

南欧大戟的化学成分研究

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摘要: **目的** 研究南欧大戟 *Euphorbia peplus* 果壳的萜类成分及其抗炎活性。**方法** 采用多种色谱技术从该植物果壳乙醇提取物的石油醚萃取部位分离萜类成分, 利用波谱分析(1D/2D NMR、HRMS)及单晶 X 射线衍射等方法鉴定化合物结构, 并通过检测脂多糖诱导的 RAW264.7 巨噬细胞中一氧化氮(NO)产生评价其抗炎活性。**结果** 从南欧大戟果壳的乙醇提取物的石油醚萃取部位共分离得到 13 个萜类化合物, 包括 4 个 paraliane 型二萜(1~4)、1 个 pepluane 型二萜(5)、3 个 jatrophone 型二萜(6~8)、2 个 ingenane 型二萜(9、10)、1 个 abietane 型二萜(11)、1 个 ursane 型三萜(12)和 1 个二降单环二萜(13)。分别鉴定为 (2S,3S,4R,5R,6R,8S,12S,13S,15R)-8 β -acetyl-paralianone D (1)、(1R,2R,3S,4R,5R,6R,8S,12S,13S,14R,15R)-1,5,8,14-tetraacetoxy-3-benzoyloxy-15-hydroxy-9-oxo-paraliane (2)、(2S,3S,4R,5R,6R,8S,12S,13S,14R,15R)-5,8,14-triacetoxy-3-benzoyloxy-15-hydroxy-9-oxo-parapaliane (3)、paralianone A (4)、(2S,3S,4R,5R,6R,8R,9R,10R,12S,13S,14R,15R)-5,8,9,10,14-pentaacetoxy-3-benzoyloxy-15-hydroxy-pepluane (5)、euphepluane A (6)、euphepluane D (7)、(2S,3S,4R,5R,7S,8R,13S,15R)-5 α ,7 β ,8 α -triacetoxy-3 β -benzoyloxy-15 β -hydroxyjatropha-6(17),11E-diene-9,14-dione (8)、20-去氧巨大戟醇(9)、20-O-(2'E,4'Z-decadienyl)ingenol (10)、helioscopinolide D (11)、熊果酸(12)和 (3R,6R,7E,9E,11E)-3-hydroxy-13-apo- α -caroten-13-one (13)。化合物 1 的结构通过单晶 X 衍射得以确认。抗炎活性筛选结果显示, 仅化合物 2 表现出一定的抗炎活性, 其半数抑制浓度(median inhibition concentration, IC₅₀)值为(37.6 \pm 8.2) μ mol/L。**结论** 化合物 1、2、10 和 13 为首次从该植物中分离得到, 化合物 2 具有一定的抗炎活性。丰富了南欧大戟的萜类化学成分, 为其抗炎活性研究提供了依据。

关键词: 大戟科; 南欧大戟; 二萜; 抗炎; 20-去氧巨大戟醇; 熊果酸; (2S,3S,4R,5R,6R,8S,12S,13S,15R)-8 β -acetyl-paralianone D

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Chemical constituents of *Euphorbia peplus*

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Abstract: Objective To investigate the terpenoid constituents of fruit shells of *Euphorbia peplus* and evaluate their anti-inflammatory activities. **Methods** Various chromatographic techniques were applied to isolate terpenoids from the petroleum ether-soluble fraction of the ethanol extract of *E. peplus* fruit shells. The chemical structures of all isolates were elucidated by comprehensive spectroscopic analyses (1D/2D NMR, HRMS) combined with single-crystal X-ray diffraction. Anti-inflammatory activities were assessed by measuring the inhibition of nitric oxide (NO) production in lipopolysaccharide (LPS)-induced RAW264.7 macrophages. **Results** A total of 13 terpenoids were isolated from the petroleum ether fraction of *E. peplus* fruit shells, including four paraliane-type diterpenoids (1–4), one pepluane-type diterpenoid (5), three jatrophone-type diterpenoids (6–8), two ingenane-type diterpenoids (9 and 10), one abietane-type diterpenoid (11), one ursane-type triterpenoid (12), and one dinor-monocyclic diterpenoid (13). They were respectively identified as (2S,3S,4R,5R,6R,8S,12S,13S,15R)-8 β -acetyl-paralianone D (1), (1R,2R,3S,4R,5R,6R,8S,12S,13S,14R,15R)-1,5,8,14-tetraacetoxy-3-benzoyloxy-15-hydroxy-9-oxo-paraliane (2), (2S,3S,4R,5R,6R,8S,12S,13S,14R,15R)-5,8,14-triacetoxy-3-benzoyloxy-15-hydroxy-9-oxo-parapaliane (3), paralianone A (4), (2S,3S,4R,5R,6R,8R,9R,10R,12S,13S,14R,15R)-5,8,9,10,14-

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pentaacetoxy-3-benzoyloxy-15-hydroxyepluane (5), euphepluone A (6), euphepluone D (7), (2*S*,3*S*,4*R*,5*R*,7*S*,8*R*,13*S*,15*R*)-5 α ,7 β ,8 α -triacetoxy-3 β -benzoyloxy-15 β -hydroxyjatropa-6(17),11*E*-diene-9,14-dione (8), 20-deoxyingenol (9), 20-*O*-(2'*E*,4'*Z*-decadienyl)ingenol (10), helioscopinolide D (11), ursolic acid (12) and (3*R*,6*R*,7*E*,9*E*,11*E*)-3-hydroxy-13-apo- α -caroten-13-one (13). The structure of compound 1 was confirmed by single-crystal X-ray diffraction. In the anti-inflammatory activity screening, only compound 2 exhibited inhibitory activity against NO production, with an IC₅₀ value of (37.6 ± 8.2) μ mol/L. **Conclusion** Compounds 1, 2, 10, and 13 were isolated from *E. peplus* for the first time. Compound 2 demonstrated moderate anti-inflammatory activity. This study enriches the terpenoid chemical diversity of terpenoids from *E. peplus* and provides an experimental basis for further research on its anti-inflammatory substances.

