多穗金粟兰的化学成分及其抗炎活性研究

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摘　要:对多穗金粟兰(*Chloranthus multistachys* Pei)全草的化学成分及其抗炎活性进行研究。利用硅胶柱色谱等多种色谱方法进行分离纯化和波谱学方法进行结构鉴定,从多穗金粟兰中分离了 22 个化合物,分别鉴定为:(7*S*,8*R*)-dihydrodehydrodiconiferyl alcohol(**1**)、7-ketositosterol(**2**)、6β-羟基豆甾-4-烯-3-酮(**3**)、6α-羟基豆甾-4-烯-3-酮(**4**)、4β,8β-二羟基-5α(H)-桉叶-7(11)-烯-8,12-内酯(**5**)、13-epitorulosol(**6**)、15-nor-14-oxolabda-8(17),12*E*-dien-19-oic acid(**7**)、4α-hydroxy-8,12-epoxyeudesma-7,11-diene-1,6-dione(**8**)、金粟兰素 A(**9**)、fortunilide K(**10**)、(1*E*,4*Z*)-8-hydroxy-6-oxogermacra-1(10),4,7(11)-trieno-12,8-1actone(**11**)、henrilabdane B(**12**)、2′-羟基-4,3′,4′,6′-四甲氧基查尔酮(**13**)、curcolonol(**14**)、zederone epoxide(**15**)、银线草醇 B(**16**)、环银线草醇 A(**17**)、henrilabdane A(**18**)、12-(3-methyl-furan)-labd-8(17)-en-19-oic acid(**19**)、ent-8(9)-pimarene-20-hydroxy-16-nor-15-oic acid(**20**)、反式-*N*-阿魏酰酪胺(**21**)、grossamide(**22**)。其中化合物化合物 **2**、**4**、**21** 和 **22** 为首次从金粟兰属中分离得到、化合物 **1**~**10**、**18**~**22** 为首次从多穗金粟兰中分离得到。此外,采用脂多糖(LPS)诱导的 RAW264.7 细胞对化合物 **5**~**17** 进行了抗炎活性筛选。结果表明化合物 **5**、**10**、**11** 和 **13** 有较好的抗炎活性,其一氧化氮(NO)抑制率分别为 41.22% ±8.28%、40.32% ±15.14%、58.79% ±8.16%、43.85% ±10.04%。

关键词:多穗金粟兰;抗炎活性;结构鉴定;化学成分;倍半萜类

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Chemical constituents from *Chloranthus multistachys* and their anti-inflammatory activity

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Abstract: *Chloranthus multistachys* Pei is a perennial herb and has been used as folk medicine to treat bone fracture, hemostasis swelling pain and pruritus cutanea for centuries in China. In this paper, the chemical constituents of *C. multistachys* and their anti-inflammatory activities were investigated. Twenty-two compounds were isolated by a variety of chromatographic techniques and identified as (7*S*,8*R*)-dihydrodehydrodiconiferyl alcohol (**1**), 7-ketositosterol (**2**), 6β-hydroxystigmast-4-en-3-one (**3**), 6α-hydroxystigmast-4-en-3-one (**4**), 4β,8β-dihydroxy-5α(H)-eudesm-7(11)-en-8,12-olide (**5**), 13-epitorulosol (**6**), 15-nor-14-oxolabda-8(17),12*E*-dien-19-oic acid (**7**), 4α-hydroxy-8,12-epoxyeudesma-7,11-diene-1,6-dione (**8**), spicachlorantin A (**9**), fortunilide K (**10**), (1*E*,4*Z*)-8-hydroxy-6-oxogermacra-1(10),4,7(11)-trieno-12,8-1actone (**11**), henrilabdane B (**12**), 2′-hydroxy-4,3′,4′,6′-tetramethoxychalcone (**13**), curcolonol (**14**), zederone epoxide (**15**), shizukaol B (**16**), cycloshizukaol A (**17**), henrilabdane A (**18**), 12-(3-methyl-furan)-labd-8(17)-en-19-oic acid (**19**), ent-8(9)-pimarene-20-hydroxy-16-nor-15-oic acid (**20**), *N*-trans-feruloyltyramine (**21**) and grossamide (**22**). Compounds **2**, **4**, **21** and **22** were isolated from the genus Chloranthus for the first time, compounds **1**-**10** and **18**-**22** were isolated from *C. multistachys* for the first time. Additionally, compounds **5**-**17** were screened for anti-inflammatory activity by LPS-induced RAW264.7 cells. The results showed that compounds **5**, **10**, **11** and **13** exhibited moderate anti-inflammatory activity with the NO inhibi-

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tion rates of 41.22% ±8.28%, 40.32% ±15.14%, 58.79% ±8.16% and 43.85% ±10.04%, respectively.

Key words: *Chloranthus multistachys* Pei; anti-inflammatory activity; structural identification; chemical composition; sesquiterpenoids

多穗金粟兰(*Chloranthus multistachys* Pei)为金粟兰科(Chloranthaceae)金粟兰属(*Chloranthus* Sw.)植物,又名四块瓦、大四块瓦、四叶对、白毛七等,广泛分布于我国南方地区。该植物常以全草入药,其性味辛、苦、有小毒,具有祛湿散寒、活血止痛、散瘀解毒等功效,主治风寒咳嗽、瘀血肿痛、腰腿痛、疖肿、皮肤瘙痒等病症,是江西民间常用中草药之一[1]。多穗金粟兰的药理学研究表明,其具有抗炎、抑菌、抗肿瘤等作用[2]。目前对于多穗金粟兰的化学成分研究报道较少,只见少量的倍半萜类、酰胺、甾醇等类型化合物的研究报道[3],致使其药效物质基础不清楚,严重影响了该药的研究与开发。因此,对该植物进行系统的化学成分研究与药理活性筛选十分必要。本课题组在前期的活性筛选中发现,多穗金粟兰的二氯甲烷部位有较好的抗炎活性。为进一步阐明其抗炎活性的有效活性成分,为其临床合理用药提供科学依据,我们对多穗金粟兰的二氯甲烷部物的化学成分进行了较深入的研究,并对部分化合物进行了抗炎活性研究,以期为多穗金粟兰的进一步开发和利用提供一定的参考依据。

1 材料与方法

1.1 仪器与材料

Bruker AVANCE III HD 600MHz 型核磁共振波谱仪(Bruker,瑞士);AB SCIEX Triple TOF5600 + 型高分辨飞行时间质谱联用仪(AB SCIEX,美国);RAW264.7 细胞株(中科院上海生命科学研究院);脂多糖(LPS);Griess 试剂(碧云天公司);酶标仪(BioTek 公司,Synergy 4 MLFPTAD);氨基胍(Aminoguanidine);胰蛋白酶(Gibco);离心机(Beckman 公司,AllegraX-15R);培养皿(Corning)、培养瓶(Corning)、48 孔板(Corning);Waters 2695-2998 型高效液相(Waters,美国);Waters 515 制备型液相(Waters,美国);葡聚糖凝胶 Sephadex LH-20(Amersham Pharmacia Biotech,美国);YMC-Pack ODS-A 制备色谱柱(250 mm×20 mm,5 μm,YMC,日本);Buchi 中压制备液相色谱仪(Buchi,瑞士);YMC ODS 反相色谱填料(50 μm,YMC,日本);PRP 512 A 树脂(75 ~ 100 μm,北京聚福树脂厂);AB-104N 型分析天平(METTLER TOLEDO,瑞士);薄层硅胶板 GF_{254}(青岛海洋化工厂);柱色谱用硅胶(100 ~ 200,200 ~ 300 目)青岛海洋化工厂;纯净水(哇哈哈,杭州);甲醇(星可,上海)为色谱纯,其他所用试剂均为分析纯(西陇科学股份有限公司)。

