

白背叶榕木芽苞中三萜类成分及抗气道炎症活性研究

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摘 要: 目的 研究白背叶榕木 *Aralia chinensis* var. *nuda* 芽苞中三萜类化学成分及其抗气道炎症活性。方法 白背叶榕木芽苞 70%乙醇提取物采用硅胶、ODS、Sephadex LH-20、半制备液相色谱进行分离纯化, 根据理化特征及核磁数据对化合物进行结构鉴定。采用脂多糖 (lipopolysaccharide, LPS) 诱导气道上皮细胞 (16HBE) 建立体外气道炎症模型, 测定化合物对炎症因子白细胞介素-6 (interleukin-6, IL-6) 释放的影响。结果 从白背叶榕木芽苞 70%乙醇提取物中分离得到 20 个三萜类化合物, 分别鉴定为 2 β ,3 β -dihydroxyolean-12-en-28-oic acid 28-*O*- β -*D*-glucopyranoside (1)、chikusetsusaponin V methyl ester (2)、*pseudo*-ginsenoside-RT₁ (3)、hemsloside Mal (4)、momordin IIa (5)、3-*O*- β -*D*-glucopyranosyl-(1 $\rightarrow$ 3)- β -*D*-glucuronopyranoside-28-*O*- β -*D*-glucopyranosyl oleanolic acid methyl ester (6)、3-*O*-[β -*D*-glucopyranosyl-(1 $\rightarrow$ 2)- β -*D*-(6'-*O*-ethyl)-glucuronopyranosyl]-oleanolic acid 28-*O*- β -*D*-glucopyranoside (7)、ginsenoside-Ro-6'-*O*-butyl ester (8)、姜状三七皂苷 R₁ (9)、oleanolic acid 3 β -*O*- β -*D*-glucopyranosyl-(1 $\rightarrow$ 2)- β -*D*-(6'-*O*-methyl-glucuronopyranoside) (10)、*pseudo*-ginsenoside-RP₁ (11)、momordin Ia (12)、银莲花苷 (13)、narcissiflorine methyl ester (14)、人参皂苷 Ro (15)、齐墩果酸 (16)、hederagenin 3-*O*- β -*D*-glucuronopyranoside-6'-*O*-methyl ester (17)、quinoasaponin 9 (18)、hederagenin 3-*O*- β -*D*-glucuronopyranosyl methyl ester-28-*O*- β -*D*-glucopyranoside (19)、3-*O*-[β -*D*-glucopyranosyl-(1 $\rightarrow$ 2)- β -*D*-glucuronopyranosyl] hederagenin 28-*O*- β -*D*-glucopyranoside (20)。化合物 3、9~14、17 能有效降低 LPS 诱导的 16HBE 气道上皮细胞中 IL-6 水平。结论 化合物 1、5、7、8、12、19 为首次从五加科植物中分离得到, 1、4~8、12、17~20 首次在榕木属中分离得到, 20 个化合物均为首次在白背叶榕木中分离得到; 部分化合物可显著抑制炎症因子 IL-6 的释放。

关键词: 白背叶榕木; 芽苞; 三萜; 抗气道炎症活性; momordin Ia; 银莲花苷; 人参皂苷 Ro

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Triterpenoids from buds of *Aralia chinensis* var. *nuda* and their anti-inflammatory effects in airways

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Abstract: Objective To study the triterpenoids from the buds of *Aralia chinensis* var. *nuda* and their anti-inflammatory activity in airway. **Methods** The 70% ethanol extract of the buds of *A. chinensis* var. *nuda* was isolated and purified by silica gel, ODS, Sephadex LH-20 and semi-preparative HPLC. The compounds structure was identified based on the physicochemical properties and nuclear magnetic resonance data. The *in vitro* airway inflammation model established by LPS-induced airway epithelium (16HBE) was used

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to determine the effect of the compound on the release of inflammatory factor interleukin-6 (IL-6). **Results** A total of 20 triterpene compounds were isolated from the 70% ethanol extract of the buds of *A. chinensis* var. *nuda* and identified as 2 β ,3 β -dihydroxyolean-12-en-28-oic acid 28-*O*- β -D-glucopyranoside (**1**), chikusetsusaponin V methyl ester (**2**), *pseudo*-ginsenoside-RT₁ (**3**), hemsloside Mal (**4**), momordin IIa (**5**), 3-*O*- β -D-glucopyranosyl-(1 $\rightarrow$ 3)- β -D-glucuronopyranoside-28-*O*- β -D-glucopyranosyl oleanolic acid methyl ester (**6**), 3-*O*-[β -D-glucopyranosyl-(1 $\rightarrow$ 2)- β -D-(6'-*O*-ethyl)-glucuronopyranosyl]-oleanolic acid 28-*O*- β -D-glucopyranoside (**7**), ginsenoside-Ro-6'-*O*-butyl ester (**8**), zingibroside R₁ (**9**), oleanolic acid 3 β -*O*- β -D-glucopyranosyl-(1 $\rightarrow$ 2)- β -D-(6'-*O*-methyl-glucuronopyranoside) (**10**), *pseudo*-ginsenoside-RP₁ (**11**), momordin Ia (**12**), narcissiflorine (**13**), narcissiflorine methyl ester (**14**), ginsenoside Ro (**15**), oleanolic acid (**16**), hederagenin 3-*O*- β -D-glucuronopyranoside-6'-*O*-methyl ester (**17**), quinoasaponin 9 (**18**), hederagenin 3-*O*- β -D-glucuronopyranosyl methyl ester-28-*O*- β -D-glucopyranoside (**19**), 3-*O*-[β -D-glucopyranosyl-(1 $\rightarrow$ 2)- β -D-glucuronopyranosyl] hederagenin 28-*O*- β -D-glucopyranoside (**20**). Compounds **3**, **9**—**14**, **17** could effectively reduce the level of inflammatory factor IL-6 in LPS-induced 16HBE cells. **Conclusion** Compounds **1**, **5**, **7**, **8**, **12**, and **19** were isolated from Araliaceae plants for the first time, compounds **1**, **4**—**8**, **12** and **17**—**20** were isolated from *Aralia* genus for the first time. All compounds were isolated from *A. chinensis* var. *nuda* for the first time. Some compounds could significantly inhibited the release of the inflammatory factor IL-6.

Key words: *Aralia chinensis* var. *nuda* Nakai; bud; triterpenoid; anti-inflammatory activity in airway; momordin Ia; narcissiflorine; ginsenoside Ro

白背叶榕木 *Aralia chinensis* var. *nuda* Nakai 为五加科榕木属植物榕木的变种，俗称刺老苞椿头、刺头菜和刺老包，主要分布在云南、四川、陕西东部及广东中部，其嫩叶芽苞常作为野菜食用^[1-3]。其味甘、微苦，性平，归肝、胃、肾经，具有活血止痛、补气安神之功，主治风热咳嗽、跌打损伤、水肿等症^[4-7]。白背叶榕木中化合物类型包括三萜、挥发油、甾醇、黄酮、有机酸及其酯类等^[8-10]，其中三萜及其苷类是其主要成分。课题组前期对白背叶榕木醋酸乙酯部位进行了系统研究，发现了黄酮、木脂素等中等极性成分^[11]。后续又从正丁醇部位中发现 5 个具有显著抗哮喘气道炎症活性的三萜类化合物^[12]。为了进一步丰富白背叶榕木的化学成分并评价其抗气道炎症活性，本实验对白背叶榕木芽苞中的三萜类化学成分进行研究，从白背叶榕木芽苞的 70% 乙醇提取物中分离得到 20 个三萜类化学成分，分别鉴定为 2 β ,3 β -dihydroxyolean-12-en-28-oic acid 28-*O*- β -D-glucopyranoside (**1**)、chikusetsusaponin V methyl ester (**2**)、*pseudo*-ginsenoside-RT₁ (**3**)、hemsloside Mal (**4**)、momordin IIa (**5**)、3-*O*- β -D-glucopyranosyl (1 $\rightarrow$ 3)- β -D-glucuronopyranoside-28-*O*- β -D-glucopyranosyl oleanolic acid methyl ester (**6**)、3-*O*-[β -D-glucopyranosyl-(1 $\rightarrow$ 2)- β -D-(6'-*O*-ethyl)-glucuronopyranosyl]-oleanolic acid 28-*O*- β -D-glucopyranoside (**7**)、ginsenoside-Ro-6'-*O*-butyl ester (**8**)、姜状三七皂苷 R₁ (zingibroside R₁, **9**)、oleanolic acid 3 β -*O*- β -D-glucopyranosyl-(1 $\rightarrow$ 2)- β -D-(6'-*O*-methyl-glucuronopyranoside) (**10**)、*pseudo*-

