Miss M. Ninomiya, and Mrs. E. Tanaka for infrared spectral data, and to the members of the Analysis Center of this Faculty for microanalytical and ultraviolet spectral data.

Summary

Alkylation of 1,1'-dimethyl-3,3'-bioxindole (V) was carried out. A higher-melting isomer (VIIa) was obtained by dimethylation of (V) with sodium hydride in benzene, while a lower-melting isomer (VIIb) was obtained by dimethylation of (V) with sodium amide in liquid ammonia. Cyanomethylation of (V) with sodium hydride in benzene afforded (VIIIa), which was further cyanomethylated by chloroacetonitrile with potassium carbonate, sodium iodide, and acetone to give (IX), which was also obtained by direct biscyanomethylation with the latter reagents. Two other 3,3'-disubstituted 3,3'-bioxindoles (X, XII) were also prepared by analogous alkylation.

The compound (III), which was considered to be an attractive intermediate for the synthesis of (I) and (II), was obtained by catalytic reduction of (IX).

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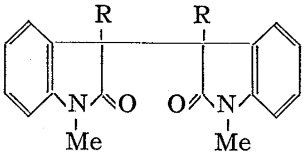
UDC 547.94 : 582.675

153. **Tôhru Hino**: Synthetic Approaches to Calycanthaceae Alkaloids. III.[*1] Reductive Cyclization of 3,3'-Bioxindoles. (1). A Formation of 5,7-Dimethyl-11b,11c-bis(2-dimethylaminoethyl)-5,5a,6a,7,11b,11c-hexahydrofuro[2,3-*b*:5,4-*b'*]diindole.

(*Faculty of Pharmaceutical Sciences, University of Tokyo*[*2])

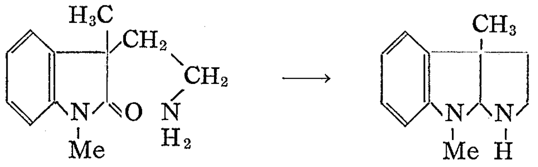
In the preceding paper,[*1] the author reported the synthesis of several kinds of 3,3'-disubstituted bioxindoles including (Ia, b), (II), and (III). Now the reductive cyclization of these compounds was investigated. Julian[1] reported, in his brilliant synthesis of physostigmine, that the reductive cyclization of (IV) with sodium in ethanol gave (V). Sugasawa



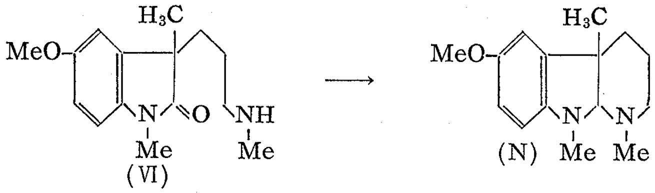
(I) R: CH_3

(II) R: $CH_2CH_2NH_2$

(III) R: $CH_2CH_2N{<}^{CH_3}_{CH_3}$



(IV) (V)



(VI) (N)

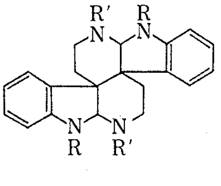
[*1] Part II. This Bulletin, 9, 979 (1961).

[*2] Hongo, Tokyo (日野 亨).

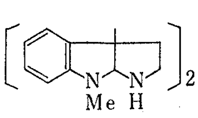
1) P.L. Julian, J. Pikl, *et al.* : J. Am. Chem. Soc., 57, 539, 564, 755 (1935).

and Murayama,[2] and Preobrazhenskii, *et al.*[3] have shown that this method is also effective for cyclization of (VI) to (VII).

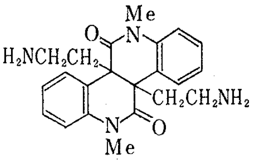
The compound (VIII), for which the isomeric (VIII′) was proposed for calycanthine by Robinson, *et al.*,[4] might be obtained by applying this method to the compound (II), though the alternative cyclization to (IX) is also possible. Further, it would be possible to obtain true calycanthine[5] skeleton if the bioxindole (II) could be isomerized to (X) before the reductive cyclization.



