[Chem. Pharm. Bull. 24(7)1490—1496(1976)]
UDC 547.94.04 : 547.834.2.04 : 541.14

A Synthesis of (±)-Dihydrodeoxyepiallocernuine by Application of a Facile Hofmann-Loeffler Type of Photocyclization[1)]

Yoshio Ban, Masayuki Kimura,[2)] and Takeshi Oishi[2a)]

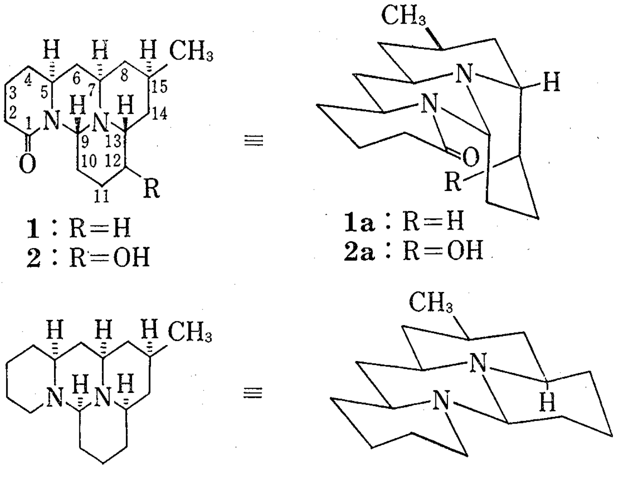
Faculty of Pharmaceutical Sciences, Hokkaido University[2)]

(Received September 10, 1975)

Pelletierine which was established to be a precursor in the biosynthesis of cernuine (**1**), was converted into the quinolizidine (**22**), whose N-chloro derivative (**27**) was irradiated with 300 W high pressure mercury lamp in ether in the absence of any strong acid to readily afford the entitled compound (**3**) as the free base with no base treatment. The present photocyclization is thus different from the known Hofmann-Loeffler reaction in several respects, which are demonstrated for discussion.

Cernuine (**1**) and lycocernuine (**2**) are alkaloids isolated from *Lycopodium cernum* L., whose structures were proposed by Ayer, *et al.* to be **1a** and **2a**, respectively. They also succeeded in the synthesis of (±)-dihydrodeoxyepiallocernuine (**3**), providing the strong support to the stereochemistry assigned to these alkaloids.[3)]

In 1970, Spenser, *et al.* reported that only one unit of pelletierine[4)] was incorporated into these alkaloids as a precursor[5a,b)] in the biosynthesis of cernuine (**1**) and lycopodine on revision of the former proposal.[5c)]



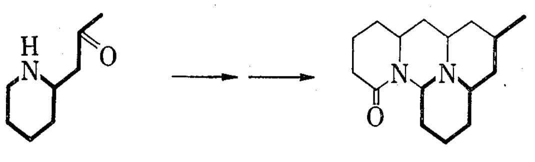
1 : R=H
2 : R=OH

1a : R=H
2a : R=OH

3

3a

Chart 1



4

1

Chart 2

A new synthesis of the entitled compound (**3**) starting from pelletierine (**4**)[4)] has been described in this paper. A starting material, pelletierine (**4**), was prepared by condensation of the iminoether (**5**) derived from piperid-2-one with acetylacetone followed by reduction

---

[1)] A preliminary communication of this paper has appeared in *Heterocycles*, **2**, 323 (1974).

[2)] Location: *Kita, 12-jo, Nishi 6-chome, Kita-ku, Sapporo, 060, Japan*; *a*) Present address: *The Institute of Physical and Chemical Research, Wako-shi, Saitama-ken, 351, Japan.*

[3)] *a*) W.A. Ayer, J.K. Jenkins, S. Valverde-Lopez, and R.H. Burnell, *Can. J. Chem.*, **45**, 433 (1967); *b*) W.A. Ayer, J.K. Jenkins, K. Piers, and S. Valverde-Lopez, *ibid.*, **45**, 445 (1967); *c*) W.A. Ayer and K. Piers, *ibid.*, **45**, 451 (1967).

[4)] 2-Piperidylpropanone (**4**) which was known as isopelletierine for many years, is referred to as pelletierine in the present paper to accord with that in the related literature,[5a)] although the same compound was referred to as isopelletierine in the communication.[1)] [R.E. Gilman and L. Marion, *Bull. Soc. Chim. France*, **1961**, 1993].