ginsenoside-RP₁ (**11**)、momordin Ia (**12**)、银莲花苷 (narcissiflorine, **13**)、narcissiflorine methyl ester (**14**)、人参皂苷 Ro (ginsenoside Ro, **15**)、齐墩果酸 (oleanolic acid, **16**)、hederagenin 3-*O*- β -D-glucuronopyranoside-6'-*O*-methyl ester (**17**)、quinoasaponin 9 (**18**)、hederagenin 3-*O*- β -D-glucuronopyranosyl methyl ester-28-*O*- β -D-glucopyranoside (**19**) 3-*O*-[β -D-glucopyranosyl-(1 $\rightarrow$ 2)- β -D-glucuronopyranosyl] hederagenin 28-*O*- β -D-glucopyranoside (**20**)。结构见图 1。其中化合物 **1**、**5**、**7**、**8**、**12**、**19** 首次在五加科植物中分离得到；化合物 **1**、**4**—**8**、**12**、**17**—**20** 首次在榕木属中分离得到。化合物 **3**、**9**—**14**、**17** 能有效降低脂多糖 (lipopolysaccharide, LPS) 诱导的 16HBE 气道上皮细胞中炎症因子 IL-6 水平，具有显著的抗气道炎症活性。

1 仪器与材料

Hei-VAP Core HL/G3 型旋转蒸发仪 (德国 Heidolph 公司)；DLSB-5L/25 型低温冷却液循环泵 (巩义市予华仪器有限责任公司)；SK6200H 超声清洗器 (上海科导超声仪器有限公司)；ME204TE 型电子天平 (瑞士梅特勒-托利多公司)；UV2401PC 型紫外可见光分光光度计 (日本 Shimadzu 公司)；400 MHz、500 MHz、600 MHz 核磁共振仪 (Bruker 公司)；20~200 μ L 移液器 (德国 Eppendorf 公司)；多功能酶标仪 (美国 Bio-Tek 公司)；Agilent 1260 infinity II Prep 液相色谱仪 (美国 Agilent 公司)。

柱色谱用硅胶 (80~100、100~200、200~300 目；中国青岛海洋化工厂)；Eclipse XDB-C₁₈ 反相

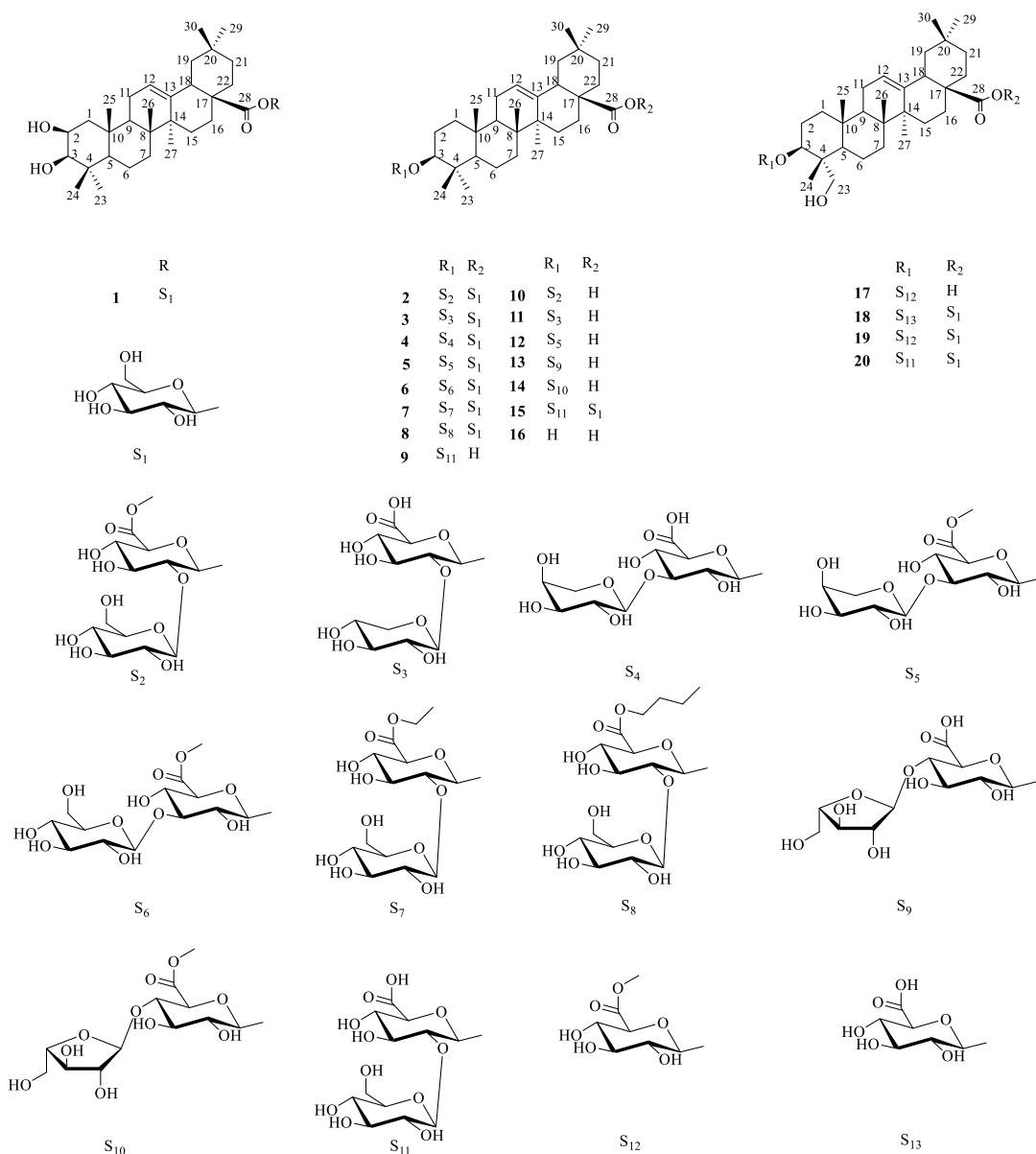


图 1 化合物 1~20 的结构

Fig. 1 Structures of compounds 1—20

谱柱 (250 mm×4.6 mm, 5 μm, 美国 Agilent 公司); 柱色谱用 ODS 填料 (美国 Millipore 公司); SephadexLH-20 葡聚糖凝胶 (美国 GE Healthcare 公司); 薄层色谱硅胶板 GF₂₅₄ (青岛海洋化工厂); 工业级、分析级溶剂 (昆明利研科技有限公司); 色谱级甲醇、乙腈 (上海星可高纯溶剂公司); DMEM 培养基 (C3113-0500)、胎牛血清 (C04001)、双抗 (C340) 均购自 VivaCell 公司; IL-6 ELISA 试剂盒 (A10631142, 联科生物); CCK8 试剂盒 (BC09224883, Bioss 公司); 地塞米松 (批号 D4902, 美国 Sigma 公司); 培养箱 (恒苏净科学仪器有限公司); 16HBE 支气管上皮细胞 (上海 Whelab 生物科

技公司); LPS (Solarbio 公司)。

实验用白背叶榕木样品于 2019 年 4 月自云南怒江泸水县采集, 经云南中医药大学李艳平教授鉴定为白背叶榕木 *A. chinensis* var. *nuda* 的干燥芽苞, 标本 (201904SM) 存放于云南省高校中药民族药质量标准研究重点实验室。

2 提取与分离

将 20 kg 干燥白背叶榕木芽苞粉碎, 于 70%乙醇中浸提 3 次, 滤液合并浓缩得乙醇提取物浸膏 4.70 kg。浸膏加水混悬后依次用石油醚、醋酸乙酯、正丁醇进行萃取, 浓缩得正丁醇部位 1.75 kg。取正丁醇部位经 100~200 目硅胶柱色谱, 以氯仿-甲醇-水