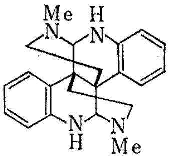
(VIII) R : CH_3, R′ : H
(VIII′) R : H, R′ : CH_3



(IX)

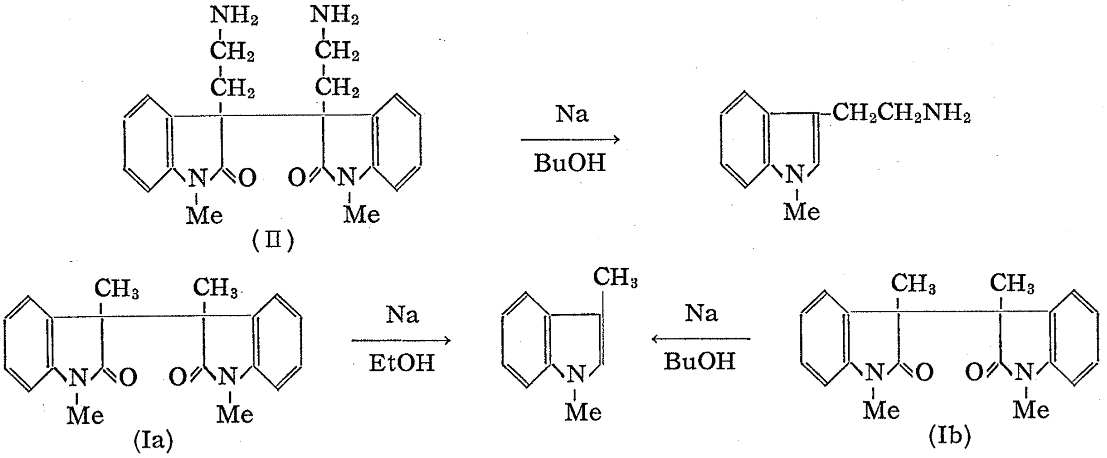


(X)



Calycanthine

When (II) was dissolved in butanol and treated with metallic sodium following Julian's method,[1] a basic compound was obtained as a brown oil. Its infrared spectrum did not show C=O absorption which is characteristic to the starting oxindole derivative. However, its ultraviolet maxima at 224 and 288 mμ[2] in ethanol and ethanolic hydrochloric acid solution do not favor the structure Ph-N-C-N-, but rather strongly supports indole type of structure. Actually, the oil showed positive Ehrlich test and gave dark red picrate, m.p. 171~173°. The picrate[2] and a phthaloyl derivative,[2] m.p. 178~179°, were respectively identical with those of 1-methyltryptamine on admixture.



(II)

(Ia) higher-melting isomer

Chart 1.

(Ib) lower-melting isomer

The formation of the indole is well known[2,6] in the Ladenburg reduction of the oxindole having hydrogen atom at 3-position, which fact, however, does not hold in the present case and a reductive cleavage of 3,3′-bioxindole occurred. Therefore, the same reaction was carried out with the two diastereoisomers (a and b) of (I) and the same 1,3-dimethylindole, identified as its picrate, was obtained from both isomers. The higher-melting isomer (Ia) was reduced in ethanol to the indole, recovering a small amount of

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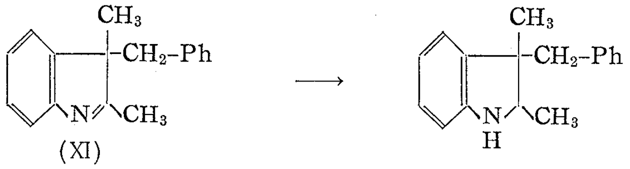
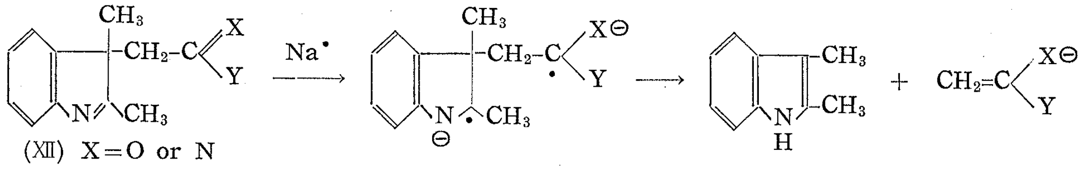
2) S. Sugasawa, M. Murayama : This Bulletin, **6**, 194, 200 (1958).
3) M. N. Kolosov, L. I. Metreveli, N. A. Preobrazhenskii : Zhur. Obshchei Khim., **23**, 2027 (1953).
4) R. Robinson, H. J. Teuber : Chem. & Ind. (London), **1954**, 783.
5) R. B. Woodward, J. Harley-Mason, *et al.* : Proc. Chem. Soc., **1960**, 76.
6) E. Wenkert, B. S. Bernstein, J. H. Udelhofen : J. Am. Chem. Soc., **80**, 4899 (1958); A. Stóll, J. Rutschmann : Helv. Chim. Acta, **33**, 67 (1950), **34**, 382 (1951).

