

臭椿树根化学成分研究

图斯库¹, 张树军¹, 李涛², 王金兰¹, 赵明¹

1. 齐齐哈尔大学化学与化学工程学院, 黑龙江 齐齐哈尔 161006

2. 齐齐哈尔医学院, 黑龙江 齐齐哈尔 161042

摘要: 目的 研究臭椿 *Ailanthus altissima* 根部的化学成分。方法 采用硅胶柱色谱和 HPLC 等分离方法, 对臭椿树根正己烷萃取物的化学成分进行分离, 并经波谱数据分析鉴定结构。结果 分离得到了 14 个化合物, 分别鉴定为 20 β -羟基达玛烷-24-烯-3-酮 (1)、 β -谷甾醇 (2)、ocotillone (3)、5,6,7,8-四甲氧基香豆素 (4)、尼洛替星 (5)、isofouquierone peroxide (6)、20S,24S-二羟基达玛烷-25-烯-3-酮 (7)、匹西狄醇 A (8)、eichlerianic acid (9)、二氢尼洛替星 (10)、12 β ,20 β -二羟基达玛烷-24-烯-3-酮 (11)、铁屎米-6-酮 (12)、12 β -hydroxy ocotillone (13)、20S,25-epoxy-24R-hydroxy-3-dammaranone (14)。

结论 化合物 3、4、6、9、10、13 系首次从该植物中分离得到。

关键词: 臭椿; 5,6,7,8-四甲氧基香豆素; 匹西狄醇 A; 二氢尼洛替星; 铁屎米-6-酮

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Chemical constituents from roots of *Ailanthus altissima*

TUSKUL Solovyev¹, ZHANG Shu-jun¹, LI Tao², WANG Jin-lan¹, ZHAO Ming¹

1. Institute of Chemistry and Chemistry Engineering, Qiqihar University, Qiqihar 161006, China

2. Qiqihar Medical College, Qiqihar 161042, China

Abstract: **Objective** To study the chemical constituents from the roots of *Ailanthus altissima*. **Methods** Compounds were isolated and purified by silica gel column chromatography and HPLC, and their structures were identified by spectral analysis. **Results** Fourteen compounds were isolated and identified as 20-hydroxydammar-24-en-3-one (1), β -sitosterol (2), ocotillone (3), 5,6,7,8-tetramethoxycoumarin (4), niloticin (5), isofouquierone peroxide (6), 20S,24S-dihydroxydammar-25-en-3-one (7), piscidinol A (8), eichlerianic acid (9), dihydroniloticin (10), dammar-24-ene-12 β ,20 β -diol-3-one (11), canthin-6-one (12), 12 β -hydroxy ocotillone (13), and 20S,25-epoxy-24R-hydroxy-3-dammaranone (14). **Conclusion** Compounds 3, 4, 6, 9, 10, and 13 are isolated from this plant for the first time.

Key words: *Ailanthus altissima* (Mill.) Swingle; 5,6,7,8-tetramethoxycoumarin; piscidinol A; dihydroniloticin; canthin-6-one

臭椿 *Ailanthus altissima* (Mill.) Swingle 为苦木科 (Simaroubaceae) 臭椿属 *Ailanthus* Desf. 落叶乔木, 又名山椿、樗树、白椿等, 是中国本土树种, 除少数省区外, 全国各地均有分布。臭椿皮也称樗白皮, 臭椿根皮也称椿根皮, 具有清热燥湿、收涩固肠、抗肿瘤、抗菌、抗病毒等作用, 是我国民间常用的中草药^[1]。此外, 臭椿根部表现出极强的化感活性, 根部周围土壤提取物能够明显抑制多种植物种子发芽和生根, 树皮及根皮提取物具有较强的杀虫活性, 也可做为除虫剂^[2]。为进一步开发利用臭椿植物资源, 在前期对臭椿树枝化学成分研究^[3]

