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见血封喉树叶化学成分研究

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摘要:从见血封喉(*Antiaris toxicaria* (Pers.) Lesch.)树叶中分离得到了6个化合物,经波谱数据分析,分别鉴定其结构为:(3*S*,5*R*,6*S*,7*E*,9*R*)-3,6-dihydroxy-5,6-dihydro-β-ionol (**1**)、(5*R*)-4,5-二氢布卢门醇A (**2**)、槲皮素-3-*O*-β-D-葡萄糖苷(**3**)、异鼠李素-3-*O*-β-D-芸香糖苷(**4**)、山柰甲黄素-3-*O*-β-D-葡萄糖苷(**5**)和环氧松柏醇(**6**),以上化合物均为首次从该种植物中分离得到。

关键词:见血封喉; 树叶; 化学成分
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Chemical Constituents from the Leaves of *Antiaris toxicaria*

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Abstract: Six compounds were isolated from the leaves of *Antiaris toxicaria*. On the basis of spectral data, they were identified as (3*S*,5*R*,6*S*,7*E*,9*R*)-3,6-dihydroxy-5,6-dihydro-β-ionol (**1**), (5*R*)-4,5-dihydroblumenol A (**2**), quercetin-3-*O*-β-D-glucopyranoside (**3**), narcissin (**4**), kaempferide-3-*O*-β-D-glucopyranosdie (**5**) and epoxyconiferyl alcohol (**6**). All the compounds were isolated from *Antiaris toxicaria* for the first time.
Key words: *Antiaris toxicaria*; Leave; Chemical constituent

见血封喉(*Antiaris toxicaria* (Pers.) Lesch.)为桑科(Moraceae)见血封喉属植物[1],别名加布、剪刀树和箭毒木,是世界上木本植物中最毒的树种之一,在我国主要分布于海南、云南、广东和广西等地,已被列为三级珍稀保护植物[2]。其鲜树汁为乳白色,有剧毒,民间入药用于强心、催吐、泻下、麻醉等[3]。在印度尼西亚、马来西亚、缅甸等国,以及我国的海南和云南等地,当地人用见血封喉的乳汁作箭毒,猎杀野兽[4]。国外研究表明,其乳汁和种子中均富含强心苷类化合物,具有强心作用;其根皮中富含黄酮类化合物,有些具有抗炎和抗肿瘤活性[5]。我们曾报道了海南产见血封喉乳汁的脂溶性成分及其抗氧化活性[6],其树叶的化学成分至今未见报道。我们对见血封喉树叶进行了化学成分分析,为见血封喉资源的开发利用提供科学依据。

1 材料和方法

1.1 材料

见血封喉(*Antiaris toxicaria* (Pers.) Lesch.)树叶于2007年8月采自海南省陵水县,经中国热带农业科学院热带作物品种资源研究所王祝年副研究员鉴定,凭证标本(AN200708)存放于中国热带农业科学院热带生物技术研究所。柱层析硅胶(200~300目)和薄层层析硅胶为青岛海洋化工厂产品,Sephadex LH-20为Merck公司产品。

1.2 仪器

熔点用北京泰克X-5型显微熔点仪测定(温度未校正);MS谱在Autospec-3000质谱仪上测定;

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NMR 用 Brucker AV-400 型超导核磁仪测定,以 TMS 为内标。比旋光度用 Autopol 旋光仪测定。