(Ia), while the lower-melting isomer (Ib) was reduced in butanol to only the indole, presumably due to the difference in the reaction temperature. These results clarified that reductive cleavage of 3,3′-bioxindole derivatives was rather common.

The formation of indole in this reduction may be considered simply as the hydrogenolysis of dibenzyl type in 3,3′-bioxindole, followed by further reduction to indole. However, Nakazaki⁷⁾ reported that the compound (XI) was not cleaved by sodium and ethanol, and he explained the mechanism of reductive cleavage of the general type of indolenine (XII) to indole as nucleophilic attack of electron of metallic sodium to form 1,4-biradical which was cleaved to the indole.

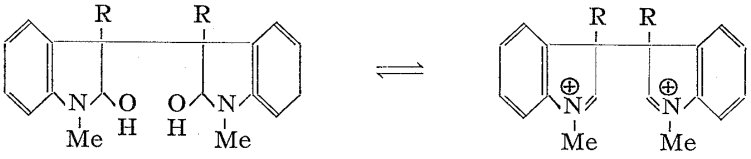


(XI)



(XII) X=O or N

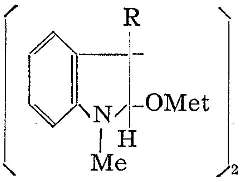
In the reduction of bioxindole, the intermediate structure (XIIIa and XIIIb) might be possible, which may be considered to be equivalent to (XII) in alkaline media, taking into account the fact that the Ladenburg reduction of 1,3,3-trimethyloxindole gives rise to 1,3,3-trimethyl-2-indolinol.⁸⁾



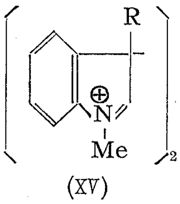
(XIIIa) (XIIIb)

(XIIIb) could now be cleaved according to Nakazaki's scheme. Since the Ladenburg reduction of (II) to (VIII) has thus far been unsuccessful, the lithium aluminium hydride reduction of (II) was undertaken as an alternative route to obtain (VIII).

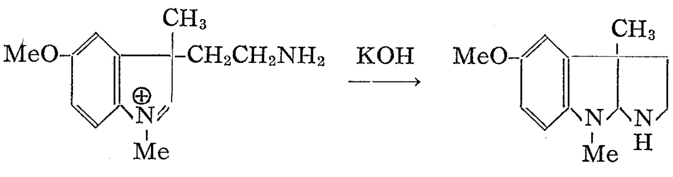
In the lithium aluminium hydride reduction of bioxindole, (XIV) or (XV) might be considered as intermediates.



(XIV) Met: LiAl/4



(XV)



(XVI) (XVII)

Then the basic property of lithium aluminium hydride may catalyse the cyclization of C=N or C-O-Met with H_2N group in R, which are close enough to each other, as was shown by King and Robinson⁹⁾ in a spontaneous cyclization of (XVI) to noresermethole (XVII) with potassium hydroxide. Furthermore, the fact reported by Newman, *et al.*¹⁰⁾ that

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7) M. Nakazaki: Bull. Chem. Soc. Japan, 32, 588 (1959).

8) G. Ciamician, A. Piccinini: Ber., 29, 2465 (1896).

9) R. R. King, R. Robinson, M. Liguori: J. Chem. Soc., **1933**, 1475; **1934**, 1416.

10) M. S. Newman, T. Fukunaga: J. Am. Chem. Soc., 82, 693 (1960).

nitriles were formed in the reaction of hindered primary amide with lithium aluminium hydride (1/2 mole), probably by the removal of Met_2O from the complex, renders the cyclization of C-O-Met with N-Met (in the side-chain R) in (XIV) possible.

