

## 云上杜鹃花化学成分及其抑制 NO 生成活性研究

段苑婷<sup>1</sup>,程琪<sup>1</sup>,毕晓旭<sup>1</sup>,  
王莹<sup>1</sup>,陈冰<sup>1</sup>,栾杰<sup>2</sup>,张高红<sup>1</sup>,何江波<sup>1\*</sup><sup>1</sup>昆明学院医学院,昆明 650214;<sup>2</sup>云南省疾病预防控制中心理化检测中心,昆明 650022

**摘要:**研究云上杜鹃花中的化学成分及其抗炎活性。采用系统分离方法(硅胶柱色谱、凝胶 Sephadex LH-20 柱色谱、半制备液相色谱)对云上杜鹃花乙酸乙酯萃取相进行分离与纯化,再采用<sup>1</sup>H NMR、<sup>13</sup>C NMR 和 MS 等现代波谱学方法对化合物的结构进行鉴定。利用 LPS 诱导 RAW 264.7 巨噬细胞建立炎症模型,评价化合物抗炎活性。从乙酸乙酯部位分离并鉴定 26 个化合物,分别为桉木毒素 I(1)、桉木毒素 II(2)、pieristoxin S(3)、去氢催吐萝芙木醇(4)、megastigm-5-en-3,9-diol(5)、吐叶醇(6)、5,6-epoxy-3-hydroxy-7-megastigmen-9-one(7)、hydroxy-3-oxo- $\alpha$ -ionol(8)、香叶芳樟醇(9)、neginfurool(10)、2,6,10-trimethyldodeca-6,11-diene-2,3,10-triol(11)、9,10-dihydroxy-6,10-dimethylundec-5-en-2-one(12)、(2Z)-2,6-dimethyl-2,7-octadiene-1,6-diol(13)、medioresinol(14)、松脂素(15)、4-O-甲基雪松素(16)、柚皮素(17)、6,8-di-C-methyldihydrokaempferol(18)、去甲基丁香色原酮(19)、二氢松柏醇(20)、mycophenolic methyl ester(21)、苔色酸甲酯(22)、东莨菪亭(23)、水杨醇(24)、对甲氧基苯乙酸(25)、苔黑酚(26)。活性筛选结果表明,13、16、18 抑制 LPS 诱导 RAW 264.7 细胞中 NO 生成,化合物 16 活性较强,IC<sub>50</sub> 值达 33.5  $\pm$  1.5  $\mu$ mol/L。

**关键词:**云上杜鹃;抗炎活性;吐叶醇;结构鉴定

中图分类号:R284.1

文献标识码:A

文章编号:1001-6880(2024)1-0063-09

DOI:10.16333/j.1001-6880.2024.1.007

**Chemical constituents from flowers of *Rhododendron pachypodum* Balf. f. et W. W. Sm and their inhibitory activity on NO production**DUAN Yuan-ting<sup>1</sup>, CHENG Qi<sup>1</sup>, BI Xiao-xu<sup>1</sup>,  
WANG Ying<sup>1</sup>, CHEN Bing<sup>1</sup>, LUAN Jie<sup>2</sup>, ZHANG Gao-hong<sup>1</sup>, HE Jiang-bo<sup>1\*</sup><sup>1</sup>School of Medicine, Kunming University, Kunming 650214, China; <sup>2</sup>Yunnan Center for Disease Control and Prevention Center for Physical and Chemical Testing, Kunming 650022, China

**Abstract:** To study chemical constituents from the flowers of *Rhododendron pachypodum* Balf. f. et W. W. Sm and their anti-inflammatory activities. Systematic separation methods (silica gel column chromatography, gel Sephadex LH-20 column chromatography, semi-preparative liquid chromatography) were used for the separation and purification of the ethyl acetate extract phase of *R. pachypodum*, and then the identification of compounds by modern spectroscopic methods, such as <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS. The anti-inflammatory activities of compounds were evaluated by LPS induced RAW 264.7 inflammatory cell model. Twenty six compounds were isolated from the EtOAc extracts of the flowers of this plant and identified as grayanotoxin I (1), grayanotoxin II (2), pieristoxin S (3), dehydrovomifoliol (4), megastigm-5-en-3,9-diol (5), vomifoliol (6), 5,6-epoxy-3-hydroxy-7-megastigmen-9-one (7), hydroxy-3-oxo- $\alpha$ -ionol (8), geranylinalool (9), negunfurool (10), 2,6,10-trimethyldodeca-6,11-diene-2,3,10-triol (11), 9,10-dihydroxy-6,10-dimethylundec-5-en-2-one (12), (2Z)-2,6-dimethyl-2,7-octadiene-1,6-diol (13), medioresinol (14), pinioresinol (15), 4-O-methylcedrusin (16), naringenin (17), 6,8-di-C-methyldihydrokaempferol (18), noreugenin (19), dihydroconiferyl alcohol (20), mycophenolic methyl ester (21), methyl orsellinate (22), scopoletin (23), salicyl alcohol (24), *p*-methoxyphenylacetic acid (25), and 5-methylbenzene-1,3-diol (26).

接稿日期:2023-08-31

接受日期:2023-11-15

基金项目:云南省应用基础研究计划高校联合面上基金(202001BA070001-043);昆明市春城计划青年拔尖人才项目(C201914001)

\* 通信作者 Tel:86-871-65098540; E-mail:hejiangbo@kmu.edu.cn

Compound **13**, **16** and **18** showed potential inhibitory activity on NO production. Compound **16** showed significant activity, the IC<sub>50</sub> value of compound 16 was 33.5 ± 1.5 μmol/L.

**Key words:** *Rhododendron pachypodum* Balf. f. et W. W. Sm; anti-inflammatory activities; vomifoliol; structure identification

云上杜鹃 (*Rhododendron pachypodum* Balf. f. et W. W. Sm) 为杜鹃花科杜鹃花属植物, 又名波瓣杜鹃、白豆花, 分布于滇东南、西南的大部分地区<sup>[1]</sup>。杜鹃花属植物具有清热解毒、活血止血等功效, 民间将其根、叶用作草药进行内服和外用; 该属植物化学成分种类多样、结构新颖, 主要包括萜类、黄酮类、挥发油、香豆素、酚类等化学成分, 其中以木藜芦烷型 (grayannane) 二萜为代表, 具有显著的镇痛、抗炎、抗肿瘤、抗病毒等生物活性<sup>[2,3]</sup>。目前的研究表明, 杜鹃花属植物满山红、烈香杜鹃、羊躑躅、锦绣杜鹃等植物化学成分复杂, 且具有良好的抗炎活性<sup>[4,5]</sup>, 而对于云南分布较为广泛的云上杜鹃还没有化学成分及生物活性研究。因此, 为了探索云上杜鹃花的化学成分和生物活性, 本实验通过系统分离方法从云上杜鹃花的乙酸乙酯萃取部位中分离得到 26 个化合物, 并对全部化合物进行体外抗炎活性筛选。以期阐明云上杜鹃花的抗炎物质基础, 为进一步开发云上杜鹃花的价值提供理论依据。

