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STUDIES ON ACONITUM SPECIES V.[1] CONSTITUENTS OF ACONITUM YESOENSE VAR. MACROYESOENSE (NAKAI) TAMURA[2]

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Abstract — Five new C_{20}-diterpenoid alkaloids, 12-acetyldehydroluciduscul ine, 12-acetylluciduscul ine, 15-benzoylpseudokobusine, 15-veratroylpseudokobusine, and yesoxine and 14 known alkaloids were isolated from A. yesoense var. macroyesoense (Nakai) Tamura. Structures of those compounds were determined on the basis of their spectral and chemical data. Structure of an unusual epoxide, yesoxine, was determined by X-ray analysis and was a first example having an epoxy group at C(16 and 17).

The isolation and structure elucidation of six alkaloids, dehydroluciduscul ine (1), N-deethyldehydroluciduscul ine (2), kobusine (3), pseudokobusine (4), delcosine (5), and 14-acetyldelcosine (6) from A. yesoense var. macroyesoense (Nakai) Tamura were reported in our previous paper.[2] We have continued to investigate the constituents of this plant and isolated five new diterpenoid alkaloids, 12-acetyldehydroluciduscul ine (7), 12-acetylluciduscul ine (8), 15-benzoylpseudokobusine (9), 15-veratroylpseudokobusine (10), and a novel epoxide (11) named as yesoxine, together with eight known alkaloids, luciduscul ine (12)[3,4], luciculine (13)[4], 1-acetylluciculine (14)[5], 14-acetylbrowniine (15)[6], browniine (16)[6], virescenine (17)[6], isotalatizidine

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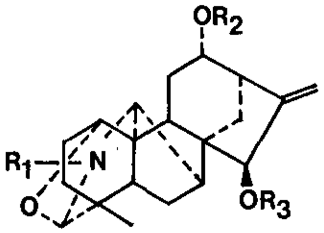

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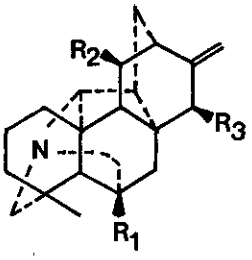
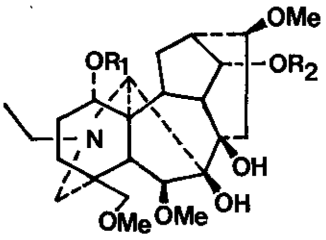
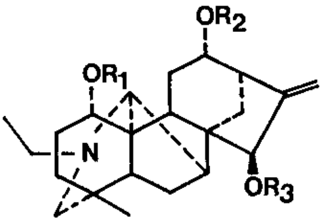
2: R_1=R_2=H, R_3=Ac
7: R_1=Et, R_2=R_3=Ac
20: R_1=Et, R_2=R_3=H



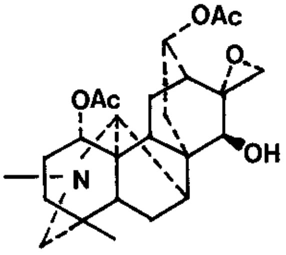
3: R_1=H, R_2=R_3=OH
4: R_1=R_2=R_3=OH
9: R_1=R_2=OH, R_3=OBz
10: R_1=R_2=OH, R_3=OVr
22: R_1=OBz, R_2=R_3=OH
23: R_1=R_3=OH, R_2=OBz
24: R_1=R_2=OBz, R_3=OH
25: R_1=R_3=OBz, R_2=OH
26: R_1=ONB, R_2=R_3=OH
27: R_1=ONB, R_2=OBz, R_3=OH
28: R_1=ONB, R_2=OH, R_3=OBz
29: R_1=ONB, R_2=R_3=OBz
Bz=Benzoyl, Vr=Veratroyl, NB=p-Nitrobenzoyl



5: R_1=R_2=H
6: R_1=H, R_2=Ac
15: R_1=Me, R_2=Ac
16: R_1=Me, R_2=H



8: R_1=H, R_2=R_3=Ac
12: R_1=R_2=H, R_3=Ac
13: R_1=R_2=R_3=H
14: R_1=Ac, R_2=R_3=H
21: R_1=R_2=R_3=Ac



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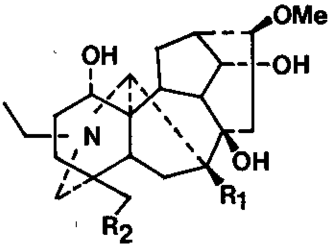

17: R_1=OH, R_2=OMe
18: R_1=H, R_2=OMe
19: R_1=R_2=H

(18)^6, and karakoline (19)^6.

Compound (13)-(19) have not previously been found in this plant. Identification of 12, 13, and 19 was carried out by comparison of their melting points and spectral data with those of their authentic samples. The structure of 14-18 was determined by comparison of spectral data with those in literature value^{5,6} and transformation of 12 into 14 according to the manner reported by S. Sakai, et al^5.

Compound (7) showed the following properties; amorphous, $[\alpha]_D$+9.3°, $C_{26}H_{35}NO_5$ (M^+ 441.2532, calcd 441.2514). The ^{1}H-nmr spectrum of 7 showed four methyl groups of δ 0.81 (s, C4-CH_3), 1.01 (t, J = 7.0 Hz, N-$CH_2C\underline{H}_3$), 2.06 and 2.14 (each s, $OCOCH_3$), two methines at δ 4.59 (m, C12β -H) and 5.48 (s, C15α -H), and the ir spectrum showed absorptions at 1670 and 890 cm^{-1} and ^{1}H-nmr signals at δ 4.98 and 5.29 (each 1H, s, C=$C\underline{H}_2$) suggested the presence of an exomethylene moiety. The molecular formula together with these spectral data suggested that the compound was a C_{20}-diterpenoid type. The ms spectrum showed following fragment peaks at m/z 382 (M^+ -OAc) as a base peak, and m/z 385 (M^+-C_3H_4O). The loss of molecule of acrolein in the ms spectrum^4, ir absorption at 1115 cm^{-1}, and ^{1}H-nmr signals at δ 3.68 (1H, s, C19-H) and 4.02 (1H, d, J = 5.0 Hz, C1-H) suggested the presence of C(1)-C(19) inner ether^2 in this new base. These spectra of 7 were very similar to those of *dehydroluciduscul ine (1)^2 and the structure was assigned to be 12-acetyldehydro*luciduscul ine, which was confirmed by acetylation of 1 to give 7 in 85% yield.

