

上的硫醇基结合,抑制琥珀酰脱氢酶的活性,从而严重影响细胞的能量代谢,最终导致细胞死亡;3-硝基丙酸在人体引起的中毒症状表现为呕吐、共济失调、抽搐、惊厥、昏迷等。文献报道的木蓝山豆根中毒症状与上述症状极为相似,因此我们认为,木蓝山豆根中所含有的大量的3-硝基丙酸、coronarion和corollin很可能是引起毒性反应的主要成分。

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Diterpenoids from *Euphorbia wallichii*

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Abstract: **Object** To study the chemical constituents of *Euphorbia wallichii*. **Methods** The constituents were repeatedly separated and purified on silica gel column. They were identified on the basis of spectral methods. **Results** Nine diterpenoids were obtained from the roots of *E. wallichii*. Among them jolkinol B (I) is lathyrane type; caudicifolin (II), helioscopinolides A (III), C (IV), and E (V) belong to abietane type; while ent-atisane-3β,16α,17-triol (VI), ent-16α,17-dihydroxyatisane-3-one (VII), ent-3β(13S)-dihydroxyatis-16-en-14-one (VIII), and ent-2-hydroxy-atis-1,16(17)-dien-3,14-dione (IX) possess an ent-atisane skeleton. **Conclusion** All of them are isolated from *E. wallichii* for the first time. **Key words:** *Euphorbia wallichii* Hook. f.; *Euphorbia* L.; lathyrane; abietane; ent-atisane

大果大戟的二萜成分

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摘要: **目的** 研究大果大戟 *Euphorbia wallichii* 的化学成分。 **方法** 采用反复硅胶柱色谱分离纯化, 通过波谱方法鉴定化合物结构。 **结果** 从大果大戟根部的乙醇提取物中分离得到 9 个二萜化合物, 其中 jolkinol B (I) 是千金二萜烷型; caudicifolin (II), helioscopinolides A (III), C (IV) 和 E (V) 是松香烷型; ent-atisane-3β,16α,17-

* 收稿日期: 2003-10-12
 基金项目: 中国科学院昆明植物研究所、植物化学与西部植物资源持续利用国家重点实验室基金资助
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trio1 (VI), *ent*-16 α , 17-dihydroxyatisan-3-one (VII), *ent*-3 β (13 S)-dihydroxyatis-16-en-14-one (VIII) 和 *ent*-2-hydroxyatis-1, 16 (17)-dien-3, 14-dione (IX) 属于对映-阿替斯烷型。结论 这些成分均为首次从该植物中分离得到。

关键词: 大果大戟; 大戟属; 千金二萜烷型; 松香烷型; 对映-阿替斯烷型

中图分类号: R284.1

文献标识码: A

文章编号: 0253-2670(2004)06-0611-04

The *Euphorbia* L. is the largest genus in the spurge family, comprising about 2 000 species. More than 80% of them are distributed in China^[1]. Various groups have been worked on the chemical constituents from the plants of this genus^[3-9], and many biological active diterpenes have been found. *E. wallichii* Hook f., a traditional medicinal plant, distributed mainly in Qinghai Province, the Tibet Autonomous Region, and Yunnan Province of China, has been used by Tibetan to cure furuncle, exanthema, and cutaneous anthrax^[2]. Its chemical constituents have not previously been investigated. From the alcohol extract of the roots of this plant, one lathyrane type (I^[3]), four abietane type (II^[5]-V^[6]), as well as four *ent*-atisane type diterpenes (VI^[7], VII, VIII^[8], IX^[9]) were obtained. In this paper the isolation and structure elucidation of these compounds are reported.

1 Apparatus and plant materials

MS spectra were obtained with a VG Auto Spec-3000 spectrometer, at 70 eV for EI. NMR spectra were recorded from a Bruker AM-400 spectrometer with TMS as internal standard. And Si gel (200-300 meshes) for column chromatography was obtained from the Qingdao Marine Chemical Industry Factory. *E. wallichii* was collected from Xinghai County, Qinghai Province of China, in July 2001. It was identified by Prof. ZHANG Xiao-feng.

2 Extraction and isolation

Air-dried root (10 kg) was extracted with EtOH (95%) for four times. After removal of the solvent by evaporation, the residues were suspended in H₂O and extracted with CHCl₃ for three times. The CHCl₃ fraction was concentrated *in vacuo* to give 100 g of the residue. The residue was separated repeatedly by chromatography on silica gel column and RP-18 to afford I (50 mg), II (10 mg), III (60 mg), IV (20 mg), V (30 mg), VI (180 mg), VII (300 mg), VIII (10 mg), IX (55

mg). Their structures are shown in Fig. 1.

