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The Structural Elucidation of *Fritillaria* Alkaloids from *Fritillaria ebeiensis* var. *purpurea*. I. The Structures of Ebeienine, Ebeiedine and Ebeiedinone

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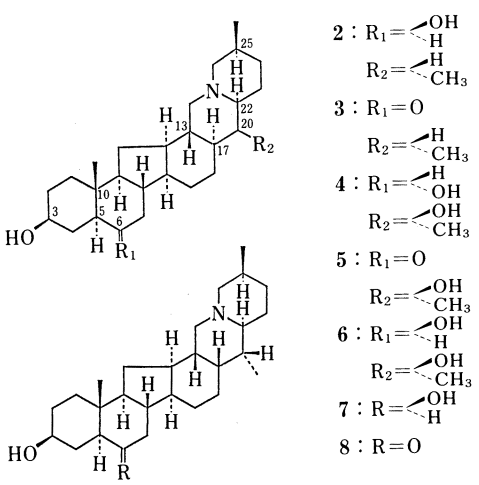
A novel (22*S*,25*R*)-13,17-didehydro-5α-cevanine alkaloid, ebeienine (**1**), was isolated from the bulbs of *Fritillaria ebeiensis* var. *purpurea*, together with (25*S*)-20-deoxy-5α-cevanin-3β,6β-diol (ebeiedine (**2**)), and (25*S*)-20-deoxy-5α-cevanin-3α-ol-6-one (ebeiedinone (**3**)). Their structures were elucidated by physical methods and finally confirmed by X-ray crystal structure determination.

Keywords——*Fritillaria*; traditional Chinese medicine; 13,17-didehydrocevanine alkaloid; 20-deoxy-5α-cevanine alkaloid; D/E *trans*-5α-cevanine alkaloid

Beimu, an important traditional Chinese medicine, is derived from many *Fritillaria* plants in mainland China, and utilized for almost the same medicinal purposes. The medicine derived from *Fritillaria ebeiensis* var. *purpurea* G. D. YU *et* P. LI,[1] which first came into use in Hupei Province, China, has been used as an antitussive and expectorant for a long time in that Province. The bulb of this plant shows a morphological form different from that of the other *Fritillaria* plants, consisting of about 21 to 64 squamae. No chemical study on its constituents has been reported up to now.



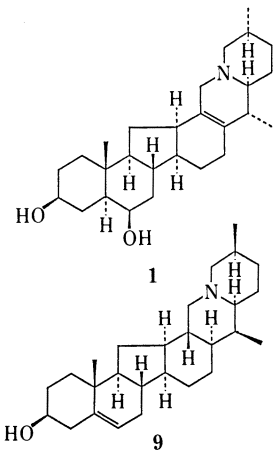


Fig. 1

In this paper, we describe the isolation of eight alkaloids from the bulbs of *Fritillaria ebeiensis* var. *purpurea* and the structural elucidation of ebeienine (**1**), ebeiedine (**2**), and ebeiedinone (**3**), in addition to verticine, verticinone and isoverticine as main alkaloids.

As described in Experimental, eight alkaloids, abbreviated as FE-2, FE-3, FE-4, FE-5, FE-6, FE-7, FE-8, and FE-9, have been isolated by silica gel column chromatography of the crude alkaloid fractionated from the hydrolysate of the aqueous acetone extract of the bulbs.

FE-5, FE-6 and FE-9 are the main alkaloids, and were deduced to be verticinone, isoverticine and verticine, respectively, from their physical constants and by mixed melting point determination.

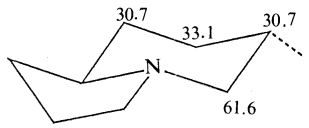
FE-8 (ebeienine, **1**) was crystallized from hexane–Et_2NH–EtOH as colorless needles, and crystallized from methanol in as rhombic form, mp 274.5—278.5 °C, $[\alpha]_D$ −2.9° ($c=0.5$, MeOH). The empirical formula of **1**, $C_{27}H_{43}NO_2 \cdot H_2O$, M.W. 431.3405 (Calcd 431.3402), was determined by high-resolution mass spectrometry, and the infrared (IR) spectrum of **1** showed hydroxyl absorptions at 3475 and 3325—3250 cm^{-1}, and a diagnostic absorption at 2750 cm^{-1} (*trans*-quinolizidine), with no carbonyl absorption. Based on the degree of unsaturation (seven) in the molecular formula, it is suggested that **1** possesses a double bond in its structure.

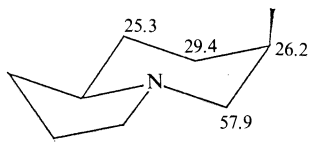
The mass spectrum (MS) of **1** revealed a molecular ion at m/z 413 (34%), and the crystal possessed 1 mol of crystal water, resulting in a peak at m/z 431 (0.8%). There were also

TABLE I. ^{13}C Chemical Shifts of Ebeienine and Delavine

Carbon No.	Ebeienine (A)	Delavine (B)	$\Delta\delta$ (A − B) (ref.)
1	39.5	39.4	
2	31.4	31.4	
3	72.0	71.9	
4	33.3	34.8	
5	47.8	48.1	
6	73.1	73.2	
7	39.3	39.6	
8	39.2	36.7	
9	56.7	57.9	
10	35.4	35.5	
11	30.8	30.8	
12	41.0	39.1	
13	131.1	39.1	
14	41.1	41.2	
15	27.8	28.7	
16	25.8	17.7	
17	128.4	41.6	
18	57.0	59.2	
19	14.8	15.7	
20	40.4	38.9	
21	16.2	14.7	
22	65.4	62.5	
23	31.1	25.0	6.1 (5.4)
24	34.8	30.3	4.5 (3.7)
25	31.5	28.4	3.1 (4.5)
26	64.0	61.7	2.3 (3.7)
27	19.8	18.3	

In ppm relative to TMS in $CDCl_3$.





fragment ions at m/z 398 (23%), 112 (36%), and 98 (100%). The base peak at m/z 98 should be formed by retro-Diels–Alder fragmentation between the E and F rings.

The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **1** exhibited a tertiary methyl signal at δ 0.95, shifted downfield compared to that of 5α-cholestanol because of 1,3-diaxial interaction with the β-axial hydroxyl group. Two secondary methyl signals appeared at δ 0.86 (27-H) and δ 0.96 (21-H). It seems reasonable to conclude that the 25α-methyl is responsible for the chemical shift of 27-H, because of the α-equatorial orientation, without a deshielding effect from the β-axial lone pair of the nitrogen atom. On the other hand, the methyl signal at C-20 was shifted downfield at δ 0.96 because of the deshielding effect from the double bond. Based on these consideration and the fact that the ^{1}H-NMR spectrum of **1** showed no olefinic proton, the double bond can be assigned between C-13 to C-17.

Two signals at δ 3.66 (m, $W_{1/2}=19$ Hz) and δ 3.86 (m, $W_{1/2}=8$ Hz) are associated with hydrogen on the carbons bearing the hydroxyl groups at 3α and 6α, respectively, being similar to those of delavine (**7**). The ^{1}H-NMR spectrum of **1** (in pyridine-d_5) displayed an H_2O signal at δ 4.98, indicating the presence of 1 mol of crystal water in the structure, this was supported by the MS.

