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A STEROIDAL ALKALOID FROM *VERATRUM OBLONGUM*

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Key Word Index—*Veratrum oblongum*; Liliaceae; roots; oblonginine; Li-lu; steroidal alkaloid; 2D NMR.

Abstract—A new alkaloid, named oblonginine, has been isolated from the roots of *Veratrum oblongum*, along with five known alkaloids. It was determined to be (22*R*,25*S*)-22,26-epiminocholest-5-en-3β-ol [(22*R*)-22, *N*-dihydroverazine] on the basis of spectroscopic evidence and was shown to be identical with a compound obtained by solanidine degradation.

INTRODUCTION

Veratrum oblongum (Chinese name Changgenglilu) is used to prepare the Chinese crude drug 'Li-lu' which has been traditionally used to treat aphasia arising from apoplexy, wind-type dysentery, jaundice, headache, scabies, chronic malaria, etc. [1]. With regard to their wide application in traditional medicine, constituents of the *Veratrum* species have been extensively studied and more than 90 steroidal alkaloids have been reported [2–4]. *Veratrum oblongum* is indigenous to China and no reports of its chemical analysis have been found so far. In this paper, we describe the isolation of a new alkaloid, oblonginine (**1**) and five known steroidal alkaloids (**3**–**7**) from this species. The structure of **1** has been elucidated mainly by NMR spectrometry. The NMR data of the known compounds, **3**–**7**, are also reported and/or completely assigned for the first time.

RESULTS AND DISCUSSION

The roots of *V. oblongum* were cut into small pieces and extracted with ethanol. The ethanolic extract was extracted successively with petrol, chloroform, acetone and methanol in a Soxhlet apparatus. The acetone-soluble portion was roughly separated by silica gel column chromatography and the fractions obtained were further separated by repeated silica gel column chromatography to give oblonginine (**1**), vanilloylzygadenine (**3**), veratroylzygadenine (**4**), angeloylzygadenine (**5**), cevadine (**6**) and shinonomenine (**7**). Of these, the five alkaloids **3**–**7** were identified by comparisons of their melting points, $[\alpha]_D$ values and/or spectral data with those reported in the literature.

Compound **1** showed a quasi-$[M]^+$ at *m/z* 400 $[C_{27}H_{45}NO + H]^+$ in the positive ion FAB-mass spectrum. The IR spectrum showed absorption at ν_{max} 3450, 3330, 2920 and 1660 cm^{-1}, but no absorption for a carbonyl group or a *trans*-quinolizidine, which are more common in this plant genus. The ^1H NMR spectrum showed signals owing to two *tert*-methyls (δ0.70 and 1.01, H_3-19 and H_3-18), two *sec*-methyls (δ0.81 and 0.90, H_3-27 and H_3-21), a hydroxyl-bearing methine (δ3.51, *tdd*, *J* = 11.5, 5.5, 4.0 Hz) and a double bond (δ, *m*, 5.34). This spectrum was very similar to that of veramiline (**2**) except for the chemical shifts of four methyl groups [**2**, two *tert*-methyls (δ0.68 and 1.0) and two *sec*-methyls (δ0.86 and 1.03)] [5].

In order to analyse the proton and carbon sequences of **1** in detail, we measured the ^1H–^1H COSY, ^1H–^{13}C COSY, ^1H–^{13}C long-range COSY (Fig. 1a) and NOE's (Fig. 1b); the results are given in Tables 1 and 2. Based on a consideration of the ^1H-splitting, pattern and coupling constants and long-range coupling and NOEs, the relative configuration of the piperidine moiety substituted with a methyl group was proposed to be that as shown in Fig. 1b.

Therefore, oblonginine (**1**) was presumed to be the 22-epimer of veramiline **1** [(22*S*)-22, *N*-dihydroverazine, **2**]. Accordingly, oblonginine was determined to be (22*R*, 25*S*)-22,26-epiminocholest-5-en-3β-ol [(22*R*-22,*N*-dihydroverazine, **1**]. The new alkaloid **1** was shown to be identical (mp, $[\alpha]_D$) with a compound obtained by the degradation of solanidine [6, 7].

