

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。

References

[1] Xiao P G. *Record of Modern Chinese Medicinal Plants* (新编中药志) [M]. Beijing: Chemical Industry Press, 2002.  
 [2] Xu G J, Xu L S. *Arrangement and Quality Study of Commonly Used Traditional Chinese Drugs* (常用中药材品种整理和质量研究) [M]. Fuzhou: Fujian Science and Technology Press, 1994.  
 [3] Thangadurai D, Ramesh N, Viswanathan M B, et al. A novel xanthone from *Indigofera longicaulis* stem [J]. *Fitoterapia*, 2001, 72(1): 92-94.  
 [4] Hasan A, Ahmad I, Khan M A, et al. Two flavonol triglycosides from flowers of *Indigofera hebetata* [J]. *Phytochemistry*, 1996, 43(5): 1115-1118.

[5] Dominguez X A, Martinez C, Calero A, et al. Mexican medicinal plants XXXI chemical components from "jiquelite" *Indigofera suffruticosa* [J]. *Planta Med*, 34(1): 172-175.  
 [6] Majak W, Benn M. Additional esters of 3-nitropropanoic acid and glucose from fruit of the New Zealand karaka tree, *Corynocarpus laevigatus* [J]. *Phytochemistry*, 1994, 35(4): 901-903.  
 [7] Mahato S B, Kundu A P. <sup>13</sup>C-NMR spectra of pentacyclic triterpenoids—a compilation and some salient features [J]. *Phytochemistry*, 1994, 37(6): 1517-1575.  
 [8] Yu D Q, Yang J S. *Handbook of Analytical Chemistry Analysis of NMR Spectra* (分析化学手册 第 7 分册 核磁共振波谱分析) [M]. Volume 7. 2nd ed. Beijing: Chemical Industry Press, 1999.  
 [9] Hanley A B, McBride J, Oehlschlager S, et al. Use of a flow cell bioreactor as a chronic toxicity model system [J]. *Toxicology in Vitro*, 1999, 13: 847-851.  
 [10] Peraica M, Radic B, Lucic A, et al. Toxic effects of mycotoxins in humans [J]. *Bull World Health Organ*, 1999, 77(9): 754-766.

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-

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trio1 (VI), *ent*-16 $\alpha$ , 17-dihydroxyatisan-3-one (VII), *ent*-3 $\beta$  (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

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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<sup>[1]</sup>. Various groups have been worked on the chemical constituents from the plants of this genus<sup>[3-9]</sup>, 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<sup>[2]</sup>. Its chemical constituents have not previously been investigated. From the alcohol extract of the roots of this plant, one lathyrane type (I<sup>[3]</sup>), four abietane type (II<sup>[5]</sup>-V<sup>[6]</sup>), as well as four *ent*-atisane type diterpenes (VI<sup>[7]</sup>, VII, VIII<sup>[8]</sup>, IX<sup>[9]</sup>) 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 H<sub>2</sub>O and extracted with CHCl<sub>3</sub> for three times. The CHCl<sub>3</sub> 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.

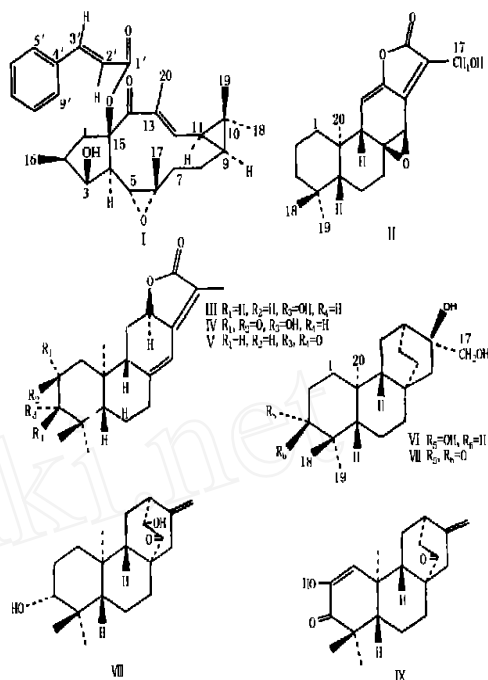


Fig. 1 Structures of diterpenoids I - IX

### 3 Identification

Jolkinol B (I): C<sub>29</sub>H<sub>36</sub>O<sub>5</sub>, colorless oil; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  3.46 (1H, dd, 7, 13.2 Hz, H-1 $\alpha$ ), 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); <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  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]<sup>+</sup> (3), 333 (13), 316 (3), 131 (100), 121 (18), 103 (75), 93 (27), 77 (40).