[5)] *a*) R.N. Gupta, Y.K. Ho, D.B. MacLean, and I.D. Spenser, *J. Chem. Soc. Chem. Comm.*, **1970**, 409; *b*) M. Castillo, R.N. Gupta, Y.K. Ho, D.B. MacLean, and I.D. Spenser, *J. Am. Chem. Soc.*, **92**, 1074 (1970); *c*) R.N. Gupta, M. Castillo D.B. MacLean, I.D. Spenser, and J.T. Wrobel, *ibid.*, **90**, 1360 (1968).

and oxidation, which method was previously published from this laboratory.[6a)] In the present synthesis where a mixture of the iminoether (**5**) and acetylacetone was heated in the presence of triethylamine in a sealed tube at 100° for 30 hr, the compound (**7**) was newly obtained along with the previously reported product (**8**).[7)] The compound (**7**) was converted into **8** on treatment with NaH in ether at room temperature. The possible intermediate (**6**) was not isolated in this case too. The product (**8**) was converted by the known procedure[6a)] into pelletierine (**4**), which was acetylated with acetyl chloride in 10% NaOH solution to afford N-acetylpelletierine (**10**) as an oil in 80% yield.

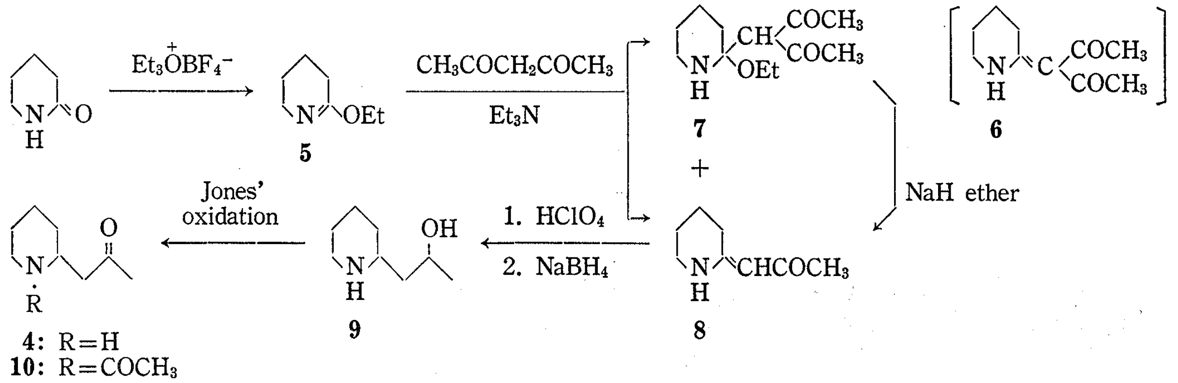


Chart 3

Meanwhile, it was also reported that the amine (**11**) was converted by the Meerwein reagent to the imminium ether salt (**12a**), which was converted into the α-ethoxy enamine (**12b**) by action of potassium *t*-butoxide. The latter (**12b**) readily underwent the intramolecular nucleophilic attack at the ester carbonyl carbon to give the cyclization product (**12c**).[6b)]

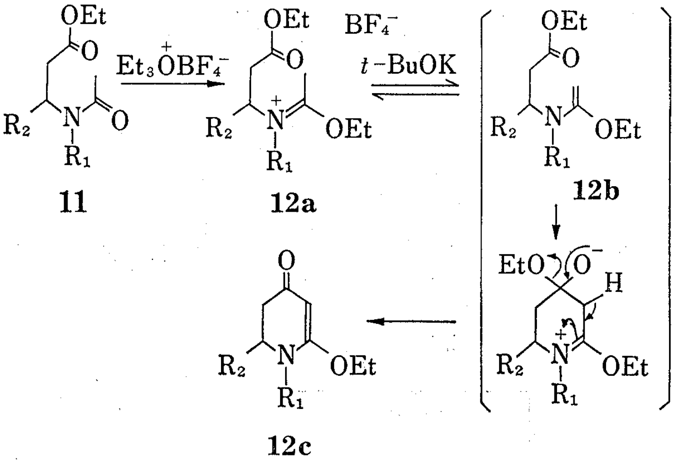


Chart 4

This useful method was now applied to the cyclization of N-acetylpelletierine (**10**) to successfully afford the compound (**15**) as an oil (UV $\lambda_{\max}^{\mathrm{EtOH}}$ 252 nm) on purification by chromatography on alumina through the following consecutive processes. At first, the compound (**10**) was refluxed with the Meerwein reagent in methylene chloride for 2 hr, providing the intermediate (**13**) in solution, to which solution was added BF_3-etherate, and the whole mixture was refluxed for 6 hr to give the compound (**14**) in 34.6% yield.