The ^1H and ^{13}C NMR data of the compounds **3**–**7** [8–14] are compiled in Tables 1 and 2, as well as in Fig. 2. Compounds **3**–**5** were found to be different owing to the substituents at C-3, while **6** was found to be the 12,17-dihydroxy derivative of **5**. The assignments for the 2, 7, 11, 14, 15, 16, 17, 23 and 24 carbon signals of **7** were not established in the papers of Kaneko *et al.* [13, 14].

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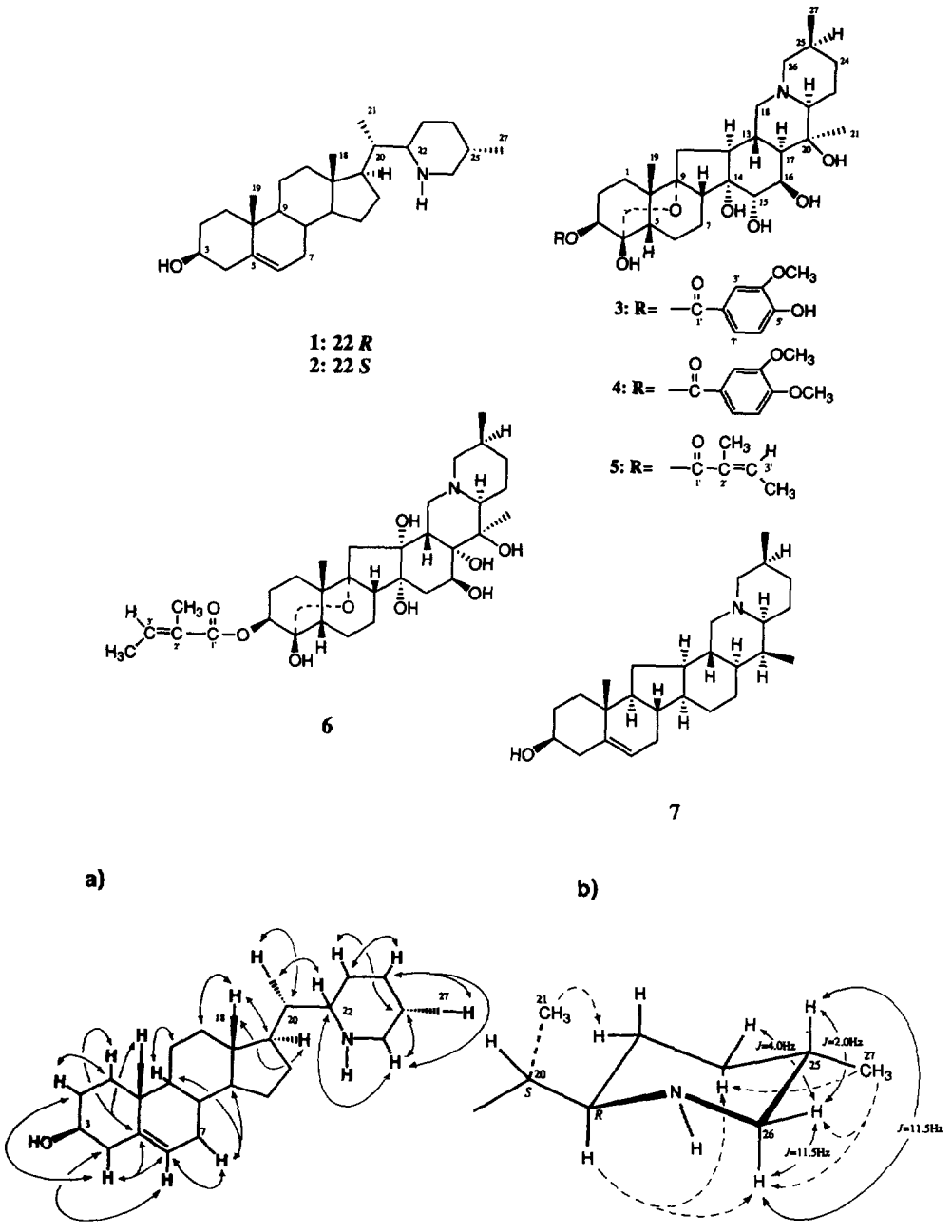