The ^{13}C-nmr spectrum of a series of dehydroluciculine type alkaloids led to the confirmation of whole assignment in 1, 2, 7, and dehydroluciculine (20) obtained from 1 by hydrolysis (Table II). The acetoxy group at C(12) shifted the C(12) resonance downfield (1.2 ppm), the C(11) and C(13) resonances upfield (4.0 and 3.3 ppm, respectively), and the C(9) and C(14) resonances downfield (1.2 and 0.9 ppm, respectively) as the result of acylation effect. The acetoxy group at C(15) shifted the C(15) resonance downfield (0.3-0.5 ppm), the C(8) and C(16) resonances upfield (0.9-1.0 and 5.9-6.8 ppm, respectively) as the result of β effect, and C(9) and C(14) resonances downfield (1.2-1.6 and 0.4-0.9 ppm, respectively) as the result of γ effect. In the another γ position, C(7) resonance was slightly shifted upfield (0.4-0.6 ppm) due to the sterically compressed effect that the ester group was close to C(7).

Compound (8) was obtained as colorless crystal, mp 144-147°C, $[\alpha]_D$-19.2°, $C_{26}H_{37}NO_5$ (M^+ 443.2659, calcd 443.2671). The ^{1}H-nmr spectrum showed two acetoxy groups at δ 2.02 and 2.12 (each 3H, s) and two acetoxy methines at δ 4.60 (1H, m, C12β -H) and

Table I. Isolated Alkaloids from Crude Base.

Alkaloids	mp (°C)	Yield (mg)[a]	Yield (mg)[b]
Dehydroluciduseuline (1)	186-189	88	77
N-Deethyldehydroluciduseuline (2)	amorphous	12	--
Kobusine (3)	262-263	201	74
Pseudokobusine (4)	273-274(decomp)	396	--
Delcosine (5)	205-207	843	902
14-Acetyldelcosine (6)	192-193	1422	2094
12-Acetyldehydroluciduseuline (7)	amorphous	--	5
12-Acetylluciduseuline (8)	144-147	--	4
15-Benzoylpseudokobusine (9)	amorphous	3	--
15-Veratroylpseudokobusine (10)	amorphous	5	--
Yesoxine (11)	184(decomp)	33	16
Luciduseuline (12)	175-177	877	723
Luciculine (13)	112-116	15	--
1-Acetylluciculine (14)	amorphous	29	--
14-Acetylbrowniine (15)	119-122	--	22
Browniine (16)	216-218(perchlorate)	72	--
Virescenine (17)	amorphous	55	--
Isotalatizidine (18)	amorphous	15	--
Karakoline (19)	180-184	11	--

In a and b column, alkaloids were obtained from their crude bases by isolation procedure-1 and 2, respectively.

Table II. ^{13}C-Chemical Shifts and Assignments for 12-Acetyldehydroluciduseuline (7), Dehydroluciduseuline (1), N-Deethyldehydroluciduseuline (2), and Dehydroluciculine (20).

Carbon	7	1	2	20	Carbon	7	1	2	20
1	67.6	67.6	67.8	67.7	14	28.6	28.1	28.1	27.7
2	29.8	29.7	29.6	29.8	15	77.9	77.7	77.7	77.4
3	24.5	24.5	23.7	24.4	16	150.7	151.7	151.6	157.5
4	37.8	37.7	37.8	37.7	17	111.8	110.4	110.5	109.3
5	45.9	45.8	45.6	45.8	18	19.0	18.9	19.0	18.9
6	23.9	23.8	23.5	23.9	19	92.8	92.8	87.8	93.0
7	48.3	48.3	48.1	48.7	20	65.6	65.6	57.5	65.9
8	49.3	49.4	49.4	50.3	N-CH_2	48.3	48.3	----	48.3
9	33.6	33.7	34.0	32.4	CH_3	14.2	14.1	----	14.2
10	51.8	51.7	50.6	51.8	O=C	170.4	170.7	170.6	----
11	26.3	30.2	30.2	30.3		170.8	----	----	----
12	77.4	76.1	76.1	76.2	CH_3	21.3	21.5	21.5	----
13	43.3	46.8	46.6	46.6		21.5	----	----	----

Previous assignments[2] of C(5), C(7), C(11), C(13), and C(14) in 1 and 2 were revised.

5.51 (1H, s, C15-H). The other nmr signals and ir absorptions were very similar to those of lucidusculine (12). The ms spectrum, furthermore, suggested the presence of two acetoxy groups by indicating fragment peaks, m/z 384 (M^+-OAc) and 324 (384-AcOH). On the basis of those spectral data, compound 8 was assigned to be 12-acetyllucidusculine. The acetylation of 12 gave 12-acetyllucidusculine (8) and triacetylluciculine (21) in 10% and 46% yield, respectively. The melting point, ir absorptions and nmr signals of the former one (8) were identical with those of the natural compound, and the structure was established.

Compound (9) showed the following properties; amorphous, $[\alpha]_D$-6.9°, $C_{27}H_{31}NO_4$ (M^+ 433.2244, calcd 433.2252). The nmr signals at δ 7.34-7.63 (3H, m) and 7.91-8.03 (2H, m) and ir absorptions at 1715 and 1265 cm^{-1}, and uv absorption at 229 nm (log ε = 3.87) suggested the presence of benzoyloxy group. Remaining carbon number of the molecule led the compound to C_{20}-diterpenoid alkaloid with an exomethylene group. The nmr spectrum of 9 was very similar to that of pseudokobusine (4) except for the ester group, which was assigned to be at C-15 on the basis of the ^1H-nmr spectral data that a signal at δ 3.85 (s) in 4 was shifted at δ 5.82 (s) in 9. The structure was also comfirmed by the transformation of 4 into 15-benzoyl-derivative. Benzoylation of 4 gave 6-benzoate (22), 11-benzoate (23), 15-benzoate (9), 6,11-dibenzoate (24), and 6,15-dibenzoate (25), in 21%, 3%, 1%, 49%, and 19% yield, respectively. It was found that this benzoylation was advantage for C-6 hydroxyl group and was not good to give 15-benzoate. Therefore, 15-benzoate was derived through the following way. Pseudokobusine (4) was treated with p-nitrobenzoyl chloride to give 6-(p-nitrobenzoyl)-derivative (26) as a major product (40% yield). Benzoylation of 26 gave 11-benzoate (27, 33%), 15-benzoate (28, 30%), and 11,15-dibenzoate (29, 22%). Hydrolysis of 28 with a mixture of 28% ammonia water, methanol, and chloroform (2:2.6:1, in volume ratio) gave 15-benzoylpseudokobusine (9) in 48% yield. The compound (9) derived from 4 was identical with the natural product in terms of nmr and ir spectra and Rf value on tlc.

Compound (10) showed the following properties; amorphous, $[\alpha]_D$-6.7°, $C_{29}H_{35}NO_6$ (M^+ 493.2464, calcd 493.2463). The nmr spectrum of 10 showed two methoxy groups at δ 3.92 and 3.94 ppm and typical 1,2,4-trisubstituted benzene pattern at δ 6.82 (d, J = 8.3 Hz), 7.53 (d, J = 2.0 Hz), and 7.62 ppm (dd, J = 8.3, 2.0 Hz). The nmr signals suggested the presence of veratroyl group. Ir absorptions at 1710 and 1270 cm^{-1} and a ms fragment peak at m/z 312 (M^+-181, loss of veratroyloxy) also suggested the presence of veratroyloxy as an ester group. The remaining carbon number of the molecule led 10 to a C_{20}-diterpenoid type. The nmr spectrum of 10 except for the ester group was very similar to that of 9. On the basis of the spectral data, structure of 10 was determined as 15-veratroylpseudokobusine.

