须花藤的化学成分

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摘 要 采用乙醇提取,硅胶柱层析分离和波谱方法鉴定结构,从须花藤 *Genianthus laurifolius*(Roxb.)Hook.f.地上部分共分离鉴定出 8 个化合物:羽扇豆醇乙酯(Ⅰ)、大黄素甲醚(Ⅱ)、β-谷甾醇(Ⅲ)、6,23-二烯-5,8-过氧麦角甾-3-醇(Ⅳ)、7,8β-epoxysinogenin-α-D-oleandropyranoside(Ⅴ)、常春藤配基(Ⅵ)、3β,23-二羟基乌索-12-烯-28-酸(Ⅶ)和胡萝卜甙(Ⅷ)。这些化合物均为首次从该属植物中分离得到。

关键词 须花藤;萝藦科;化学成分

萝藦科须花藤属植物种类不多,在我国仅有须花藤[*Genianthus laurifolius*(Roxb.)Hook.f.]一个种,其形态与同科的鲫鱼藤属(*Secamone*)和弓果藤属(*Toxocarpus*)植物相近[1],而这 2 个属的一些植物可作药用[2]。为了探索须花藤是否也具有潜在的药用价值,寻找天然活性成分,我们首次对该植物进行化学成分研究,从其地上部分乙醇提取物中共分离鉴定出以三萜和甾体为主的 8 个化合物,其结构分别为羽扇豆醇乙酯(Ⅰ)、大黄素甲醚(Ⅱ)、β-谷甾醇(Ⅲ)、6,23-二烯-5,8-过氧麦角甾-3-醇(Ⅳ)、7,8β-epoxysinogenin-α-D-oleandropyranoside(Ⅴ)、常春藤配基(Ⅵ)、3β,23-二羟基乌索-12-烯-28-酸(Ⅶ)和胡萝卜甙(Ⅷ),它们大都具有一些药理活性[3]。

1 仪器与试剂

熔点用 XRC-1 型显微熔点仪测定。ESI-MS 用 Finnigan LCQ^{DECA}型质谱仪测定。^{13}C NMR 和^{1}H NMR 用 Bruker AC-300P 型核磁共振仪测定,2D-NMR 用 Bruker AM-400 型核磁共振仪测定,TMS 为内标。薄层层析和柱层析用硅胶均为青岛海洋化工厂产品。LiChroprep RP-18 B 型反相柱为 Merck 公司产品。MCI 树脂为三菱化工产品。

2 提取分离

须花藤实验样品于 1999 年 11 月采自云南省景东县,由本所赵佐成研究员采集和鉴定。取 4.5 kg 地上部分干粉用 75%乙醇室温下浸提三次,每次 7 d,减压回收乙醇得浸膏 150 g。将其分散于水中,用石油醚脱脂后以等体积的乙酸乙酯萃取 4 次,回收溶剂后共得萃取物 95 g。该萃取物首先用硅胶柱层析(石油醚-乙酸乙酯梯度洗脱)粗分成 A～M 等 13 个组分。组分 A 和 B 经硅胶柱层析(石油醚-乙酸乙酯洗脱)分离得到化合物 Ⅰ和 Ⅱ,组分 E 经 2 次硅胶柱层析(氯仿-甲醇洗脱)分离得到化合物 Ⅲ,组分 G 通过 MCI 树脂柱层析脱去叶绿素后再反复用硅胶柱分离(氯仿-甲醇梯度洗脱)并辅以 RP-18 反相柱层析(甲醇-水梯度洗脱)纯化,得到化合物 Ⅳ和 Ⅴ。组分 H 经类似处理得到化合物 Ⅵ和 Ⅶ的混合物。组分 I 由硅胶柱层析(氯仿-甲醇梯度洗脱)分离出化合物 Ⅷ。

3 结构鉴定

3.1 化合物 Ⅰ

无色针晶,mp. 209～211 ℃,ESI-MS *m/z*:469 $[M+H]^+$,^{1}H NMR δ($CDCl_3$):4.69,4.58(each 1 H,br. s,29-H_2),4.50(1 H,m,3-H),2.38(1 H,m,19-H),2.05(3 H,s,Ac),1.69,1.04,0.95,0.86,0.85,0.84,0.79(each 3 H,s,17 ×CH_3)。^{13}C NMR δ($CDCl_3$)见表 1,与羽扇豆醇乙酯的文献值[4,5]一致。

3.2 化合物 Ⅱ

桔黄色针晶,mp. 206～208 ℃;^{1}H NMR($CDCl_3$) δ:12.32,12.12(each 1 H,s,1-OH,8-OH);7.62,7.08(each 1 H,d,*J* = 1 Hz,2-H,4-H);7.36,6.68.(each 1 H,d,*J* = 2 Hz,5-H,7-H);3.94(3 H,s,OCH_3);2.45(3 H,s,CH_3)。上述数据与大黄素甲

