einer Laktam-Bande bei 1680 cm^{-1} bestätigt. Erhitzte man jedoch XI mit 47% iger Bromwasserstoffsäure unter Rückfluß, spaltete die Ketal-Gruppe voraus und ergab unter Indolringschluß 1,2,3,4,12,12*b*-hexahydroindolo[2,3-*a*]chinolizin-6(7*H*)-on (XIII : Blättchen vom Schmp. 254~255° u. Zers. $C_{15}H_{16}ON_2$—Ber. : C, 74.97; H, 6.71; N, 11.66. Gef. : C, 74.52; H, 6.46; N, 11.87. IR ν_{max}^{KBr} cm^{-1} : 1605), welches durch Reduktion mittels $LiAlH_4$ in V übergeführt wurde. Die Konstitution von XIII wurde damit auch bestätigt.

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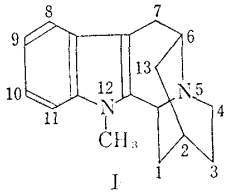
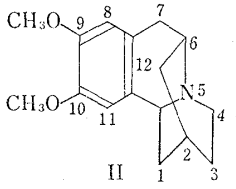
Synthesis of 12-Methyl-1,2,3,4,6,7,12,12*b*-octahydro-2,6-methanoindolo[2,3-*a*]quinolizine

In the present communication, the author wishes to report a synthesis of 12-methyl-1,2,3,4,6,7,12,12*b*-octahydro-2,6-methanoindolo[2,3-*a*]quinolizine (I), which possesses the fundamental skeleton of sarpagine (III).[1,2]



I



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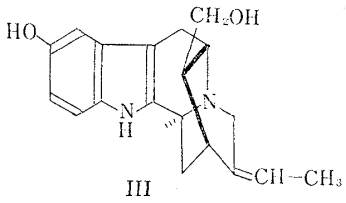
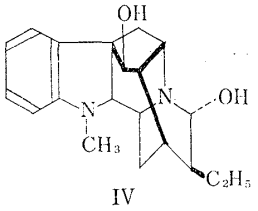
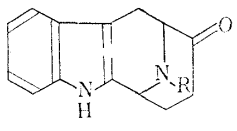


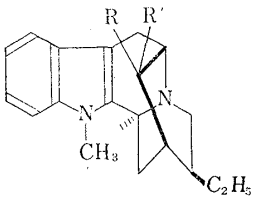
III



IV



V



VIa : R=CHO R′=H
VIb : R=H R′=CHO
VIIa : R=CH_2OH R′=H
VIIb : R=H R′=CH_2OH

Chart 1.

1) J.E. Saxton, in "The Alkaloids," ed. Manske, Vol. VII, p. 103 (1960). Academic Press, Inc., New York.
2) M.F. Bartlett, R. Sklar, W.I. Taylor, E. Schlittler, R.L.S. Amai, Peter Beak, N.V. Bringi, Ernest Wenkert : J. Am. Chem. Soc., 84, 622 (1962).

In my knowledge, no reports have been published on the synthesis of sarpagine and its congeners, and certain degradation products of ajmaline (Ⅳ),[1,2,3] *e.g.*, deoxyajmalal-A (Ⅵa) and -B (Ⅵb),[2,3] deoxyajmalol-A (Ⅶa) and -B (Ⅶb),[2] all of which have a peculiar pentacyclic ring system.