In the ^{1}H–^{1}H-two dimensional correlation spectroscopy (2D-COSY) spectrum of **1** (Fig. 3), the cross peaks indicated that the doublet signals at δ 2.55 ($J=15$ Hz) and δ 3.2 ($J=15$ Hz) could be assignable to α-axial and β-equatorial hydrogen at C-18, respectively, and both hydrogens were coupled with each other. This confirms that the double bond in **1** is located

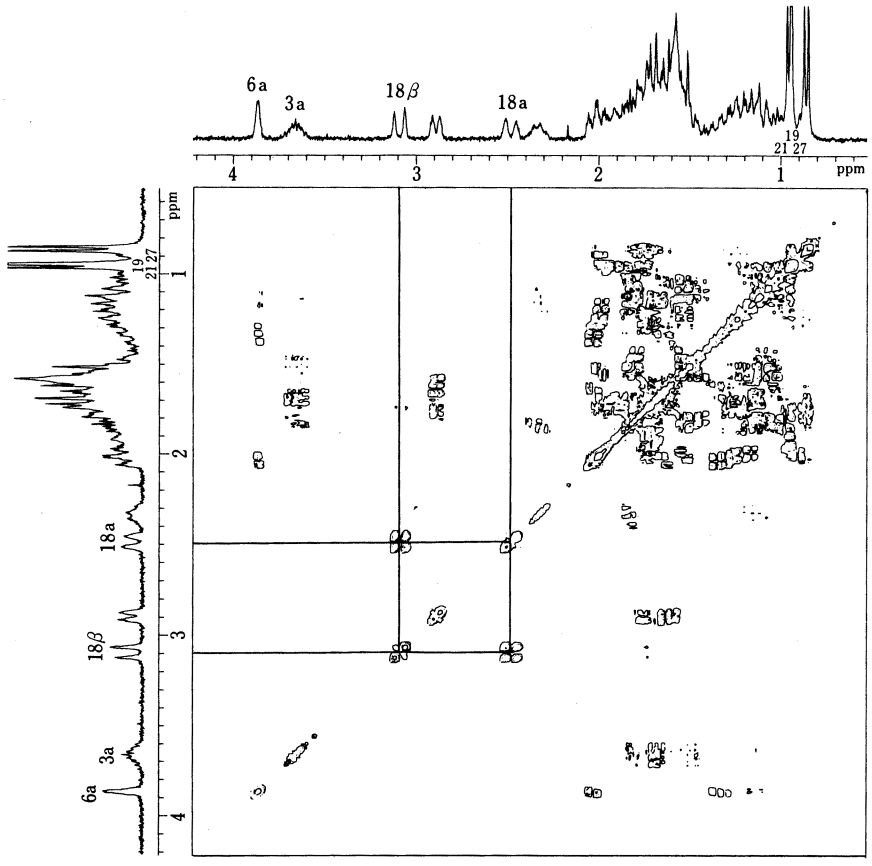


Fig. 2. ^{1}H,^{1}H-2D-COSY Spectrum of **1**

TABLE II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($Å^2 \times 10^2$) with Their e.s.d. Values in Parentheses, for Ebeienine (**1**)

	x	y	z	B_{eq}
C(1)	3266 (3)	6824 (2)	9390 (5)	343 (11)
C(2)	2574 (4)	7191 (2)	10220 (5)	354 (13)
C(3)	1485 (3)	6630 (2)	9644 (5)	324 (11)
C(4)	1462 (3)	4735 (2)	9372 (4)	323 (9)
C(5)	2132 (3)	4400 (2)	8527 (4)	298 (8)
C(6)	1978 (3)	2611 (2)	7985 (4)	357 (9)
C(7)	2599 (3)	2396 (2)	7068 (4)	409 (9)
C(8)	3702 (3)	2920 (2)	7561 (4)	303 (9)
C(9)	3777 (3)	4741 (2)	8034 (4)	273 (8)
C(10)	3258 (3)	4943 (2)	9039 (4)	273 (8)
C(11)	4905 (3)	5193 (2)	8159 (5)	298 (10)
C(12)	5043 (3)	4590 (2)	6978 (4)	283 (9)
C(13)	6125 (3)	4514 (2)	6811 (4)	284 (8)
C(14)	4442 (3)	2892 (2)	6741 (4)	316 (8)
C(15)	5145 (3)	1363 (3)	6976 (5)	375 (12)
C(16)	5957 (3)	1453 (2)	6270 (5)	413 (12)
C(17)	6502 (3)	3138 (2)	6417 (4)	316 (10)
C(18)	6675 (3)	6183 (3)	6976 (5)	323 (10)
C(19)	3813 (3)	3884 (2)	10093 (4)	354 (9)
C(20)	7538 (3)	3177 (2)	6116 (5)	354 (11)
C(21)	7457 (4)	2297 (3)	4944 (8)	512 (21)
C(22)	7950 (3)	4991 (3)	6079 (5)	340 (10)
C(23)	9104 (4)	4931 (3)	6145 (6)	481 (15)
C(24)	9556 (3)	6697 (3)	6120 (6)	493 (13)
C(25)	9320 (3)	7818 (3)	7065 (5)	416 (11)
C(26)	8168 (3)	7784 (3)	6954 (5)	364 (11)
C(27)	9703 (4)	9628 (3)	7010 (5)	564 (13)
N(1)	7776 (5)	6057 (4)	7031 (11)	306 (31)
O(1)	850 (6)	7061 (6)	10412 (11)	394 (37)
O(2)	2253 (4)	1271 (2)	8786 (5)	486 (12)
O(3)	1093 (4)	579 (3)	10564 (6)	356 (16)

e.s.d., estimated standard deviations.

TABLE III. Bond Lengths (Å) with Their e.s.d. Values in Parentheses, for Ebeienine (**1**)

C(1)–C(2)	1.545 (8)	C(1)–C(10)	1.535 (8)
C(2)–C(3)	1.528 (8)	C(3)–C(4)	1.522 (8)
C(3)–O(1)	1.439 (14)	C(4)–C(5)	1.532 (7)
C(5)–C(6)	1.539 (7)	C(5)–C(10)	1.553 (7)
C(6)–C(7)	1.541 (7)	C(6)–O(2)	1.408 (8)
C(7)–C(8)	1.518 (7)	C(8)–C(9)	1.531 (7)
C(8)–C(14)	1.560 (7)	C(9)–C(10)	1.537 (7)
C(9)–C(11)	1.536 (8)	C(10)–C(19)	1.539 (7)
C(11)–C(12)	1.538 (8)	C(12)–C(13)	1.524 (7)
C(12)–C(14)	1.551 (7)	C(13)–C(17)	1.328 (7)
C(13)–C(18)	1.496 (8)	C(14)–C(15)	1.514 (8)
C(15)–C(16)	1.539 (8)	C(16)–C(17)	1.503 (8)
C(17)–C(20)	1.528 (8)	C(18)–N(1)	1.476 (14)
C(20)–C(21)	1.537 (11)	C(20)–C(22)	1.534 (8)
C(22)–C(23)	1.542 (9)	C(22)–N(1)	1.474 (14)
C(23)–C(24)	1.519 (10)	C(24)–C(25)	1.523 (9)
C(25)–C(26)	1.529 (8)	C(25)–C(27)	1.520 (8)

TABLE IV. Bond Angles (°) with Their e.s.d. Values in Parentheses, for Ebeienine (**1**)

C(2)–C(1)–C(10)	112.9 (5)	C(1)–C(2)–C(3)	109.0 (5)
C(2)–C(3)–C(4)	110.2 (5)	C(2)–C(3)–O(1)	107.8 (7)
C(4)–C(3)–O(1)	112.4 (7)	C(3)–C(4)–C(5)	108.9 (4)
C(4)–C(5)–C(6)	113.0 (4)	C(4)–C(5)–C(10)	112.0 (4)
C(6)–C(5)–C(10)	115.7 (4)	C(5)–C(6)–C(7)	110.9 (4)
C(5)–C(6)–O(2)	114.3 (4)	C(7)–C(6)–O(2)	107.4 (4)
C(6)–C(7)–C(8)	110.4 (4)	C(7)–C(8)–C(9)	111.4 (4)
C(7)–C(8)–C(14)	118.2 (4)	C(9)–C(8)–C(14)	104.4 (4)
C(8)–C(9)–C(10)	112.4 (4)	C(8)–C(9)–C(11)	103.1 (4)
C(10)–C(9)–C(11)	122.1 (4)	C(1)–C(10)–C(5)	108.2 (4)
C(1)–C(10)–C(9)	109.7 (4)	C(1)–C(10)–C(19)	109.2 (4)
C(5)–C(10)–C(9)	104.8 (4)	C(5)–C(10)–C(19)	114.0 (4)
C(9)–C(10)–C(19)	110.8 (4)	C(9)–C(11)–C(12)	100.4 (4)
C(11)–C(12)–C(13)	117.8 (4)	C(11)–C(12)–C(14)	104.8 (4)
C(13)–C(12)–C(14)	114.8 (4)	C(12)–C(13)–C(17)	122.8 (4)
C(12)–C(13)–C(18)	114.2 (4)	C(17)–C(13)–C(18)	122.6 (5)
C(8)–C(14)–C(12)	105.1 (4)	C(8)–C(14)–C(15)	111.4 (4)
C(12)–C(14)–C(15)	111.8 (4)	C(14)–C(15)–C(16)	111.2 (5)
C(15)–C(16)–C(17)	111.8 (5)	C(13)–C(17)–C(16)	122.5 (5)
C(13)–C(17)–C(20)	121.3 (5)	C(16)–C(17)–C(20)	116.2 (4)
C(13)–C(18)–N(1)	114.2 (7)	C(17)–C(20)–C(21)	109.8 (5)
C(17)–C(20)–C(22)	112.6 (5)	C(21)–C(20)–C(22)	109.7 (6)
C(20)–C(22)–C(23)	109.8 (5)	C(20)–C(22)–N(1)	112.2 (7)
C(23)–C(22)–N(1)	109.1 (7)	C(22)–C(23)–C(24)	112.2 (6)
C(23)–C(24)–C(25)	110.8 (6)	C(24)–C(25)–C(26)	108.6 (5)
C(24)–C(25)–C(27)	111.9 (5)	C(26)–C(25)–C(27)	111.3 (5)
C(25)–C(26)–N(1)	112.7 (7)	C(18)–N(1)–C(22)	110.7 (9)
C(18)–N(1)–C(26)	108.1 (9)	C(22)–N(1)–C(26)	110.4 (9)

