UDC 547.944.7.02 : 582.675.1

100. Eiji Ochiai and Toshihiko Okamoto : The Aconite Alkaloids. XXIII.[1] The Structure of Ignavine. (3).

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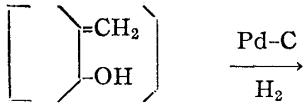
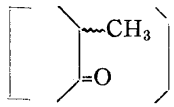
As was previously reported,[2,3] ignavine (I), $C_{27}H_{31}O_6N$, gave its alkamine, anhydroignavinol, (II), $C_{20}H_{25}O_4N$, on alkaline hydrolysis. The latter easily formed methiodide and on the Hofmann degradation, it gave des-N-methylanhydroignavinol (III), $C_{21}H_{27}O_4N$. This paper treats further studies on des-N-methylanhydroignavinol.

The existence of a terminal methylene group in ignavine (I) was proved by the analysis of its infrared spectrum and also by its oxidation with ozone.[3] On catalytic hydrogenation over palladised carbon, ignavine (I) gave a dihydro compound (IV), m.p. 173~175°,[2] $C_{27}H_{33}O_6N$. Later this reduction was reëxamined, and another dihydro compound and also a small amount of a ketone compound were obtained. The reduction products were carefully separated by alumina chromatography and as the first fraction, a ketone compound (V) of m.p. 260~262°, $C_{27}H_{29}O_5N$, was obtained. In the infrared spectrum it showed the band of six-membered ring ketone at 1692 cm^{-1} beside the acyl band at 1712 cm^{-1}. The second fraction (IV), $C_{27}H_{33}O_6N$, melted at 173~175°, showed no depression by admixture with the above-described dihydroignavine. The third fraction (VI), $C_{27}H_{31}O_5N$, showed m.p. 236~238° and these two products had only acyl bands at 1720 and 1715 cm^{-1}, respectively, so were considered as dihydro derivatives. The loss of one mole of water was observed in the formation of the ketone (V) and also the dihydro compound of m.p. 236~238°. The ketone (V) was designated as anhydrodihydroignavinone and the dihydro compound (VI) of m.p. 236~238° was named anhydrodihydroignavine. These results suggest the similarity of ignavine to hypognavine[4] or kobusine[5] which has allyl alcohol part of the type of C=Ċ-Ċ-OH in the structure. Further, to confiirm this point des-N-methylanhydroignavinol (III) was heated with 5% hydrochloric acid and a