Key words: Euphorbiaceae; *Euphorbia peplus* Linn.; diterpenoids; anti-inflammatory; 20-deoxyingenol; ursolic acid; 8 β -acetyl-paralianone D; (2*S*,3*S*,4*R*,5*R*,6*R*,8*S*,12*S*,13*S*,15*R*)-8 β -acetyl-paralianone D

南欧大戟 *Euphorbia peplus* Linn. 为大戟科大戟属 1 年生草本，多具乳汁，原产地中海沿岸（南欧至北非），归化于亚洲、美洲和澳大利亚；在我国相继发现归化植株或种群。多生于路旁、屋旁和草地。全草外涂可治癣，故又称癣草。常用于治疗各种皮肤病（晒斑、疣、鸡冠疮等）、炎症、哮喘、糖尿病和癌症^[1-2]。大戟科二萜凭借其新颖的化学骨架与卓越的成药潜力，已成为天然药物化学领域的研究热点^[3-7]。尽管已有研究对南欧大戟的化学成分进行了初步解析，但其果实中部分微量二萜类成分有待进一步分离与鉴定。本研究从南欧大戟果实的石油醚萃取部位中分离得到 13 个萜类化合物，分别鉴定为 (2*S*,3*S*,4*R*,5*R*,6*R*,8*S*,12*S*,13*S*,15*R*)-8 β -acetyl-paralianone D (1)、(1*R*,2*R*,3*S*,4*R*,5*R*,6*R*,8*S*,12*S*,13*S*,14*R*,

15*R*)-1,5,8,14-tetraacetoxy-3-benzoyloxy-15-hydroxy-9-oxo-paraliane (2)、(2*S*,3*S*,4*R*,5*R*,6*R*,8*S*,12*S*,13*S*,14*R*,15*R*)-5,8,14-triacetoxy-3-benzoyloxy-15-hydroxy-9-oxo-parapliane (3)、paralianone A (4)、(2*S*,3*S*,4*R*,5*R*,6*R*,8*R*,9*R*,10*R*,12*S*,13*S*,14*R*,15*R*)-5,8,9,10,14-pentaacetoxy-3-benzoyloxy-15-hydroxyepluane (5)、euphepluone A (6)、euphepluone D (7)、(2*S*,3*S*,4*R*,5*R*,7*S*,8*R*,13*S*,15*R*)-5 α ,7 β ,8 α -triacetoxy-3 β -benzoyloxy-15 β -hydroxyjatropa-6(17),11*E*-diene-9,14-dione (8)、20-去氧巨大戟醇 (20-deoxymorphoterol, 9)、20-*O*-(2'*E*,4'*Z*-decadienyl) ingenol (10)、熊果酸 (ursolic acid, 12) 和 (3*R*,6*R*,7*E*,9*E*,11*E*)-3-hydroxy-13-apo- α -caroten-13-one (13)。结构见图 1。化合物 1、2、10 和 13 为

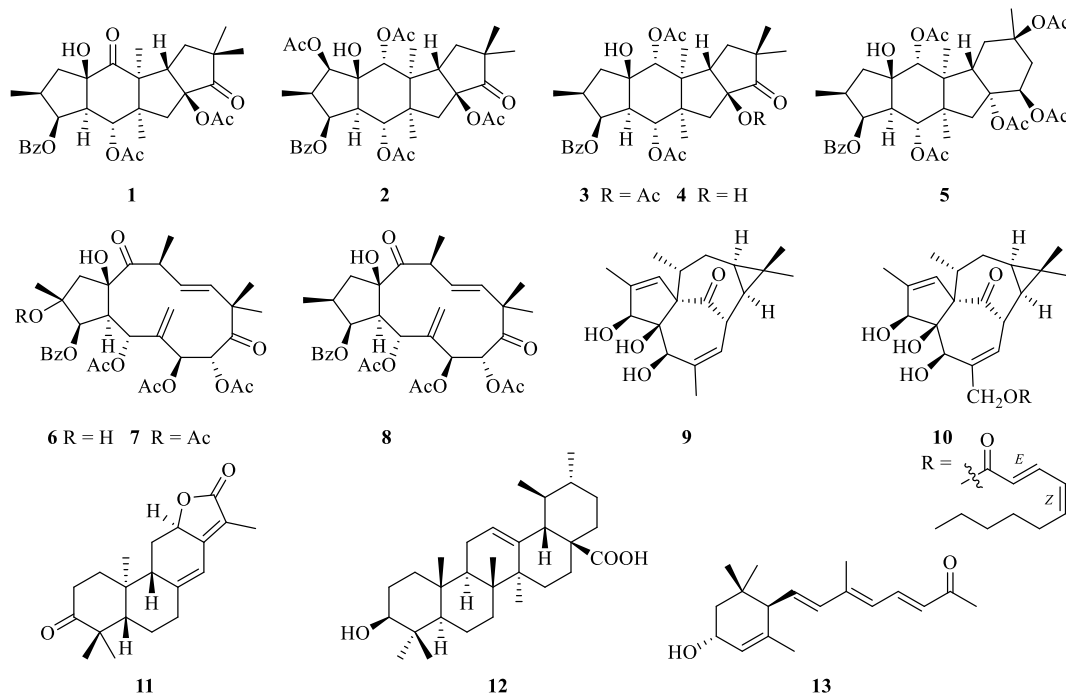


图 1 化合物 1~13 的结构

Fig. 1 Structures of compounds 1—13

首次从该植物中分离得到, 化合物 **1** 的结构通过单晶 X 衍射得以确认。并对分离得到的萜类化合物进行了 LPS 诱导的 RAW264.7 细胞 NO 抑制活性的筛选, 结果显示化合物 **2** 具有一定的抗炎活性。

1 仪器与材料

Agilent Xcalibur Nova X 射线衍射仪(安捷伦科技(中国)有限公司); SWG X-4 型显微熔点仪(上海仪电物理光学仪器有限公司); Autopol I 旋光仪(美国 Rudolph Research Analytical); Chirascan Plus 圆二色谱仪(英国 Applied Photophysics 公司); 紫外可见分光光度计(Shimadzu UV-2450); TENSOR 27 傅里叶变换红外光谱仪(Bruker 公司); AvanceIII-400、AvanceIII-500 核磁共振仪(瑞士 Bruker 公司); 液质联用仪(美国 Finnigan LCQ Deca), Waters-Micromass Q-TOF electrospray 质谱仪; LC-20AT 高效液相色谱仪(PDA SPD-M20A 检测器, 日本岛津公司); 柱色谱硅胶和 GF₂₅₄ 薄层色谱硅胶均来自青岛海洋化工有限公司; 柱色谱硅胶, Sephadex LH-20(美国 GE 公司), CHP-20 MCI(日本 Mitsubishi 公司)和反相硅胶(Merck)等均为填料。手性柱为 Phenomenex Lux cellulose-2, 250 mm×10 mm, 5 μm, 半制备柱为 YMC 公司的 YMC-pack ODS-A(250 mm×10 mm, S-5 μm, 12 nm)。SB-5200DTD 超声波清洗仪(宁波新芝生物科技股份有限公司); SHZ-DIII 型循环水多用真空泵(巩义市予华仪器有限责任公司); ZF-20D 型暗箱紫外分析仪(巩义市予华仪器有限责任公司); N-1100 型旋转蒸发器 EYELA(东京理化器械株式会社); 万分之一分析天平(瑞士 Mettler-Toledo 公司)。95%乙醇、甲醇、石油醚、醋酸乙酯、二氯甲烷(天津市致远化学试剂有限公司)、丙酮(广东广试试剂有限公司)、正丁醇(天津市大茂化学试剂厂), 以上试剂均为分析纯; 乙腈(色谱级, BCR International Trading 有限公司)。

本研究的植物材料于 2023 年 5 月采自云南省昆明市, 经中山大学药学院杨得坡教授鉴定为南欧大戟 *E. peplus* Linn. 的果壳。样品标本(20230503)存放于吉首大学药学院标本室。