的基础上, 对臭椿树根甲醇浸出液正己烷萃取物的化学成分进行了研究, 得到 14 个化合物, 分别鉴定为 20 β -羟基达玛烷-24-烯-3-酮 (20-hydroxydammar-24-en-3-one, 1)、 β -谷甾醇 (β -sitosterol, 2)、ocotillone (3)、5,6,7,8-四甲氧基香豆素 (5,6,7,8-tetramethoxycoumarin, 4)、尼洛替星 (niloticin, 5)、isofouquierone peroxide (6)、20S,24S-二羟基达玛烷-25-烯-3-酮 (20S,24S-dihydroxydammar-25-en-3-one, 7)、匹西狄醇 A (piscidinol A, 8)、eichlerianic acid (9)、二氢尼洛替星 (10)、12 β ,20 β -二羟基达玛烷-24-烯-3-酮 (dammar-24-ene-12 β ,20 β -diol-3-one, 11)、铁屎

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作者简介: 图斯库 (1989—), 男, 硕士研究生, 研究方向为天然产物化学。E-mail: manutd24@mail.ru

米-6-酮(canthin-6-one, **12**)、12 β -hydroxy ocotillone (**13**)、20S,25-epoxy-24R-hydroxy-3-dammaranone (**14**)。其中,化合物 **3**、**4**、**6**、**9**、**10**、**13** 系首次从该植物中分离得到。

1 仪器与材料

X-6 显微熔点测定仪(北京泰克仪器有限公司); Bruker AM-400 和 Bruker-600 MHz 型核磁共振仪(德国 Bruker 公司); AUTOPOL V 型旋光仪(美国鲁道夫公司); 高效液相色谱仪: HITACHI L-7100 泵, HITACHI L-3350 示差折光检测器, GL SCIRNCES Inc. Inertsil PREP-ODS (250 mm $\times$ 10 mm, 5 μ m) 不锈钢柱; 柱色谱用硅胶为青岛海洋化工厂产品(200~300 目); 薄层色谱硅胶板为烟台化工厂生产, 实验用有机溶剂均为分析纯。

实验材料 2012 年 5 月 3 日采于辽宁省凌源市, 经齐齐哈尔大学植物学教授沙伟鉴定为臭椿 *Ailanthus altissima* (Mill.) Swingle 的根, 标本(Ams-201200503)保存于齐齐哈尔大学天然产物研究室。

2 提取与分离

干燥臭椿树根 10 kg 切碎, 每次用 35 L 甲醇室温浸泡 3 d 后滤过, 重复 5 次, 合并浸出液, 减压浓缩至 2.5 L, 加水 1.9 L, 依次用正己烷、醋酸乙酯、正丁醇萃取, 浓缩萃取液得到正己烷萃取物 84.1 g、醋酸乙酯萃取物 88.7 g、正丁醇萃取物 68.3 g。

取正己烷萃取物(59.0 g)用硅胶柱色谱分离, 依次用正己烷-醋酸乙酯(9:1、1:1、0:1)洗脱, TLC 监测合并相同流分, 得到 10 个部分 F1~F10。

F6(16.7 g)用硅胶柱色谱分离, 依次用正己烷-醋酸乙酯(90:10、85:15、80:20、60:40、1:1)洗脱得到 6 个部分 F6-1~F6-6。F6-4(8.7 g)用硅胶柱色谱分离, 依次用正己烷-醋酸乙酯(8:2)、醋酸乙酯洗脱, 得化合物 **1**(416.1 mg)、**3**(433.0 mg); F6-5(3.8 g)用硅胶柱色谱分离, 依次用正己烷-醋酸乙酯(8:2、1:1)洗脱得化合物 **2**(2.0 g)和其他 5 个部分 F6-5-1~F6-5-5; F6-5-4(650.1 mg)用半制备 HPLC(正己烷-醋酸乙酯 8:2, 体积流量 4 mL/min)分离, 得到化合物 **4**(7.9 mg, t_R =13.0 min)、**5**(127.1 mg, t_R =14.8 min); F6-5-4(529.9 mg)用半制备 HPLC(正己烷-醋酸乙酯 9:1, 体积流量 4 mL/min)分离, 得化合物 **6**(9.0 mg, t_R =28.2 min)、**7**(6.4 mg, t_R =32.2 min)、**8**(8.4 mg, t_R =36.7 min)。F7(15.6 g)经硅胶柱色谱分离, 正己烷-醋酸乙酯(8:2、7:3)洗脱得化合物 **9**(450.2