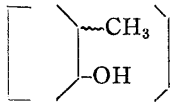


Ignavine (I)
$C_{27}H_{31}O_6N$

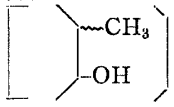
Pd-C
H_2



Anhydrodihydroignavinone (V)
$C_{27}H_{29}O_5N$



Dihydroignavine (IV)
$C_{27}H_{33}O_6N$



Anhydrodihydroignavine (VI)
$C_{27}H_{31}O_5N$

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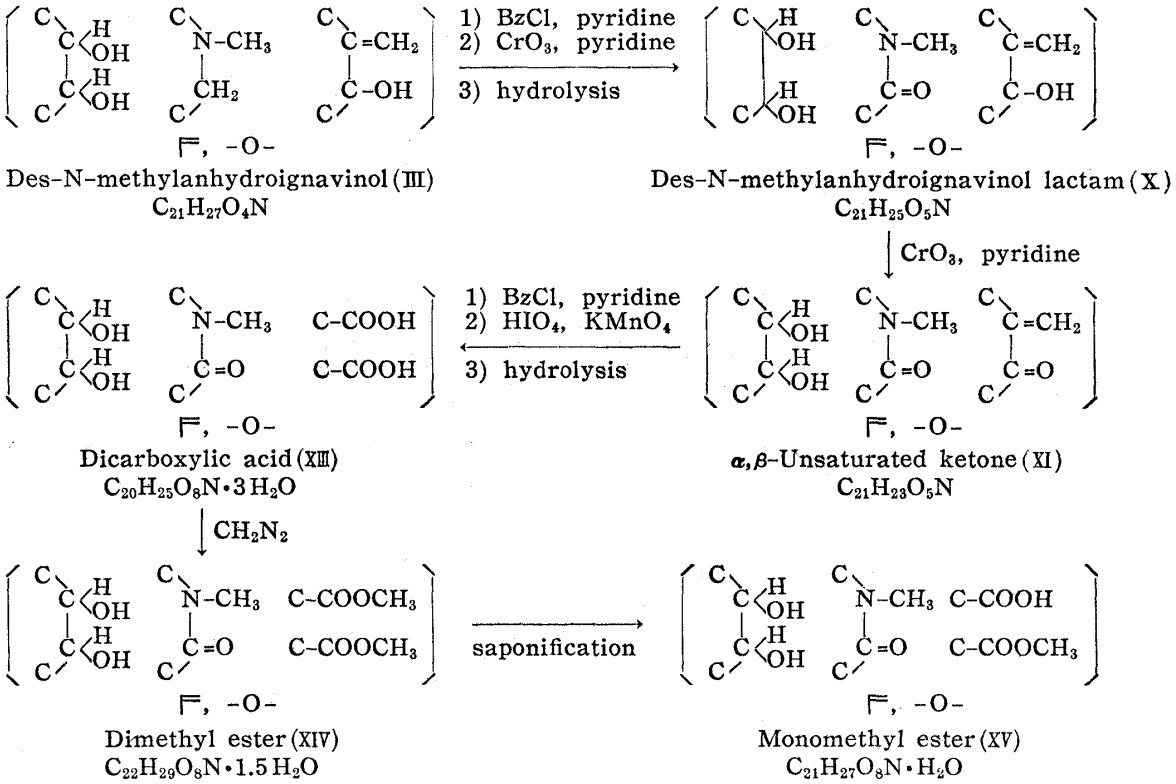
1) Part XXII : T. Okamoto, K. Mitsuoka : Yakugaku Zasshi, **79**, 214(1959).
2) E. Ochiai, *et al.* : *Ibid.*, **72**, 816 (1952).
3) E. Ochiai, *et al.* : This Bulletin, **1**, 60(1953).
4) S. Sakai : *Ibid.*, **5**, 1(1957).
5) T. Okamoto : *Ibid.*, **7**, 44(1959).

rearranged ketone (Ⅶ), $C_{21}H_{27}O_7N$, m.p. 227~230°, was obtained. This showed the band of a six-membered ring ketone at 1695 cm^{-1} in its infrared spectrum.

From these facts the existence of α-methylenecyclohexanol part in the structure of ignavine was confirmed.

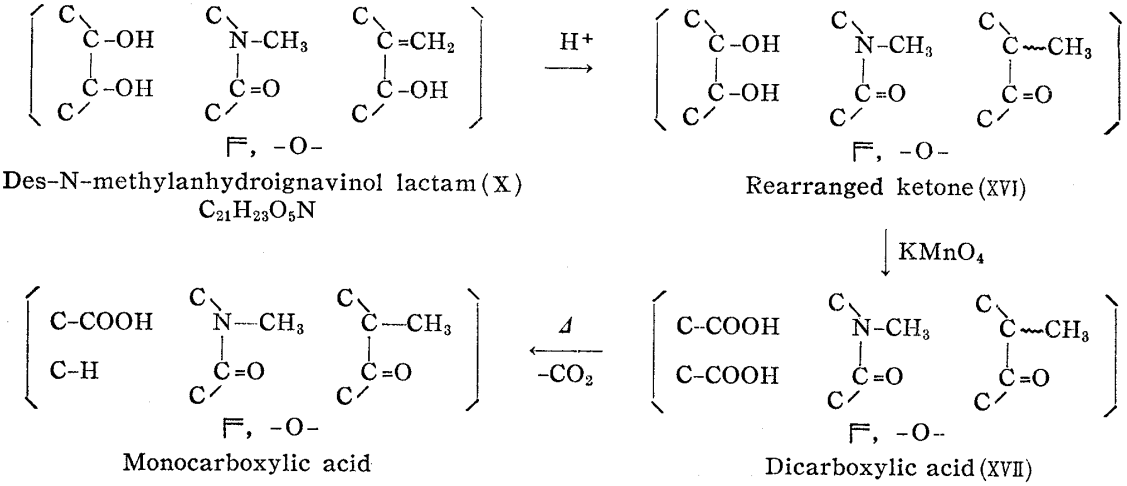
Des-N-methylanhydroignavinol (Ⅲ) gave a tribenzoyl derivative (Ⅷ), $C_{42}H_{39}O_7N$, m.p. 204~205°, by acylation with benzoyl chloride in pyridine. This tribenzoate was oxidized with chromium trioxide in pyridine at room temperature, the product was purified by alumina chromatography, and a lactam rtibenzoate (Ⅸ), $C_{42}H_{37}O_8N$, m.p. 267~269°, was obtained. Its infrared spectrum showed the band of a six-membered ring lactam at 1645 cm^{-1}. Alkaline hydrolysis of this compound gave a lactam (Ⅹ), $C_{21}H_{25}O_5N$, m.p. 306~308°(decomp.), which showed the band at 1615 cm^{-1}, corresponding to a six-membered ring lactam. Further oxidation of this lactam compound with chromium trioxide in pyridine gave the α,β-unsaturated ketone (Ⅺ), $C_{21}H_{23}O_5N$, m.p. 285~287°. Its infrared spectrum showed the bands at 1615 and 1687 cm^{-1}, corresponding to α,β-unsaturated ketone in a six-membered ring and it also showed the band of lactam in six-membered ring at 1590 cm^{-1}. This gave a dibenzoate (Ⅻ), $C_{35}H_{31}O_7N$, m.p. 200~203°, with benzoyl chloride in pyridine. Oxidation of this dibenzoate with Lemieux reagent[6] and subsequent hydrolysis gave a dicarboxylic acid (ⅩⅢ), $C_{20}H_{25}O_8N\cdot 3H_2O$, m.p. >340°, which showed the bands of carboxyl groups at 1690 and 1708 cm^{-1}, and also of a six-membered ring lactam at 1585 cm^{-1}. By titration with alkali solution it was further confirmed as dicarboxylic acid.