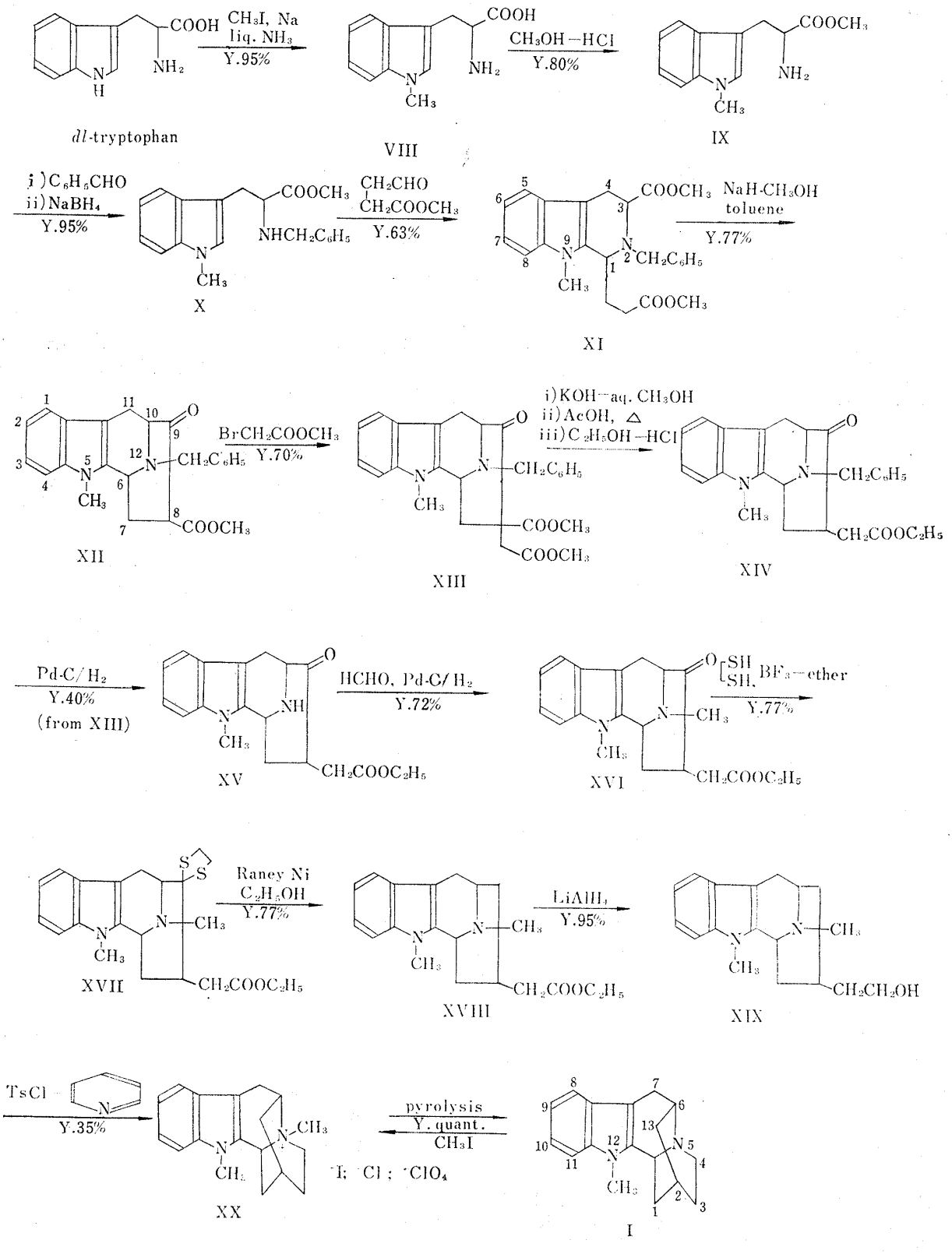


Chart 2.

In 1963 Hobson, *et al.*[4] reported syntheses of 1,2,3,4-tetrahydro-10-oxo-1,3-propano-β-carboline (V) and a number of its derivatives as useful intermediates for synthetical approaches to sarpagine and ajmaline groups.

Recently, the author reported[5] the synthesis of 9,10-dimethoxy-1,2,3,4,6,7-hexahydro-2,6-methano-11*bH*-benzo[*a*]quinolizine (II) as a preliminary to the synthesis of the title compound (I).

Thus, according to the synthetical route of II, I has now been synthesized from *dl*-tryptophan as shown in Chart 2.

Properties and analytical date of synthesized compounds in this work are given below.

1-Methyltryptophan[6] (VIII) : colorless plates (from EtOH-H_2O). m.p. 251~252° (decomp.). [lit. m.p. 250~251° (decomp.)]. *Anal.* Calcd. for $C_{12}H_{14}O_2N_2$: C, 66.04; H, 6.47; N, 12.84. Found : C, 65.97; H, 6.47; N, 12.83.

1-Methyltryptophan methyl ester (IX) : faint yellow viscous oil. HCl salt : colorless minute needles (from MeOH). m.p. 228~229° (decomp.). *Anal.* Calcd. for $C_{13}H_{17}O_2N_2Cl$: C, 58.10; H, 6.38; N, 10.42; Cl, 13.19. Found : C, 58.23; H, 6.42; N, 10.25; Cl, 13.38.