mg)和其他 9 个部分 F7-1~F7-9, F7-7(260.1 mg)用半制备 HPLC(正己烷-醋酸乙酯 9:1, 体积流量 4 mL/min)分离, 得化合物 **10**(22.7 mg, t_R =25.4 min); F7-8(4.6 g)用硅胶柱色谱分离, 依次用正己烷-醋酸乙酯(8:2、7:3)洗脱, 得化合物 **11**(2.6 g)。F8(2.1 g)用醋酸乙酯重结晶得化合物 **12**(70.0 mg); 母液用硅胶柱色谱分离, 正己烷-醋酸乙酯(8.5:1.5、6:4)洗脱, 得到 6 个部分(F8-1~F8-6)。F8-5(280.1 mg)用半制备 HPLC(正己烷-醋酸乙酯 8:2, 体积流量 4 mL/min)分离, 得化合物 **13**(130.0 mg, t_R =25.3 min)。F9(2.8 g)用硅胶柱色谱分离, 正己烷-醋酸乙酯(1:1、0:1)洗脱, 得到 5 个部分 F9-1~F9-5。F9-4(409.8 mg)用半制备 HPLC(正己烷-醋酸乙酯 7:3, 体积流量 4 mL/min)分离, 得化合物 **14**(21.9 mg, t_R =28.0 min)。

3 结构鉴定

化合物 **1**: 白色针晶(醋酸乙酯), mp 171~172 $^{\circ}$ C; $[\alpha]_D^{25}+10^{\circ}$ (c 0.5, MeOH)。 $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ : 5.12 (1H, t, J = 7.2 Hz, H-23), 2.49 (1H, m, H-2), 2.43 (1H, m, H-2), 2.05 (2H, m, H-23), 1.92 (1H, m, H-1), 1.85 (1H, m, H-1), 1.75 (2H, t, J = 7.5 Hz, H-16), 1.69 (3H, s, H-26), 1.67 (1H, m, H-5), 1.63 (3H, s, H-27), 1.60~1.20 (15H, m, H-6, 7, 9, 11, 12, 13, 15, 17, 22), 1.15 (3H, s, H-21), 1.08 (3H, s, H-18), 1.04 (3H, s, H-28), 1.00 (3H, s, H-29), 0.94 (3H, s, H-19), 0.89 (3H, s, H-30); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ : 218.1 (C-3), 131.6 (C-25), 124.7 (C-24), 75.3 (C-20), 55.3 (C-5), 50.2 (C-14), 50.0 (C-9), 49.8 (C-17), 47.4 (C-4), 42.4 (C-13), 40.4 (C-22), 40.3 (C-8), 39.9 (C-1), 36.8 (C-10), 34.5 (C-7), 34.1 (C-2), 31.1 (C-15), 27.5 (C-28), 26.7 (C-16), 25.7 (C-26), 25.5 (C-12), 24.8 (C-21), 22.5 (C-23), 22.0 (C-29), 21.0 (C-11), 19.6 (C-6), 17.7 (C-27), 16.3 (C-30), 16.0 (C-18), 15.2 (C-19)。以上数据与文献报道基本一致^[4], 故鉴定化合物 **1** 为 20 β -羟基-达玛烷-24-烯-3-酮。

化合物 **2**: 无色针晶(醋酸乙酯), mp 135.1~136.2 $^{\circ}$ C。 $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ : 5.33 (1H, dd, J = 5.0, 2.0 Hz, H-6), 3.51 (1H, tt, J = 8.5, 4.5 Hz, H-3), 1.00 (3H, s, H-19), 0.92 (3H, d, J = 6.8 Hz, H-21), 0.83 (3H, t, J = 7.3 Hz, H-26), 0.82 (3H, d, J = 6.8 Hz, H-28), 0.80 (3H, d, J = 6.8 Hz, H-29), 0.67 (3H, s, H-18)。以上数据与文献报道基本一致^[5], 故

