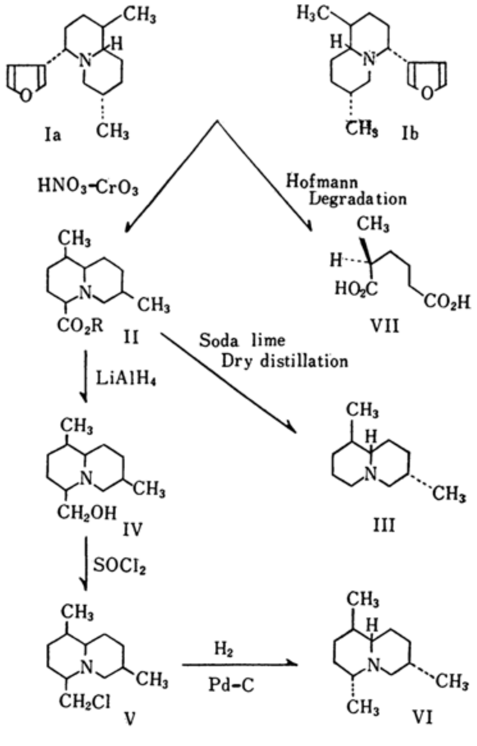
Absolute Configuration of Deoxynupharidine[1]

By Ichiro KAWASAKI and Takeo KANEKO

(Received February 19, 1962)

Recentry, the determination of the conformation of methylquinolizidine by means of the NMR spectrum was reported briefly[2]. Independently, we have prepared 1-, 3- and 4-methylquinolizidine having a definite conformation and their NMR spectra were compared in order to determine the configuration of deoxynupharidine[3,4] with those of 1, 7-dimethyl (III) and 1, 4, 7-trimethylquinolizidine (VI) which were derived from deoxynupharidine by the degragation according to the following schema:



The doublet of 350～354 c. p. s. and the other doublet of 327～333 c. p. s. in the spectrum of III were attributed to a 1-equatorial and a 3-axial methyl group, respectively. The doublet

---

1) A part of this work was presented at the 5th Meeting on Natural Organic Compounds of the Chemical Society of Japan, Sendai, October, 1961.

2) T. M. Moynehan, K. Schofield, R. A. Y. Jones and A. R. Katritzky, *Proc. Chem. Soc.*, **1961**, 218.

3) M. Kotake, S. Kusumoto and T. Ohara, *Ann.*, **606**, 148 (1957).

4) M. Kotake, I. Kawasaki, T. Okamoto, S. Kusumoto and T. Kaneko, ibid., **636**, 158 (1960).

of 337∼344 c. p. s. in the spectrum of VI was assigned to a 4-equatorial methyl group, since the intensity of the peak at 337 c. p. s. was found to be twice that of the peak at 354 c. p. s.

The absolute configuration of deoxynupharidine can thus be shown as either Ia and Ib. Since the configuration of (−)-α-methyladipic acid (VII) obtained from Hofmann degradation of deoxynupharidine was found to have the S(−) configuration[5], we reached to the conclusion that the absolute configuration of deoxynupharidine should be represented by the formula Ib. Compound (IIa R : CH_3), $[\alpha]_D$ −76.25° in EtOH. (IIb R : H), HCl salt, $[\alpha]_D$ −40.3° in EtOH, (III) obtained from IIb, (40%), b. p. 65°C/15 mmHg, $[\alpha]_D$ −34.3° in EtOH, picrate, m. p. 124∼125°C, picrolonate, m. p. 200∼204°C. (IV) obtained from IIa, (90%), b. p. 88°C/0.6 mmHg, $[\alpha]_D$ −37.1° in EtOH, methiodide, m. p. 173∼174°C. (V), (90%), b. p. 91∼93°C/1 mmHg, $[\alpha]_D$ −69.4° in EtOH. (VI), (76%), b. p. 95∼98°C/12 mmHg, $[\alpha]_D$ −47.8° in EtOH, picrolonate, m. p. 180∼184°C, methiodide, m. p. 189∼191°C. (VII), $[\alpha]_D$ −12.0° in EtOH.

TABLE OF NMR SPECTRA

Compound		c. p. s.*		
1 (equat.)-Methyl-quinolizidine	a			351∼356
1 (axial)-Me-	b	329∼334		
3 (e)-Me-	c			353∼359
3 (a)-Me-	d	329∼336		
4 (e)-Me-	e		340∼346	
4 (a)-Me-	f			348∼354
III		327∼333		350∼354
VI		330∼337∼344		354

m. p. of picrate ; a : 162∼164°C, b : 185∼188°C, c : 183∼185°C, d : 151∼153°C, e : 193∼196°C, f : 187∼190°C.

* These values were measured in benzene solution at 56.4 Mc/sec. using a Varian Associates 4300 C instrument, calculated from benzene side band.

Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka

---

[5] T. Kaneko, K. Wakabayashi and H. Katsura, This Bulletin, to be published.