Compound (11) showed the following properties; mp 184°C (decomp), $[\alpha]_D$-37.5°, $C_{25}H_{35}NO_6$ (M^+ 445.2444, calcd 445.2463). The nmr spectrum of 11 showed four methyl groups at δ 0.71 (s, angular methyl), 2.06 (6H, s, two overlapping acetoxy), and 2.30 (s, N-methyl), and three oxygenated methines at δ 4.21(s), 4.85 (dd, J = 8.3, 4.3 Hz), and 5.05 (dd, J = 10.9, 6.3 Hz). This compound seemed to be a C_{20}-diterpenoid type in view of the carbon number without ester groups of the molecule. But the ir, ^1H and ^{13}C-nmr spectra did not suggested the presence of the characteristic exomethylene moiety. Five oxygen atoms in the molecule were located to be at two acetoxy and one hydroxy groups. A remaining oxgen atom was deduced to be located at an epoxy group in place of the exomethylene group. The ^{13}C-nmr spectrum also suggested the presence of the epoxy group of which carbon signals exhibited at 64.0 (s) and 45.5 (t) ppm. We could not determine the configuration of the epoxy group and also could not confirm exactly the type of skeleton in C_{20}-diterpenoid alkaloid on the basis of the spectral data. We, therefore, turned to a single crystal X-ray analysis, which finaly confirmed the structure illustrated as 11.

X-ray crystal structure determination of yesoxine (11)

Single crystals were obtained by recrystallization from AcOEt-Hexane. A colorless crystal, 0.5 x 0.4 x 0.2 mm, was used for the X-ray study. The crystal belongs to a monoclinic system, space group $P2_1$, with a unit cell dimensions a = 18.544(4), b = 8.763(3), c = 14.469(5)Å, β = 96.99(2)°, U = 2334(1)$Å^3$, Z = 4, D_x = 1.268(1)Mg·m^{-3}, T = 293°K, μ = 0.084 mm^{-1}, F(000) = 960, Mr = 445.5. X-ray diffraction data were collected on a Rigaku automated four-circle diffractometer with graphite-monochromatized MoKα (λ = 0.71073Å) radiation. Within the range of $2\theta \leqq 55°$, 4420 reflections with $F>3\sigma$ (F) were obtained. 4141 unique reflections were used for the structure determination and refinement. The intensities were corrected for Lorenz-polarization effects and for deterioration, but no absorption correction was applied.

The structure was solved by the direct phasing method using MULTAN 78[7] and the Monte Carlo method[8]. Among 70 H atoms, 68 were located from difference fourier synthesis. 2 atoms were calculated from standard bond lengths and angles. The structure was refined by the block-diagonal least-squares method. Unit weight was given to all reflections, and anisotropic temperature factors were used for all non-hydrogen atoms. The final R and Rw values were 5.3 and 4.8%, respectively. In the final refinement the maximum ratio of parameter shift to error was 0.58 for H(23)I atom of molecule A. The final difference Fourier map showed no peaks higher than 0.24 eA^{-3}. Atomic scattering factors and anomalous scattering corrections were taken from International Tables for X-ray Crystallography[9]. Crystallographic calculations performed on a FACOM M-780 computer of the Institute using UNICS-III program system[10].

The drawing of the molecules is shown in Fig.I[11]. The final positional parameters of the non-hydrogen atoms are given in Table III. There are two crystallographically independent molecules in the unit cell. Both of them have essentially the same structure. The two molecules from a dimer by two hydrogen bonds between the hydroxyl group and epoxide. The hydrogen bond distances, O(5) of molecule A and O(6)' of molecule B, O(6) of molecule A and O(5)' of molecule B, are 2.793(5) and 2.834(5)Å, respectively. The list of the bond lengths and angles are given in Table IV and V. All the observed bond lengths and angles are normal. The torsion angles within the six-membered ring and the five-membered ring are given Table VI.

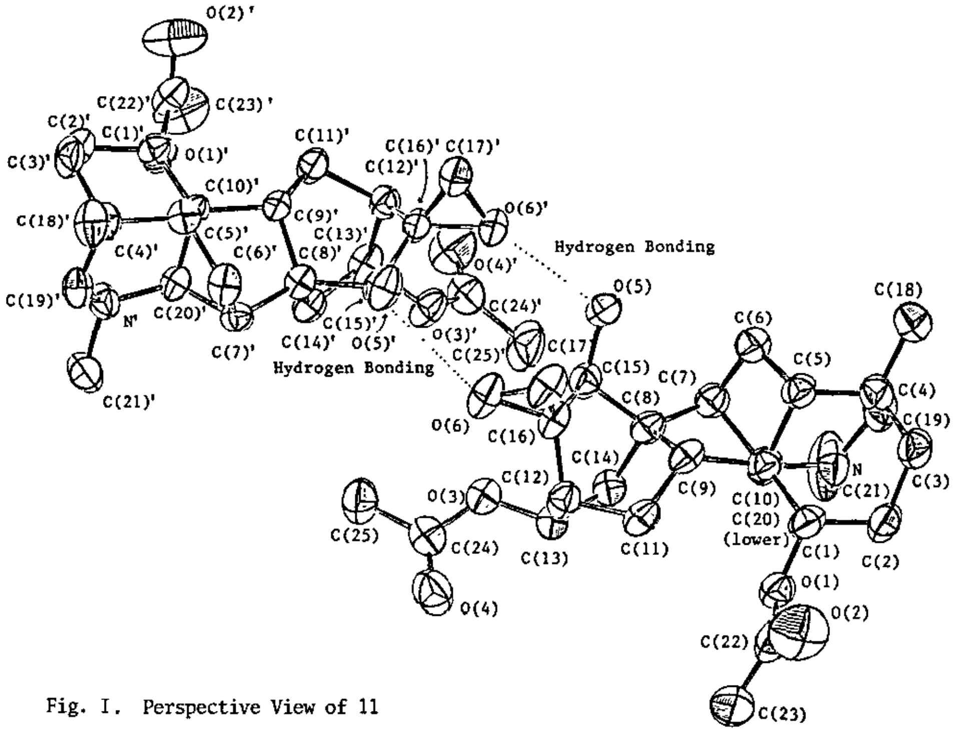

Fig. I. Perspective View of 11

Table III. Atomic Parameters.

Positional parameters are multiplied by 10^4 with estimated standard deviations in parentheses. The numbering scheme of atoms is shown in Fig. 1. The equivalent isotropic temperature factor is defined by $B_{eq} = 4/3 \cdot \Sigma_i \Sigma_j \beta_{ij} (\alpha_i \cdot \alpha_j)$.