鉴定化合物 **2** 为 β -谷甾醇。

化合物 **3**: 无色羽状晶体 (氯仿), mp 186~187.5 °C; $[\alpha]_D^{25}$ -94° (*c* 0.5, MeOH)。¹H-NMR (600 MHz, CDCl₃) δ : 3.73 (1H, t, *J* = 7.2 Hz, H-24), 2.49 (1H, m, H-2), 2.43 (1H, m, H-2), 1.21 (3H, s, H-21), 1.14 (3H, s, H-26), 1.12 (3H, s, H-27), 1.08 (3H, s, H-19), 1.04 (3H, s, H-28), 0.99 (3H, s, H-29), 0.93 (3H, s, H-30), 0.88 (3H, s, H-18); ¹³C-NMR (150 MHz, CDCl₃) δ : 218.0 (C-3), 86.3 (C-20), 83.3 (C-24), 71.4 (C-25), 55.3 (C-5), 50.1 (C-14), 50.0 (C-9), 49.5 (C-17), 47.4 (C-4), 43.8 (C-13), 40.3 (C-8), 39.9 (C-1), 36.9 (C-10), 35.7 (C-22), 34.6 (C-7), 34.1 (C-2), 31.4 (C-15), 27.5 (C-26), 27.4 (C-16), 26.7 (C-29), 26.1 (C-23), 25.7 (C-12), 24.3 (C-27), 23.6 (C-21), 22.1 (C-11), 21.0 (C-28), 19.7 (C-6), 16.4 (C-30), 16.0 (C-18), 15.1 (C-19)。以上数据与文献报道基本一致^[4], 故鉴定化合物 **3** 为 ocotillone。

化合物 **4**: 浅黄色无定形物 (醋酸乙酯), mp 54~56 °C。¹H-NMR (600 MHz, CDCl₃) δ : 7.94 (1H, d, *J* = 9.6 Hz, H-4), 6.29 (1H, d, *J* = 9.6 Hz, H-3), 4.04 (3H, s, 5-OCH₃), 3.98 (3H, s, 7-OCH₃), 3.97 (3H, s, 6-OCH₃), 3.90 (3H, s, 8-OCH₃); ¹³C-NMR (150 MHz, CDCl₃) δ : 160.4 (C-2), 150.7 (C-7), 145.1 (C-6), 144.3 (C-5), 142.4 (C-8), 138.8 (C-4), 136.9 (C-9), 114.1 (C-3), 109.5 (C-10), 62.1 (5-OCH₃), 61.9 (7-OCH₃), 61.8 (6-OCH₃), 61.5 (8-OCH₃)。以上数据与文献报道基本一致^[6], 故鉴定化合物 **4** 为 5,6,7,8-四甲氧基香豆素。

化合物 **5**: 无色针晶 (醋酸乙酯), mp 146.2~147.6 °C。¹H-NMR (600 MHz, CDCl₃) δ : 5.32 (1H, brd, *J* = 3.0 Hz, H-7), 3.58 (1H, dt, *J* = 8.2, 6.4 Hz, H-23), 2.74 (1H, dt, *J* = 14.5, 5.6 Hz, H-2a), 2.64 (1H, d, *J* = 8.2 Hz, H-24), 2.27 (1H, m, H-2b), 2.23 (1H, dt, *J* = 14.0, 3.3 Hz, H-6a), 2.07 (2H, m, H-6b, 9), 2.03 (1H, m, H-1a), 1.98 (1H, m, H-1b), 1.80 (1H, m, H-5), 1.34 (3H, s, H-26), 1.32 (3H, s, H-27), 1.12 (3H, s, H-19), 1.05 (3H, s, H-28), 1.02 (3H, s, H-30), 1.01 (3H, s, H-29), 0.96 (1H, d, *J* = 6.1 Hz, H-21), 0.81 (3H, s, H-18); ¹³C-NMR (150 MHz, CDCl₃) δ : 216.9 (C-3), 145.7 (C-8), 118.0 (C-7), 69.3 (C-23), 68.4 (C-24), 60.3 (C-25), 53.3 (C-17), 52.4 (C-5), 51.2 (C-14), 48.5 (C-9), 47.9 (C-4), 43.6 (C-13), 40.7

