Communications to the Editor

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STRUCTURE OF TWO NEW DITERPENE ALKALOIDS, 3-EPI-IGNAVINOL AND 2,3-DEHYDRODELCOSINE

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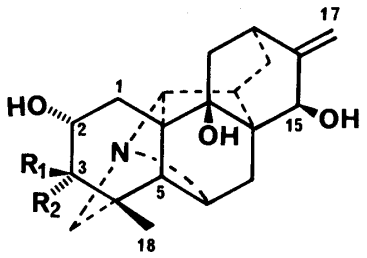
The structure of two new diterpene alkaloids, 3-epi-ignavinol (**1**) and 2,3-dehydrodelcosine (**3**), isolated from Aconitum japonicum var. montanum Nakai collected at Mt. Arafune, were elucidated.

KEYWORDS——Aconitum japonicum; diterpene alkaloid; 3-epi-ignavinol; 2,3-dehydrodelcosine; ^{13}C-NMR; X-ray analysis

No previous chemical or taxonomic studies have been reported on an Aconitum species native to Mt. Arafune (Gunma prefecture). Chemical investigation of the roots of this plants (Aconitum japonicum var. montanum Nakai, so-called Yamatori-kabuto) resulted in the isolation of two new diterpene alkaloids, along with the eight known bases, talatizamine, delcosine, neoline, isotalatizidine, hypaconitine, 14-O-acetyldelcosine, takaosamine and kobusine. Here we describe the structure of two new alkaloids.

The new alkaloid (**1**) was obtained as colorless prisms, mp 292-293.5°C(dec.), $[\alpha]_D^{23}$ +49.1°(c=0.11, MeOH), whose high resolution mass spectrum showed the M^+324.1935, corresponding to the formula $C_{20}H_{27}NO_4$. The mass spectral fission pattern of this alkaloid paralleled that for ignavinol (**2**).[1] The IR spectrum indicated the presence of hydroxy groups (3520, 3350, and 3280 cm^{-1}). The ^{1}H-NMR spectrum showed the characteristic signals in C_{20} type diterpene alkaloid due to C(18)-H_3(δ1.14, 3H, s.), C(17)-H_2 (δ4.99, 2H, d, J=1.7Hz), and C(15)-αH (δ3.98, 1H, t-like). From spin decoupling studies between δ4.08(1H, m, C(2)-H) and δ3.37(1H, d, J=4.6Hz, C(3)-H), the presence of vicinal secondary hydroxy groups was deduced. In the ^{13}C-NMR spectra (see Table I), the signals due to C(1) and C(5) of (**1**) appeared farther downfield (3.1ppm and 4.7ppm, respectively) than the corresponding signals of ignavinol (**2**). This indicates the presence of an α-equatorial hydroxy group on C(3) in (**1**) instead of a β-axial hydroxy group on C(3) as in ignavinol (**2**). The structure of (**1**) proposed by the spectroscopic analysis was confirmed by X-ray analysis. The crystal of (**1**) had the following features: monoclinic, $P2_1$, a=8.677(2)Å, b=11.627(2)Å, c=8.733(2)Å, z=2, Cell volume=864.0Å^3, Dc=1.40 gcm^{-3}. A total of 4198 unique independent intensities were measured within the range of $3° \leqq 2\theta \leqq 70°$, on a 4-circle diffractometer (Rigaku AFC-

5) using MoKα radiation. The structure was derived by the direct method using MULTAN and refined anisotropically (isotropically for H) by the least-squares method to an R value of 0.046, using the 3670 reflections for which $F(0) > 3\sigma(Fo)$. The ORTEP drawing of compound **1** is shown in Fig. 1.



1 R_1=H, R_2=OH : **3-epi-ignavinol**

2 R_1=OH, R_2=H : **ignavinol**

Table I. ^{13}C Chemical Shifts of **1** and **2**

Carbon	1[a]	2[b]
1	31.6	28.5
2	70.5	73.0
3	75.3	74.3
4	43.0	42.3
5	56.7	52.0
6	64.9	65.3
7	30.1	30.2
8	45.1	44.7
9	80.5	80.1
10	51.9	52.0
11	39.9	39.6
12	36.6	36.0
13	34.1	33.9
14	43.2	42.6
15	73.8	74.0
16	156.1	156.6
17	110.1	109.6
18	26.8	26.6
19	60.7	62.4
20	73.2	73.0

Chemical shifts in ppm downfield from TMS.
a) in CD_3OD, b) in pyridine-D_5.

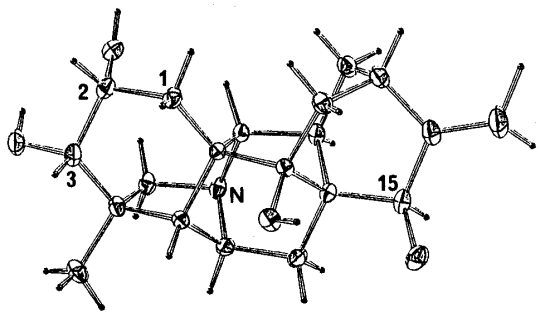
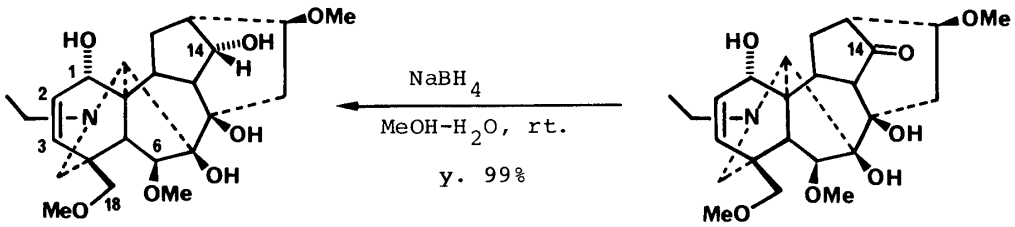


Fig. 1. ORTEP Drawing of 1

The new alkaloid (**3**) was isolated as an amorphous solid, $[\alpha]_D^{12}$ +86.2° (c 0.09, $CHCl_3$). The mass spectrum of **3** presents the molecular ion m/z 451.2533 ($C_{24}H_{37}NO_7$), which is 2 a.m.u. lower than the corresponding peak in the spectrum of delcosine (**4**). And cleavage pattern appears exactly similar to **4**. The presence of hydroxy groups was indicated by the IR absorption at 3520 and 3430 cm^{-1}. In the ^1H-NMR spectrum, in addition to the some readily assignable signals due to N-$CH_2\underline{CH}_3$ (δ1.06, 3H, t, J=7.3Hz), OMex3 (δ3.36, 3.37, 3.39, each 3H, s.), C(18)-H_2 (δ3.46 and 3.18, each 1H, d, J=9.0Hz), C(6)-H (δ3.95, 1H, s.), and C(14)-H (δ4.12, 1H, t, J=5Hz), two olefinic protons occur at δ5.86 (1H, d, J=9.4Hz) and δ5.90(1H, dd, J=9.4 and 3.3Hz). The latter is coupled to C(1)-βH (δ3.74, 1H, d, J=3.3Hz). From these spectroscopic data, we formulated the new alkaloid as 2,3-dehydrodelcosine. This was confirmed by a direct correlation with 2,3-dehydrodelcosine obtained by the $NaBH_4$ reduction of takaonine (**5**).[2] (Chart 1)



2,3-dehydrodelcosine 3 **takaonine 5**

Chart 1

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