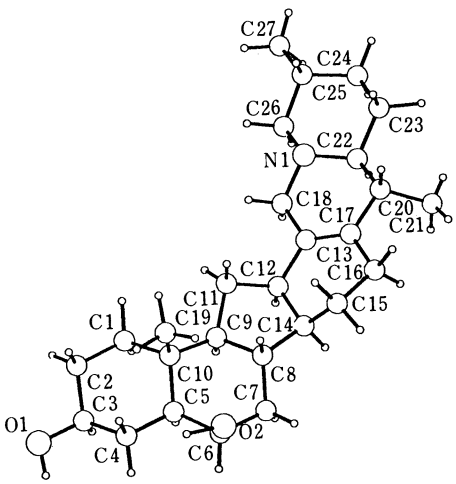


Fig. 3. Perspective Drawing of Ebeienine (**1**)

between C-13 and C-17.

In the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **1** (Table I, Fig. 1), the resonances of C-1 to C-11, C-14 to C-15, and C-18 to C-19 are in good agreement with those of **7**,[2] suggesting that **1** has a 5α-cevanine-3β,6β-diol structure.

The chemical shifts of C-12, C-16 and C-20 to C-22 were shifted downfield, compared to those in delavine (**7**), because of the deshielding effect of the double bond at C-13 to C-17. As

can be seen in Table I, the $\Delta\delta$ values from C-23 to C-26 between **1** and **7** showed the same relationship as those of α- and β-oriented methyl groups on the indolizine system.[3)]

These spectral properties of **1** suggest that **1** possesses a 5α-cevanine skeleton with 3β,6β-substituted hydroxyl groups, a double bond between C-13 and C-17, and an α-equatorial methyl group at C-25. The structure is, namely, (22*S*,25*R*)-20-deoxy-13,17-didehydro-5α-cevanine-3β,6β-diol.

The relative stereostructure of **1** was confirmed by X-ray crystal structure elucidation. The structure of the molecule is shown in Fig. 3.

The crystal of ebeienine (**1**), $C_{27}H_{43}NO_2 \cdot H_2O$, M.W. 431, mp 278.5 °C, belongs to the monoclinic system with space group $P2_1$, and the cell dimensions are $a=13.508$ (1), $b=7.853$ (1), $c=11.912$ (1) Å; $\beta=104.18°$ (1), $V=1225.1$ (2) Å^3, $Z=2$, $d=1.170$ g/cm^3, $\mu=5.9$ cm^{-1}. The crystal size is $0.4\times0.15\times0.1$ mm. Three-dimensional intensity data were collected on Rigaku AFC-5 Diffractometer and 2240 unique reflections were measured for $|F_O|>3\sigma(F_O)$ by the ω–2θ scan method with CuK_α radiation. The structure was determined by a direct method and refined by a block-diagonal anisotropic least-squares technique to $R=0.042$, $R_w=0.060$ and $S=1.221$ for 2125 reflections. The crystallographic details are given in Experimental.

The results showed that all rings are in the chair conformation. The ring fusions are as follows: A/B *trans*, B/C *trans*, C/D *cis*, E/F *trans*. The configurations at the chiral centers have been determined as 3-OH β-equatorial, 6-OH β-axial, 10-Me β-axial, 20-Me α-equatorial, 25-Me α-equatorial and the lone pair on the nitrogen β-axial.

Ebeiedine (**2**) was crystallized from hexane–Et_2NH–EtOH as colorless needles, mp 118—120 °C $[\alpha]_D$ −37.9° ($c=0.97$, $CHCl_3$). The empirical formula of **1**, $C_{27}H_{45}NO_2$, M.W. 415.34283 (Calcd 415.34523) was determined by high-resolution mass spectrometry, and the IR spectrum of **2** displayed hydroxyl absorption at 3300 cm^{-1} and a diagnostic absorption at 2750 cm^{-1} (*trans*-quinolizidine).

The MS of **2** showed a parent ion at m/z 415 (M^+, 29%) and fragment ions at m/z 400 (7%), 359 (9%), 111 (100%), 112 (45%) and 98 (11%). The base peak at m/z 111 is compatible with the absence of a hydroxyl group at C-20 in the structure.[2)]

The ^{1}H-NMR spectrum of **2** revealed the presence of two secondary methyl groups appearing as 3H-doublets at δ 0.83 ($J=6$ Hz) and δ 1.08 ($J=7$ Hz) and one tertiary methyl group at δ 1.02 (s, 3H). The chemical shift at δ 0.83, ascribable to 21-H, further corroborated the absence of a hydroxyl group at C-20. The signal at δ 1.08 showed the presence of a β-axial

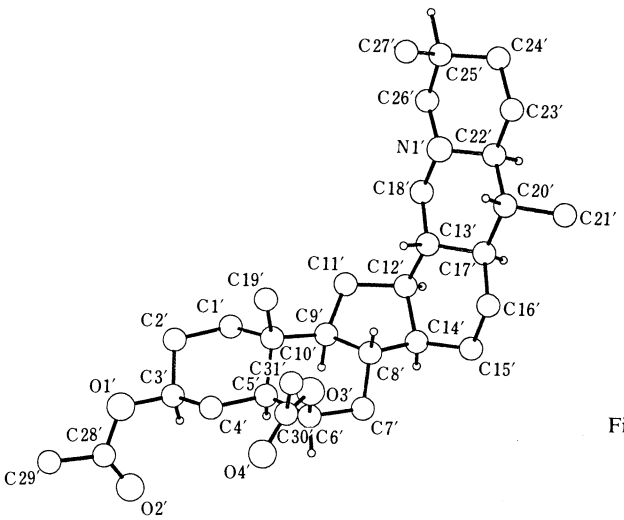


Fig. 4. Perspective Drawing of Ebeiedine-3,6-diacetate

TABLE V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factor (Å$^2 \times 10$) with e.s.d. Values in Parentheses for Ebeiedine Diacetate

