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# 毛山小橘枝叶中生物碱类成分的研究

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**摘要:** 为了解毛山小橘(*Glycosmis craibii*)的化学成分, 采用硅胶柱层析、ODS 柱层析、Sephadex LH-20 凝胶柱层析和高效液相色谱等现代色谱分离技术, 从毛山小橘枝叶 95%乙醇提取物中分离得到 9 个生物碱类化合物。根据化合物的理化性质和波谱数据, 其结构分别鉴定为 de-*N*-methyl-*O*-noracronycine (**1**)、去甲山油柑碱(**2**)、glycocitrine II (**3**)、acrifoline (**4**)、3-hydroxy-2,4-dimethoxy-10-methyl-9-acridanone (**5**)、阿塔宁(**6**)、glycosolone (**7**)、3-(3',3'-dimethylallyl)-4,8-dimethoxy-*N*-methyl-quinolin-2-one (**8**)和 4-methoxy-*N*-methyl-2-quinolone (**9**)。所有化合物均为首次从该植物中分离, 其中化合物 **2**、**3**、**5**、**6** 和 **9** 为首次从山小橘属植物中分离得到。

**关键词:** 芸香科; 山小橘属; 毛山小橘; 生物碱

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## Studies on the Alkaloids from Twigs and Leaves of *Glycosmis craibii*

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**Abstract:** In order to clarify the alkaloids in the twigs and leaves of *Glycosmis craibii*, nine alkaloids were isolated from 95% ethanol extract of *G. craibii* by several column chromatographic techniques, such as MPLC, MCI-gel, silica gel, Sephadex LH-20 and preparative HPLC. Based on physicochemical properties and NMR spectral data, their structures were identified as de-*N*-methyl-*O*-noracronycine (**1**), noracronycine (**2**), glycocitrine II (**3**), acrifoline (**4**), 3-hydroxy-2,4-dimethoxy-10-methyl-9-acridanone (**5**), atanine (**6**), glycosolone (**7**), 3-(3',3'-dimethylallyl)-4,8-dimethoxy-*N*-methyl-quinolin-2-one (**8**) and 4-methoxy-*N*-methyl-2-quinolone (**9**). It is the first report of all the alkaloids isolated from this species and compounds **2**, **3**, **5**, **6** and **9** from the genus *Glycosmis*.

**Key words:** Rutaceae; *Glycosmis*; *G. craibii*; Alkaloid

毛山小橘(*Glycosmis craibii*)是芸香科(Rutaceae)山小橘属植物, 常见于云南南部(元江等地), 在泰国东北部也有分布<sup>[1]</sup>。本属药用植物在民间用于治疗多种疾病, 如印度民间 *G. arborea* 用作降体温、肝部不适及其他疾病<sup>[2]</sup>, *G. citrifolia* 用作治疗皮肤瘙痒、疥疮和皮肤溃疡<sup>[2]</sup>。山小橘(*G. pentaphylla*)

醇提取物展示出显著的杀蚊虫和护肝作用<sup>[3]</sup>, 但是关于毛山小橘植物化学成分研究尚未见文献报道。本课题组一直从事热带药用植物活性成分研究<sup>[4]</sup>, 前期从毛山小橘中分离得到一个抗肿瘤活性显著的新颖吲哚生物碱和四个具有抗炎活性的肟类化合物<sup>[5-6]</sup>。为了进一步从该植物中寻找活性成分, 阐

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明其药效作用的物质基础,本课题组对毛山小橘枝叶的化学成分进行了系统研究。本文报道从毛山小橘枝叶95%乙醇提取物中分离得到的9个生物碱类化合物。

