℃减压干燥后用无水乙醇重结晶，得白色针状结晶 5 mg。将此针晶与薯蓣皂苷元对照品进行 TLC 分析，Rf 值完全一致。将此再同做 IR 谱，图谱完全重叠，证明皂苷元为薯蓣皂苷元。

将上述酸水解液用 1 mol/L NaOH 液中和，浓缩后进行 TLC 分析，用展开剂⑥展开，显色剂⑤显色，*D*-葡萄糖与 *L*-鼠李糖作对照品，从水解液中检出葡萄糖与鼠李糖。

皂苷 D 的部分水解：取约 150 mg 皂苷 D 于 10 mL 试管中，加 3 mL 1 mol/L HCl 溶液溶解。置此试管于沸水浴中加热 20 min，冷却。滤出沉淀，用 1 mL 甲醇溶解，与皂苷 A、B、C 和次生苷 Ⅰ、Ⅱ同做硅胶 H、TLC 分析，用展开剂②展开，显色剂①显色。水解物呈现 7 个斑点，其中极性小的 5 个斑点的 Rf 值均与皂苷 A、B、C 和次生苷 Ⅰ、Ⅱ完全一致，另换两种展开剂①、③展开，作相同对照操作，仍得到完全相同结果。取硅胶 H 制备色谱板（20 cm × 10 cm × 0.1 cm）一块，用微量注射器吸取上述沉淀溶解的甲醇液 500 μL，成条状（2 cm）点样于板底部，挥去溶剂后于层析缸中用展开剂②展开。展开完全后取出，挥干溶剂再展开 1 次，取出晾干，置碘缸中碘蒸气显色 3～5 min，取出立即用铅等划出极性小的 5 条色带的边界。挥去碘用刮刀刮下各色带的吸附剂，分别置于 G_3 玻沙漏斗中用 5 mL 甲醇洗脱，抽滤。滤液置 10 mL 蒸发皿内蒸干溶剂，刮下各残留物以 KBr 压片分别做 IR 光谱。所得的 IR 谱分别与次生苷 Ⅰ、Ⅱ，皂苷 A、B、C 的 IR 谱完全重合。此确定了皂苷 D 部分水解所得的 7 个次生苷中有 5 个分别为次生苷 Ⅰ、Ⅱ，皂苷 A、B、C。

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References:

[1] Xu X M, Wang J, Yang H, *et al*. Studies on the saponin constituents from the seeds of *Trigonella foenum-graecum* L. (Ⅰ)—Isolation and structural elucidation for a new saponin A and its secondary glucosides Ⅰ, Ⅱ [J]. *Chin Tradit Herb Drugs* (中草药), 2003, 34(8): 678-682.

[2] Xu X M, Wang J, Yang H, *et al*. Studies on the saponins constituents from the seeds of *Trigonella foenum-graecum* L. (Ⅱ) — Isolation and structural elucidation for two new saponins B and C [J]. *Chin Tradit Herb Drugs* (中草药), 2004, 35(2): 127-130.

[3] Breitmaier E, Haas G, Voeleer W, *et al*. *Atlas of Carbon-13NMR Data* [M]. Vol Ⅰ. Philadelphia: Heyolen and Son Ltd, 1979.

Two compounds from *Drymaria diandra*

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Abstract: **Objective** To investigate the chemical costituents from *Drymaria diandra*. **Methods** Compounds were separated and purified by repeated column chromatographies on macroporous resin D-101, silica gel, and RP-18. Two compounds were identified by spectral analysis. **Results** Two compounds were isolated from *D. diandra*. Their structures were identified as 6-carboxymethyl-5, 7, 4′-trihydroxyflavone (Ⅰ) and 1-*O*-β-*D*-glucopyranosyl-(2*S*, 3*R*, 4*E*, 8*E*)-*Z*-*N*-(2′-hydroxypalmitoyl) octadecasphinga-4, 8-dienine (soya cerebroside Ⅰ, Ⅱ). **Conclusion** Compound Ⅰ is a new compound. Compound Ⅱ is obtained from this plant for the first time.

Key words: *Drymaria diandra* Blume; Caryophyllaceae; flavone

二蕊荷莲豆中的两个化合物

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摘 要：**目的** 研究二蕊荷莲豆 *Drymaria diandra* 的化学成分。**方法** 采用大孔树脂 D-101，硅胶柱色谱和 PR-18 进行反复分离纯化，通过波谱分析方法鉴定化合物结构。**结果** 分离并鉴定了 2 个化合物：6-羧甲基-5,7,4′-三羟基黄酮（Ⅰ）和 4[*E*],8[*E*]-*N*-[2′-*D*-羟基-十六烷酰基]-1-*O*-*D*-吡喃葡萄糖基-4,8-二烯-十八鞘氨醇（大豆脑苷 Ⅰ，Ⅱ）。**结论** 化合物 Ⅰ 为新化合物，化合物 Ⅱ 首次从该植物中分离得到。