(C-22), 38.6 (C-1), 35.0 (C-10), 34.9 (C-2), 34.0 (C-15), 33.6 (C-12), 33.5 (C-20), 28.8 (C-16), 27.4 (C-30), 24.9 (C-28), 24.6 (C-27), 24.4 (C-6), 21.8 (C-29), 21.6 (C-26), 19.9 (C-21), 19.8 (C-19), 18.3 (C-11), 12.8 (C-18)。以上数据与文献报道基本一致^[7], 故鉴定化合物 **5** 为尼洛替星。

化合物 **6**: 无色针晶 (醋酸乙酯), mp 80~81 °C; $[\alpha]_D^{25}$ +37° (*c* 0.3, CHCl₃)。 ¹H-NMR (600 MHz, CDCl₃) δ : 5.79 (1H, dt, *J* = 15.8, 7.4 Hz, H-23), 5.62 (1H, d, *J* = 15.8 Hz, H-24), 2.53 (1H, m, H-2a), 2.43 (1H, m, H-2b), 2.20 (2H, m, H-22), 1.92 (1H, m, H-1), 1.86 (1H, m, H-1), 1.74 (2H, m, H-5, 16a), 1.68 (1H, m, H-16b), 1.60~1.40 (7H, m, H-6, 7, 12, 13, 17), 1.38 (1H, m, H-15), 1.36 (3H, s, H-26), 1.35 (3H, s, H-27), 1.35~1.20 (4H, m, H-9, 11, 15), 1.14 (3H, s, H-21), 1.11 (1H, m, H-12), 1.08 (3H, s, H-30), 1.04 (1H, m, H-29), 1.00 (3H, s, H-28), 0.94 (3H, s, H-19), 0.88 (3H, s, H-18); ¹³C-NMR (150 MHz, CDCl₃) δ : 218.1 (C-3), 137.3 (C-24), 127.2 (C-23), 82.1 (C-25), 75.0 (C-20), 55.3 (C-5), 50.2 (C-14), 50.1 (C-9), 49.9 (C-17), 47.4 (C-4), 43.3 (C-13), 42.5 (C-22), 40.3 (C-8), 39.9 (C-1), 36.8 (C-10), 34.5 (C-7), 34.1 (C-2), 31.1 (C-15), 27.5 (C-27), 26.7 (C-26), 25.8 (C-12), 24.8 (C-16), 24.4 (C-28), 24.1 (C-21), 21.9 (C-11), 21.0 (C-29), 19.6 (C-6), 16.3 (C-30), 16.0 (C-18), 15.2 (C-19)。以上数据文献报道一致^[8], 故鉴定化合物 **6** 为 isofouquierone peroxide。

化合物 **7**: 无色针晶 (醋酸乙酯), mp 92~93.5 °C; $[\alpha]_D^{25}$ +60° (*c* 1.25, MeOH)。¹H-NMR (600 MHz, CDCl₃) δ : 5.02 (2H, m, H-26), 4.29 (1H, t, *J* = 6.0 Hz, H-24), 2.51 (1H, dt, *J* = 14.0, 7.5 Hz, H-2a), 2.43 (1H, dt, *J* = 14.0, 4.5 Hz, H-2b), 1.92 (1H, m, H-1), 1.82 (1H, m, H-1), 1.76 (3H, s, H-27), 1.14 (3H, s, H-21), 1.08 (3H, s, H-18), 1.04 (3H, s, H-28), 0.99 (3H, s, H-29), 0.94 (3H, s, H-19), 0.88 (3H, s, H-30); ¹³C-NMR (150 MHz, CDCl₃) δ : 218.1 (C-3), 143.6 (C-25), 114.2 (C-26), 76.4 (C-24), 75.1 (C-20), 55.7 (C-5), 50.6 (C-9), 50.5 (C-17), 50.4 (C-14), 47.6 (C-4), 42.8 (C-13), 40.6 (C-8), 40.2 (C-1), 37.1 (C-10), 37.0 (C-22), 34.8 (C-7), 34.3 (C-2), 31.4 (C-15), 29.4 (C-23), 27.7 (C-12), 26.9 (C-28), 25.1 (C-16), 25.0 (C-21), 22.3 (C-11), 21.1 (C-29), 19.9 (C-6), 17.6 (C-27), 16.5 (C-30), 16.1 (C-18), 15.3