多穗金粟兰全草于 2018 年 11 月采自江西井冈山,由江西中医药大学药学院邓可众副教授鉴定为金粟兰科金粟兰属多穗金粟兰(*Chloranthus multistachys* Pei)的全草。凭证标本(20181128)保存于江西中医药大学药学院中药化学科研室。

1.2 提取与分离

多穗金粟兰全草 20 kg,切碎后加 4 倍量的 95% 乙醇提取 2 次,合并提取液,减压浓缩至无醇味,得浸膏 1 100 g。取部分总浸膏经硅藻土柱色谱,依次用石油醚、二氯甲烷、乙酸乙酯、甲醇洗脱,各洗脱液分别减压浓缩后得石油醚部位 130 g、二氯甲烷部位 375 g、乙酸乙酯部位 30 g、甲醇部位 300 g。

二氯甲烷部位浸膏经 PRP 512 A 树脂柱色谱分离(梯度依次为 30%、50%、70%、95% 乙醇)得到 4 个组分 A ~ D。其中 B 组分(100 g)经硅胶(100 ~ 200 目)柱色谱分离,以石油醚∶乙酸乙酯(20∶1→0∶1)为流动相梯度洗脱,经薄层色谱合样后得到 10 个组分 Fr1 ~ Fr10。Fr8(8 g)通过中压 ODS 柱色谱(甲醇-水)、葡聚糖凝胶 Sephadex LH-20 柱色谱(甲醇)和重结晶分离纯化得到化合物 **5**(20 mg)、**11**(20 mg)、**14**(9 mg)、**15**(8 mg)。Fr9(14.9 g)经硅胶柱色谱分离(二氯甲烷-甲醇,50∶1→0∶1)、中压 ODS 柱色谱(甲醇-水)和制备液相柱色谱(甲醇-水)分离纯化得到化合物 **9**(10 mg)、**10**(11 mg)、**21**(2 mg)、**22**(4 mg);其中 C 组分(107 g)经硅胶(100 ~ 200 目)柱色谱分离,以石油醚∶乙酸乙酯(30∶1→0∶1)为流动相梯度洗脱,经薄层色谱合样后得到 8 个组分 Fr1 ~ Fr8。Fr4(18 g)通过硅胶柱色谱分离(二氯甲烷-甲醇,50∶1→0∶1)、中压 ODS 柱色谱(甲醇-水)、葡聚糖凝胶 Sephadex LH-20 柱色谱(甲醇)和重结晶分离纯化得到化合物 **1**(2 mg)、**6**(15 mg)、**7**(14 mg)、**12**(13 mg)、**13**(10 mg)、**16**(11 mg)、**17**(12 mg)、**18**(4 mg)、**19**(3 mg)、**20**(4 mg);其中 D 组分(30 g)经硅胶(100 ~ 200 目)柱色谱分离,以石油醚

∶乙酸乙酯(50∶1→0∶1)为流动相梯度洗脱,经薄层色谱合样后得到5个组分Fr1~Fr5。Fr4(4.2 g)通过葡聚糖凝胶Sephadex LH-20柱色谱(甲醇)、薄层制备色谱和重结晶得到化合物**2**(3 mg)、**3**(3 mg)、**4**(3 mg)、**8**(9 mg)。

1.3 抗炎活性筛选方法

本实验采用脂多糖(LPS)诱导的RAW264.7细胞炎症筛选模型,对分离得率较高的化合物(**5**~**17**)进行了抗炎活性检测,采用Griess试剂法测定其中产生一氧化氮(NO)的含量[4]以评价化合物的抗炎活性。取对数生长期的RAW264.7细胞经胰蛋白酶消化后重悬得到1×10^6个/mL的细胞悬液,铺板于48孔板中,每孔200 μL,在37 ℃、5% CO_2培养箱中常规培养12 h。再用10 μmol/L的单体化合物预处理1 h,再加入1 μg/mL LPS(终浓度)进行刺激,同时设置空白对照组(培养液)、非样品组(LPS+培养液)、阳性对照组(氨基胍+LPS+培养液),继续培养持续刺激18 h。每组实验在相同条件下设置3个复孔。取100 μL细胞培养液,加入等量Griess试剂(含A B液分别50 μL,碧云天公司),经摇床避光充分混匀15 min后,用酶标仪于570 nm波长下测定各孔OD值,计算化合物的NO生成抑制率[5]。

2 实验结果

2.1 结构鉴定

化合物1 白色无定型粉末;HR-ESI-MS:*m/z* 383.146 2 [M+Na]$^+$(calcd for $C_{20}H_{24}O_6Na$, 383.146 5),分子式为$C_{20}H_{24}O_6$;^{1}H NMR(600 MHz, CD_3OD)δ:6.94(1H,d,*J*=1.8 Hz,H-2),6.75(1H,d,*J*=8.1 Hz,H-5),6.82(1H,dd,*J*=8.1,2.1 Hz,H-6),5.48(1H,d,*J*=6.3 Hz,H-7),3.82(1H,m,H-8),3.75(1H,dd,*J*=11.1,7.2 Hz,H-9a),3.46(1H,q,*J*=6.3 Hz,H-9b),6.72(2H,s,H-2′,6′),2.62(2H,dd,*J*=8.7,6.9 Hz,H-7′),1.80(2H,m,H-8′),3.56(2H,t,*J*=6.5 Hz,H-9′),3.81(3H,s,3-OCH_3),3.85(3H,s,3′-OCH_3);^{13}C NMR(150 MHz, CD_3OD)δ:134.8(C-1),110.5(C-2),149.1(C-3),147.5(C-4),116.1(C-5),119.7(C-6),89.0(C-7),55.5(C-8),65.0(C-9),136.9(C-1′),114.0(C-2′),145.2(C-3′),147.5(C-4′),129.9(C-5′),117.9(C-6′),32.9(C-7′),35.8(C-8′),62.2(C-9′),56.3(3-OCH_3),56.7(3′-OCH_3)。以上数据与文献[6]对照基本一致,故鉴定化合物**1**为(7*S*,8*R*)-dihydrodehydrodiconiferyl alcohol。

化合物2 无色针状结晶(甲醇);HR-ESI-MS:*m/z* 429.372 2 [M+H]$^+$(calcd for $C_{29}H_{49}O_2$, 429.372 7),分子式为$C_{29}H_{48}O_2$;^{1}H NMR(600 MHz, $CDCl_3$)δ:3.68(1H,m,H-3),5.69(1H,br s,H-6),2.45(3H,m),2.24(1H,ddd,*J*=12.6,10.8,2.4 Hz),2.09~1.02(17H,m,包括1.19(3H,H-19)),0.69(3H,s,H-18),0.93(3H,d,*J*=6.6 Hz,H-21),0.83(3H,d,*J*=6.6 Hz,H-26),0.81(3H,d,*J*=6.6 Hz,H-27),0.85(3H,d,*J*=7.2 Hz,H-29);^{13}C NMR(150 MHz,$CDCl_3$)δ:36.5(C-1),31.3(C-2),70.7(C-3),41.9(C-4),165.2(C-5),126.3(C-6),202.5(C-7),45.6(C-8),50.1(C-9),38.8(C-10),21.4(C-11),38.4(C-12),43.2(C-13),50.1(C-14),26.5(C-15),28.7(C-16),54.8(C-17),12.1(C-18),17.5(C-19),36.2(C-20),19.1(C-21),34.1(C-22),26.2(C-23),45.9(C-24),29.2(C-25),19.2(C-26),20.0(C-27),23.2(C-28),12.1(C-29)。以上数据与文献[7]对照基本一致,故鉴定化合物**2**为7-ketositosterol。