Fig. 1. (a) Significant long range correlations observed in ^1H–^{13}C long range COSY of **1**. (b) Partial structure of **1** (↷ coupling and long range coupling observed in ^1H–^1H COSY; ↶ NOE observed in NOE experiments).

However. our spectral information confirmed the complete assignment for shinonomenine (**7**). The complete assignment of the ^1H and ^{13}C NMR signals for the known steroidal alkaloids **3**–**7** has not been reported before.

EXPERIMENTAL

Mps: uncorr. IR spectra were recorded in KBr, UV spectra in EtOH solns. NMR spectra were recorded in $CDCl_3$ soln with TMS as int. standard. Chemical shifts were recorded in δ values and coupling constants are expressed in Hz. Multiplicities of ^{13}C NMR spectra were determined by the DEPT method. ^1H–^1H COSY, ^1H–^{13}C COSY, ^1H–^{13}C long-range COSY were obtained with standard pulse-sequences. CC was done with Wako-gel C-200 silica gel. Prep. TLC was carried out on Merck Kieselgel GF_{254} plates and spots detected under UV light. TLC analyses were done on Merck Kieselgel GF_{254} plates and spots detected using 1% $Ce(SO_4)_2$–aq. H_2SO_4 (10%) reagent.

Table 1. ^{1}H NMR spectral data for steroidal alkaloids from *Veratrum oblongum* (δ values in $CDCl_3$)