On standing with diazomethane in ether-methanol mixture the dicarboxylic acid gave a dimethyl ester (ⅩⅣ), $C_{22}H_{29}O_8N\cdot 1.5H_2O$, m.p. 257~259°. Its infrared spectrum showed the bands at 1708 and 1732 cm^{-1} corresponding to ester carbonyl groups and the band at 1620 cm^{-1} was observed as that of a six-membered ring lactam. By alkaline saponification, the dimethyl ester gave a monomethyl ester (ⅩⅤ), $C_{21}H_{27}O_8N\cdot H_2O$, m.p. 203~206°, and from these facts, one of the carboxyl groups of the dicarboxylic acid was considered as tertiary.



6) R. U. Lemieux, E. von Rudloff: Can. J. Chem., **33**, 1701, 1710(1955).

The presence of a glycol in anhydroignavinol was already proved by its periodate oxidation.[3] Oxidative cleavage of the glycol part was studied and the rearranged ketone of the lactam compound (X) was taken as the compound for the oxidation. The lactam compound (X) was heated with 5% hydrochloric acid and purification of the product by alumina chromatography gave an amorphous rearranged ketone (XVI) which showed the band at 1700 cm^{-1}, corresponding to a six-membered ring ketone. This ketone was oxidized with potassium permanganate at 0° to 5° and an amorphous dicarboxylic acid (XVII) was obtained. This acid eliminated carbon dioxide by pyrolysis at about 140°.



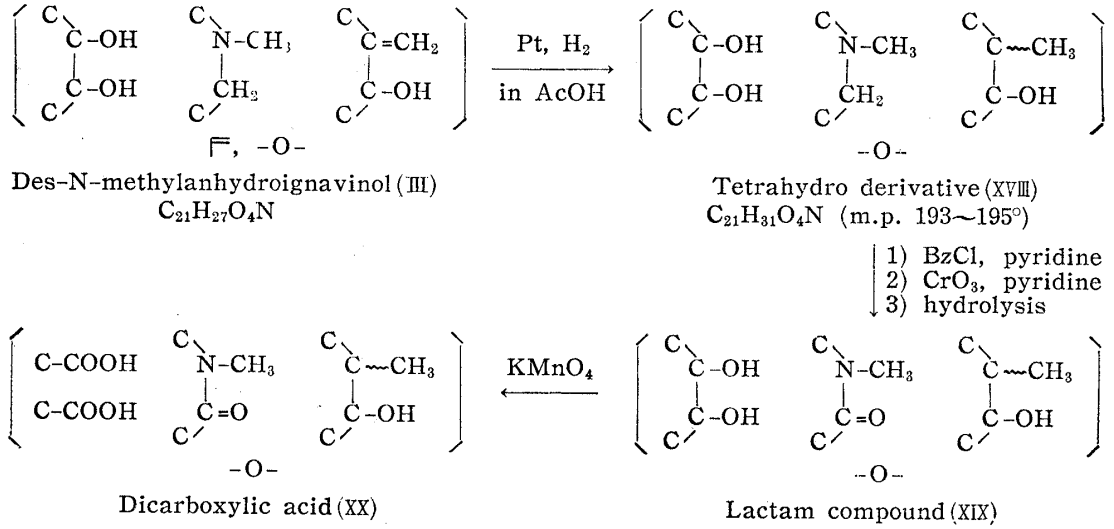
Des-N-methylanhydroignavinol lactam (X)
$C_{21}H_{23}O_5N$