化合物3 无色针状结晶(甲醇);HR-ESI-MS:*m/z* 429.372 4 [M+H]$^+$(calcd for $C_{29}H_{49}O_2$, 429.372 7),分子式为$C_{29}H_{48}O_2$;^{1}H NMR(600 MHz, $CDCl_3$)δ:5.82(1H,d,*J*=0.9 Hz,H-4),4.35(1H,m,H-6),2.03(1H,m,H-7),0.74(3H,s,H-18),1.38(3H,s,H-19),0.92(3H,d,*J*=6.6 Hz,H-21),1.70(1H,m,H-25),0.81(3H,m,H-26),0.84(3H,m,H-27),0.85(3H,d,*J*=7.5 Hz,H-29);^{13}C NMR(150 MHz,$CDCl_3$)δ:37.2(C-1),34.4(C-2),200.6(C-3),126.5(C-4),168.6(C-5),73.4(C-6),38.7(C-7),29.9(C-8),53.7(C-9),38.1(C-10),21.1(C-11),39.7(C-12),42.6(C-13),56.2(C-14),24.3(C-15),28.3(C-16),56.0(C-17),12.2(C-18),19.7(C-19),36.3(C-20),18.9(C-21),34.0(C-22),26.7(C-23),46.0(C-24),29.3(C-25),20.0(C-26),19.2(C-27),23.2(C-28),12.1(C-29)。以上数据与文献[8]对照基本一致,故鉴定化合物**3**为6β-羟基豆甾-4-烯-3-酮。

化合物4 无色针状结晶(甲醇);HR-ESI-MS:*m/z* 429.372 4 [M+H]$^+$(calcd for $C_{29}H_{49}O_2$, 429.372 7),分子式为$C_{29}H_{48}O_2$;^{1}H NMR(600 MHz, $CDCl_3$)δ:6.17(1H,d,*J*=1.8 Hz,H-4),4.33(1H,ddd,*J*=12.3,5.7,1.8 Hz,H-6),0.71(3H,s,H-

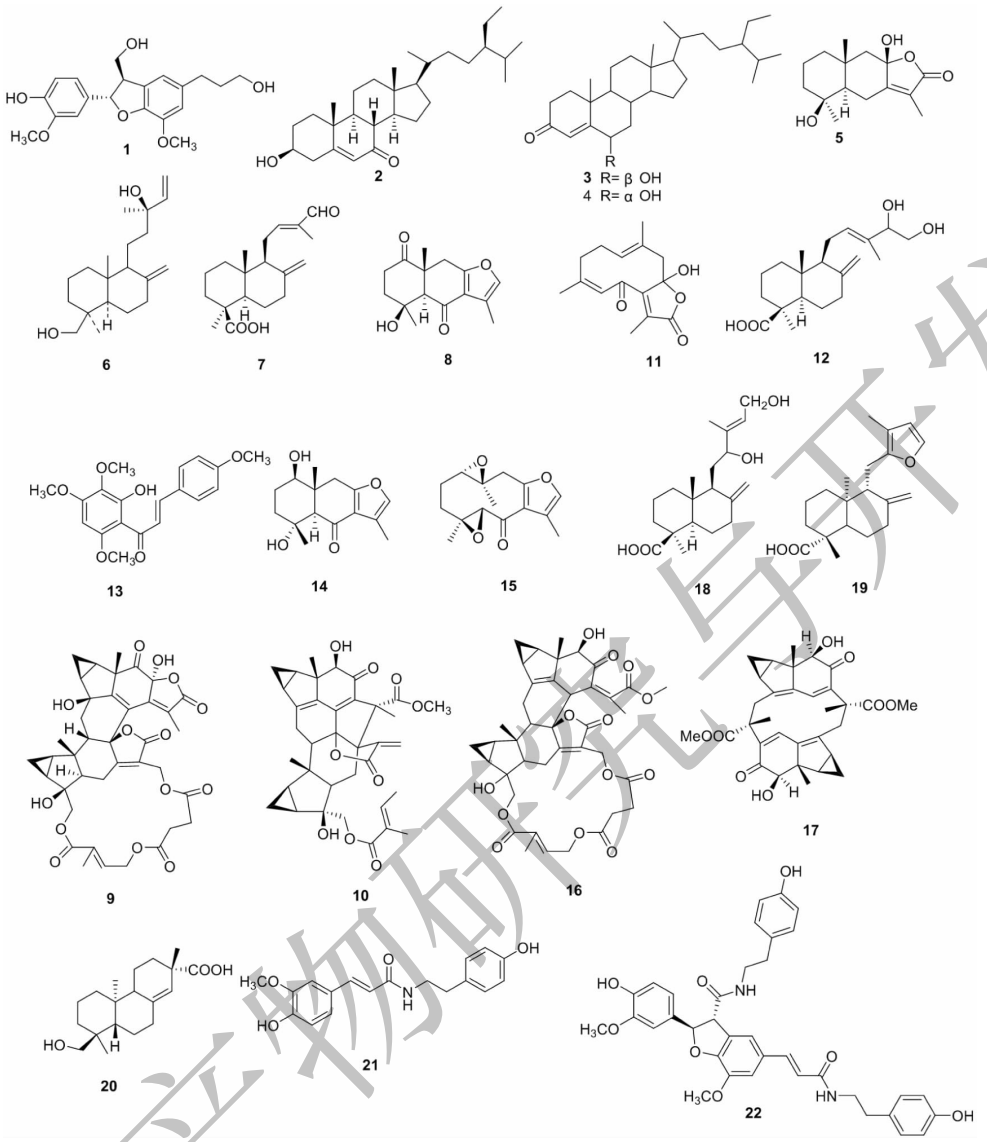

图 1 化合物 1 ~ 22 的结构

Fig. 1 Chemical structures of compounds **1-22**

18),1.18(3H,s,H-19),0.92(3H,d,J = 6.6 Hz,H-21),0.83(3H,d,J = 6.9 Hz,H-26),0.81(3H,d,J = 6.9 Hz,H-27),0.85(3H,d,J = 7.5 Hz,H-29);^{13}C NMR(150 MHz,$CDCl_3$)δ:36.4(C-1),34.3(C-2),199.6(C-3),119.8(C-4),171.7(C-5),68.9(C-6),41.6(C-7),34.0(C-8),53.9(C-9),39.2(C-10),21.2(C-11),39.6(C-12),42.6(C-13),55.7(C-14),24.3(C-15),28.3(C-16),56.1(C-17),12.1(C-18),18.4(C-19),36.2(C-20),18.8(C-21),34.0(C-22),26.2(C-23),45.9(C-24),29.3(C-25),20.0(C-26),19.2(C-27),23.2(C-28),12.1(C-29)。以上数据与文献[9]对照基本一致,故鉴定化合物 **4** 为 6α-羟基豆甾-4-烯-3-酮。