(1:0:0~5:5:0.8)梯度洗脱得 6 个流分(A~F)。

根据液相分析结果,对 B 段(27 g)组分进行 ODS 反相柱色谱(甲醇-水梯度洗脱),收集 50% 甲醇洗脱部位,后经半制备液相色谱(乙腈-水-甲酸,45:55:0.05),得到化合物 **1** ($t_R=17.2$ min, 3 mL/min, 6.4 mg)。对 C 段(132 g)组分进行硅胶柱分离以氯仿-甲醇-水(1:0:0~6:4:0.5)梯度洗脱,得到 13 个亚流分 C1~C13,亚流分 C2 经半制备液相色谱(乙腈-水-甲酸 32:68:0.05),得到化合物 **15** ($t_R=13.2$ min, 3 mL/min, 7.1 mg),亚流分 C13 经半制备液相色谱(乙腈-水-甲酸 40:60:0.01),得到化合物 **2** ($t_R=24.0$ min, 3 mL/min, 20.7 mg);亚流分 C3 经半制备液相色谱(乙腈-水-甲酸 37:63:0.01),得到化合物 **6** ($t_R=15.4$ min, 3 mL/min, 5.1 mg)和化合物 **7** ($t_R=16.6$ min, 3 mL/min, 5.1 mg)。对 D 段(198 g)组分进行硅胶柱色谱,以氯仿-甲醇-水(9:1:0~5:5:0.8)梯度洗脱,得到 10 个亚流分 D1~D10,亚流分 D1 经半制备液相色谱(33.5%乙腈-水),得到化合物 **3** ($t_R=13.7$ min, 3 mL/min, 14.9 mg);亚流分 D2 经半制备液相色谱(40%乙腈-水),得到化合物 **5** ($t_R=29$ min, 3 mL/min, 4.5 mg);亚流分 D4 经半制备液相色谱(乙腈-水-甲酸 43:57:0.05),得到化合物 **9** ($t_R=17.8$ min, 3 mL/min, 10.9 mg);亚流分 D6 经半制备液相色谱(乙腈-水-甲酸 50:50:0.01),得到化合物 **10** ($t_R=16.9$ min, 3 mL/min, 5.9 mg)和化合物 **17** ($t_R=18.9$ min, 3 mL/min, 4.9 mg);亚流分 D7 经 Sephadex LH-20 葡聚糖凝胶处理后,析出白色粉末,经鉴定得到化合物 **11** (5.3 mg);亚流分 D8 直接析晶得到化合物 **16** (7.7 mg),剩余样品经半制备液相色谱(60%乙腈-水),得到化合物 **12** ($t_R=24.5$ min, 3 mL/min, 6.9 mg);亚流分 D9 经半制备液相色谱(乙腈-水-甲酸 33:67:0.05),得到化合物 **18** ($t_R=28.9$ min, 3 mL/min, 35.6 mg);亚流分 D10 经半制备液相色谱(40%乙腈-水),得到化合物 **19** ($t_R=29.0$ min, 3 mL/min, 5.1 mg)。E 组分(64 g)经氯仿-甲醇-水(9:1:0.1~5:5:0.5)硅胶柱色谱和甲醇-水(2:8~8:2)ODS 反相柱色谱,最终得到 8 个亚流分 E1~E8,亚流分 E2 经半制备液相色谱(33.5%乙腈-水),得到化合物 **4** ($t_R=14.1$ min, 3 mL/min, 22.7 mg);亚流分 E4 经半制备液相色谱(乙腈-水-甲酸 42:58:0.01),得到化合物 **8** ($t_R=18.3$ min, 3 mL/min,

17.1 mg);亚流分 E6 经半制备液相色谱(乙腈-水-甲酸 45:55:0.01),得到化合物 **13** ($t_R=19.4$ min, 3 mL/min, 12.1 mg);亚流分 E7 经半制备液相色谱(乙腈-水-甲酸 63:37:0.06),得到化合物 **14** ($t_R=24.5$ min, 3 mL/min, 6.0 mg);亚流分 E8 经半制备液相色谱(乙腈-水-甲酸 37:63:0.05),得到化合物 **20** ($t_R=15.8$ min, 3 mL/min, 5.3 mg)。

3 结构鉴定

化合物 **1**: 白色无定型粉末, ESI-MS m/z : 633.4 $[M-H]^-$, 分子式 $C_{36}H_{58}O_9$ 。 1H -NMR (600 MHz, CD_3OD) δ : 5.37 (1H, d, $J=8.2$ Hz, H-1'), 5.26 (1H, brs, H-12), 3.81 (1H, d, $J=12.1$ Hz, H-6'a), 3.67 (1H, dd, $J=12.1, 4.0$ Hz, H-6'b), 1.15 (3H, s, H-27), 1.00 (6H, s, H-24, 25), 0.93 (3H, s, H-30), 0.90 (3H, s, H-29), 0.80 (6H, s, H-23, 26); ^{13}C -NMR (150 MHz, CD_3OD) δ : 178.1 (C-28), 145.0 (C-13), 123.6 (C-12), 95.7 (C-1'), 84.5 (C-3), 78.7 (C-5'), 78.3 (C-3'), 73.9 (C-2'), 71.1 (C-4'), 69.5 (C-2), 62.4 (C-6'), 56.4 (C-5), 49.6 (C-9), 47.9 (C-1), 47.7 (C-17), 46.9 (C-19), 42.7 (C-14), 42.3 (C-18), 40.5 (C-8), 40.2 (C-4), 39.0 (C-10), 34.6 (C-21), 33.6 (C-7), 33.5 (C-29), 32.9 (C-22), 31.3 (C-20), 29.3 (C-23), 28.6 (C-15), 26.3 (C-27), 24.3 (C-11), 24.0 (C-30), 23.7 (C-16), 19.3 (C-6), 17.7 (C-24), 17.5 (C-26), 17.2 (C-25)。以上数据与文献数据一致^[13], 故鉴定化合物 **1** 为 2 β ,3 β -dihydroxyolean-12-en-28-oic acid 28-*O*- β -D-glucopyranoside。

化合物 **2**: 白色粉末, ESI-MS m/z : 969.5 $[M-H]^-$, 分子式 $C_{49}H_{78}O_{19}$ 。 1H -NMR (500 MHz, CD_3OD) δ : 5.39 (1H, d, $J=8.1$ Hz, H-1'''), 5.26 (1H, brs, H-12), 4.69 (1H, d, $J=7.7$ Hz, H-1''), 4.53 (1H, d, $J=7.6$ Hz, H-1'), 3.78 (3H, s, H-7'), 1.16 (3H, s, H-27), 1.08 (3H, s, H-23), 0.96 (3H, s, H-25), 0.94 (3H, s, H-30), 0.92 (3H, s, H-29), 0.86 (3H, s, H-24), 0.81 (3H, s, H-26); ^{13}C -NMR (125 MHz, CD_3OD) δ : 178.1 (C-28), 171.1 (C-6'), 144.8 (C-13), 123.8 (C-12), 105.6 (C-1''), 104.4 (C-1'), 95.7 (C-1'''), 91.8 (C-3), 80.4 (C-2'), 78.7 (C-3''), 78.4 (C-5''), 78.3 (C-5'''), 77.9 (C-3'''), 77.7 (C-3'), 76.5 (C-2''), 76.3 (C-5'), 73.9 (C-2'''), 73.0 (C-4'), 71.9 (C-4''), 71.1 (C-4'''), 63.1 (C-6'''), 62.4 (C-6''), 57.0 (C-5), 52.8 (C-7'), 49.0 (C-9), 48.0 (C-17), 47.2 (C-19), 42.9 (C-14), 42.6 (C-18), 40.7 (C-8), 40.4 (C-4), 39.8 (C-1), 37.9 (C-10), 34.9 (C-7), 33.9 (C-21), 33.5 (C-29), 33.1 (C-22), 31.5 (C-20), 28.9 (C-15), 28.4 (C-23),

27.1 (C-2), 26.3 (C-27), 24.6 (C-11), 24.0 (C-16), 24.0 (C-30), 19.3 (C-6), 17.7 (C-26), 16.9 (C-24), 16.0 (C-25)。以上数据与文献数据一致^[14], 故鉴定化合物 **2** 为 chikusetsusaponin V methyl ester。