1.3 提取和分离

见血封喉树叶晒干后加工成粉末(9.3 kg),用 95% 乙醇浸提 3 次。将乙醇提取液减压浓缩至无乙醇味后加水分散成悬浊液,依次用石油醚、乙酸乙酯萃取,浓缩后分别得到石油醚浸膏(163.7 g)和乙酸乙酯浸膏(50.0 g),剩余水相部分过滤后经大孔吸附树脂(D-101)柱层析,先后用水和甲醇洗脱,收集甲醇洗脱液,减压浓缩得到甲醇浸膏(57.9 g)。乙酸乙酯浸膏(50.0 g)经减压硅胶柱层析,以氯仿-甲醇(100: 1~0: 1)梯度洗脱,得到 9 个组分(Fr. 1~9)。Fr. 5 (13.0 g)经硅胶柱层析,以氯仿-甲醇(100: 1~25: 1) 梯度洗脱得到化合物 **1** (11.0 mg)、**2** (32.5 mg)和 **6** (14.2 mg)。甲醇浸膏(57.9 g)经减压硅胶柱层析,以氯仿-甲醇(100: 1~0: 1)梯度洗脱得到 8 个组分(Fr. M1 ~ M8)。Fr. M5 (3.9 g)依次经 Sephadex LH-20 凝胶(95% 乙醇)和硅胶(氯仿-甲醇 5: 1)柱层析得到化合物 **3** (23.0 mg)和 **4** (98.2 mg)。Fr. M6 (19.7 g)依次经 Sephadex LH-20 凝胶(95% 乙醇)和反复硅胶(氯仿-甲醇 15: 1)柱层析得到化合物 **5** (7.8 mg)。

1.4 结构鉴定

(*3S*,*5R*,*6S*,*7E*,*9R*)-3,6-dihydroxy-5,6-dihydro-β-ionol (1)　无色油状物, $[\alpha]_D^{25}$ = -10.1° (*c* 0.85, $CHCl_3$); EI-MS *m/z*: 228 $[M]^+$; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.61 (1H, d, *J* = 12.1 Hz, H-2a), 1.50 (1H, m, H-2b), 3.83 (1H, m, H-3), 1.34 (1H, d, *J* = 12.0 Hz, H-4a), 1.75 (1H, d, *J* = 12.4 Hz, H-4b), 1.90 (1H, m, H-5), 5.54 (1H, d, *J* = 15.7 Hz, H-7), 5.73 (1H, dd, *J* = 15.7, 6.0 Hz, H-8), 4.35 (1H, d, *J* = 6.0 Hz, H-9), 1.27 (3H, d, *J* = 6.4 Hz, H-10), 0.95 (3H, s, H -11), 0.86 (3H, s, H-12), 0.77 (3H, d, *J* = 6.8 Hz, H-13); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 39.1 (C-1), 45.1 (C-2), 66.6 (C-3), 39.4 (C-4), 34.0 (C-5), 76.9 (C-6), 132.8 (C-7), 134.4 (C-8), 68.4 (C-9), 23.8 (C-10), 25.1 (C-11), 24.5 (C-12), 15.8 (C-13)。上述波谱数据与文献[7]报道的(3*S*,5*R*,6*S*,7*E*,9*R*)-3,6-dihydroxy-5,6-dihydro-β-ionol 数据基本一致。

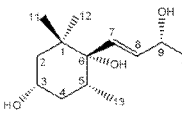
(*5R*)-4,5-二氢布卢门醇 A [(*5R*)-4,5-dihydroblumeno0l A, 2]　黄色油状物, $[\alpha]_D^{25}$ = +2.0° (*c* 0.85, $CHCl_3$); EI-MS *m/z*: 226 $[M]^+$; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.83 (1H, d, *J* = 13.6 Hz, H-2a), 1.90 (1H, d, *J* = 13.6 Hz, H-2b), 2.41 (1H, d, *J* = 12.4 Hz, H-4a), 2.20 (1H, m, H-4b), 2.26 (1H, m, H-5), 5.69 (1H, d, *J* = 15.8 Hz, H-7), 5.76 (1H, dd, *J* = 15.8, 5.8 Hz, H-8), 4.42 (1H, m, H-9), 1.31 (3H, d, *J* = 6.4 Hz, H-10), 0.93 (3H, s, H-11), 0.95 (3H, s, H-12), 0.87 (3H, d, *J* = 6.3 Hz, H-13); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 42.6 (C-1), 51.4 (C-2), 211.4 (C-3), 45.1 (C-4), 36.4 (C-5), 77.0 (C-6), 131.8 (C-7), 135.2 (C-8), 68.3 (C-9), 23.9 (C-10), 24.5 (C-11), 24.4 (C-12), 15.9 (C-13)。上述波谱数据与文献[8]报道的(5*R*)-4,5-二氢布卢门醇 A 数据基本一致。