	x	y	z	B_{eq}		x	y	z	B_{eq}
C(1)	4601 (3)	8672 (10)	1140 (4)	57 (3)	C(1′)	1296 (3)	2708 (9)	3040 (3)	47 (2)
C(2)	4251 (3)	9491 (10)	516 (4)	59 (3)	C(2′)	1208 (2)	3709 (10)	3497 (3)	49 (2)
C(3)	4323 (3)	8951 (10)	−19 (4)	57 (3)	C(3′)	1333 (3)	2787 (9)	4076 (3)	45 (2)
C(4)	4250 (3)	7221 (10)	−102 (3)	53 (3)	C(4′)	1864 (3)	2285 (8)	4427 (3)	45 (2)
C(5)	4620 (2)	6434 (10)	534 (3)	46 (2)	C(5′)	1947 (3)	1287 (9)	3977 (3)	47 (2)
C(6)	4654 (3)	4741 (10)	458 (3)	50 (2)	C(6′)	2417 (3)	403 (9)	4284 (3)	52 (2)
C(7)	5032 (3)	3957 (11)	1069 (4)	56 (3)	C(7′)	2453 (3)	−701 (9)	3835 (4)	56 (3)
C(8)	4956 (2)	4406 (10)	1603 (3)	48 (2)	C(8′)	2350 (3)	106 (10)	3241 (3)	52 (2)
C(9)	4953 (3)	6157	1668 (3)	50 (2)	C(9′)	1859 (2)	930 (9)	2932 (3)	43 (2)
C(10)	4541 (2)	6917 (9)	1078 (3)	45 (2)	C(10′)	1832 (2)	2143 (9)	3363 (3)	45 (2)
C(11)	4988 (3)	6360 (10)	2315 (3)	54 (3)	C(11′)	1755 (3)	1338 (11)	2277 (3)	53 (3)
C(12)	5227 (3)	4886 (11)	2698 (3)	55 (3)	C(12′)	2048 (3)	212 (11)	2121 (3)	54 (3)
C(13)	4877 (3)	4045 (11)	2852 (3)	54 (3)	C(13′)	2427 (3)	990 (10)	2024 (3)	53 (3)
C(14)	5357 (3)	3943 (11)	2278 (4)	54 (3)	C(14′)	2265 (3)	−918 (10)	2692 (4)	59 (3)
C(15)	5437 (3)	2243 (10)	2415 (4)	67 (3)	C(15′)	2709 (4)	−1824 (12)	2778 (4)	72 (3)
C(16)	5045 (3)	1559 (11)	2526 (4)	59 (3)	C(16′)	3070 (3)	−905 (12)	2689 (4)	70 (3)
C(17)	5024 (3)	2410 (10)	3046 (4)	61 (2)	C(17′)	2807 (3)	−92 (11)	2042 (4)	61 (3)
C(18)	4828 (4)	4928 (11)	3344 (4)	69 (3)	C(18′)	2181 (3)	1849 (11)	1415 (3)	54 (3)
C(19)	4026 (2)	6464 (10)	963 (3)	47 (2)	C(19′)	2176 (3)	3510 (9)	3478 (3)	51 (2)
C(20)	4671 (3)	1685 (10)	3225 (3)	58 (3)	C(20′)	3155 (3)	778 (12)	1878 (5)	68 (3)
C(21)	4846 (5)	35 (14)	3486 (6)	96 (5)	C(21′)	3503 (4)	−425 (15)	1841 (6)	96 (5)
C(22)	4624 (3)	2658 (13)	3691 (4)	70 (3)	C(22′)	2872 (3)	1702 (13)	1282 (4)	66 (3)
C(23)	4243 (4)	1954 (13)	3814 (5)	85 (4)	C(23′)	3230 (4)	2638 (15)	1170 (5)	87 (4)
C(24)	4126 (7)	2909 (20)	4229 (7)	136 (7)	C(24′)	2939 (4)	3652 (14)	567 (6)	94 (5)
C(25)	3941 (7)	4607 (16)	3917 (7)	128 (7)	C(25′)	2570 (4)	4679 (13)	614 (5)	78 (4)
C(26)	4398 (7)	5156 (16)	3890 (7)	124 (6)	C(26′)	2245 (3)	3639 (12)	737 (4)	65 (3)
C(27)	3447 (7)	4560 (21)	3289 (9)	143 (8)	C(27′)	2817 (4)	5888 (15)	1125 (6)	96 (5)
C(28)	4043 (3)	9856 (12)	−1069 (4)	65 (3)	C(28′)	1115 (4)	3003 (13)	4858 (4)	71 (3)
C(29)	3633 (4)	10635 (12)	−1640 (4)	70 (3)	C(29′)	1027 (5)	4097 (17)	5257 (5)	96 (5)
C(30)	3910 (3)	3514 (9)	−330 (3)	46 (2)	C(30′)	3079 (3)	1861 (11)	5152 (3)	61 (3)
C(31)	3446 (3)	2849 (11)	−448 (4)	58 (3)	C(31′)	3495 (3)	2878 (16)	5316 (5)	87 (4)
N(1)	4475 (3)	4166 (9)	3457 (3)	73 (3)	N(1′)	2524 (2)	2705 (9)	1307 (3)	57 (2)
O(1)	3943 (2)	9676 (7)	−600 (3)	61 (2)	O(1′)	1242 (2)	3721 (7)	4483 (2)	57 (2)
O(2)	4418 (3)	9478 (13)	−1008 (4)	114 (4)	O(2′)	1079 (4)	1672 (11)	4855 (5)	126 (4)
O(3)	4181 (2)	3999 (7)	259 (2)	51 (2)	O(3′)	2846 (2)	1421 (7)	4539 (2)	57 (2)
O(4)	4019 (2)	3665 (9)	−722 (3)	80 (2)	O(4′)	2948 (2)	1473 (9)	5515 (2)	73 (2)

$B_{eq} = 4/3 \sum_i \sum_j \beta_{ij} \boldsymbol{a}_i \boldsymbol{a}_j$.

methyl group at C-25. The tertiary methyl group at δ 1.02 is shifted downfield, compared with that of 5α-cholestanol, because of the 1,3-diaxial interaction with the β-axial hydroxyl groups. Two signals at δ 3.66 (1H, m, $W_{1/2} = 19$ Hz, 3α-H) and δ 3.87 (1H, br s, $W_{1/2} = 8$ Hz, 6α-H) are ascribed to the hydrogens on carbon bearing a hydroxyl group. On acetylation these two signals were shifted downfield to δ 4.73 and 5.00, respectively.

All of these spectral properties are similar to those of delavine (**7**), suggesting that **2** possesses a (25*S*)-5α-cevanine skeleton, with two hydroxyl groups in 3β and 6β orientation, respectively, and no hydroxyl group at C-20.

Nuriddinov *et al.*[5,6] isolated 20-deoxy-5α-cevanine-3β,6β-diol (edpetilidine) from *Petilum eduardi*, and although **2** corresponds to edpetilidine in planar structure, the chemical shifts of the methyl groups in the ^{1}H-NMR spectra are in a striking contrast.

In the ^{13}C-NMR spectrum of **2** (Table IX), the chemical shifts of carbons are in good agreement with those in **7**,[2] except C-16, C-18, and C-22. The chemical shifts of C-18 and C-

TABLE VI. Bond Lengths (Å) with e.s.d. Values in Parentheses for Ebeiedine Diacetate

C(1)–C(2)	1.54 (1)	C(1)–C(10)	1.55 (1)
C(2)–C(3)	1.53 (1)	C(3)–C(4)	1.54 (1)
C(3)–O(1)	1.46 (1)	C(4)–C(5)	1.56 (1)
C(5)–C(6)	1.51 (1)	C(5)–C(10)	1.55 (1)
C(6)–C(7)	1.52 (1)	C(6)–O(3)	1.48 (1)
C(7)–C(8)	1.52 (1)	C(8)–C(9)	1.55 (1)
C(8)–C(14)	1.54 (1)	C(9)–C(10)	1.52 (1)
C(9)–C(11)	1.56 (1)	C(10)–C(19)	1.57 (1)
C(11)–C(12)	1.55 (1)	C(12)–C(13)	1.55 (1)
C(12)–C(14)	1.55 (1)	C(13)–C(17)	1.51 (1)
C(13)–C(18)	1.52 (2)	C(14)–C(15)	1.53 (1)
C(15)–C(16)	1.54 (1)	C(16)–C(17)	1.52 (1)
C(17)–C(20)	1.55 (1)	C(18)–N(1)	1.46 (2)
C(20)–C(21)	1.57 (2)	C(20)–C(22)	1.51 (2)
C(22)–C(23)	1.53 (2)	C(22)–N(1)	1.43 (2)
C(23)–C(24)	1.52 (3)	C(24)–C(25)	1.65 (3)
C(25)–C(26)	1.57 (3)	C(25)–C(27)	1.54 (3)
C(26)–N(1)	1.50 (2)	C(28)–C(29)	1.50 (2)
C(28)–O(1)	1.36 (1)	C(28)–O(2)	1.18 (2)
C(30)–C(31)	1.48 (1)	C(30)–O(3)	1.32 (1)
C(30)–O(4)	1.20 (1)	C(1′)–C(2′)	1.57 (1)
C(1′)–C(10′)	1.55 (1)	C(2′)–C(3′)	1.51 (1)
C(3′)–C(4′)	1.52 (1)	C(3′)–O(1′)	1.44 (1)
C(4′)–C(5′)	1.55 (1)	C(5′)–C(6′)	1.50 (1)
C(5′)–C(10′)	1.56 (1)	C(6′)–C(7′)	1.53 (1)
C(6′)–O(3′)	1.48 (1)	C(7′)–C(8′)	1.51 (1)
C(8′)–C(9′)	1.53 (1)	C(8′)–C(14′)	1.53 (1)
C(9′)–C(10′)	1.54 (1)	C(9′)–C(11′)	1.52 (1)
C(10′)–C(19′)	1.55 (1)	C(11′)–C(12′)	1.55 (1)
C(12′)–C(13′)	1.52 (1)	C(12′)–C(14′)	1.56 (1)
C(13′)–C(17′)	1.53 (1)	C(13′)–C(18′)	1.49 (1)
C(14′)–C(15′)	1.54 (2)	C(15′)–C(16′)	1.52 (2)
C(16′)–C(17′)	1.54 (1)	C(17′)–C(20′)	1.57 (2)
C(18′)–N(1′)	1.47 (1)	C(20′)–C(21′)	1.57 (2)
C(20′)–C(22′)	1.51 (2)	C(22′)–C(23′)	1.55 (2)
C(22′)–N(1′)	1.45 (1)	C(23′)–C(24′)	1.56 (2)
C(24′)–C(25′)	1.54 (2)	C(25′)–C(26′)	1.53 (2)
C(25′)–C(27′)	1.52 (2)	C(26′)–N(1′)	1.47 (1)
C(28′)–C(29′)	1.51 (2)	C(28′)–O(1′)	1.35 (1)
C(28′)–O(2′)	1.18 (2)	C(30′)–C(31′)	1.48 (2)
C(30′)–O(3′)	1.35 (1)	C(30′)–O(4′)	1.22 (1)

22, which are carbons adjacent to a nitrogen atom, and C-16 were shifted downfield at δ 61.8, 69.0, and 25.6 compared with those of **7** at δ 59.2, 62.5 and 17.7, and correspond very well with those in shinonomenine (**9**)[7] at δ 62.6, 68.0 and 24.9 respectively. These supported the presence of the D/E *trans* juncture in **2**.