(C-19)。以上数据与文献报道基本一致^[9], 故鉴定化合物 **7** 为 20S,24S-二羟基达玛烷-25-烯-3-酮。

化合物 **8**: 无色针晶 (丙酮), mp 179~180 °C; $[\alpha]_D^{25}$ -176° (*c* 0.5, MeOH)。¹H-NMR (400 MHz, CDCl₃) δ : 5.31 (1H, t, *J* = 4.5 Hz, H-7), 4.12 (1H, dd, *J* = 4.4, 8.8 Hz, H-23), 3.17 (1H, s, H-24), 1.32 (3H, s, H-26), 1.31 (3H, s, H-27), 1.12 (3H, s, H-19), 1.05 (3H, s, H-29), 1.02 (3H, s, H-28), 1.01 (3H, s, H-30), 0.94 (3H, d, *J* = 6.4 Hz, H-21), 0.82 (3H, s, H-18); ¹³C-NMR (100 MHz, CDCl₃) δ : 217.1 (C-3), 145.7 (C-8), 117.9 (C-7), 75.1 (C-24), 74.3 (C-25), 69.7 (C-23), 53.8 (C-17), 52.3 (C-5), 51.2 (C-14), 48.4 (C-9), 47.8 (C-13), 43.5 (C-4), 40.5 (C-22), 38.5 (C-1), 35.0 (C-10), 34.9 (C-2), 34.0 (C-12), 33.8 (C-15), 33.7 (C-20), 28.4 (C-16), 27.3 (C-27), 27.3 (C-30), 26.2 (C-26), 24.5 (C-28), 24.3 (C-6), 22.0 (C-18), 21.5 (C-29), 18.9 (C-21), 18.3 (C-11), 12.7 (C-19)。以上数据与文献报道基本一致^[10], 故鉴定化合物 **8** 为匹西狄醇 A。

化合物 **9**: 白色脂状物; $[\alpha]_D^{25}$ +41° (*c* 0.96, CHCl₃)。¹H-NMR (600 MHz, CDCl₃) δ : 4.85 (1H, s, H-28), 4.66 (1H, s, H-28), 3.74 (1H, t, *J* = 7.2 Hz, H-24), 2.38 (1H, m, H-2), 2.19 (1H, m, H-2), 1.97 (1H, brd, *J* = 10.7 Hz, H-5), 1.73 (3H, s, H-29), 1.20 (3H, s, H-27), 1.13 (3H, s, H-26), 1.12 (3H, s, H-21), 0.99 (3H, s, H-18), 0.89 (3H, s, H-30), 0.84 (3H, s, H-19); ¹³C-NMR (150 MHz, CDCl₃) δ : 179.8 (C-3), 147.5 (C-4), 113.5 (C-28), 86.4 (C-20), 83.3 (C-24), 71.6 (C-25), 50.8 (C-17), 50.4 (C-14), 49.5 (C-9), 43.0 (C-13), 41.1 (C-5), 40.0 (C-8), 39.1 (C-10), 35.8 (C-22), 34.3 (C-2), 33.9 (C-7), 31.5 (C-6), 31.5 (C-15), 27.4 (C-27), 27.2 (C-16), 26.2 (C-23), 25.7 (C-12), 24.6 (C-1), 24.2 (C-26), 23.5 (C-21), 23.2 (C-29), 22.1 (C-11), 20.1 (C-19), 16.4 (C-30), 15.3 (C-18)。以上数据与文献报道基本一致^[4], 故鉴定化合物 **9** 为 eichlerianic acid。

化合物 **10**: 无色针晶 (醋酸乙酯), mp 177.5~178.5 °C。¹H-NMR (600 MHz, CDCl₃) δ : 5.27 (1H, dd, *J* = 6.4, 3.0 Hz, H-7), 3.58 (1H, dt, *J* = 8.2, 6.4 Hz, H-23), 3.24 (1H, dd, *J* = 11.6, 4.1 Hz, H-3), 2.67 (1H, d, *J* = 8.2 Hz, H-24), 2.19 (1H, m, H-6a), 2.14 (1H, m, H-6b), 2.03 (1H, m, H-9), 1.96 (1H, m, H-2a), 1.80 (1H, m, H-2b), 1.34 (3H, s, H-26), 1.32 (3H, s, H-27),