槲皮素-3-*O*-β-D-葡萄糖苷(Quercetin-3-*O*-β-D-glucopyranoside, 3)　黄色针晶(氯仿), mp: 220 ~ 222℃, FAB-MS *m/z*: 463 $[M-H]^-$; ^{1}H NMR (CD_3OD, 400 MHz): δ 6.18 (1H, d, *J* = 2.0 Hz, H-6), 6.37 (1H, d, *J* = 2.0 Hz, H-8), 7.71 (1H, d, *J* = 2.0 Hz, H-2'), 6.85 (1H, d, *J* = 8.4 Hz, H-5'), 7.56 (1H, dd, *J* = 8.4, 2.0 Hz, H-6'), 5.23 (1H, d, *J* = 7.2 Hz, H-1''); ^{13}C NMR (CD_3OD, 100 MHz): δ 158.4 (C-2), 135.7 (C-3), 179.5 (C-4), 163.0 (C-5), 100.0 (C-6), 166.0 (C-7), 94.8 (C-8), 159.1 (C-9), 105.7 (C-10), 123.1 (C-1'), 116.0 (C-2'), 145.9 (C-3'), 149.8 (C-4'), 117.7 (C-5'), 123.2 (C-6'), 104.5 (C-1''), 75.7 (C-2''), 78.1 (C-3''), 71.3 (C-4''), 78.3 (C-5''), 62.6 (C-6'')。上述波谱数据与文献[9]报道的槲皮素-3-*O*-β-D-葡萄糖苷数据基本一致。

异鼠李素-3-*O*-β-D-芸香糖苷(Narcissin, 4)　黄色针晶(甲醇),FAB-MS *m/z*: 623 $[M-H]^-$; ^{1}H NMR (CD_3OD, 400 MHz): δ 6.18 (1H, d, *J* = 2.0 Hz, H-6), 6.37 (1H, d, *J* = 2.0 Hz, H-8), 7.71 (1H, d, *J* = 2.0 Hz, H-2'), 6.85 (1H, d, *J* = 8.4 Hz, H-5'), 7.56 (1H, dd, *J* = 8.4, 2.0 Hz, H-6'), 5.23 (1H, d, *J* = 7.2 Hz, H-1''), 3.61 (3H, s, OCH_3); ^{13}C NMR (CD_3OD, 100 MHz): δ 158.4 (C-2), 135.7 (C-3), 179.5 (C-4), 163.0 (C-5), 100.0 (C-6), 166.0 (C-7), 94.8 (C-8), 159.1 (C-9), 105.7 (C-10), 123.1 (C-1'), 116.0 (C-2'), 146.9 (C-3'), 149.8 (C-4'), 117.7 (C-5'), 123.2 (C-6'), 104.5 (C-1''), 75.7 (C-2''), 78.2 (C-3''), 71.4 (C-4''), 77.2 (C-5''), 68.6 (C-6''), 100.0 (C-1'''), 72.1 (C-2'''), 72.3 (C-3'''), 74.0 (C-4'''), 69.7 (C-5'''), 17.9 (C-6'''), 55.7 (OCH_3)。上述波谱数据与文献[10]报道的异鼠李素-3-*O*-β-D-芸香糖苷基本一致。