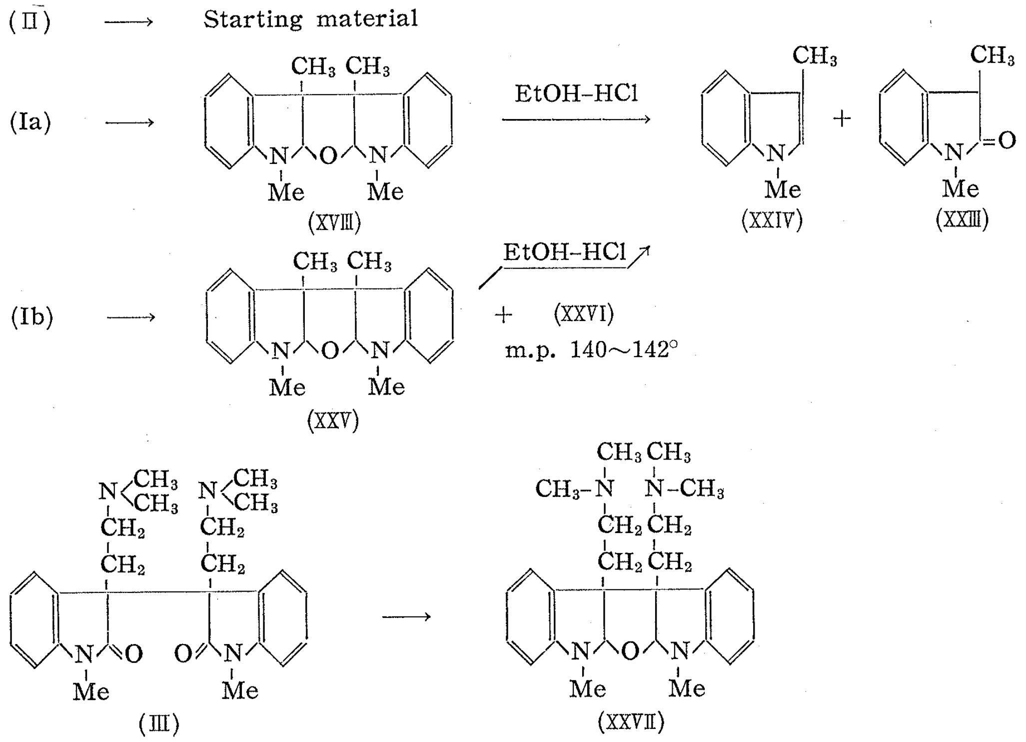

Chart 2. $LiAlH_4$ Reduction in Dioxane-Ether

When the compound (II) was heated with 4 moles of lithium aluminium hydride in dioxane-ether mixture at the boiling point of ether for 4 hours, as showh in Chart 2, only the starting material was recovered, probably due to the insolubility of lithium aluminium hydride complex of (II).*[3] However, a compound (XVIII) of m.p. 116～118° was obtained in a fair yield from (Ia) by using 2 moles of lithium aluminium hydride in dioxane-ether as above. The infrared spectrum of this compound showed neither C=O band nor OH band, but showed aromatic N-methyl absorption at 2820 cm^{-1} which was not observed in the starting material (Ia) of N-methyloxindole type, and absorptions at 888, 954, 1005, 1054, and 1070 cm^{-1} are probably due to C-O-C- vibration.[11] The ultraviolet spectrum showed the maxima at 246 mμ (log ε 4.2), and 298 mμ (log ε 3.7) in ethanol, but the maxima changed to 226 mμ (log ε 4.5), 253 mμ (log ε 4.0), and 279 mμ (log ε 3.8) by the addition of ethanolic hydrochloric acid. Only the starting material (XVIII) was recovered when (XVIII) was further treated with lithium aluminium hydride in ether for 4 hours.

The formation of (XVIII) can be considered as a cyclization by the removal of Met_2O from the hypothetical intermediate (XIV) in which both C-OMet may be close to each other. A compound (XIX) having the same ring system has been reported by Hodson, Smith, and

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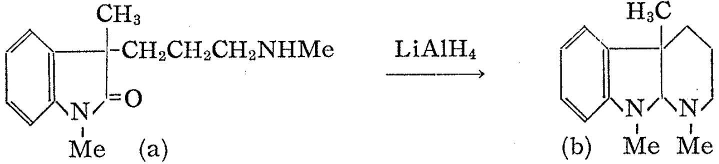
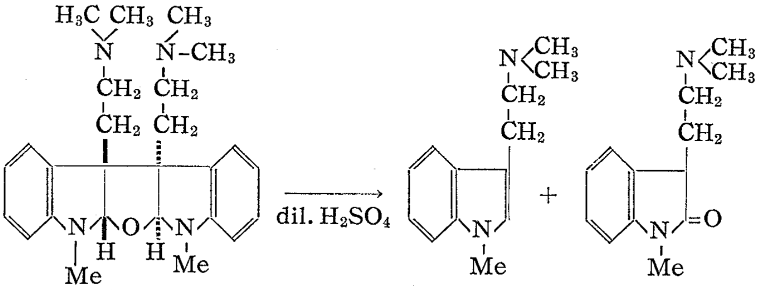
*[3] The reductive cyclization of (a) to (b) with $LiAlH_4$ in ether has been successful.



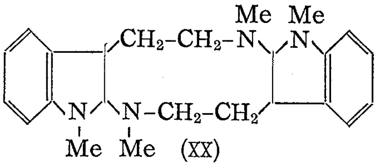
The details will be reported in a separate paper by T. Hino and K. Ogawa.

[11] L. J. Bellamy : "The Infra-red Spectra of Complex Molecules," 114 (1958). John Wiley & Sons, Inc., New York.

