mg. (73%) of small colorless needles, m.p. 201～202°. *Anal.* Calcd. for $C_{16}H_{20}N_2O$: C, 75.00; H, 7.81; N, 10.93. Found: C, 74.98; N, 7.85; N, 10.77.

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Summary

10-Methoxy-6,7-dihydro-12*H*-indolo[2,3-*a*]quinolizinium salts were prepared in ca. 90% yield through condensation of 6-methoxytryptophol tosylate with 2-bromopyridine, which is the best record so far described for this type of condensations. The above salt was hydrogenated to the octahydroindolo[2,3-*a*]quinolizine derivative.

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The Synthesis of 3-Spirooxindole Derivatives. IV.[*1] The Conversion of 3-Spirooxindole to Indole Derivative.

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In the previous paper of this series,¹⁾ there was reported a synthesis of the 3-spirooxindole (I), which was identified with the Julian's compound, m.p. 182°.²⁾ This identification conclusively established Belleau's formula (I)³⁾ for the above substance, to which Julian had given the formula (II).²⁾ Meanwhile, Julian reduced this compound with the limited amount of lithium aluminum hydride and then treated it with hydrochloric acid to obtain the indole derivative (III).²ᵇ⁾ Based upon the correct formula (I) for the starting material, this conversion is interpreted to progress as is indicated in the Chart (I→III), which may be accepted as a typical Wagner-Meerwein rearrangement.

These works prompted us to try the conversion of 3-spirooxindole (IV) to the indole derivative (VI) *via* the intermediate (V), as a preliminary for the chemical correlation of N-methylrhynchophyllane (X) with N-methyldihydrocorynantheane (XI).

Thus, the 3-spirooxindole (IV) which was prepared by us,⁴⁾ was subjected to the reduction with 3/4 molar equivalent of lithium aluminum hydride, followed by treatment of hydrochloric acid to afford a mixture of the crude bases, which were separated by chromatography. Elution with benzene gave colorless prisms, m.p. 58～60°, which were identified with the indoline (IX).⁴⁾ The combined fractions eluted with benzene-

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[*1] Part III, This Bulletin, **11**, 451 (1963).

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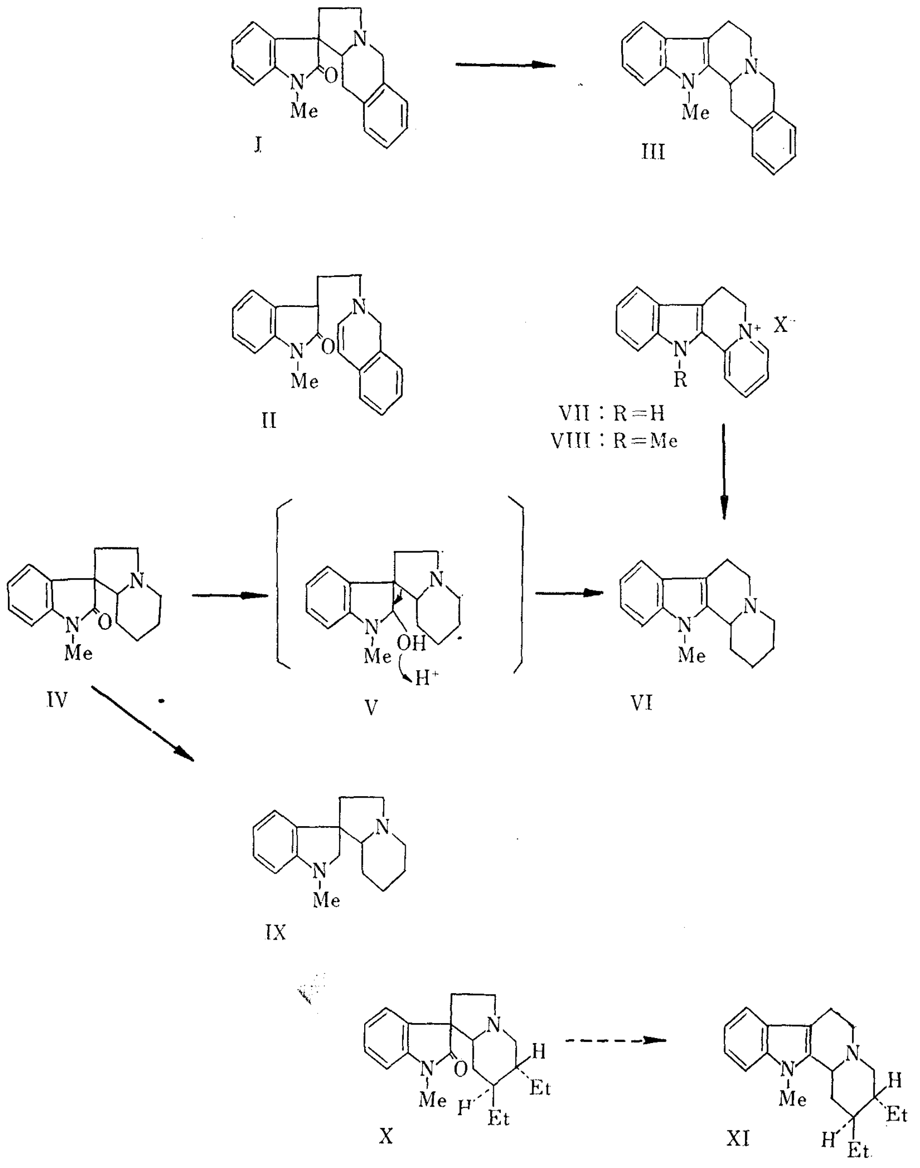

Chart 1.

ether (1:1) and subsequently with ether, afforded the colorless oil which formed a picrate, yellow prisms, m.p. 195~196°, purified from ethanol.