收稿日期:2001-10-15 修回日期:2001-11-12
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醚的文献报道[6]一致。

3.3 化合物 Ⅲ

无色针晶,mp.137～139 ℃,其 TLC 的 R_f 值同β-谷甾醇标准品一致。

3.4 化合物 Ⅳ

白色粉末,^{1}H NMR($CDCl_3$) δ:6.51,6.24(each 1 H,d,J = 8 Hz,6-H,7-H),5.22,5.14(each 1 H,d,J = 7,15 Hz,22-H,23-H),3.97(1 H,m,3-H),1.00,0.91,0.83,0.81(each 3 H,d,J = 7 Hz,21,26,27,28-H_3),0.89,0.82(each 3 H,s,18,19-H_3)。^{13}C NMR($CDCl_3$)见表 1。上述数据与 6,22-二烯-5,8-过氧-麦角甾-3-醇的文献值[7]一致。2D-NMR 分析(图 1)也与该结构吻合。

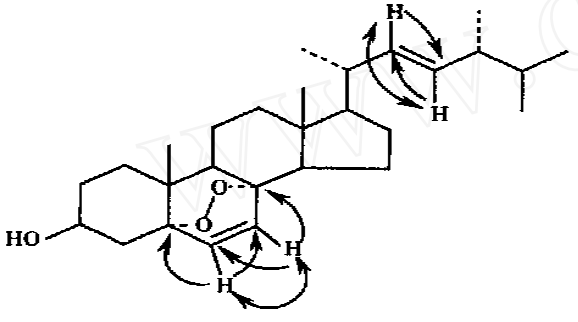

图 1 化合物 Ⅳ的重要 HMBC 碳氢远程相关和 ^{1}H-^{1}H COSY 氢氢相关

Fig.1 The key HMBC and ^{1}H-^{1}H COSY correlations for compound Ⅳ

3.5 化合物 Ⅴ

白色粉末,ESI-MS m/z:563[M + H]$^+$,^{1}H NMR(DMSO-d_6) δ:5.92(s,22-H),4.86(3 H,m,21-H_2,1′-H),4.53(d,J = 12 Hz,11-H),3.91(m,17-H),3.69(br.s,3-H),3.25(3 H,s,OCH_3),1.07(3 H,s,19-H_3),1.05(3 H,d,J = 6 Hz,6′-H_3),0.91(3 H,s,18-H_3)。^{13}C NMR(C_5D_5N)见表 1。结合 HMQC 碳氢相关和 HMBC 碳氢远程相关(图 2)分析,将该化合物鉴定为 7,8β-epoxysinogenin-α-D-oleandropyranoside,该结构曾有 X-单晶衍射分析的报道[8]。

3.6 化合物 Ⅵ和 Ⅶ

白色针晶,ESI-MS m/z:471[M - H]$^-$,^{13}C NMR(C_5D_5N)见表 1。分别与常春藤配基(3β,23-二羟基齐墩果-12-烯-28-酸)和 3β,23-二羟基乌索-12-烯-28-酸[5]的文献报道一致。

3.7 化合物 Ⅷ

白色粉末,mp.290～292 ℃,ESI-MS(+) m/z:599[M + Na]$^+$,397[M-glc]$^+$;ESI-MS(-) m/z:575[M-H]$^-$。其 TLC 的 R_f 值同胡萝卜甙标准品一致。