Wrobel[12] as an alkaline degradation product of folicanthine methiodide and they deduced that the structure (XX) proposed for folicanthine by themselves became untenable, because there exists direct β,β-linkage of two indolins in (XIX). They also reported that (XIX) could be cleaved quantitatively by dil. H_2SO_4 to give two kinds of product, which were isolated on alumina column and were proved to be oxindole (XXI) and indole (XXII). Therefore, the compound (XVIII) should be cleaved to the oxindole (XXIII) and the indole (XXIV) by acid. As a matter of fact, merely the addition of hydrochloric acid to the ethanolic solution of (XVIII) in the cold caused its fission to (XXIII) and (XXIV), as evidenced by the ultraviolet absorption change described above (cf. Fig. 1). Further, when the acidified solution was warmed, there was obtained a faint yellow oil, in which the presence of a mixture of (XXIII) and (XXIV) was also supported by its infrared absorption spectrum. In fact, they were isolated by chromatographic separation and were identified with the authentic specimens.



(XIX) (XXII) (XXI)



folicanthine: Hodson, Smith, 1957

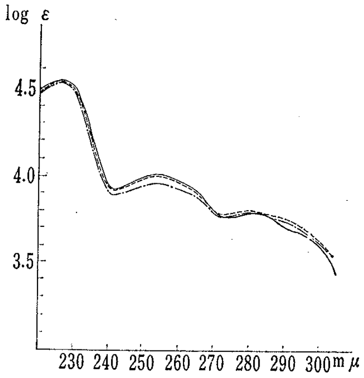


Fig. 1. Ultraviolet Spectra

—— 1,3-Dimethyloxindole (XXIII) + 1,3-Dimethylindole (XXIV) (in EtOH)
------ (XVIII) (in EtOH-HCl)
·—·—· (XXV) (in EtOH-HCl warm)

In the case of (Ib), the lower-melting isomer, (XXV) was obtained by the same lithium aluminium hydride reduction accompanied with another product (XXVI). The compound (XXV), m.p. 170°, showed similar infrared and ultraviolet spectra as those of (XVIII), but the ultraviolet spectra (Fig. 1) changed to the mixed curve of (XXIII) and (XXIV) after boiling the ethanolic solution containing hydrochloric acid for one minute (Fig. 1). The infrared spectrum of the oil obtained by the treatment of (XXV) with ethanolic hydrochloric acid was also identical with that of the mixture of (XXIII) and (XXIV).

The by-product from reduction of (Ib), (XXVI), m.p. 140~142°, showed ultraviolet maxima at 254 mμ (log ε 4.2) and 306 mμ (log ε 3.8), no C=O or OH absorption in its infrared spectra, and the analytical data showed the absence of oxygen. Its structure is still obscure, except that the ring system of (XVIII) or (XXII) is not present in it.

The above-mentioned lithium aluminium hydride reduction technique was now applied to (III) to obtain (XXVII) having the same plane structure as (XIX). When (III) was heated with lithium aluminium hydride (3 moles) in dioxane-ether at the boiling point of ether

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[12] R. H. F. Hodson, G. F. Smith, J. T. Wrobel: Chem. & Ind. (London), **1958**, 1551.

for 5 hours, a partially crystallized oil was obtained as a hexane-soluble portion, which showed medium C=O absorption in its infrared spectrum. (XXVII), m.p. 139~141°, was obtained after chromatographic separation on alumina. The ultraviolet absorption (Fig. 2) showed the same behavior as (XVIII) and (XXV), and its infrared spectrum showed aromatic N-methyl at 2820 cm^{-1}, aliphatic N-methyl at 2780 cm^{-1}, and absorptions at 880, 987 and 1050 cm^{-1} are probably due to C-O-C- vibration. Though the configuration of (XXVII) could not be established, it is certain that (XXVII) has the same plane structure as (XIX) obtained from folicanthine.

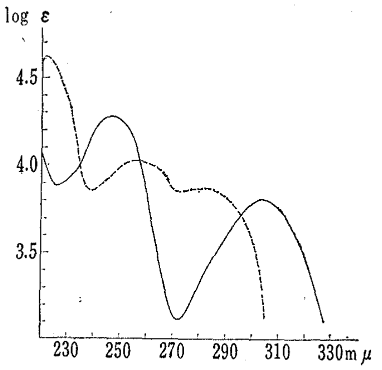

Fig. 2. Ultraviolet Spectra of (XXVII)

—— (in EtOH)
------ (in warm EtOH-HCl)

The reductive cyclization of (II) to (VIII) did not succeed by the Ladenburg method or lithium aluminium hydride but hexahydrofuro-diindole derivatives were obtained by lithium aluminium hydride reduction of (I) and (III). Experiments on the stereochemical problems of (XVIII), (XXV), and (XXVII) are now in progress.