N-Benzyl-1-methyltryptophan methyl ester (X) : colorless viscous oil ($b.p._{1.0}$ 200~205°). HCl salt : colorless needles (from MeOH). m.p. 232° (decomp.). *Anal.* Calcd. for $C_{20}H_{23}O_2N_2Cl$: C, 66.94; H, 6.46; N, 7.81; Cl, 9.88. Found : C, 66.90; H, 6.40; N, 8.01; Cl, 10.18. Picrate : yellow needles (from MeOH). m.p. 176~177°. *Anal.* Calcd. for $C_{26}H_{25}O_9N_5$: C, 56.62; H, 4.57; N, 12.70. Found : C, 56.32; H, 4.52; N, 13.09.

Methyl 2-benzyl-3-methoxycarbonyl-9-methyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]-indole-1-propionate (XI) : α-isomer (major product) : colorless prisms (from MeOH). m.p. 144~145°. IR ν_{max}^{Nujol} cm^{-1} : 1730 (ester). β-isomer (minor product) : colorless plates (from MeOH). m.p. 195~196° (decomp.). IR ν_{max}^{Nujol} cm^{-1} : 1730, 1715 (ester). *Anal.* Calcd. for $C_{25}H_{28}O_4N_2$: C, 71.41; H, 6.72; N, 6.66; OMe, 14.76. Found : α-isomer : C, 71.09; H, 6.80; N, 6.66; OMe, 14.47. β-isomer : C, 71.12; H, 6.22; N, 7.06. Picrate : α-isomer : yellow-orange needles (from MeOH). m.p. 149~150°. β-isomer : yellow needles (from MeOH). m.p. 178~179° (decomp.). *Anal.* Calcd. for $C_{31}H_{31}O_{11}N_5$: C, 57.32; H, 4.81; N, 10.78. Found : α-isomer : C, 57.22; H, 4.74; N, 10.77. β-isomer : N, 11.01.

Methyl 5-methyl-9-oxo-12-benzyl-6,7,8,9,10,11-hexahydro-6,10-imino-5*H*-cycloöct[*b*]-indole-8-carboxylate (XII) : colorless plates (from MeOH-AcOEt). m.p. 150.5~151.5°. IR ν_{max}^{Nujol} cm^{-1} : 1670, 1625 (enol-form of β-keto-ester). *Anal.* Calcd. for $C_{24}H_{24}O_3N_2$: C, 74.20; H, 6.23; N, 7.21. Found : C, 74.23; H, 6.15; N, 7.15. Picrate : faint yellow needles (from AcOH). m.p. 207° (decomp.). *Anal.* Calcd. for $C_{30}H_{27}O_{10}N_5$: C, 58.34; H, 4.41; N, 11.34. Found : C, 58.78; H, 4.20; N, 11.32.

Methyl 5-methyl-8-methoxycarbonyl-9-oxo-12-benzyl-6,7,8,9,10,11-hexahydro-6,10-imino-5*H*-cycloöct[*b*]indole-8-acetate (XIII) : colorless syrup. Picrate : yellow-orange prisms (from MeOH). m.p. 171~172° (decomp.). *Anal.* Calcd. for $C_{33}H_{31}O_{12}N_5$: C, 57.47; H, 4.53; N, 10.16. Found : C, 57.56; H, 4.60; N, 10.16.

Ethyl 5-methyl-9-oxo-12-benzyl-6,7,8,9,10,11-hexahydro-6,10-imino-5*H*-cycloöct[*b*]-indole-8-acetate (XIV) : faint yellow syrup. HCl salt : colorless plates (from EtOH-ether). m.p. 210~211° (decomp.). *Anal.* Calcd. for $C_{26}H_{29}O_3N_2Cl$: C, 68.94; H, 6.45; N, 6.18; Cl, 7.83. Found : C, 68.82; H, 6.55; N, 6.14; Cl, 7.62.

Ethyl 5-methyl-9-oxo-6,7,8,9,10,11-hexahydro-6,10-imino-5*H*-cycloöct[*b*]indole-8-acetate (XV) : faint yellow prisms (from EtOH). m.p. 141.5~143°. IR ν_{max}^{Nujol} cm^{-1} : 3200 (N-H),

3) R.B. Woodward : Angew. Chem., **68**, 13 (1956).
4) J.D. Hobson, J. Raines, R.J. Whiteoak : J. Chem. Soc., **1963**, 3495.
5) N. Yoneda : This Bulletin, **12**, 1478 (1964).
6) E. Leete : J. Org. Chem., **23**, 631 (1958).