^{1}H	1*	3*	4	5	6*	7*
1	1.05 (*m*), 1.85 (*m*)	1.64 (*m*), 1.77 (*m*)	1.63 (*m*), 1.72 (*m*)	1.55 (*m*), 1.67 (*m*)	1.60 (2H, *m*)	1.27 (*td*, *J* = 13.0, 3.5) 1.74 (*dt*, *J* = 13.0, 3.5)
2	1.55 (*m*), 1.82 (*m*)	1.74 (*m*), 2.22 (*m*)	1.74 (*m*), 2.25 (*m*)	1.67 (*m*), 2.20 (*m*)	1.66 (*m*), 2.10 (*m*)	1.74 (*m*), 1.84 (*m*)
3	3.51 (*tdd*, *J* = 11.5, 5.5, 4.0)	5.13 (*br d*, *J* = 4.0)	5.14 (*br d*, *J* = 4.5)	5.01 (*br d*, *J* = 4.5)	5.01 (*br d*, *J* = 4.5)	3.57 (*tt*, *J* = 11.5, 4.5)
4	2.22 (*m*), 2.28 (*m*)	—	—	—	—	2.35 (*dq*, *J* = 12.5, 2.5), 2.21 (*m*)
5	—	2.12 (*t*, *J* = 2.5)	2.13 (*t*, *J* = 2.0)	2.06 (*t*, *J* = 3.0)	2.03 (*t*, *J* = 3.0)	—
6	5.34 (*m*)	1.75 (*m*), 1.92 (*m*)	1.77 (*m*), 1.94 (*m*)	1.75 (*m*), 1.93 (*m*)	1.73 (*m*), 1.96 (*m*)	5.38 (*m*)
7	1.96 (*m*), 1.50 (*m*)	1.61 (*m*), 1.97 (*m*)	1.64 (*m*), 1.98 (*m*)	1.62 (*m*), 1.99 (*m*)	1.76 (*m*)	2.18 (2H, *m*)
8	1.45 (*m*)	2.53 (*dd*, *J* = 11.0, 6.0)	2.52 (*dd*, *J* = 11.5, 6.0)	2.50 (*dd*, *J* = 11.0, 6.0)	2.68 (*t*, *J* = 5.0)	1.24 (*m*)
9	0.93 (*m*)	—	—	—	—	1.10 (*m*)*
11	1.49 (2H, *m*)	1.56 (*m*) 2.20 (*dd*, *J* = 15.0, 9.0)	1.59 (*m*) 2.21 (*dd*, *J* = 14.5, 8.0)	1.56 (*dd*, *J* = 15.0, 5.0) 2.18 (*dd*, *J* = 15.0, 9.0)	1.82 (*d*, *J* = 16.0) 2.20 (*d*, *J* = 16.0)	1.47 (2H, *m*)
12	2.01 (*ddd*, *J* = 12.5, 4.0, 2.5) 1.16 (*m*)	1.86 (*m*)	1.86 (*m*)	1.88 (*m*)	—	2.04 (*m*)
13	—	1.55 (*m*)	1.55 (*m*)	1.53 (*m*)	2.14 (*dd*, *J* = 7.5, 3.0)	1.70 (*m*)
14	0.99 (*m*)	—	—	—	—	1.68 (*br t*, *J* = 5.5)
15	1.08 (*m*), 1.60 (*m*)	3.74 (*d*, *J* = 3.0)	3.74 (*d*, *J* = 3.5)	3.73 (*d*, *J* = 3.0)	1.94 (*m*), 1.89 (*m*)	1.12 (*m*), 1.72 (*m*)
16	1.74 (*m*), 1.35 (*m*)	4.43 (*br s*)	4.42 (*dd*, *J* = 3.0, 2.0)	4.41 (*dd*, *J* = 3.0, 2.0)	4.15 (*t*, *J* = 3.0)	1.15 (*m*), 1.59 (*m*)
17	1.21 (*m*)	1.44 (*br d*, *J* = 12.0)	1.44 (*br d*, *J* = 12.0)	1.43 (*br d*, *J* = 12.0)	—	1.42 (*dd*, *J* = 11.5, 5.0)