Experimental[*4]

1-Methyl-3(2-aminoethyl)indole——The Ladenburg reduction of (II): To a boiling solution of (II)[*1] (1.0 g.) in dehyd. BuOH (100 cc.), Na pieces (5.0 g.) were added during 1.5 hr. with stirring. Transient purple color was observed when the first piece of Na was added to the solution. After the addition, the mixture was refluxed for 1 hr., until all of Na disappeared, giving a pale brown solution. After cool, H_2O (50 cc.) was added to the mixture and the aqueous layer was extracted with benzene. The combined BuOH-benzene solution was washed several times with satd. NaCl solution, dried, and evaporated *in vacuo*, leaving a brown oil (1.0 g.).

The oil was dissolved in benzene (100 cc.) and extracted 4 times with 5% HCl. The acid solution was basified with NaOH solution after treatment with charcoal and extracted with benzene. The benzene solution was washed with H_2O, dried, and evaporated, leaving a pale brown oil (600 mg.), which showed no C=O absorption in its IR spectrum. A part of the oil was distilled *in vacuo*, giving a pale yellow oil, $b.p_5$ 150~170° (bath temp.). UV $\lambda_{max}^{EtOH(J.P.)}$ mμ (log ε): 224 (4.49), 290 (3.75).
Dipicrate: Dark red pillars, m.p. 171~173° (from EtOH) (reported[2)] m.p. 167~168°). *Anal.* Calcd. for $C_{11}H_{14}N_2 \cdot 2C_6H_3O_7N_3$: C, 43.68; H, 3.19; N, 17.72. Found: C, 44.23; H, 3.39; N, 17.81.
Phthaloyl derivative: Pale yellow needles, m.p. 177~178° (from EtOH) (reported[2)] m.p. 175~176°). The dipicrate and the phthaloyl derivative were identical with authentic samples[*5] on admixture and in IR spectra.

The same reduction of (II) in dehyd. EtOH only gave the starting material.

1,3-Dimethylindole; the Ladenburg Reduction of (I)——a) From (Ia): To a boiling solution of (Ia)[*1] (1.5 g.) in dehyd. EtOH (100 cc.), small pieces of Na (7.5 g.) were added during 45 min. After the addition, the mixture was further refluxed for 15 min,, chilled, and added with H_2O (75. cc.). EtOH was evaporated *in vacuo*, separating a brown oil which was extracted with benzene and Et_2O. The benzene-Et_2O solution was washed with satd. NaCl solution, dried, and evaporated, leaving a reddish brown oil (1.2 g.), from which some crystals separated on standing. The oil showed positive Ehrlich test. UV $\lambda_{max}^{EtOH(J.P.)}$ 226, 290 mμ.

[*4] All melting points are not corrected. Infrared spectra were taken by Koken DS-301 spectrophotometer and ultraviolet spectra were taken by Carry Model 11 spectrophotometer.

[*5] Both samples were kindly donated by Dr. Murayama (cf. reference 2) to whom the author's thanks are due.

Picrate : Red needles (iso-PrOH), m.p. 143~144°, *Anal.* Calcd. for $C_{10}H_{11}N \cdot C_6H_3O_7N_3$: C, 51.34; H, 3.74; N, 14.97. Found : C, 51.41; H, 3.83; N, 14.57. This sample showed no depression on admixture with the picrate of authentic 1,3-dimethylindole.[*6]

The crystals (50 mg.) were collected and washed with EtOH, and it was identical with the starting material on admixture and in IR spectra.

b) From (Ib) : (Ib)[*1] (1.2 g.) was treated with Na (6.0 g.) and dehyd. BuOH (120 cc.) as in the case of (II). A brown oil (800 mg.) was obtained when the BuOH-benzene solution was evaporated *in vacuo.* A part of the oil was distilled *in vacuo,* giving a pale yellow oil, b.p$_{20}$ 140~150°(bath temp.). UV $\lambda_{max}^{EtOH(J.P.)}$ mμ (log ε) : 226 (4.507), 290 (3.70). The picrate, m.p. 143~144°, was identical with the authentic sample.

