

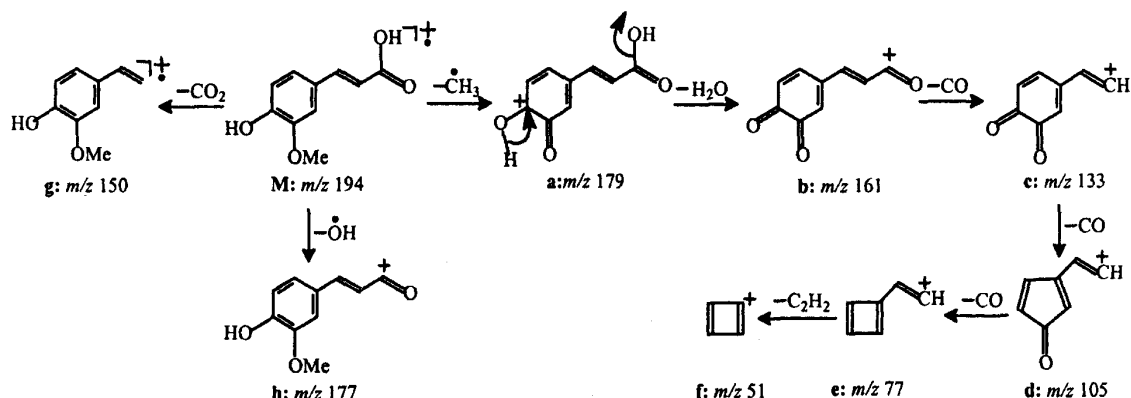


图3 阿魏酸的飞行时间质谱裂解途径

Fig. 3 TOFMS fragmentation pathway of ferulic acid

提取物中阿魏酸的相对质量分数为5%；利用飞行时间质谱所提供的具有精确质量的分子离子峰和8个特征碎片离子峰，参考谱图检索结果可以确认阿魏酸的分子结构。

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黄亮囊吾的苯并呋喃类化合物

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摘要:目的 研究黄亮囊吾根和根茎的化学成分。方法 利用硅胶、Sephadex LH-20 柱色谱分离等方法进行分离和纯化, 根据化合物的理化常数和波谱数据鉴定其结构。结果 从黄亮囊吾的根和根茎中分离到8个化合物, 分别鉴定为: 泽兰素(euparin, I)、6-甲氧基泽兰素(6-methoxy-euparin, II)、2-羟基-4, 5-二甲氧基苯甲醛(4, 5-dimethoxy-2-hydroxybenzaldehyde, III)、2-乙酰-5, 6-二甲氧基苯并呋喃(2-acetyl-5, 6-dimethoxybenzofuran, IV)、对羟基苯乙酮(4-hydroxyacetophenone, V)、2-isopropenyl-5, 6-dimethoxy-2, 3-hydrocumarin (VI)、8β-hydroxy-7(11)-eremophilen-12, 8α-olide (VII)、羽扇豆醇(lupeol, VIII)。结论 8个化合物均为首次从黄亮囊吾中分离得到。主要成分为苯并呋喃类化合物, 特别是化合物I和II是两个重要的成分, 具有杀虫和昆虫拒食活性, 这和黄亮囊吾民间用于驱虫有相关性。

关键词:黄亮囊吾; 苯并呋喃; 杀虫活性

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Benzofuran compounds from *Ligularia caloxantha*LI Yun-sen¹, WANG Zheng-tao¹, ZHANG Mian¹, TAN Ai-min¹, CHEN Lin²

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Abstract: Objective To study the benzofuran compounds from roots and rhizomes of *Ligularia caloxantha*, which is a folk medicine used in the Naxi Nationality in Yunnan Province. **Methods** Compounds were separated and purified by silica gel and Sephadex LH-20 column chromatography. Their structures were elucidated by physicochemical properties and spectral analysis. **Results** Eight compounds are isolated from ethanolic extracts of the roots and rhizomes. They were identified as euparin (I), 6-methoxy-euparin (II), 4, 5-dimethoxy-2-hydroxybenzaldehyde (III), 2-acetyl-5, 6-dimethoxy-benzofuran (IV), 4-hydroxyacetophenone (V), 2-isopropenyl-5, 6-dimethoxy-2, 3-hydrocumaran (VI), 8 β -hydroxy-7(11)-eremophilene-12, 8 α -olide (VII), lupeol (VIII). **Conclusion** All the eight compounds were obtained from *L. caloxantha* for the first time as benzofurans. Compounds I and II are two major ones with insecticide and insect food refusal-induced activities. That is the relative reason of *L. caloxantha* used for folk anti-insect.

