Hz, H-1''), 4.29~3.48 (4H, m, H-2'', 3'', 4'', 5''), 0.92 (3H, d, J = 4.9 Hz, H-6''); ¹³C-NMR (CD₃OD, 100 MHz) δ : 179.3 (C-4), 165.9 (C-2), 162.9 (C-4'), 161.5 (C-9), 159.3 (C-7), 158.3 (C-5), 135.2 (C-3), 132.2 (C-2', 6'), 122.7 (C-1'), 116.7 (C-3', 5'), 105.6 (C-10), 103.4 (C-1''), 100.0 (C-6), 94.8 (C-8), 78.0 (C-3''), 75.8 (C-5''), 72.1 (C-2''), 72.0 (C-4''), 17.7 (C-6'')。与文献对照^[7], 鉴定化合物 **4** 为山柰酚-3-*O*- β -*L*-吡喃鼠李糖苷。

化合物 **5**: 黄色无定型粉末, C₂₁H₂₀O₁₂。FAB-MS m/z : 463 [M-H]⁻。¹H-NMR (CD₃OD, 400 MHz) δ : 7.84 (1H, dd, J = 8.0, 2.0 Hz, H-6'), 7.70 (1H, d, J = 2.0 Hz, H-2'), 7.59 (1H, d, J = 8.0 Hz, H-5'), 6.87 (1H, d, J = 1.5 Hz, H-8), 6.85 (1H, d, J = 1.5 Hz, H-6), 6.39 (1H, d, J = 8.0 Hz, H-1''); ¹³C-NMR (CD₃OD, 100 MHz) δ : 179.5 (C-4), 166.2 (C-2), 163.1 (C-9), 159.0 (C-7), 158.5 (C-5), 150.0 (C-3'), 146.9 (C-4'), 135.6 (C-3), 123.2 (C-1'), 123.1 (C-6'), 117.8 (C-2'), 116.1

(C-5'), 105.7 (C-10), 104.3 (C-1''), 100.0 (C-6), 94.8 (C-8), 78.4 (C-3''), 75.8 (C-5''), 71.2 (C-2''), 70.0 (C-4''), 62.6 (C-6'')。与文献对照^[8-9], 鉴定化合物 **5** 为槲皮素-3-*O*- β -*D*-吡喃半乳糖苷。

化合物 **6**: 黄色无定型粉末, C₂₁H₂₀O₁₁。FAB-MS m/z : 447 [M-H]⁻。¹H-NMR (CD₃OD, 400 MHz) δ : 7.82 (1H, dd, J = 7.9, 2.0 Hz, H-6'), 7.69 (1H, d, J = 2.0 Hz, H-2'), 7.57 (1H, d, J = 7.9 Hz, H-5'), 6.83 (1H, d, J = 1.8 Hz, H-8), 6.80 (1H, d, J = 1.8 Hz, H-6), 6.35 (1H, d, J = 7.8 Hz, H-1''), 0.96 (3H, d, J = 5.2 Hz, CH₃); ¹³C-NMR (CD₃OD, 100 MHz) δ : 179.6 (C-4), 165.9 (C-9), 163.2 (C-2), 159.3 (C-7), 158.5 (C-5), 149.8 (C-3'), 146.4 (C-4'), 136.2 (C-3), 122.9 (C-1'), 122.8 (C-6'), 118.9 (C-2'), 116.9 (C-5'), 105.9 (C-10), 103.5 (C-1''), 99.8 (C-6), 94.7 (C-8), 79.5 (C-3''), 73.2 (C-5''), 72.1 (C-2''), 71.9 (C-4''), 17.6 (C-6'')。与文献对照^[9], 鉴定化合物 **6** 为槲皮素-3-*O*- β -*L*-吡喃鼠李糖苷。

