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Pingbeinone, A Novel Steroidal Alkaloid having C-18 nor Cevane Skeleton from *Fritillaria ussuriensis* Maxim.

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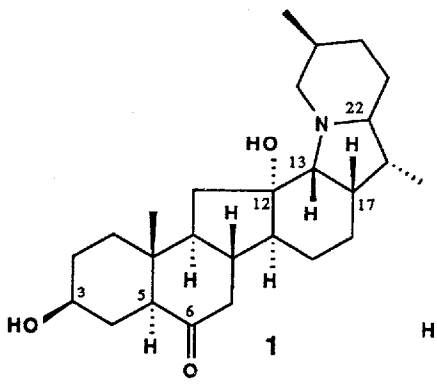
Abstract: A novel stroidal alkaloid, having C-18 nor cevane skeleton, pingbeinone (**1**), was isolated from *Fritillaria ussuriensis* Maxim. The structure was established by X-ray crystallographic analysis of its hydrogen iodide.

An important Chinese medicine "Bei-mu", dried bulbs of *Fritillaria* genus, has been used for an antitussive, expectorant and sedative.[1] As many *Fritillaria* genus are cultivated in China, we have been studying the alkaloids in many kinds of "Bei-mu" to clarify the relation between the chemical constituents and the original plants.[2] In the previous communication,[3] we have reported a new steroidal alkaloid with 7-ring system, ussurienine (**2**), isolated from *Fritillaria ussuriensis*. In this communication, we report additional new stroidal alkaloid, pingbeinone (**1**), having a novel skeleton, isolated from *F. ussuriensis*.

The alkaloid containing fraction obtained from the 50% aqueous acetone extract of the dried bulbs of *F. ussuriensis*[4] was repeatedly chromatographied on silica gel to give a new alkaloid (**1**), along with known alkaloids, ussuriedine,[4] ussuriedinone,[4] solanidine and verticine.

Pingbeinone (**1**) was obtained as white needles from MeOH; mp 200-202°C; HR-MS $C_{26}H_{41}NO_3$ (found 415.3076, calcd. 415.3086); $[\alpha]_D$ -22° (*c* 0.8, $CHCl_3$); EI-MS (*m/z*) 415 (M^+), 400, 220, 164(base peak); IR $\nu_{max}(CHCl_3)$ 3500(OH), 2810, 1730(carbonyl). The HR-MS and ^{13}C-NMR spectra showed that **1** has 26 carbons in the molecule which is one carbon



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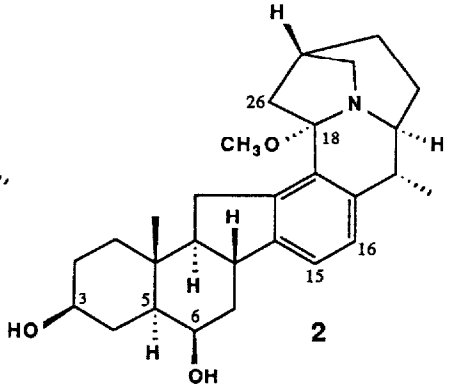

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Table ^1H and ^{13}C-NMR Chemical Shifts of **1** ($CDCl_3$)

Carbon No.	δ_C	δ_H	Carbon No.	δ_C	δ_H
1	37.2	1.42 (t, J=9.3Hz), 1.60	14	52.3	1.71
2	30.4	1.60, 1.65	15	26.9	0.80 (ddd, J=2, 10, 24Hz), 1.82
3	70.8	3.60 ($W_{1/2}$=23Hz)	16	21.4	1.20 (ddd, J=2, 12.9, 24.1Hz), 1.43
4	30.0	1.45, 1.92	17	42.0	2.40
5	56.4	2.25 (dd, J=2.5, 12.7Hz)	19	12.6	0.70 (s)
6	211.2		20	36.1	2.06 (tq, J=8.5, 9.8Hz)
7	46.4	2.19 (t, J=13.0Hz),	21	13.5	0.86 (d, J=7.0Hz)
		2.51 (dd, J=4.7, 13.0Hz)	22	63.5	2.67 (dt, J=5.0, 8.5Hz)
8	47.9	1.45	23	23.8	1.63, 1.69
9	52.5	1.96	24	28.4	1.13, 1.56
10	38.3		25	30.6	1.67
11	44.5	1.34 (t, J=12.3Hz), 1.9	26	58.4	2.40 (dd, J=9.1, 11.5Hz),
12	77.5				2.79 (dd, J=2.9, 11.5Hz)
13	73.1	2.89 (d, J=9.8Hz)	27	20.0	0.92 (d, J=6.8Hz)

lesser than those of normal 5α-cevane alkaloids. The absolute structure of **1** was established by X-ray crystallographic analysis of its hydrogen iodide[5] as shown in Figure. All signals of the ^1H- and ^{13}C-NMR spectra were assigned as shown in Table using ^1H-^1H and ^1H-^{13}C 2D NMR technique.

Compound **1** is the first example of the C_{26} alkaloid from *Fritillaria* species, and has a novel skeleton lacking C-18 of 5α-cevane skeleton. Moreover, it is notable that *Fritillaria ussuriensis* contains novel alkaloids which have the skeletons derived from the modification at C-18 of 5α-cevane skeleton. Compound **1** was also isolated from the glycoside fraction, after hydrolysis with ß-glucosidase. The biogenesis and pharmacological activitiy of **1** are now under investigation.

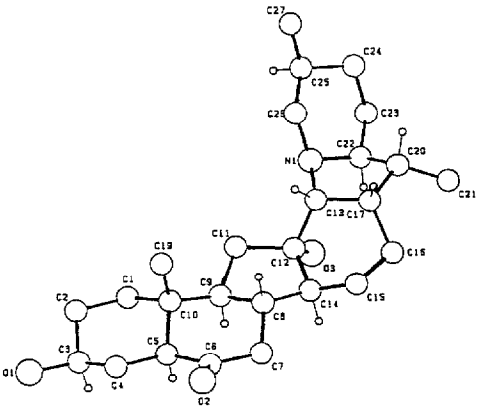

Figure Perspective Drawing of **1** hydrogen iodide

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4) Y. Kitamura, M. Nishizawa, K. Kaneko, M. Ikura, K. Hikishi, M. Shiro, Y.-P. Chen and H.-Y. Hsu, *Tetrahedron*, accepted.

5) The crystal of **1** hydrogen iodide belongs to the orthorhombic system with space group $p2_12_12_1$, and the cell dimentions a=15.064(6), b=17.546(4), c=11.178(3) Å^3, V=2954(1)Å^3, R=0.074 for 1769 reflections. Table of structural data are available from the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

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