## 1 材料与方法

### 1.1 材料

Avance 600 核磁共振仪 (Bruker 公司, TMS 作为内标); 质谱仪 (安捷伦, 6540 UHD Q-TOF/MS); Hanbon-NP7000C 液相 (汉邦仪器公司), 半制备柱 (YMC-Triart C<sub>18</sub>, 250 mm × 10.0 mm, 5 μm); 硅胶 (200 ~ 300 目) 及薄层层析硅胶板 (GF 254, 50 mm × 100 mm) 均为青岛海洋化工厂生产; Sephadex LH-20 (25 ~ 100 μm, 美国 GE 公司, 批号: 17009002); ODS-A (30 ~ 50 μm, 日本 YMC 公司产品, 批号: 15340); 色谱试剂: 甲醇 (上海星可高纯溶剂有限公司)。显色剂为 H<sub>2</sub>SO<sub>4</sub> (10%) 乙醇溶液。RAW 264.7 细胞 (上海药物研究所); DMEM 培养基 (公司: Biological Industries, 批号: 06-1055-57-1 ACS); 胎牛血清 (Bio-Channel 公司, 批号: BC-SE-FBS07); 双抗 (Biosharp 公司, 批号: BL505A); DMSO (索莱宝公司, 批号: D8371)、LPS (Sigma 公司, 批号: L2880-25 mg); Griess 试剂盒碧 (云天公司, 批号: S0023); MTT (碧云天公司, 批号: ST1537-1 g); 地塞米松 (Sigma 公司, 批号: D4902-25 mg)。

云上杜鹃花于 2020 年 5 月采自云南省大理白

族自治州石门关, 经国家林业和草原局昆明勘察设计研究院王浩波研究员鉴定证实为杜鹃花科杜鹃花属云上杜鹃 (*Rhododendron pachypodum* Balf. f. et W. W. Sm) 的花部位, 样品凭证标本 (标本编号 2020-XB) 现封存放于昆明学院医学楼药理学实验室。

### 1.2 提取分离

云上杜鹃花部位 38.0 kg, 粉碎, 采用工业甲醇加热回流提取, 2 h/次, 提取 3 次, 提取液减压浓缩回收甲醇得到浸膏。浸膏采用热水溶解, 然后依次采用等体积石油醚、乙酸乙酯、正丁醇溶剂各萃取 3 次; 其中乙酸乙酯萃取液减压浓缩回收乙酸乙酯后, 得到 1.1 kg 浸膏, 然后采用硅胶柱色谱进行分离, 硅胶 (200 ~ 300 目, 800 g) 拌样, 柱体积硅胶 4.0 kg, 硅胶柱 (16 cm × 120 cm)。依次用氯仿甲醇 (100% → 50%) 梯度洗脱, 每 1 000 mL 收集为 1 个流分。根据 TLC 检测, 总共得到 8 个流分 (XB-1 ~ XB-8)。

其中组分 XB-2 (31 g) 采用硅胶柱色谱 (石油醚: 丙酮, 20: 1) 洗脱, 得到组分 XB-2 (1 ~ 2), 其中 XB-2-1 利用正相硅胶柱色谱分离, 再通过半制备液相 (YMC-Triart C<sub>18</sub>, 250 mm × 10.0 mm, 5 μm), 90% 乙腈洗脱得到化合物 **9** (1.8 mg, *t<sub>R</sub>* = 17.38 min); XB-3 (40 g) 组分经正相硅胶柱色谱 (石油醚: 丙酮, 20: 1 → 1: 1) 梯度洗脱得到 XB-3 (1 ~ 2); XB-3-1 用凝胶 Sephadex LH-20 柱分离, 得到化合物 **21** (6.7 mg) 和 **22** (3.1 mg); XB-3-2 用凝胶 Sephadex LH-20 柱分离和 ODS-A (甲醇: 水, 10% → 100%) 梯度洗脱, 得到 XB-3-2 (1 ~ 5), XB-3-2-1 用正相硅胶柱色谱, 采用石油醚: 乙酸乙酯, 5: 1 等度洗脱, 获得化合物 **7** (6.2 mg), XB-3-2-2 经过凝胶 Sephadex LH-20 柱纯化得到化合物 **19** (16.7 mg), XB-3-2-3 经过反相半制备液相纯化 (40% 甲醇, 3 mL/min) 得到化合物 **23** (22.7 mg, *t<sub>R</sub>* = 13.62 min), XB-3-2-4 采用反相半制备液相纯化 (YMC-Triart C<sub>18</sub>, 250 mm × 10.0 mm, 5 μm), 50% 甲醇洗脱得到化合物 **24** (3.4 mg, *t<sub>R</sub>* = 10.95 min), XB-3-2-5 经过硅胶柱色谱 (石油醚: 乙酸乙酯, 2: 1) 等度洗脱获得化合物 **14** (43.4 mg) 和 **15** (108 mg); 组分 XB-4 (48 g) 经过 ODS-A (甲醇: 水, 10% → 100%) 梯度洗脱和凝胶 Sephadex LH-20 柱分离, 得到 XB-4 (1 ~ 6), XB-4-1 采用正相硅胶柱

色谱分离,以石油醚:丙酮,6:1等度洗脱,获得化合物 **10** (10.7 mg)、**17** (3.5 mg),XB-4-2 经过凝胶 Sephadex LH-20 柱纯化,得到化合物 **4** (13.2 mg),XB-4-3 经过硅胶柱色谱(石油醚:丙酮,5:1)等度洗脱得到化合物 **5** (4.5 mg)、**18** (8.3 mg),XB-4-4 经过凝胶 Sephadex LH-20 柱纯化,得到化合物 **20** (5.8 mg),XB-4-5 经过反相半制备液相(YMC-Triart C<sub>18</sub>, 250 mm × 10.0 mm, 5 μm), 80% 甲醇洗脱得到化合物 **6** (35 mg, *t<sub>R</sub>* = 16.79 min),XB-4-6 利用反相半制备液相(YMC-Triart C<sub>18</sub>, 250 mm × 10.0 mm, 5 μm), 60% 甲醇洗脱得到化合物 **1** (15.2 mg, *t<sub>R</sub>* = 12.19 min) 与 **3** (6.8 mg, *t<sub>R</sub>* = 13.56 min);组分 XB-5 (31 g) 经过 ODS-A (甲醇:水, 10% → 100%) 梯度洗脱和 Sephadex LH-20 (甲醇) 柱色谱洗脱得到 XB-5 (1 ~ 6), 其中 XB-5-1 采用正相硅胶柱,用石油醚:乙酸乙酯,3:1 等度纯化得化合物 **2** (9.1 mg)、**16** (22.6 mg),XB-5-2 经过硅胶柱色谱(石油醚:丙酮,10:1) 等度洗脱获得化合物 **25** (14 mg),XB-5-3 经过硅胶柱色谱(石油醚:丙酮,8:1) 等度洗脱得到化合物 **26** (3.2 g),XB-5-4 经过半制备液相(YMC-Triart C<sub>18</sub>, 250 mm × 10.0 mm, 5 μm), 65% 甲醇洗脱得到化合物 **11** (9.6 mg, *t<sub>R</sub>* = 12.68 min),XB-5-5 经过半制备液相纯化(YMC-Triart C<sub>18</sub>, 250 mm × 10.0 mm, 5 μm), 50% 甲醇洗脱得到化合物 **12** (1.8 mg, *t<sub>R</sub>* = 18.09 min) 和 **13** (2.3 mg, *t<sub>R</sub>* = 21.52 min),XB-5-5 采用凝胶 Sephadex LH-20 柱纯化,得到化合物 **8** (26.5 mg)。