2 方法

2.1 提取与分离

于室温 25 °C 条件下, 取 8 kg 南欧大戟果壳干燥粉末, 用 25 L 95%乙醇进行浸提, 重复浸提 3 次(每次浸提 4 h), 最终浓缩得到 1.2 kg 浸膏。用 1 L

水分散, 依次用石油醚(3×4 L)和醋酸乙酯(3×4 L)进行萃取。将石油醚浸膏(0.18 kg)用大孔树脂柱(甲醇-水 4:6→10:0)粗分得到 3 个组分(I~III)。Fr. II(4.0 g)经硅胶柱(石油醚-二氯甲烷 1:0→20:1)和 Sephadex LH-20(甲醇)得到化合物 **12**(4.5 mg)。Fr. III(78.0 g)由硅胶柱(石油醚-二氯甲烷 1:0→1:1)分为 4 个组分(IIIa~III d)。Fr. IIIa(5.0 g)经硅胶柱(石油醚-二氯甲烷 1:0→5:1)得到 3 个部分(IIIa1~IIIa3)。Fr. IIIa 由半制备 HPLC 柱(乙腈-水 7:3, 3 mL/min)纯化得到化合物 **13**(7 mg, $t_R=8$ min)。Fr. IIIb 通过重结晶得到化合物 **6**(17 mg)。Fr. IIIc 由 Sephadex LH-20(甲醇)纯化得到化合物 **9**(120 mg)。Fr. IIIb(13.0 g)经 RP-C₁₈ 柱(甲醇-水 4:6→10:0)得到 3 个部分(IIIb1~IIIb3)。Fr. IIIb1 通过重结晶得到化合物 **1**(20 mg)。Fr. IIIb2 再次经 Sephadex LH-20(甲醇)分为 3 个部分(IIIb2a~IIIb2c), 其中 Fr. IIIb2a 经过硅胶柱(二氯甲烷-甲醇 1:0→200:1)和半制备 HPLC 柱(甲醇-水 7.5:2.5, 3 mL/min)纯化得到化合物 **4**(6 mg)。Fr. IIIb2b 经半制备 HPLC 柱(乙腈-水 6.5:3.5, 3 mL/min)纯化得到化合物 **3**(28 mg, $t_R=20$ min)、**7**(18 mg, $t_R=21$ min)和 **8**(19 mg, $t_R=22$ min)。Fr. IIIb2c 由半制备 HPLC 柱(乙腈-水 6.5:3.5, 3 mL/min)纯化得到化合物 **5**(26 mg, $t_R=13$ min)和 **2**(8 mg, $t_R=18$ min)。Fr. IIIc(1.0 g)经 Sephadex LH-20(甲醇)和硅胶柱(二氯甲烷-甲醇 1:0→200:1)纯化得到 **11**(42 mg)。Fr. III d(2.0 g)由硅胶柱(二氯甲烷-甲醇 1:0→200:1)和半制备 HPLC 柱(乙腈-水 8:2, 3 mL/min)分别纯化得到 **10**(108 mg, $t_R=22$ min)。

2.2 NO 抑制活性测试

采用 Griess 法^[8]检测化合物对脂多糖(lipopolysaccharide, LPS)诱导的 RAW264.7 巨噬细胞一氧化氮(NO)生成的抑制作用。将 RAW264.7 细胞以 4×10^4 个/孔的密度接种于 96 孔板中, 37 °C、5% CO₂ 培养 24 h。实验设空白组、模型组(LPS)及给药组。空白组细胞不做处理; LPS 模型组细胞加入 1 μg/mL LPS 刺激 24 h。受试化合物组先以不同浓度样品预处理 30 min, 再加入 1 μg/mL LPS 继续培养 24 h。随后取 50 μL 的细胞上清液与 100 μL 的 Griess 试剂室温避光反应 10 min, 于 540 nm 测定吸光度(A)值。根据下列公式计算 NO 抑制率, 实验重复 3 次, 槲皮素作为阳性对照。

$$\text{抑制率} = 1 - (A_{\text{给药}} - A_{\text{空白}}) / (A_{\text{模型}} - A_{\text{空白}})$$

3 结果

3.1 结构鉴定

化合物 **1**: 无色晶体 (甲醇), mp 304~305 °C; $[\alpha]_D^{20} -2$ (c 0.3, MeCN); UV (MeCN) λ_{max} ($\log \epsilon$) 195 (4.61), 229 (4.07), 273 (2.97), 280 (2.89) nm; ECD (c 1.1×10^{-4} M, MeCN) λ_{max} ($\Delta \epsilon$) 199 (+3.20), 219 (-0.24), 275(+2.79), 296 (+2.22), 314 (+2.50), 362 (+1.25), 395(+0.37) nm; IR $\nu_{\text{max}}^{\text{KBr}}$ (cm^{-1}): 3 462, 1 747, 1 715, 1 453 的吸收表明化合物存在羟基, 羰基及苯环等基团; 氢谱和碳谱数据见表 1; ESIMS m/z 577 $[\text{M} + \text{Na}]^+$, HRESIMS m/z 577.240 2 $[\text{M} + \text{Na}]^+$ (calcd for $\text{C}_{31}\text{H}_{38}\text{O}_9\text{Na}$, 577.240 8)。结合高分辨质谱和碳谱推测其分子式为 $\text{C}_{31}\text{H}_{38}\text{O}_9$, 对应 13 个不饱和度。化合物 **1** 的核磁谱图显示有 2 个乙酰氧基、1 个苯

甲酰氧基、5 个甲基、3 个亚甲基、5 个次甲基 (2 个连氧 δ_{H} 6.33, 5.83)、5 个季碳 (2 个连氧 δ_{C} 86.1, 92.0) 和 2 个羰基 (δ_{C} 216.9, 207.5)。上述的这些基团占据其中的 9 个不饱和度, 剩余的 4 个不饱和度表明化合物 **1** 为 1 个四环体系。分析发现化合物 **1** 的核磁数据与 8 β -acetyl-paralianone D^[9] 的平面结构一致, 是 1 个 paraliane 二萜。相对构型是由 NOESY 谱图确定, H-AA' (of 3-OBz)/H-5, H-5/OAc-8, H-5/HO-15, H-AA' (of 3-OBz)/HO-15, HO-15/H-12, H-12/H₃-16, H-12/H₃-18 的 NOE 信号表明 OBz, H-5, H-8, H-12, OH-15, H₃-16 和 H₃-18 共面, 并被任意定为 β -朝向。相应地, H-4/H₃-17, H₃-17/H₃-20 的 NOE 信号则表示这些氢为 α -朝向。以上信息确定该化合物的结构与 8 β -acetyl-paralianone D 一致, 并首次由单晶确定其绝对构型为 2*S*,3*S*,4*R*,5*R*,6*R*, 8*S*,12*S*,13*S*,15*R*。

表 1 化合物 **1** 的氢谱和碳谱核磁数据 (400/100 MHz, CDCl₃)

Table 1 ¹H- and ¹³C-NMR data of compound **1** (400/100 MHz, CDCl₃)