The relative stereostructure of **2** was confirmed by an X-ray crystal analysis of its acetate (mp 143.5—146 °C). The structure of the molecule is shown in Fig. 4. The crystal of ebeiedine-3,6-diacetate belongs to the monoclinic system with space group $C2$, and the cell dimensions, are $a=31.994\,(6)$, $b=8.802\,(1)$, $c=24.745\,(4)$ Å; $\beta=121.36\,(1)$, $Z=8$, $d=1.115$ g/cm^3. The crystal size is $0.7\times0.1\times0.1$ mm. Three-dimensional intensity data were collected on Rigaku AFC-5 diffractometer and 5387 unique reflections were measured for 3210 [F_O $3\sigma(F_O)$] by the ω–2θ scan method with CuK_α ($\lambda=1.5417$ Å) radiation. The structure was determined by a direct method and refined by a block-diagonal anisotropic least-squares technique to $R=0.072$,

TABLE VII. Bond Angles (°) with e.s.d. Values in Parentheses for Ebeiedine Diacetate

C(2)–C(1)–C(10)	112.3 (8)	C(1)–C(2)–C(3)	111.4 (8)
C(2)–C(3)–C(4)	110.0 (8)	C(2)–C(3)–O(1)	107.0 (8)
C(4)–C(3)–O(1)	108.1 (8)	C(3)–C(4)–C(5)	108.9 (8)
C(4)–C(5)–C(6)	112.3 (7)	C(4)–C(5)–C(10)	111.9 (7)
C(6)–C(5)–C(10)	115.6 (7)	C(5)–C(6)–C(7)	113.2 (8)
C(5)–C(6)–O(3)	110.4 (7)	C(7)–C(6)–O(3)	106.1 (7)
C(6)–C(7)–C(8)	110.0 (8)	C(7)–C(8)–C(9)	111.2 (7)
C(7)–C(8)–C(14)	117.1 (8)	C(9)–C(8)–C(14)	101.4 (7)
C(8)–C(9)–C(10)	112.8 (7)	C(8)–C(9)–C(11)	102.7 (7)
C(10)–C(9)–C(11)	120.0 (8)	C(1)–C(10)–C(5)	106.9 (7)
C(1)–C(10)–C(9)	110.0 (7)	C(1)–C(10)–C(19)	109.5 (7)
C(5)–C(10)–C(9)	105.1 (7)	C(5)–C(10)–C(19)	113.7 (7)
C(9)–C(10)–C(19)	111.4 (7)	C(9)–C(11)–C(12)	106.3 (8)
C(11)–C(12)–C(13)	111.1 (8)	C(11)–C(12)–C(14)	104.9 (8)
C(13)–C(12)–C(14)	113.0 (8)	C(12)–C(13)–C(17)	112.8 (8)
C(12)–C(13)–C(18)	110.0 (8)	C(17)–C(13)–C(18)	112.1 (9)
C(8)–C(14)–C(12)	102.9 (8)	C(8)–C(14)–C(15)	116.7 (8)
C(12)–C(14)–C(15)	116.7 (8)	C(14)–C(15)–C(16)	111.4 (8)
C(15)–C(16)–C(17)	110.9 (8)	C(13)–C(17)–C(16)	110.1 (8)
C(13)–C(17)–C(20)	109.3 (8)	C(16)–C(17)–C(20)	113.5 (8)
C(13)–C(18)–N(1)	109.3 (10)	C(17)–C(20)–C(21)	110.0 (9)
C(17)–C(20)–C(22)	111.3 (8)	C(21)–C(20)–C(22)	111.6 (9)
C(20)–C(22)–C(23)	109.2 (9)	C(20)–C(22)–N(1)	111.3 (9)
C(23)–C(22)–N(1)	108.9 (9)	C(22)–C(23)–C(24)	114.4 (12)
C(23)–C(24)–C(25)	109.9 (16)	C(24)–C(25)–C(26)	100.6 (17)
C(24)–C(25)–C(27)	112.3 (18)	C(26)–C(25)–C(27)	117.1 (18)
C(25)–C(26)–N(1)	110.7 (16)	C(29)–C(28)–O(1)	112.1 (9)
C(29)–C(28)–O(2)	125.6 (11)	O(1)–C(28)–O(2)	122.2 (11)
C(31)–C(30)–O(3)	111.2 (8)	C(31)–C(30)–O(4)	124.8 (9)
O(3)–C(30)–O(4)	123.9 (9)	C(18)–N(1)–C(22)	112.1 (9)
C(18)–N(1)–C(26)	107.5 (12)	C(22)–N(1)–C(26)	113.3 (12)
C(3)–O(1)–C(28)	116.4 (8)	C(6)–O(3)–C(30)	118.8 (7)
C(2′)–C(1′)–C(10′)	111.9 (7)	C(1′)–C(2′)–C(3′)	108.9 (7)
C(2′)–C(3′)–C(4′)	111.4 (8)	C(2′)–C(3′)–O(1′)	107.9 (7)
C(4′)–C(3′)–O(1′)	109.8 (8)	C(3′)–C(4′)–C(5′)	108.3 (8)
C(4′)–C(5′)–C(6′)	115.6 (8)	C(4′)–C(5′)–C(10′)	112.7 (7)
C(6′)–C(5′)–C(10′)	114.2 (8)	C(5′)–C(6′)–C(7′)	113.4 (8)
C(5′)–C(6′)–O(3′)	111.4 (8)	C(7′)–C(6′)–O(3′)	107.0 (7)
C(6′)–C(7′)–C(8′)	110.4 (8)	C(7′)–C(8′)–C(9′)	111.0 (8)
C(7′)–C(8′)–C(14′)	115.8 (8)	C(9′)–C(8′)–C(14′)	100.0 (7)
C(8′)–C(9′)–C(10′)	113.3 (7)	C(8′)–C(9′)–C(11′)	104.1 (7)
C(10′)–C(9′)–C(11′)	120.9 (7)	C(1′)–C(10′)–C(5′)	107.1 (7)
C(1′)–C(10′)–C(9′)	108.1 (7)	C(1′)–C(10′)–C(19′)	109.5 (7)
C(5′)–C(10′)–C(9′)	105.6 (7)	C(5′)–C(10′)–C(19′)	114.2 (7)
C(9′)–C(10′)–C(19′)	111.9 (7)	C(9′)–C(11′)–C(12′)	106.9 (7)
C(11′)–C(12′)–C(13′)	112.9 (8)	C(11′)–C(12′)–C(14′)	102.9 (8)
C(13′)–C(12′)–C(14′)	114.5 (8)	C(12′)–C(13′)–C(17′)	113.8 (8)
C(12′)–C(13′)–C(18′)	110.1 (8)	C(17′)–C(13′)–C(18′)	109.8 (8)
C(8′)–C(14′)–C(12′)	102.6 (8)	C(8′)–C(14′)–C(15′)	117.1 (9)
C(12′)–C(14′)–C(15′)	113.4 (9)	C(14′)–C(15′)–C(16′)	114.8 (10)
C(15′)–C(16′)–C(17′)	110.6 (9)	C(13′)–C(17′)–C(16′)	108.4 (8)
C(13′)–C(17′)–C(20′)	110.5 (8)	C(16′)–C(17′)–C(20′)	114.7 (9)
C(13′)–C(18′)–N(1′)	113.1 (8)	C(17′)–C(20′)–C(21′)	107.8 (10)
C(17′)–C(20′)–C(22′)	111.8 (10)	C(21′)–C(20′)–C(22′)	112.9 (10)
C(20′)–C(22′)–C(23′)	109.8 (10)	C(20′)–C(22′)–N(1′)	111.8 (9)
C(23′)–C(22′)–N(1′)	109.9 (9)	C(22′)–C(23′)–C(24′)	110.2 (11)
C(23′)–C(24′)–C(25′)	111.3 (11)	C(24′)–C(25′)–C(26′)	106.9 (10)
C(24′)–C(25′)–C(27′)	112.7 (11)	C(26′)–C(25′)–C(27′)	111.5 (10)
C(25′)–C(26′)–N(1′)	113.0 (9)	C(29′)–C(28′)–O(1′)	112.2 (11)
C(29′)–C(28′)–O(2′)	126.1 (13)	O(1′)–C(28′)–O(2′)	121.7 (12)
C(31′)–C(30′)–O(3′)	112.0 (9)	C(31′)–C(30′)–O(4′)	125.0 (10)
O(3′)–C(30′)–O(4′)	123.0 (9)	C(18′)–N(1′)–C(22′)	111.1 (8)
C(18′)–N(1′)–C(26′)	108.9 (8)	C(22′)–N(1′)–C(26′)	113.4 (8)
C(3′)–O(1′)–C(28′)	117.1 (8)	C(6′)–O(3′)–C(30′)	120.0 (7)