Molecule A

	x	y	z	$B_{eq}(\mathring{A}^2)$
O(1)	-367(2)	-66(4)	3170(2)	4.1
O(2)	-1530(2)	254(7)	2603(4)	8.6
O(3)	1787(2)	-2851(4)	808(2)	4.2
O(4)	1032(2)	-4746(5)	312(3)	5.7
O(5)	1972(2)	2097(4)	670(2)	4.4
O(6)	1301(2)	-350(5)	-679(2)	5.0
N	1274(3)	1804(5)	4355(3)	4.9
C(1)	-218(2)	1540(6)	3022(3)	4.0
C(2)	-330(3)	2411(7)	3900(4)	4.9
C(3)	-73(3)	4042(7)	3839(4)	5.2
C(4)	717(3)	4176(6)	3630(3)	4.6
C(5)	800(3)	3360(6)	2705(3)	3.8
C(6)	1608(3)	3175(6)	2527(3)	4.0
C(7)	1785(2)	1468(6)	2753(3)	3.6
C(8)	1497(2)	487(6)	1909(3)	3.3
C(9)	673(2)	931(6)	1805(3)	3.4
C(10)	557(2)	1656(6)	2760(3)	3.5
C(11)	233(2)	-428(7)	1383(3)	3.9
C(12)	706(2)	-1237(6)	715(3)	3.8
C(13)	1227(2)	-2229(6)	1339(3)	3.8
C(14)	1599(2)	-1247(6)	2130(3)	3.7
C(15)	1765(2)	611(6)	929(3)	3.6
C(16)	1139(2)	-23(6)	264(3)	3.8
C(17)	794(3)	857(8)	-521(3)	5.0
C(18)	910(3)	5874(7)	3572(4)	5.7
C(19)	1259(3)	3460(7)	4396(3)	5.6
C(20)	1208(3)	1088(6)	3437(3)	3.7
C(21)	1895(4)	1201(10)	4966(4)	7.8
C(22)	-1045(3)	-557(8)	2885(4)	5.3
C(23)	-1093(3)	-2255(8)	2973(5)	6.8
C(24)	1595(3)	-4102(6)	294(3)	4.3
C(25)	2187(3)	-4532(8)	-275(4)	5.7

Molecule B

	x	y	z	$B_{eq}(\mathring{A}^2)$
O(1)'	5412(2)	-1919(4)	-2887(2)	3.6
O(2)'	6105(2)	100(6)	-3104(3)	7.6
O(3)'	3947(2)	-1245(5)	510(2)	4.3
O(4)'	4985(2)	-579(6)	1339(2)	7.0
O(5)'	2345(2)	20(5)	-1938(2)	4.4
O(6)'	3182(2)	1741(5)	-288(2)	4.7
N'	3912(2)	-4411(5)	-3691(2)	3.6
C(1)'	4843(2)	-1403(6)	-3615(3)	3.2
C(2)'	4928(3)	-2265(7)	-4505(3)	4.4
C(3)'	4273(3)	-2004(6)	-5223(3)	4.3
C(4)'	3546(3)	-2395(6)	-4879(3)	3.9
C(5)'	3458(2)	-1404(6)	-4017(3)	3.4
C(6)'	2813(2)	-1921(6)	-3483(3)	3.6
C(7)'	3177(2)	-2768(5)	-2612(3)	3.1
C(8)'	3471(2)	-1607(5)	-1855(3)	3.0
C(9)'	3963(2)	-607(5)	-2419(3)	2.8

Table III continued.

C(10)'	4117(2)	-1666(5)	-3252(2)	2.8
C(11)'	4561(2)	125(6)	-1738(3)	3.6
C(12)'	4256(2)	340(6)	-791(3)	3.5
C(13)'	4306(2)	-1228(7)	-336(3)	3.7
C(14)'	3936(2)	-2382(6)	-1013(3)	3.4
C(15)'	2967(2)	-522(6)	-1368(3)	3.3
C(16)'	3460(2)	788(6)	-990(3)	3.6
C(17)'	3268(3)	2393(7)	-1199(4)	4.8
C(18)'	2936(3)	-2097(7)	-5674(3)	4.9
C(19)'	3503(3)	-4074(6)	-4599(3)	3.8
C(20)'	3918(2)	-3285(5)	-2948(3)	2.9
C(21)'	3755(3)	-5946(6)	-3386(3)	4.8
C(22)'	6000(2)	-1046(7)	-2700(3)	4.4
C(23)'	6497(3)	-1638(9)	-1899(4)	6.5
C(24)'	4359(3)	-899(6)	1300(3)	4.4
C(25)'	3931(4)	-1014(9)	2121(3)	6.4

Table IV. Intramolecular bond distances (Å) with e.s.d.'s in parentheses.

	A	B		A	B
O(1) -C(1)	1.455(6)	1.469(5)	C(5) -C(6)	1.560(7)	1.567(6)
O(1) -C(22)	1.346(6)	1.333(6)	C(5) -C(10)	1.565(7)	1.561(5)
O(2) -C(22)	1.180(7)	1.190(8)	C(6) -C(7)	1.558(7)	1.545(6)
O(3) -C(13)	1.470(6)	1.463(5)	C(7) -C(8)	1.535(6)	1.545(6)
O(3) -C(24)	1.348(6)	1.330(5)	C(7) -C(20)	1.578(7)	1.577(6)
O(4) -C(24)	1.190(6)	1.189(7)	C(8) -C(9)	1.567(6)	1.564(6)
O(5) -C(15)	1.420(6)	1.417(5)	C(8) -C(14)	1.559(7)	1.559(6)
O(6) -C(16)	1.461(5)	1.456(6)	C(8) -C(15)	1.563(6)	1.560(6)
O(6) -C(17)	1.452(7)	1.464(6)	C(9) -C(10)	1.559(6)	1.569(6)
N -C(19)	1.453(8)	1.466(5)	C(9) -C(11)	1.528(7)	1.532(6)
N -C(20)	1.461(6)	1.459(6)	C(10)-C(20)	1.541(6)	1.551(7)
N -C(21)	1.462(8)	1.456(7)	C(11)-C(12)	1.554(7)	1.557(6)
C(1) -C(2)	1.518(7)	1.517(7)	C(12)-C(13)	1.514(7)	1.522(7)
C(1) -C(10)	1.535(7)	1.521(6)	C(12)-C(16)	1.526(7)	1.521(6)
C(2) -C(3)	1.513(8)	1.516(6)	C(13)-C(14)	1.528(6)	1.513(7)
C(3) -C(4)	1.537(8)	1.532(7)	C(15)-C(16)	1.520(6)	1.526(7)
C(4) -C(5)	1.541(7)	1.545(6)	C(16)-C(17)	1.456(7)	1.473(8)
C(4) -C(18)	1.535(8)	1.534(6)	C(22)-C(23)	1.497(10)	1.484(7)
C(4) -C(19)	1.537(7)	1.530(8)	C(24)-C(25)	1.498(8)	1.510(8)

Table V. Intramolecular bond angles(°) with e.s.d.'s in parentheses.