碳位	δ_{H}	δ_{C} , type	碳位	δ_{H}	δ_{C} , type
1	2.60 (m, H- α)	42.6, CH ₂	15		86.1, C
	1.67 (dd, $J = 14.1, 4.0$ Hz, H- β)		16	1.07 (s)	16.2, CH ₃
2	2.53 (m)	36.3, CH	17	1.08 (s)	17.9, CH ₃
3	5.83 (t, $J = 4.6$ Hz)	76.9, CH	18	1.26 (s)	28.4, CH ₃
4	2.30 (m)	52.4, CH	19	1.14 (s)	26.8, CH ₃
5	6.33 (d, $J = 12.0$ Hz)	68.8, CH	20	1.08 (s)	17.9, CH ₃
6		55.4, C	3-OBz		165.8, C
7	1.74 (m, H- α), 2.27 (m, H- β)	44.1, CH ₂		7.58 (t, $J = 7.3$ Hz, H-C)	133.4, CH
8		92.0, C			130.0, C
9		216.9, C		7.95 (d, $J = 7.9$ Hz, H-AA')	129.6 \times 2, CH
10		45.1, C		7.44 (t, $J = 7.5$ Hz, H-BB')	128.6 \times 2, CH
11	1.74 (dd, $J = 14.4, 4.3$ Hz)	125.8, CH ₂	5-OAc	1.98, s	169.6, C
	2.08 (dd, $J = 14.4, 11.1$ Hz)				21.0, CH ₃
12	4.25 (dd, $J = 11.1, 4.3$ Hz)	51.7, CH	8-OAc	1.91, s	170.0, C
13		62.0, C			20.5, CH ₃
14		207.5, C	15-OH	3.25, s	

单晶数据如下: $M = 554.61$, $a = 10.25814(5)$ Å ($1 \text{ Å} = 0.1 \text{ nm}$), $b = 14.29951(8)$ Å, $c = 19.08281(10)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 2799.13(7)$ Å³, $T = 100.01(10)$ K, 空间群 $P2_12_12_1$, $Z = 4$, $\mu(\text{Cu K}\alpha) = 0.793 \text{ mm}^{-1}$ 。共收集 28 483 个衍射点, 其中独立衍射点 5 815 个 ($R_{\text{int}} = 0.0341$, $R\sigma = 0.0209$)。最终 R_1 值为 0.028 0 [$I > 2\sigma(I)$], wR_2 值为 0.073 8 [$I > 2\sigma(I)$]。基于全部数据的 $R_1 = 0.0285$, $wR_2 = 0.0743$ 。

对 F^2 的拟合优度为 1.038。Flack 参数 = -0.03 (4)。化合物 **1** 的 X-射线单晶衍射分析结构见图 2, 结构确定为 (2*S*,3*S*,4*R*,5*R*,6*R*,8*S*,12*S*,13*S*,15*R*)-8 β -acetyl-paralianone D。

化合物 **2**: 白色粉末, m/z 657.3 $[\text{M} + \text{H}]^+$, 分子式 $\text{C}_{35}\text{H}_{44}\text{O}_{12}$, ¹H-NMR (400 MHz, CDCl₃) δ : 0.69 (3H, s, H-20), 0.84 (3H, d, $J = 7.6$ Hz, H-16), 1.06 (3H, s, H-17), 1.11 (3H, s, H-18), 1.26 (3H, s, H-19), 1.78

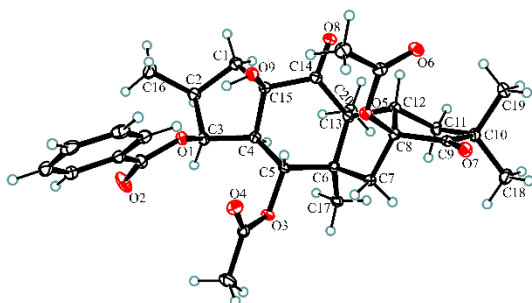


图2 化合物1的单晶图

Fig. 2 X-ray single crystal diffraction patterns of compound 1

(1H, dd, $J = 14.3, 3.1$ Hz, H-11 α), 1.88 (3H, s, 14-OAc), 1.90 (3H, s, 8-OAc), 1.91 (1H, m, H-7 α), 2.10 (3H, s, 1-OAc), 2.12 (3H, s, 5-OAc), 2.16 (1H, dd, $J = 14.3, 11.4$ Hz, H-11 β), 2.15 (1H, m, H-7 β), 2.37 (1H, dd, $J = 11.9, 5.1$ Hz, H-4), 2.86 (1H, s, 15-OH), 2.87 (1H, m, H-2), 4.39 (1H, dd, $J = 11.3, 3.1$ Hz, H-12), 4.82 (1H, s, H-14), 5.05 (1H, d, $J = 10.0$ Hz, H-1 α), 5.76 (1H, dd, $J = 6.9, 5.1$ Hz, H-3), 5.98 (1H, d, $J = 11.9$ Hz, H-5), 7.42 (2H, t, $J = 7.5$ Hz, 3-OBz BB'), 7.55 (1H, t, $J = 7.5$ Hz, 3-OBz C), 8.03 (2H, d, $J = 7.5$ Hz, 3-OBz AA'); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 215.7 (C-9), 170.1 (1-OAc C=O), 169.9 (5-OAc C=O), 169.8 (14-OAc C=O), 169.7 (8-OAc C=O), 166.1 (3-OBz C=O), 133.2 (3-OBz C-1), 130.0 (3-OBz C-2), 129.9 (3-OBz C-4), 129.9 (3-OBz C-3), 128.4 (3-OBz C-5), 128.4 (3-OBz C-6), 90.8 (C-8), 82.7 (C-15), 74.6 (C-1), 73.2 (C-3), 72.2 (C-14), 69.0 (C-5), 52.3 (C-6), 52.0 (C-13), 49.5 (C-12), 46.3 (C-10), 43.5 (C-4), 40.7 (C-7), 38.0 (C-2), 33.5 (C-11), 28.9 (C-18), 25.2 (C-19), 21.0 (1-OAc CH₃), 20.9 (5-OAc CH₃), 20.9 (8-OAc CH₃), 20.7 (14-OAc CH₃), 16.6 (C-20), 16.5 (C-17), 10.2 (C-16)。以上核磁数据与文献报道一致^[10], 鉴定化合物 2 为 (1*R*,2*R*,3*S*,4*R*,5*R*,6*R*,8*S*,12*S*,13*S*,14*R*,15*R*)-1,5,8,14-tetraacetoxy-3-benzoyloxy-15-hydroxy-9-oxo-paraliane。

化合物 3: 白色粉末, m/z 599.3 $[\text{M}+\text{H}]^+$, 分子式 $\text{C}_{33}\text{H}_{42}\text{O}_{10}$, $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 0.73 (3H, s, H-20), 1.04 (3H, d, $J = 7.2$ Hz, H-16), 1.08 (3H, s, H-17), 1.11 (3H, s, H-18), 1.24 (3H, s, H-19), 1.47 (1H, dd, $J = 14.3, 5.6$ Hz, H-1b), 1.78 (1H, dd, $J = 14.4, 3.1$ Hz, H-11a), 1.82 (3H, s, 8-OAc), 1.85 (1H, d, $J = 16.2$ Hz, H-7a), 1.96 (3H, s, 5-OAc), 2.08 (1H, d, $J = 16.2$ Hz, H-7b), 2.11 (3H, s, 14-OAc), 2.14 (1H, dd, $J = 14.4,$