18	0.70 (*s*)	1.71 (*m*) 2.69 (*dd*, *J* = 11.0, 3.5)	1.71 (*m*) 2.68 (*dd*, *J* = 12.0, 4.0)	1.70 (*m*) 2.68 (*dd*, *J* = 11.0, 4.0)	2.62 (2H, *m*)	2.01 (*m*) 2.14 (*br d*, *J* = 11.0)
19	1.01 (*s*)	1.02 (*s*)	1.04 (*s*)	1.01 (*s*)	1.01 (*s*)	1.00 (*s*)
20	1.51 (*m*)	—	—	—	—	1.81 (*m*)
21	0.90 (*d*, *J* = 6.5)	1.24 (*s*)	1.24 (*s*)	1.23 (*s*)	1.15 (*s*)	1.07 (*d*, *J* = 7.0)
22	2.45 (*dt*, *J* = 11.0, 2.5)	1.78 (*br d*, *J* = 6.0)	1.80 (*br d*, *J* = 5.5)	1.72 (*dd*, *J* = 15.0, 3.0)	2.05 (*br d*, *J* = 9.0)	1.27 (*m*)
23	1.49 (*m*), 1.11 (*m*)	1.54 (*m*), 1.66 (*m*)	1.54 (*m*), 1.65 (*m*)	1.52 (*m*), 1.62 (*m*)	1.90 (2H, *m*)	1.26 (*m*), 1.65 (*m*)
24	0.96 (*m*), 1.79 (*m*)	1.50 (*m*), 1.60 (*m*)	1.53 (*m*), 1.63 (*m*)	1.50 (*m*). 1.58 (*m*)	1.57 (2H, *m*)	1.50 (*m*), 1.69 (*m*)
25	1.43 (*m*)	1.90 (*m*)	1.91 (*m*)	1.89 (*m*)	1.91 (*m*)	1.82 (*m*)
26	3.02 (*ddd*, *J* = 11.5, 4.0, 2.0) 2.26 (*t*, *J* = 11.5)	2.28 (*dd*, *J* = 11.5, 3.5) 2.65 (*br d*, *J* = 11.5)	2.28 (*dd*, *J* = 11.5, 3.0) 2.64 (*br d*, *J* = 11.5)	2.27 (*dd*, *J* = 11.0, 3.0) 2.64 (*dd*, *J* = 11.0, 3.5)	2.43 (*br d*, *J* = 9.0) 2.65 (*m*)	2.20 (*m*) 2.50 (*br d*, *J* = 11.0)
27	0.81 (*d*, *J* = 6.5)	1.08 (*d*, *J* = 7.5)	1.09 (*d*, *J* = 7.0)	1.08 (*d*, *J* = 7.0)	1.10 (*d*, *J* = 7.0)	0.97 (*d*, *J* = 6.0)
3′	—	7.53 (*d*, *J* = 2.0)	7.52 (*d*, *J* = 2.0)	6.12 (*qq*, *J* = 7.0, 1.5)	6.14 (*qq*, *J* = 7.0, 1.5)	—
6′	—	6.93 (*d*, *J* = 8.0)	6.88 (*d*, *J* = 8.0)	—	—	—
7′	—	7.62 (*dd*, *J* = 8.0, 2.0)	7.67 (*dd*, *J* = 8.0, 2.0)	—	—	—
Me-2′	—	—	—	1.90 (*quintet*, *J* = 1.5)	1.89 (*quintet*, *J* = 1.5)	—
Me-3′	—	—	—	2.00 (*dq*, *J* = 7.0, 1.5)	2.00 (*dq*, *J* = 7.0, 1.5)	—
OMe-4′	—	3.95 (*s*)	3.93 (*s*)	—	—	—
OMe-5′	—	—	3.95 (*s*)	—	—	—
OH-4	—	—	—	3.74 (*s*)	3.99 (*brs*)	—
OH-14	—	—	—	—	4.65 (*s*)	—
OH-15	—	4.21 (*s*)	—	3.72 (*s*)	—	—
OH-16	—	3.27 (*s*)	—	4.19 (*s*)	—	—
OH-20	—	4.70 (*s*)	3.32 (*s*)	4.72 (*s*)	4.72 (*s*)	—