Key words: *Ligularia caloxantha* (Diels) Hand.-Mazz.; benzofurans; insecticidal activity

黄亮橐吾 *Ligularia caloxantha* (Diels) Hand.-Mazz. 为菊科橐吾属植物,其根和根茎在云南省丽江地区被纳西族口服用于驱蛔虫,外用治疗跌打损伤。为了探寻其效用的物质基础,为其资源开发提供化学基础,本实验研究了其药用部位的化学成分。初步分离了8个化合物,均为首次从黄亮橐吾中分离得到。主要成分为泽兰素(I),6-甲氧基泽兰素(II)等苯并呋喃类成分,具有橐吾属橐吾组短梗系特征性。文献报道苯并呋喃类化合物对昆虫、家畜有细胞毒的生物活性,特别是化合物I和II是两个重要的成分,具有杀虫和昆虫拒食活性^[1],这和黄亮橐吾民间用于驱虫有相关性。

1 仪器与材料

四川大学科仪厂生产XRC-1型显微熔点仪测定熔点;旋光用Dip-360旋光仪测定;EI-MS用VG Auto Spec-3000型质谱仪测定(70 eV);NMR用Bruker AM-400型超导核磁共振仪测定,CDCl₃作溶剂,TMS为内标。柱色谱用硅胶为青岛海洋化工厂生产,Rp18为Merck公司生产,Sephadex LH-20为日本三菱化成公司生产。黄亮橐吾 *L. caloxantha* (Diels) Hand.-Mazz. 采自云南省丽江市白沙(2000年8月),经中国药科大学药学研究室张勉博士鉴定。

2 提取和分离

黄亮橐吾干燥根和根茎6.5 kg,粉碎,95%乙醇冷浸(20 L×3),回收乙醇得棕黑色浸膏400.0 g,浸膏加适量水成混悬液后用氯仿(2 L×3)萃取,得

萃取物300.0 g,氯仿部分经硅胶(200~300目)柱色谱分离,氯仿-醋酸乙酯梯度洗脱,通过TLC检视,合并相同流份得8个组分。组分2经硅胶H加压、减压柱色谱分离,以石油醚-醋酸乙酯(40:1)分离得化合物I(450 mg)。组分3中析出白色针晶(VI, 300 mg),组分4中析出白色片晶(谷甾醇,300 mg)。组分5经硅胶H加压柱色谱分离,以石油醚-醋酸乙酯(10:1)为洗脱剂分离,再经Sephadex LH-20(氯仿为膨胀剂)分离得化合物II(40 mg)、III(30 mg)。组分4经硅胶H加压柱色谱分离,石油醚-醋酸乙酯(8:1)为洗脱剂分离得化合物IV(60 mg)、化合物V(20 mg)、化合物VII(20 mg)。组分6经硅胶H加压柱色谱分离,氯仿-丙酮(15:1)洗脱分离得化合物VIII(100 mg)。组分8中析出白色粉末(胡萝卜苷,50 mg)。

3 鉴定

化合物I: C₁₃H₁₂O₃, 黄色针状结晶(丙酮)。¹H-NMR(400 MHz, CDCl₃) δ : 12.48(1H, s, 与酮基形成氢键的6位酚羟基), 7.83(1H, s, H-4), 6.92(1H, s, H-3), 6.49(1H, s, H-7), 5.72(1H, s, H-11a), 5.19(1H, s, H-11b), 2.63(3H, s, H-14), 2.07(3H, s, H-12)。¹³C-NMR(100 MHz, CDCl₃) δ : 203.9(s, C=O), 161.6(s, C-8), 159.6(s, C-6), 157.9(s, C-2), 132.2(s, C-10), 123.5(d, C-4), 121.9(s, C-5), 116.8(s, C-9), 113.6(t, C-11), 102.4(d, C-7), 99.3(d, C-3), 26.7(q, C-14), 19.1(q, C-12)。¹H-NMR、¹³C-NMR数据参考文献的数据^[2], 化合物

I 为泽兰素。

化合物 II: 黄色块状结晶(醋酸乙酯)。¹H-NMR (400 MHz, CDCl₃) δ: 7.70 (1H, s, H-4), 6.88 (1H, s, H-3), 6.40 (1H, s, H-7), 5.68 (1H, s, H-11a), 5.14 (1H, s, H-11b), 2.60 (3H, s, H-14), 2.05 (3H, s, H-12), 3.93 (3H, s, -OMe)。¹³C-NMR (100 MHz, CDCl₃) δ: 202.6 (s, C=O), 161.0 (s, C-8), 160.2 (s, C-6), 157.0 (s, C-2), 130.5 (s, C-10), 122.0 (d, C-4), 120.1 (s, C-5), 115.7 (s, C-9), 111.9 (t, C-11), 101.8 (d, C-7), 98.9 (d, C-3), 26.0 (q, C-14), 19.0 (q, C-12), 56.0 (q, -OMe)。¹H-NMR、¹³C-NMR数据参考文献^[1], 化合物 II 为 6-甲氧基泽兰素。

化合物 III: 红色针晶(丙酮)。¹H-NMR (400 MHz, CDCl₃) δ: 11.38 (1H, s, 与酮基形成氢键的 7 位酚羟基), 9.69 (1H, s, 醛基氢), 6.90 (1H, s, H-3), 6.46 (1H, s, H-6), 3.92 (3H, s, -OMe), 3.87 (3H, s, -OMe)。¹³C-NMR (100 MHz, CDCl₃) δ: 194.0 (d, C-1), 159.4 (s, C-4), 157.3 (s, C-5), 113.3 (d, C-3), 112.9 (s, C-7), 100.1 (d, C-6), 56.5 (s, -OMe), 56.3 (s, -OMe)。¹H-NMR、¹³C-NMR数据参考文献^[3]化合物 III 为 2-羟基-4,5-二甲氧基苯甲醛。