### 1.3 抑制 NO 生成活性研究

参考 Lei 等<sup>[6]</sup>的方法,采用 MTT 法检测各化合物对 RAW 264.7 细胞活力的影响。消化对数期生长的 RAW 264.7 细胞,计数,以  $1 \times 10^5$  个细胞/孔铺 96 孔板,置于 5% CO<sub>2</sub>, 37°C 培养箱培养过夜,次日加浓度为 100 μmol/L 的不同药物和地塞米松(DXM)预处理 2 h,空白对照加 DMSO 处理,2 h 之后再加 LPS (1 μg/mL),继续培养 24 h,紫色结晶充分溶解后,在 490 nm 测 OD 值计算抑制率。然后采用 Griess 法检测 RAW 264.7 细胞释放 NO 的含量。每孔里面换 1 mL 的无血清 DMEM 培养基,加入稀释好的化合物,浓度均为 3.3、11、33、100 μmol/L,空白加等体积的 DMSO,阳性对照加地塞米松(33 μmol/L)预处理 2 h 后,用无血清的 DMEM 培养基稀释标准品,其浓度分别是:0.1、2.5、10、20、40、60、和 100 μmol/L。取待测样品和标准品各 50 μL,加

到新 96 孔板,每个样品设 3 个复孔,之后每孔加入 50 μL Griess Reagent I,接着再加入 Griess Reagent II,540 nm 处测吸光值,然后计算化合物的 IC<sub>50</sub> 值。

## 2 结果

### 2.1 结构鉴定

**化合物 1** 无色油状;ESI-MS: *m/z* 435 [M + Na]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD) δ: 5.46 (1H, s, H-14), 3.59 (1H, dd, *J* = 11.5, 4.5 Hz, H-3), 3.20 (1H, overlap, H-1), 2.62 (1H, dd, *J* = 11.9, 4.5 Hz, H-2), 2.10 (3H, s, -COMe), 1.36 (3H, s, H-20), 1.32 (3H, s, H-19), 1.17 (3H, s, H-17), 0.96 (3H, s, H-18); <sup>13</sup>C NMR (150 MHz, CD<sub>3</sub>OD) δ: 51.6 (C-1), 35.7 (C-2), 83.2 (C-3), 52.4 (C-4), 84.9 (C-5), 74.3 (C-6), 43.8 (C-7), 51.3 (C-8), 56.8 (C-9), 79.2 (C-10), 22.8 (C-11), 27.8 (C-12), 55.5 (C-13), 83.8 (C-14), 60.8 (C-15), 79.9 (C-16), 24.1 (C-18), 19.4 (C-19), 27.9 (C-20), 21.6 (C-21), 172.7 (C-22)。以上数据与文献<sup>[7]</sup>报道一致,故鉴定为桉木毒素 I。

**化合物 2** 无色油状;ESI-MS: *m/z* 375 [M + Na]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 5.34 (1H, s, H-14), 5.11 (1H, s, H-20β), 4.99 (1H, s, H-20α), 4.05 (1H, dd, *J* = 9.2, 2.6 Hz, H-6), 3.65 (1H, d, *J* = 6.7 Hz, H-3), 2.97 (1H, m, H-1), 2.67 (1H, t, *J* = 7.4 Hz, H-9), 2.03 (1H, d, *J* = 14.9 Hz, H-15α), 1.97 (1H, d, *J* = 14.9 Hz, H-15β), 1.90 (1H, m, H-12α), 1.74 (1H, m, H-12β), 1.69 (2H, m, H-11), 1.42 (3H, s, H-17), 1.23 (3H, s, H-19), 1.02 (3H, s, H-18); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 44.4 (C-1), 38.9 (C-2), 82.4 (C-3), 49.3 (C-4), 82.9 (C-5), 70.1 (C-6), 40.5 (C-7), 50.7 (C-8), 51.1 (C-9), 151.5 (C-10), 24.1 (C-11), 25.6 (C-12), 53.0 (C-13), 80.3 (C-14), 60.5 (C-15), 81.8 (C-16), 24.0 (C-17), 23.6 (C-18), 18.5 (C-19), 113.9 (C-20)。以上数据与文献<sup>[8]</sup>报道一致,故鉴定为桉木毒素 II。

**化合物 3** 无色油状;ESI-MS: *m/z* 375 [M + Na]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD) δ: 5.07 (1H, s, H-20α), 5.00 (1H, s, H-20β), 3.78 (1H, dd, *J* = 9.6, 1.8 Hz, H-6), 3.60 (1H, dd, *J* = 6.6, 2.4 Hz, H-3), 2.97 (1H, t, *J* = 9.0 Hz, H-1), 2.49 (1H, t-like, H-9), 2.39 (1H, m, H-2α), 1.19 (3H, s, H-19), 1.12 (3H, s, H-17), 0.97 (3H, s, H-18); <sup>13</sup>C NMR (150 MHz, CD<sub>3</sub>OD) δ: 45.2 (C-1), 38.8 (C-2), 82.4 (C-

3), 51.3 (C-4), 84.0 (C-5), 71.7 (C-6), 47.0 (C-7), 40.9 (C-8), 49.0 (C-9), 153.1 (C-10), 28.2 (C-11), 32.4 (C-12), 81.0 (C-13), 60.3 (C-15), 78.8 (C-16), 21.4 (C-17), 24.4 (C-18), 19.0 (C-19), 119.7 (C-20)。以上数据与文献<sup>[9]</sup>报道一致,故鉴定为 pieristoxin S。

**化合物 4** 无色油状;ESI-MS:  $m/z$  245 [M + Na]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 6.83 (1H, d,  $J$  = 15.7 Hz, H-7), 6.47 (1H, d,  $J$  = 15.7 Hz, H-8), 5.96 (1H, t-like, H-4), 2.31 (3H, s, H-10), 1.11 (3H, s, H-11), 1.02 (3H, s, H-12); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 41.6 (C-1), 49.8 (C-2), 197.6 (C-3), 128.1 (C-4), 160.4 (C-5), 79.5 (C-6), 145.1 (C-7), 130.6 (C-8), 197.1 (C-9), 28.6 (C-10), 24.5 (C-11), 23.1 (C-12), 18.9 (C-13)。以上数据与文献<sup>[10]</sup>报道一致,故鉴定为去氢催吐萝芙木醇。

**化合物 5** 无色油状;ESI-MS:  $m/z$  213 [M + H]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.94 (1H, m, H-3), 3.80 (1H, m, H-9), 2.24 (1H, dd,  $J$  = 16.2, 5.3 Hz, H-4 $\alpha$ ), 2.18 (2H, m, H-7), 1.71 (1H, m, H-4 $\beta$ ), 1.67 (1H, m, H-2 $\alpha$ ), 1.62 (3H, s, H-13), 1.51 (2H, m, H-8), 1.42 (1H, m, H-2 $\beta$ ), 1.21 (3H, d,  $J$  = 6.2 Hz, H-10), 1.03 (3H, s, H-11); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 37.9 (C-1), 48.5 (C-2), 65.3 (C-3), 42.3 (C-4), 124.1 (C-5), 136.8 (C-6), 24.4 (C-7), 39.7 (C-8), 68.8 (C-9), 23.4 (C-10), 28.5 (C-11), 29.7 (C-12), 19.7 (C-13)。以上数据<sup>[11]</sup>与文献报道一致,故鉴定该化合物为 megastigm-5-en-3,9-diol。