The compound (**14**) was heated with potassium *t*-butoxide in *t*-butanol for 3 hr to furnish **15** in 78% yield. A better yield (62%) of **15** from **10** was obtained when the crude product (**13**) which was provided after evaporation of methylene chloride in the foregoing procedure, was heated with potassium *t*-butoxide in *t*-butanol at 90° for 2.5 hr to directly afford **15**. Moreover, when heated with aluminum *t*-butoxide in xylene at 150°, the compound (**10**) gave the other oily product (**17**, UV $\lambda_{\max}^{\mathrm{EtOH}}$ 323 nm) as a result of an alternative aldol condensation.

---

6) *a*) T. Oishi, M. Nagai, T. Ohnuma, H. Moriyama, M. Ochiai, and Y. Ban, *Chem. Pharm. Bull.* (Tokyo), **17**, 2306 (1969); *b*) T. Oishi, M. Ochiai, T. Nakayama, and Y. Ban, *ibid.*, **17**, 2314 (1969).

7) In the previous experiment under the same condition, heating was continued for 50 hr.[6a)]

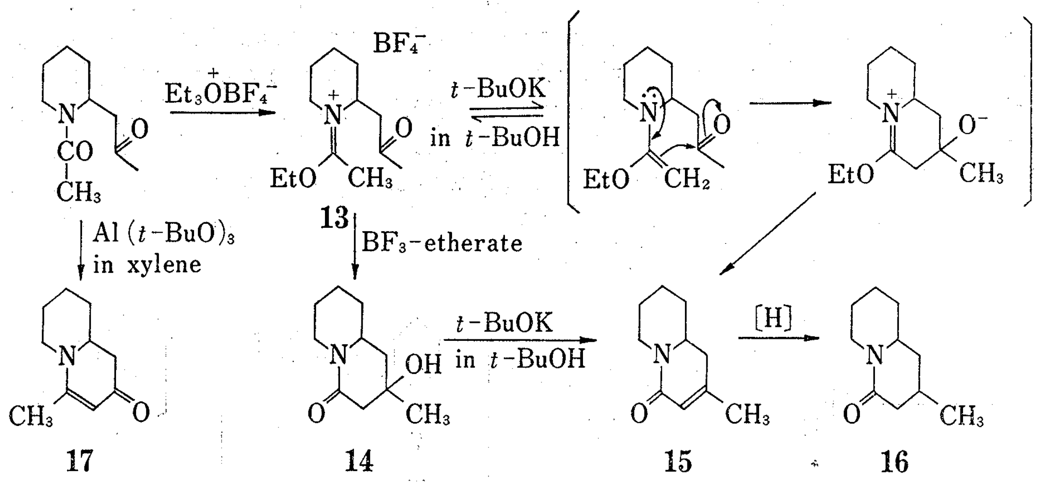


Chart 5

The lactam (**16**) as an oil (*ca.* 100% yield) was obtained by hydrogenation of **15** at 4 atmospheric pressure of hydrogen with Adams' catalyst in ethanol.[8]

As for the subsequent condensation of the lactam (**16**) with α-picolyl lithium, the preliminary experiments were carried out to confirm that a similar condensation does not require any activation of the lactam part. Namely, the compound (**18**) was obtained by condensation of N-methyl-2-pyrrolidone with α-picolyl lithium in THF kept at −40° for 3 hr.

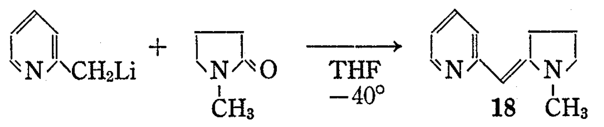


Chart 6

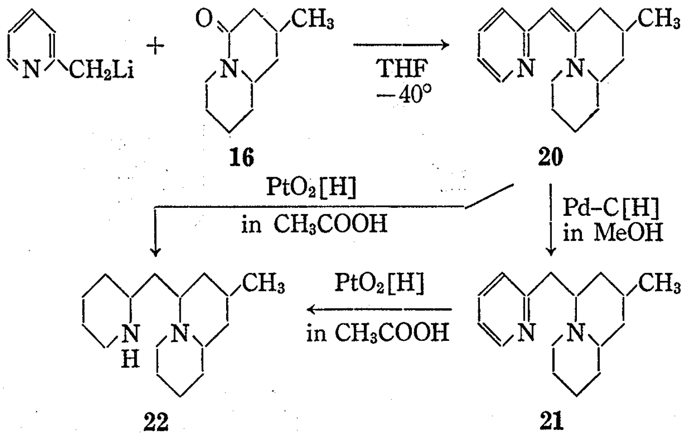


Chart 7

Based upon these results, the lactam (**16**) was condensed with α-picolyl lithium to afford the compound (**20**), colorless oil, in 89.8% yield, which was submitted to hydrogenation with palladium on charcoal in methanol to yield **21** as an oil (*ca.* 100% Yield). The pyridine part of **21** was hydrogenated at 4 atmospheric pressure of hydrogen with Adams' catalyst in acetic acid to afford the piperidylmethyl quinolizidine (**22**) as an oil in 80% yield.