^{1}H–^{1}H shift correlation spectra were measured. *Difference NOE sepctra were measured.

Table 2. ^{13}C NMR spectral data for steroidal alkaloids from *Veratrum oblongum* (δ values in $CDCl_3$)

C	1*	3†	4‡	5‡	6†	7†
1	37.3 *t*	32.8 *t*	32.9 *t*	32.8 *t*	32.4 *t*	38.6 *t*
2	31.7 *t*	26.9 *t*	26.9 *t*	26.9 *t*	26.7 *t*	31.7 *t*
3	71.7 *d*	75.9 *d*	75.9 *d*	75.1 *d*	75.1 *d*	72.1 *d*
4	42.4 *t*	105.0 *s*	104.9 *s*	105.0 *s*	105.1 *s*	41.9 *t*
5	140.9 *s*	46.5 *d*	46.5 *d*	46.4 *d*	46.1 *d*	142.3 *s*
6	121.6 *d*	19.1 *t*	19.1 *t*	19.0 *t*	18.3 *t*	123.0 *d*
7	32.0 *t*	17.2 *t*	17.2 *t*	17.2 *t*	16.9 *t*	33.0 *t*
8	32.0 *d*	44.0 *d*	44.0 *d*	43.9 *d*	44.7 *d*	39.5 *d*
9	50.2 *d*	96.3 *s*	96.3 *s*	96.2 *s*	94.5 *s*	55.8 *d*
10	36.5 *s*	45.9 *s*	45.9 *s*	45.7 *s*	45.5 *s*	37.0 *s*
11	21.1 *t*	33.3 *t*	33.3 *t*	33.2 *t*	42.1 *t*	30.5 *t*
12	39.9 *t*	46.3 *d*	46.4 *d*	46.3 *d*	81.7 *s*	43.3 *d*
13	42.5 *s*	34.2 *d*	34.2 *d*	34.1 *d*	36.9 *d*	38.6 *d*
14	56.7 *d*	80.8 *s*	80.8 *s*	80.8 *s*	80.3 *s*	42.2 *d*
15	24.3 *t*	69.8 *d*	69.9 *d*	69.8 *d*	31.6 *t*	26.9 *t*
16	27.8 *t*	70.3 *d*	70.4 *d*	70.3 *d*	71.0 *d*	25.5 *t*
17	53.2 *d*	44.3 *d*	44.3 *d*	44.2 *d*	72.0 *s*	42.8 *d*
18	11.8 *q*	61.7 *t*	61.7 *t*	61.8 *t*	51.4 *t*	62.4 *t*
19	19.4 *q*	19.1 *q*	19.1 *q*	19.0 *q*	19.0 *q*	18.8 *q*
20	41.0 *d*	73.3 *s*	73.3 *s*	73.2 *s*	75.8 *s*	35.2 *d*
21	13.6 *q*	19.9 *q*	19.9 *q*	19.8 *q*	15.5 *q*	17.8 *q*
22	59.1 *d*	70.3 *d*	70.2 *d*	69.7 *d*	63.6 *d*	68.4 *d*
23	25.3 *t*	18.4 *t*	18.4 *t*	18.4 *t*	18.9 *t*	25.5 *t*
24	34.0 *t*	29.0 *t*	29.0 *t*	28.9 *t*	29.0 *t*	32.3 *t*
25	32.8 *d*	27.4 *d*	27.4 *d*	27.4 *d*	27.5 *d*	28.0 *d*
26	55.3 *t*	61.4 *t*	61.4 *t*	61.3 *t*	61.2 *t*	61.7 *t*
27	19.6 *q*	17.1 *q*	17.1 *q*	17.1 *q*	17.1 *q*	16.0 *q*
1′	—	167.3 *s*	167.2 *s*	168.4 *s*	168.7 *s*	—
2′	—	121.8 *s*	122.3 *s*	127.6 *s*	127.4 *s*	—
3′	—	112.1 *d*	110.2 *d*	138.9 *d*	139.5 *d*	—
4′	—	146.4 *s*	148.8 *s*	—	—	—
5′	—	150.6 *s*	153.4 *s*	—	—	—
6′	—	114.2 *d*	112.3 *d*	—	—	—
7′	—	124.4 *d*	123.8 *d*	—	—	—
Me-2′	—	—	—	20.6 *q*	20.6 *q*	—
Me-3′	—	—	—	15.9 *q*	16.0 *q*	—
OMe-4′	—	56.2 *q*	56.1 *q*	—	—	—
OMe-5′	—	—	56.0 *q*	—	—	—

Multiplicities of carbon signals determined by distortionless enhancement using polarization (DEPT).

*^1H–^{13}C COSY and ^1H–^{13}C long-range COSY spectra.

†^1H–^{13}C COSY and HMBC spectra.

‡Only complete decoupling spectrum was measured.