TABLE VIII. Anisotropic Thermal Parameters ($\times 10^4$) with e.s.d. Values in Parentheses for Ebeiedine Diacetate

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	21 (1)	168 (14)	31 (2)	−6 (4)	13 (1)	2 (5)
C(2)	24 (2)	147 (13)	33 (2)	−3 (4)	15 (1)	−4 (4)
C(3)	18 (1)	184 (15)	36 (2)	0 (4)	15 (1)	17 (5)
C(4)	18 (1)	209 (15)	22 (2)	4 (3)	10 (1)	0 (4)
C(5)	15 (1)	149 (12)	28 (2)	−5 (3)	12 (1)	3 (4)
C(6)	14 (1)	201 (15)	29 (2)	0 (3)	12 (1)	−12 (4)
C(7)	15 (1)	222 (16)	30 (2)	5 (4)	11 (1)	−1 (5)
C(8)	12 (1)	180 (13)	27 (2)	4 (3)	9 (1)	9 (4)
C(9)	16 (1)	175 (14)	26 (2)	−4 (3)	10 (1)	−13 (4)
C(10)	12 (1)	174 (14)	27 (2)	−5 (3)	10 (1)	−5 (4)
C(11)	19 (1)	158 (13)	29 (2)	−14 (3)	10 (1)	−7 (4)
C(12)	14 (1)	216 (16)	25 (2)	−9 (3)	5 (1)	−3 (4)
C(13)	18 (1)	194 (15)	27 (2)	−12 (4)	11 (1)	−9 (4)
C(14)	13 (1)	212 (15)	31 (2)	2 (3)	9 (1)	1 (5)
C(15)	18 (1)	167 (15)	49 (3)	10 (4)	13 (1)	19 (5)
C(16)	21 (1)	173 (14)	30 (2)	12 (4)	11 (1)	7 (5)
C(17)	17 (1)	158 (14)	33 (2)	−4 (3)	5 (1)	14 (5)
C(18)	30 (2)	219 (18)	31 (2)	−32 (5)	18 (2)	−24 (5)
C(19)	13 (1)	159 (12)	31 (2)	−2 (3)	12 (1)	−2 (4)
C(20)	24 (1)	144 (13)	27 (2)	−3 (4)	11 (1)	12 (4)
C(21)	36 (2)	222 (21)	75 (5)	21 (6)	34 (3)	46 (8)
C(22)	25 (2)	259 (19)	32 (2)	−2 (5)	15 (1)	25 (6)
C(23)	36 (2)	250 (21)	50 (3)	0 (6)	27 (2)	15 (7)
C(24)	75 (5)	398 (33)	71 (5)	−45 (12)	60 (4)	−23 (12)
C(25)	79 (5)	264 (24)	92 (6)	−47 (9)	74 (5)	−47 (10)
C(26)	75 (5)	244 (24)	79 (6)	−26 (9)	62 (5)	−29 (10)
C(27)	53 (4)	372 (34)	121 (9)	10 (10)	61 (5)	9 (15)
C(28)	24 (2)	232 (18)	35 (2)	6 (4)	18 (1)	0 (5)
C(29)	30 (2)	212 (17)	27 (2)	15 (5)	13 (1)	7 (5)
C(30)	19 (1)	138 (12)	27 (2)	2 (3)	13 (1)	−6 (4)
C(31)	19 (1)	195 (15)	31 (2)	−14 (4)	12 (1)	−5 (5)
N(1)	36 (2)	191 (14)	38 (2)	−14 (4)	24 (1)	−15 (4)
O(1)	20 (1)	216 (11)	32 (1)	3 (2)	13 (1)	14 (3)
O(2)	34 (2)	565 (26)	54 (2)	69 (5)	30 (1)	84 (7)
O(3)	18 (1)	190 (9)	27 (1)	−8 (2)	13 (1)	−16 (3)
O(4)	28 (1)	347 (16)	34 (2)	−30 (4)	19 (1)	−27 (4)
C(1′)	15 (1)	155 (12)	25 (2)	3 (3)	9 (1)	8 (4)
C(2′)	13 (1)	190 (14)	22 (2)	6 (3)	6 (1)	−3 (4)
C(3′)	16 (1)	122 (11)	34 (2)	−1 (3)	15 (1)	−12 (4)
C(4′)	20 (1)	125 (11)	23 (2)	−1 (3)	12 (1)	1 (4)
C(5′)	16 (1)	159 (13)	21 (2)	−9 (3)	8 (1)	8 (4)
C(6′)	18 (1)	126 (12)	29 (2)	9 (3)	9 (1)	22 (4)
C(7′)	24 (2)	103 (11)	36 (2)	19 (3)	15 (1)	7 (4)
C(8′)	19 (1)	157 (13)	28 (2)	3 (3)	12 (1)	7 (4)
C(9′)	13 (1)	159 (12)	24 (2)	−1 (3)	10 (1)	−9 (4)
C(10′)	14 (1)	146 (12)	22 (2)	−2 (3)	7 (1)	0 (4)
C(11′)	17 (1)	205 (15)	25 (2)	12 (4)	10 (1)	0 (4)
C(12′)	17 (1)	217 (15)	25 (2)	−3 (4)	11 (1)	−12 (5)
C(13′)	14 (1)	220 (16)	26 (2)	−4 (3)	9 (1)	−23 (4)
C(14′)	20 (1)	173 (14)	34 (2)	−8 (4)	13 (1)	−17 (5)
C(15′)	27 (2)	195 (17)	42 (3)	14 (4)	18 (2)	−15 (6)
C(16′)	22 (2)	211 (17)	41 (3)	5 (4)	14 (1)	−12 (6)
C(17′)	16 (1)	212 (16)	36 (2)	1 (4)	10 (1)	−26 (5)
C(18′)	14 (1)	246 (17)	25 (2)	1 (3)	11 (1)	−10 (5)

TABLE VIII. (continued)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(19′)	16 (1)	160 (13)	27 (2)	−12 (3)	9 (1)	4 (4)
C(20′)	13 (1)	249 (18)	51 (3)	−10 (4)	16 (1)	−43 (6)
C(21′)	26 (2)	314 (25)	77 (5)	−4 (6)	31 (2)	−45 (9)
C(22′)	20 (1)	246 (18)	40 (3)	−17 (4)	17 (1)	−41 (6)
C(23′)	26 (2)	290 (23)	67 (4)	−6 (6)	30 (2)	−23 (8)
C(24′)	34 (2)	276 (23)	80 (5)	−43 (6)	41 (3)	−35 (9)
C(25′)	29 (2)	258 (20)	54 (3)	−34 (5)	28 (2)	−32 (7)
C(26′)	20 (1)	265 (19)	33 (2)	−7 (4)	15 (1)	−7 (6)
C(27′)	32 (2)	272 (25)	64 (4)	−16 (6)	25 (2)	−28 (8)
C(28′)	31 (2)	234 (18)	40 (3)	−5 (5)	25 (2)	3 (6)
C(29′)	39 (3)	362 (28)	47 (3)	9 (7)	30 (2)	−24 (8)
C(30′)	18 (1)	224 (17)	27 (2)	32 (4)	8 (1)	8 (5)
C(31′)	18 (2)	330 (24)	49 (3)	−17 (5)	11 (2)	−37 (8)
N(1′)	16 (1)	211 (13)	37 (2)	−3 (3)	16 (1)	−14 (4)
O(1′)	19 (1)	202 (10)	32 (1)	2 (2)	14 (1)	−5 (3)
O(2′)	73 (3)	274 (15)	85 (3)	−15 (6)	66 (3)	4 (7)
O(3′)	16 (1)	238 (11)	22 (1)	17 (2)	6 (1)	10 (3)
O(4′)	24 (1)	286 (13)	29 (1)	20 (3)	12 (1)	5 (4)

The temperature factor is of the form: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

$R_W=0.093$ and $S=1.141$ for 3181 reflections. The crystallographic details are described in Experimental. The results showed that all the rings are in the chair conformation. The ring fusions are as follows: A/B *trans*, B/C *trans*, C/D *cis*, D/E *trans*. The configurations at the chiral center have been determined as 3-OAc β-equatorial, 6-OAc β-axial, 10-Me β-axial, 20-Me α-equatorial, 25-Me β-axial, and the lone pair on the nitrogen β-axial.