11.3 Hz, H-11b), 2.15 (1H, dd, $J = 14.3, 7.1$ Hz, H-1a), 2.36 (1H, dd, $J = 12.0, 4.2$ Hz, H-4), 2.48 (1H, m, H-2), 3.24 (1H, s, OH), 4.42 (1H, dd, $J = 11.3, 3.1$ Hz, H-12), 4.94 (1H, s, H-14), 5.77 (1H, dd, $J = 5.6, 4.2$ Hz, H-3), 5.95 (1H, d, $J = 12.0$ Hz, H-5), 7.44 (2H, t, $J = 7.5$ Hz, 3-OBz BB'), 7.56 (1H, t, $J = 7.5$ Hz, 3-OBz C), 7.92 (2H, d, $J = 7.5$ Hz, 3-OBz AA'); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 216.4 (C-9), 170.0 (5-OAc C=O), 169.9 (14-OAc C=O), 169.9 (8-OAc C=O), 165.8 (3-OBz C=O), 133.3 (3-OBz C-4), 130.1 (3-OBz C-1), 129.5 (3-OBz C-3), 129.5 (3-OBz C-5), 128.6 (3-OBz C-2), 128.6 (3-OBz C-6), 91.1 (C-8), 84.5 (C-15), 76.7 (C-3), 73.6 (C-14), 69.3 (C-5), 52.7 (C-13), 52.1 (C-6), 49.6 (C-12), 48.2 (C-4), 46.2 (C-10), 44.7 (C-1), 41.4 (C-7), 36.3 (C-2), 33.6 (C-11), 28.8 (C-19), 25.6 (C-18), 21.0 (5-OAc CH₃), 21.0 (14-OAc CH₃), 20.8 (8-OAc CH₃), 17.2 (C-20), 16.7 (C-17), 16.3 (C-16)。以上核磁数据与文献报道一致^[11], 鉴定化合物 3 为 (2*S*,3*S*,4*R*,5*R*,6*R*,8*S*,12*S*,13*S*,14*R*,15*R*)-5,8,14-triacetoxy-3-benzoyloxy-15-hydroxy-9-oxo-paraliane。

化合物 4: 白色粉末, m/z 557.3 $[\text{M}+\text{H}]^+$, 分子式 $\text{C}_{31}\text{H}_{40}\text{O}_9$, $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 0.64 (3H, s, H-20), 1.07 (3H, s, H-17), 1.07 (3H, d, $J = 7.3$ Hz, H-16), 1.09 (3H, s, H-18), 1.29 (3H, s, H-19), 1.51 (1H, dd, $J = 14.1, 4.9$ Hz, H-1b), 1.69 (1H, d, $J = 15.7$ Hz, H-7a), 1.72 (1H, dd, $J = 14.3, 3.9$ Hz, H-11a), 1.83 (1H, d, $J = 15.7$ Hz, H-7b), 2.01 (3H, s, 5-OAc), 2.06 (1H, dd, $J = 14.3, 11.0$ Hz, H-11b), 2.11 (3H, s, 14-OAc), 2.14 (1H, m, H-1a), 2.45 (1H, dd, $J = 11.9, 4.6$ Hz, H-4), 2.56 (1H, m, H-2), 3.12 (1H, s, 15-OH), 3.40 (1H, s, 8-OH), 4.22 (1H, dd, $J = 11.0, 3.9$ Hz, H-12), 4.93 (1H, s, H-14), 5.83 (1H, dd, $J = 6.0, 4.6$ Hz, H-3), 5.92 (1H, d, $J = 11.9$ Hz, H-5), 7.47 (2H, t, $J = 7.4$ Hz, 3-OBz BB'), 7.58 (1H, t, $J = 7.4$ Hz, 3-OBz C), 7.92 (2H, t, $J = 7.4$ Hz, 3-OBz AA'); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 222.1 (C-9), 172.2 (5-OAc C=O), 169.9 (14-OAc C=O), 165.9 (3-OBz C=O), 133.6 (3-OBz C-4), 129.6 (3-OBz C-1), 129.5 (3-OBz C-3), 129.5 (3-OBz C-5), 128.9 (3-OBz C-2), 128.9 (3-OBz C-6), 85.5 (C-8), 84.6 (C-15), 76.5 (C-3), 73.7 (C-14), 70.4 (C-5), 53.3 (C-13), 52.0 (C-6), 51.4 (C-12), 47.9 (C-4), 46.4 (C-10), 44.5 (C-7), 44.3 (C-1), 36.2 (C-2), 33.9 (C-11), 29.5 (C-19), 24.1 (C-18), 21.2 (5-OAc CH₃), 21.0 (14-

OAc CH₃), 16.7 (C-16), 16.5 (C-17), 16.5 (C-20), 以上核磁数据与文献报道一致^[12], 鉴定化合物 4 为 paralianone A。

化合物 5: 白色粉末, MS (*m/z* 701.3 [M+H]⁺), 分子式 C₃₇H₄₈O₁₃, ¹H-NMR (400 MHz, CDCl₃) δ: 0.88 (3H, s, H-20), 1.05 (3H, d, *J* = 7.1 Hz, H-16), 1.06 (3H, s, H-17), 1.50 (1H, dd, *J* = 14.1, 4.9 Hz, H-1b), 1.56 (3H, s, H-19), 1.56 (1H, d, *J* = 15.7 Hz, H-7a), 1.61 (1H, m, H-11a), 1.65 (3H, s, 9-OAc), 1.79 (1H, m, H-18a), 1.94 (3H, s, 5-OAc), 2.02 (3H, s, 14-OAc), 2.05 (3H, s, 10-OAc), 2.11 (3H, s, 8-OAc), 2.37 (1H, m, H-11b), 2.41 (1H, m, H-18b), 2.44 (1H, d, *J* = 15.7 Hz, H-7b), 2.12 (1H, dd, *J* = 14.1, 11.3 Hz, H-1a), 2.36 (1H, dd, *J* = 12.0, 4.3 Hz, H-4), 2.51 (1H, m, H-2), 3.09 (1H, s, 15-OH), 4.13 (1H, dd, *J* = 13.2, 5.9 Hz, H-12), 5.02 (1H, s, H-14), 5.75 (1H, dd, *J* = 5.9, 4.3 Hz, H-3), 5.80 (1H, d, *J* = 5.8 Hz, H-9), 5.82 (1H, d, *J* = 12.0 Hz, H-5), 7.34 (2H, t, *J* = 7.5 Hz, 3-OBz BB'), 7.51 (1H, t, *J* = 7.5 Hz, 3-OBz C), 7.94 (2H, t, *J* = 7.5 Hz, 3-OBz AA'); ¹³C-NMR (100 MHz, CDCl₃) δ: 171.1 (10-OAc), 170.4 (9-OAc), 169.9 (5-OAc), 169.8 (8-OAc), 169.0 (14-OAc), 165.6 (3-OBz C=O), 133.1 (3-OBz C-4), 130.4 (3-OBz C-1), 129.4 (3-OBz C-3), 129.4 (3-OBz C-5), 128.3 (3-OBz C-2), 128.3 (3-OBz C-6), 87.2 (C-8), 84.1 (C-15), 80.0 (C-10), 76.3 (C-3), 73.8 (C-14), 69.8 (C-5), 67.4 (C-9), 51.2 (C-13), 49.0 (C-6), 48.5 (C-4), 46.6 (C-12), 44.7 (C-1), 40.1 (C-7), 38.4 (C-18), 36.0 (C-2), 31.2 (C-11), 28.6 (C-19), 22.3 (10-OAc CH₃), 22.3 (9-OAc CH₃), 21.5 (8-OAc CH₃), 21.0 (5-OAc CH₃), 21.0 (14-OAc CH₃), 16.5 (C-17), 16.4 (C-16), 16.2 (C-20)。以上核磁数据与文献报道一致^[13], 鉴定化合物 5 为 (2*S*,3*S*,4*R*,5*R*,6*R*,8*R*,9*R*,10*R*,12*S*,13*S*,14*R*,15*R*)-5,8,9,10,14-pentaacetoxy-3-benzoyloxy-15-hydroxyeupluane。