化合物 5 白色粉末;HR-ESI-MS:m/z 267.1597 $[M+H]^+$(calcd for $C_{15}H_{23}O_4$,267.1596),分子式为 $C_{15}H_{22}O_4$;^{1}H NMR(600 MHz,CD_3OD)δ:1.11(1H,m,H-1a),1.51(1H,m,H-1b),1.39(1H,m,H-2a),1.93(1H,m,H-2b),1.42(1H,m,H-3a),1.70(1H,m,H-3b),1.09(1H,t,J = 3.5 Hz,H-5),2.44(1H,m,H-6a),2.82(1H,dd,J = 13.2,2.7 Hz,H-6b),1.35(1H,d,J = 8.4 Hz,H-9a),2.06(1H,d,J = 13.2 Hz,H-9b),1.79(3H,d,J = 1.5 Hz,H-13),1.32(3H,d,J = 3.9 Hz,H-14),1.24(3H,s,H-15);^{13}C NMR(150 MHz,CD_3OD)δ:42.6(C-1),

18.7(C-2),41.7(C-3),72.3(C-4),55.8(C-5),23.1(C-6),164.4(C-7),105.8(C-8),54.9(C-9),36.1(C-10),121.9(C-11),174.6(C-12),7.9(C-13),19.7(C-14),30.4(C-15)。以上数据与文献[10]对比基本一致,故鉴定化合物**5**为4β,8β-二羟基-5α(H)-桉叶-7(11)-烯-8,12-内酯。

化合物6 白色块状结晶(甲醇);HR-ESI-MS:*m/z* 307.263 4 [M+H]$^+$(calcd for $C_{20}H_{35}O_2$,307.263 1),分子式为$C_{20}H_{34}O_2$;^{1}H NMR(600 MHz,$CDCl_3$)δ:1.05(1H,m,H-1a),1.78(1H,m,H-1b),1.48(2H,m,H-2),1.02(1H,m,H-3a),1.72(1H,m,H-3b),1.22(1H,m,H-5),1.29(1H,m,H-6a),1.82(1H,m,H-6b),2.38(1H,ddd,*J*=12.6,4.2,2.4 Hz,H-7a),1.93(1H,td,*J*=12.6,5.1 Hz,H-7b),1.54(1H,m,H-9),1.36(1H,m,H-11a),1.52(1H,m,H-11b),1.24(1H,m,H-12a),1.76(1H,m,H-12b),5.92(1H,m,H-14),5.21(1H,dd,*J*=17.4,1.2 Hz,H-15a),5.06(1H,m,H-15b),1.28(3H,s,H-16),4.81(1H,q,*J*=1.5 Hz,H-17a),4.47(1H,q,*J*=1.5 Hz,H-17b),0.96(3H,s,H-18),3.73(1H,d,*J*=10.8 Hz,H-19a),3.36(1H,dd,*J*=10.8,1.2 Hz,H-19b),0.63(3H,s,H-20);^{13}C NMR(150 MHz,$CDCl_3$)δ:39.1(C-1),19.1(C-2),35.5(C-3),39.0(C-4),56.4(C-5),24.5(C-6),38.7(C-7),148.3(C-8),57.4(C-9),39.8(C-10),17.9(C-11),41.4(C-12),73.8(C-13),145.2(C-14),111.8(C-15),27.2(C-16),106.7(C-17),28.2(C-18),65.1(C-19),15.4(C-20)。以上数据与文献[11]对照基本一致,故鉴定化合物**6**为13-epitorulosol。

化合物7 白色粉末;HR-ESI-MS:*m/z* 305.210 6 [M+H]$^+$(calcd for $C_{19}H_{29}O_3$,305.211 1),分子式为$C_{19}H_{28}O_3$;^{1}H NMR(600 MHz,$CDCl_3$)δ:1.15(1H,m,H-1a),1.82(1H,m,H-1b),1.54(1H,m,H-2a),2.17(1H,m,H-3a),1.37(1H,dd,*J*=12.0,2.7 Hz,H-5),1.99(1H,m,H-6a),2.42(1H,dt,*J*=9.9,2.5 Hz,H-7a),1.90(1H,m,H-9),2.56(1H,m,H-11a),6.42(1H,ddd,*J*=7.4,5.9,1.5 Hz,H-12a),9.32(1H,s,H-14),1.74(3H,d,*J*=1.2 Hz,H-16a),4.38(1H,s,H-17a),4.85(1H,br s,H-17b),1.25(3H,s,H-18),0.67(3H,s,H-20);^{13}C NMR(150 MHz,$CDCl_3$)δ:39.4(C-1),20.0(C-2),37.9(C-3),44.3(C-4),56.2(C-5),25.8(C-6),38.4(C-7),147.7(C-8),55.9(C-9),40.5(C-10),24.6(C-11),156.4(C-12),139.0(C-13),195.5(C-14),9.5(C-16),108.0(C-17),29.1(C-18),184.1(C-19),13.0(C-20)。以上数据与文献[12]对照基本一致,故鉴定化合物**7**为15-nor-14-oxolabda-8(17),12*E*-dien-19-oic acid。

化合物8 无色油状;HR-ESI-MS:*m/z* 263.127 4 [M+H]$^+$(calcd for $C_{15}H_{19}O_4$,263.127 7),分子式为$C_{15}H_{18}O_4$;^{1}H NMR(600 MHz,$CDCl_3$)δ:2.45(1H,ddd,*J*=15.3,4.5,3.0 Hz,H-2a),2.73(1H,td,*J*=15.3,6.0 Hz,H-2b),1.91(1H,td,*J*=14.4,4.5 Hz,H-3a),2.03(1H,ddd,*J*=13.5,6.0,3.0 Hz,H-3b),2.89(1H,s,H-5),3.07(1H,d,*J*=17.7 Hz,H-9a),2.95(1H,d,*J*=17.7 Hz,H-9b),7.12(1H,s,H-12),2.20(3H,d,*J*=1.2 Hz,H-13),1.73(3H,s,H-14),1.27(3H,s,H-15);^{13}C NMR(150 MHz,$CDCl_3$)δ:211.1(C-1),34.8(C-2),39.0(C-3),70.4(C-4),62.2(C-5),195.5(C-6),119.4(C-7),165.9(C-8),35.7(C-9),51.2(C-10),119.1(C-11),140.3(C-12),9.1(C-13),23.9(C-14),20.5(C-15)。以上数据与文献[13]对照基本一致,故鉴定化合物**8**为4*a*-hydroxy-8,12-epoxyeudesma-7,11-diene-1,6-dione。