	A	B		A	B
C(1) -O(1) -C(22)	116.8(4)	117.9(4)	C(5) -C(6) -C(7)	104.4(4)	104.9(3)
C(13)-O(3) -C(24)	115.7(4)	116.4(4)	C(6) -C(7) -C(8)	109.1(4)	110.1(4)
C(16)-O(6) -C(17)	60.0(3)	60.6(3)	C(6) -C(7) -C(20)	101.1(4)	101.4(3)
C(19)-N -C(20)	117.7(4)	118.7(4)	C(8) -C(7) -C(20)	100.6(4)	99.3(3)
C(19)-N -C(21)	110.7(5)	110.9(4)	C(7) -C(8) -C(9)	100.2(4)	100.2(3)
C(20)-N -C(21)	111.5(5)	112.7(4)	C(7) -C(8) -C(14)	111.2(4)	112.4(4)
O(1) -C(1) -C(2)	108.4(4)	108.4(4)	C(7) -C(8) -C(15)	124.4(4)	122.8(3)
O(1) -C(1) -C(10)	107.5(4)	107.2(3)	C(9) -C(8) -C(14)	110.7(4)	110.5(3)
C(2) -C(1) -C(10)	113.6(4)	114.1(4)	C(9) -C(8) -C(15)	108.0(3)	108.2(4)
C(1) -C(2) -C(3)	110.5(5)	110.5(4)	C(14)-C(8) -C(15)	102.2(4)	102.5(3)
C(2) -C(3) -C(4)	113.5(5)	114.1(4)	C(8) -C(9) -C(10)	104.7(3)	104.2(3)
C(3) -C(4) -C(5)	109.5(4)	108.6(4)	C(8) -C(9) -C(11)	108.1(4)	108.8(3)
C(3) -C(4) -C(18)	108.5(5)	108.5(4)	C(10)-C(9) -C(11)	123.2(4)	123.6(3)
C(3) -C(4) -C(19)	112.5(4)	112.2(4)	C(1) -C(10)-C(5)	111.1(4)	112.6(3)
C(5) -C(4) -C(18)	110.8(4)	111.7(4)	C(1) -C(10)-C(9)	115.2(4)	115.6(3)
C(5) -C(4) -C(19)	108.2(4)	108.2(4)	C(1) -C(10)-C(20)	120.5(4)	118.9(4)
C(18)-C(4) -C(19)	107.4(4)	107.7(4)	C(5) -C(10)-C(9)	105.8(4)	105.2(3)
C(4) -C(5) -C(6)	113.0(4)	113.4(4)	C(5) -C(10)-C(20)	97.6(4)	98.0(3)
C(4) -C(5) -C(10)	109.8(4)	110.1(4)	C(9) -C(10)-C(20)	104.5(4)	104.5(3)
C(6) -C(5) -C(10)	101.3(4)	100.8(3)	C(9) -C(11)-C(12)	106.9(4)	107.2(3)

Table V continued.

C(11)-C(12)-C(13)	105.0(4)	105.2(4)	C(12)-C(16)-C(17)	119.9(4)	119.3(4)
C(11)-C(12)-C(16)	108.3(4)	108.3(3)	C(15)-C(16)-C(17)	122.0(5)	121.7(4)
C(13)-C(12)-C(16)	108.9(4)	108.8(4)	O(6) -C(17)-C(16)	60.3(3)	59.5(3)
O(3) -C(13)-C(12)	110.0(4)	111.2(4)	N -C(19)-C(4)	113.1(4)	113.2(4)
O(3) -C(13)-C(14)	108.6(4)	108.6(4)	N -C(20)-C(7)	119.5(4)	119.5(3)
C(12)-C(13)-C(14)	108.7(4)	108.9(3)	N -C(20)-C(10)	114.3(4)	113.2(3)
C(8) -C(14)-C(13)	111.3(4)	112.3(4)	C(7) -C(20)-C(10)	94.1(3)	94.0(3)
O(5) -C(15)-C(8)	115.4(4)	115.6(3)	O(1) -C(22)-O(2)	124.0(6)	124.3(4)
O(5) -C(15)-C(16)	112.3(4)	111.5(4)	O(1) -C(22)-C(23)	110.8(5)	111.9(5)
C(8) -C(15)-C(16)	104.2(4)	104.8(3)	O(2) -C(22)-C(23)	125.3(5)	123.8(5)
O(6) -C(16)-C(12)	116.1(4)	115.7(3)	O(3) -C(24)-O(4)	123.2(5)	123.4(4)
O(6) -C(16)-C(15)	115.8(4)	115.8(4)	O(3) -C(24)-C(25)	110.2(4)	111.0(5)
O(6) -C(16)-C(17)	59.7(3)	60.0(3)	O(4) -C(24)-C(25)	126.6(5)	125.6(4)
C(12)-C(16)-C(15)	112.7(4)	113.5(4)			

Table VI. Torsion angle(°) with e.s.d.'s in parentheses.

