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STRUCTURE OF DEOXYJESACONITINE. A NEW DITERPENE ALKALOID FROM ACONITUM SUBCUNEATUM NAKAI

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Abstract —— A new diterpene alkaloid, deoxyjesaconitine, was isolated from *Aconitum subcuneatum* and its structure was determined on the basis of spectral data. This compound along with deoxyaconitine and hypaconitine was purified with high performance liquid chromatography, and ^{13}C-NMR spectra of those compounds were measured to afford the relationship with each compound.

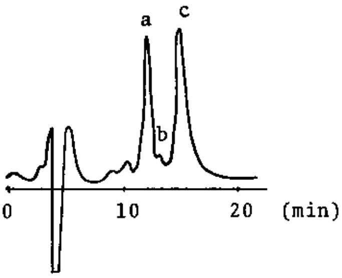
A new diterpene alkaloid, deoxyjesaconitine (**1**), was isolated together with deoxyaconitine (**2**) and hypaconitine (**3**) with high performance liquid chromatography (HPLC) from less polar fraction than that containing aconitine (**4**), mesaconitine (**5**), and jesaconitine (**6**) as main alkaloids from *Aconitum subcuneatum* Nakai.1) The HP-liquid chromatogram was given at chart 1. Few papers have been published on the alkaloids having anisoyl group except for jesaconitine (**6**).2)

The object of the present paper is to report the structure elucidation of a new compound having an anisoyl group at C-14, deoxyjesaconitine, on the basis of spectral data.

Deoxyjesaconitine (**1**) showed the following properties; mp 174-176° (acetone), $[\alpha]_D = +52°$ (c = 0.065, MeOH), $C_{35}H_{49}NO_{11}$, m/e 659 (M^+). UV spectrum of **1** showed an absorption maximum at 257 nm (log ε = 4.23) indicating the presence of anisoyl group. IR spectrum showed absorptions at 3500 cm^{-1} (OH), 1715 (C=O), 1710 (C=O), and 1605 (aromatic C=C). 100 MHz ^{1}H-NMR spectrum showed two methyl groups at δ 1.08 (t, J = 7.0 Hz, N-$CH_2\underline{CH_3}$) and δ 1.43 (s, acetyl group), four methoxyl groups at δ 3.17, 3.28, 3.30, and 3.74, an aromatic methoxyl at δ 3.88, a methine attached to an ester group at δ 4.83 (d, J = 5.0 Hz) assigned to be at C_{14}-H, and aromatic protons with A_2B_2 pattern at δ 6,92 (2H, d, J = 8.0 Hz) and 7.97 (2H, d, J = 8.0 Hz). The ^{13}C-NMR spectrum of **1** was given at table 1 together with those of deoxyaconitine (**2**) and jesaconitine (**6**). In these spectra signals of anisoyl group of

1 were identical with those of **6**. The other signals of **1** were similar to those of **2**. These spectral data of **1** are related to deoxyaconitine (**2**) and jesaconitine (**6**) having 3α-hydroxyl group and the structure of deoxyjesaconitine is given to **1**.

Chart 1 High Performance Liquid Chromatogram of Deoxy Derivatives



Column; Nucleosil 10-C_{18} (8 x 30 mm)
Solvent; CH_3CN : H_2O : MeOH : AcOH : NH_3
(30 : 20 : 5 : 2 : 1)
Flow Rate; 2.5 ml/min
Detector; 231 nm
a --- Deoxyaconitine
b --- Hypaconitine
c --- Deoxyjesaconitine

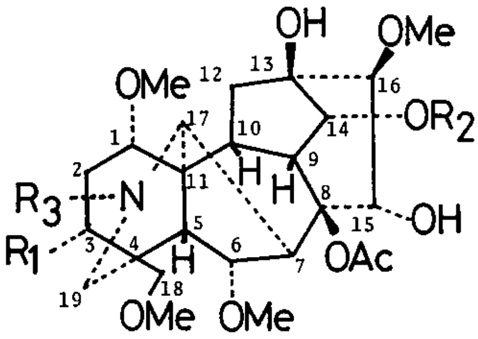
Table 1 ^{13}C-Chemical Shifts and Assignments for Deoxyjesaconitine (**1**) and Related Alkaloids

Carbon Atom	**1**	**2**3)	**6**
1	85.2	85.0	83.3
2	26.4	26.3	33.6
3	35.2	35.2	70.9
4	39.0	39.0	43.1
5	49.2	49.1	46.6
6	83.3	83.3	82.3
7	45.2*	45.1*	44.6*
8	92.1	92.0	91.9
9	44.1*	44.6*	44.2*
10	41.0	41.0	40.8
11	49.9	49.9	49.9
12	36.6	36.7	35.8
13	74.2	74.0	74.0
14	78.7**	78.8**	78.6**
15	78.8**	79.0**	78.8**
16	90.2	90.2	90.0
17	61.4	61.2	60.9
18	80.3	80.2	75.8
19	53.2	53.3	46.9
N-CH_2	49.1	49.1	48.9
CH_3	13.4	13.4	13.3
1'	56.2	56.0	55.8
6'	58.0	57.9	57.9
16'	61.1	60.9	61.1
18'	59.1	59.0	59.0
O=C	172.4	172.2	172.4
CH_3	21.5	21.3	21.5
O=C	165.8	165.9	165.7
C_6 1"	122.3	129.9	122.1
2",6"	131.6	129.5	131.6
3",5"	113.8	128.5	113.8
4"	163.4	133.1	163.5
OCH_3(p)	55.5		55.4

a) δ (ppm) downfield from TMS in $CDCl_3$

b) Assignments with the same asterisk may be interchanged in each column.

Fig. 1



1 R_1= H, R_2= COC_6H_4-OCH_3(p), R_3= C_2H_5

2 R_1= H, R_2= COC_6H_5, R_3= C_2H_5

3 R_1= H, R_2= COC_6H_5, R_3= CH_3

4 R_1= OH, R_2= COC_6H_5, R_3= C_2H_5

5 R_1= OH, R_2= COC_6H_5, R_3= CH_3

6 R_1= OH, R_2= COC_6H_4-OCH_3(p), R_3= C_2H_5

REFERENCES

1. R. Majima and S. Morio, Chem. Ber., 57 1472 (1924); H. Suginome and S. Imato, J. Fac. Sci., Hokkaido Univ., Ser. 3, 4 33 (1950).

2. H. Takayama, M. Ito, M. Koga, S. Sakai, and T. Okamoto, Heterocycles, 15 403 (1981); C. Wei-shin and E. Breitmaier, Chem. Ber., 114 394 (1981); C. Szu-Ying, C. A., 91 20833f (1979).

3. S. W. Pelletier and Z. Djarmati, J. Am. Chem. Soc., 98 2626 (1976).

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