表 2 化合物Ⅵ的 NMR 数据(CD_3OD)

H	δ	J_{HZ}	C	δ
2	6.26(d)	16.6	1	168.87
3	7.55(d)	16.6	2	114.74
5	7.05(d)	1.1	3	146.45
8	6.77(d)	8.1	4	127.67
9	6.99(d)	8.1	5	115.22
3′	8.22(s)		6	146.89
4′	8.02(d)	6.5	7	149.66
5′	6.47(d)	6.5	8	116.53
1″	4.76(d)	2.8	9	123.07
			1′	173.97
			2′	146.30
			3′	145.79
			4′	157.92
			5′	117.04
			1″	99.06
			2″	74.65
			3″	77.09
			4″	71.50
			5″	75.84
			6″	66.41

h, 可明显减少 TNF-α 诱导的 CMSMC 对 MNC 的粘附作用($P < 0.01$)。提示它可能为灯盏花治疗脑血管疾病的机制之一, 这为进一步的药物开发提供了理论依据。

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New alkaloid isolated from *Fritillaria pallidiflora*

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Abstract: **Object** To elucidate the structure of a new alkaloid isolated from *Fritillaria pallidiflora* Schrenk. **Methods** By means of IR, MS and NMR. **Results** The new alkaloid was ascertained as *N*-(1′, 4′-dihydroxy-1′, 2′, 3′, 4′-tetrahydronaphthyl)-propyl-*N*-diphenylmethyl-*N*-3, 3-dimethylbutylamine. **Conclusion** This alkaloid was found for the first time from the natural plant. Its skeleton and structure is very different from all known *Fritillaria* alkaloids.

Key words: *Fritillaria pallidiflora* Schrenk; structure elucidation; *N*-(1′, 4′-dihydroxy-1′, 2′, 3′, 4′-tetrahydronaphthyl)-propyl-*N*-diphenylmethyl-*N*-3, 3-dimethylbutylamine

摘 要: 目的 确证从伊贝母中分离得到一种新的生物碱的结构。方法 IR, MS 及 NMR。结果 其结构被鉴定为 *N*-(1′, 4′-二羟基-1′, 2′, 3′, 4′-四氢化萘基)-丙基-*N*-二苯基甲基-*N*-3, 3-二甲基丁胺。结论 这种生物碱为首次从植物中分离得到, 它在骨架结构上与已知的贝母生物碱截然不同。

关键词: 伊贝母; 结构解析; *N*-(1′, 4′-二羟基-1′, 2′, 3′, 4′-四氢化萘基)-丙基-*N*-二苯基甲基-*N*-3, 3-二甲基丁胺
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1 Introduction

The bulb of *Fritillaria* plants (Chinese name Beimu) is a traditional Chinese medicine commonly used as antitussive and expectorant. The active constituents of this medicine are the alkaloids confirmed by chemical and pharmacological studies[1].

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Up to the present, more than a hundred and thirty alkaloids were isolated from different *Fritillaria* species, and eight of the alkaloids were isolated from *Fritillaria pallidiflora* Schrenk[2~5]. Though most of them were isosteroidal alkaloids, there are also a few other types of alkaloids such as steroidal alkaloids *et al*. The present paper reports the structural elucidation of a new alkaloid which is very different from the known *Fritillaria* alkaloids either in structure or in alkaloid skeleton.

2 Experiment

2.1 General procedures: Mps: 148.5 ℃ uncorr., as determined by a XII-5 apparatus: ^{1}H and ^{13}CNMR (300 and 75 MHz respectively) and ^{1}H-^{13}C shift correlated spectrum were recorded at a Bruker Am-300 instrument and TMS in $CDCl_3$ was used as internal standard. MS spectra were measured with ZAB-HS spectrophotometer. IR spectral data were obtained from a Bio-Rad FTS-135 spectrometer with KBr pellets. CC was carried out on Qingdao silica gel, TLC was performed on self prepared and precoated silica gel plates.

2.2 Plant material: The bulbs of *F. pallidifloria* were collected in Xinjiang autonomous district of China, and identified by Prof. LI Ping, the voucher specimen is deposited in the Herbarium of China Pharmaceutical University, Nanjing, China.

2.3 Extraction and isolation: Ground *F. pallidiflora* bulbs (10 kg) were extracted with 70% alcohol (20 L×3), and the combined extract were concentrated to 1 L, after adjusting its pH to 11. The solution was extracted with chloroform (0.5 L×3) and the chloroform layer was combined and dried under reduced pressure. Forty two grams of crude alkaloid was obtained. The crude alkaloid was chromatographed on silica gel (800 g) and eluted with cyclohexane-EtOAc-diethylamine (6∶3∶1). Three fractions were obtained and the last fraction was subjected to silica gel column using chloroform-methanol-diethylamine (9∶1∶1, lower phase) for elution. Thus compound Ⅰ (100 mg) was obtained.