	A	B
C(1) -C(2) -C(3) -C(4)	-54.6(6)	-54.8(5)
C(2) -C(3) -C(4) -C(5)	58.2(6)	59.1(5)
C(3) -C(4) -C(5) -C(10)	-57.0(5)	-56.4(5)
C(4) -C(5) -C(10)-C(1)	55.3(5)	53.7(5)
C(2) -C(1) -C(10)-C(5)	-53.2(5)	-50.6(5)
C(10)-C(1) -C(2) -C(3)	52.0(6)	49.7(5)
C(4) -C(5) -C(10)-C(20)	-71.6(4)	-72.2(4)
C(5) -C(10)-C(20)-N	63.0(5)	62.8(4)
C(19)-N -C(20)-C(10)	-51.3(6)	-50.3(5)
C(20)-N -C(19)-C(4)	38.4(6)	37.4(5)
C(5) -C(4) -C(19)-N	-44.4(6)	-42.9(5)
C(19)-C(4) -C(5) -C(10)	65.9(5)	65.6(5)
C(5) -C(6) -C(7) -C(8)	81.2(4)	80.2(4)
C(6) -C(7) -C(8) -C(9)	-57.8(4)	-54.9(4)
C(7) -C(8) -C(9) -C(10)	-17.8(4)	-20.8(4)
C(8) -C(9) -C(10)-C(5)	83.2(4)	85.7(4)
C(6) -C(5) -C(10)-C(9)	-59.4(4)	-59.6(4)
C(10)-C(5) -C(6) -C(7)	-14.0(4)	-14.0(4)
C(8) -C(9) -C(11)-C(12)	-33.1(5)	-29.3(4)
C(9) -C(11)-C(12)-C(13)	81.5(4)	78.8(4)
C(11)-C(12)-C(13)-C(14)	-51.5(5)	-52.9(5)
C(12)-C(13)-C(14)-C(8)	-15.6(5)	-13.0(5)
C(9) -C(8) -C(14)-C(13)	62.2(5)	61.3(5)
C(14)-C(8) -C(9) -C(11)	-33.3(5)	-35.7(4)
C(8) -C(9) -C(11)-C(12)	-33.1(5)	-29.3(4)
C(9) -C(11)-C(12)-C(16)	-34.7(5)	-37.3(5)
C(11)-C(12)-C(16)-C(15)	74.3(5)	72.2(5)
C(8) -C(15)-C(16)-C(12)	-30.1(5)	-26.4(5)
C(9) -C(8) -C(15)-C(16)	-39.9(4)	-42.6(4)
C(15)-C(8) -C(9) -C(11)	77.8(4)	75.9(4)
C(8) -C(15)-C(16)-C(12)	-30.1(5)	-26.4(5)
C(13)-C(12)-C(16)-C(15)	-39.3(5)	-41.6(5)
C(16)-C(12)-C(13)-C(14)	64.3(5)	62.9(5)
C(12)-C(13)-C(14)-C(8)	-15.6(5)	-13.0(5)
C(15)-C(8) -C(14)-C(13)	-52.6(5)	-53.9(4)
C(14)-C(8) -C(15)-C(16)	76.9(4)	74.2(4)
C(7) -C(8) -C(9) -C(10)	-17.8(4)	-20.8(4)
C(8) -C(9) -C(10)-C(20)	-19.2(4)	-16.9(4)
C(9) -C(10)-C(20)-C(7)	46.5(4)	46.2(4)
C(8) -C(7) -C(20)-C(10)	-58.8(4)	-60.0(3)
C(20)-C(7) -C(8) -C(9)	48.0(4)	50.9(4)
C(5) -C(6) -C(7) -C(20)	-24.2(4)	-24.2(4)
C(6) -C(7) -C(20)-C(10)	53.2(4)	52.8(4)
C(5) -C(10)-C(20)-C(7)	-62.0(4)	-61.8(3)

Table VI continued.

C(6) -C(5) -C(10)-C(20)	48.1(4)	47.8(4)
C(10)-C(5) -C(6) -C(7)	-14.0(4)	-14.0(4)

EXPERIMENTAL

All melting points are uncorrected. Ir spectra in KBr disks were taken with a JASCO IRA-2 spectrometer, and uv spectra were measured in EtOH solution with a Shimazu D-300 spectrometer. Nmr spectra were measured in $CDCl_3$ solution with JEOL FX-100 and JEOL GX-270 spectrometers using TMS as an internal standard. Ms spectra were measured with a Shimazu LKB-9000B spectrometer, and HR-ms spectra were measured with JMS-D300 mass spectrometer. HPLC was performed with Shimazu LC-3A apparatus.

Isolation Procedure -- 1) The rhizoma of the title plant were collected at Jozankei, Sapporo city, in august 1984. Dried ground rhizoma (1.5 kg) were extracted with EtOH (14 l) at room temperature and the solution was evaporated in vaccuo to give the extract, which was partitioned between 5% HCl (500 ml) and hexane (250 ml x 3). The water layer was made alkaline (PH 10) with 28% ammonia water and extracted with $CHCl_3$ (300 ml x 7) followed by evaporation to give the crude alkaloid-1. The hexane layer was evaporated to give hexane extract, which was partitioned again between 5% HCl (100 ml) and hexane (90 ml x 2). The water layer was made alkaline (PH 10) with 28% ammonia water and extracted with $CHCl_3$ (100 ml x 7) followed by evaporation to give the crude alkaloid-2. Combined crude alkaloid-1 and 2 (9.4 g) was chromatographed repeatedly on silica gel. A mixture of hexane and ether saturated with 28% ammonia water and another mixture of hexane and chloroform saturated 28% ammonia water were used as eluting solvent systems; the content of ether and chloroform were gradually increased monitoring each fraction with tlc. Purification of compound (9) and (10) was performed by HPLC. The condition was follows; retention time (min); 17.9 (10) and 21.3 (9), column; nucleosil 10-C_{18} (8 x 300 mm), mobile phase; CH_3CN:H_2O:MeOH:AcOH:28% ammonia water (12:30:3:2:1 in volume ratio), flow rate; 3.0 ml/min, detector; uv(254 nm). Seventeen alkaloids were isolated and listed in Table I. 2) The rhizoma of the title plant were collected at the same area in august 1985 and 1986. Dried ground rhizoma (2.1 kg) were treated by the same procedure as above to give a combined crude alkaloid (13.9 g). The crude alkaloid was separated as the same manner as above. Purified comounds were listed in Table I and unidentified compound are remained to investigate.

12-Acetyldehydroluciduscouline (7) -- amorphous, $[\alpha]_D$+9.3° (c = 0.43, EtOH). HR-ms

: Calcd for $C_{26}H_{35}NO_5$ 441.2514, Found 441.2532. ms (m/z): 441 (M^+), 385 (M^+-C_3H_4O), 382 (M^+-OAc, base peak). ir ν (max): 1750, 1670, 1240, 1115, 890. ^{1}H-nmr (δ): 0.81 (3H, s), 1.01(3H, t, J = 7.0 Hz), 2.06 (3H, s), 2.14 (3H, s), 3.68 (1H, s), 4.2 (1H, d, J = 5.0 Hz), 4.59 (1H, m), 4.98 (1H, s), 5.29 (1H, s), 5.48 (1H, s).

12-Acetyllucidusculine (8) -- mp 144-147°C, $[\alpha]_D$-19.2°(c = 0.5, EtOH). HR-ms: Calcd for $C_{26}H_{37}NO_5$ 443.2671, Found 443.2659. ms (m/z): 443 (M^+, base peak), 384 (M^+-OAc), 324 (384-AcOH). ir ν (max): 3450, 1750, 1670, 1240, 895. ^{1}H-nmr (δ): 0.77 (3H, s), 1.08 (3H, t, J = 7.0 Hz), 2.02 (3H, s), 2.12 (3H, s), 3.89 (1H, t, J = 7.0 Hz), 4.60 (1H, m), 4.98 (1H, s), 5.25 (1H, s), 5.51 (1H, s).

15-Benzoylpseudokobusine (9) -- amorphous, $[\alpha]_D$-6.9°(c = 0.13, EtOH). HR-ms: Calcd for $C_{27}H_{31}NO_4$ 433.2252, Found 433.2244. ms (m/z): 433 (M^+, base peak), 312 (M^+-$C_6H_5CO_2$). ir ν ($CHCl_3$, max): 3550, 1715, 1580, 1265. uv(λ , nm): 229 (log ε = 3.87). ^{1}H-nmr (δ): 1.33 (3H, s), 4.07 (1H, d, J = 4.6 Hz), 5.27 (1H, s), 5.48 (1H, s), 5.82 (1H, s), 7.34-7.63 (3H, m), 7.91-8.03 (2H, m).