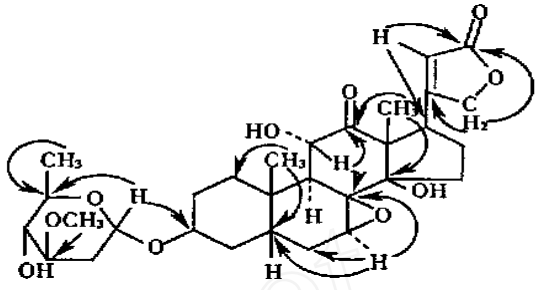

图 2 化合物 Ⅴ的重要 HMBC 碳氢远程相关

Fig.2 The key HMBC correlations for compound Ⅴ

表 1 化合物 Ⅰ和 Ⅳ～Ⅶ的^{13}C-NMR 化学位移

Table 1 The chemical shifts of compounds Ⅰ and Ⅳ～Ⅶ

C	Ⅰ[a]	Ⅳ	Ⅴ[b]	Ⅵ	Ⅶ
1	38.4	34.7t	32.7t	38.7t	38.9t
2	23.7	30.1t	27.0t	27.6t	27.6t
3	81.0	66.4d	71.3d	73.5d	73.5d
4	37.8	36.9t	33.3t	42.8s	42.8s
5	55.4	82.1s	36.2d	48.6d	48.0d
6	18.2	135.4d	27.2t	18.5t	18.6t
7	34.2	130.7d	52.0d	33.1t	33.1t
8	40.9	79.4s	63.7s	39.4s	39.7s
9	50.4	51.1d	34.4d	48.7d	48.6d
10	37.1	37.0s	34.8s	37.4s	37.2s
11	20.9	20.6t	74.3d	23.8t	23.9t
12	25.1	39.4t	212.8s	122.5d	125.6d
13	38.0	44.5s	64.5s	144.8s	139.2s
14	42.8	51.7d	81.4s	42.1s	42.8s
15	27.4	23.4t	36.2t	28.3t	27.6t
16	35.6	28.6t	28.4t	23.9t	24.8t
17	43.0	56.2d	42.4d	46.6s	46.6s
18	48.3	12.9q	18.4q	42.1d	53.5d
19	48.0	18.2q	23.7q	46.4t	39.2d
20	151.0	39.8d	175.0s	31.0s	39.4d
21	29.8	20.9q	74.4t	34.2t	30.9t
22	40.0	135.2d	117.6d	33.2t	37.2t
23	27.9	132.3d	174.6s	68.1t	68.1t
24	16.5	42.8d		13.0q	13.0q
25	16.2	33.1d		15.9q	15.9q
26	16.0	19.6q		17.5q	17.5q
27	14.5	19.9q		26.1q	23.9q
28	18.0	17.6q		180.0s	180.0s
29	109.3			33.2q	17.4q
30	19.3			23.9q	21.4q

a. Ac:171.0,21.3; b. sugar moiety:95.6,35.7,78.2,76.3,68.6,18.3,57.2,

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CHEMICAL CONSTITUENTS OF GENIANTHUS LAURIFOLIUS

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Abstract From the ethanol extract of aerial parts of *Genianthus laurifolius* (Roxb.) Hook f., eight compounds were isolated and identified as lupeol acetate (Ⅰ), physcione (Ⅱ), β-sitosterol (Ⅲ), 6,22-diene-5,8-epidioxyergosta-3-ol (Ⅳ), 7,8β-epoxysinogenin-α-D-oleandropyranoside (Ⅴ), hederagenin (Ⅵ), 3β,23-dihydroxy-urs-12-en-28-oic acid (Ⅶ) and daucosterol (Ⅷ), respectively. These compounds were isolated from *Genianthus* species for the first time.

Key words *Genianthus laurifolius*; Asclepiadaceae; chemical constituent

天然药物信息(医学期刊扫描:文摘和评论)

Natural Medicine Information (Medical Journal Watch: Abstract and Comments)

L-Carnitine Improves Exercise Tolerance Among Angina Patients

Iyer RN, Khan AA, et al. L-carnitine moderately improves the exercise tolerance in chronic stable angina. *J Assoc Phys India* 48(11):1050～1052,2000.

Forty-seven men and women aged 48 to 64 years who had chronic stable angina took 2 g of L-carnitine or placebo daily for 3 months. Those taking L-carnitine had a moderate improvement in exercise duration, with no side effects.

■ NP **Notes:** *Carnitine plays a critical role in the metabolic use of fat to produce energy. Increasing the supply of nutrients involved in the production of energy, such as those that yield adenosine triphosphate, can increase cellular energy levels. Other helpful nutrients include coenzyme Q10 and alpha-lipoic acid.*

Coenzyme Q10 Deficiency Found in Cases of Cerebellar Ataxia

Musumeci O, Naini A, et al. Familial cerebellar ataxia with muscle coenzyme Q10 deficiency. *Neurology* 56(7):849～855, 2001.

Coenzyme Q10 (CoQ10) deficiency was found in muscle biopsies of six patients with hereditary ataxia, a condition that affects coordination and speech. Supplementation with Co Q10 improved the condition of all the patients.

■ NP **Notes:** *Like carnitine, CoQ10 plays a key role in cellular energy production. Other studies have found that supplementation with CoQ10 can increase heart function and improve cognitive performance. However, some of the dosages of CoQ10 used in this study of ataxia were extremely high, ranging from 300 to 3,000 mg daily.*

Obese Children Have Increased Levels of C-Reactive Protein

Ford ES, Galuska DA, et al. C-reactive protein and body mass index in children: Findings from the Third National Health and Nutrition Examination Survey. *J. Pediatr* 138(4):486～492,2001.

These investigators reported that obese children had increased blood levels of C-reactive protein (CRP), a marker of systemic inflammation. The implication is that excess body weight may be associated with chronic low-grade inflammation in children as well as in adults.

■ NP **Notes:** *Abdominal adipose cells produce large amounts of CRP, in effect making obesity an inflammatory disorder. This increase in CRP may explain some of the increased risk of heart disease among obese persons.*