**化合物 6** 白色粉末;ESI-MS:  $m/z$  247 [M + Na]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 5.91 (1H, s, H-4), 5.86 (1H, m, H-8), 5.79 (1H, d,  $J$  = 15.8 Hz, H-7), 4.41 (1H, m, H-9), 2.45 (1H, dd,  $J$  = 17.0, 4.7 Hz, H-2 $\alpha$ ), 2.25 (1H, d,  $J$  = 17.0 Hz, H-2 $\beta$ ) 1.91 (3H, s, H-13), 1.30 (3H, d,  $J$  = 6.7 Hz, H-10), 1.08 (3H, s, H-11), 1.01 (3H, s, H-12); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 41.4 (C-1), 49.9 (C-2), 198.3 (C-3), 127.1 (C-4), 163.1 (C-5), 79.3 (C-6), 129.1 (C-7), 135.9 (C-8), 68.2 (C-9), 24.3 (C-10), 23.1 (C-11), 24.0 (C-12), 19.1 (C-13)。以上数据与文献<sup>[12]</sup>报道一致,故鉴定为吐叶醇。

**化合物 7** 无色油状;ESI-MS:  $m/z$  247 [M + Na]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.03 (1H, d,  $J$  = 15.4 Hz, H-7), 6.29 (1H, d,  $J$  = 15.4 Hz, H-8), 2.28

(3H, s, H-10), 1.58 (3H, s, H-13) 1.19 (3H, s, H-11), 0.98 (3H, s, H-12); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 35.1 (C-1), 40.6 (C-2), 64.0 (C-3), 47.0 (C-4), 67.3 (C-5), 69.5 (C-6), 142.4 (C-7), 132.6 (C-8), 197.4 (C-9), 28.3 (C-10), 29.4 (C-11), 25.0 (C-12), 19.9 (C-13)。以上数据与文献<sup>[13]</sup>报道一致,故鉴定为 5,6-epoxy-3-hydroxy-7-megastigmen-9-one。

**化合物 8** 无色油状;ESI-MS:  $m/z$  223 [M - H]<sup>-</sup>; <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD)  $\delta$ : 5.90 (1H, s, H-4), 5.80 ~ 5.83 (2H, m, H-7/8), 4.34 (1H, m, H-9), 2.52 (1H, dd,  $J$  = 16.9, 3.5 Hz, H-2 $\alpha$ ), 2.19 (1H, d,  $J$  = 16.3 Hz, H-2 $\beta$ ), 1.94 (3H, dd,  $J$  = 5.3, 1.1 Hz, H-13); <sup>13</sup>C NMR (150 MHz, CD<sub>3</sub>OD)  $\delta$ : 42.5 (C-1), 50.8 (C-2), 201.3 (C-3), 127.1 (C-4), 167.5 (C-5), 80.0 (C-6), 137.0 (C-7), 130.0 (C-8), 68.8 (C-9), 24.5 (C-10), 23.9 (C-11), 23.5 (C-12), 19.6 (C-13)。以上数据与文献<sup>[14]</sup>报道一致,故鉴定为 hydroxy-3-oxo-a-ionol。

**化合物 9** 无色油状;ESI-MS:  $m/z$  291 [M + H]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 5.94 (1H, dd,  $J$  = 17.3, 10.7 Hz, H-2), 5.24 (1H, d,  $J$  = 17.3 Hz, H-1 $\beta$ ), 5.16 (1H, t,  $J$  = 7.2 Hz, H-6), 5.13 (2H, m, H-10, 14), 5.09 (1H, d,  $J$  = 10.7 Hz, H-1 $\alpha$ ), 2.04 (10H, m, H-5, H-8, H-9, H-12, H-13), 1.70 (3H, s, H-16), 1.63 (6H, s, H-18, 19), 1.62 (3H, s, H-20), 1.58 (2H, m, H-4); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 111.9 (C-1), 145.3 (C-2), 73.7 (C-3), 42.3 (C-4), 22.9 (C-5), 124.6 (C-6), 135.9 (C-7), 39.9 (C-8), 27.0 (C-9), 124.4 (C-10), 135.3 (C-11), 39.9 (C-12), 26.8 (C-13), 124.3 (C-14), 131.5 (C-15), 25.9 (C-16), 28.1 (C-17), 16.3 (C-18), 16.2 (C-19), 17.9 (C-20)。以上数据与文献<sup>[15]</sup>报道一致,故鉴定为香叶芳樟醇。

**化合物 10** 无色油状;ESI-MS:  $m/z$  293 [M + K]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 5.92 (1H, dd,  $J$  = 17.4, 10.7 Hz, H-2), 5.60 (1H, m, H-5), 5.60 (1H, m, H-6), 5.20 (1H, d,  $J$  = 17.3 Hz, H-1 $\alpha$ ), 5.06 (1H, d,  $J$  = 10.7 Hz, H-1 $\beta$ ), 1.81 (2H, q,  $J$  = 7.2 Hz, H-9), 1.31 (3H, s, H-14), 1.26 (3H, s, H-12), 1.21 (3H, s, H-15), 1.12 (3H, s, H-13); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 112.2 (C-1), 145.0 (C-2), 72.8 (C-3), 45.4 (C-4), 122.3 (C-5), 140.5 (C-6), 82.9 (C-7), 38.1 (C-8), 26.6 (C-9), 85.7 (C-10), 71.4

(C-11), 27.4 (C-12), 24.3 (C-13), 27.4 (C-14), 27.6 (C-15)。以上数据与文献<sup>[16]</sup>报道一致,故鉴定为 *negunfurol*。

**化合物 11** 无色油状;ESI-MS: $m/z$  279 [M + Na]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 5.91 (1H, dd,  $J$  = 17.3, 11.0 Hz, H-11), 5.22 (1H, d,  $J$  = 17.4 Hz, H-12 $\alpha$ ), 5.21 (1H, m, H-7), 5.07 (1H, dd,  $J$  = 10.7, 1.4 Hz, H-12 $\beta$ ), 3.35 (1H, dd,  $J$  = 10.7, 2.0 Hz, H-3), 2.23 (1H, m, H-5 $\alpha$ ), 2.05 (3H, m, H-5 $\beta$ , 8), 1.62 (3H, s, H-14); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 26.4 (C-1), 73.0 (C-2), 78.2 (C-3), 29.6 (C-4), 36.8 (C-5), 135.1 (C-6), 125.0 (C-7), 22.7 (C-8), 41.9 (C-9), 73.5 (C-10), 145.0 (C-11), 111.8 (C-12), 23.2 (C-13), 15.9 (C-14), 28.0 (C-15)。以上数据与文献<sup>[17]</sup>报道一致,故鉴定为 2,6,10-trimethyldodeca-6,11-diene-2,3,10-triol。