On the other hand, the indoloquinolizinium salt (VII)[5)] was methylated by the procedure of Swan[5b)] to yield VIII, which was hydrogenated with Adams' catalyst to afford a colorless oil, forming a picrate, yellow prisms, m.p. 198~199°, recrystallized from ethanol. The infrared absorption spectrum of the free base (VI) was identical with that of the foregoing product (VI) obtained from IV, and both picrates showed no depression on a mixed melting point determination.

These experiments suggested the possibility of chemical correlation of N-methylrhynchophyllane (X) with N-methyldihydrocorynantheane (XI). The studies on this problem are now in progress.

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Experimental[*3]

12-Methyl-1,2,3,4,6,7,12,12*b*-octahydroindolo[2,3-*a*]pyridocoline (VI)

a) By the Reduction of 1-Methylspiro[indoline-3,1'-indolizidine]-2-one (IV), followed by Rearrangement——To a solution of the 3-spirooxindole (IV, 200 mg.) in Et_2O (30 ml.) cooled to −10° by an ice-salt mixture, $LiAlH_4$ (28 mg., 3/4 molar equivalent calculated as 100% purity) was added in one portion under vigorous stirring, and the mixture was stirred, first for 30 min. at −10°, and then for 80 min. at room temperature. Subsequently, the mixture was gently refluxed for an additional 20 min., then 1 ml. of H_2O was added under ice-cooling, and the mixture was stirred for 30 min. The Et_2O was separated by decantation, and the insoluble resinous material was washed well with Et_2O. The combined Et_2O solution was dried over anhyd. Na_2SO_4 overnight, and the solvent was evaporated to leave 186 mg. of a pale yellow oil, which was dissolved in 10% HCl (5 ml.), and the resulting solution heated on a water bath for 30 min. On cooling, the solution was extracted with Et_2O and the aqueous layer was treated with charcoal, filtered and basified with K_2CO_3, followed by extraction with benzene. The benzene extract was washed with H_2O, and dried over anhyd. Na_2SO_4 overnight. The benzene was removed *in vacuo* to leave a pale yellow oil (156 mg.) which was subjected to alumina chromatography. Elution with benzene gave 32 mg. of colorless prisms, m.p. 58~60°, which were identified with indoline (IX).[4] The combined fractions eluted with benzene-Et_2O (1:1) and subsequently with Et_2O, afforded 70 mg. of a colorless oil, the IR spectrum of which was in good agreement with that of the sample prepared from VIII. This base set to color on standing 3 or 4 hr. and afterwards changed to yellow color acceleratively. The base formed a picrate, yellow prisms, m.p. 195~196° (decomp.). *Anal.* Calcd. for $C_{22}H_{23}N_5O_7$: C, 56.29; H, 4.90; N, 14.92. Found: C, 56.66; H, 5.21; N, 14.78.

b) By the Hydrogenation of 12-Methyl-6,7-dihydro-12*bH*-indolo[2,3-*a*]quinolizinium Salt (VIII)——To a solution of the iodide (VIII, X=I; 120 mg.) in EtOH (70 ml.) was added AgCl freshly prepared from 1 g. of $AgNO_3$, and the resulting mixture was refluxed for 3 hr. After filtration of AgI and the excess AgCl, the filtrate was treated with charcoal, filtered, and subjected to the hydrogenation over Adams' catalyst in the usual manner. After 3 hr., the catalyst was filtered off, and the EtOH was removed *in vacuo* to leave a residual oil which was dissolved in benzene, extracted with 10% HCl and the aqueous extract basified with K_2CO_3 liberated the based. The oil was taken up in benzene and worked up in the usual manner to yield a colorless oil which formed a picrate, yellow prisms, m.p. 198~199°, recrystallized from EtOH. The picrate showed no depression of the melting point on admixture with the for egoing picrate prepared by (a) method. *Anal.* Calcd. for $C_{22}H_{23}N_5O_7$: C, 56.29; H, 4.90. Found: C, 56.27; H, 5.22.

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Summary

The conversion of 1-methylspiro(indoline-3,1'-indolizine)-2-one to 12-methyl-1,2,3,4,6,7,12,12*b*-octahydroindolo[2,3-*a*]quinolizine is described as a preliminary for the chemical correlation of N-methylrhynchophyllane with N-methyldihydrocorynantheane.

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[*3] All melting points are not corrected.