化合物 **3**: 白色结晶 (甲醇), ESI-MS m/z : 925.5 $[M-H]^-$, 分子式 $C_{47}H_{74}O_{18}$ 。 1H -NMR (500 MHz, CD_3OD) δ : 5.38 (1H, d, $J = 8.1$ Hz, H-1'''), 5.25 (1H, brs, H-12), 4.53 (1H, d, $J = 7.5$ Hz, H-1''), 4.48 (1H, d, $J = 7.5$ Hz, H-1'), 1.16 (3H, s, H-27), 1.05 (3H, s, H-23), 0.95 (3H, s, H-25), 0.94 (3H, s, H-30), 0.91 (3H, s, H-29), 0.84 (3H, s, H-24), 0.80 (3H, s, H-26); ^{13}C -NMR (125 MHz, CD_3OD) δ : 178.1 (C-28), 173.3 (C-6'), 144.8 (C-13), 123.9 (C-12), 106.3 (C-1''), 105.5 (C-1'), 95.7 (C-1'''), 91.2 (C-3), 82.9 (C-2'), 78.7 (C-3'''), 78.3 (C-5'''), 78.2 (C-3'), 77.8 (C-5'), 77.8 (C-3''), 76.3 (C-2''), 73.9 (C-2'''), 73.2 (C-4'), 71.2 (C-4'''), 71.1 (C-4''), 67.2 (C-5''), 62.4 (C-6'''), 57.1 (C-5), 49.0 (C-9), 48.0 (C-17), 47.2 (C-19), 42.9 (C-14), 42.6 (C-18), 40.7 (C-8), 40.3 (C-4), 39.9 (C-1), 37.9 (C-10), 34.9 (C-21), 34.0 (C-7), 33.5 (C-29), 33.1 (C-22), 31.5 (C-20), 28.9 (C-15), 28.2 (C-23), 27.1 (C-2), 26.3 (C-27), 24.6 (C-16), 24.0 (C-30), 24.0 (C-11), 19.3 (C-6), 17.7 (C-26), 16.6 (C-24), 16.0 (C-25)。以上数据与文献数据一致^[15], 故鉴定化合物 **3** 为 *pseudo-ginsenoside-RT*₁。

化合物 **4**: 白色结晶 (甲醇), ESI-MS m/z : 925.5 $[M-H]^-$, 分子式 $C_{47}H_{74}O_{18}$ 。 1H -NMR (500 MHz, CD_3OD) δ : 5.38 (1H, d, $J = 8.1$ Hz, H-1'''), 5.25 (1H, brs, H-12), 4.54 (1H, d, $J = 6.9$ Hz, H-1'), 4.42 (1H, d, $J = 7.6$ Hz, H-1''), 1.16 (3H, s, H-27), 1.05 (3H, s, H-23), 0.95 (3H, s, H-25), 0.94 (3H, s, H-30), 0.92 (3H, s, H-29), 0.84 (3H, s, H-24), 0.80 (3H, s, H-26); ^{13}C -NMR (125 MHz, CD_3OD) δ : 178.1 (C-28), 173.6 (C-6'), 144.8 (C-13), 123.8 (C-12), 106.6 (C-1'), 105.4 (C-1''), 95.7 (C-1'''), 91.1 (C-3), 86.1 (C-3'), 78.7 (C-5'''), 78.3 (C-3'''), 76.5 (C-5'), 74.8 (C-2'), 74.1 (C-3''), 73.9 (C-2'''), 72.8 (C-4'), 71.8 (C-2''), 71.1 (C-4'''), 69.7 (C-4''), 67.3 (C-5''), 62.4 (C-6'''), 57.0 (C-5), 49.0 (C-9), 48.0 (C-17), 47.2 (C-19), 42.9 (C-14), 42.6 (C-18), 40.7 (C-8), 40.2 (C-4), 39.8 (C-1), 37.9 (C-10), 34.9 (C-21), 34.0 (C-7), 33.5 (C-29), 33.1 (C-22), 31.5 (C-20), 28.9 (C-15), 28.5 (C-23), 26.9 (C-2), 26.3 (C-27), 24.6 (C-11), 24.0 (C-16), 24.0 (C-30), 19.3 (C-6), 17.7 (C-26), 17.0 (C-24), 16.0 (C-25)。以上数据与文献数据一

致^[16], 故鉴定化合物 **4** 为 hemsloside Mal。

化合物 **5**: 白色粉末, ESI-MS m/z : 939.5 $[M-H]^-$, 分子式 $C_{48}H_{76}O_{18}$ 。 1H -NMR (600 MHz, CD_3OD) δ : 5.37 (1H, d, $J = 8.2$ Hz, H-1'''), 5.24 (1H, br s, H-12), 4.51 (1H, d, $J = 7.1$ Hz, H-1''), 4.43 (1H, d, $J = 7.9$ Hz, H-1'), 3.76 (3H, s, H-7'), 1.14 (3H, s, H-27), 1.03 (3H, s, H-23), 0.94 (3H, s, H-25), 0.92 (3H, s, H-30), 0.90 (3H, s, H-29), 0.82 (3H, s, H-24), 0.79 (3H, s, H-26); ^{13}C -NMR (150 MHz, CD_3OD) δ : 178.1 (C-28), 171.1 (C-6'), 144.8 (C-13), 123.8 (C-12), 106.7 (C-1''), 105.6 (C-1'), 95.7 (C-1'''), 91.2 (C-3), 86.0 (C-3'), 78.7 (C-5'''), 78.3 (C-3'''), 76.3 (C-5'), 74.8 (C-3''), 74.2 (C-2''), 73.9 (C-2'''), 72.9 (C-4'), 71.7 (C-2''), 71.1 (C-4'''), 69.6 (C-4''), 67.3 (C-5''), 62.4 (C-6'''), 57.0 (C-5), 52.9 (C-7'), 49.0 (C-9), 48.0 (C-17), 47.2 (C-19), 42.9 (C-14), 42.6 (C-18), 40.7 (C-8), 40.2 (C-4), 39.7 (C-1), 37.9 (C-10), 34.9 (C-21), 33.9 (C-7), 33.5 (C-29), 33.1 (C-22), 31.5 (C-20), 28.9 (C-15), 28.4 (C-23), 27.0 (C-2), 26.3 (C-27), 24.6 (C-11), 24.0 (C-16), 24.0 (C-30), 19.3 (C-6), 17.7 (C-26), 16.9 (C-24), 16.0 (C-25)。以上数据与文献数据一致^[17], 故鉴定化合物 **5** 为 momordin IIa。

化合物 **6**: 白色粉末, ESI-MS m/z : 969.5 $[M-H]^-$, 分子式 $C_{49}H_{78}O_{19}$ 。 1H -NMR (500 MHz, CD_3OD) δ : 5.38 (1H, d, $J = 8.2$ Hz, H-1'''), 5.25 (1H, brs, H-12), 4.57 (1H, d, $J = 7.8$ Hz, H-1''), 4.44 (1H, d, $J = 7.9$ Hz, H-1'), 3.77 (3H, s, H-7'), 1.15 (3H, s, H-27), 1.04 (3H, s, H-23), 0.95 (3H, s, H-25), 0.93 (3H, s, H-30), 0.91 (3H, s, H-29), 0.83 (3H, s, H-24), 0.80 (3H, s, H-26); ^{13}C -NMR (125 MHz, CD_3OD) δ : 178.1 (C-28), 171.1 (C-6'), 144.9 (C-13), 123.8 (C-12), 106.6 (C-1'), 105.1 (C-1''), 95.7 (C-1'''), 91.2 (C-3), 86.5 (C-3'), 78.7 (C-3'''), 78.3 (C-5'''), 78.2 (C-3''), 77.8 (C-5'), 76.3 (C-5'), 75.5 (C-2''), 74.8 (C-2'), 73.9 (C-2'''), 71.8 (C-4'''), 71.6 (C-4'), 71.1 (C-4''), 62.7 (C-6''), 62.4 (C-6'''), 57.0 (C-5), 52.8 (C-7'), 49.0 (C-9), 48.0 (C-17), 47.2 (C-19), 42.9 (C-14), 42.6 (C-18), 40.7 (C-8), 40.2 (C-4), 39.7 (C-1), 37.9 (C-10), 34.9 (C-21), 33.9 (C-7), 33.5 (C-29), 33.1 (C-22), 31.5 (C-20), 28.9 (C-15), 28.4 (C-23), 27.0 (C-2), 26.3 (C-27), 24.6 (C-11), 24.0 (C-16), 24.0 (C-30), 19.3 (C-6), 17.7 (C-26), 17.0 (C-24), 16.0 (C-25)。以上数据与文献数据一致^[18], 故鉴定化合物 **6** 为 3-*O*- β -*D*-glucopyranosyl(1 $\rightarrow$ 3)- β -*D*-glucuronopyranoside-28-*O*- β -*D*-glucopyranosyl oleanolic acid