**化合物 12** 无色油状;ESI-MS: $m/z$  251 [M + Na]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 5.15 (1H, dt,  $J$  = 7.1, 1.5 Hz, H-5), 3.33 (1H, d,  $J$  = 10.6 Hz, H-9), 2.48 (2H, t,  $J$  = 7.3 Hz, H-3), 2.28 (2H, m, H-4), 2.14 (3H, s, H-1), 1.98 ~ 2.10 (2H, m, H-7), 1.64 (3H, s, H-11), 1.37 ~ 1.43 (2H, m, H-8), 1.20 (3H, H-12), 1.16 (3H, H-13); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 30.0 (C-1), 208.9 (C-2), 43.6 (C-3), 22.4 (C-4), 123.3 (C-5), 136.2 (C-6), 36.8 (C-7), 29.6 (C-8), 78.2 (C-9), 73.0 (C-10), 15.9 (C-11), 26.4 (C-12), 23.3 (C-13)。以上数据与文献<sup>[18]</sup>报道一致,故鉴定为 9,10-dihydroxy-6,10-dimethylundec-5-en-2-one

**化合物 13** 无色油状;ESI-MS: $m/z$  171 [M + H]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 5.90 (1H, dd,  $J$  = 17.3, 10.7 Hz, H-7), 5.31 (1H, t,  $J$  = 7.5 Hz, H-3), 5.22 (1H, dd,  $J$  = 17.4, 0.9 Hz, H-8 $\alpha$ ), 5.07 (1H, dd,  $J$  = 10.7, 1.0 Hz, H-8 $\beta$ ), 4.12 (2H, dd,  $J$  = 11.9, 5.1 Hz, H-1), 2.12 (2H, m, H-4), 1.79 (3H, d,  $J$  = 1.6 Hz, H-9), 1.41 (2H, m, H-5), 1.29 (3H, s, H-10); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 61.6 (C-1), 134.6 (C-2), 128.5 (C-3), 22.4 (C-4), 42.0 (C-5), 73.5 (C-6), 144.9 (C-7), 111.9 (C-8), 21.5 (C-9), 28.2 (C-10)。以上数据与文献<sup>[19]</sup>报道一致,故鉴定为 (2*Z*)-2,6-dimethyl-2,7-octadiene-1,6-diol。

**化合物 14** 黄色粉末;ESI-MS: $m/z$  411 [M + Na]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$ : 11.12 (1H, s,

4'-OH), 10.84 (1H, s, 4-OH), 7.30 (1H, d,  $J$  = 8.1 Hz, H-5'), 7.28 (1H, s, H-2'), 7.12 (1H, d,  $J$  = 8.0 Hz, H-6'), 7.02 (2H, s, H-2, 6), 4.40 (2H, s, H-7, 7'), 4.08 (2H, m, H-9, 9'), 3.86 (6H, s, 3,5-OMe), 3.80 (3H, s, 3'-OMe), 3.31 (2H, m, H-8, 8'); <sup>13</sup>C NMR (150 MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$ : 132.9 (C-1), 105.4 (C-2, 6), 57.1 (3,5-OMe), 149.9 (C-3, 5), 56.6 (3'-OMe), 137.9 (C-4), 87.3 (C-7), 55.7 (C-8), 72.8 (C-9), 133.8 (C-1'), 111.6 (C-2'), 149.5 (C-3'), 148.5 (C-4'), 117.1 (C-5'), 120.4 (C-6'), 87.1 (C-7'), 55.4 (C-8'), 72.5 (C-9')。以上数据与文献<sup>[20]</sup>报道一致,故鉴定为 *medioresinol*。

**化合物 15** 无色油状;ESI-MS: $m/z$  381 [M + Na]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 6.91 (2H, d,  $J$  = 2.0 Hz, H-2/2'), 6.89 (2H, d,  $J$  = 8.3 Hz, H-5/5'), 6.82 (2H, dd,  $J$  = 8.3, 2.0 Hz, H-6/6'), 4.74 (2H, d,  $J$  = 4.3 Hz, H-7/7'), 4.25 (2H, m, H-9 $\beta$ /9' $\beta$ ), 3.90 (6H, s, 2  $\times$  -OMe), 3.88 (2H, dd,  $J$  = 9.2, 3.6 Hz, H-9 $\alpha$ /9' $\alpha$ ), 3.11 (2H, m, H-8/8'); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 133.1 (C-1/1'), 108.8 (C-2/2'), 146.9 (C-3/3'), 145.4 (C-4/4'), 114.5 (C-5/5'), 119.2 (C-6/6'), 86.1 (C-7/7'), 54.4 (C-8/8'), 71.9 (C-9/9'), 56.2 (2  $\times$  -OMe)。以上数据与文献<sup>[21]</sup>报道一致,故鉴定为松脂素。

**化合物 16** 无色油状;ESI-MS: $m/z$  383 [M + Na]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD)  $\delta$ : 6.95 (1H, d,  $J$  = 1.9 Hz, H-2), 6.82 (1H, dd,  $J$  = 8.1, 1.9 Hz, H-5), 6.76 (1H, d,  $J$  = 8.1 Hz, H-6), 6.72 (2H, s, H-2'/6'), 5.49 (1H, d,  $J$  = 6.2 Hz, H-7), 3.84 (3H, s, 4-OMe), 3.82 (1H, overlap, H-9 $\beta$ ), 3.81 (3H, s, 3-OMe), 3.75 (1H, m, H-8), 3.57 (2H, t,  $J$  = 6.5 Hz, H-9'), 3.47 (1H, dd,  $J$  = 6.3, 6.1 Hz, H-9 $\alpha$ ), 2.62 (2H, t,  $J$  = 8.0 Hz, H-7'), 1.82 (2H, m, H-8'); <sup>13</sup>C NMR (150 MHz, CD<sub>3</sub>OD)  $\delta$ : 137.1 (C-1/1'), 110.7 (C-2), 149.2 (C-3), 147.6 (C-4), 114.2 (C-5), 119.9 (C-6), 89.1 (C-7), 55.6 (C-8), 65.1 (C-9), 116.3 (C-2'), 134.9 (C-3'), 145.4 (C-4'), 130.0 (C-5'), 118.1 (C-6'), 33.1 (C-7'), 36.0 (C-8'), 62.9 (C-9'), 56.9 (3-OMe), 56.5 (4-OMe)。以上数据与文献<sup>[22]</sup>报道一致,故鉴定 4-*O*-甲基雪松素。

**化合物 17** 黄色粉末;ESI-MS: $m/z$  273 [M + H]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD)  $\delta$ : 7.31 (2H, d,  $J$  = 8.6 Hz, H-2'/6'), 6.82 (2H, d,  $J$  = 8.6 Hz, H-3'/

5'), 5.89 (1H, d,  $J = 2.4$  Hz, H-6), 5.88 (1H, d,  $J = 2.4$  Hz, H-8), 2.68 (1H, dd,  $J = 17.2, 3.0$  Hz, H-3 $\alpha$ );  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : 80.6 (C-2), 44.2 (C-3), 198.0 (C-4), 165.6 (C-5), 97.2 (C-6), 168.5 (C-7), 96.3 (C-8), 165.0 (C-9), 103.5 (C-10), 131.2 (C-1'), 129.2 (C-2'/6'), 116.5 (C-3'/5'), 159.2 (C-4'). 以上数据与文献<sup>[23]</sup>报道一致, 故鉴定该柚皮素。