化合物9 黄色油状;HR-ESI-MS:*m/z* 731.228 3 [M-H]$^-$(calcd for $C_{39}H_{39}O_{14}$,731.229 4),分子式为$C_{39}H_{40}O_{14}$;^{1}H NMR(600 MHz,$CDCl_3$)δ:2.28(1H,d,*J*=5.7 Hz,H-1),1.22(1H,d,*J*=5.1 Hz,H-2a),1.02(1H,q,*J*=8.1 Hz,H-2b),1.78(H,m,H-3),1.81(3H,s,H-13),1.16(3H,s,H-14),2.68(1H,m,H-15a),1.75(1H,t,*J*=12.3 Hz,H-15b),1.55(1H,d,*J*=9.3 Hz,H-1′),1.26(1H,m,H-2′a),0.63(1H,q,*J*=7.8 Hz,H-2′b),1.46(1H,s,H-3′),2.23(1H,dd,*J*=12.6,6.6 Hz,H-5′),3.04(1H,dd,*J*=18.3,12.6 Hz,H-6′a),2.39(1H,dd,*J*=18.3,6.6 Hz,H-6′b),2.60(1H,td,*J*=10.8,5.7 Hz,H-9′),5.40(1H,d,*J*=12.0 Hz,H-13′a),4.51(1H,d,*J*=12.0 Hz,H-13′b),0.95(3H,s,H-14′),4.32(1H,d,*J*=11.4 Hz,H-15′a),4.03(1H,d,*J*=11.4 Hz,H-15′b),6.57(1H,t,*J*=5.7 Hz,H-3′′),4.75(1H,dd,*J*=14.7,5.4 Hz,H-4′′a),4.63(1H,dd,*J*=14.7,6.0 Hz,H-4′′b),1.86(3H,s,H-5′′),2.79(1H,m,H-2′′′a),2.52(1H,m,H-2′′′b),2.71(1H,m,H-3′′′a),2.48(1H,m,H-3′′′b);^{13}C NMR

(150 MHz, $CDCl_3$) δ: 24.4 (C-1), 9.5 (C-2), 30.3 (C-3), 77.6 (C-4), 160.9 (C-5), 122.8 (C-6), 148.0 (C-7), 94.3 (C-8), 200.3 (C-9), 57.1 (C-10), 129.2 (C-11), 170.4 (C-12), 11.5 (C-13), 21.1 (C-14), 40.2 (C-15), 26.8 (C-1′), 10.1 (C-2′), 29.4 (C-3′), 77.4 (C-4′), 55.1 (C-5′), 24.1 (C-6′), 173.7 (C-7′), 85.7 (C-8′), 52.1 (C-9′), 45.2 (C-10′), 123.9 (C-11′), 171.3 (C-12′), 53.5 (C-13′), 24.4 (C-14′), 74.3 (C-15′), 168.0 (C-1″), 129.5 (C-2″), 136.6 (C-3″), 61.9 (C-4″), 13.0 (C-5″), 172.3 (C-1‴), 29.0 (C-2‴), 29.0 (C-3‴), 172.3 (C-4‴)。以上数据与文献[14]对照基本一致,故鉴定化合物**9**为金粟兰素 A。

化合物 10　黄色油状; HR-ESI-MS: *m/z* 639.256 1 [M + Na]$^+$ (calcd for $C_{36}H_{40}O_9Na$, 639.256 4),分子式为 $C_{36}H_{40}O_9$; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.18 (1H, dt, *J* = 8.7, 4.8 Hz, H-1), 1.19 (1H, m, H-2a), 0.63 (1H, m, H-2b), 1.96 (1H, ddd, *J* = 8.4, 5.4, 3.0 Hz, H-3), 3.95 (1H, s, H-9), 1.36 (3H, s, H-13), 1.16 (3H, s, H-14), 2.96 (1H, dd, *J* = 18.0, 7.2 Hz, H-15a), 2.31 (1H, dd, *J* = 18.0, 9.6 Hz, H-15b), 1.66 (1H, m, H-1′), 0.66 (1H, m, H-2′a), 1.22 (1H, m, H-2′b), 1.66 (1H, m, H-3′), 1.65 (1H, m, H-5′), 2.46 (1H, d, *J* = 11.7 Hz, H-6′a), 1.71 (1H, d, *J* = 14.1 Hz, H-6′b), 2.65 (1H, dd, *J* = 9.6, 7.2 Hz, H-9′), 5.52 (1H, s, H-13′a), 6.21 (1H, s, H-13′b), 0.95 (3H, s, H-14′), 4.24 (1H, d, *J* = 11.1 Hz, H-15′a), 4.19 (1H, d, *J* = 11.1 Hz, H-15′b), 6.86 (1H, m, H-2″), 1.82 (3H, s, H-4″), 1.83 (3H, s, H-5″), 3.45 (3H, s, 12-OCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 28.5 (C-1), 15.8 (C-2), 26.6 (C-3), 151.3 (C-4), 135.4 (C-5), 151.4 (C-6), 129.7 (C-7), 197.1 (C-8), 83.2 (C-9), 57.6 (C-10), 65.3 (C-11), 172.0 (C-12), 18.9 (C-13), 14.9 (C-14), 29.3 (C-15), 26.6 (C-1′), 10.3 (C-2′), 29.8 (C-3′), 79.0 (C-4′), 55.7 (C-5′), 27.8 (C-6′), 59.1 (C-7′), 95.6 (C-8′), 52.2 (C-9′), 43.0 (C-10′), 145.9 (C-11′), 168.4 (C-12′), 123.1 (C-13′), 24.0 (C-14′), 69.6 (C-15′), 167.9 (C-1″), 128.2 (C-2″), 138.7 (C-3″), 14.7 (C-4″), 12.3 (C-5″), 52.2 (12-OCH_3)。以上数据与文献[15]对照基本一致,故鉴定化合物**10**为 fortunilide K。

化合物 11　淡黄色无定型粉末; HR-ESI-MS: *m/z* 285.109 8 [M + Na]$^+$ (calcd for $C_{15}H_{18}O_4Na$, 285.109 7),分子式为 $C_{15}H_{18}O_4$; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 4.87 (1H, m, H-1), 2.15 (1H, m, H-2a), 2.02 (1H, m, H-2b), 2.68 (1H, m, H-3a), 2.03 (1H, m, H-3b), 6.30 (1H, s, H-5), 2.70 (1H, d, *J* = 12.6 Hz, H-9a), 2.39 (1H, d, *J* = 12.6 Hz, H-9b), 1.91 (3H, s, H-13), 1.85 (3H, d, *J* = 1.5 Hz, H-14), 1.58 (3H, s, H-15); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 127.8 (C-1), 25.5 (C-2), 29.4 (C-3), 147.9 (C-4), 129.0 (C-5), 190.8 (C-6), 154.7 (C-7), 109.3 (C-8), 48.2 (C-9), 135.4 (C-10), 135.4 (C-11), 170.2 (C-12), 9.9 (C-13), 24.5 (C-14), 17.8 (C-15)。以上数据与文献[16]对照基本一致,故鉴定化合物 **11** 为 (1*E*, 4*Z*)-8-hydroxy-6-oxogermacra-1(10), 4, 7(11)-trieno-12, 8-1actone。