Rearranged ketone (XVI)

Monocarboxylic acid

Dicarboxylic acid (XVII)

Further, a similar result was also obtained in the following case. Des-N-methylanhydroignavinol (III) was hydrogenated over platinum catalyst in acetic acid and after consuming two moles of hydrogen, isomers of tetrahydro derivative were obtained. One of the tetrahydro compound (XVIII) of m.p. 193~195°, $C_{21}H_{31}O_4N$, was oxidized to a lactam compound using the same methods obtaining des-N-methylanhydroignavinol lactam (X). The tetrahydro compound (XVIII) was acylated to benzoyl derivative, subsequently oxidized



Des-N-methylanhydroignavinol (III)
$C_{21}H_{27}O_4N$

Tetrahydro derivative (XVIII)
$C_{21}H_{31}O_4N$ (m.p. 193~195°)

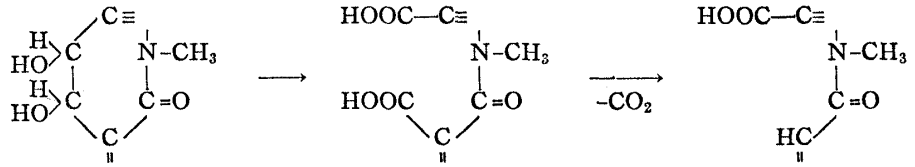
Dicarboxylic acid (XX)

Lactam compound (XIX)

Monocarboxylic acid (XXI)

to a lactam benzoate and followed by hydrolysis to give a lactam compound (XIX). This lactam was oxidized to a dicarboxylic acid (XX) with potassium permanganate. Although all compounds at each stage were amorphous, the final product (XX) was characterized by the analysis of its infrared spectrum and also by alkali titration. The infrared spectrum of (XX) showed the band of carboxyl group at 1708 cm^{-1} and the band corresponding to lactam group at 1637 cm^{-1}. The dicarboxylic acid (XX) gave a monocarboxylic acid (XXI) by pyrolysis at about 140~170°, losing carbon dioxide. This monocarboxylic acid showed the bands at 1712 and 1620 cm^{-1} which correspond to carboxyl and lactam groups, respectively. Further this acid (XXI) was confirmed as a monocarboxylic acid by titration.

These easy elimination of carbon dioxide suggests the presence of a malonamide structure in the acids (XVII, XX) and the partial structure around nitrogen should be represented as follows :



The authors are indebted to Dr. J. Matsumura of Hokuriku Hygienic Chemical Laboratory for his kind help for the collection of aconite roots. They are also indebted to Mr. K. Tanikawa of this Faculty for the determination of infrared spectra and to the members of the Central Microanalysis Room of this Faculty for microanalyses.

Experimental

Catalytic Reduction of Ignavine over Pd-C—300 mg. of ignavine was reduced over Pd-C (prepared from 5 cc. of 1% $PdCl_2$ solution and 50 mg. of carbon) in MeOH and 12.5 cc. of hydrogen was consumed in 2 hr. at 15° (calcd. for 1 mole of hydrogen, 14.4 cc.). After filtration of the catalyst, the solvent was evaporated and 274 mg. of resinous product was obtained. This was separated by alumina chromatography (Al_2O_3, 10 cc.) using $CHCl_3$ (containing 1% of MeOH) as the solvent.

Fract. No.	Product	
	mg.	m.p.(°C)
1~ 9	6	260~262
10~12	24	170~240 (mixture)
13~18	95	173~175
19~28	70	170~220 (mixture)
29~33	29	230~235

Fraction Nos. 1~9, m.p. 260~262°, was recrystallized from acetone to needles, m.p. 260~262°. IR λ_{max}^{Nujol} cm^{-1} : 1695 (C=O in six-membered ring), 1710 (ϕ-CO). *Anal.* Calcd. for $C_{27}H_{29}O_5N$: C, 72.46; H, 6.53. Found : C, 72.15; H, 7.11.