Caudicifolin (II): C<sub>20</sub>H<sub>26</sub>O<sub>4</sub>, colorless needles; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  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); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) see Table 1; EIMS *m/z*: 330 [M]<sup>+</sup> (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): C<sub>20</sub>H<sub>28</sub>O<sub>3</sub>, colorless needles; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 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); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) is seen in Table 1.

Helioscopinolide C (IV): C<sub>20</sub>H<sub>26</sub>O<sub>4</sub>, colorless needles; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 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); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) is seen in Table 1.

**Table 1** <sup>13</sup>C-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 CD<sub>3</sub>N, while other compounds in CDCl<sub>3</sub> with TMS as internal standard

Helioscopinolide E (V): C<sub>20</sub>H<sub>26</sub>O<sub>3</sub>, colorless needles; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 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); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) is seen in Table 1; EIMS *m/z*: 314 [M]<sup>+</sup> (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): C<sub>20</sub>H<sub>34</sub>O<sub>3</sub>, white powders; <sup>1</sup>H-NMR (CD<sub>3</sub>N): 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); <sup>13</sup>C-NMR (CD<sub>3</sub>N) is seen in Table 1; EIMS *m/z*: 322 [M]<sup>+</sup> (< 1), 291 (100), 273 (79), 255 (20), 229 (15), 135 (30), 57 (24).

*ent*-16α, 17-Dihydroxyatisan-3-one (VII): C<sub>20</sub>H<sub>32</sub>O<sub>3</sub>, colorless needles; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 2.31 (1H, m, H-2α), 2.56 (1H, m, H-2β), 3.40, 3.53 (2H, Abq, 10.8 Hz, H-17); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) is seen in Table 1; EIMS *m/z*: 320 [M]<sup>+</sup> (< 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): C<sub>20</sub>H<sub>30</sub>O<sub>3</sub>, white powders; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 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); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) is seen in Table 1; EIMS *m/z*: 318 [M]<sup>+</sup> (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): C<sub>20</sub>H<sub>30</sub>O<sub>3</sub>, white powders; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 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); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) is seen in Table 1; EIMS *m/z*: 314 [M]<sup>+</sup> (100), 300 (32), 243 (5), 187 (25), 154 (14), 55 (7).

**References**

- [1] Shi Y P, Jia Z J. Recent studies on diterpene esters and their bioactivities from *Euphorbia* genus in China [J]. *Chem J Chin Univ* (高等学校化学学报), 1997, 18(7): 1107-1112.
- [2] Northwest Institute of Plateau Biology, Chinese Academy of Science. *Tibetan Medicine Glossary* (藏药志) [M]. Xining: Qinghai People's Publishing House, 1991.
- [3] Shi J G, Jia Z J, Yang L. Diterpenoids from *Euphorbia microactina* [J]. *Chem J Chin Univ* (高等学校化学学报), 1994, 15(6): 861-863.
- [4] Lal A R, Cambie R C, Rutledge P S, et al. *Ent*-pinarane and *ent*-abietane diterpenes from *Euphorbia fidjiana* [J]. *Phytochemistry*, 1990, 29 (7): 2239-2246.
- [5] Satti N K, Suri O P, Dhar K L, et al. High resolution NMR and X-ray crystallography data of caudicifolin from *Euphorbia*

- acaulis* [J]. *Phytochemistry*, 1986, 25 (6): 1411-1431.
- [6] Borghi D, Baumer L, Ballabio M, et al. Structure elucidation of helioscopinolides D and E from *Euphorbia calytrata* cell cultures [J]. *J Nat Prod*, 1991, 54(6): 1503-1508.
- [7] Jia Z, Ding Y L. New diterpenoids from *Euphorbia sieboldiana* [J]. *Planta Med*, 1991, 57, 569-571.
- [8] Lal A R, Cambie R C, Rutledge P S, et al. Entatisane diterpenes from *Euphorbia fidjiana* [J]. *Phytochemistry*, 1990, 29(6): 1925-1935.
- [9] Appendino G, Bellro E, Tron G C, et al. Polycyclic from *Euphorbia characias* [J]. *Fitoterapia*, 2000, 71 (2): 134-142.

## 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  $6.65 \times 10^5$  和  $7.45 \times 10^4$ 。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

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### 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  $6.65 \times 10^5$  and  $7.45 \times 10^4$  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<sup>[1]</sup>。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<sup>[2,3]</sup>。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

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