

STRUCTURE OF DEOXYJESAONITINE. 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 hyaconitine was purified with high performance liquid chromatography, and ^{13}C -NMR spectra of those compounds were measured to afford the relationship with each compound.

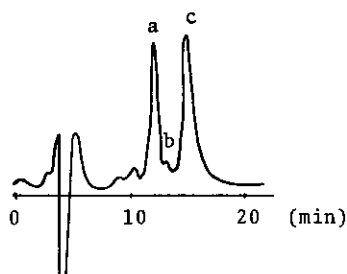
A new diterpene alkaloid, deoxyjesaconitine (1), was isolated together with deoxyaconitine (2) and hyaconitine (3) with high performance liquid chromatography (HPLC) from less polar fraction than that containing aconitine (4), mesaconitine (5), and jesaconitine (6) as main alkaloids from Aconitum subcuneatum 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), $[\alpha]_D = +52^\circ$ ($c = 0.065$, MeOH), $\text{C}_{35}\text{H}_{49}\text{NO}_{11}$, m/e 659 (M^+). UV spectrum of 1 showed an absorption maximum at 257 nm ($\log \epsilon = 4.23$) indicating the presence of anisoyl group. IR spectrum showed absorptions at 3500 cm^{-1} (OH), 1715 ($\text{C}=\text{O}$), 1710 ($\text{C}=\text{O}$), and 1605 (aromatic $\text{C}=\text{C}$). 100 MHz ^1H -NMR spectrum showed two methyl groups at δ 1.08 (t, $J = 7.0$ Hz, $\text{N-CH}_2\text{CH}_3$) 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 $\text{C}_{14}\text{-H}$, 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 3 α -hydroxyl group and the structure of deoxyjesaconitine is given to 1.

Chart 1 High Performance Liquid Chromatogram of Deoxy Derivatives



Column; Nucleosil 10-C₁₈ (8 x 30 mm)

Solvent; CH₃CN : H₂O : MeOH : AcOH : NH₃
(30 : 20 : 5 : 2 : 1)

Flow Rate; 2.5 ml/min

Detector; 231 nm

a --- Deoxyaconitine

b --- Hypaconitine

c --- Deoxyjesaconitine

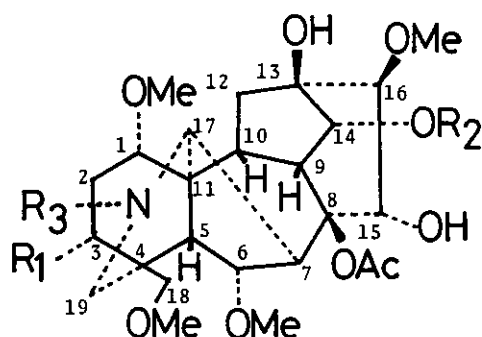
Table 1 ¹³C-Chemical Shifts and Assignments for Deoxyjesaconitine (1) and Related Alkaloids

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

a) δ (ppm) downfield from TMS in CDCl₃

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

Fig. 1



- 1 $\sim$ $R_1 = H$, $R_2 = \text{COC}_6\text{H}_4\text{-OCH}_3(p)$, $R_3 = \text{C}_2\text{H}_5$
- 2 $\sim$ $R_1 = H$, $R_2 = \text{COC}_6\text{H}_5$, $R_3 = \text{C}_2\text{H}_5$
- 3 $\sim$ $R_1 = H$, $R_2 = \text{COC}_6\text{H}_5$, $R_3 = \text{CH}_3$
- 4 $\sim$ $R_1 = \text{OH}$, $R_2 = \text{COC}_6\text{H}_5$, $R_3 = \text{C}_2\text{H}_5$
- 5 $\sim$ $R_1 = \text{OH}$, $R_2 = \text{COC}_6\text{H}_5$, $R_3 = \text{CH}_3$
- 6 $\sim$ $R_1 = \text{OH}$, $R_2 = \text{COC}_6\text{H}_4\text{-OCH}_3(p)$, $R_3 = \text{C}_2\text{H}_5$

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