0.99 (3H, s, H-19), 0.98 (3H, s, H-30), 0.96 (1H, d, *J* = 6.1 Hz, H-21), 0.86 (3H, s, H-28), 0.82 (3H, s, H-29), 0.75 (3H, s, H-18); ¹³C-NMR (150 MHz, CDCl₃) δ : 145.6 (C-8), 118.1 (C-7), 79.3 (C-3), 69.3 (C-23), 68.5 (C-24), 60.3 (C-25), 53.3 (C-17), 51.2 (C-14), 50.6 (C-5), 48.9 (C-9), 43.6 (C-13), 40.7 (C-22), 39.0 (C-4), 37.2 (C-1), 34.9 (C-10), 34.0 (C-12), 33.6 (C-15), 33.6 (C-20), 28.8 (C-2), 27.7 (C-16), 27.6 (C-28), 27.2 (C-30), 24.9 (C-27), 24.0 (C-6), 21.8 (C-18), 20.0 (C-21), 19.9 (C-26), 18.2 (C-11), 14.7 (C-29), 13.1 (C-19)。以上数据与文献报道一致^[10], 故鉴定化合物 **10** 为二氢尼洛替星。

化合物 **11**: 白色针晶 (醋酸乙酯), mp 188.9~191.0 °C; $[\alpha]_D^{25}$ +80° (*c* 0.5, MeOH)。¹H-NMR (600 MHz, CDCl₃) δ : 5.17 (1H, t, *J* = 7.2 Hz, H-24), 3.61 (1H, ddd, *J* = 10.4, 10.4, 5.2 Hz, H-12), 2.51 (1H, m, H-2), 2.43 (1H, m, H-2), 2.17 (1H, m, H-1), 2.05 (2H, m, H-22), 1.97 (1H, m, H-1), 1.85 (2H, m, H-11), 1.75 (1H, t, *J* = 10.6 Hz, H-5), 1.70 (3H, s, H-26), 1.64 (3H, s, H-27), 1.60~1.23 (13H, m, H-6, 7, 9, 13, 15, 16, 17, 22), 1.20 (3H, s, H-21), 1.08 (3H, s, H-18), 1.04 (3H, s, H-28), 1.02 (3H, s, H-29), 0.98 (3H, s, H-19), 0.89 (3H, s, H-30); ¹³C-NMR (150 MHz, CDCl₃) δ : 217.8 (C-3), 132.0 (C-25), 124.8 (C-24), 74.6 (C-20), 70.6 (C-12), 55.3 (C-5), 53.3 (C-17), 51.6 (C-14), 49.3 (C-9), 48.0 (C-13), 47.4 (C-4), 39.7 (C-1), 39.7 (C-8), 36.8 (C-10), 34.1 (C-2), 34.2 (C-7), 34.3 (C-22), 31.5 (C-15), 30.9 (C-11), 27.0 (C-28), 26.7 (C-21), 26.4 (C-16), 25.7 (C-26), 22.3 (C-23), 21.0 (C-29), 19.6 (C-6), 17.7 (C-27), 16.7 (C-30), 15.9 (C-18), 15.4 (C-19)。以上数据与文献报道基本一致^[3], 故鉴定化合物 **11** 为 12 β ,20 β -二羟基-达玛烷-24-烯-3-酮。

化合物 **12**: 无色针晶 (醋酸乙酯), mp 156~157 °C。¹H-NMR (600 MHz, CDCl₃) δ : 8.81 (1H, d, *J* = 5.0 Hz, H-2), 8.64 (1H, d, *J* = 8.2 Hz, H-8), 8.18 (1H, d, *J* = 8.2 Hz, H-11), 8.01 (1H, d, *J* = 9.7 Hz, H-4), 7.92 (1H, d, *J* = 5.0 Hz, H-1), 7.69 (1H, t, *J* = 8.2 Hz, H-9), 7.52 (1H, t, *J* = 8.2 Hz, H-10), 6.98 (1H, d, *J* = 9.7 Hz, H-5); ¹³C-NMR (150 MHz, CDCl₃) δ : 159.4 (C-6), 145.8 (C-2), 139.6 (C-4), 139.4 (C-3a), 136.2 (C-7a), 131.9 (C-11c), 130.8 (C-11b), 130.2 (C-5), 128.9 (C-11a), 125.6 (C-9), 124.3 (C-11), 122.6