## 1 材料和方法

### 1.1 仪器和材料

瑞士布鲁克公司生产的Bruker AV-400 MHz超导核磁共振仪;德国Finnigan公司生产的Finnigan-MAT-95-MS质谱仪;日本东京理化公司生产的N-1100D-W直立式旋转蒸发仪;武汉药科新技术开发有限公司生产的YOKO-ZX紫外分析暗箱;上海青浦沪西仪器有限公司生产的BSZ-100自动部分收集器;美国安捷伦公司生产Agilent 1260分析型高效液相色谱仪、Agilent 1260制备型高效液相色谱仪;美国Amersham Biosciences公司生产Sephadex LH-20凝胶;美国Merck公司生产的ODS柱色谱材料(C<sub>18</sub>, 10~40 μm);青岛海洋化工厂生产的柱层析硅胶(200~300和300~400目),所用试剂均为分析纯,购买于西陇化工股份有限公司。

试验材料于2018年8月采自中国科学院西双版纳热带植物园,由浙江省丽水市林业科学研究院王军峰副研究员鉴定为芸香科山小橘属植物毛山小橘(*Glycosmis craibii*)的干燥枝叶,凭证标本(No. W180801)保存于台州学院高等研究院天然药物与健康产品研究所标本室。

### 1.2 提取和分离

取10.0 kg毛山小橘新鲜枝叶晾干,粉碎成粗粉,用95%乙醇浸泡3次,溶剂体积依次为20.0、

15.0和15.0 L,每次浸泡1周,合并浸泡液,减压浓缩至无醇味得总浸膏。将总浸膏分散于温水混悬后依次分别用石油醚和乙酸乙酯进行萃取,减压回收溶剂后得石油醚萃取部位(69.0 g)和乙酸乙酯萃取部位(90.0 g)。将石油醚部位经硅胶柱色谱分离,以石油醚-丙酮为洗脱剂[80:20→50:50, V/V]梯度洗脱,收集洗脱流份,每份1 L,减压浓缩至干,TLC检测合并主点相同的流份,得组分Fr.1~Fr.5。组分Fr.3(10.3 g)经ODS柱色谱进行分离,以甲醇-水为洗脱剂[20:80→100:0, V/V]进行梯度洗脱,得到8个亚组分Fr.3A~Fr.3H。Fr.3B经葡聚糖凝胶柱色谱(氯仿-甲醇,1:1)分离,经制备型HPLC纯化,以乙腈-水(55:45)为流动相,流速20 mL/min,制得化合物4(t<sub>R</sub>=14.8 min, 2.8 mg)、6(t<sub>R</sub>=22.3 min, 17.4 mg)、7(t<sub>R</sub>=25.6 min, 13.8 mg)和8(8.8 mg)。Fr.3D经硅胶柱色谱分离,以石油醚-丙酮为洗脱剂[25:75→50:50, V/V]进行梯度洗脱,洗脱组分经葡聚糖凝胶柱色谱(石油醚-氯仿-甲醇,40:20:20)分离纯化,经制备HPLC纯化,以乙腈-水(45:55)为流动相,流速20 mL/min,制备获得化合物1(t<sub>R</sub>=11.2 min, 55.7 mg)和3(t<sub>R</sub>=13.2 min, 89.7 mg)。Fr.3E经硅胶柱色谱分离,以石油醚-乙酸乙酯(20:80→0:100, V/V)为洗脱剂进行梯度洗脱,洗脱组分经Sephadex LH-20凝胶柱色谱(氯仿-甲醇,50:50)纯化,以甲醇-水(80:20)为流动相,经制备型HPLC进行制备得到化合物2(t<sub>R</sub>=21.3 min, 19.0 mg)、5(t<sub>R</sub>=16.5 min, 32.4 mg)和9(t<sub>R</sub>=23.5 min, 4.8 mg)(图1)。