化合物 IV: 黄色针晶(丙酮)。¹H-NMR (400 MHz, CDCl₃) δ: 7.41 (1H, s, H-3), 7.04 (2H, s, H-5, H-8), 3.95 (3H, s, -OMe), 3.93 (3H, s, -OMe), 2.54 (3H, s, -CH₃)。¹³C-NMR (100 MHz, CDCl₃) δ: 187.6 (s, C=O), 152.4 (s), 151.7 (s), 151.4 (s), 147.8 (s), 119.1 (s), 113.8 (d), 102.8 (d), 95.1 (d), 56.3 (q, 2 个甲氧基), 26.1 (q, -CH₃)。¹H-NMR、¹³C-NMR数据参考文献化合物 IV 为 2-乙酰-5,6-二甲氧基苯呋喃^[1]。

化合物 V: C₈H₈O₂, 白色针状结晶(丙酮), mp 109 °C。MS *m/z*: 136[M]⁺ (65), 121 (100, 基峰), 107 (15), 93 (61), 77 (26), 74 (15), 65 (65), 53 (32)。¹H-NMR (CDCl₃) δ: 7.91 (2H, dd, *J* = 8.9, 2.2 Hz, H-2, 6), 6.98 (2H, dd, *J* = 8.9, 2.2 Hz, H-3, 5), 2.59 (3H, s, -Me)。¹³C-NMR (CDCl₃) δ: 162.1 (s, C-1), 131.5 (d, C-2), 115.9 (d, C-3), 129.6 (s, C-4), 115.6 (d, C-5), 131.5 (d, C-6), 199.4 (s, C=O), 26.4 (q, -Me)。mp、EI-MS、¹H-NMR、¹³C-NMR数据同参考文献^[3], 化合物 V 为对羟基苯乙酮。

化合物 VI: 白色针晶(石油醚-醋酸乙酯)。¹H-NMR (CDCl₃) δ: 7.01 (1H, s, H-4), 6.95 (1H, s, H-3), 6.52 (1H, s, H-7), 5.67 (1H, s, H-11a), 5.07

(1H, s, H-11b), 3.90 (3H, s, -OMe), 3.89 (3H, s, -OMe), 2.08 (3H, s, H-12)。¹³C-NMR (CDCl₃) δ: 156.5 (s, C-2), 149.6 (s, C-8), 148.3 (s, C-6), 146.5 (s, C-5), 132.9 (s, C-10), 120.8 (s, C-9), 111.5 (t, C-11), 102.8 (d, C-3), 102.4 (d, C-4), 95.2 (d, C-7), 56.4 (q, -OMe), 56.2 (q, -OMe), 19.3 (q, C-12)。¹H-NMR、¹³C-NMR数据见文献中 2-isopropenyl-5,6-dimethoxy-2,3-hydrocumarane 数据, 化合物 VI 为 2-isopropenyl-5,6-dimethoxy-2,3-hydrocumarane^[2]。

化合物 VII: C₁₅H₂₂O₃, 白色针晶(丙酮), mp 78~80 °C。TLC 5% 硫酸乙醇烘烤显紫红色。IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3 440、1 790、1 710。EI-MS *m/z* (%): 250 [M]⁺ (23), 232 [M-H₂O]⁺ (29), 222 (61), 217 (6), 205 (13), 189 (9), 177 (6), 161 (11), 141 (5), 126 (34), 109 (100), 98 (13), 91 (29), 81 (30), 67 (31), 55 (54)。¹H-NMR (400 MHz, CDCl₃) δ: 0.65 (3H, 类似 d 峰, C₄-Me), 0.90 (3H, s, C₅-Me), 1.64 (3H, s, C₁₁-Me)。¹³C-NMR (100 MHz, CDCl₃) δ: 20.4 (t, C-1), 26.1 (t, C-2), 30.5 (t, C-3), 29.5 (d, C-4), 40.2 (s, C-5), 34.9 (t, C-6), 160.0 (s, C-7), 104.3 (s, C-8), 38.8 (t, C-9), 39.5 (d, C-10), 121.7 (s, C-11), 173.2 (s, C-12), 7.9 (q, C-13), 21.2 (q, C-14), 15.8 (q, C-15)。mp、EI-MS、¹H-NMR、¹³C-NMR数据参考文献中的数据^[4], 化合物 VII 为 8 α -hydroxy-7 (11)-eremophilene-12,8 β -olide。

化合物 VIII: C₃₀H₅₀O, 白色针晶(醋酸乙酯), mp 213~214 °C, [α]_D²⁵ = +27.6° (CHCl₃, c = 0.646)。Liebermann-Burchard 反应呈红色。mp、EI-MS、¹H-NMR、¹³C-NMR数据参考文献^[6,7]中的数据, 推断化合物 VIII 为羽扇豆醇。

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