In order to obtain the compound (**3**) from **22**, the mercuric acetate oxidation of a similar ring system (**23**) was investigated. It has been demonstrated in the preliminary work that a model compound (**23**) afforded the lactam (**24**) on mercuric acetate oxidation with or without ethylene diamine tetraacetic acid (EDTA) reagent. In the meantime, the same oxidation of the diamine of a general formula (**25**) in the presence of EDTA, was proved by Möhrle to afford the amide (**26**).[9] Therefore, the mercuric acetate oxidation of the diamines (**22**, **23** or **25**) seemed not to be appropriate for formation of the 1,3-diaza ring system.

---

[8] E. Ochiai, K. Tsuda, and J. Yokoyama, *Chem. Ber.*, **68**, 2291 (1935).

[9] *a*) H. Möhrle and S. Mayer, *Arch. Pharmaz.*, **306**, 210 (1973); *b*) H. Möhrle and R. Engelsing, *Chem. Ber.*, **106**, 1172 (1973).

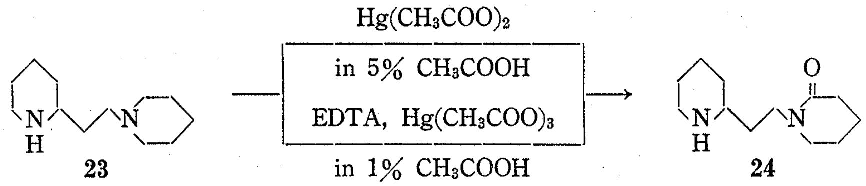


Chart 8

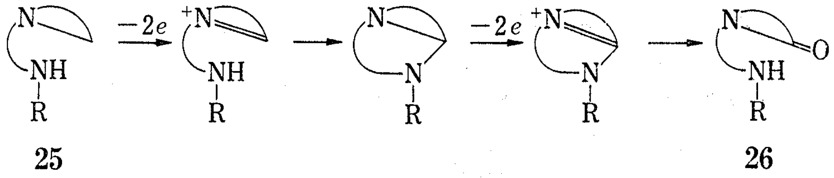


Chart 9

Consequently, the Hofmann-Loeffler type of photocyclization of 22 was tried with an aim to have the compound (3=3a) in preference to an alternative product (28), because the easiness of abstraction of a hydrogen at the carbon adjacent to the nitrogen atom was anticipated,[10] although generation of a five-membered ring is favored in the usual Hofmann-Loeffler reaction.[11–13] Formation of 29 might be also excluded on account of difficult steric requirement, though the high selectivity for the tertiary hydrogen abstraction to form the radical at C-13 should be possible. Thus, the compound (27) which was prepared from 22 by action of N-chlorosuccinimide in ether,[11] was irradiated with a 300 W high pressure mercury lamp in 95% sulfuric acid or in trifluoroacetic acid,[12] but any appreciable amount of product was not obtained.

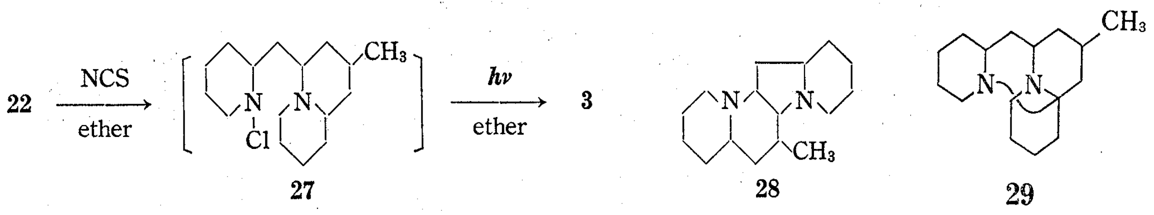


Chart 10

Therefore, the amine (22) was mixed with N-chlorosuccinimide in ether *in situ*, and the mixture was immediately irradiated with the above mercury lamp in a current of nitrogen at room temperature for 5 hr, during which time the colorless precipitate (22-dihydrochloride) deposited. After the precipitate was filtered off and the solvent was removed from the filtrate, the residue was extracted with *n*-pentane to separate the insoluble succinimde, and *n*-pentane was evaporated from the extract to furnish the cyclized product (3=3a) as the free base, mp 63—64.5° (lit.[3c] mp 62—64°), picrate, mp 177—178°, in 30% yield, which was identified with the authentic specimen generously provided by Professor Ayer by mixed melting point determination and by direct comparisons of the spectral data of both samples.