methyl ester。

化合物 **7**: 白色粉末, ESI-MS m/z : 983.5 $[M-H]^-$, 分子式 $C_{50}H_{80}O_{19}$ 。 1H -NMR (600 MHz, pyridine- d_5) δ : 6.18 (1H, d, $J = 8.2$ Hz, H-1'''), 5.27 (1H, brs, H-12), 5.26 (1H, d, $J = 7.7$ Hz, H-1''), 4.85 (1H, d, $J = 7.6$ Hz, H-1'), 4.21 (2H, q, $J = 7.1$ Hz, H-1'''), 1.08 (3H, t, $J = 7.2$ Hz, H-2'''), 1.15 (3H, s, H-23), 1.14 (3H, s, H-27), 0.98 (3H, s, H-26), 0.96 (3H, s, H-24), 0.80 (3H, s, H-29), 0.77 (3H, s, H-30), 0.72 (3H, s, H-25); ^{13}C -NMR (150 MHz, pyridine- d_5) δ : 176.8 (C-28), 170.7 (C-6'), 144.9 (C-13), 123.4 (C-12), 106.5 (C-1''), 105.6 (C-1'), 95.7 (C-1'''), 89.6 (C-3), 82.7 (C-2'), 79.6 (C-3'''), 79.1 (C-5'''), 78.4 (C-5''), 78.3 (C-3''), 77.7 (C-3'), 77.3 (C-2''), 77.1 (C-5'), 74.4 (C-2'''), 73.0 (C-4'), 71.9 (C-4''), 71.3 (C-4'''), 62.9 (C-6''), 62.3 (C-6'''), 61.4 (C-1'''), 56.0 (C-5), 48.1 (C-9), 47.1 (C-17), 46.3 (C-19), 42.4 (C-14), 42.0 (C-18), 40.1 (C-8), 39.7 (C-4), 38.7 (C-1), 37.1 (C-10), 34.2 (C-21), 33.5 (C-29), 33.4 (C-22), 32.9 (C-7), 30.9 (C-20), 28.4 (C-15), 28.2 (C-23), 26.7 (C-2), 26.3 (C-27), 24.0 (C-16), 23.9 (C-30), 23.6 (C-11), 18.8 (C-6), 17.7 (C-26), 16.9 (C-24), 15.7 (C-25), 14.4 (C-2'''). 以上数据与文献数据一致^[19], 故鉴定化合物 **7** 为 3-*O*-[β -*D*-glucopyranosyl-(1 $\rightarrow$ 2)- β -*D*-(6'-*O*-ethyl)-glucuronopyranosyl]-oleanolic acid 28-*O*- β -*D*-glucopyranoside。

化合物 **8**: 白色粉末, ESI-MS m/z : 1 011.5 $[M-H]^-$, 分子式 $C_{52}H_{84}O_{19}$ 。 1H -NMR (500 MHz, CD_3OD) δ : 5.40 (1H, d, $J = 8.1$ Hz, H-1'''), 5.27 (1H, brs, H-12), 4.69 (1H, d, $J = 7.6$ Hz, H-1''), 4.53 (1H, d, $J = 7.5$ Hz, H-1'), 4.21 (2H, t, $J = 6.4$ Hz, H-1'''), 1.17 (3H, s, H-27), 1.09 (3H, s, H-23), 0.97 (3H, s, H-25), 0.96 (3H, t, $J = 7.0$ Hz, H-4'''), 0.95 (3H, s, H-30), 0.93 (3H, s, H-29), 0.87 (3H, s, H-24), 0.81 (3H, s, H-26); ^{13}C -NMR (125 MHz, CD_3OD) δ : 178.0 (C-28), 170.6 (C-6'), 144.9 (C-13), 123.8 (C-12), 105.6 (C-1''), 104.5 (C-1'), 95.7 (C-1'''), 91.8 (C-3), 80.4 (C-2'), 78.7 (C-3'''), 78.4 (C-5'''), 78.3 (C-5''), 77.9 (C-3''), 77.7 (C-3'), 76.6 (C-2''), 76.3 (C-5'), 73.9 (C-2'''), 72.9 (C-4'), 71.9 (C-4''), 71.1 (C-4'''), 63.1 (C-6''), 62.4 (C-6'''), 66.1 (C-1'''), 57.0 (C-5), 49.0 (C-9), 48.0 (C-17), 47.2 (C-19), 42.9 (C-14), 42.6 (C-18), 40.7 (C-8), 40.4 (C-4), 39.8 (C-1), 37.9 (C-10), 34.9 (C-21), 33.9 (C-7), 33.5 (C-29), 33.1 (C-22), 31.7 (C-2'''), 31.5 (C-20), 28.9 (C-15), 28.4 (C-

23), 27.1 (C-2), 26.3 (C-27), 24.6 (C-11), 24.0 (C-30), 24.0 (C-16), 20.1 (C-3'''), 19.3 (C-6), 17.7 (C-26), 16.9 (C-24), 16.0 (C-25), 14.1 (C-4''')。以上数据与文献数据一致^[20], 故鉴定化合物 **8** 为 ginsenoside-Ro-6'-*O*-butyl ester。

化合物 **9**: 白色结晶 (甲醇) ESI-MS m/z : 793.4 $[M-H]^-$, 分子式 $C_{42}H_{66}O_{14}$ 。 1H -NMR (500 MHz, CD_3OD) δ : 5.24 (1H, brs, H-12), 4.68 (1H, d, $J = 7.7$ Hz, H-1''), 4.49 (1H, d, $J = 6.4$ Hz, H-1'), 3.82 (1H, dd, $J = 11.5, 2.0$ Hz, H-6''a), 3.62 (1H, dd, $J = 11.5, 5.9$ Hz, H-6''b), 1.16 (3H, s, H-27), 1.08 (3H, s, H-23), 0.95 (3H, s, H-25), 0.94 (3H, s, H-30), 0.91 (3H, s, H-29), 0.86 (3H, s, H-24), 0.82 (3H, s, H-26); ^{13}C -NMR (125 MHz, CD_3OD) δ : 181.9 (C-28), 172.7 (C-6'), 145.2 (C-13), 123.7 (C-12), 105.5 (C-1''), 104.6 (C-1'), 91.5 (C-3), 81.0 (C-2'), 78.3 (C-3''), 78.1 (C-5''), 77.8 (C-2''), 77.2 (C-5'), 76.3 (C-3'), 73.4 (C-4'), 71.9 (C-4''), 63.1 (C-6''), 57.0 (C-5), 49.6 (C-9), 47.7 (C-17), 47.2 (C-19), 42.9 (C-14), 42.8 (C-18), 40.6 (C-8), 40.4 (C-4), 39.8 (C-1), 37.9 (C-10), 34.9 (C-21), 34.0 (C-22), 33.8 (C-7), 33.6 (C-29), 31.6 (C-20), 28.8 (C-15), 28.5 (C-23), 27.0 (C-2), 26.4 (C-27), 24.6 (C-16), 24.1 (C-11), 24.0 (C-30), 19.3 (C-6), 17.7 (C-26), 16.9 (C-24), 16.0 (C-25)。以上数据与文献数据一致^[21], 故鉴定化合物 **9** 为姜状三七皂苷 R_1 。

化合物 **10**: 白色粉末, ESI-MS m/z : 807.5 $[M-H]^-$, 分子式 $C_{43}H_{68}O_{14}$ 。 1H -NMR (600 MHz, CD_3OD) δ : 5.23 (1H, brs, H-12), 4.68 (1H, d, $J = 7.7$ Hz, H-1''), 4.52 (1H, d, $J = 7.7$ Hz, H-1'), 3.77 (3H, s, H-7'), 1.15 (3H, s, H-27), 1.07 (3H, s, H-23), 0.95 (3H, s, H-25), 0.94 (3H, s, H-30), 0.90 (3H, s, H-29), 0.85 (3H, s, H-24), 0.81 (3H, s, H-26); ^{13}C -NMR (150 MHz, CD_3OD) δ : 180.5 (C-28), 171.1 (C-6'), 145.3 (C-13), 123.5 (C-12), 105.6 (C-1''), 104.4 (C-1'), 91.8 (C-3), 80.4 (C-2'), 78.4 (C-5''), 77.9 (C-3''), 77.7 (C-2''), 76.5 (C-5'), 76.3 (C-3'), 73.0 (C-4'), 71.9 (C-4''), 63.1 (C-6''), 56.9 (C-5), 52.8 (C-7'), 49.6 (C-9), 47.8 (C-17), 47.3 (C-19), 42.9 (C-14), 42.8 (C-18), 40.6 (C-8), 40.4 (C-4), 39.7 (C-1), 37.9 (C-10), 35.0 (C-21), 34.0 (C-22), 33.9 (C-7), 33.6 (C-29), 31.6 (C-20), 28.9 (C-15), 28.4 (C-23), 27.1 (C-2), 26.4 (C-27), 24.6 (C-16), 24.1 (C-11), 24.0 (C-30), 19.3 (C-6), 17.8 (C-26), 16.9 (C-24), 15.9 (C-25)。以上数据与文献数据一致^[22], 故鉴定化合物 **10**