化合物 6: 无色晶体, ESI-MS *m/z* 629.3 [M+H]⁺, 分子式 C₃₃H₄₀O₁₂, ¹H-NMR (400 MHz, CDCl₃) δ: 6.33 (1H, dd, *J* = 7.7, 3.8 Hz, H-5), 5.97 (1H, d, *J* = 15.9 Hz, H-11), 5.96 (1H, d, *J* = 1.9 Hz, H-7), 5.81 (1H, dd, *J* = 15.9, 9.8 Hz, H-12), 5.54 (1H, d, *J* = 3.5 Hz, H-3), 5.38 (1H, s, H-8), 5.32 (1H, brs, H-17), 5.60 (1H, brs, H-17), 4.38 (1H, dq, *J* = 9.8, 6.5 Hz, H-13), 4.30 (1H, brs, 15-OH), 3.54 (1H, m, H-4), 2.47 (1H, d, *J* = 15.6 Hz, H-1), 2.23 (1H, d, *J* = 15.6 Hz, H-1), 2.08 (3H,

s, 8-OAc), 2.05 (3H, s, 7-OAc), 1.81 (3H, s, 2-OH), 1.68 (3H, s, 5-OAc), 1.38 (3H, s, H-16), 1.36 (3H, s, H-20), 1.34 (3H, s, H-18), 1.22 (3H, s, H-19), 8.12 (2H, d, *J* = 7.4 Hz, 3-OBz AA'), 7.57 (1H, t, *J* = 7.4 Hz, 3-OBz C), 7.46 (2H, t, *J* = 7.7 Hz, 3-OBz BB'); ¹³C-NMR (100 MHz, CDCl₃) δ: 213.4 (C-14), 205.0 (C-9), 170.6 (8-OAc C=O), 170.1 (7-OAc C=O), 169.0 (5-OAc C=O), 165.7 (3-OBz C=O), 138.5 (C-6), 138.5 (3-OBz C-1), 136.2 (C-11), 133.5 (3-OBz C-4), 133.2 (C-12), 130.1 (3-OBz C-3, 5), 128.7 (3-OBz C-2, 6), 85.2 (C-15), 81.1 (C-3), 79.3 (C-5), 79.3 (C-2), 72.8 (C-8), 65.2 (C-7), 52.4 (C-1), 49.7 (C-10), 47.8 (C-4), 42.9 (C-13), 25.4 (C-18), 24.1 (C-19), 23.3 (C-16), 20.9 (5-OAc CH₃), 20.8 (7-OAc CH₃), 20.8 (8-OAc CH₃), 20.6 (C-20)。以上核磁数据与文献报道一致^[14], 鉴定化合物 6 为 euphepluone A。

化合物 7: 无色晶体 (甲醇), ESI-MS *m/z* 671.3 [M+H]⁺, 分子式 C₃₅H₄₂O₁₃, ¹H-NMR (400 MHz, CDCl₃) δ: 8.14 (2H, d, *J* = 7.4 Hz, 3-OBz AA'), 7.58 (1H, t, *J* = 7.4 Hz, 3-OBz C), 7.46 (2H, t, *J* = 7.7 Hz, 3-OBz BB'), 5.96 (1H, m, H-5), 5.95 (1H, d, *J* = 16.0 Hz, H-11), 5.93 (1H, m, H-3), 5.82 (1H, dd, *J* = 16.0, 9.5 Hz, H-12), 5.43 (1H, s, H-17), 5.37 (1H, s, H-7), 5.37 (1H, s, H-8), 5.33 (1H, s, H-17), 4.31 (1H, s, 15-OH), 3.77 (1H, dq, *J* = 13.3, 6.5 Hz, H-13), 3.28 (1H, m, H-4), 3.17 (1H, d, *J* = 16.4 Hz, H-1), 2.29 (1H, d, *J* = 16.4 Hz, H-1), 2.19 (3H, s, 7-OAc), 2.07 (3H, s, 8-OAc), 2.05 (3H, s, 5-OAc), 1.66 (3H, d, *J* = 8.4 Hz, 2-OAc), 1.61 (3H, s, H-16), 1.36 (3H, s, H-20), 1.34 (3H, s, H-18), 1.22 (3H, s, H-19); ¹³C-NMR (100 MHz, CDCl₃) δ: 212.2 (C-14), 204.6 (C-9), 170.4 (5-OAc C=O), 170.1 (8-OAc C=O), 169.9 (7-OAc C=O), 169.0 (2-OAc C=O), 165.3 (3-OBz C=O), 138.5 (3-OBz C-1), 138.0 (C-6), 136.6 (C-11), 133.6 (3-OBz C-4), 132.3 (C-12), 130.2 (3-OBz C-3, 5), 128.7 (3-OBz C-2, 6), 88.5 (C-2), 85.4 (C-15), 78.1 (C-3), 78.1 (C-5), 72.7 (C-8), 65.6 (C-7), 49.8 (C-1), 49.8 (C-10), 48.0 (C-4), 43.9 (C-13), 25.1 (C-18), 24.0 (C-19), 20.9 (5-OAc CH₃), 20.8 (7-OAc CH₃), 20.8 (8-OAc CH₃), 20.6 (C-20), 19.1 (C-16)。以上核磁数据与文献报道一致^[14], 鉴定化合物 7 为 euphepluone D。

化合物 8: 白色粉末, ESI-MS *m/z* 613.3 [M+H]⁺, 分子式 C₃₃H₄₀O₁₁, ¹H-NMR (400 MHz, CDCl₃)