The features of the present photocyclization are remarkably different from those of the known Hofmann-Loeffler reaction in the following respects:

---

10) *a*) S.G. Cohen and R.J. Baumgarten, *J. Am. Chem. Soc.*, **89**, 3471 (1967); *b*) *idem*, *ibid.*, **87**, 2996 (1965).
11) E.J. Corey and W.R. Hertler, *J. Am. Chem. Soc.*, **82**, 1657 (1960).
12) M.E. Wolff, *Chem. Rev.*, **63**, 55 (1963).
13) *a*) S. Wawzonek and P.J. Thelen, *J. Am. Chem. Soc.*, **72**, 2118 (1950), *b*) S. Wawzonek, M.F. Nelson, Jr. and P.J. Thelen, *ibid.*, **73**, 2806 (1951); *c*) S. Wawzonek and T.P. Culbertson, *ibid.*, **81**, 3367 (1959).

1. The 1,3-diaza six membered ring (**3**) was exclusively generated instead of the five membered ring seen in **28**, suggesting that the present cyclization did not involve the intramolecular 1,5-hydrogen shift.
2. Any strong acid was absent, which means that the aminium radical as an key intermediate for the propagation sequence was not present in this reaction.
3. Cyclization readily occurred without base treatment to give the free base of the product.

These features suggest that the present reaction may not have proceeded *via* the mechanism for the usual Hofmann-Loeffler reaction proposed by Wawzonek[13] and thoroughly investigated by Corey.[11] The availability of the present procedure should be limited to generation of 1,3-diaza, -oxaza and -thiaza cyclic derivatives, which is now under investigation.

Experimental[14,15]

2-Piperidylideneacetone (8) and 2-Ethoxy-2-diacetylmethyl-piperidine (7)——A mixture of 23 g of the iminoether (**5**), 20 g of acetylacetone and 3.4 g of triethylamine was heated in a sealed tube for 30 hr at 100° (bath temp). After the unreacted materials were evaporated under reduced pressure, the residual brown oil was distilled to furnish the compounds, (**8**, 16.5 g. 65.7%) and (**7**, 13.4 g, 32.8%). 2-Piperidylideneacetone (**8**), bp 80—85° (5 mmHg)[6a] and 2-ethoxy-2-diacetylmethyl-piperidine (**7**), bp 140—145° (5 mmHg). IR $\nu_{\max}^{\text{neat}}$ cm^{-1}: 3480 (NH), 1740, 1612, 1590. NMR (CCl_4) δ: 1.22 (3H, t, J=6.9 Hz $-OCH_2CH_3$), 4.5 (2H, q, J=6.9 Hz $-OCH_2CH_3$), 10.7 (1H, broad, NH). Mass Spectrum *m/e*: 227 (M^+), 139 (100%).

Preparation of 2-Piperidylideneacetone (8) from the Compound (7)——To a solution of 1.5 g of NaH in ether was added 6 g of **7** and the resulting mixture was stirred at room temperature for 10 hr. After reaction, the mixture was mixed with ethanol and water, extracted with CH_2Cl_2 and the extract was dried over anhydrous Na_2SO_4. After the solvent was evaporated under reduced pressure, the residual oil was distilled to give 3.25 g (86.4%) of **8**, bp 80—85° (5 mmHg).

N-Acetylpelletierine (10)——Pelletierine (**4**) was prepared from the foregoing compound (**8**) by the known procedure.[6a] To a solution of 380 mg of pelletierine in 50 ml of CH_2Cl_2 and 5 ml of 10% NaOH solution was added 380 mg of acetyl chloride at 0° under stirring. After 1 hr, the CH_2Cl_2 layer was separated from the aqueous phase, and the aqueous phase was extracted with CH_2Cl_2. The extracts were combined, dried over anhydrous Na_2SO_4 and the solvent was removed by evaporation to leave 400 mg (80.7%) of the pale yellow oil (**10**). Which indicated a single spot on tlc. IR $\nu_{\max}^{\text{neat}}$ cm^{-1}: 1710 (C=O), 1630 (N–C=O). NMR ($CDCl_3$): 2.08 and 2.11 (3H, s and s, $N-COCH_3$),[16] 2.17 (3H, s, $-CH_2COCH_3$). Mass Spectrum *m/e*: 183 (M^+). Semicarbazone, mp 171°. *Anal.* Calcd. for $C_{11}H_{20}O_2N_4$: C, 54.78; H, 8.39; N, 23.32. Found: C, 54.76; H, 8.45; N, 23.27.