为 oleanolic acid 3 β -O- β -D-glucopyranosyl-(1 $\rightarrow$ 2)- β -D-(6'-O-methyl-glucuronopyranoside)。

化合物 **11**: 白色粉末, ESI-MS m/z : 763.4 [M-H]⁻, 分子式 C₄₁H₆₄O₁₃。 ¹H-NMR (600 MHz, CD₃OD) δ : 5.24 (1H, brs, H-12), 4.52 (1H, d, J = 7.5 Hz, H-1''), 4.45 (1H, d, J = 7.6 Hz, H-1'), 3.80 (1H, dd, J = 11.5, 5.4 Hz, H-5''a), 3.62 (1H, m, H-5''b), 1.15 (3H, s, H-27), 1.05 (3H, s, H-23), 0.95 (3H, s, H-25), 0.94 (3H, s, H-30), 0.91 (3H, s, H-29), 0.84 (3H, s, H-24), 0.81 (3H, s, H-26); ¹³C-NMR (150 MHz, CD₃OD) δ : 181.9 (C-28), 173.4 (C-6'), 145.2 (C-13), 123.7 (C-12), 106.4 (C-1''), 105.4 (C-1'), 91.0 (C-3), 83.1 (C-2'), 78.0 (C-5''), 77.8 (C-3'), 77.8 (C-3''), 76.3 (C-2''), 73.4 (C-4'), 71.2 (C-4''), 67.2 (C-5'), 57.1 (C-5), 49.0 (C-9), 47.7 (C-17), 47.2 (C-19), 42.9 (C-14), 42.7 (C-18), 40.6 (C-8), 40.3 (C-4), 39.8 (C-1), 37.9 (C-10), 34.9 (C-7), 34.0 (C-21), 33.8 (C-22), 33.6 (C-29), 31.6 (C-20), 28.8 (C-15), 28.2 (C-23), 27.0 (C-2), 26.4 (C-27), 24.6 (C-11), 24.1 (C-16), 24.0 (C-30), 19.3 (C-6), 17.7 (C-26), 16.6 (C-24), 16.0 (C-25)。以上数据与文献数据一致^[23], 故鉴定化合物 **11** 为 *pseudo-ginsenoside-RP*₁。

化合物 **12**: 白色粉末, ESI-MS m/z : 777.5 [M-H]⁻, 分子式 C₄₂H₆₆O₁₃。 ¹H-NMR (400 MHz, pyridine-*d*₅) δ : 5.46 (1H, brs, H-12), 5.32 (1H, d, J = 7.1 Hz, H-1''), 5.00 (1H, d, J = 7.8 Hz, H-1'), 4.08 (1H, dd, J = 12.0, 2.8 Hz, H-5''a), 3.94 (3H, s, H-7'), 3.80 (1H, dd, J = 12.0, 4.4 Hz, H-5''b), 1.28 (3H, s, H-27), 1.01 (3H, s, H-23), 0.99 (6H, s, H-25, 30), 0.97 (3H, s, H-29), 0.96 (3H, s, H-24), 0.80 (3H, s, H-26); ¹³C-NMR (100 MHz, pyridine-*d*₅) δ : 180.0 (C-28), 169.8 (C-6'), 144.7 (C-13), 122.3 (C-12), 106.6 (C-1''), 105.6 (C-1'), 89.2 (C-3), 85.5 (C-3'), 76.4 (C-5'), 74.3 (C-2'), 74.2 (C-3''), 72.6 (C-4'), 71.0 (C-2''), 69.0 (C-4''), 66.9 (C-5''), 55.5 (C-5), 52.0 (C-7'), 47.9 (C-9), 46.5 (C-17), 46.4 (C-19), 42.0 (C-14), 41.8 (C-18), 39.6 (C-8), 39.3 (C-4), 38.4 (C-1), 36.9 (C-10), 34.2 (C-21), 33.1 (C-22), 33.0 (C-7), 32.9 (C-29), 30.9 (C-20), 28.2 (C-15), 28.0 (C-23), 26.4 (C-2), 26.1 (C-27), 23.6 (C-11), 23.6 (C-16), 23.5 (C-30), 18.2 (C-6), 17.1 (C-26), 16.8 (C-24), 15.3 (C-25)。以上数据与文献数据一致^[24], 故鉴定化合物 **12** 为 momordin Ia。

化合物 **13**: 白色粉末, ESI-MS m/z : 763.4 [M-H]⁻, 分子式 C₄₁H₆₄O₁₃。 ¹H-NMR (500 MHz, CD₃OD)

δ : 5.24 (1H, brs, H-12), 5.09 (1H, d, J = 1.5 Hz, H-1''), 4.36 (1H, d, J = 7.6 Hz, H-1'), 1.16 (3H, s, H-27), 1.05 (3H, s, H-23), 0.94 (6H, s, H-25, 30), 0.91 (3H, s, H-29), 0.84 (3H, s, H-24), 0.81 (3H, s, H-26); ¹³C-NMR (125 MHz, CD₃OD) δ : 181.9 (C-28), 173.3 (C-6'), 145.2 (C-13), 123.7 (C-12), 109.2 (C-1''), 106.9 (C-1'), 90.9 (C-3), 86.6 (C-4''), 82.8 (C-2''), 79.0 (C-3''), 78.6 (C-4'), 76.4 (C-3'), 75.4 (C-2'), 75.4 (C-5'), 63.2 (C-5''), 57.0 (C-5), 49.0 (C-9), 47.7 (C-17), 47.2 (C-19), 42.9 (C-14), 42.8 (C-18), 40.6 (C-8), 40.2 (C-4), 39.8 (C-1), 37.9 (C-10), 34.9 (C-21), 34.0 (C-22), 33.8 (C-7), 33.6 (C-29), 31.6 (C-20), 28.8 (C-15), 28.5 (C-23), 27.0 (C-2), 26.4 (C-27), 24.5 (C-16), 24.1 (C-11), 24.0 (C-30), 19.3 (C-6), 17.7 (C-26), 17.0 (C-24), 16.0 (C-25)。以上数据与文献数据一致^[25], 故鉴定化合物 **13** 为银莲花苷。

化合物 **14**: 白色粉末, ESI-MS m/z : 777.5 [M-H]⁻, 分子式 C₄₂H₆₆O₁₃。 ¹H-NMR (600 MHz, CD₃OD) δ : 5.23 (1H, brs, H-12), 4.91 (1H, d, J = 1.5 Hz, H-1''), 4.41 (1H, d, J = 7.8 Hz, H-1'), 3.79 (3H, s, H-7'), 1.16 (3H, s, H-27), 1.05 (3H, s, H-23), 0.95 (3H, s, H-25), 0.94 (3H, s, H-30), 0.91 (3H, s, H-29), 0.85 (3H, s, H-24), 0.82 (3H, s, H-26); ¹³C-NMR (150 MHz, CD₃OD) δ : 180.9 (C-28), 171.2 (C-6'), 145.3 (C-13), 123.6 (C-12), 109.2 (C-1''), 106.9 (C-1'), 91.2 (C-3), 86.7 (C-4''), 82.9 (C-2''), 78.5 (C-3''), 78.5 (C-4'), 76.0 (C-3'), 75.1 (C-5'), 75.0 (C-2'), 63.0 (C-5''), 57.0 (C-5), 53.1 (C-7'), 49.1 (C-9), 47.7 (C-17), 47.3 (C-19), 42.9 (C-14), 42.8 (C-18), 40.6 (C-8), 40.2 (C-4), 39.7 (C-1), 37.9 (C-10), 34.9 (C-21), 34.0 (C-22), 33.9 (C-7), 33.6 (C-29), 31.6 (C-20), 28.9 (C-15), 28.4 (C-23), 27.0 (C-2), 26.4 (C-27), 24.5 (C-16), 24.1 (C-11), 24.0 (C-30), 19.3 (C-6), 17.8 (C-26), 16.9 (C-24), 15.9 (C-25)。以上数据与文献数据一致^[26], 故鉴定化合物 **14** 为 narcissiflorine methyl ester。