Ebeiedinone (**3**) was crystallized from hexane–Et_2NH–EtOH as colorless needles, mp 102—105 °C, $[\alpha]_D$ −62.2° ($c=0.89$, $CHCl_3$).

The empirical formula of **3**, $C_{27}H_{43}NO_2$, M.W. 413.32830 (Calcd 413.32959), was measured by high-resolution mass spectrometry, and the IR spectrum of **3** showed, besides the absorptions at 3525, 3350 cm^{-1} (hydroxyl) and 2750 cm^{-1} (*trans*-quinolizidine system), a six membered ketone system at 1686 cm^{-1}.

The MS of **3** revealed a parent ion at m/z 413 (M^+, 19%), and fragment ions at m/z 398 (5%), 357 (7%), 112 (38%), 111 (100%) and 98 (11%).

The ^{1}H-NMR spectrum of **3** displayed three methyl signals at δ 0.76 (3H, s, 19-H), δ 0.83 (3H, d, $J=6$ Hz, 21-H) and δ 1.08 (3H, d, $J=7$ Hz, 27-H), and a signal of hydrogen on carbon bearing a hydroxyl group at δ 3.58 (1H, m, $W_{1/2}=19$ Hz, 3α-H) (on acetylation, this signal was shifted downfield to δ 4.68).

The above data allowed us to conclude that 3 is structurally similar to **2**, possessing a (25*S*)-20-deoxy-5α-cevanine skeleton.

On the other hand, the ^{13}C-NMR spectrum of ebeiedinone (**3**) (Table IX), showed that the chemical shifts of carbons, except C-16, C-18 and C-22, whose signals were shifted downfield at δ 25.1, 62.1 and 69.0 compared with those of delavinone (**8**) at δ 17.1, 59.3 and 62.4, are in good accordance with those of delavinone (**8**). Furthermore, in the ^{1}H-NMR spectrum, the signal of 19-H in **2** exhibited an upfield shift at δ 0.75 compared with that in **2**, and was very close to that in delavinone (**8**). The presence of a carbonyl group at C-6 was also corroborated by the ^{13}C-NMR spectrum, which displayed low-field signals at δ 211.3 assignable to C-6. Reduction of **3** with $NaBH_4$, furnished the diol derivative whose physical and chemical properties coincided with those in **2** and whose melting point was not depressed by admixture with **2**.

TABLE IX. ^{13}C Chemical Shifts of Cevanine Alkaloids

Carbon No.	2	3	7	8	9	Carbon No.	2	3	7	8	9
1	38.1	37.0	39.4	37.6	38.1	15	26.9	25.3	28.7	26.8	25.1
2	31.2	30.5	31.4	30.6	31.4	16	25.6	25.1	17.7	17.1	24.9
3	71.7	70.8	71.9	70.9	72.0	17	46.5	46.4	41.6	46.9	45.5
4	34.9	30.1	34.8	30.3	41.8	18	61.8	62.1	59.2	59.3	62.6
5	48.3	56.8	48.1	56.7	142.4	19	15.0	12.8	15.7	12.7	19.1
6	72.8	211.3	73.2	211.0	122.3	20	43.3	43.7	38.9	35.7	36.2
7	39.1	46.1	39.6	47.0	31.2	21	14.8	14.7	14.7	15.6	8.6
8	35.0	40.3	36.7	39.7	38.6	22	69.0	69.0	62.5	62.4	68.0
9	57.7	56.7	57.9	56.7	54.4	23	24.8	24.6	25.0	24.9	24.3
10	35.5	38.4	35.5	38.3	37.0	24	29.2	28.9	30.3	30.4	28.9
11	30.2	30.1	30.8	30.0	30.3	25	28.4	28.3	28.4	28.4	28.3
12	40.4	41.4	39.1	39.5	41.5	26	62.0	61.7	61.7	61.8	63.9
13	40.3	40.4	39.1	39.3	37.9	27	18.3	18.3	18.3	18.3	17.9
14	44.0	44.3	41.2	41.0	45.3						

In ppm relative to TMS in $CDCl_3$.

Experimental

The melting points were taken on a Leitz Wetzlar micro-melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 digital polarimeter. IR spectra were run on an A-102 infrared spectrophotometer. The MS were recorded on a JEOL JMS-D300 mass spectrometer. The ^1H- and ^{13}C-NMR spectra were taken on a JEOL JNM GX-270 spectrophotometer (270 MHz for ^1H-NMR, 67.5 MHz for ^{13}C-NMR).

The dried bulbs of *F. ebeiensis* var. *purpurea* were collected in Hupei Province, China, in June 1985. The ground bulbs (5 kg) were extracted three times with 50% aqueous acetone. After removal of the acetone under reduced pressure, the aqueous fraction was passed through a Diaion HP-20 column which was eluted gradually with H_2O containing increasing concentrations of methanol. The fractions eluted with 50% methanol and methanol afforded free alkaloids and their glycodises. The residue of these fractions was hydrolyzed with 1 N HCl in methanol for 6 h. The hydrolysate was extracted with ether after being made alkaline with 10% NaOH. The combined ether phase was extracted with 5% aqueous tartaric acid. The aqueous solution was made alkaline and then extracted with chloroform. The chloroform extract was evaporated and the residue (crude alkaloid, 21 g) was chromatographed on silica gel, followed by repeated column chromatography using hexane–Et_2NH–EtOH (120 : 1 : 1—120 : 7 : 7), cyclohexane–EtOAc–Et_2NH (60 : 10 : 2—60 : 20 : 5) and hexane–EtOAc–MeOH (150 : 2 : 1—2 : 2 : 1) as eluents to give FE-2, FE-3, FE-4, FE-5, FE-6, FE-7, FE-8 and FE-9. The yields were: FE-2 (5 mg), FE-3 (10 mg), FE-4 (200 mg), FE-5 (1.8 g), FE-6 (321 mg), FE-7 (234 mg), FE-8 (151 mg) and FE-9 (1.5 g). All the products were obtained as crystalline solids.

FE-8, named ebeienine (**1**), was crystallized from *n*-hexane–Et_2NH–EtOH as colorless needles, and crystallized from methanol in rhombic form, mp 274.5—278.5 °C, $[\alpha]_D$ −2.9° (c=0.5, MeOH). IR ν_{max}^{Nujol} cm^{-1}: 3475, 3250—3325 (hydroxyl), 2750 (*trans*-quinolizidine system). MS m/z: 431 ($M^+ + H_2O$), 413 (M^+), 398 ($M^+ - CH_3$). 190, 112, 98 (base peak). ^1H-NMR ($CDCl_3$) δ: 0.86 (3H, d, J=6 Hz, 27-H), 0.95 (3H, s, 19-H), 0.96 (3H, d, J=7 Hz, 21-H), 3.66 (1H, m, $W_{1/2}$=19 Hz, 3α-H), 3.86 (1H, m, $W_{1/2}$=8 Hz, 6α-H). ^{13}C-NMR (Table I).

FE-9, verticine (**4**), was crystallized from hexane–Et_2NH–EtOH as colorless needles, mp 215—220 °C, mmp 213—220 °C (mixed melting point with an authentic specimen), $[\alpha]_D$ −26.2° (c=0.96, $CHCl_3$). IR: 3325 (hydroxyl), 2780 (*trans*-quinolizidine system). MS m/z: 431 ($C_{27}H_{45}NO_3$, M^+), 412, 386, 112 (base peak), 98. ^1H-NMR ($CDCl_3$) δ: 0.82 (3H, s, 19-H), 1.03 (3H, s, 21-H), 1.08 (3H, d, J=7 Hz, 27-H), 3.44 (1H, m, $W_{1/2}$=20 Hz, 6β-H), 3.60 (1H, m, $W_{1/2}$=20 Hz, 3α-H).