化合物 12　白色粉末; HR-ESI-MS: *m/z* 359.218 8 [M + Na]$^+$ (calcd for $C_{20}H_{32}O_4Na$, 359.219 2),分子式为 $C_{20}H_{32}O_4$; ^{1}H NMR (600 MHz, CD_3OD) δ: 1.16 (1H, m, H-1a), 1.88 (1H, m, H-1b), 1.50 (1H, m, H-2a), 1.86 (1H, m, H-2b), 1.07 (1H, td, *J* = 13.2, 4.0 Hz, H-3a), 2.13 (1H, m, H-3b), 1.36 (1H, dd, *J* = 12.0, 3.0 Hz, H-5), 1.94 (2H, m, H-6), 1.85 (1H, m, H-7a), 2.38 (1H, m, H-7b), 1.74 (1H, m, H-9), 2.00 (1H, m, H-11a), 2.32 (1H, m, H-11b), 5.38 (1H, t, *J* = 6.6 Hz, H-12), 3.94 (1H, dd, *J* = 7.2, 5.1 Hz, H-14), 3.45 (2H, m, H-15), 1.61 (3H, d, *J* = 1.5 Hz, H-16), 4.47 (1H, s, H-17a), 4.82 (1H, s, H-17b), 1.19 (3H, s, H-18), 0.66 (3H, s, H-20); ^{13}C NMR (150 MHz, CD_3OD) δ: 40.6 (C-1), 21.2 (C-2), 39.4 (C-3), 45.4 (C-4), 57.5 (C-5), 27.4 (C-6), 39.7 (C-7), 149.6 (C-8), 57.9 (C-9), 41.4 (C-10), 23.6 (C-11), 129.3 (C-12), 135.1 (C-13), 79.1 (C-14), 65.9 (C-15), 12.3 (C-16), 107.9 (C-17), 29.6 (C-18), 181.3 (C-19), 13.4 (C-20)。以上数据与文献[17]对照基本一致,故鉴定化合物**12**为 henrilabdane B。

化合物 13　红色块状结晶(甲醇); HR-ESI-MS: *m/z* 345.133 3 [M + H]$^+$ (calcd for $C_{19}H_{21}O_6$, 345.133 2),分子式为 $C_{19}H_{20}O_6$; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.56 (2H, m, H-2, 6), 6.93 (2H, m, H-3,

5),6.01(1H,s,H-5′),7.77(1H,d,J = 15.6 Hz,H-a),7.81(1H,d,J = 15.6 Hz,H-b),3.84(3H,s,4-OCH_3),3.86(3H,s,3′-OCH_3),3.96(6H,d,J = 0.9 Hz,4′,6′-OCH_3);^{13}C NMR(150 MHz,$CDCl_3$)δ:128.3(C-1),130.3(C-2,6),161.6(C-4),114.5(C-3,5),107.1(C-1′),158.3(C-2′),131.0(C-3′),158.6(C-4′),87.2(C-5′),159.5(C-6′),125.2(C-a),143.0(C-b),193.3(C=O),55.6,56.1,56.2,60.9(OCH_3)。以上数据与文献[18]对照基本一致,故鉴定化合物**13**为2′-羟基-4,3′,4′,6′-四甲氧基查尔酮。

化合物 14 白色粉末;HR-ESI-MS:m/z 265.143 0 $[M+H]^+$(calcd for $C_{15}H_{21}O_4$,265.143 4),分子式为$C_{15}H_{20}O_4$;^{1}H NMR(600 MHz,CD_3OD)δ:3.69(1H,m,H-1),1.82(1H,m,H-2a),1.76(1H,m,H-2b),1.63(2H,m,H-3),2.56(1H,s,H-5),3.09(1H,d,J = 17.1 Hz,H-9a),2.72(1H,dt,J = 17.1,0.9 Hz,H-9b),7.08(1H,s,H-12),2.19(3H,d,J = 1.5 Hz,H-13),1.48(3H,s,H-14),1.02(3H,s,H-15);^{13}C NMR(150 MHz,CD_3OD)δ:78.3(C-1),28.5(C-2),38.3(C-3),71.2(C-4),62.1(C-5),197.3(C-6),119.4(C-7),166.4(C-8),40.0(C-9),44.7(C-10),139.7(C-11),119.2(C-12),9.2(C-13),24.6(C-14),14.7(C-15)。以上数据与文献[3]对照基本一致,故鉴定化合物**14**为curcolonol。

化合物 15 无色透明结晶(甲醇);HR-ESI-MS:m/z 285.109 9 $[M+Na]^+$(calcd for $C_{15}H_{18}O_4Na$,285.109 7),分子式为$C_{15}H_{18}O_4$;^{1}H NMR(600 MHz,$CDCl_3$)δ:2.91(1H,br d,J = 11.1 Hz,H-1),2.22(1H,br d,J = 14.1 Hz,H-2a),1.53(1H,m,H-2b),2.40(1H,br d,J = 14.1 Hz,H-3a),1.48(1H,m,H-3b),3.76(1H,s,H-5),2.80(1H,d,J = 17.1 Hz,H-9a),3.67(1H,d,J = 17.1 Hz,H-9b),7.08(1H,s,H-12),2.16(3H,s,H-13),1.31(3H,s,H-14),1.14(3H,s,H-15);^{13}C NMR(150 MHz,$CDCl_3$)δ:70.0(C-1),24.5(C-2),36.9(C-3),64.9(C-4),64.7(C-5),192.3(C-6),123.4(C-7),159.2(C-8),39.9(C-9),59.1(C-10),124.4(C-11),140.0(C-12),10.9(C-13),15.6(C-14),17.0(C-15)。以上数据与文献[3]对照基本一致,故鉴定化合物**15**为zederone epoxide。

化合物 16 黄色油状;HR-ESI-MS:m/z 755.267 1 $[M+Na]^+$(calcd for $C_{40}H_{44}O_{13}Na$,755.267 4),分子式为$C_{40}H_{44}O_{13}$;^{1}H NMR(600 MHz,$CDCl_3$)δ:2.05(1H,m,H-1),1.00(1H,m,H-2a),0.32(1H,m,H-2b),1.87(1H,m,H-3),3.95(1H,J = 3.9 Hz,H-6),3.87(1H,s,H-9),1.94(3H,d,J = 0.6 Hz,H-13),1.03(3H,s,H-14),2.80(1H,m,H-15a),2.58(1H,m,H-15b),1.60(1H,m,H-1′),0.73(1H,m,H-2′a),1.35(1H,m,H-2′b),1.39(1H,m,H-3′),1.85(1H,m,H-5′),2.50(1H,m,H-6′a),2.71(1H,m,H-6′b),1.84(1H,m,H-9′),4.53(1H,d,J = 12.0 Hz,H-13′a),5.09(1H,m,H-13′b),0.82(3H,s,H-14′),3.63(1H,d,J = 11.7 Hz,H-15′a),4.62(1H,m,H-15′b),6.61(1H,ddq,J = 6.6,5.1,1.2 Hz,H-c),4.63(1H,d,J = 12.0 Hz,H-da),5.07(1H,m,H-db),1.92(3H,d,J = 1.2 Hz,H-e),2.47(1H,m,H-ga),2.89(1H,m,H-gb),2.67(1H,m,H-ha),2.77(1H,m,H-hb),3.71(3H,S,12-OCH_3);^{13}C NMR(150 MHz,$CDCl_3$)δ:26.1(C-1),16.1(C-2),24.9(C-3),142.6(C-4),132.2(C-5),41.2(C-6),131.5(C-7),200.9(C-8),80.1(C-9),51.1(C-10),147.6(C-11),170.3(C-12),20.3(C-13),15.4(C-14),25.5(C-15),25.7(C-1′),11.8(C-2′),27.9(C-3′),77.2(C-4′),61.4(C-5′),23.5(C-6′),174.7(C-7′),93.4(C-8′),55.6(C-9′),45.1(C-10′),123.5(C-11′),171.7(C-12′),54.5(C-13′),26.2(C-14′),72.1(C-15′),167.2(C-a),129.3(C-b),135.6(C-c),61.4(C-d),13.1(C-e),171.7(C-f),28.8(C-g),29.3(C-h),172.1(C-i),52.5(12-OCH_3)。以上数据与文献[19]对照基本一致,故鉴定化合物**16**为银线草醇B。