Isolation of alkaloids. Dried roots (9.8 kg) of *Veratrum oblongum Loes. f.* collected at Shennongjia in Hu-bei province, China, in July 1992, were cut into small pieces and extracted × 3 (3 hr) with boiling 95% EtOH (15 l). The EtOH solns were combined and concd *in vacuo*. The residue was further extracted successively with petrol (3 l), $CHCl_3$ (3 l), Me_2CO (3 l) and MeOH (3 l) in a Soxhlet apparatus to give petrol (185 g), $CHCl_3$ (50 g), Me_2CO (143 g) and MeOH extracts (289 g). The Me_2CO extract was subjected to CC on silica gel (1.2 kg). Elution with $CHCl_3$, $CHCl_3$–MeOH [49:1 (6 l); 9:1 (4 l); 22:3 (3 l); 17:13 (3 l); 73:21 (5 l)] gave fr. I (4 g), II (12 g), III (17 g), IV (10 g), V (23 g) and VI (95 g). TLC analysis with hexane–Me_2CO–NH_4OH (80:20:1), C_6H_6–Me_2CO–NH_4OH (80:20:1) and C_6H_6–Me_2CO–NH_4OH (60:40:1) gave spots of frs III, IV and V, which were indicated alkaloid-positive by spraying Dragendorff's reagent. Fr. III (17 g) was chromatographed over silica gel (120 g) with hexane–Me_2CO–NH_4OH (80:20:1). Eluates were monitored by TLC and sepd into 6 frs. Fr. 3 was recrystallized from Me_2CO–hexane to give oblongiinine (**1**) (121 mg). Fr. IV (10 g) was chromatographed over silica gel (400 g) with C_6H_6–Me_2CO–NH_4OH (80:20:1 and 60:40:1) and sepd into 4 frs. Fr. 3 was further purified by silica gel CC [120 g, C_6H_6–Me_2CO–NH_4OH (80:20:1)] to give cevadine (**6**) (130 mg), angeloylzygadenine (**5**) (11 mg) and veratroylzygadenine (**4**) (9 mg). Fr. V (23 g) was chromatographed

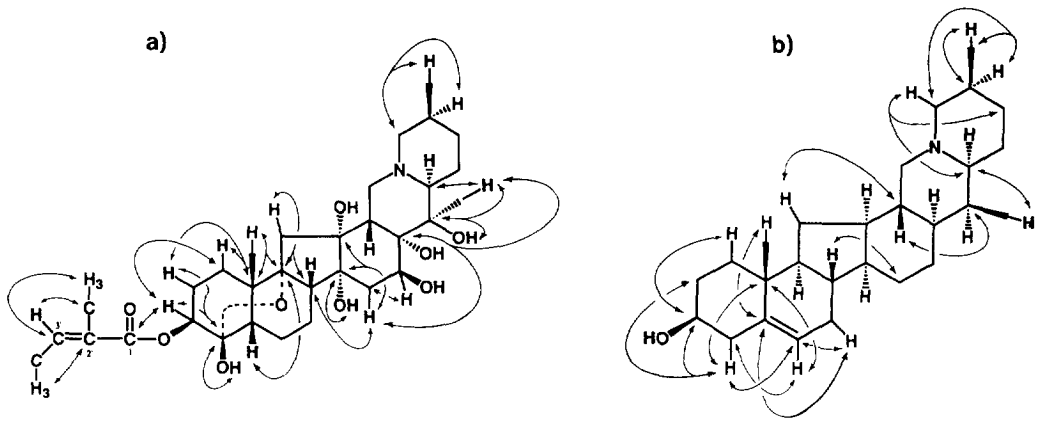

Fig. 2. (a) Significant long range correlations observed in ^{1}H–^{13}C long range COSY experiment of **6**. (b) Significant long range correlations observed in HMBC experiment of **7**.

over silica gel (400 g) with $CHCl_3$–Me_2CO–MeOH–NH_4OH (100:10:10:1) and sepd into 6 frs. Fr. 2 was recrystallized from Me_2CO–hexane to give shinonomenine (**7**) (25 mg). Fr. 3 was subjected repeatedly to prep. TLC with C_6H_6–Me_2CO–NH_4OH (60:30:1) to give vanilloylzylgadenine (**3**) (19 mg).