4-Methyl-1,6,7,8,9,9a-hexahydro-2H-quinolizin-2-one (17)——A mixture of 300 mg of N-acetylpelletierine (**10**) and 242 mg of Al(O-*tert*.Bu)$_3$ in 50 ml of xylene was heated at 150° (bath temperature) for 5 hr. On cooling, the mixture was mixed with water, extracted with CH_2Cl_2 and the extract was dried over anhydrous Na_2SO_4. The solvent was evaporated to leave the crude product, which was chromatographed on alumina to give 171 mg (57%) of an oil (**17**). IR $\nu_{\max}^{\text{neat}}$ cm^{-1}: 1630 (N–C=C–C=O). NMR (CCl_4) δ: 1.95 (3H, s, CH_3), 4.75 (1H, s, vinyl-H). UV $\lambda_{\max}^{\text{EtOH}}$ nm: 323. Mass Spectrum *m/e*: 165 (M^+), 150, 137, 136 (100%), 122.

2-Methyl-1,6,7,8,9,9a-hexahydro-4H-quinolizin-4-one (15)——Method A): The compound (**15**) was prepared from **10** *via* 2-methyl-2-hydroxy-octahydro-quinolizin-4-one (**14**). A mixture of 434 mg of N-acetylpelletierine (**10**) and 800 mg of triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$) in 10 ml of CH_2Cl_2 was refluxed at 45° for 2 hr. To this solution was added 586 mg of BF_3-etherate and the whole mixture was refluxed at the same temperature for 6 hr. The mixture was made alkaline with 5 N K_2CO_3, extracted with CH_2Cl_2 and the extract was dried over anhydrous K_2CO_3. After evaporation of the solvent, the product

---

14) Melting points were measured with a hot stage microscope (Yanaco MP-J2) and uncorrected. Spectra reported herein were measured on a Hitachi EPS-3T spectrophotometer, JASCO DS-701G and 215 Hitachi grating infrared (IR) spectrophotometers, a Hitachi R-20B (NMR, 60 MHz), and a Hitachi RMU-7M double forcussing mass spectrometer. The authors are indebted to Misses H. Kakizaki, M. Satoh, A. Maeda, and C. Ohara for microanalyses, to Mmes. M. Ohnuma and K. Tsuta, and Miss S. Okayama for obtaining nuclear magnetic resonance (NMR) spectra and to Miss Masako Takahashi for mass spectral measurements.

15) The following abbreviations are used: b=broad, d=doublet, m=multiplet, q=quartet, s=singlet, t=triplet. DMSO=dimethyl sulfoxide. THF=tetrahydrofuran.

16) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, 1969, p. 361.

was chromatographed on alumina to give 150 mg (34.6%) of 2-methyl-2-hydroxy-octahydro-quinolizin-4-one (**14**), colorless solid, and 250 mg (47.2%) of the starting material (**10**) was recovered. The compound (**14**), mp 133°. IR $\nu_{\text{max}}^{\text{nujol}}$ cm^{-1}: 3280 (OH), 1625 (N–C=O). NMR ($CDCl_3$) δ: 1.23 and 1.27 (3H, CH_3, doubling due to an isomeric mixture), 2.85 (1H, s, OH). Mass Spectrum *m/e*: 183 (M^+), 165, 150 (100%). *Anal.* Calcd. for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.27; H, 9.50; N, 7.56.

A mixture of 70 mg of **14** and 128 mg of *t*-BuOK in 10 ml of *t*-BuOH was refluxed at 90° for 3 hr. The solvent was evaporated under reduced pressure, the residue was mixed with water, and extracted with CH_2Cl_2. The extract was dried over anhydrous K_2CO_3 and the solvent was evaporated to give an oil, which was subjected to chromatography on alumina to afford 50 mg (78.9%) of an oil (**15**). IR $\nu_{\text{max}}^{\text{neat}}$ cm^{-1}: 1680, 1630. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 255. Mass Spectrum *m/e*: 165 (M^+), 150, 136, 126, 84 (100%). NMR ($CDCl_3$) δ: 1.85 (3H, s, CH_3), 5.55 (1H, s, vinyl-H).

Method B): A mixture of 1 g of N-acetylpelletierine (**10**) and 1.05 g of $Et_3O^+BF_4^-$ in 30 ml CH_2Cl_2 was refluxed at 45° for 3 hr. Evaporation of the solvent gave the crude salt (**13**), which without purification, was dissolved in 50 ml of *t*-BuOH. To this solution was added 1.84 g of *t*-BuOK, the whole mixture was refluxed at 90° for 2.5 hr. The solvent was evaporated under reduced pressure, the residue was mixed with water, and extracted with CH_2Cl_2. The extract was dried over anhydrous K_2CO_3 and the solvent was evaporated to give an oil, which was subjected to chromatography on alumina to afford 533 mg (62%) of an oil, which was indentified with the foregoing compound (**15**).