### 1.3 结构鉴定

**化合物1** 黄色油状物,与改良的碘化铋钾反应显色呈阳性,ESI-MS m/z: 316.1 [M+Na]<sup>+</sup>, 分

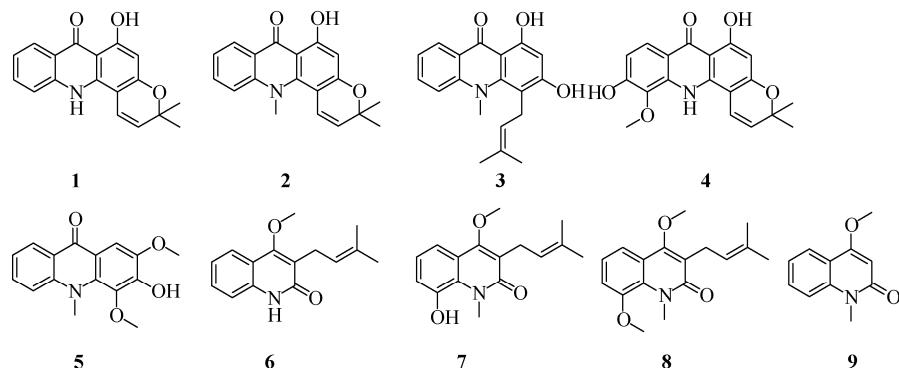


图1 化合物1~9结构式

Fig. 1 Structures of compounds 1~9

子式为  $C_{18}H_{15}NO_3$ ,  $^1H$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta_H$  14.68 (1H, s, OH-1), 11.16 (1H, s, NH-10), 8.15 (1H, dd,  $J$  = 8.0, 1.6 Hz, H-8), 7.79 (1H, td,  $J$  = 8.0, 1.6 Hz, H-6), 7.74 (1H, dd,  $J$  = 8.0, 1.6 Hz, H-5), 7.28 (1H, td,  $J$  = 8.0, 1.6 Hz, H-7), 7.10 (1H, d,  $J$  = 10.4 Hz, H-1'), 6.04 (1H, s, H-2), 5.72 (1H, d,  $J$  = 10.4 Hz, H-2'), 1.43 (3H, s, 4'-CH<sub>3</sub>), 1.43 (3H, s, 5'-CH<sub>3</sub>);  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta_C$  180.6 (C-9), 163.8 (C-3), 159.2 (C-1), 141.0 (C-10a), 137.9 (C-4a), 133.9 (C-6), 125.6 (C-8), 124.9 (C-2'), 121.8 (C-7), 118.9 (C-8a), 117.6 (C-1'), 116.1 (C-5), 104.0 (C-4), 98.1 (C-9a), 96.2 (C-2), 77.1 (C-3'), 27.5 (4'-CH<sub>3</sub>), 27.5 (5'-CH<sub>3</sub>)。以上波谱数据与文献[7]报道的一致, 故鉴定为 de-*N*-methyl-*O*-noracronycine。

**化合物 2** 黄色不定形粉末, 与改良的碘化铋钾反应显色呈阳性, ESI-MS  $m/z$ : 330.1 [M + Na]<sup>+</sup>, 分子式为  $C_{19}H_{17}NO_3$ ,  $^1H$  NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_H$  14.70 (1H, s, OH-1), 8.37 (1H, dd,  $J$  = 8.0, 1.6 Hz, H-8), 7.71 (1H, td,  $J$  = 8.0, 1.6 Hz, H-6), 7.43 (1H, dd,  $J$  = 8.0, 1.6 Hz, H-5), 7.30 (1H, td,  $J$  = 8.0, 1.6 Hz, H-7), 7.55 (1H, d,  $J$  = 10.4 Hz, H-1'), 6.26 (1H, s, H-2), 5.50 (1H, d,  $J$  = 10.4 Hz, H-2'), 4.90 (3H, s, N-CH<sub>3</sub>), 1.53 (3H, s, 4'-CH<sub>3</sub>), 1.53 (3H, s, 5'-CH<sub>3</sub>);  $^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_C$  181.3 (C-9), 165.4 (C-3), 161.7 (C-1), 145.1 (C-10a), 144.6 (C-4a), 134.1 (C-6), 126.4 (C-8), 123.1 (C-2'), 122.2 (C-7), 122.1 (C-8a), 121.7 (C-1'), 116.3 (C-5), 107.1 (C-4), 101.1 (C-9a), 98.0 (C-2), 76.5 (C-3'), 43.8 (N-CH<sub>3</sub>), 27.0 (4'-CH<sub>3</sub>), 27.0 (5'-CH<sub>3</sub>)。以上波谱数据与文献[8]报道的一致, 故鉴定为 noracronycine。