δ : 1.06 (3H, d, $J = 6.5$ Hz, H-16), 1.24 (3H, s, H-19), 1.33 (3H, s, H-18), 1.42 (3H, d, $J = 6.6$ Hz, H-20), 1.72 (3H, s, 5-OAc), 1.97 (1H, dd, $J = 14.1, 11.8$ Hz, H-1b), 2.04 (3H, s, 7-OAc), 2.10 (3H, s, 8-OAc), 2.37 (1H, m, H-2), 2.48 (1H, dd, $J = 14.1, 8.5$ Hz, H-1a), 2.87 (1H, dd, $J = 8.7, 3.6$ Hz, H-4), 3.62 (1H, dd, $J = 9.6, 6.6$ Hz, H-13), 5.34 (1H, s, H-8), 5.35 (1H, s, H-5), 5.52 (1H, s, H-17b), 5.63 (1H, s, H-17a), 5.80 (1H, dd, $J = 16.1, 9.6$ Hz, H-12), 5.81 (1H, d, $J = 3.6$ Hz, H-3), 5.92 (1H, s, H-7), 6.01 (1H, d, $J = 16.1$ Hz, H-11), 7.45 (2H, t, $J = 7.5$ Hz, 3-OBz BB'), 7.55 (1H, t, $J = 7.5$ Hz, 3-OBz C), 8.12 (2H, t, $J = 7.5$ Hz, 3-OBz AA'); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 212.4 (C-14), 204.7 (C-9), 170.5 (7-OAc C=O), 170.1 (5-OAc C=O), 169.0 (8-OAc C=O), 166.0 (3-OBz C=O), 138.2 (C-6), 136.4 (C-11), 133.3 (3-OBz C-4'), 132.4 (C-12), 130.0 (3-OBz C-1'), 130.0 (3-OBz C-2', 6'), 128.6 (3-OBz C-3', 5'), 85.0 (C-15), 77.4 (C-3), 73.1 (C-5), 73.1 (C-8), 63.6 (C-7), 50.8 (C-4), 49.6 (C-10), 46.6 (C-1), 44.1 (C-13), 38.9 (C-2), 25.6 (C-18), 24.0 (C-19), 21.1 (C-20), 20.9 (5,7-OAc CH_3), 20.6 (8-OAc CH_3), 14.1 (C-16)。以上核磁数据与文献报道一致^[15], 鉴定化合物 **8** 为 (2*S*,3*S*,4*R*,5*R*,7*S*,8*R*,13*S*,15*R*)-5 α ,7 β ,8 α -triacetoxy-3 β -benzoyloxy-15 β -hydroxyjatropa-6(17),11*E*-diene-9,14-dione。

化合物 **9**: 无色油状物, ESI-MS m/z 333.2 [$\text{M} + \text{H}$]⁺, 分子式 $\text{C}_{20}\text{H}_{28}\text{O}_4$, $^1\text{H-NMR}$ (400 MHz, CD_3OD) δ : 0.68 (1H, dd, $J = 11.9, 8.4$ Hz, H-1), 0.79 (3H, d, $J = 7.0$ Hz, H-16), 0.95 (1H, m, H-11a), 0.97 (3H, s, H-18), 1.02 (3H, s, H-19), 1.56 (1H, m, H-11b), 1.61 (3H, s, H-20), 1.69 (3H, s, H-17), 2.23 (1H, m, H-12a), 2.32 (1H, m, H-4), 4.02 (1H, d, $J = 14.6$ Hz, H-13), 4.11 (1H, d, $J = 5.4$ Hz, H-5), 4.49 (1H, s, H-14), 5.62 (1H, d, $J = 1.5$ Hz, H-2), 5.66 (1H, d, $J = 5.4$ Hz, H-6); $^{13}\text{C-NMR}$ (100 MHz, CD_3OD) δ : 206.9 (C-3), 139.5 (C-1), 139.2 (C-7), 127.8 (C-2), 122.2 (C-6), 84.6 (C-15), 79.0 (C-14), 75.4 (C-5), 71.9 (C-13), 43.1 (C-8), 38.2 (C-10), 30.5 (C-4), 28.4 (C-9), 23.3 (C-16), 23.1 (C-17), 22.6 (C-11), 22.3 (C-12), 17.1 (C-18), 15.5 (C-19), 15.4 (C-20)。以上核磁数据与文献报道一致^[16], 鉴定化合物 **9** 为 20-去氧巨大戟醇。

化合物 **10**: 无色油状物, ESI-MS m/z 499.3 [$\text{M} + \text{H}$]⁺, 分子式 $\text{C}_{30}\text{H}_{42}\text{O}_6$, $^1\text{H-NMR}$ (400 MHz, CDCl_3)

δ : 0.69 (1H, dd, $J = 14.8, 8.6$ Hz, H-13), 0.89 (1H, t, $J = 7.0$ Hz, H-10'), 0.95 (1H, m, H-14), 0.97 (1H, d, $J = 6.9$ Hz, H-18), 1.05 (3H, s, H-16), 1.11 (3H, s, H-17), 1.29 (2H, m, H-8', 9'), 1.40 (1H, m, H-7'), 1.76 (1H, m, H-12b), 1.85 (3H, d, $J = 1.3$ Hz, H-19), 2.28 (1H, m, H-12a), 2.29 (1H, m, H-6'), 2.34 (1H, m, H-11), 3.69 (1H, d, $J = 10.4$ Hz, H-5), 4.12 (1H, dd, $J = 12.6, 7.3$ Hz, H-8), 4.43 (1H, d, $J = 6.3$ Hz, H-3), 4.61 (1H, d, $J = 12.9$ Hz, H-20b), 4.80 (1H, d, $J = 12.9$ Hz, H-20a), 5.87 (1H, d, $J = 15.2$ Hz, H-2'), 5.89 (1H, m, H-5'), 5.93 (1H, d, $J = 1.5$ Hz, H-1), 6.11 (1H, m, H-7), 6.12 (1H, m, H-4'), 7.61 (1H, dd, $J = 15.2, 11.7$ Hz, H-3'); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 206.9 (C-9), 167.6 (C-1'), 142.4 (C-5'), 140.4 (C-3'), 139.0 (C-2), 136.9 (C-6), 130.1 (C-1), 128.5 (C-7), 126.5 (C-4'), 120.8 (C-2'), 84.5 (C-4), 80.8 (C-3), 73.9 (C-5), 72.7 (C-10), 66.5 (C-20), 44.2 (C-8), 39.9 (C-11), 31.5 (C-8'), 31.1 (C-12), 29.2 (C-7'), 28.6 (C-16), 28.4 (C-6'), 24.1 (C-15), 23.3 (C-14), 23.1 (C-13), 22.6 (C-9'), 17.5 (C-18), 15.6 (C-19), 15.5 (C-17), 14.2 (C-10')。以上核磁数据与文献报道一致^[17], 鉴定化合物 **10** 为 20-*O*-(2'*E*,4'*Z*)-decadienoyl)ingenol。