2-Methyl-octahydro-4H-quinolizin-4-one (16)——A solution of 400 mg of **15** in ethanol was hydrogenated at 4 atmospheric pressure of hydrogen with Adams' catalyst. The catalyst was removed by filtration, and the solvent was evaporated to leave 400 mg (98%) of colorless oil (**16**).[8] IR $\nu_{\text{max}}^{\text{neat}}$ cm^{-1}: 1630 (N–C=O). Mass Spectrum *m/e*: 167 (M^+), 152, 126, 97, 84 (100%). NMR ($CDCl_3$) δ: 0.98 (3H, d, $J=5.3$ Hz, CH_3).

1-Methyl-2-(2-pyridylmethylidene)-pyrrolidine (18)——To a solution of 8 g of α-picoline in 100 ml of THF, was slowly added 35 ml of 20% solution of *n*-butyllithium in *n*-hexane at −40° in a current of nitrogen. The color of the reaction mixture immediately changed from colorless to dark red brown. After the solution was stirred at −40° for 1 hr, a solution of 5 g of N-methylpyrrolidone in 20 ml of THF was added at the same temperature, during which time the color of the solution changed to pale yellow. The mixture was stirred for further 3 hr and kept to stand at room temperature overnight. Water was added to the reaction mixture, which was extracted with CH_2Cl_2. The extract was dried over anhydrous K_2CO_3 and concentrated to give 8.5 g (97.1%) of an colorless oil, which was purified by chromatography on alumina to give the compound (**18**). IR $\nu_{\text{max}}^{\text{neat}}$ cm^{-1}: 1620 (C=C), 1580. 1540. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 267, 325. NMR (CCl_4) δ: 2.78 (3H, s, NCH_3), 4.9 (1H, s, vinyl-H), 6.4—7.5 (3H, m, pyridyl-H), 8.2 (1H, d, $J=4.5$ Hz, pyridyl-H). Mass Spectrum *m/e*: 174 (M^+), 107 (100%).

2-Methyl-4-(2-pyridylmethylidene)-quinolizidine (20)——According to the foregoing procedure, 8 g of α-picoline, 30 ml of *n*-butyllithium (20% in hexane) and 2.7 g of **16** yielded 3.5 g (89.8%) of **20** as an oil. IR $\nu_{\text{max}}^{\text{neat}}$ cm^{-1}: 2800, 1610, 1590, 1545. UV $\lambda_{\text{max}}^{\text{EtOH}}$: 320 nm, which was shifted to 265 nm in an acidic medium. Mass Spectrum *m/e*: 242 (M^+), 241, 227 (100%), 150, 134, 124, 119, 106, 93. NMR ($CDCl_3$) δ: 0.95 (3H, d, $J=4.5$ Hz, CH_3), 5.35 (1H, s, vinyl-H), 6.6—7.6 (3H, m, pyridyl-H), 8.38 (1H, d, $J=4.5$ Hz, pyridyl-H).

2-Methyl-4-(2-pyridylmethyl)-quinolizidine (21)——A solution of 15 mg of **20** in methanol was hydrogenated at atmospheric pressure of hydrogen with 20 mg of 5% palladium on charcoal until the uptake of hydrogen ceased. After removal of the catalyst and evaporation of methanol, 180 mg (*ca.* 100%) of the product (**21**) was obtained as colorless oil. IR $\nu_{\text{max}}^{\text{neat}}$ cm^{-1}: 2800 −2750 (Bohlmann's absorption), 1590, 1582. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 264. Mass Spectrum *m/e*: 244 (M^+), 152 (100%). NMR ($CDCl_3$) δ: 0.8 (3H, d, $J=4.5$ Hz, $C\underline{H}_3$), 6.9—7.2 (3H, m, pyridyl-$\underline{H}$), 8.48 (1H, d, $J=4.5$ Hz, pyridyl-$\underline{H}$). Dipicrate, mp 152°. *Anal.* Calcd. for $C_{28}H_{30}O_{14}N_8$: C, 47.86; H, 4.27; N, 15.96; Found: C, 47.79; H, 4.56; N, 15.41. C, 48.26; H, 4.46; N, 15.56.