化合物 **15**: 白色结晶(甲醇), ESI-MS m/z : 955.5 [M-H]⁻, 分子式 C₄₈H₇₆O₁₉。 ¹H-NMR (500 MHz, CD₃OD) δ : 5.37 (1H, d, J = 8.0 Hz, H-1'''), 5.24 (1H, brs, H-12), 4.66 (1H, d, J = 7.3 Hz, H-1''), 4.46 (1H, d, J = 7.2 Hz, H-1'), 1.14 (3H, s, H-27), 1.06 (3H, s, H-23), 0.94 (3H, s, H-25), 0.92 (3H, s, H-30), 0.90 (3H, s, H-29), 0.84 (3H, s, H-24), 0.79 (3H, s, H-26); ¹³C-NMR (125 MHz, CD₃OD) δ : 178.1 (C-28), 172.4 (C-6'), 144.8 (C-13), 123.9 (C-12), 105.5 (C-1''), 104.7 (C-1'), 95.7 (C-1'''), 91.4 (C-3), 81.2 (C-2'), 78.7 (C-5'''),

78.3 (C-5''), 78.2 (C-3'), 77.8 (C-3'''), 76.4 (C-3''), 76.2 (C-2''), 75.5 (C-5'), 73.9 (C-2'''), 73.6 (C-4'), 71.9 (C-4'''), 71.1 (C-4''), 63.1 (C-6'''), 62.4 (C-6''), 57.0 (C-5), 49.0 (C-9), 48.0 (C-17), 47.2 (C-19), 42.9 (C-14), 42.6 (C-18), 40.7 (C-8), 40.4 (C-4), 39.9 (C-1), 37.9 (C-10), 34.9 (C-21), 34.0 (C-7), 33.5 (C-29), 33.2 (C-22), 31.6 (C-20), 28.9 (C-15), 28.5 (C-23), 27.0 (C-2), 26.3 (C-27), 24.6 (C-11), 24.0 (C-16), 24.0 (C-30), 19.3 (C-6), 17.7 (C-26), 16.9 (C-24), 16.1 (C-25)。以上数据与文献数据一致^[27], 故鉴定化合物 **15** 为人参皂昔 Ro。

化合物 **16**: 白色结晶(甲醇), ESI-MS m/z : 455.4 $[M-H]^-$, 分子式 $C_{30}H_{48}O_3$ 。 1H -NMR (500 MHz, CD_3OD) δ : 5.24 (1H, brs, H-12), 1.16 (3H, s, H-27), 0.97 (3H, s, H-23), 0.95 (3H, s, H-24), 0.94 (3H, s, H-30), 0.91 (3H, s, H-29), 0.82 (3H, s, H-26), 0.78 (3H, s, H-25); ^{13}C -NMR (125 MHz, CD_3OD) δ : 180.3 (C-28), 145.3 (C-13), 123.6 (C-12), 79.7 (C-3), 56.8 (C-5), 49.0 (C-9), 47.7 (C-17), 47.3 (C-19), 42.9 (C-14), 42.8 (C-18), 40.6 (C-8), 39.8 (C-1), 38.2 (C-4), 34.9 (C-7), 34.8 (C-10), 34.0 (C-22), 33.9 (C-21), 33.6 (C-29), 31.6 (C-20), 28.9 (C-15), 28.7 (C-23), 27.9 (C-2), 26.4 (C-27), 24.5 (C-11), 24.1 (C-16), 24.0 (C-30), 19.5 (C-6), 17.8 (C-26), 16.3 (C-24), 15.9 (C-25)。以上数据与文献数据一致^[28], 故鉴定化合物 **16** 为齐墩果酸。

化合物 **17**: 白色无定型粉末, ESI-MS m/z : 661.4 $[M-H]^-$, 分子式 $C_{37}H_{58}O_{10}$ 。 1H -NMR (600 MHz, pyridine- d_5) δ : 5.47 (1H, brs, H-12), 5.23 (1H, d, $J = 7.8$ Hz, H-1'), 3.70 (3H, s, H-7'), 1.24 (3H, s, H-27), 1.01 (3H, s, H-26), 1.00 (3H, s, H-24), 0.94 (3H, s, H-25), 0.93 (3H, s, H-29), 0.90 (3H, s, H-30); ^{13}C -NMR (150 MHz, pyridine- d_5) δ : 180.1 (C-28), 170.7 (C-6'), 144.7 (C-13), 122.4 (C-12), 106.3 (C-1'), 82.1 (C-3), 77.7 (C-3'), 77.2 (C-5'), 75.4 (C-2'), 73.1 (C-4'), 64.2 (C-23), 51.9 (C-7'), 48.0 (C-9), 47.4 (C-5), 46.5 (C-17), 46.3 (C-19), 43.4 (C-4), 42.0 (C-14), 41.8 (C-18), 39.6 (C-8), 38.5 (C-1), 36.8 (C-10), 34.1 (C-21), 33.1 (C-29), 33.1 (C-22), 32.7 (C-7), 30.8 (C-20), 28.2 (C-15), 26.1 (C-27), 25.9 (C-2), 23.7 (C-16), 23.6 (C-30), 23.5 (C-11), 18.0 (C-6), 17.3 (C-26), 15.9 (C-25), 13.5 (C-24)。以上数据与文献数据一致^[29], 故鉴定化合物 **17** 为 hederagenin 3-*O*- β -*D*-glucuronopyranoside-6'-*O*-methyl ester。

化合物 **18**: 白色无定型粉末, ESI-MS m/z : 809.4

$[M-H]^-$, 分子式 $C_{42}H_{66}O_{15}$ 。 1H -NMR (600 MHz, CD_3OD) δ : 5.37 (1H, d, $J = 8.2$ Hz, H-1''), 5.24 (1H, brs, H-12), 4.43 (1H, d, $J = 7.9$ Hz, H-1'), 3.81 (1H, d, $J = 11.6$ Hz, H-6''a), 3.62 (1H, d, $J = 11.6$ Hz, H-6''b), 1.16 (3H, s, H-27), 0.97 (3H, s, H-25), 0.92 (3H, s, H-30), 0.90 (3H, s, H-29), 0.79 (3H, s, H-26), 0.69 (3H, s, H-24); ^{13}C -NMR (150 MHz, CD_3OD) δ : 178.1 (C-28), 172.9 (C-6'), 144.9 (C-13), 123.8 (C-12), 105.2 (C-1'), 95.7 (C-1''), 82.3 (C-3), 78.7 (C-5''), 78.6 (C-3''), 78.3 (C-3'), 78.1 (C-5'), 75.1 (C-2'), 73.9 (C-2''), 73.6 (C-4'), 71.1 (C-4''), 64.8 (C-23), 62.4 (C-6''), 49.6 (C-9), 48.1 (C-5), 48.0 (C-17), 47.2 (C-19), 43.9 (C-4), 43.0 (C-14), 42.6 (C-18), 40.7 (C-8), 39.6 (C-1), 37.7 (C-10), 34.9 (C-21), 33.5 (C-29), 33.4 (C-7), 33.2 (C-22), 31.5 (C-20), 28.9 (C-15), 26.4 (C-27), 26.2 (C-2), 24.6 (C-11), 24.0 (C-16), 24.0 (C-30), 18.9 (C-6), 17.8 (C-26), 16.5 (C-25), 13.4 (C-24)。以上数据与文献数据一致^[30], 故鉴定化合物 **18** 为 quinoasaponin 9。

