## Communications to the Editor

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# THE TRANSFORMATION OF MESACONITINE TO ISODELPHININE: DEOXYGENATION OF BRIDGEHEAD HYDROXYL

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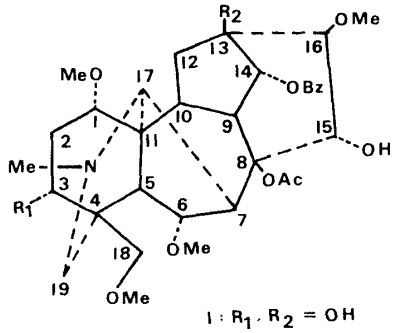
A trifluoromethanesulfonate of anhydromesaconitine was subjected to photochemical reaction, which contains replacement of the bridgehead hydroxyl at C(13) by hydrogen, followed by catalytic hydrogenation, yielding isodelphinine.

KEYWORDS——— mesaconitine; isodelphinine; deoxygenation; bridgehead hydroxyl; photolysis

In order to convert aconitine-type alkaloids possessing bridgehead hydroxyl at C(13) to isodelphinine-type alkaloids,[1] replacement of this hydroxyl group by hydrogen is an important step. We wish to report the conversion of mesaconitine (I) to isodelphinine (II) which had been isolated from Aconitum miyabei Nakai.[2,3] Recently a study of the partial synthesis of II has been published.[4] The transformation of I to II involves a radical-type deoxygenation of the bridgehead hydroxyl by acylation with trifluoromethanesulfonic anhydride and subsequent photolysis.[5]

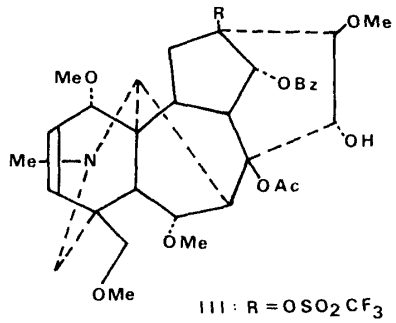
By treatment with trifluoromethanesulfonic anhydride in pyridine, the trifluoromethanesulfonyl group was easily introduced to the bridgehead hydroxyl at C(13) of I with simultaneous elimination of water, and a trifluoromethanesulfonate (III) of anhydromesaconitine (IV)[6] was obtained in 82% yield. Mass spectrometry of III, mp 162-163°C, confirmed the molecular fomula as $C_{34}H_{42}NO_{12}SF_3$ [m/z 745 ($M^+$)]. The $^1$H-NMR spectrum (100 MHz, $CDCl_3$, $\delta$) revealed the presence of an acetoxyl group (1.40, s, 3H), an N-methyl group (2.37, s, 3H), four methoxyl groups (3.18, s, 3H, 3.33, s, 6H, and 3.77, s, 3H), olefinic protons (5.77, d, J=10.0 Hz, and 6.04, dd, J=10.0 Hz, 4.0 Hz, each 1H), and a benzoyl group (7.40-8.08, m, 5H). The infrared spectrum (KBr) exhibited bands due to a hydroxyl group at 3500, acyl carbonyl groups at 1725 $cm^{-1}$. A solution of III dissolved in aqueous hexamethylphosphoric triamide was irradiated by a 2537 Å lamp at room temperature for 3 hours and worked up in the usual manner.[5] A dehydrocompound (V) was obtained in 10% yield and the other residue was starting material. Mass spectrometry of V, amorphous, confirmed the molecular formula as $C_{33}H_{43}NO_9$ [m/z 597 ($M^+$)]. The $^1$H-NMR spectrum revealed the presence of an acetoxyl group (1.46, s, 3H), an N-methyl group (2.38, s, 3H), four methoxyl groups (3.20, s, 3.33, s, 3.34, s, and 3.56, s, each 3H), and olefinic protons (5.80, d, J=10.0 Hz, and 6.08, dd, J=10.0 Hz, 3.4 Hz, each 1H), and a benzoyl group (7.40-8.20, m, 5H). The infrared spectrum exhibited bands due to a hydroxyl group at 3500, acyl carbonyl groups at 1720 $cm^{-1}$. On hydrogenation over platinum in EtOH, compound V was absorbed one mol of hydrogen to

give isodelphinine (II), mp 159-161°C, $[\alpha]_D^{16}$ = +20.0° (c=0.13), in 55% yield. This compound was identical with the authentic sample[4] in IR, $^1H$ and $^{13}C$-NMR, MS spectrometry and mixture melting point test. The carbon atoms of III, IV and V are assigned in the Table.



I: $R_1, R_2$ = OH

II: $R_1, R_2$ = H



III: R = $OSO_2CF_3$

IV: R = OH

V: R = H

Table. $^{13}C$-Chemical Shifts and Assignments [a]

| | Carbon atom | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| III | 81.2 | 124.9 | 137.5 | 40.9 | 46.2 | 83.5 | 42.7 | 93.8 | 41.4 | 40.9 | 48.4 | 32.6 |
| IV | 81.3 | 125.0 | 137.3 | 40.8 | 46.4 | 83.5 | 44.0 | 92.0 | 41.5 | 41.0 | 48.4 | 33.8 |
| V | 81.3 | 125.1 | 137.4 | 40.8 | 46.1 | 84.0 | 44.6 | 92.1 | 44.1 | 38.6 | 48.5 | 26.9 |

| | 13 | 14 | 15 | 16 | 17 | 18 | 19 | $N-CH_3$ | 1' | 6' | 16' | 18' |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| III | 91.1 | 77.9 | 79.1 | 87.5 | 62.5 | 76.4 | 53.1 | 42.7 | 56.6 | 58.0 | 60.1 | 59.2 |
| IV | 74.1 | 78.8 | 78.8 | 89.7 | 62.6 | 78.1 | 53.3 | 42.7 | 56.7 | 57.9 | 61.1 | 59.2 |
| V | 41.5 | 76.3 | 78.1 | 88.8 | 62.5 | 75.4 | 53.3 | 42.7 | 56.6 | 57.5 | 57.9 | 59.2 |

| | $-\underline{C}OCH_3$ | $-CO\underline{C}H_3$ | $-\underline{C}OC_6H_5$ | $-CO\underline{C}_6H_5$ | $-SO_2CF_3$ |
|---|---|---|---|---|---|
| III | 172.3 | 21.1 | 165.5 | 136.6, 129.8, 127.7 | 124.6 |
| IV | 172.3 | 21.3 | 165.9 | 133.2, 129.5, 128.5 | ----- |
| V | 172.2 | 21.4 | 165.9 | 133.1, 129.8, 129.5, 128.5 | ----- |

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

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