

*The Synthesis of dl-4-(3-Furyl)-1-methyl
Quinolizidine; Demethyl Analogue of
Deoxynupharidine*

By Munio KOTAKE, Ichiro KAWASAKI,
Tadashi OKAMOTO, Shiro KUSUMOTO
and Takeo KANEKO

(Received June 30, 1959)

In 1956, structure (I) was assigned by Kotake, Kusumoto and Ohara¹⁾ to deoxynupharidine; an alkaloid isolated from the roots of *Nuphar japonica* DC. A synthesis of *dl*-4-(3-furyl)-1-methyl quinolizidine is

now reported which establishes the synthetic routes to the *dl*-deoxynupharidine*. The stages involved in the synthesis are as follows:

Compound II²⁾, b. p. 133°C/10⁻² mmHg; III, (62%) b. p. 130°C/10⁻² mmHg, I. R. bands at 1645 (amide), 1735 cm⁻¹ (ester). *Anal.* Found: C, 64.78; H, 8.89; N, 5.80. Calcd. for C₁₃H₂₁O₃N: C, 65.24; H, 8.85; N, 5.85%; IV, (95%) m. p. 102~106°C. *Anal.* Found: C, 53.69; H, 9.13; N, 6.20. Calcd. for C₁₀H₁₉O₂N·HCl: C, 54.17; H, 9.09; N, 6.33%; V, (48%) b. p. 154°C/10⁻³ mmHg, I. R. bands at 875, 1505, 3110 (furan), 1573 (conjugated furan), 1625 (amide), 1735 cm⁻¹ (ester). *Anal.* Found: C, 65.94; H, 8.24; N, 4.51. Calcd. for C₁₇H₂₅O₄N: C, 66.42; H, 8.20; N, 4.56%; VI³⁾, (56%) b. p. 81~84°C/10⁻³ mmHg, I. R. bands at 875, 1505, 3110 (furan), 1588 (conjugated furan), 1640 cm⁻¹ (double bond); VII, (50%) b. p. 87~89°C/10⁻² mmHg. Perchlorate, m. p. 193~194°C. *Anal.* Found: C, 52.56; H, 6.82; N, 4.34. Calcd. for C₁₄H₂₁ON·HClO₄: C, 52.57; H, 6.93; N, 4.38%. Picrate, m. p. 172~174°C. *Anal.* Found: C, 53.30; H, 5.40; N, 12.79. Calcd. for C₂₀H₂₄O₈N₄: C, 53.57; H, 5.39; N, 12.50%.

The I. R. spectra of compound VII are similar to that of the deoxynupharidine as indicated in Fig. 1.

The authors wish to express their thanks to Professor Takeo Sakan, Professor Takashi Kubota and Professor Yasuhide Yukawa for their encouragement throughout this work.

Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka

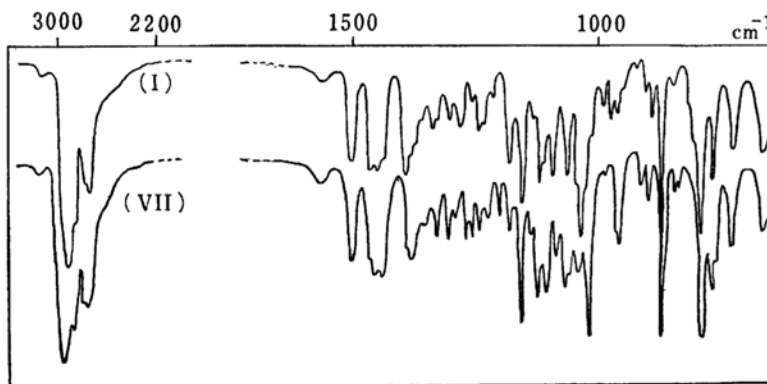
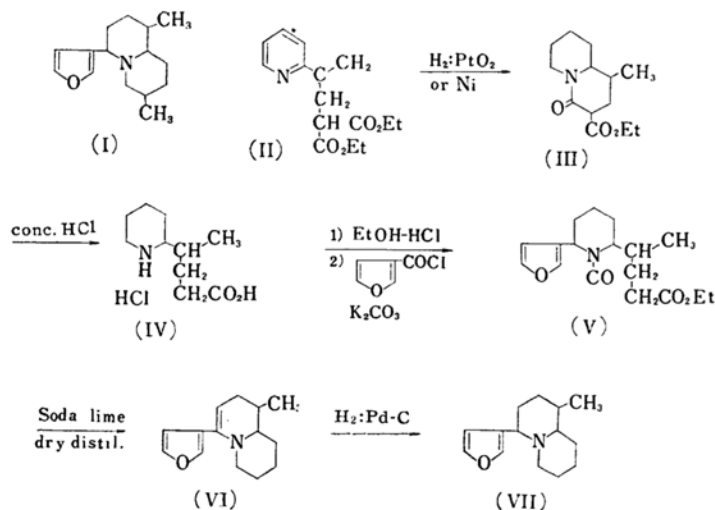


Fig. 1.



* The synthesis of *dl*-deoxynupharidine was reported elsewhere.

1) M. Kotake, S. Kusumoto and T. Ohara, *Ann.*, **606**, 148 (1957); *This Bulletin*, **29**, 157 (1957); *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **77**, 1302 (1956); **78**, 488 (1957).

2) F. Bohlmann, N. Ottawa and R. Keller, *Ann.*, **587**, 162 (1954); E. E. v. Tamellen and J. S. Baran, *J. Am. Chem. Soc.*, **80**, 4659 (1958).

3) I. Murakoshi, *J. Pharm. Soc. Japan (Yakugaku Zasshi)*, **78**, 594 (1958).