化合物 **11**: 白色粉末, ESI-MS m/z 315.2 [$\text{M} + \text{H}$]⁺, 分子式 $\text{C}_{20}\text{H}_{26}\text{O}_3$, $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 1.06 (3H, s, H-18), 1.08 (3H, s, H-19), 1.14 (3H, s, H-17), 1.65 (3H, s, H-16), 1.85 (3H, d, $J = 1.3$ Hz, H-20), 1.56 (1H, m, H-1ax), 1.65 (2H, m, H-5ax, 6ax), 1.77 (1H, m, H-11ax), 1.77 (1H, m, H-6eq), 1.84 (1H, m, H-5eq), 2.19 (1H, m, H-1eq), 2.58 (2H, m, H-7eq, 9ax), 2.65 (1H, m, H-2ax), 4.89 (1H, dd, $J = 13.3, 4.9$ Hz, H-12), 2.47 (1H, dd, $J = 15.7, 3.6$ Hz, H-2eq), 6.34 (1H, brs, H-14); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 215.7 (C-3), 175.2 (C-16), 155.7 (C-13), 150.3 (C-8), 117.3 (C-15), 114.9 (C-14), 75.8 (C-12), 54.9 (C-5), 50.8 (C-9), 47.7 (C-4), 41.1 (C-10), 37.5 (C-1), 36.7 (C-7), 34.6 (C-2), 27.9 (C-11), 26.7 (C-17), 24.7 (C-6), 22.0 (C-18), 16.2 (C-19), 8.5 (C-20)。以上核磁数据与文献报道一致^[9], 鉴定化合物 **11** 为 helioscopinolide D。

化合物 **12**: 白色粉末, ESI-MS m/z 447.4 [$\text{M} + \text{H}$]⁺, 分子式 $\text{C}_{30}\text{H}_{48}\text{O}_3$, $^1\text{H-NMR}$ (400 MHz, CD_3OD) δ : 0.99 (3H, s, H-27), 1.06 (3H, s, H-26), 1.12 (3H, d, $J = 6.3$ Hz, H-30), 1.19 (1H, d, $J = 11.6$ Hz, H-15 α), 1.21 (3H, s, H-24), 1.23 (3H, s, H-25), 1.35 (3H, s, H-

23), 1.70~1.90, 2.10~2.30 (16H, m, H-1, 2, 6, 7, 15, 16, 21, 22), 2.42 (1H, d, $J = 11.2$ Hz, H-16 α), 2.81 (1H, brs, H-18), 4.60 (1H, d, $J = 4.4$ Hz, H-3), 5.45 (1H, d, $J = 11.7$ Hz, H-12), 12.3 (1H, s, -COOH); $^{13}\text{C-NMR}$ (100 MHz, CD_3OD) δ : 178.3 (C-28), 138.2 (C-13), 124.6 (C-12), 76.8 (C-3), 54.8 (C-5), 52.4 (C-18), 47.0 (C-17), 46.8 (C-9), 41.6 (C-14), 38.5 (C-19), 38.4 (C-8, 20), 38.2 (C-1), 36.5 (C-4), 36.3 (C-22), 32.7 (C-7), 30.2 (C-21), 28.3 (C-23), 27.5 (C-15), 27.0 (C-2), 23.8 (C-16), 23.3 (C-27), 22.9 (C-11), 21.1 (C-30), 18.0 (C-6), 17.0 (C-26), 16.9 (C-29), 16.1 (C-25), 15.2 (C-24)。以上核磁数据与文献报道一致^[18], 鉴定化合物 **12** 为熊果酸。

化合物 **13**: 淡黄色粉末, ESI-MS m/z 275.2 $[\text{M} + \text{H}]^+$, 分子式 $\text{C}_{18}\text{H}_{26}\text{O}_2$, $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 0.85 (3H, s, H-15), 1.00 (3H, s, H-15), 1.38 (1H, dd, $J = 13.3, 6.7$ Hz, H-2ax), 1.61 (3H, s, H-17), 1.83 (1H, dd, $J = 13.3, 5.9$ Hz, H-2eq), 2.00 (3H, s, H-18), 2.29 (3H, s, H-14), 2.44 (1H, d, $J = 9.7$ Hz, H-16), 4.25 (1H, brs, H-3), 5.57 (1H, brs, H-4), 5.69 (1H, dd, $J = 15.5, 9.9$ Hz, H-7), 6.15 (1H, d, $J = 10.9$ Hz, H-10), 6.18 (2H, d, $J = 14.0$ Hz, H-8, 12), 7.53 (1H, dd, $J = 14.0, 10.9$ Hz, H-11); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 198.6 (C-13), 144.5 (C-9), 139.0 (C-11), 137.2 (C-5), 136.9 (C-8), 133.7 (C-7), 129.8 (C-12), 127.8 (C-10), 125.0 (C-4), 65.8 (C-3), 54.9 (C-6), 44.5 (C-2), 34.0 (C-1), 29.5 (C-15), 27.8 (C-14), 24.9 (C-16), 22.8 (C-17)。以上核磁数据与文献报道一致^[19], 鉴定化合物 **13** 为 (3R,6R,7E,9E,11E)-3-hydroxy-13-apo- α -caroten-13-one。

3.2 化合物的 NO 抑制活性研究

对南欧大戟分离得到的部分二萜 (**1**~**10**) 进行了针对 LPS 诱导的 RAW264.7 细胞 NO 抑制活性的筛选, 测试结果如图 3 所示。结果显示, 化合物 **2** 具有一定的抗炎活性, IC_{50} 为 $(37.6 \pm 8.2) \mu\text{mol/L}$, 弱于阳性对照药[槲皮素 IC_{50} 为 $(8.8 \pm 1.4) \mu\text{mol/L}$], 其余化合物均未显示活性 (浓度为 $50 \mu\text{mol/L}$ 时, NO 抑制率 $< 50\%$)。

4 讨论

本研究从南欧大戟果壳的乙醇提取物中分离并鉴定了 13 个萜类化合物 (**1**~**13**), 包括 4 个 paraliene 型二萜、1 个 pepluane 型二萜、3 个 jatrophone 型二萜 (**6**~**8**)、2 个 ingenane 型二萜 (**9**、**10**)、1 个 abietane 型二萜 (**11**)、1 个 ursane 型三萜

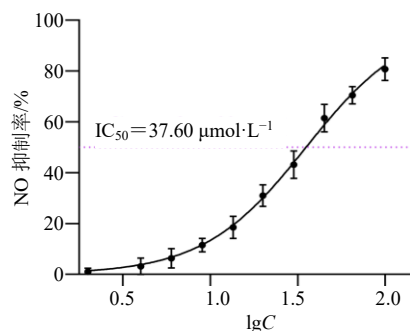


图 3 化合物 **2** 的 NO 抑制曲线

Fig. 3 NO inhibitory curve of compound **2**

(**12**) 和 1 个降单环二萜化合物 (**13**)。其中化合物 **1**、**2**、**10** 和 **13** 为首次从南欧大戟中分离得到。抗炎活性评价结果表明, 多数二萜化合物对 NO 生成仅表现出微弱抑制活性, 仅化合物 **2** 显示出中等程度的抑制作用。本研究不仅丰富了南欧大戟中萜类成分的结构多样性, 还初步揭示了其抗炎潜力, 为其作为抗炎药物的研发提供了科学依据。

利益冲突 所有作者均声明不存在利益冲突

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