Fraction Nos. 13~18, m.p. 173~175°, was again purified by alumina chromatography and recrystallized from acetone to needles, m.p. 173~175°. IR λ_{max}^{Nujol} 1718 cm^{-1} (ϕ-CO). *Anal.* Calcd. for $C_{27}H_{31}O_5N$: C, 69.36; H, 7.11. Found : C, 68.91; H, 7.35.

Fraction Nos. 29~33, m.p. 230~235°, was purified again by alumina chromatography and recrystallized from acetone to prisms, m.p. 236~238°. IR λ_{max}^{Nujol} 1718 cm^{-1} (ϕ-CO). *Anal.* Calcd. for $C_{27}H_{31}O_5N$: C, 72.14; H, 6.95. Found : C, 72.37; H, 7.81.

Rearrangement of Des-N-methylanhydroignavinol (III) to the Ketone Compound (VII)—100 mg. of (III) was heated with 5% HCl on a steam bath for 3 hr., after evaporation of HCl, NH_4OH was added, and extracted with $CHCl_3$-MeOH mixture. The residue was purified by chromatography on alumina, using $CHCl_3$ (MeOH, 3~6%) as the solvent.

Fract. No.	Product	
	mg.	m.p.
1~ 5	71	225~230°
6~18	14	amorphous

The fraction Nos. 1~5 was recrystallized from CH_2Cl_2 to needles, m.p. 228~230°. IR λ_{max}^{Nujol} 1695 cm^{-1} (six-membered ring ketone). *Anal.* Calcd. for $C_{21}H_{27}O_4N$: C, 70.56; H, 7.61. Found : C, 69.70; H, 7.54.

Hydrochloride : Needles from MeOH-acetone mixture, m.p. 257~259°(decomp.). *Anal.* Calcd. for $C_{21}H_{29}O_4N \cdot HCl \cdot H_2O$: C, 61.00; H, 7.50. Found : C, 60.97; H, 7.71.

Oxidation of Tribenzoyl-des-N-methylanhydroignavinol (VIII) to the Lactam Tribenzoate (IX)—To a suspension of CrO_3 (400 mg.) in pyridine (5 cc.), 500 mg. of (VIII) was added, the mixture was allowed to stand over night, poured into water, and extracted with CH_2Cl_2-MeOH mixture. After removal of the solvent the residue was purified by passing through Al_2O_3 in CH_2Cl_2 solution. The residue was recrystallized several times from MeOH and gave needles of m.p. 267~269°. Yield, 290 mg. IR λ_{max}^{Nujol} cm^{-1} : 1720 (ϕ-CO), 1690 (six-membered ring lactam). *Anal.* Calcd. for $C_{42}H_{37}O_8N$: C, 73.78; H, 5.45. Found : C, 73.33; H, 5.46.

The mother liquid of (IX) was separated by alumina chromatography and as a less-adsorbed fraction a small amount of another product was separated. This was recrystallized from acetone to needles, m.p. 237~239°. *Anal.* Calcd. for $C_{42}H_{37}O_8N \cdot H_2O$: C, 71.80; H, 5.56. Found : C, 71.90; H, 5.42.

Hydrolysis of the Lactam Tribenzoate (IX) to the Lactam (X)—200 mg. of the lactam tribenzoate (IX) was heated in alkali solution (100 mg. KOH, in 10 cc. MeOH) for 30 min. on a steam bath. After removal of the solvent 10 cc. of water was added and this solution was passed through Amberlite IR-120 (5 cc.) and extracted with ether. The aqueons layer was concentrated and evaporated *in vacuo* the residue was recrystallized from a small amount of water and gave prisms of m.p. 306~308° (decomp.). IR λ_{max}^{Nujol} 1615 cm^{-1} (six-membered ring lactam). *Anal.* Calcd. for $C_{21}H_{25}O_5N$: C, 67.90; H, 6.78. Found : C, 67.55; H, 7.89.