15-Veratroylpseudokobusine (10) -- amorphous, $[\alpha]_D$-6.7°(c = 0.18, EtOH). HR-ms: Calcd for $C_{29}H_{35}NO_6$ 493.2463, Found 493.2464. ms (m/z): 493 (M^+), 312 (M^+-veratroyloxy), 165 (base peak). uv(λ , nm): 260 (log ε = 3.91), 290 (log ε = 3.62). ir ν (max): 3550, 1710, 1605, 1270. ^{1}H-nmr (δ): 1.35 (3H, s), 3.92 (3H, s), 3.94 (3H, s), 4.06 (1H, d, J = 4.6 Hz), 5.27 (1H, s), 5.45 (1H, s), 5.86 (1H, s), 6.82 (1H, d, J = 8.3 Hz), 7.53 (1H, d, J = 2.0 Hz), 7.62 (1H, dd, J = 8.3, 2.0 Hz).

Yesoxine (11) -- mp 184°C(decomp), $[\alpha]_D$-37.5°(c = 0.32, EtOH). HR-ms: Calcd for $C_{25}H_{35}NO_6$ 445.2463, Found 445.2444. ms (m/z): 445 (M^+), 386 (M^+-OAc, base peak). ir ν (max) 3400, 1730, 1720, 1240, 910. ^{1}H-nmr (δ): 0.71 (3H, s), 2.06 (6H, s), 2.30 (3H, s), 2.42 (1H, d, J = 4.9 Hz), 3.10 (1H, d, J = 4.9 Hz), 4.21 (1H, s), 4.85 (1H, dd, J = 8.3, 4.3Hz), 5.05 (1H, dd, J = 10.9, 6.3 Hz). ^{13}C-nmr (ppm): 170.7 (s), 170.6 (s), 76.3 (d), 74.0 (d), 71.4 (d), 69.0 (d), 64.0 (s), 59.1 (t), 52.4 (d), 48.2 (s), 45.5 (t), 43.8 (d), 43.3 (s), 41.4 (d), 41.0 (q), 38.5 (d), 37.9 (t), 36.0 (t), 33.5 (s), 26.4 (t), 25.6 (q), 23.4 (t), 22.9 (t), 21.9 (q), 21.3 (q).

Acetylation of 1 -- A mixture of 1 (10 mg), pyridine (1 ml), and acetic anhydride (0.5 ml) was left for 3 h at room temperature. Usual work up and purification afforded 12-acetyldehydrolucidusculine (9.4 mg) in 85% yield. Rf value on tlc and ir and nmr spectra of the acetate were identical with those of the natural compound (7).

Dehydroluciculine (20) -- Dehydroluciduscul ine (1, 50 mg) was dissolved in 5% KOH/MeOH (5 ml) for 3.5 h at room temperature. Usual work up gave 20 quantitatively. mp 92-92.5°C. ms (m/z): 357 (M^+), 301 ($M^+-C_3H_4O$). ir ν (max): 3350, 1640, 1110, 890. ^{1}H-nmr (δ): 0.82, (3H, s), 1.02 (3H, t, J = 7.1 Hz), 3.64 (1H, t, J = 7.0 Hz), 3.69 (1H, s), 4.06 (1H, d, J = 4.4 Hz), 4.22 (1H, s), 5.17 (2H, bs). ^{13}C-nmr spectrum was shown in Table II.

Acetylation of 12 -- A mixture of 12 (300 mg), pyridine (3 ml), and acetic anhydride (3 ml) was left over night at room temperature. Usual work up and purification by column chromatography on silica gel afforded 12-acetyllucidusculine (8, 32 mg) and 1,12,15-triacetylluciculine (21, 167 mg) in 10 and 46% yield, respectively. Mp and ir and nmr spectra of 8 were identical with those of the natural product.

1,12,15-Triacetylluciculine (21) -- mp 152-156°C. ms (m/z): 485 (M^+), 426 (M^+-OAc, base peak). ir ν (max): 1720, 1650, 1230, 895. ^{1}H-nmr (δ): 0.73 (3H, s), 1.08 (3H, t, J = 7.0 Hz), 2.02 (3H, s), 2.06 (3H, s), 2.12 (3H, s), 4.48 (1H, m), 5.00 (1H, s), 5.03 (1H, dd, J = 11.0, 7.0 Hz), 5.27 (1H, s), 5.49 (1H, s).

Benzoylation of 4 -- A mixture of 4 (300 mg), pyridine (8 ml), and benzoyl chloride (0.16 ml) was refluxed for 5 h. After cooling, usual work up and purification by column chromatography on silica gel afforded 6-benzoate (22, 82 mg), 11-benzoate (23, 10 mg), 15-benzoate (9, 4 mg), 6,11-dibenzoate (24, 239 mg), and 6,15-dibenzoate (25, 93 mg) in 21, 3, 1, 49, and 19% yield, respectively. Rf value on tlc and ir and nmr spectra of the 15-benzoate (9) were identical with those of the natural product.

6-Benzoylpseudokobusine (22) -- mp 238-239°C. HR-ms: Calcd for $C_{27}H_{31}NO_4$ 433.2252, Found 433.2254. ms (m/z): 433 (M^+), 328 ($M^+-C_6H_5CO$, base peak), 105. ir ν (max): 3400, 1715, 1600, 1285. ^{1}H-nmr (δ): 0.99 (3H, s), 3.96 (1H, s), 4.06 (1H, d, J = 4.6 Hz), 5.12 (1H, s), 5.22 (1H, s), 7.31-7.63 (3H, m), 7.94-8.12 (2H, m).

11-Benzoylpseudokobusine (23) -- amorphous. HR-ms: Calcd for $C_{27}H_{31}NO_4$ 433.2252, Found 433.2234. ms (m/z): 433 (M^+, base pek), 328 ($M^+-C_6H_5CO$), 105. ir ν (max): 3350, 1705, 1595, 1270. ^{1}H-nmr (δ): 1.38 (3H, s), 4.02 (1H, s), 5.37 (1H, d, J = 4.6 Hz), 5.15 (1H, s), 5.32 (1H, s), 7.31-7.61 (3H, m), 7.87-8.01 (2H, m).

6,11-Dibenzoylpseudokobusine (24) -- mp 211-213°C. HR-ms: Calcd for $C_{34}H_{35}NO_5$ 537.2514, Found 537.2510. ms (m/z): 537 (M^+), 432 ($M^+-C_6H_5CO$), 105 (base peak). ir ν (max): 3400, 1715, 1705, 1595, 1280, 1270. ^{1}H-nmr (δ): 1.00 (3H, s), 4.04 (1H, d, J = 8.5 Hz, changed into s after addition of D_2O), 5.40 (1H, d, J = 4.6 Hz), 5.11 (1H, s), 5.29 (1H, s), 7.32-7.59 (6H, m), 7.89-8.10 (4H, m).