化合物 **7**: 黄色无定型粉末, C₂₁H₂₀O₁₀。FAB-MS m/z : 431 [M-H]⁻。¹H-NMR (C₅D₅N, 500 MHz) δ : 8.31 (2H, d, J = 7.5 Hz, H-2', 6'), 7.26 (2H, d, J = 7.5 Hz, H-3', 5'), 6.79 (1H, s, H-3), 6.73 (1H, s, H-8), 5.97 (1H, d, J = 7.9 Hz, H-1''); ¹³C-NMR (C₅D₅N, 125 MHz) δ : 183.1 (C-4), 164.9 (C-7), 164.6 (C-2), 162.8 (C-4'), 162.4 (C-5), 157.4 (C-9), 129.7 (C-2', 6'), 123.8 (C-1'), 116.9 (C-3', 5'), 106.2 (C-10), 105.4 (C-6), 103.3 (C-3), 99.2 (C-8), 83.6 (C-1''), 80.9 (C-3''), 75.6 (C-5''), 73.1 (C-2''), 72.4 (C-4''), 63.1 (C-6'')。与文献对照^[7], 鉴定化合物 **7** 为山柰酚-6-*C*- β -*D*-吡喃葡萄糖苷。

化合物 **8**: 黄色无定型粉末, C₂₃H₂₂O₁₂。FAB-MS m/z : 489 [M-H]⁻。¹H-NMR (CD₃OD, 400 MHz) δ : 7.35 (1H, dd, J = 8.0, 2.0 Hz, H-6'), 7.21 (1H, d, J = 2.0 Hz, H-2'), 6.92 (2H, d, J = 8.0 Hz, H-5'), 6.37 (1H, s, H-8), 6.19 (1H, s, H-6), 5.35 (1H, d, J = 7.2 Hz, H-1''), 2.08 (3H, s, H-2''), 0.96 (6H, d, J = 6.4 Hz, 6''); ¹³C-NMR (CD₃OD, 100 MHz) δ : 179.5 (C-4), 172.7 (C-1''), 166.0 (C-7), 163.2 (C-5), 159.3 (C-2), 158.5 (C-9), 149.8 (C-3'), 146.5 (C-4'), 136.1 (C-3), 123.0 (C-6'), 122.9 (C-1'), 116.7 (C-2'), 116.4 (C-5'), 105.8 (C-10), 103.2 (C-1''), 99.9 (C-6), 94.7 (C-8), 75.3 (C-4''), 72.1 (C-2''), 70.4 (C-5''), 69.7 (C-3''), 21.1 (C-2''), 17.7 (C-6'')。与文献对照^[10], 鉴定化合

物 **8** 为槲皮素-3-*O*- β -*L*-吡喃鼠李糖苷-2"-乙酸酯。

化合物 **9**: 黄色无定型粉末, $C_{39}H_{32}O_{15}$ 。FAB-MS m/z : 739 $[M-H]^-$ 。 1H -NMR (CD_3OD , 500 MHz) δ : 8.05 (2H, d, $J = 16.0$ Hz, H-7''', 7'''), 7.57 (6H, d, $J = 8.5$ Hz, H-2', 6', 2''', 6'', 2''', 6'''), 6.96 (6H, d, $J = 8.5$ Hz, H-3', 5', 3''', 5'', 3''', 5'''), 6.50 (2H, d, $J = 16.0$ Hz, H-8''', 8'''), 6.33 (1H, d, $J = 2.0$ Hz, H-6), 6.15 (1H, d, $J = 2.0$ Hz, H-8), 5.64 (1H, d, $J = 8.0$ Hz, H-1''); ^{13}C -NMR (CD_3OD , 100 MHz) δ : 179.4 (C-4), 168.8 (C-9'''), 168.7 (s, C-9'''), 165.6 (C-2), 163.0 (C-4'), 161.4 (C-4'''), 161.2 (C-4'''), 161.1 (C-9), 158.4 (C-5), 158.2 (C-7), 147.0 (C-7'''), 146.6 (d, C-7'''), 134.8 (C-3), 132.2 (C-2''', 6'', 2''', 6'''), 131.2 (C-2', 6'), 127.2 (C-1'''), 127.0 (C-1'''), 122.7 (C-1'), 116.8 (C-3', 5'), 116.3 (C-3''', 5'', 3''', 5'''), 115.2 (C-8'''), 114.5 (C-8'''), 105.7 (C-10), 101.0 (1''), 100.0 (C-6), 94.7 (C-8), 75.0 (C-3''), 74.0 (C-5''), 73.1 (C-4''), 71.0 (C-2''), 64.2 (C-6'')。与文献对照^[11], 鉴定化合物 **9** 为山柰酚-3-*O*- β -*D*-吡喃葡萄糖苷-3'', 6''-二-*E*-(4-羟基)-肉桂酸酯。