2.4 Compound Ⅰ, $C_{32}H_{41}NO_2$, colorless filamentary needlem, exhibits positive reaction to Dragendorff's reagent, mp: 148.5 ℃; IR (cm^{-1}), 3 400 (br.), 2 960, 1 890, 740, 690. EIMS (m/z), (rel. int), 471 (23), 435 (5), 280 (100), 262 (11), 183 (15), 105 (19), 96 (11), 85 (20), 77 (8), 57 (20), 44 (11). ^{1}HNMR (TMS in $CDCl_3$, 75 Hz), δ 7.46~7.51 (4H, m, H-6~H-9), 7.24~7.33 (8H, m, H-22, 23, 25, 26, H-28, 29, 31, 32), 7.16~7.19 (2H, m, H-24, H-30), 4.59 (1H, dd, J= 7.5 Hz, 2.5 Hz, H-1), 3.14 (1H, d, J= 11 Hz, H-2a), 2.97 (1H, d, J= 11 Hz, H-3a), 3.06 (1H, m, H-20), 2.39 (2H, m, H-13), 1.29 (9H, s, $3CH_3$). Chemical shift of other H were overlapped at δ 1.48~2.07. ^{13}CNMR, MS in $CDCl_3$, δ 149.4 (C-9), 146.1 (C-21), 146.0 (C-27), 142.7 (C-10), 128.2 (C-23, C-25, C-29, C-31), 126.4 (C-5, C-8), 125.7 (C-26, C-32), 125.4 (C-6, C-7), 125.0 (C-24, C-30), 79.2 (C-1), 73.4 (C-4), 58.8 (C-13), 54.6 (C-2), 53.3 (C-3), 41.2 (C-20), 39.6 (C-14), 34.4 (C-16), 31.4 (C-17, C-18, C-19), 25.9 (C-11), 25.8 (C-12), 24.1 (C-15).

3 Structure elucidation

Compound Ⅰ, was obtained as a colorless filament-like needle, had a formula of $C_{32}H_{41}O_2$ as determined from EIMS molecular ion peak at m/z 471 and DEPT data. It showed a UV maximum at 254 nm indicating the presence of phenyl group, which was confirmed by IR absorption at 1 800~1 900, 690 and 740 cm^{-1}.

In the EIMS spectrum, M^+ (471) showed that compound Ⅰ was an alkaloid with one or odd nitrogen, which $(M^+ + 1)/M^+ \times 100\% = 36.5\%$ and $(M^+ + 2)/M^+ \times 100\% = 0.063\%$ suggests 32 carbons and no S, P, X existed in the molecule; the fragments of ion peak at m/z 77 and 105 were the further evidences for the presence of phenyl groups in the molecule. The base peak at m/z 280 arising from a cleavage indicated that compound Ⅰ was very different from the known *Fritillaria* alkaloids in its skeletal structure; and the fragments of m/z 435 ($M^+ - 2H_2O$) suggested that there were two hydroxy groups in its structure as supported by the signals of methine and methylene linked with hydroxy at δ 79.2 and 73.4 in ^{13}CNMR spectrum.

The main MS cleavage of compound Ⅰ was shown in Figure 1.

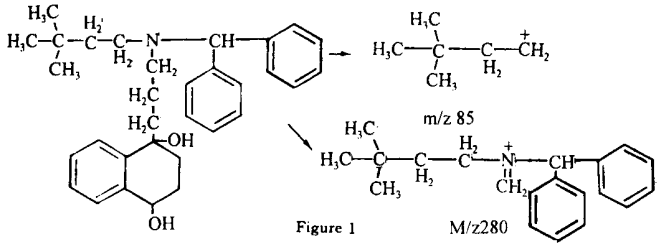

Figure 1

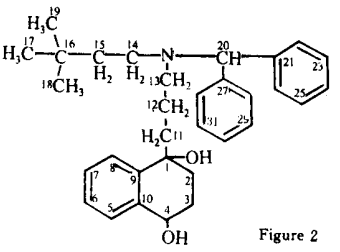

Figure 2

DEPT spectrum of compound Ⅰ suggested three methyls, seven methylenes, 16 methines, six quaternary carbons in the molecule. The assignment of ^{1}H and $^{13}CNMR$ signals of compound Ⅰ were achieved on the basis of 1D and 2D techniques. In the lower field of $^{13}CNMR$, the spectral region between δ 124.9 and 149.4 correlatd with δ 7.1 and 7.5 in the $^{1}HNMR$, were the carbon resonances of a two-substituted and two single substituted phenyls. The cross peak at δ 1.29/ δ 31.38 was the signal of three chemically equivalent methyls.

The formula $C_{32}H_{41}NO_2$ revealed that compound Ⅰ had 13 rings and double bonds all together (degree of unsaturation), besides the three phenyl rings, there remained one ring other than double bonds evidenced from $^{1}HNMR$.

From the facts above, compound Ⅰ can be ascertained as *N*-(1′, 4′-dihydroxy-1′, 2′, 3′, 4′-tetrahydronaphthyl)-propyl-*N*-diphenylmethyl-*N*-3, 3-dimethylbutylamine. Its structure is shown in Figure 2.

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超临界 CO_2 萃取法与水蒸气蒸馏法提取当归挥发油的比较

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摘 要: 目的 考察当归挥发油的不同提取方法。方法 超临界 CO_2 流体萃取法及水蒸气蒸馏法。结果 两者的成分及(*Z*)-藁本内酯的含量基本一致, 而超临界 CO_2 萃取所得当归油的收率约为水蒸气蒸馏收率的 2 倍。结论 超临界 CO_2 流体萃取法是当归挥发油较好的提取方法。

关键词: 超临界 CO_2 流体; 水蒸气蒸馏; 当归挥发油

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Extraction of essential oil from *Angelica sinensis* by supercritical-CO_2 fluid in comparison with that by steam distillation

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