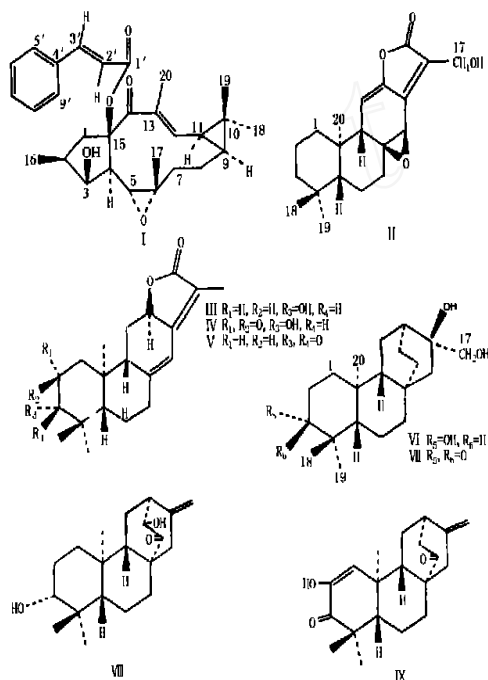


Fig. 1 Structures of diterpenoids I - IX

3 Identification

Jolkinol B (I): C₂₉H₃₆O₅, colorless oil; ¹H-NMR (CDCl₃): δ 3.46 (1H, dd, 7, 13.2 Hz, H-1 α), 3.61 (1H, d, 9.6 Hz, H-5), 4.09 (1H, br s, H-3), 6.38 (1H, d, 16.0 Hz, H-2), 6.94 (1H, d, 11.0 Hz, H-12), 7.2-7.4 (5H, m), 7.59 (1H, d, 16.0 Hz, H-3); ¹³C-NMR (CDCl₃): δ 44.9 (C-1), 29.6 (C-2), 78.2 (C-3), 52.1 (C-4), 58.4 (C-5), 64.1 (C-6), 38.6 (C-7), 23.2 (C-8), 33.7 (C-9), 26.2 (C-10), 38.5 (C-11), 144.2 (C-12), 133.8 (C-13), 195.1 (C-14), 91.9 (C-15), 13.2 (C-16), 19.9 (C-17), 28.9 (C-18), 16.1 (C-19), 12.3 (C-20), 165.5 (C-1), 117.4 (C-2), 146.3 (C-3), 133.9 (C-4), 128.0 (C-5), 128.8 (C-6), 130.5 (C-7), 128.8 (C-8), 128.0 (C-9); EIMS *m/z*: 464 [M]⁺ (3), 333 (13), 316 (3), 131 (100), 121 (18), 103 (75), 93 (27), 77 (40).

Caudicifolin (II): C₂₀H₂₆O₄, colorless needles; ¹H-NMR (CDCl₃): δ 0.71, 0.83, 0.92 (each

3H, s, Me × 3), 2.63 (1H, d, 5.5 Hz, H-9), 4.00 (1H, br s, H-14), 4.62 (2H, br s, H-17), 5.55 (1H, d, 5.5 Hz, H-11); ¹³C-NMR (CDCl₃) see Table 1; EIMS *m/z*: 330 [M]⁺ (9), 312 (19), 230 (23), 188 (33), 175 (84), 162 (43), 147 (18), 137 (51), 123 (37), 109 (36), 95 (84), 81 (86), 69 (100), 55 (68).

Helioscopinolide A (III): C₂₀H₂₈O₃, colorless needles; ¹H-NMR (CDCl₃): δ 0.80, 0.92, 1.01 (each 3H, s, Me × 3), 1.81 (3H, d, 1.4 Hz, H-17), 3.26 (1H, dd, 4.4, 11.8 Hz, H-3), 4.84 (1H, dd, 6.3, 12.6 Hz, H-12), 6.25 (1H, br s, H-14); ¹³C-NMR (CDCl₃) is seen in Table 1.

Helioscopinolide C (IV): C₂₀H₂₆O₄, colorless needles; ¹H-NMR (CDCl₃): δ 0.68, 0.91, 1.23 (each 3H, s, Me × 3), 1.84 (3H, d, 1.4 Hz, H-17), 3.95 (1H, br s, H-3), 4.84 (1H, dd, 6.3, 12.6 Hz, H-12), 6.32 (1H, br s, H-14); ¹³C-NMR (CDCl₃) is seen in Table 1.