(C-10), 117.2 (C-8), 116.3 (C-1)。以上数据与文献对照基本一致^[3], 故鉴定化合物 **12** 为铁屎米-6-酮。

化合物 **13**: 针状透明晶体 (醋酸乙酯), mp 172~173 °C。¹H-NMR (600 MHz, CDCl₃) δ : 3.88 (1H, dd, J = 10.8, 5.4 Hz, H-24), 3.54 (1H, m, H-12), 2.51 (1H, m, H-2), 2.44 (1H, m, H-2), 1.28 (3H, s, H-26), 1.24 (3H, s, H-27), 1.11 (3H, s, H-21), 1.08 (3H, s, H-19), 1.05 (3H, s, H-28), 1.04 (3H, s, H-29), 0.97 (3H, s, H-30), 0.92 (3H, s, H-18); ¹³C-NMR (150 MHz, CDCl₃) δ : 217.8 (C-3), 87.5 (C-24), 87.1 (C-20), 70.4 (C-12), 70.1 (C-25), 55.3 (C-5), 52.2 (C-14), 49.6 (C-9), 49.0 (C-13), 48.9 (C-17), 47.4 (C-4), 39.7 (C-1), 39.6 (C-8), 36.9 (C-10), 34.1 (C-7), 32.2 (C-2), 32.1 (C-11), 31.7 (C-15), 29.7 (C-22), 28.9 (C-27), 28.5 (C-23), 28.1 (C-21), 26.7 (C-28), 25.1 (C-16), 24.3 (C-26), 20.1 (C-29), 19.7 (C-6), 17.7 (C-18), 16.1 (C-30), 15.1 (C-19)。以上数据与文献报道基本一致^[11], 故鉴定化合物 **13** 为 12 β -hydroxy ocotillone。

化合物 **14**: 针状透明晶体 (醋酸乙酯), mp 175~176 °C。¹H-NMR (600 MHz, CDCl₃) δ : 3.40 (1H, brd, J = 10.2 Hz, H-24), 2.50 (1H, m, H-2), 2.43 (1H, m, H-2), 1.92 (1H, m, H-1), 1.82 (1H, m, H-12), 1.77 (1H, m, H-17), 1.73 (1H, m, H-22), 1.67~1.25 (18H, m, H-1, 5, 6, 7, 9, 11, 12, 13, 15, 16, 22, 23), 1.23 (3H, s, H-27), 1.18 (3H, s, H-26), 1.16 (3H, s, H-21), 1.08 (3H, s, H-28), 1.04 (3H, s, H-29), 1.00 (3H, s, H-18), 0.95 (3H, s, H-18), 0.89 (3H, s, H-30); ¹³C-NMR (150 MHz, CDCl₃) δ : 218.1 (C-3), 78.8 (C-24), 75.5 (C-20), 73.1 (C-25), 55.3 (C-5), 50.3 (C-14), 49.8 (C-17), 48.9 (C-9), 47.4 (C-4), 42.6 (C-13), 40.2 (C-8), 39.8 (C-1), 37.1 (C-22), 36.8 (C-10), 34.5 (C-7), 34.1 (C-2), 31.1 (C-15), 27.4 (C-12), 26.7 (C-28), 26.5 (C-27), 25.6 (C-16), 25.2 (C-21), 24.9 (C-23), 23.3 (C-26), 22.0 (C-29), 20.9

(C-11), 19.6 (C-6), 16.3 (C-30), 16.0 (C-19), 15.2 (C-18)。以上数据与文献报道一致^[3], 故鉴定化合物 **14** 为 20S,25-epoxy-24R-hydroxy-3-dammaranone。

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