化合物 17 黄色油状;HR-ESI-MS:m/z 549.246 5 $[M+H]^+$(calcd for $C_{32}H_{37}O_8$,549.248 3),分子式为$C_{32}H_{36}O_8$;^{1}H NMR(600 MHz,$CDCl_3$)δ:1.83(1H,m,H-1,1′),0.87(1H,m,H-2,2′a),0.21(1H,q,J = 3.9 Hz,H-2,2′b),1.96(1H,d,J = 7.2 Hz,H-3,3′),7.16(1H,s,H-6,6′),3.80(1H,s,H-9,9′),1.50(3H,s,H-13,13′),0.99(3H,s,H-14,14′),2.95(1H,d,J = 13.5 Hz,H-15,15′a),2.60(1H,d,J = 13.5 Hz,H-15,15′b),3.64(3H,s,12,12′-OCH_3);^{13}C NMR(150 MHz,$CDCl_3$)δ:24.8(C-

1,1′),14.1(C-2,2′),28.1(C-3,3′),147.5(C-4,4′),136.0(C-5,5′),138.5(C-6,6′),137.4(C-7,7′),199.2(C-8,8′),81.1(C-9,9′),58.6(C-10,10′),47.9(C-11,11′),175.6(C-12,12′),28.7(C-13,13′),16.1(C-14,14′),38.4(C-15,15′),52.2(12,12′-OCH_3)。以上数据与文献[19]对照基本一致,故鉴定化合物**17**为环银线草醇A。

化合物18 白色无定型粉末;HR-ESI-MS:*m/z* 337.237 3 [M + H]$^+$(calcd for $C_{20}H_{33}O_4$,337.237 3),分子式为$C_{20}H_{32}O_4$;^{1}H NMR(600 MHz,CD_3OD)δ:1.19(3H,s,H-1a),1.79(1H,m,H-1b),1.49(1H,m,H-2a),1.88(1H,m,H-2b),1.08(1H,td,*J* = 13.5,4.2 Hz,H-3a),2.06(1H,m,H-3b),1.40(1H,d,*J* = 12.3,Hz,H-5),2.01(1H,m,6a),1.91(1H,m,H-6b),1.97(1H,m,7a),2.41(1H,m,H-7b),2.13(1H,m,H-9),1.52(1H,m,H-11a),1.62(1H,m,H-11b),3.97(1H,d,*J* = 10.2 Hz,H-12),5.52(1H,t,*J* = 6.6 Hz,H-14),4.11(2H,d,*J* = 6.6 Hz,H-15),1.66(3H,s,H-16),4.49(1H,d,*J* = 1.8 Hz,H-17a),4.86(1H,s,H-17b),1.20(3H,s,H-18),0.61(3H,s,H-20);^{13}C NMR(150 MHz,CD_3OD)δ:40.3(C-1),21.1(C-2),39.4(C-3),45.2(C-4),57.6(C-5),27.6(C-6),39.9(C-7),150.3(C-8),53.2(C-9),41.2(C-10),31.5(C-11),75.9(C-12),142.4(C-13),124.7(C-14),59.2(C-15),12.1(C-16),107.0(C-17),29.6(C-18),181.3(C-19),13.5(C-20)。以上数据与文献[17]对照基本一致,故鉴定化合物**18**为henrilabdane A。

化合物19 黄色油状;HR-ESI-MS:*m/z* 315.196 1 [M-H]$^-$(calcd for $C_{20}H_{27}O_3$,315.196 0),分子式为$C_{20}H_{28}O_3$;^{1}H NMR(600 MHz,$CDCl_3$)δ:1.87(1H,m,H-1a),1.26(H,s,H-1b),1.90(1H,m,H-2a),1.54(1H,m,H-2b),2.17(1H,m,H-3a),1.10(1H,td,*J* = 13.5,4.2 Hz,H-3b),1.43(1H,m,H-5),2.00(1H,m,H-6a),1.89(1H,m,H-6b),2.36(1H,m,H-7a),1.92(1H,m,H-7b),2.30(1H,m,H-9),2.74(1H,dd,*J* = 15.3,3.3 Hz,H-11a),2.63(1H,dd,*J* = 15.3,10.4 Hz,H-11b),6.11(1H,d,*J* = 1.8 Hz,H-14),7.17(1H,d,*J* = 1.8 Hz,H-15),1.96(3H,d,*J* = 0.6 Hz,H-16),4.79(1H,d,*J* = 1.5 Hz,H-17a),4.59(1H,s,H-17b),1.26(3H,s,H-18),0.70(3H,s,H-20);^{13}C NMR(150 MHz,$CDCl_3$)δ:39.2(C-1),20.1(C-2),38.1(C-3),44.3(C-4),56.3(C-5),26.0(C-6),38.6(C-7),148.1(C-8),53.8(C-9),40.5(C-10),21.8(C-11),150.8(C-12),113.5(C-13),113.0(C-14),139.5(C-15),10.3(C-16),107.1(C-17),29.2(C-18),182.9(C-19),12.8(C-20)。以上数据与文献[20]对照基本一致,故鉴定化合物**19**为12-(3-methyl-furan)-labd-8(17)-en-19-oic acid。

化合物20 无色无定型粉末;HR-ESI-MS:*m/z* 307.226 4 [M + H]$^+$(calcd for $C_{19}H_{31}O_3$,307.226 7),分子式为$C_{19}H_{30}O_3$;^{1}H NMR(600 MHz,CD_3OD)δ:1.04(1H,td,*J* = 12.6,5.4 Hz,H-1a),1.70(1H,m,H-1b),1.52(2H,m,H-2),1.25(2H,m,H-3),1.32(1H,m,H-5),1.45(1H,d,*J* = 5.1 Hz,H-6a),1.32(1H,d,*J* = 1.5 Hz,H-6b),2.26(1H,m,H-7a),2.11(1H,m,H-7b),1.80(1H,m,H-9),1.66(2H,m,H-11),1.76(1H,m,H-12a),1.67(2H,m,H-12b),5.53(1H,s,H-14),1.22(3H,s,H-17),3.34(1H,d,*J* = 10.8 Hz,H-18a),2.99(1H,d,*J* = 10.8 Hz,H-18b),0.78(3H,s,H-19),0.85(3H,s,H-20);^{13}C NMR(150 MHz,CD_3OD)δ:40.1(C-1),19.4(C-2),36.5(C-3),38.8(C-4),48.5(C-5),23.3(C-6),36.6(C-7),139.7(C-8),49.6(C-9),39.1(C-10),19.6(C-11),32.8(C-12),43.8(C-13),126.2(C-14),181.6(C-15,16),25.2(C-17),72.0(C-18),18.5(C-19),16.1(C-20)。以上数据与文献[21]对照基本一致,故鉴定化合物**20**为ent-8(9)-pimarene-20-hydroxy-16-nor-15-oic acid。