化合物 **10**: 黄色无定型粉末, $C_{30}H_{26}O_{11}$ 。FAB-MS m/z : 561 $[M-H]^-$ 。 1H -NMR (CD_3OD , 500 MHz) δ : 7.98 (1H, d, $J = 16.0$ Hz, H-7'''), 7.41 (2H, d, $J = 8.2$ Hz, H-2''', 6'''), 7.32 (2H, d, $J = 8.5$ Hz, H-2', 6'), 6.83 (2H, d, $J = 8.2$ Hz, H-3''', 5'''), 6.80 (2H, d, $J = 8.5$ Hz, H-3', 5'), 6.68 (1H, d, $J = 16.0$ Hz, H-8'''), 6.09~6.05 (4H, m, H-5, 6, 7, 8), 5.24 (1H, d, $J = 7.5$ Hz, H-1''); ^{13}C -NMR (CD_3OD , 100 MHz) δ : 179.4 (C-4), 168.4 (C-9'''), 166.2 (C-2), 161.5 (C-4'), 161.2 (C-9), 159.3 (C-4'''), 146.6 (C-7'''), 135.1 (C-3), 133.8 (C-5), 132.2 (C-2', 6', 2''', 6'''), 127.0 (C-1'''), 122.7 (C-1'), 116.7 (C-3', 5'), 116.0 (C-3''', 5'''), 115.7 (C-8'''), 114.7 (C-8), 105.0 (C-10), 103.9 (C-1''), 100.0 (C-6), 94.8 (C-7), 78.0 (C-3''), 75.8 (C-5''), 75.7 (C-2''), 71.7 (C-4''), 64.2 (C-6'')。与文献对照^[12], 鉴定化合物 **10** 为 4'-hydroxyflavone-3-*O*-(6-*O*-*trans*-*p*-coumaroyl)- β -*D*-glucopyranoside。

化合物 **11**: 黄色无定型粉末, $C_{30}H_{26}O_{13}$ 。FAB-MS m/z : 593 $[M-H]^-$ 。 1H -NMR (CD_3OD , 400 MHz) δ : 7.98 (1H, d, $J = 15.8$ Hz, H-7'''), 7.28 (4H, d, $J = 8.4$ Hz, H-2', 6', 2''', 6'''), 6.92 (4H, d, $J = 8.4$ Hz, H-3', 5', 3''', 5'''), 6.80 (1H, d, $J = 15.8$ Hz, H-8'''), 6.26 (1H, d, $J = 2.0$ Hz, H-6), 6.17 (1H, d, $J = 2.0$ Hz,

H-8), 6.10 (1H, d, $J = 7.9$ Hz, H-1''); ^{13}C -NMR (CD_3OD , 100 MHz) δ : 179.3 (C-4), 168.8 (C-9'''), 165.9 (C-2), 162.9 (C-4'), 161.5 (C-9), 161.4 (C-4'''), 159.3 (C-7), 158.3 (C-5), 146.6 (C-7'''), 135.2 (C-3), 132.2 (C-2', 6', 2''', 6'''), 127.0 (C-1'''), 122.7 (C-1'), 116.7 (C-3', 5', 3''', 5'''), 114.7 (C-8'''), 105.7 (C-10), 103.4 (C-1''), 100.0 (C-6), 94.8 (C-8), 78.0 (C-3''), 75.8 (C-5''), 72.1 (C-2''), 72.0 (C-4''), 64.4 (C-6'')。与文献对照^[13], 鉴定化合物 **11** 为山柰酚-3-*O*- β -*D*-吡喃葡萄糖苷-6''-*E*-(4-羟基)-肉桂酸酯。

化合物 **12**: 白色无定型粉末, $C_{30}H_{48}O_3$ 。FAB-MS m/z : 457 $[M+H]^+$ 。 1H -NMR (CD_3OD , 500 MHz) δ : 5.23 (1H, s, H-11), 3.16 (1H, m, H-3), 1.07 (3H, s, H-24), 0.98 (3H, s, H-25), 0.92 (3H, s, H-26), 0.89 (3H, d, $J = 6.0$ Hz, H-29), 0.84 (3H, d, $J = 6.4$ Hz, H-30), 0.80 (3H, s, H-27), 0.77 (3H, s, H-28); ^{13}C -NMR (CD_3OD , 125 MHz) δ : 181.4 (C-23), 139.2 (C-9), 126.5 (C-11), 79.4 (C-3), 56.3 (C-21), 53.9 (C-18), 48.6 (C-5), 47.5 (C-14), 47.0 (C-4), 41.0 (C-17), 40.5 (C-1), 37.6 (C-12), 33.6 (C-10), 31.3 (C-15), 29.1 (C-22), 28.7 (C-20), 27.4 (C-2), 25.5 (C-19), 24.0 (C-25), 21.5 (C-29, 30), 19.1 (C-28), 17.5 (C-27), 17.3 (C-26), 17.1 (C-24)。与文献对照^[14], 鉴定化合物 **12** 为 3 β -hydroxy-9(11)-fernen-23-oic acid。