化合物 **19**: 白色无定型粉末, ESI-MS m/z : 823.5 $[M-H]^-$, 分子式 $C_{43}H_{68}O_{15}$ 。 1H -NMR (600 MHz, CD_3OD) δ : 5.37 (1H, d, $J = 8.2$ Hz, H-1''), 5.24 (1H, brs, H-12), 4.45 (1H, d, $J = 7.9$ Hz, H-1'), 3.84 (1H, d, $J = 9.8$ Hz, H-6''a), 3.77 (3H, s, H-7'), 3.50 (1H, t, $J = 9.4$ Hz, H-6''b), 1.16 (3H, s, H-27), 0.97 (3H, s, H-25), 0.93 (3H, s, H-30), 0.91 (3H, s, H-29), 0.80 (3H, s, H-26), 0.70 (3H, s, H-24); ^{13}C -NMR (150 MHz, CD_3OD) δ : 178.1 (C-28), 171.5 (C-6'), 144.9 (C-13), 123.8 (C-12), 106.1 (C-1'), 95.7 (C-1''), 83.5 (C-3), 78.7 (C-3''), 78.3 (C-5''), 77.6 (C-3'), 76.7 (C-5'), 75.2 (C-2'), 73.9 (C-2''), 73.2 (C-4'), 71.1 (C-4''), 64.6 (C-23), 62.4 (C-6''), 52.8 (C-7'), 49.6 (C-9), 48.1 (C-5), 48.0 (C-17), 47.2 (C-19), 43.9 (C-4), 43.0 (C-14), 42.6 (C-18), 40.7 (C-8), 39.5 (C-1), 37.7 (C-10), 34.9 (C-21), 33.5 (C-29), 33.4 (C-22), 33.2 (C-7), 31.5 (C-20), 28.9 (C-15), 26.4 (C-2), 26.3 (C-27), 24.6 (C-16), 24.0 (C-11), 24.0 (C-30), 18.8 (C-6), 17.8 (C-26), 16.5 (C-25), 13.4 (C-24)。以上数据与文献数据一致^[31], 故鉴定化合物 **19** 为 hederagenin 3-*O*- β -*D*-glucuronopyranosyl methyl ester-28-*O*- β -*D*-glucopyranoside。

化合物 **20**: 白色无定型粉末, ESI-MS m/z : 971.5 $[M-H]^-$, 分子式 $C_{48}H_{76}O_{20}$ 。 1H -NMR (600 MHz, CD_3OD) δ : 5.38 (1H, d, $J = 8.2$ Hz, H-1'''), 5.23 (1H, brs, H-12), 4.69 (1H, d, $J = 7.8$ Hz, H-1''), 4.51 (1H, d,

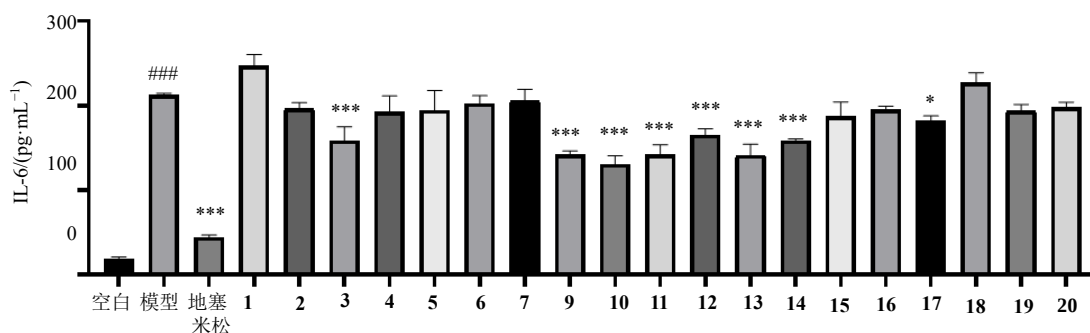
$J = 7.6$ Hz, H-1'), 1.17 (3H, s, H-27), 0.98 (3H, s, H-25), 0.93 (3H, s, H-30), 0.90 (3H, s, H-29), 0.83 (3H, s, H-26), 0.72 (3H, s, H-24); ^{13}C -NMR (150 MHz, CD_3OD) δ : 178.1 (C-28), 173.0 (C-6'), 145.7 (C-13), 123.3 (C-12), 104.5 (C-1''), 104.5 (C-1'), 95.7 (C-1'''), 84.2 (C-3), 81.4 (C-2'), 78.7 (C-5''), 78.5 (C-5'''), 78.4 (C-3'''), 78.3 (C-3''), 77.9 (C-3'), 77.7 (C-5'), 76.2 (C-2''), 73.9 (C-2'''), 73.6 (C-4'), 71.8 (C-4''), 71.5 (C-4'''), 64.8 (C-23), 63.0 (C-6'''), 62.8 (C-6''), 49.9 (C-9), 48.3 (C-5), 48.0 (C-17), 47.5 (C-19), 44.1 (C-4), 43.1 (C-14), 42.9 (C-18), 40.5 (C-8), 39.5 (C-1), 37.7 (C-10), 35.1 (C-21), 33.7 (C-29), 33.5 (C-7), 31.7 (C-22), 30.8 (C-20), 28.9 (C-15), 26.5 (C-27), 26.5 (C-2), 24.6 (C-11), 24.2 (C-16), 24.1 (C-30), 18.9 (C-6), 18.0 (C-26), 16.4 (C-25), 13.4 (C-24)。以上数据与文献数据一致^[32], 故鉴定化合物 **20** 为 3-*O*-[β -*D*-glucopyranosyl-(1 $\rightarrow$ 2)- β -*D*-glucurono-

pyranosyl] hederagenin 28-*O*- β -*D*-glucopyranoside。

4 对 16HBE 气道上皮细胞中炎症因子 IL-6 的影响

采用 CCK-8 法测定化合物对 16HBE 细胞活力的影响, 具体实验操作参考文献方法^[33-34]。结果表明, 除化合物 **8** 外, 其他化合物在 12 $\mu\text{mol/L}$ 浓度下对 16HBE 细胞活力均无显著影响。

采用 ELISA 法评价 LPS 诱导的 16HBE 细胞中炎症因子 IL-6 的水平。取对数生长期的 16HBE 细胞以 2×10^4 个/孔接种于 96 孔板上孵育 24 h, 空白组加入不含药物的培养基, 模型组加入 5 $\mu\text{g/mL}$ LPS^[35], 阳性药物组加入质量浓度为 4 $\mu\text{g/mL}$ 地塞米松, 药物组加入浓度为 12 $\mu\text{mol/L}$ 的待测化合物, 每个浓度设 3 个复孔。培养 24 h 后取细胞上清液, 按照试剂盒说明进行检测。结果表明, 化合物 **3**、**9**~**14**、**17** 能明显降低 16HBE 气道上皮细胞中炎症因子 IL-6 的水平, 具有显著的抗气道炎症活性 (图 2)。



与空白组比较: **** $P < 0.001$; 与模型组比较: * $P < 0.05$ *** $P < 0.001$.
**** $P < 0.001$ vs control group; * $P < 0.05$ *** $P < 0.001$ vs model group.

图 2 化合物对 LPS 诱导的 16HBE 细胞中 IL-6 水平的影响 ($\bar{x} \pm s, n = 3$)

Fig. 2 Effect of compounds on IL-6 levels in LPS induced 16HBE ($\bar{x} \pm s, n = 3$)

5 讨论

从白背叶楸木正丁醇部位中共分离并鉴定了 20 个三萜类化合物, 化合物 **1**、**5**、**7**~**8**、**12**、**19** 首次在五加科植物中分离得到, 化合物 **1**、**4**~**8**、**12**、**17**~**20** 首次在三萜类中分离得到。其中化合物 **1** 为奥古斯丁酸型三萜皂苷; 化合物 **2**~**16** 为齐墩果酸型三萜皂苷, 该类型皂苷为五加科楸木属中最常见的皂苷类型; 化合物 **17**~**20** 为常春藤型三萜皂苷。体外抗气道炎症活性筛选结果表明, 化合物 **3**、**9**~**14**、**17** 能明显降低 LPS 诱导的 16HBE 气道上皮细胞中炎症因子 IL-6 的水平, 具有显著的抗气道炎症活性。构效关系分析表明, 白背叶楸木中三萜类成分抑制气道上皮细胞 IL-6 水平与苷元母核及所连糖数目类型均有关; 其中苷元活性: 齐墩果酸型 > 常

春藤皂苷元型 > 奥古斯丁酸型; 在齐墩果酸型三萜皂苷中, 相比于 3 位、28 位双糖链皂苷, 3 位单糖链皂苷更容易产生抗气道炎症活性。本研究丰富了白背叶楸木三萜类成分分类群并明确了其抗气道炎症活性, 为其阐明药效物质基础提供了科学依据, 对进一步开发利用该药食两用资源打下了坚实基础。

利益冲突 所有作者均声明不存在利益冲突

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