Table 1 ¹³C-NMR spectral data for compounds II- IX (10 MHz)

C	II	III	IV	V	VI	VII	VIII	IX
1	40.3 t	37.4 t	51.2 t	37.3 t	38.0 t	37.9 t	36.3 t	124.9 d
2	18.8 t	27.5 t	209.4 s	34.3 t	27.9 t	34.0 t	26.8 g	144.1 s
3	41.9 t	78.5 d	82.4 d	215.5 s	78.2 d	217.5 s	78.8 d	200.7 s
4	33.9 s	39.0 s	45.0 s	47.5 s	39.2 s	47.6 s	38.6 s	43.8 s
5	54.0 d	54.3 d	53.4 d	54.6 d	55.7 d	55.6 d	54.5 d	53.2 d
6	21.2 t	23.4 t	23.0 t	24.5 t	18.9 t	19.6 t	18.8 t	19.1 t
7	34.3 t	36.8 t	36.3 t	36.5 t	40.1 t	38.7 t	30.7 t	31.0 t
8	61.7 s	151.4 s	149.4 s	150.2 s	37.7 s	32.8 s	47.4 s	48.0 s
9	52.2 d	51.5 d	51.3 d	50.5 d	52.1 d	50.8 d	51.9 d	48.8 d
10	41.9 s	41.2 s	46.9 s	40.8 s	33.0 s	37.2 s	37.8 s	39.1 s
11	106.9 d	27.5 t	27.6 t	27.7 t	23.6 t	23.2 t	25.2 t	28.0 t
12	147.8 s	75.9 d	75.3 d	75.6 d	32.8 d	32.1 d	44.8 d	38.0 d
13	147.0 s	156.0 s	155.0 s	155.5 s	23.8 t	23.4 t	75.0 d	44.5 t
14	54.8 d	114.2 d	115.2 d	114.6 d	27.7 t	27.4 t	218.4 s	216.4 s
15	127.8 s	116.4 s	117.5 s	116.9 s	53.5 t	52.4 t	43.8 t	42.5 t
16	169.6 s	175.3 s	174.9 s	175.0 s	73.7 s	74.2 s	142.7 s	146.5 s
17	56.8 t	8.2 q	8.3 q	8.3 q	69.3 t	68.9 t	110.7 t	107.6 t
18	33.9 q	28.6 q	29.5 q	26.4 q	28.6 q	26.1 q	28.4 q	26.9 q
19	22.3 q	15.6 q	16.4 q	21.7 q	16.3 q	21.6 q	15.6 q	21.9 q
20	15.5 q	16.7 q	17.3 q	16.2 q	14.2 q	13.4 q	14.0 q	17.2 q

Compound VI was measured in CD₃N, while other compounds in CDCl₃ with TMS as internal standard

Helioscopinolide E (V): C₂₀H₂₆O₃, colorless needles; ¹H-NMR (CDCl₃): δ 1.02, 1.04, 1.09, 1.80 (each 3H, s, Me × 3), 4.84 (1H, m, H-12), 6.30 (1H, s, H-14); ¹³C-NMR (CDCl₃) is seen in Table 1; EIMS *m/z*: 314 [M]⁺ (80), 296 (45), 204 (30), 177 (56), 164 (100), 151 (20), 138

(60), 123 (97), 109 (19), 96 (20), 81 (14), 69 (8), 55 (14).

ent-A tisan-3β 16α, 17-triol (VI): C₂₀H₃₄O₃, white powders; ¹H-NMR (CD₃N): δ 0.98, 1.03, 1.20 (each 3H, s, Me × 3), 3.42 (1H, dd, 4.8, 11.3 Hz, H-3), 3.81, 3.90 (2H, Abq, 10.8 Hz, H-17); ¹³C-NMR (CD₃N) is seen in Table 1; EIMS *m/z*: 322 [M]⁺ (< 1), 291 (100), 273 (79), 255 (20), 229 (15), 135 (30), 57 (24).

ent-16α, 17-Dihydroxyatisan-3-one (VII): C₂₀H₃₂O₃, colorless needles; ¹H-NMR (CDCl₃): δ 2.31 (1H, m, H-2α), 2.56 (1H, m, H-2β), 3.40, 3.53 (2H, Abq, 10.8 Hz, H-17); ¹³C-NMR (CDCl₃) is seen in Table 1; EIMS *m/z*: 320 [M]⁺ (< 1), 289 (52), 271 (17), 247 (25), 107 (37), 95 (45), 81 (47), 69 (52), 55 (100).