**化合物 3** 黄色不定形粉末, 与改良的碘化铋钾反应显色呈阳性, ESI-MS  $m/z$ : 332.1 [M + Na]<sup>+</sup>, 分子式为  $C_{19}H_{19}NO_3$ ,  $^1H$  NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_H$  14.59 (1H, s, OH-1), 8.34 (1H, dd,  $J$  = 8.0, 1.6 Hz, H-8), 7.69 (1H, td,  $J$  = 8.0, 1.6 Hz, H-6), 7.39 (1H, dd,  $J$  = 8.0, 1.6 Hz, H-5), 7.26 (1H, td,  $J$  = 8.0, 1.6 Hz, H-7), 6.38 (1H, s, H-2), 5.41 (1H, t,  $J$  = 6.4 Hz, H-2'), 3.47 (2H, d,  $J$  = 6.4 Hz, H-1'), 3.83 (3H, s, N-CH<sub>3</sub>), 1.81 (3H, s, 4'-CH<sub>3</sub>), 1.68 (3H, s, 5'-CH<sub>3</sub>);  $^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_C$  181.7 (C-9), 163.9 (C-3), 163.5 (C-1), 147.7 (C-4a), 146.6 (C-10a), 134.7 (C-6), 130.7 (C-3'), 126.2 (C-8), 123.5 (C-2'), 121.8 (C-7), 121.7 (C-8a), 116.5 (C-5), 107.5 (C-4), 104.7 (C-9a), 97.9

(C-2), 44.3 (N-CH<sub>3</sub>), 27.3 (C-1'), 25.9 (4'-CH<sub>3</sub>), 18.3 (5'-CH<sub>3</sub>)。经与文献[7]比较, 鉴定化合物 3 为 glycocitrine II。

**化合物 4** 黄色不定形粉末, 与改良的碘化铋钾反应显色呈阳性, ESI-MS  $m/z$ : 362.1 [M + Na]<sup>+</sup>, 分子式为  $C_{19}H_{17}NO_5$ ,  $^1H$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta_H$  14.65 (1H, s, OH-1), 9.60 (1H, s, NH), 7.78 (1H, d,  $J$  = 8.8 Hz, H-8), 6.91 (1H, d,  $J$  = 8.8 Hz, H-7), 7.03 (1H, d,  $J$  = 10.4 Hz, H-1'), 6.03 (1H, s, H-2), 5.69 (1H, d,  $J$  = 10.4 Hz, H-2'), 3.93 (3H, s, 5-OCH<sub>3</sub>), 1.43 (3H, s, 4'-CH<sub>3</sub>), 1.43 (3H, s, 5'-CH<sub>3</sub>);  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta_C$  180.1 (C-9), 163.8 (C-1), 159.0 (C-3), 153.9 (C-6), 137.1 (C-4a), 135.9 (C-10a), 133.1 (C-5), 125.5 (C-2'), 121.0 (C-8), 116.2 (C-2'), 113.3 (C-7), 113.0 (C-8), 103.3 (C-9a), 98.4 (C-4), 96.4 (C-2), 77.1 (C-3'), 60.4 (5-OCH<sub>3</sub>), 27.5 (4'-CH<sub>3</sub>), 27.5 (5'-CH<sub>3</sub>)。以上波谱数据与文献[9]报道的一致, 故鉴定为 acrifoline。