化合物21 黄色油状;HR-ESI-MS:*m/z* 314.138 8 [M + H]$^+$(calcd for $C_{18}H_{19}NO_4$,314.138 6),分子式为$C_{18}H_{18}NO_4$;^{1}H NMR(600 MHz,CD_3OD)δ:7.10(1H,d,*J* = 1.8 Hz,H-2),6.78(1H,d,*J* = 8.1 Hz,H-5),7.01(1H,dd,*J* = 8.1,2.1 Hz,H-6),7.42(1H,d,*J* = 15.6 Hz,H-7),6.39(1H,d,*J* = 15.6 Hz,H-8),7.05(1H,d,*J* = 2.1 Hz,H-2′),6.71(1H,d,*J* = 2.1 Hz,H-3′),6.70(1H,d,*J* = 2.1 Hz,H-5′),7.04(1H,d,*J* = 2.1 Hz,H-6′),2.74(2H,t,*J* = 7.5 Hz,H-7′),3.45(2H,t,*J* = 7.5 Hz,H-8′),3.87(3H,s,3-OCH_3);^{13}C NMR(150 MHz,CD_3OD)δ:128.1(C-1),111.5(C-2),150.0(C-3),149.3(C-

4),116.5(C-5),123.2(C-6),142.1(C-7),118.6(C-8),169.2(C-9),131.3(C-1′),130.7(C-2′),116.3(C-3′),157.0(C-4′),116.2(C-5′),130.7(C-6′),35.8(C-7′),42.6(C-8′),56.4(3-OCH_3)。以上数据与文献[22]对照基本一致,故鉴定化合物**21**为反式-*N*-阿魏酰酪胺。

化合物22 白色粉末;HR-ESI-MS:*m/z* 625.2540 $[M+H]^+$(calcd for $C_{36}H_{37}N_2O_8$,625.2544),分子式为 $C_{36}H_{36}N_2O_8$;^{1}H NMR(600 MHz,DMSO-d_6)δ:7.13(1H,s,H-2),6.89(1H,s,H-6),7.35(1H,d,*J*=15.6 Hz,H-7),6.46(1H,d,*J*=15.6 Hz,H-8),7.02(2H,m,H-2′,6′),6.68(2H,d,*J*=3.9 Hz,H-3′,5′),2.66(2H,d,*J*=8.1 Hz,H-7′),3.33(2H,m,H-8′),6.99(2H,d,*J*=8.4 Hz,H-2″,6″),6.67(2H,d,*J*=3.9 Hz,H-3″,5″),2.64(2H,d,*J*=7.5 Hz,H-7″),3.32(2H,m,H-8″),6.89(1H,s,H-2‴),6.78(1H,d,*J*=8.1 Hz,H-5‴),6.71(1H,dd,*J*=8.1,2.1 Hz,H-6‴),5.88(1H,d,*J*=8.1 Hz,H-7‴),4.21(1H,d,*J*=8.1 Hz,H-8‴),3.83(3H,s,3-OCH_3),3.75(3H,s,3‴-OCH_3),9.21(1H,s,4-OH),9.18(1H,s,4″-OH),9.15(1H,s,4‴-OH),8.06(1H,t,*J*=5.7 Hz,9′-NH),8.39(1H,t,*J*=5.7 Hz,9″-NH);^{13}C NMR(150 MHz,DMSO-d_6)δ:128.6(C-1),111.7(C-2),144.1(C-3),148.7(C-4),128.5(C-5),115.9(C-6),138.7(C-7),119.7(C-8),129.6(C-1′),129.6(C-2′,6′),115.1(C-3′,5′),155.6(C-4′),34.4(C-7′),40.9(C-8′),165.2(C-9′),129.3(C-1″),129.5(C-2″,6″),115.2(C-3″,5″),155.7(C-4″),34.2(C-7″),40.7(C-8″),169.5(C-9″),130.6(C-1‴),110.4(C-2‴),147.7(C-3‴),146.9(C-4‴),115.5(C-5‴),118.8(C-6‴),87.7(C-7‴),55.9(C-8‴),55.8(3-OCH_3),55.7(3‴-OCH_3)。以上数据与文献[23]对照基本一致,故鉴定化合物**22**为grossamide。

2.2 抗炎活性筛选结果

本实验采用脂多糖(LPS)诱导的RAW264.7细胞炎症筛选模型,以氨基胍为阳性对照,对多穗金粟兰中分离得率较高的13个化合物(**5**~**17**)进行了抗炎活性检测。结果显示,当化合物浓度为10 μmol/L时化合物**5**、**8**、**9**、**10**、**11**、**13**、**14**、**15**、**16**、**17**具有一定的NO生成抑制作用,表现出一定的抗炎活性,其中化合物**5**、**10**、**11**和**13**有较好的NO生成抑制作用,表现出中等的抗炎活性,结果见表1。

表1 化合物5~17的抗炎活性大小

Table 1 The anti-inflammatory activity of compounds **5-17**

化合物 Compound	NO生成抑制率 Inhibition rate of NO production(%)
5	41.22±8.28
6	<0
7	<0
8	27.33±14.35
9	17.27±2.19
10	40.32±15.14
11	58.79±8.16
12	<0
13	43.85±10.04
14	9.79±6.05
15	31.67±16.63
16	17.79±6.26
17	34.52±12.71
氨基胍 Aminoguanidine	66.45±2.09

注:每组数据在3次独立实验的基础上用平均值±SD表示。以氨基胍为阳性对照。

Note:Each group of data are represented as means±SD based on three independent experiments. Aminoguanidine was used as the positive control.

3 结论

本实验从多穗金粟兰具有抗炎活性的二氯甲烷部位中分离得到22个化合物,包括9个倍半萜类(**5**、**8**~**11**、**14**~**17**)、6个二萜(**6**、**7**、**12**、**18**~**20**)、2个酰胺(**21**、**22**),3个甾醇(**2**~**4**)、1个查尔酮(**13**)、1个木脂素(**1**),其中化合物**2**、**4**、**21**、**22**为首次从金粟兰属中分离得到,化合物**1**~**10**、**18**~**22**为首次从多穗金粟兰中分离得到。并采用脂多糖(LPS)诱导的小鼠巨噬细胞RAW264.7释放一氧化氮(NO)免疫炎症细胞模型,对多穗金粟兰中得率较高的13个化合物(**5**~**17**)进行了抗炎活性测定,结果表明:9个倍半萜类化合物和查尔酮(化合物**13**)都有一定的抗炎活性,其中化合物**5**、**10**、**11**、**13**表现出较好的抗炎活性。通过比较倍半萜化合物(**5**、**8**、**11**、**14**、**15**)的抗炎活性大小,可以发现倍半萜内酯化合物(**5**、**11**)的抗炎活性明显优于其他倍半萜化合物(**8**、**14**、**15**),并且所分离的化合物中倍半萜内酯的得率也是最高的,据此初步推测倍半萜内酯类化合物可

能是多穗金粟兰抗炎的主要活性成分。且此前也有大量文献表明倍半萜内酯类化合物具有较好的抗肿瘤、强心等药理活性[24],因此,应更加注重多穗金粟兰中倍半萜内酯类化学成分及其药理活性的研究。本文进一步丰富了多穗金粟兰植物的研究内容,同时也为抗炎活性较好的先导化合物的发现、创新药物的研发,以及该药用植物资源的开发和利用提供了一定的参考依据。

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