1725 (ester), 1685 (ketone). *Anal.* Calcd. for $C_{19}H_{22}O_3N_2$: C, 69.92; H, 6.79; N, 8.58. Foumd : C, 70.07; H, 6.61; N, 8.84.

Ethyl 9-oxo-5,12-dimethyl-6,7,8,9,10,11-hexahydro-6,10-imino-5*H*-cycloöct[*b*]indole-8-acetate (XVI) : colorless syrup.

Cyclic ethylene thioacetal (XVII) of XVI : colorless plates (from benzene-hexane). m.p. 154.5~156.5°. *Anal.* Calcd. for $C_{22}H_{28}O_2N_2S_2$: C, 63.43; H, 6.77; N, 6.72; S, 15.39. Found : C, 63.47; H, 6.27; N, 6.83; S, 15.26.

Ethyl 5,12-dimethyl-6,7,8,9,10,11-hexahydro-6,10-imino-5*H*-cycloöct[*b*]indole-8-acetate (XVIII) : colorless syrup.

5,12-Dimethyl-6,7,8,9,10,11-hexahydro-6,10-imino-5*H*-cycloöct[*b*]indole-8-ethanol (XIX) : colorless syrup. Methiodide : yellow-orange plates (from MeOH-ether). m.p. 230~231° (decomp.). *Anal.* Calcd. for $C_{19}H_{27}ON_2I \cdot H_2O$: C, 51.01; H, 6.53; N, 6.26; I, 29.04. Found : C, 50.54; H, 6.24; N, 6.41; I, 28.98.

5,12-Dimethyl-1,2,3,4,6,7,12,12*b*-octahydro-2,6-methanoindolo[2,3-*a*]quinolizinium (XX) -iodide : yellow-orange needles (from MeOH-ether). m.p. 250~252° (decomp.). *Anal.* Calcd. for $C_{18}H_{23}N_2I$: C, 54.42; H, 5.84; N, 7.05; I, 32.70. Found : C, 54.92; H, 5.81; N, 7.22; I, 32.54.

XX-perchlorate : pale yellow needles (from EtOH-ether). m.p. 217~218° (decomp.). *Anal.* Calcd. for $C_{18}H_{23}O_4N_2Cl$: C, 58.93; H, 6.32; N, 7.64; Cl, 9.67. Found : C, 59.12; H, 6.25; N, 7.69; Cl, 9.68. XX-chloride : colorless prisms (from MeOH-ether). m.p. 278~280° (decomp.). *Anal.* Calcd. for $C_{18}H_{23}N_2Cl$: N, 9.25; Cl, 11.71. Found : N, 9.27; Cl, 11.30.

12-Methyl-1,2,3,4,6,7,12,12*b*-octahydro-2,6-methanoindolo[2,3-*a*]quinolizine (I) : colorless prisms (from hexane). m.p. 142~143°. *Anal.* Calcd. for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99; N, 11.10; mol. wt., 252.36. Found : C, 80.61; H, 7.57; N, 11.26; mol. wt., 256 (micro Rast). UV λ_{max}^{EtOH} mμ (log ε) : 229~230 (4.60), 285 (3.90); shld. 278 (3.86); plat. 291~293 (3.86). λ_{min}^{EtOH} mμ (log ε) : 251 (3.40).

In the original attempt the compound (XIV) was directly converted to the corresponding ethylene thioketal derivative (compare XVII : N^2-$CH_2C_6H_5$ for N^2-CH_3), which was then submitted to Mozingo desulfurization reaction to afford (XVIII, as above). However, the product obtained under a variety of working conditions sofar investigated was always a mixture of compounds, which were probably produced by concomittant hydrogenolysis of debenzylation type around N^2. Attempted isolation of any one of the reaction products from the mixture invariably failed. This difficulty was, however, circumvented by working with N^2-CH_3 derivative (XVI) prepared from XIV as shown in Chart 2. Thus the synthesis of I should be more conveniently achieved starting from N,1-dimethyltryptophan, and work along this line is now under progress.

A synthetical approach to sarpagine and its derivatives and to degradation products of ajmaline is now under investigation according to this route.

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