Oxidation of the Lactam (X) to α,β-Unsaturated Ketone (XI)—To a suspension of CrO_3 (200 mg.) in pyridine (10 cc.), 300 mg. of the lactam (X) was added, the mixture was allowed to stand over night, poured into water, and extracted with $CHCl_3$-MeOH mixture. After evaporation of the solvent the residue (312 mg.) was separated by alumina chromatography using $CHCl_3$ (5% MeOH) as the solvent.

Fract. No.	Product	
	mg.	m.p.
1~ 7	39	amorphous
8~11	101	280~285°
12~20	9	amorphous

Fraction Nos. 8~11 was recrystallized from MeOH to plates, m.p. 285~287° (negative to Tollens' reagent). IR λ_{max}^{Nujol} cm^{-1} : 1590 (lactam in six-membered ring), 1615, 1685 (α,β-unsaturated ketone). *Anal.* Calcd. for $C_{21}H_{23}O_5N \cdot H_2O$: C, 65.10; H, 6.50. Found : C, 64.07; H, 6.59.

Fraction Nos. 1~7 was positive to Tollens' reagent and also triphenyltetrazolium chloride, so were considered as a ketol.

Acylation of α,β-Unsaturated Ketone (XI) to Dibenzoate (XII)—A solution of 20 mg. of the α,β-unsaturated ketone (XI) dissolved in 2 cc. of pyridine, added with 100 mg. of BzCl, was allowed to stand over night, poured into water, and a small amount of NH_4OH was added. After standing for 30 min., the mixture was extracted with $CHCl_3$, purified by alumina chromatography using CH_2Cl_2 as the solvent, and the benzoate was obtained as needles from acetone, m.p. 200~203°. Yield, 15 mg. *Anal.* Calcd. for $C_{35}H_{31}O_7N$: C, 72.77; H, 5.41. Found : C, 72.31; H, 6.04.

Oxidation of the Dibenzoate (XII) to the Dicarboxylic Acid (XIII)—To 16 mg. of the dibenzoate (XII) dissolved in 2 cc. of pyridine, $NaIO_4$ solution (45 mg. $NaIO_4$ in 2 cc. H_2O) was added. To this clear solution $KMnO_4$ solution (2 mg. $KMnO_4$ in 2 cc. H_2O) was added, allowed to stand over night, a small amount of AcOH was added, and the reaction mixture was evaporated to dryness *in vacuo* at below 50°. The residue was extracted several times with 1% Na_2CO_3 solution (10 cc.) at room temperature. After filtration, the solution was acidified with 10% HCl and the separated amorphous-precipitate (10 mg.) was collected.

76 mg. of the above-described precipitated acid was hydrolysed by heating in KOH-MeOH solution (100 mg. KOH in 10 cc. MeOH) on a steam bath for 20 min. After removal of the solvent, the residue was dissolved in water, the solution was passed through Amberlite IR-120, and the effluent solution was extracted with ether. The water layer was evaporated to dryness and the residue was crystallized from a small amount of water to prisms, m.p. over 340°. During determination of the melting point, no change in crystals was observed. IR λ_{max}^{Nujol} cm^{-1} : 1585 (six-membered ring lactam), 1690, 1708 (carboxyl groups). *Anal.* Calcd. for $C_{20}H_{23}O_8N \cdot 3H_2O$: C, 52.29; H, 6.32. Found : C, 52.71; H, 5.93. Titration of the dicarboxylic acid : Sample, 8.549 mg. 0.02*N* NaOH (F=1.00), 1.97 cc. Calcd. for 2-COOH : 1.86 cc.

***Dimethyl* Ester (XIV) of the Dicarboxylic Acid (XIII)**—To a suspension of 10 mg. of the dicarboxylic acid in 5 cc. of ether-MeOH mixture (ca. 30% MeOH), excess of CH_2N_2 was added, the mix-

ture was allowed to stand over night, and trace of undissolved material was filtered off. After removal of the solvent the residue was purified by alumina chromatography using $CHCl_3$ (2% MeOH) as the solvent and crystallized from water as needles, m.p. 255~257°. *Anal.* Calcd. for $C_{22}H_{29}O_8N \cdot 1.5H_2O$: C, 57.39; H, 6.52. Found : C, 57.62; H, 6.43.