ent-3β (13S)-Dihydroxyatis-16-en-14-one (VIII): C₂₀H₃₀O₃, white powders; ¹H-NMR (CDCl₃): δ 3.18 (1H, dd, 4.3, 11.6 Hz, H-3), 3.82 (1H, d, 3.0 Hz, H-13), 4.81 (1H, d, 1.0 Hz, H-17), 4.97 (1H, br s, H-17); ¹³C-NMR (CDCl₃) is seen in Table 1; EIMS *m/z*: 318 [M]⁺ (53), 300 (9), 243 (22), 136 (80), 121 (65), 107 (66), 97 (30), 91 (70), 81 (61), 69 (70), 57 (100).

ent-2-Hydroxy-atis-1, 16 (17)-dien-3, 14-dione (IX): C₂₀H₃₀O₃, white powders; ¹H-NMR (CDCl₃): δ 2.75 (1H, t, 2.9 Hz, H-12), 4.66 (1H, br s, H-17b), 4.89 (1H, br s, H-17a), 6.01 (1H, s, OH), 6.06 (1H, s, H-1); ¹³C-NMR (CDCl₃) is seen in Table 1; EIMS *m/z*: 314 [M]⁺ (100), 300 (32), 243 (5), 187 (25), 154 (14), 55 (7).

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两种毛大丁草多糖 Gbp 和 Gcp 的组成研究

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摘要: 目的 从毛大丁草的根中分离提取多糖, 测定其组成。方法 毛大丁草根的水提取物经脱蛋白、脱色、乙醇沉淀得两种粗多糖, 再经过 Sephadex G-75 和 Sephadex G-50 凝胶柱色谱纯化得到两种纯多糖 Gbp 和 Gcp, 用高效凝胶色谱 (HPGPC) 测定 Gbp 和 Gcp 相对分子质量, 通过完全酸水解后, 进行三甲基硅醚化的 GC-MS 分析, 测定两种多糖的组成。结果 Gbp 和 Gcp 重均相对分子质量分别为 6.65×10^5 和 7.45×10^4 。Gbp 是由木糖、来苏糖、鼠李糖、核糖、葡萄糖和半乳糖组成, 其比例约为 3 : 3 : 3 : 2 : 6 : 2; Gcp 主要由果糖组成, 还有少量葡萄糖和木糖, 其比例为 24 : 4 : 1。结论 通过凝胶柱色谱分析, 所提取两种多糖 Gbp 和 Gcp 均为单一、纯净的多糖。

关键词: 毛大丁草; 多糖; 三甲基硅醚化反应

中图分类号: R 284.1

文献标识码: A

文章编号: 0253 - 2670(2004)06 - 0614 - 03

Study on composition of two polysaccharides Gbp and Gcp from root of *Gerbera piloselloides*

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Abstract: **Object** To study the composition of two polysaccharides Gbp and Gcp which were isolated and purified from *Gerbera piloselloides* (L.) Cass. **Methods** The polysaccharides were extracted with hot water and precipitated by alcohol. Protein in the precipitates was removed by Sevag method. The products were further purified with column chromatography on Sephadex-75 and Sephadex-50. The molecular weights of Gbp and Gcp were measured by HPGPC. Their compositions were studied by using GC-MS after acid hydrolysis and trimethylsilylation. **Results** The weight-average molecular weights of Gbp and Gcp are 6.65×10^5 and 7.45×10^4 respectively (with polyoxyethylene glycol as a reference). Gbp is consisted of lyxose, xylose, robitose, glucose, and galactose, the rate is 3 : 3 : 3 : 2 : 6 : 2. Gcp is composed of fructose, glucose, and xylose (24 : 4 : 1). **Conclusion** Gbp and Gcp are shown to be homogeneous by gel permeation chromatography.

Key words: *Gerbera piloselloides* (L.) Cass.; polysaccharide; trimethylsilylation

多糖是一类重要的生命大分子物质, 在生物体内有重要的生物功能和良好的生物活性, 在生命科学和医药科学中有广泛的应用, 因而多糖成为具有吸引力的研究领域^[1]。我们从鲍鱼和海洋微生物的

菌体中分离出多种有生物活性的多糖, 并对其组成、结构和药理活性进行了研究^[2,3]。近来又从中药毛大丁草的根部分离出两种多糖 Gbp 和 Gcp, 药理实验显示这两种多糖是良好的免疫调节作用。毛大丁草

* 收稿日期: 2003-10-19
 基金项目: 广东省中医药局科研资助项目 (101028)
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