关键词：二蕊荷莲豆；石竹科；黄酮

中图分类号：R284.1 **文献标识码**：A **文章编号**：0253-2670(2005)06-0808-03

Drymaria diandra Blume (Caryophyllaceae) grows under trees or near rivers. In China, it is used as a folk medicine for treatment of acute hepatitis[1]. It was reported previously that three new cyclic peptides, a novel flavonoid glycoside (drymariatin A, which had two additional olefinic carbons compared with general flavone), alkaloids, terpenes, and long chain fatty acides had been isolated from this plant collected in Xishuangbanna, Yunnan Province[2-5]. As a series of investigation on bioactive compounds, a chemical study on this plant was carried out. A new flavone (compound Ⅰ) and a cerebroside (compound Ⅱ) were obtained from the ethyl acetate fraction of its ethanol extract by column chromatography.

1 Apparatus and materials

NMR spectra were obtained on DRX-500 MHz spectrometer. VG Auto Spec-3000 spectrometer was used to record MS spectrum. IR spectra were recorded with a Bio-Rad FTS-135 spectrometer. Melting points were determined on kolfler block and uncorrected. 200-300 and 300-400 meshes silica gel, macroporous resin D-101 and RP-18 were used for column chromatography.

2 Extration and isolation

The whole plants of *D. diandra* (15.2 kg) were extracted with hot ethanol three times to afford a extract that was suspended in water, then extracted with petroleum, ethyl acetate, and *n*-butanol, respectively. The ethyl acetate residue was chromatographyed on macroporous resin D-101 using H_2O-MeOH (from 9∶1 to 1∶9) gradient system. The fraction eluted with 70% MeOH was further subjected to silica gel column chromatography using $CHCl_3$-MeOH system (from 98∶2 to 50∶50) and purified repeatedly on RP-18 (H_2O-MeOH, 10∶90) to afford compound Ⅰ (5 mg) and compound Ⅱ (72 mg).

3 Identification

Compound Ⅰ: $C_{17}H_{12}O_7$, yellow needles (CH_3OH), FAB-MS *m/z* (%): 327 (100), 169 (5), 80 (4), HR-FAB-MS $[M-H]^-$ *m/z*: 327.050 6 (calcd: 327.050 4); ^{13}C-NMR (125 MHz, CD_3OD) and ^{1}H-NMR (500 MHz, CD_3OD) are listed in Table 1.

Table 1 NMR data of compound Ⅰ [in CD_3OD, 500 MHz for δ_H and 125 MHz for δ_C]

Compound Ⅰ	δ_C	δ_H	Compound Ⅰ	δ_C	δ_H
2	164.8		10	103.7	
3	102.5	6.60(1H,s)	1′	122.0	
4	182.5		2′,6′	128.3	7.85(1H,d,8.8 Hz)
5	159.3		3′,5′	115.6	6.94(1H,d,8.8 Hz)
6	105.7		4′	161.3	
7	162.7		1″	27.3	3.66(2H,s)
8	92.8	6.52(1H,s)	2″	176.0	
9	156.7				

Compound Ⅱ: $C_{40}H_{75}NO_9$, white amorphous powder, mp 180-182 ℃; FAB-MS *m/z* (%): 713 (100), 550(9), 431(3), 367 (7), 296 (15), $IR\nu_{max}^{KBr}$ cm^{-1}: 3 724.3(OH), 1 645.2, 2 918.4, 2 849.9, 1 529.1, 1 468.0, 1 081.7; ^{1}H-NMR (500 MHz, $CDCl_3$∶CD_3OD=3∶2) δ: 4.07 (1H, dd, *J*=10.0, 5.0 Hz, H-1a), 3.74 (1H, dd, *J*=10.0, 3.0 Hz, H-1b), 3.19 (1H, m, H-2), 4.03 (1H, m, H-3), 5.47 (1H, dd, *J*=15.0, 10.0 Hz, H-4), 5.44 (1H, br, d, *J*=15.0 Hz, H-5), 2.06 (2H, m, H-6), 2.06 (2H, m, H-7), 5.41 (1H, m, H-8), 5.44 (1H, m, H-9), 1.97 (2H, m, H-10), 1.39 (2H, m, H-11), 1.26 (12H, m, H-12-17), 0.88 (6H, t, *J*=5.0 Hz, H-18, 16′), 4.10 (1H, m, H-2′), 1.55 (1H, m, H-3′a), 1.74 (1H, m, H-3′b), 1.35 (2H, m, H-4′), 1.26 (22H, m, H-5′-15′), glucose moiety: 4.22 (1H, d, *J*=5.0 Hz, H-1″), 3.24 (1H, m, H-2″), 3.26 (1H, m, H-3″), 3.29 (1H, m, H-4″), 3.30 (1H, m, H-5″), 3.85 (1H, dd, *J*=10.0, 1.5 Hz, H-6″a), 3.71 (1H, dd, *J*=10.0, 5.0 Hz, H-6″b); ^{13}C-NMR (125 MHz, $CDCl_3$∶CD_3OD=3∶2) δ:

68.9 (C-1), 53.8 (C-2), 72.5 (C-3), 131.5 (C-4), 134.2 (C-5), 33.0 (C-6), 32.6 (C-7), 129.6 (C-8), 129.5 (C-9), 32.3 (C-10), 32.6 (C-11), 30.2—29.7 (C-12—17), 14.3 (C-18), 175.3 (C-1′), 74.0 (C-2′), 35.1 (C-3′), 23.0—33.0 (C-4′—15′), 14.3 (C-16′), glucose moiety: 103.6 (C-1″), 74.0 (C-2″), 76.8 (C-3″), 70.6 (C-4″), 78.0 (C-5″), 62.0 (C-6″). It was identified as soya-cerebroside I by spectral analysis and compared with data of literature[6].

4 Results and Discussion

Compound I, yellow needle, its negative FAB-MS exhibited the molecular ion peak at m/z: 327 ($[M-H]^-$, base peak). According to HR-FAB-MS (m/z: 327.050 6 calcd: 327.050 4), its molecular formula was established as $C_{17}H_{12}O_7$, indicating 12 degrees of unsaturation. The ^{1}H-NMR spectrum of this compound revealed a singlet at δ 3.66, two aromatic singlets at δ 6.60 and 6.52, an AX pair of aromatic doublets at δ 7.85 (2H, J=8.8 Hz) and 6.94 (2H, J=8.8 Hz) characteristic of a para disubstituted aromatic ring. The ^{13}C-NMR and DEPT spectra showed two carbonyl, eight quarternary carbon, six methine carbon and one methylene carbon signals. This information indicated that compound I was a flavone. Comparison with ^{13}C-NMR signals of 5, 7, 4′-trihydroxyflavone[7] and taking its molecular formular into account, compound I has one additional carboxymethyl. The HMBC spectrum (Fig. 1) showed correlations between the methylene proton H-1″ (δ 3.66, s) of carboxymethyl and C-6 (δ 105.7), H-1″ and C-2″ (δ 176.0), H-1″ and C-5 (δ 157.3), H-1″ and C-7 (δ 162.7). This indicated that the methylene carbon was linked to C-6. Therefore the structure of compound I was determined as 6-C-carboxymethyl-5, 7, 4′-trihydroxyflavone. It was a novel flavone and its total assignment of protons and carbons were assigned with the aid of HMQC and HMBC spectra (Table 1).

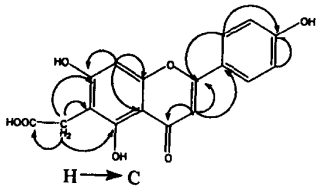

Fig. 1 HMBC of compound I

Compound II was obtained as amorphous powder. By analysis of its ^{1}H-NMR and ^{13}C-NMR data, it was determined as soya-cerebroside I, which was reported that it had ionophoretic and anti-ulcerogenic activity[7,8], and it was from *D. diandra* for the first time.

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References:

[1] Wu C Y. *A Compedium of New China (Xinhua) Herbal* (新华本草纲要) [M]. Vol II. Shanghai: Shanghai Scientific and Technical Publishers, 1990.

[2] Ding Z T, Zhou J, Tan N H. A novel flavonid glycoside from *Drymaria diandra* [J]. *Planta Med*, 1999, 65(6): 578-579.

[3] Ding Z T, Zhou J, Tan N H. Two new cyclopeptides from *Drymaria diandra* [J]. *Planta Med*, 2000, 66(4): 386-388.

[4] Ding Z T, Zhou J, Tan N H. Structure of a new cyclopeptide from *Drymaria diandra* [J]. *J Yunnan Univ* (云南大学学报), 2000, 22(2): 123-125.

[5] Yang X Q, Huang R, Bao Z J, *et al*. Study on chemical constituents from *Drymaria diandra* Bl. [J]. *J Yunnan Univ* (云南大学学报), 2003, 25(4): 358-360.

[6] Shibuya H, Kawashima K, Sakagami M, *et al*. Sphingolipids and glycerolipids I. Chemical structures and ionophoretic activities of soyacerebrosides I and II from soybean [J]. *Chem Pharm Bull*, 1990, 38(11): 2933-2938.

[7] Gong Y H. *^{13}C-NMR Data of Natural Products* (天然有机化合物的 C13 核磁共振化学位移) [M]. Kunming: Yunnan Science and Technology Press, 1986.

[8] Okuyama E, Yamazaki M. The priciples of tetragonia tetragonoides having anti-ulcerogenic activity II. Isolation and structures of cerebrosides [J]. *Chem Pharm Bull*, 1983, 31(7): 2209-2219.