Saponification of the Dimethyl Ester (XIV) to the Monomethyl Ester (XV)—To a solution of 7.869 mg. of the dimethyl ester in 10 cc. of MeOH, 10 cc. of 0.05*N* NaOH, (F=1.009) was added, heated on a steam bath for 1.5 hr., concentrated to 1 cc., and 10 cc. of water was added. The solution was titrated with 0.05*N* HCl (F=1.031) : 9.05 cc. Blank test with the same condition : 9.30 cc. The difference : 0.25 cc. Calcd. for 1-COOH : 0.33 cc. The titrated solution was passed through Amberlite IR-120, evaporated to dryness *in vacuo*, and the residue was recrystallized from water as needles, m.p. 203~206°. *Anal.* Calcd. for $C_{21}H_{25}O_8N \cdot H_2O$: C, 57.66; H, 6.22. Found : C, 57.91; H, 7.97.

Rearrangement of the Lactam (X) to the Ketone (XVI)—A mixture of 80 mg. of the lactam in 5 cc. of 5% HCl was heated on a steam bath for 2 hr. After evaporating to dryness, the residue was purified by alumina chromatography and amorphous ketone (51 mg.) was obtained. IR λ_{max}^{Nujol} 1700 cm^{-1} (six-membered ring ketone).

Oxidation of the Ketone (XVI) to the Acid (XVII)—To a solution of 26 mg. of the ketone (XVI) dissolved in 2 cc. of 5% NaOH, 60 mg. of $KMnO_4$ was added in 2 hr. at 0° to 5°. The color of $KMnO_4$ still remained after 30 min. of standing. After decomposition of excess of $KMnO_4$ the reaction solution was passed through Amberlite IR-120, the effluent was evaporated to dryness *in vacuo*, and an amorphous acid product was obtained. This acid (25 mg.) was heated in a stream of N_2 and eliminated gas was bubbled through 10 cc. of 0.02*N* $Ba(OH)_2$ solution. At ca. 140°, elimination of CO_2 was observed. The acid was heated for 1 hr. at 140~170° and the $Ba(OH)_2$ solution was titrated with 0.02*N* HCl (F=1.06); 6.00 cc. Blank test : 8.25 cc. The difference : 2.25 cc. Calcd. for 1 mole CO_2 : 6.07 cc.

Reduction of Des-N-methylanhydroignavinol—400 mg. of des-N-methylanhydroignavinol (III) was hydrogenated over Pt catalyst (PtO_2 : 50 mg.) in 10 cc. of AcOH and 59 cc. of hydrogen was consumed in 4 hr. at 20° (Calcd. for 2 moles of hydrogen : 54 cc.). After filtering off the catalyst, the solvent was evaporated to dryness. A small amount of NH_4OH solution was added to the residue and the product was taken up in $CHCl_3$ (containing ca. 3% of MeOH). After evaporation of the solvent the residue (380 mg.) was separated by alumina chromatography (Al_2O_3 : ca. 20 cc.) using $CHCl_3$ (containing 2~3% MeOH) as the solvent.

Fract.No.	Product	
	mg.	m.p.(°C)
1~ 5	—	—
6~ 9	37	165~175
10~12	81	amorphous
13~29	200	185~190
30~40	51	215~218
41~	2	—

Fractions 30~40 were collected and recrystallized from acetone to needles of m.p. 218~220°. *Anal.* Calcd. for $C_{21}H_{31}O_4N$: C, 69.81; H, 8.59. Found : C, 69.77; H, 9.80.

Fractions 13~29 (200 mg.) were collected and separated again by alumina chromatography (Al_2O_3: ca. 20 cc.) using $CHCl_3$ (MeOH, 2%) as the solvent.

Fract. No.	Product	
	mg.	m.p.(°C)
1~ 4	—	—
5~ 8		amorphous
9	70	175~185
10~16	64	193~195
17~	21	180~185

Fractions 10~16 were collected and recrystallized from acetone to needles of m.p. 193~195°. *Anal.* Calcd. for $C_{21}H_{31}O_4N$: C, 69.81; H, 8.59. Found : C, 69.54; H, 9.07. On further hydrogenation over Pt catalyst in AcOH this compound did not consume any more hydrogen.

Oxidation of the Tetrahydro Compound (XVIII) to the Dicarboxylic Acid (XX)—To a solution of 80 mg. of the tetrahydro compound (XVII), m.p. 193~195°, in 3 cc. of pyridine, 0.2 cc. of BzCl was added, the mixture was allowed to stand over night at room temperature, and heated on a steam bath for about 2 hr. The reaction mixture was diluted with water and NH_4OH solution added. The product was taken up in $CHCl_3$, purified by alumina chromatography using $CHCl_3$ as the solvent, and amorphous benzoate was obtained. Yield, 77 mg.