2-Methyl-4-(2-piperidylmethyl)-quinolizidine (22)——A solution of 150 mg of **21** in acetic acid was hydrogenated at 4 atmospheric pressure of hydrogen with Adams' catalyst until the uptake of hydrogen ceased. The solvent was evaporated under reduced pressure to leave the residue, to which was added water. The aqueous solution was made alkaline with 6 N NaOH, extracted with CH_2Cl_2 and the extract was dried over anhydrous K_2CO_3. The solvent was evaporated under reduced pressure to leave 120 mg (80%) of an oil (**22**), which indicated a single spot on TLC. IR $\nu_{\text{max}}^{\text{neat}}$ cm^{-1}: 3300 (NH), 2800—2750 (Bohlmann's absorption). Mass Spectrum *m/e*: 250 (M^+), 152 (100%), 110, 84. The spectral data of the present compound (22) were indentified on direct comparisons with those of the authentic specimen provided by Professor Ayer.

1-[2-(2-piperidyl)ethyl]-piperid-2-one (24)——Method A): A solution of 300 mg of 2-[2-(1-piperidyl)-ethyl]piperidine (**23**) and 2.44 g of mecuric acetate in 30 ml of 5% acetic acid was heated in a current of nitrogen at 90° for 24 hr. The precipitated mercurous acetate was collected on filtration, washed with dilute acetic acid and the washings were combined with the filtrate. The filtrate was saturated with hydrogen sulfide and the precipitated mercurous sulfide was removed on filtration. The precipitate was washed with dilute acetic acid and with water. The washings were combined with the filtrate, and the whole filtrate was basified with 20% NaOH under cooling in an ice-bath. The aqueous solution was extracted with CH_2Cl_2, and the extract was dried over anhydrous $MgSO_4$. The solution was removed by evaporation to leave 150 mg (46.7%) of **24** as pale yellow oil, which was purified by chromatography on alumina. IR $\nu_{\text{max}}^{\text{neat}}$ cm^{-1}: 3275 (NH), 1620 (CONH). Mass Spectrum *m/e*: 210 (M^+), 129, 128, 127, 126, 113, 112, 111, 110, 98, 84 (100%).

NMR (CCl_4) δ: 3.0—3.5 (4H, m, $-CH_2-\overset{|}{N}-\underset{\underset{O}{\|}}{C}-CH_2-$). Picrate, mp 180—181°. *Anal.* Calcd. for $C_{18}H_{25}O_8N_5$: C, 49.20; H, 5.69; N, 15.95. Found: C, 49.04; H, 5.74; N, 15.98.

Method B): To a solution of 1.96 g of **23** in 40 ml of 1% acetic acid were added 9.31 g of (ethylene diamine)tetraacetic acid disodium salt dihydrate (EDTA) and 7.97 g of mercuric acetate. The mixture was stirred in an oil bath kept at 110° for 1.5 hr, during which time matallic Hg deposited. After cooling, the reaction mixture was made alkaline with 20% NaOH, extracted with CH_2Cl_2, and the extract was dried over anhydrous $MgSO_4$. The solvent was evaporated to give 850 mg (44.8%) of **24** as a pale yellow oil, which was subjected to chromatography on alumina.

(±)-**Dihydrodeoxyepiallocernuine** (3)——The amine (22, 900 mg) was mixed with 480 mg of N-chloro succinimide in 200 ml of ether *in situ*, and the mixture was immediately irradiated with a 300 W high pressure mercury lamp in a current of nitrogen at room temperature for 5 hr, during which time the colorless precipitate (22-dihydrochloride) deposited. After the precipitate was filtered off and the solvent was removed from the filtrate, the residue was extracted with *n*-pentane to separate the insoluble succinimide, and *n*-pentane was evaporated to afford 270 mg (30%) of colorless crystals, which were recrystallized from *n*-hexane to give the entitled compound (3) as colorless plates, mp 63—64.5°. IR $\nu_{\text{max}}^{\text{nujol}}$ cm^{-1}: 2800, 2720 (Bohlmann's absorption). NMR ($CDCl_3$) δ: 0.84 (3H, d, J=4.5 Hz, CH_3), 3.20 (1H, m, $\rangle N-\overset{|}{C}H-N\langle$). Mass Spectrum *m/e*: 248 (M^+), 247, 218, 219 (100%), 218, 206, 205. *Anal.* Calcd. for $C_{16}H_{28}N_2$: C, 47.58; H, 4.82; N, 15.86. Found: C, 47.58; 4.90; N, 15.59. This compound was identified with the authentic specimen generously provided by Professor Ayer by mixed melting point determination and by direct comparisons of the spectral data of both samples.

Acknowledgement The authors express their gratitude to Professor W.A. Ayer, The University of Alberta, for the generous donation of the authentic sample of (±)-dihydrodeoxyepiallocernuine and the spectral data. The work was supported by the Grant-in-Aid from the Ministry of Education, Science and Culture, and from the Mitsubishi Foundation, which are gratefully acknowledged.