化合物 **13**: 白色无定型粉末, $C_{30}H_{48}O_3$ 。ESI-MS m/z : 457 $[M+H]^+$ 。 1H -NMR (CD_3OD , 500 MHz) δ : 5.24 (1H, s, H-11), 3.97 (1H, m, H-2), 3.24 (1H, m, H-1), 1.08 (6H, s, H-23, 24), 0.98 (5H, s, H-25, 28), 0.95 (6H, s, H-26, 27), 0.89 (6H, d, $J = 6.5$ Hz, H-29), 0.86 (3H, d, $J = 6.5$ Hz, H-30); ^{13}C -NMR (CD_3OD , 125 MHz) δ : 207.0 (C-3), 137.9 (C-9), 125.8 (C-11), 79.1 (C-2), 77.3 (C-1), 55.2 (C-21), 52.7 (C-18), 47.9 (C-14), 47.6 (C-4), 45.6 (C-5), 44.5 (C-8), 41.5 (C-13), 38.8 (C-16), 38.7 (C-12), 33.7 (C-10, 17), 31.3 (C-15), 29.1 (C-22), 27.6 (C-7, 20), 25.5 (C-19, 6), 24.0 (C-25), 23.6 (C-29, 30), 21.2 (C-28), 18.3 (C-27), 17.0 (C-26), 15.6 (C-24), 15.5 (C-23)。与文献对照^[15-16], 鉴定化合物 **13** 为 1, 2-dihydroxy-9(11)-arborinen-3-one。

化合物 **14**: 白色无定型粉末, $C_{27}H_{46}O_3$ 。ESI-MS m/z : 419 $[M+H]^+$ 。 1H -NMR (CD_3OD , 500 MHz) δ : 5.30 (1H, d, $J = 3.5$ Hz, H-6), 3.31~3.63 (4H, m, H-2, 3, 21), 3.31 (1H, m, H-3), 1.21 (3H, s, H-19),

1.16 (3H, s, H-18), 0.92 (6H, d, $J = 7.0$ Hz, H-26, 27); ^{13}C -NMR (CD_3OD , 125 MHz) δ : 145.0 (C-5), 122.8 (C-6), 69.3 (C-2), 68.3 (C-3), 66.1 (C-21), 49.5 (C-14), 48.4 (C-1), 48.0 (C-17), 45.5 (C-13), 43.3 (C-25), 42.7 (C-4), 41.5 (C-10), 39.4 (C-24), 38.3 (C-9), 35.5 (C-12), 33.5 (C-11), 31.4 (C-20), 31.0 (C-8), 26.3 (C-22, 7), 24.3 (C-23, 16), 24.1 (C-15), 19.0 (C-27, 26), 18.9 (C-19), 14.9 (C-18)。与文献对照^[17], 鉴定化合物 **14** 为 cholest-5-ene-2, 3, 21-triol。

化合物 **15**: 白色针晶 (甲醇), 喷 10% 硫酸-乙醇显色剂加热为紫红色。Liebermann-Burchard 反应呈阳性。在石油醚-醋酸乙酯、石油醚-丙酮、氯仿-丙酮 3 种不同展开条件下, 其 R_f 值和显色行为与 β -谷甾醇一致, 鉴定化合物 **15** 为 β -谷甾醇。

化合物 **16**: 白色无定型粉末, 喷 10% 硫酸-乙醇显色剂加热为紫红色, 在氯仿-丙酮、氯仿-甲醇、氯仿-甲醇-水 3 种不同展开条件下, 其 R_f 值和显色行为与胡萝卜苷一致, 鉴定化合物 **16** 为胡萝卜苷。

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