**化合物 18** 黄色粉末; ESI-MS:  $m/z$  339 [M + Na]<sup>+</sup>;  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : 7.36 (2H, d,  $J = 8.6$  Hz, H-2'/6'), 6.84 (2H, d,  $J = 8.6$  Hz, H-3'/5'), 4.91 (1H, d,  $J = 11.5$  Hz, H-3), 4.51 (1H, d,  $J = 11.5$  Hz, H-2), 2.00 (3H, s, H-11), 1.94 (3H, s, H-12);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : 72.6 (C-2), 83.5 (C-3), 197.3 (C-4), 158.9 (C-5), 104.1 (C-6), 162.7 (C-7), 103.3 (C-8), 157.9 (C-9), 100.1 (C-10), 128.6 (C-1'), 129.0 (C-2'/6'), 114.9 (C-3'/5'), 157.8 (C-4'), 6.3 (C-11), 6.8 (C-12)。以上数据与文献<sup>[24]</sup>报道一致, 故鉴定为 6,8-di-*C*-methyl-dihydrokaempferol。

**化合物 19** 黄色粉末; ESI-MS:  $m/z$  191 [M-H]<sup>-</sup>;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 12.81 (1H, s, 5-OH), 6.31 (1H, d,  $J = 2.1$  Hz, H-8), 6.16 (1H, d,  $J = 2.1$  Hz, H-6), 6.15 (1H, s, H-3), 2.33 (3H, s, H-11);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 167.7 (C-2), 107.9 (C-3), 181.8 (C-4), 161.5 (C-5), 98.7 (C-6), 164.1 (C-7), 93.7 (C-8), 157.8 (C-9), 103.4 (C-10), 19.9 (C-11)。以上数据与文献<sup>[25]</sup>报道一致, 故鉴定为去甲基丁香色原酮。

**化合物 20** 黄色油状; ESI-MS:  $m/z$  181 [M-H]<sup>-</sup>;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.84 (1H, d,  $J = 8.1$  Hz, H-5), 6.70 (1H, d,  $J = 2.0$  Hz, H-2), 6.69 (1H, dd,  $J = 8.1, 2.0$  Hz, H-6), 5.48 (1H, s, 4-OH), 3.88 (3H, s, 3-OMe), 3.68 (2H, m, H-3'), 2.65 (2H, t,  $J = 7.7$  Hz, H-1'), 1.87 (2H, m, H-2');  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 133.7 (C-1), 110.9 (C-2), 146.4 (C-3), 143.7 (C-4), 114.2 (C-5), 120.9 (C-6), 34.5 (C-1'), 31.8 (C-2'), 62.3 (C-3'), 55.9 (3-OMe)。以上数据与文献<sup>[26]</sup>报道一致, 故鉴定为二氢松柏醇。

**化合物 21** 黄色粉末; ESI-MS:  $m/z$  357 [M + Na]<sup>+</sup>;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.23 (1H, td,  $J = 7.2, 1.2$  Hz, H-5), 5.20 (2H, s, H-13), 3.76 (3H,

s, H-17), 3.62 (3H, s, H-18), 3.38 (2H, d,  $J = 6.6$  Hz, H-6), 2.40 (2H, dd,  $J = 9.0, 6.6$  Hz, H-2), 2.30 (2H, dd,  $J = 8.6, 7.2$  Hz, H-3), 2.15 (3H, s, H-16), 1.80 (3H, s, H-15);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 174.1 (C-1), 33.1 (C-2), 34.8 (C-3), 134.4 (C-4), 122.9 (C-5), 22.8 (C-6), 122.4 (C-7), 153.9 (C-8), 106.6 (C-9), 116.9 (C-10), 144.2 (C-11), 163.9 (C-12), 70.3 (C-13), 173.2 (C-14), 16.3 (C-15), 11.2 (C-16), 61.2 (C-17), 51.7 (C-18)。以上数据与文献<sup>[27]</sup>报道一致, 故鉴定为 mycophenolic methyl ester。

**化合物 22** 无色晶状; ESI-MS:  $m/z$  183 [M + H]<sup>+</sup>;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 11.74 (1H, s, 2-OH), 6.28 (1H, d,  $J = 2.1$  Hz, H-5), 6.23 (1H,  $J = 2.1$  Hz, H-3), 5.23 (1H, s, 4-OH), 3.92 (3H, s, COOMe), 2.49 (3H, s, Me-8);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 105.9 (C-1), 160.4 (C-2), 101.5 (C-3), 165.6 (C-4), 111.5 (C-5), 144.2 (C-6), 172.3 (C-7), 24.5 (C-8), 52.1 (COOMe)。以上数据与文献<sup>[28]</sup>报道一致, 故鉴定为苔色酸甲酯。

**化合物 23** 无色油状; ESI-MS:  $m/z$  191 [M-H]<sup>-</sup>;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 7.89 (1H, d,  $J = 9.4$  Hz, H-4), 6.76 (1H, s, H-8), 6.19 (1H, d,  $J = 9.3$  Hz, H-3), 3.50 (3H, s, H-11);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 160.7 (C-2), 111.4 (C-3), 144.5 (C-4), 109.5 (C-5), 145.4 (C-6), 149.6 (C-7), 102.8 (C-8), 151.5 (C-9), 110.3 (C-10), 56.0 (C-11)。以上数据与文献<sup>[29]</sup>报道一致, 故鉴定为东莨菪亭。

**化合物 24** 无色油状; ESI-MS:  $m/z$  123 [M-H]<sup>-</sup>;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.22 (1H, t,  $J = 7.8$  Hz, H-4), 7.05 (1H, d,  $J = 7.5$  Hz, H-6), 6.90 (1H, d,  $J = 8.1$  Hz, H-3);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 124.7 (C-1), 156.4 (C-2), 116.8 (C-3), 128.0 (C-4), 120.3 (C-5), 129.8 (C-6), 65.0 (C-7)。以上数据与文献<sup>[30]</sup>报道一致, 故鉴定为水杨醇。

**化合物 25** 无色油状; ESI-MS:  $m/z$  189 [M + Na]<sup>+</sup>;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.11 (2H, d,  $J = 8.5$  Hz, H-2, 6), 6.75 (2H, d,  $J = 8.5$  Hz, H-3, 5), 3.70 (3H, s, 4-OMe), 3.56 (2H, s, H-7);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 130.7 (C-1), 126.0 (C-2, 6), 115.8 (C-3, 5), 155.2 (C-4), 40.5 (C-7), 173.3 (C-8), 52.4 (4-OMe)。以上数据与文献<sup>[31]</sup>报道一致, 故鉴定为甲氧基苯乙酸。

化合物 26 无色油状;ESI-MS: $m/z$  125 [M + H]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 6.24 (2H, d,  $J$  = 2.3 Hz, H-4/6), 6.17 (1H, t,  $J$  = 2.3 Hz, H-2), 2.24 (3H, s, H-7); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 156.8

(C-1/3), 100.1 (C-2), 108.9 (C-4, 6), 141.2 (C-5), 21.6 (C-7)。以上数据与文献<sup>[32]</sup>报道一致,故鉴定为荜黑酚。