$LiAlH_4$ reduction of (II)——To a suspension of $LiAlH_4$(400 mg., 4 mol. equiv.) in dehyd. Et_2O (30 cc.) and dehyd. dioxane (40 cc.) (II)[*1](1.0 g.) in dehyd. dioxane (60 cc.) was added dropwise during 1 hr., under reflux with stirring. The mixture was refluxed for 5 hr. after the addition, giving a white suspension. The mixture was chilled in ice and H_2O, and the excess $LiAlH_4$ and complexes were decomposed[13] with H_2O (0.5 g.) in dioxane (3 cc.), 10% NaOH (1 cc.), and H_2O (2 cc.). The mixture was then filtered, the precipitate was washed with Et_2O, and the Et_2O-dioxane solution was dried over Na_2SO_4 and solid KOH. The Et_2O and dioxane were evaporated *in vacuo,* leaving a brown resinous oil (900 mg.) which partially solidified on standing. The semi-solid was recrystallized from tetrahydrofuran to colorless prisms, m.p. 215~218°, which showed no depression on admixture with the starting material and the same IR spectrum.

5,7,11b,11c-Tetramethyl-5,5a,6a,7,11b,11c-hexahydrofuro[2,3-*b*:5,4-*b'*]diindole (XVIII) by $LiAlH_4$ Reduction of (Ia)——To a suspension of $LiAlH_4$(400 mg., 2 mol. equiv.) in dehyd. Et_2O (20 cc.) and dehyd. dioxane (20 cc.), (Ia)[*1](1.6 g.) in dehyd. dioxane (30 cc.) was added dropwise during 50 min. under gentle boiling. After the addition, the mixture was refluxed for 4 hr. and then chilled in ice and H_2O. An excess of $LiAlH_4$ and complexes were decomposed as above, the mixture was filtered, and the insoluble salt was washed with Et_2O. The combined Et_2O-dioxane solution was dried over Na_2SO_4 and KOH, and evaporated *in vacuo* leaving a greenish oil (1.1 g.) which soon solidified to m.p. 85~100°. Recrystallization once from EtOH and twice from hexane gave colorless prisms, m,p, 116~118°. *Anal.* Calcd. for. $C_{20}H_{22}ON_2$: C, 78.40; H, 7.24; N, 9.14. Found : C, 78.77; H, 7.13; N, 8.92. UV $\lambda_{max}^{EtOH(J.P.)}$ mμ (log ε) : 246.6 (4.21), 298 (3.73); $\lambda_{max}^{EtOH-HCl}$ mμ (log ε) : 226 (4.54), 253 (4.01), 279 (3.80) (Fig. 1). IR ν_{max}^{KBr} cm^{-1} : 2820 (sh) ($N-CH_3$); 1610, 1490 (benzene); 1054, 1035, 1005, 954, 898. (C–O–C ?); 740 (*o*-disubstituted benzene).

Acid Cleavage of (XVIII); Formation of 1,3-Dimethylindole (XXIV) and Oxindole (XXIII)——To a warm ethanolic solution (10 cc.) of (XVIII) (350 mg.), a few drops of conc. HCl were added and the clear mixture was boiled for 1~2 min. After cool, benzene (80 cc.) was added to the mixture, the benzene-EtOH mixture was washed with satd. NaCl solution and dried. The benzene-EtOH solution was evaporated *in vacuo,* yielding a pale brown oil (320 mg.). The IR spectrum of the oil in liq. film was superimposable with those of the equimolar mixture of 1,3-dimethylindole[*6](28.5 mg.) and oxindole[*6](30.5 mg.).

The oil (180 mg.) was chromatographed over Al_2O_3 column. From the fraction eluted with hexane-benzene (3:1), pale brown oil (70 mg.), which showed positive Ehrlich test, was obtained. UV $\lambda_{max}^{EtOH(J.P.)}$ mμ (log ε) : 226 (4.51), 290 (3.65). It formed a red picrate (from EtOH), m.p. 143~144°, which showed no depression on admixture with the authentic sample[*6].

From the fraction eluted with hexane-benzene (1:1) colorless oil (60 mg.) was obtained, which soon solidified by seeding with authentic 1,3-dimethyloxindole. It was recrystallized from petr. ether to colorless prisms, m.p. 56~58°, which was identical with authentic sample[*6] on admixture and in IR spectrum.

$LiAlH_4$ Reduction of (XVIII)——(XVIII) (150 mg.) was treated with $LiAlH_4$(50 mg.) in dehyd. Et_2O (30 cc.) for 4 hr. at the boiling point of Et_2O. A colorless oil (120 mg.) was obtained by the same procedure as above and it soon solidified, m.p. 106~112°. It was recrystallized from EtOH to colorless prisms, m.p. 113~116°, which was identical with the starting material on admixture and in IR spectrum.