6,15-Dibenzoylpseudokobusine (25) -- mp 249-251°C. HR-ms: Calcd for $C_{34}H_{35}NO_5$ 537.2514, Found 537.2497. ms (m/z): 537 (M^+), 432 (M^+-C_6H_5CO), 105 (base peak). ir ν (max): 3375, 1715, 1705, 1595, 1285, 1260. ^{1}H-nmr (δ): 0.99 (3H, s), 4.07 (1H, d, J = 4.6 Hz), 5.26 (1H, s), 5.45 (1H, s), 5.75 (1H, s), 7.29-7.66 (6H, m), 7.90-8.12 (4H, m).

6-p-Nitrobenzoylpseudokobusine (26) -- A mixture of 4 (100 mg), pyridine (2 ml), and p-nitrobenzoylchloride (170 mg) was stirred for 5 min at room temperature. Usual work up and purification by column chromatography on silica gel afforded 26 (58 mg) in 40% yield. mp 216-217°C. HR-ms: Calcd for $C_{27}H_{30}N_2O_6$ 478.2103, Found 478.2127. ms (m/z): 478 (M^+), 328(M^+-$COC_6H_4NO_2$, base peak). ir ν (max): 3400, 1720, 1600, 1520, 1340, 1270. ^{1}H-nmr (δ): 0.98 (3H, s), 3.97 (1H, s), 4.09 (1H, d, J = 5.0 Hz), 5.15 (1H, s), 5.25 (1H, s), 8.21 (2H, d, J = 8.9 Hz), 8.29 (2H, d, J = 8.9 Hz).

Benzoylation of 26 -- A mixture of 26 (22 mg), pyridine (0.6 ml), and benzoyl chloride (16 μl) was stirred for 40 min at room temperature. Usual work up and purification by column chromatography on silica gel afforded 11-benzoate (27, 9 mg), 15-benzoate (28, 8 mg), 11,15-dibenzoate (29, 7 mg) in 33, 30, and 22% yield, respectively.

11-Benzoyl-6-(p-nitrobenzoyl)-pseudokobusine (27) -- mp 211-214°C. HR-ms: Calcd for $C_{34}H_{34}N_2O_7$ 582.2365, Found 582.2351. ms (m/z): 582 (M^+), 432 (M^+-$COC_6H_4NO_2$), 105 (base peak). ir ν (max): 3400, 1705, 1590, 1520, 1340, 1270. ^{1}H-nmr (δ): 0.98 (3H, s), 4.04 (1H, bs), 5.14 (1H, s), 5.31 (1H, s), 5.40 (1H, d, J = 4.9 Hz), 7.45 (2H, t, J = 7.0 Hz), 7.58 (1H, t, J = 7.0 Hz), 7.96 (2H, d, J = 7.0 Hz), 8.20 (2H, d, J = 8.9 Hz), 8.28 (2H, d, J = 8.9 Hz).

15-Benzoyl-6-(p-nitrobenzoyl)-pseudokobusine (28) -- mp 218-221°C. HR-ms: Calcd for $C_{34}H_{34}N_2O_7$ 582.2365, Found 582.2377. ms (m/z): 582 (M^+), 432 (M^+-$COC_6H_4NO_2$), 105 (base peak). ir ν (max): 3350, 1705, 1590, 1520, 1340, 1260. ^{1}H-nmr (δ): 0.96 (3H, s), 4.12 (1H, dd, J = 9.2, 4.0 Hz), 5.24 (1H, s), 5.45 (1H, s), 5.76 (1H, s), 7.47 (2H, t, J = 7.0 Hz), 7.60 (1H, t, J = 7.0 Hz), 8.03 (2H, d, J = 7.0 Hz), 8.13 (2H, d, J = 8.9 Hz), 8.24 (2H, d, J = 8.9 Hz).

11,15-Dibenzoyl-6-(p-nitrobenzoyl)-pseudokobusine (29) -- amorphous. HR-ms: Calcd for $C_{41}H_{38}N_2O_8$ 686.2627, Found 686.2651. ms (m/z): 686 (M^+), 536 (M^+-$COC_6H_4NO_2$), 105 (base peak). ir ν (max): 1705, 1590, 1520, 1340, 1275, 1260. ^{1}H-nmr (δ): 0.96 (3H, s), 5.16 (1H, s), 5.39 (1H, s), 5.48 (1H, d J = 4.9 Hz), 5.83 (1H, s), 7.18 (4H, m), 7.45 (2H, m), 7.95 (4H, m), 8.13 (1H, d, J = 8.9 Hz), 8.23 (2H, d, J = 8.9 Hz).

Hydrolysis of 28 -- Compound (*28*, *10.6 mg*) was *dissolved in a mixture of 28%* ammonia water, MeOH, and $CHCl_3$ (2, 2.6, and 1 ml, respectively) and stirred at 40°C for 2 d. After evaporation of the solution, the residue was purified by column chromatography on silica gel to afford 15-benzoylpseudokobusine (9, 3.8 mg) in 48% yield. Rf value on tlc and ir and nmr spectra of the product were identical with those of the natural product.

REFERENCES

1. Part IV: H. Bando, K. Wada, M. Watanabe, T. Mori, and T. Amiya, Chem. Pharm. Bull., 33, 4717 (1985).
2. K. Wada, H. Bando, and T. Amiya, Heterocycles, 23, 2473 (1985).
3. T. Okamoto, M. Natsume, Y. Iitaka, A. Yoshino, and T. Amiya, Chem. Pharm. Bull., 13, 1270 (1965).
4. S. W. Pelletier and N. V. Mody, "The Alkaloids", Vol. XVIII, ed. by R. H. F. Manske and R. G. Rodrigo, Academic Press, New York, 1981, p. 99.
5. H. Takayama, A. Tokita, M. Ito, S. Sakai, F. Kurosaki, and T. Okamoto, Yakugaku Zasshi, 102, 245 (1982).
6. S. W. Pelletier, N. V. Mody, B. S. Joshi, and L. C. Schramm, "Alkaloids: Chemical and Biological Perspectives", Vol. 2, ed. by S. W. Pelletier, Wiley-Interscience, New York, 1984, p, 205.
7. P. Main, S. E. Hull, L, Lessinger, G, Germain, J. -P. Declercq, and M. M. Woolfson, MULTAN. A Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univ. of York, England, and Louvain, Belgium, 1978.
8. A. Furusaki, Acta Cryst., A35, 220 (1978).
9. International Tables for X-ray Crystallography, Vol IV, Birmingham: Kynoch Press, 1974.
10. T. Sakurai and K. Kobayashi, Rikagaku Kenkyusho Hokoku, 55, 69 (1979).
11. C. K. Johnson, ORTEP. Report ORNL-3794. Oak Ridge Nation Laboratory, Tennessee.

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