化合物 1~26 结构式见图 1。

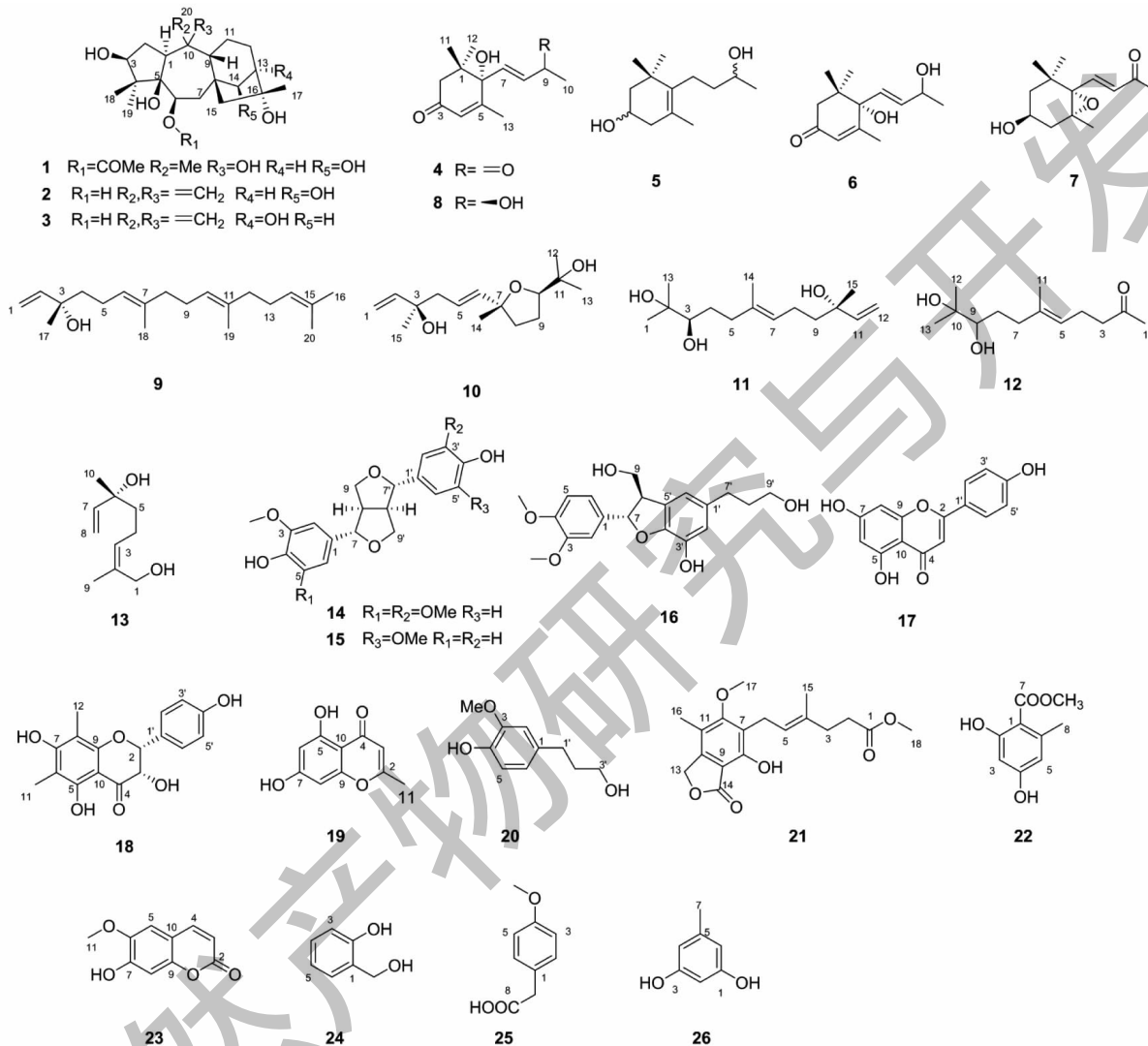


图 1 云上杜鹃花的化学结构

Fig. 1 The chemical structures from flower of *R. pachyodum*

## 2.2 抑制 NO 生成活性研究结果

根据 MTT 法检测各化合物对 RAW 264.7 细胞活性影响,在 490 nm 测 OD 值计算抑制率,结果显示浓度为 100  $\mu\text{mol/L}$  时化合物 4、16、17、18、23 对细胞活力均无显著影响;Griess 法检测 RAW 264.7 细胞释放 NO 的含量,阳性药物选用地塞米松,加入稀释好的化合物 4、13、14、16、18、23 浓度均为 3.3、11、33、100  $\mu\text{mol/L}$ ,空白加等体积的 DMSO,阳性对照加地塞米松 (33  $\mu\text{mol/L}$ );抗炎活性实验结果显

示化合物 13、16 和 18 均能抑制 LPS 诱导的 RAW 264.7 释放 NO 而表现出较好的抗炎活性,其  $\text{IC}_{50}$  分别是:  $75.4 \pm 2.7$ 、 $33.5 \pm 1.5$  和  $85.4 \pm 4.3$   $\mu\text{mol/L}$ ,阳性药物地塞米松在 33.0  $\mu\text{mol/L}$  下显著抑制 LPS 激活的 RAW 264.7 细胞释放 NO。

## 3 结论

杜鹃花在云南分布广泛,资源丰富,云南拥有包含亚种和变种在内的杜鹃花 320 种,占全中国的 56%,世界的 31%<sup>[33]</sup>。云南民族地区食花习俗由来

已久,长期野外实践表明杜鹃花颜色越深毒性越大,人们通常只食用少数白色和浅色的杜鹃花,故白色的云上杜鹃花也存在于云南人的食谱当中<sup>[34]</sup>。云上杜鹃因其仅在云南部分地区分布,尚无成分与活性的研究报道。为研究云上杜鹃花作为菜食花的安全性以及探索其中的抗炎成分,本课题组对云上杜鹃花化学成分进行研究,结果分离得到 26 个化合物。查阅相关文献发现,我们报道的化合物均没有相关抗炎活性报道。因此,对部分单体化合物进行 NO 释放抑制活性筛选,发现化合物(2*Z*)-2,6-dimethyl-2,7-octadiene-1,6-diol (**13**)、4-*O*-甲基雪松素(**16**)、6,8-di-*C*-methyl-dihydrokaempferol (**18**)能对 LPS 诱导 RAW 264.7 巨噬细胞中 NO 的释放有抑制作用,其中化合物 4-*O*-甲基雪松素表现出明显的抗炎活性,IC<sub>50</sub> 值达到 33.5 ± 1.5 μmol/L。此外,本次研究从云上杜鹃花中分离得到 3 个木藜芦烷型毒素(化合物 **1** ~ **3**),文献<sup>[35]</sup>报道这 3 个化合物具有显著的镇痛活性,但是这类化合物属于神经心脏系统毒素,能够增强心肌收缩力,也能引发心脏快速心律失常以致抑制心脏跳动而致死<sup>[3]</sup>。关于木藜芦毒素的研究,国外研究者报道较多,特别是在一些蜂蜜中会检测到该类毒素的存在。因此云上杜鹃花的食用安全性还有待进一步的研究。