山柰甲黄素-3-*O*-β-D-葡萄糖苷(Kaempferide-3-*O*-β-D-glucoside, 5) 黄色粉末, FAB-MS *m/z*: 461 $[M-H]^-$; ^{1}H NMR (CD_3OD, 400 MHz): δ 6.18 (1H, s, H-6), 6.37 (1H, s, H-8), 5.21 (1H, d, *J* = 7.2 Hz, H-1'), 8.01 (1H, d, *J* = 8.8 Hz, H-2'), 6.87 (1H, dd, *J* = 8.7, 2.2 Hz, H-3'), 6.87 (1H, dd, *J* = 8.7, 2.2 Hz, H-5'), 8.01 (1H, d, *J* = 8.8 Hz, H-6'), 3.91 (3H, s, OCH_3); ^{13}C NMR (CD_3OD, 100 MHz): δ 158.5 (C-2), 135.5 (C-3), 179.5 (C-4), 163.1 (C-5), 100.0 (C-6), 166.0 (C-7), 94.8 (C-8), 159.1 (C-9), 105.7 (C-10), 123.1 (C-1'), 132.3 (C-2'), 116.1 (C-3'), 161.6 (C-4'), 116.6 (C-5'), 132.3 (C-6'), 104.5 (C-1''), 75.7 (C-2''), 78.1 (C-3''), 71.3 (C-4''), 78.3 (C-5''), 62.6 (C-6''), 56.8 (OCH_3)。该化合物的^{13}C NMR 数据与文献[11]报道的山柰甲黄素-3-*O*-β-D-葡萄糖苷数据基本一致。

环氧松柏醇(Epoxyconiferyl alcohol, 6) 黄色粉末, EI-MS *m/z*: 196 $[M]^+$; ^{1}H NMR (Acetone-d_6, 400 MHz): δ 6.89 (1H, d, *J* = 1.8 Hz, H-2), 6.76 (1H, dd, *J* = 8.0, 1.7 Hz, H-5), 6.78 (1H, d, *J* = 8.1 Hz, H-6), 4.13 (1H, dd, *J* = 8.9, 6.8 Hz, H-1'), 3.80 (1H, dd, *J* = 9.1, 3.6 Hz, H-1'), 3.08 (1H, dd, *J* = 6.5, 4.4 Hz, H-2'), 3.83 (3H, s, OCH_3); ^{13}C NMR (Acetone-d_6, 100 MHz): δ 133.3 (C-1), 108.4 (C-2), 146.6 (C-3), 144.8 (C-4), 114.2 (C-5), 118.7 (C-6), 72.5 (C-1'), 56.0 (C-2'), 87.6 (C-3'), 56.1 (OCH_3)。上述波谱数据与文献[12]报道的环氧松柏醇数据基本一致。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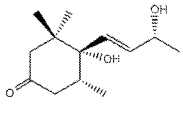
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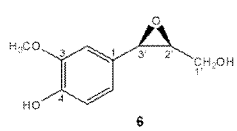
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2 结果和讨论

见血封喉是世界上最毒的木本植物之一,但民间观察到动物食用其树苗的叶子却未见中毒的现象。前人研究表明其毒性是由其乳汁和种子中所含的强心苷类成分引起的,故推测其树叶中可能不含强心苷类成分。本研究对见血封喉树叶的各提取物经 kedde 试剂检测后均呈阴性反应,证明树叶中不含强心苷类化合物。对其化学成分进行分析,从其乙醇提取物中分离鉴定了 6 个化合物,分别为:(3*S*,5*R*,6*S*,7*E*,9*R*)-3,6-dihydroxy-5,6-dihydro-β-ionol (**1**)、(5*R*)-4,5-二氢布卢门醇 A (**2**)、槲皮素-3-*O*-β-D-葡萄糖苷(**3**)、异鼠李素-3-*O*-β-D-芸香糖苷(**4**)、山柰甲黄素-3-*O*-β-D-葡萄糖苷(**5**)和环氧松柏醇(**6**)。其中化合物 **1** 和 **2** 为降倍半萜类化合物,化合物 **3**、**4** 和 **5** 为黄酮类化合物,化合物 **6** 为苯丙素类化合物,而未发现强心苷类化合物,以上化合物均为首次从该植物中分离得到。

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