**化合物 5** 黄色不定形粉末, 与改良的碘化铋钾反应显色呈阳性, ESI-MS  $m/z$ : 308.1 [M + Na]<sup>+</sup>, 分子式为  $C_{16}H_{15}NO_4$ ,  $^1H$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta_H$  8.28 (1H, d,  $J$  = 8.0 Hz, H-8), 7.83 (1H, m, overlap, H-6), 7.83 (1H, m, overlap, H-6, H-5), 7.34 (1H, t,  $J$  = 8.0 Hz, H-7), 6.62 (1H, s, H-1), 4.00 (3H, s, 2-OCH<sub>3</sub>), 3.90 (3H, s, N-CH<sub>3</sub>), 3.73 (3H, s, 4-OCH<sub>3</sub>);  $^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_C$  179.7 (C-9), 159.3 (C-2), 154.9 (C-3), 141.8 (C-10a), 140.2 (C-4a), 134.3 (C-5), 129.4 (C-4), 125.4 (C-8), 121.5 (C-7), 119.6 (C-8a), 116.1 (C-6), 88.2 (C-1), 59.9 (4-OCH<sub>3</sub>), 56.1 (2-OCH<sub>3</sub>), 34.2 (N-CH<sub>3</sub>)。以上波谱数据与文献[10]报道的一致, 故鉴定为 3-hydroxy-2,4-dimethoxy-10-methyl-9-acridanone。

**化合物 6** 无色晶体粉末, 与改良的碘化铋钾反应显色呈阳性, ESI-MS  $m/z$ : 266.1 [M + Na]<sup>+</sup>, 分子式为  $C_{15}H_{17}NO_2$ ,  $^1H$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta_H$  7.68 (1H, dd,  $J$  = 8.0, 2.0 Hz, H-5), 7.47 (1H, td,  $J$  = 8.0, 2.0 Hz, H-7), 7.32 (1H, dd,  $J$  = 8.0, 2.0 Hz, H-8), 7.19 (1H, td,  $J$  = 8.0, 2.0 Hz, H-6), 5.16 (1H, td,  $J$  = 6.8, 3.2 Hz, H-2'), 3.86 (3H, s, 4-OCH<sub>3</sub>), 3.22 (2H, d,  $J$  = 6.8 Hz, H-1'), 1.73 (3H, s, 5'-CH<sub>3</sub>), 1.63 (3H, s, 4'-CH<sub>3</sub>);  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta_C$  163.3 (C-2), 160.6 (C-4), 137.7 (C-8a), 131.3 (C-3'), 130.0 (C-7), 122.5 (C-5), 122.0 (C-3), 121.8 (C-6), 121.7

(C-2'), 116.0 (C-4a), 115.2 (C-8), 61.5 (4-OCH<sub>3</sub>), 25.5 (C-1'), 23.0 (5'-CH<sub>3</sub>), 17.8 (4'-CH<sub>3</sub>)。以上波谱数据与文献[11]报道的一致, 故鉴定为阿塔宁。

**化合物7** 无色晶体粉末, 与改良的碘化铋钾反应显色呈阳性, ESI-MS *m/z*: 296.1 [M + Na]<sup>+</sup>, 分子式为 C<sub>16</sub>H<sub>19</sub>NO<sub>3</sub>。<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ<sub>H</sub> 7.23 (1H, dd, *J* = 8.0, 2.0 Hz, H-5), 7.08 (1H, td, *J* = 8.0, 2.0 Hz, H-6), 7.04 (1H, dd, *J* = 8.0, 2.0 Hz, H-7), 5.15 (1H, td, *J* = 6.8, 3.2 Hz, H-2'), 3.86 (3H, s, 4-OCH<sub>3</sub>), 3.81 (3H, s, N-CH<sub>3</sub>), 3.24 (2H, d, *J* = 6.8 Hz, H-1'), 1.73 (3H, s, 5'-CH<sub>3</sub>), 1.63 (3H, s, 4'-CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ<sub>C</sub> 163.5 (C-2), 159.6 (C-4), 146.1 (C-8), 131.3 (C-3'), 128.5 (C-8a), 122.7 (C-3), 121.8 (C-6), 121.2 (C-2'), 119.5 (C-4a), 117.3 (C-5), 113.8 (C-7), 61.5 (4-OCH<sub>3</sub>), 34.7 (N-CH<sub>3</sub>), 25.5 (C-1'), 23.8 (5'-CH<sub>3</sub>), 17.8 (4'-CH<sub>3</sub>)。以上波谱数据与文献[12]报道的一致, 故鉴定为 glycosolone。