5,7,11b,11c-Tetramethyl-5,5a,6a,7,11b,11c-hexahydrofuro[2,3-*b*:5,4-*b'*]diindole (XXV) by $LiAlH_4$ Reduction of (Ib)——(Ib)[*1](3.2 g.) in dehyd. dioxane (40 cc.) was reduced with $LiAlH_4$(770 mg., 2 mol. equiv.) in dehyd. dioxane (40 cc.) and dehyd. Et_2O (40 cc.), as in the case of (Ia). A brown solid (3.0 g.), m.p. 120~140°, was obtained when the Et_2O-dioxane solution was evaporated. It was recrys-

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[*6] 1,3-Dimethylindole was prepared from 1,3-dimethyloxindole, which was synthesized by Stolle's method (cf. P. L. Julian, Pikl, D. Boggess : J. Am. Chem. Soc., 56, 1797 (1934)), by the Ladenburg reduction. The work has been carried out by Mr. K. Ogawa in this laboratory to whom the author's thanks are due.

13) V. M. Micovic, M. L. Michailovic : J. Org. Chem., 18, 1190 (1953).

tallized twice from hexane to crude (XXV) (1.0 g.), m.p. 155~165°, which gave pure (XXV) on repeated recrystallization from EtOH as colorless pillars, m.p. 169~170°. *Anal.* Calcd. for $C_{20}H_{22}ON_2$: C, 78.40; H, 7.24; N, 9.14. Found : C, 78.74; H, 6.81; N, 9.31. UV $\lambda_{\max}^{\text{EtOH(J.P.)}}$ mμ (log ε) : 246.5 (4.25), 300.4 (3.76); $\lambda_{\max}^{\text{EtOH-HCl(warm)}}$ mμ (log ε) : 226 (4.55), 253 (3.96), 280 (3.79) (Fig. 1). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 2820 (N-Me); 1610, 1490 (benzene); 1060, 1045, 977, 958 (C-O-C ?), 740 (*o*-substituted benzene).

When (XXV) (150 mg.) was boiled for a few minutes in EtOH-HCl solution as in the case of (XVIII), a pale brown oil (100 mg.) was obtained, whose IR spectrum was identical with that of a mixture of (XXIII) and (XXIV).

From the mother liquor of hexane recrystallization, a crude (XXVI) (700 mg.), m.p. 113~140°, was obtained after chromatographic separation on Al_2O_3. It was recrystallized from hexane to colorless prisms, m.p. 140~142°. *Anal.* found : C, 82.61; H, 8.06; N, 9.96. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε) : 257 (4.16), 306 (3.70).

5,7-Dimethyl-11b,11c-bis(2-dimethylaminoethyl)5,5a,6a,7,11b,11c-hexahydrofuro[2,3-*b*; 5,4-*b*′] diindole (XXVII) by LiAlH$_4$ Reduction of (III)——(III)[*1] (1.0 g.) was treated with $LiAlH_4$ (250 mg., 2.5 mol. equiv.) in dehyd. dioxane (40 cc.) and Et_2O (20 cc.) for 5 hr. at the boiling point of Et_2O as in above cases. A brown oil (900 mg.) was obtained as a crude product. Its hexane-soluble portion (600 mg.), which partially crystallized on standing, was chromatographed over Al_2O_3. From the fractions eluted with benzene : $CHCl_3$ (3:1 and 1:1), colorless crystals (200 mg.), m.p. 130~135°, were obtained and recrystallized 3 times from petr. ether to colorless prisms, m.p. 139~141°. *Anal.* Calcd. for $C_{22}H_{36}ON_4$: C, 74.25; H, 8.63; N, 13.22. Found : C, 73.79; H, 8.27; N, 13.61. UV $\lambda_{\max}^{\text{EtOH(J.P.)}}$ mμ (log ε) : 246 (4.28), 304 (3.82); $\lambda_{\max}^{\text{EtOH-HCl(warm)}}$ mμ (log ε) : 222 (4.62), 255 (4.07), 280 (3.65) (Fig. 2). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 2820 (arom. N-Me); 2780 (aliph. N-Me); 1610, 1495 (benzene); 1053, 1043, 1020, 982, 880 (C-O-C ?), 740 (*o*-disubstituted benzene).

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Summary

The Ladenburg reduction and lithium aluminium hydride reduction of 3,3′-disubstituted 3,3′-bioxindole were carried out. By the former method, (I) and (II) gave 1,3-dimethylindole and 1-methyl-3-(2-aminoethyl)indole respectively, while by the latter method, (I) gave furo[2,3-*b*:5,4-*b*′]diindoles (XVIII, XXV). The compound (XXVII), which has the same planar structure as the product (XIX) obtained from folicanthine, was obtained by the lithium aluminium hydride reduction of (III).

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