FE-5, verticinone (**5**), was crystallized from hexane–Et_2NH–EtOH and recrystallized from EtOH–H_2O as colorless needles, mp 210—212 °C, mmp 209—211 °C (mixed melting point with an authentic specimen), $[\alpha]_D$ −75.2° (c=0.92, $CHCl_3$). IR: 3380 (hydroxyl), 2760 (*trans*-quinolizidine system), 1700 (six-membered ketone). MS m/z: 429 ($C_{27}H_{43}NO_3$, M^+), 411 ($M^+ - H_2O$), 384, 112 (base peak), 98. ^1H-NMR δ: 0.77 (3H, s, 19-H), 1.02 (3H, s, 21-H), 1.07 (3H, d, J=7 Hz, 27-H), 3.56 (1H, m, $W_{1/2}$=24 Hz, 3α-H).

Verticinone (FE-5) Monoacetate: Verticinone was acetylated in the usual manner to give a monoacetate, mp 172—175 °C. IR: 3480 (hydroxyl), 2800 (*trans*-quinolizidine system), 1700, 1715 (six-membered ketone). MS m/z: 471 (M^+), 453, 426, 392, 112 (base peak), 98. ^1H-NMR δ: 0.77 (3H, s, 19-H), 1.02 (3H, s, 21-H), 2.03 (3H, s, –OAc), 4.70 (1H, m, $W_{1/2}$=20 Hz, 3α-H).

FE-6, isoverticine (**6**), was crystallized from EtOAc–acetone as colorless needles, mp 216.5—219.5 °C, mmp 207—216.5 °C, (mixed melting point with an authentic specimen) $[\alpha]_D$ −43.9° (c=0.82, $CHCl_3$). IR: 3500 (hydroxyl),

2825 (*trans*-quinolizidine system). MS *m/z*: 431 ($C_{27}H_{45}NO_3$, M^+), 412, 386, 154, 124, 112 (base peak), 111, 98. ^{1}H-NMR δ: 1.03 (6H, s, 19-H and 21-H), 1.08 (3H, d, J=7 Hz, 27-H), 3.63 (1H, m, $W_{1/2}$=20 Hz, 3α-H), 3.85 (1H, br s, $W_{1/2}$=9 Hz, 6α-H).

FE-7, named ebeiedine (**2**), was crystallized from hexane–Et_2NH–EtOH as colorless needles, mp 118—120 °C, $[\alpha]_D$ −37.9° (c=0.97, $CHCl_3$). IR ν_{max}^{Nujol} cm^{-1}: 3300 (hydroxyl), 2750 (*trans*-quinolizidine). MS *m/z*: 415 (M^+, 29%), 400 (M^+-CH_3, 7%), 359 (9%), 112 (45%), 111 (100%), 98 (11%). ^{1}H-NMR δ: 0.83 (3H, d, J=6 Hz, 21-H), 1.08 (3H, d, J=7 Hz, 27-H), 1.02 (3H, s, 19-H), 3.66 (1H, m, $W_{1/2}$=19 Hz, 3α-H), 3.87 (1H, br s, $W_{1/2}$=8 Hz, 6α-H). ^{13}C-NMR (shown in Table I).

Ebeiedine Diacetate: Acetylation of ebeiedine (**2**) with Ac_2O in pyridine gave diacetylebeiedine, mp 143.5—146.5 °C. IR ν_{max}^{Nujol} cm^{-1}: 2800 (*trans*-quinolizidine system), 1750, 1250 (carbonyl group). MS *m/z*: 499 (M^+, 21%), 484 (M^+-CH_3, 5%), 443 (6%), 112 (45%), 111 (100%), 98 (10%). ^{1}H-NMR δ: 0.84 (3H, d, J=7 Hz, 21-H), 1.02 (3H, s, 19-H), 1.09 (3H, d, J=7 Hz, 27-H), 2.02 (3H, s, –OAc), 2.03 (3H, s, –OAc), 4.73 (1H, m, $W_{1/2}$=19 Hz, 3α-H), 5.0 (1H, m, $W_{1/2}$=8 Hz, 6α-H).

FE-4, named ebeiedinone (**3**), was crystallized from hexane–Et_2NH–EtOH as colorless needles, mp 102—105 °C, $[\alpha]_D$ −62.2° (c=0.89, $CHCl_3$). IR ν_{max}^{Nujol} cm^{-1}: 3525, 3350 (hydroxy), 2750 (*trans*-quinolizidine), 1686 (six-membered ketone). MS *m/z*: 413 (M^+, 19%), 398 (M^+-CH_3, 5%), 357 (7%), 112 (38%), 111 (100%), 98 (11%). ^{1}H-NMR δ: 0.76 (3H, s, 19-H), 0.83 (3H, d, J=6 Hz, 21-H), 1.08 (3H, d, J=7 Hz, 27-H), 3.58 (1H, m, $W_{1/2}$=19 Hz, 3α-H).

Ebeiedinone Monoacetate: Ebeiedinone (**3**) was acetylated with Ac_2O in pyridine to yield a monoacetate, mp 88—91.5 °C. MS *m/z*: 455 (M^+, 27%), 440 (M^+-CH_3, 6%), 399 (8%), 112 (41%), 111 (100%), 98 (10%). ^{1}H-NMR δ: 0.78 (3H, s, 19-H), 0.83 (3H, d, J=6 Hz, 21-H), 1.08 (3H, d, J=7 Hz, 27-H), 2.03 (3H, s, –OAc), 4.68 (1H, m, $W_{1/2}$= 19 Hz, 3α-H).

Reduction of Ebeiedinone (**3**): Ebeiedinone (**3**) was converted to **1** by reduction with $NaBH_4$, mp 117—120 °C, mmp 117—120 °C. IR ν_{max}^{Nujol} cm^{-1}: 3350 (hydroxyl), 2800 (*trans*-quinolizidine). MS *m/z*: 415 (M^+, 28%), 400 (M^+-CH_3, 7%), 359 (10%), 112 (44%), 111 (100%), 98 (11%). ^{1}H-NMR δ: 0.83 (3H, d, J=6 Hz, 21-H), 1.02 (3H, s, 19-H), 1.08 (3H, d, J=7 Hz, 27-H), 3.66 (1H, m, $W_{1/2}$=19 Hz, 3α-H), 3.87 (1H, m, $W_{1/2}$=8 Hz, 6α-H).

Crystallographic Details of Ebeienine (1), and Ebeiedine (2) Diacetate——The authors have deposited atomic coordinates for these structures with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from the Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1 EW, UK.

	Ebeienine (**1**)	Ebeiedine (**2**) diacetate
Formula	$C_{27}H_{43}NO_2 \cdot H_2O$	$C_{31}H_{49}NO_4$
Formula w.t.	431.7	499.7
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$C2$
a (Å)	13.508 (1)	31.994 (6)
b (Å)	7.853 (1)	8.802 (1)
c (Å)	11.912 (1)	24.745 (4)
α (deg)	—	—
β (deg)	104.18 (1)	121.36 (1)
τ (deg)	—	—
Z	2	8
Density calcd (g/cm^3)	1.170	1.115
Crystal size (mm)	0.4 × 0.15 × 0.1	0.7 × 0.1 × 0.1
μ (cm^{-1})	5.9 (CuK_α)	—
Radiation	CuK_α (λ=1.54178 Å)	CuK_α (λ=1.54178 Å)
Data collection method	ω–2θ scan	ω–2θ scan
No. of unique reflcns.	2240	5387
No. of observed reflcns.	2173 [$\|F_O\| > 3\sigma(F_O)$]	3210 [$\|F_O\| > 3\sigma(F_O)$]
Least-squares method	Block-diagonal approximation [$\sum(w\|\Delta F\|^2)$ minimized	Block-diagonal approximation [$\sum(w\|\Delta F\|^2)$ minimized
Weighting expression	$[\sigma^2(F_O)+0.00431(F_O)^2]^{-1}$	$[\sigma^2(F_O)+0.00431(F_O)^2]^{-1}$
No. of reflections used in the last stage of least-squares refinement	2125	3181
R	0.042	0.072
R_w	0.60	0.093
S	1.221	1.141

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