The benzoate (77 mg.) was added to a suspension of CrO_3 (80 mg.) in pyridine (5 cc.), allowed to

stand over night at room temperature, diluted with water, and a small amount of NH_4OH was added. The crude product was taken up in $CHCl_3$ and after evaporation of the solvent the residue was purified by alumina chromatography to give an amorphous product. Yield, 50 mg.

Fifty mg. of the above compound was hydrolyzed with MeOH-KOH solution (50 mg. of KOH in 10 cc. of MeOH) heating on a steam bath for about 30 min. The reaction solution was diluted with water and passed through Amberlite IR-120 column. After extraction of the resulting BzOH with ether the aqueous solution was evaporated to dryness *in vacuo* and 12 mg. of amorphous neutral compound was obtained.

This neutral compound (XIX)(12 mg.) was dissolved in pyridine-water mixture (1 cc. of pyridine and 3 cc. of water) and 13 mg. of $KMnO_4$ was added during 2 hr. at 0° to 5°. After standing at room temperature for further 30 min., the color of MnO_4^- was still observed. After filtration of MnO_2, the reaction solution was evaporated to dryness *in vacuo* at below 50°. The residue was dissolved in water, passed through Amberlite IR-120 column, and the aqueous solution was evaporated to leave an amorphous dicarboxylic acid (XX). Yield, 9 mg. This acid was titrated with 0.02*N* NaOH (F=1.00) and 2.35 cc. of alkali was consumed. Calcd. for 2-COOH : 2.22 cc. IR λ_{max}^{KBr} cm^{-1} : 1708(COOH), 1637 (>N-CO-).

Pyrolysis of the Dicarboxylic Acid (XX)—7 mg. of the acid (XX) was heated in a stream of N_2 and eliminated gas was bubbled through $Ba(OH)_2$ solution. From about 140° precipitation of $BaCO_3$ was observed. After heating up to 170° for about 1 hr., the residue (5.2 mg.) was dissolved in 20% MeOH, and titrated with 0.02*N* NaOH solution (F=1.00). 0.65 cc. of NaOH solution was consumed. Calcd. for 1-COOH : 0.72 cc. IR λ_{max}^{KBr} cm^{-1} : 1712 (COOH), 1620 (>N-CO-).

Summary

The presence of α-methylenecyclohexanol grouping in ignavine or des-N-methylanhydroignavinol was proved by rearrangement reaction to ketone. Oxidative cleavage of the cyclohexanol ring in des-N-methylanhydroignavinol gave a dicarboxylic and one of the carboxyl groups in this acid was confirmed as tertiary. α-Glycol group which is another functional group in des-N-methylanhydroignavinol was also cleaved by oxidation to give a dicarboxylic acid and the glycol was proved to exist at carbons γ ond δ to the nitrogen.

(Received December 22, 1958)

UDC 547.944.7.02

101. Eiji Ochiai and Toshihiko Okamoto : Aconite Alkaloids. XXIV.[1] The Structure of Ignavine. (4).

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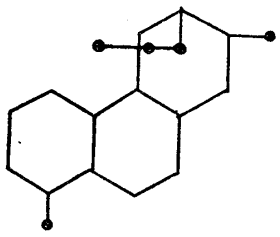
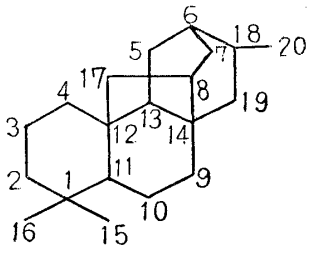
Previously, the authors reported the isolation of an alkylphenanthrene of m.p. 89~90°, $C_{19}H_{20}$, as a dehydrogenation product of anhydroignavinol,[2] $C_{20}H_{25}O_4N$. Recently, this alkylphenanthrene was identified by syhthesis as 1,7-dimethyl-6-propylphenanthrene.[3]



(I)



(II)

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1) Part XXIII : This Bulletin, **7**, 550(1959).

2) E. Ochiai, *et al.* : *Ibid.*, **2**, 388(1954).

3) E. Ochiai, *et al.* : *Ibid.*, **6**, 327(1958).