**化合物8** 黄色油状物, 与改良的碘化铋钾反应显色呈阳性, ESI-MS *m/z*: 310.1 [M + Na]<sup>+</sup>, 分子式为 C<sub>17</sub>H<sub>21</sub>NO<sub>3</sub>, <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ<sub>H</sub> 7.44 (1H, dd, *J* = 8.0, 2.0 Hz, H-5), 7.16 (1H, td, *J* = 8.0, 2.0 Hz, H-6), 7.04 (1H, dd, *J* = 8.0, 2.0 Hz, H-7), 5.25 (1H, td, *J* = 6.8, 3.2 Hz, H-2'), 3.96 (3H, s, N-CH<sub>3</sub>), 3.89 (3H, s, 8-OCH<sub>3</sub>), 3.88 (3H, s, 4-OCH<sub>3</sub>), 3.40 (2H, d, *J* = 6.8 Hz, H-1'), 1.80 (3H, s, 5'-CH<sub>3</sub>), 1.60 (3H, s, 4'-CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ<sub>C</sub> 165.2 (C-2), 160.2 (C-4), 148.9 (C-8), 132.6 (C-3'), 130.7 (C-8a), 122.8 (C-3), 122.6 (C-6), 121.6 (C-2'), 120.4 (C-4a), 116.1 (C-5), 113.6 (C-7), 61.8 (8-OCH<sub>3</sub>), 56.8 (4-OCH<sub>3</sub>), 35.7 (N-CH<sub>3</sub>), 24.5 (C-1'), 25.8 (5'-CH<sub>3</sub>), 18.1 (4'-CH<sub>3</sub>)。以上波谱数据与文献[13]报道的一致, 故鉴定为 3-(3',3'-dimethylallyl)-4,8-dimethoxy-N-methyl-quinolin-2-one。

**化合物9** 无色晶体粉末, 与改良的碘化铋钾反应显色呈阳性, ESI-MS *m/z*: 212.1 [M + Na]<sup>+</sup>, 分子式为 C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub>。<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ<sub>H</sub> 7.88 (1H, dd, *J* = 8.0, 2.0 Hz, H-5), 7.65 (1H, td, *J* = 8.0, 2.0 Hz, H-7), 7.51 (1H, dd, *J* = 8.0, 2.0 Hz, H-8), 7.26 (1H, td, *J* = 8.0, 2.0 Hz, H-6), 6.04 (1H, s, H-3), 3.95 (3H, s, 4-OCH<sub>3</sub>), 3.56 (3H, s, N-CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ<sub>C</sub> 162.3 (C-2), 161.8 (C-4), 139.4 (C-8a), 131.4 (C-7), 122.6 (C-5), 121.5 (C-6), 115.5 (C-4a), 114.7 (C-8), 96.3 (C-3), 56.1 (4-OCH<sub>3</sub>),

28.6 (N-CH<sub>3</sub>)。以上波谱数据与文献[14]报道的一致, 故鉴定为 4-methoxy-N-methyl-2-quinolone。

## 2 结果和讨论

本研究从毛山小橘枝叶的 95%工业乙醇提取物分离鉴定了 9 个生物碱类化合物, 包括 5 个吖啶酮类生物碱和 4 个喹诺酮类生物碱, 其中化合物 **2**、**3**、**5**、**6** 和 **9** 均为从山小橘属植物中首次发现。据报道, 化合物 **1**、**2**、**3** 和 **4** 具有抗血小板聚集活性, 带有吡喃环的 acridone 母核是其活性的主要因素<sup>[15]</sup>; 此外, 这些吖啶酮化合物可作为 HL-60 细胞分化的诱导剂, 预示它们具有潜在的癌症预防作用<sup>[16]</sup>。在过敏反应评价中, 化合物 **5** 对肥大细胞脱粒显示出较强的抑制作用<sup>[10]</sup>。本研究结果在一定程度上阐明了毛山小橘的生物碱类, 可为山小橘属植物资源的开发利用提供科学依据。

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