#### 参考文献

- 1 Editorial committee of flora of China. Flora Reipublicae Popularis Sinicae: Vol 1 (中国植物志:第一卷) [M]. Beijing: Science Press, 1999;46.
- 2 Tan CB, Chen XL, Liu X, et al. Research advance of *Rhododendron* [J]. Chin Wild Plant Res (中国野生植物资源), 2021, 40:29-36.
- 3 Chen LX, Yang X, Li H, et al. A review on the research hotspots of Ericaceae [J]. Guizhou For Sci Technol (贵州林业科技), 2022, 50:45-50, 39.
- 4 Yao YM, Fang X, Li J, et al. Study on anti-inflammatory effects of diterpenoids and different polarity fractions from *Rhododendron molle* G. Don *in vivo* and *in vitro* [J]. J Shanghai Univ Tradit Chin Med (上海中医药大学学报), 2019, 33:84-88.
- 5 Zhang N, Xiong LL, Sun DJ, et al. Anti-inflammatory scapemic chromanoids and chromenoids from *Rhododendron dauricum* [J]. Fitoterapia, 2022, 162:105300.
- 6 Lei H, Bi X, Lin, X, et al. Heterocornols from the sponge-derived fungus *Pestalotiopsis heterocornis* with anti-inflammatory activity [J]. Mar Drugs, 2021, 19:585.
- 7 Burke JW, Doskotch RW. High Field <sup>1</sup>H and <sup>13</sup>C NMR assignments of grayanotoxin I, IV, and XIV Isolated from *Kalmia angustifolia* [J]. J Nat Prod, 1990, 53:131-137.
- 8 Li HM, Pan YY, Li RT, et al. Study on chemical constituents of *Pieris formosa* [J]. J Kunming Univ Sci Technol (昆明理工大学学报), 2011, 36:56-63.
- 9 Niu CS, Li Y, Liu YB, et al. Analgesic diterpenoids from the twigs of *Pieris formosa* [J]. Tetrahedron, 2016, 72:44-49.
- 10 Kisiel W, Michalska K, Szneler E. Norisoprenoids from aerial parts of *Cichorium pumilum* [J]. Biochem Syst Ecol, 2004, 32:343-346.
- 11 Lin TC, Fang JM, Cheng YS. Terpenes and lignans from leaves of *Chamaecyparis formosensis* [J]. Phytochemistry, 1999, 51:793-801.
- 12 Siddiqui BS, Nadeem KM, Tariq AS, et al. Two new and a known compound from *Lausonia inermis* [J]. Helv Chim Acta, 2003, 86:2164-2169.
- 13 D'Abrosca B, Dellagrecia M, Fiorentino A, et al. Structure elucidation and phytotoxicity of C<sub>13</sub> nor-isoprenoids from *Cestrum parqui* [J]. Phytochemistry, 2004, 65:497-505.
- 14 Wang C. Separation and identification of lipase inhibiting activity components in *Nelumbinis folium* [D]. Shanghai: Shanghai University of Traditional Chinese Medicine (上海中医药大学), 2020.
- 15 Guella G, Pietra F. A new-skeleton diterpenoid, new prenyl-bisabolanes, and their putative biogenetic precursor, from the red seaweed *Laurencia microcladia* from II rogiolo: assigning the absolute configuration when two chiral halves are connected by single bonds [J]. Helv Chim Acta, 2000, 83:2946-2952.
- 16 Zheng CJ, Pu J, Zhang H, et al. Sesquiterpenoids and nortriterpenoids from *Vitex negundo* [J]. Fitoterapia, 2012, 83:49-54.
- 17 Zhong MJ, Kang HH, Ma LY, et al. Study on the secondary metabolites from *Aspergillus pseudoglaucus* derived from offshore mud in dandong [J]. Chin J Mar Drugs (中国海洋药物), 2021, 40:16-22.
- 18 Gliszczynska A, Warzenczyk C. Oxidative biotransformation of farnesol and 10,11-epoxyfarnesol by fungal strains [J]. J Mol Catal B-Enzym, 2008, 52-53:40-48.
- 19 Wang LN, Jin MY, Feng D, et al. Hydrosoluble chemical constituents in *Sanguisorba officinalis* (II) [J]. Chin Tradit Herb Drugs (中草药), 2019, 50:3017-3023.
- 20 Liang RL, Shi GR, Yu SS. Lignans from seed of *Hydnocarpus anthelminthica* [J]. China J Chin Mater Med (中国中药杂志), 2019, 44:1397-1402.
- 21 Kong LY, Min ZD. Studies on chemical constituents of roots



- of *Euphorbia pekinensis* [J]. Acta Pharm Sin (药学报), 1996, 31:45-50.
- 22 Pieter L, Bruyne T, Claeys M, et al. Isolation of a dihydrobenzofuran lignan from south american dragon's blood (*Croton* spp.) as an inhibitor of cell proliferation [J]. J Nat Prod, 1993, 56:899-906.
- 23 Khalid SA, Yagi SM, Khristoca P, et al. (+)-Catechin-5-galloyl ester as a novel natural polyphenol from the bark of *Acacia nilotica* of sudanese origin [J]. Planta Med, 1989, 55:556-558.
- 24 Zeng H, Qian HQ, Liang ZC, et al. Chemical constituents in twigs and leaves of *Rhododendron fortunei* [J]. Chin Tradit Herb Drugs (中草药), 2013, 44:3123-3126.
- 25 Li XD, Wu LJ, Zang XY, et al. Studies on chemical constituents of *Sorbaria sorbifolia* [J]. China J Chin Mater Med (中国中药杂志), 2002, 27:40-42.
- 26 Li JJ, Ren FC, Hu JM, et al. Chemical constituents and cytotoxic activities of *Dendrobium wardianum* [J]. Chin Tradit Herb Drugs (中草药), 2020, 51:1819-1824.
- 27 Rovirosa J, Diaz-Marrero A, Darias J, et al. Secondary metabolites from marine *Penicillium brevicompactum* [J]. J Chil Chem Soc, 2006, 51:775-778.
- 28 Li XF, Jin HZ, Yang M, et al. A new methyl orsellinate glycoside from the aerial parts of *Rhododendron primulaeflorum* [J]. Chin J Nat Med, 2008, 6:336-338.
- 29 Wu YB, Zheng CJ, Qin LP, et al. Antiosteoporotic activity of anthraquinones from *Morinda officinalis* on osteoblasts and osteoclasts [J]. Molecules, 2009, 14:573-593.
- 30 Ding LF, Wang HY, Wang K, et al. Chemical constituents from *Fokienia hodginsii* [J]. Chin Tradit Herb Drugs (中草药), 2017, 48:639-643.
- 31 Zhang J, Liu HX, Liu ZM, et al. Secondary metabolites of endophytic fungus *Letendreaa helminthicola* derived from *Amomum villosum* [J]. Nat Prod Res Dev (天然产物研究与开发), 2021, 33:773-778.
- 32 Gan Q, Xu X, Zhang XM, et al. Study on secondary metabolites of a mangrove endophytic fungus *Stachybotrys chartarum* HDN16-358 [J]. Chin J Mar Drugs (中国海洋药物), 2019, 38:48-52.
- 33 Zhou WW. National *Rhododendron* germplasm resource bank in Yunnan agricultural university [J]. Chin Flow Hort (中国花卉园艺), 2020, 23:36-37.
- 34 Ma JQ. Yunnan People like to eat *Rhododendron* as vegetable [J]. Yunnan Agric Sci Technol (云南农业科技), 2022, 1:52.
- 35 Yan HM. Studies on the chemical constituents and pharmacological activity of *Rhododendron micranthum* Turcz [D]. Shijiazhuang: Hebei Medical University (河北医科大学), 2017.