Oblonginine (**1**). Pillars, mp 219–220°. $[\alpha]_D$ − 40.7° ($CHCl_3$; *c* 0.11). UV λ_{max} nm (log ε): 213 (2.78). IR ν_{max} cm^{-1}: 3450, 3330, 2970, 2920, 2850, 1660. ^{1}H and ^{13}C NMR in Tables 1 and 2. Positive-ion FAB-MS, *m/z*: 400 $[M + H]^+$.

Vanilloylzygadenine (**3**). Needles, mp 235–238°. $[\alpha]_D$ − 30.8° ($CHCl_3$; *c* 0.05). [Lit. [8], mp 258–259°. $[\alpha]_D$ − 27.5° ($CHCl_3$)]. UV λ_{max} nm (log ε): 210 (4.00), 220 (4.05), 262 (3.89), 292 (3.54). IR ν_{max} cm^{-1}: 3360, 2890, 2750, 1710, 1660. ^{1}H and ^{13}C NMR in Tables 1 and 2. Positive-ion FAB-MS, *m/z*: 644 $[M + H]^+$.

Veratroylzygadenine (**4**). Needles, mp 260–262°. $[\alpha]_D$ − 27.9° ($CHCl_3$; *c* 0.07) [Lit. [8], mp 278–280°, $[\alpha]_D$ − 27° ($CHCl_3$)]. UV λ_{max} nm (log ε): 220 (4.16), 262 (3.99), 292 (3.70). IR ν_{max} cm^{-1}: 3460, 2960, 2930, 2850, 2760, 1720, 1610. ^{1}H and ^{13}C NMR in Tables 1 and 2. Positive-ion FAB-MS, *m/z*: 658 $[M + H]^+$.

Angeloylzygadenine (**5**). Needles, mp 225–226°. $[\alpha]_D$ − 32.4° ($CHCl_3$; *c* 0.06) [Lit. [9, 10], mp 222–224°, $[\alpha]_D$ − 35° ($CHCl_3$)]. UV λ_{max} nm (log ε): 245 (3.85). IR ν_{max} cm^{-1}: 3450, 2950, 2920, 2850, 2810, 2770, 2760, 1710, 1645. ^{1}H and ^{13}C NMR in Tables 1 and 2. Positive-ion FAB-MS, *m/z*: 576 $[M + H]^+$.

Cevadine (**6**). Needles, mp 206–209°. $[\alpha]_D$ + 10.0° (EtOH, *c* 0.20) [Lit. [11, 12]. mp 213–214°, $[\alpha]_D$ + 13° (EtOH; *c* 0.97)]. UV λ_{max} nm (log ε): 220 (3.91), 262 (3.48), 292 (3.18). IR ν_{max} cm^{-1}: 3410, 2920, 2890, 2840, 2780, 1710, 1640. ^{1}H and ^{13}C NMR in Tables 1 and 2. EI-MS *m/z*: 591 ($[M]^+$), 573, 572, 556, 548, 509, 492, 154, 140, 128, 112, 98. HR-MS *m/z*: 591.3372 $[M]^+$, $C_{32}H_{49}NO_9$ (calcd 591.3337).

Shinonomenine (**7**). Needles, mp 99–100°. $[\alpha]_D$ − 80.7° ($CHCl_3$; *c* 0.40) [Lit. [13, 14], mp 95–96°, {$[\alpha]_D$ − 90.7° ($CHCl_3$; *c* 0.33)}]. UV λ_{max} nm (log ε): 218 (3.94), 270 (3.12). IR ν_{max} cm^{-1}: 3400, 2950, 2920, 2850, 2790, 2750, 2740, 2700, 2650, 1650. ^{1}H and ^{13}C NMR in Tables 1 and 2. Positive-ion FAB-MS, *m/z*: 398 $[M + H]^+$.

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