*Studies on Pelletierine. II. On the Structure of the So-called Pelletierine Proposed by Hess**,***

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As reported in the previous paper[1], the author has isolated pelletierine by tracing the same method as that of Hess and Eichel and has compared it with synthetic samples of 3-(2-piperidyl)-propionaldehyde and 1-(2-piperidyl)-2-propanone in the form of urethane, as the result of which he has reached the conclusion that pelletierine is the same as isopelletierine, 1-(2-piperidyl)-2-propanone.

But the problem remains that the chemical reactions of pelletetierine, on the basis of which Hess and Eichel have assigned to it the structure of 3-(2-piperidyl)-propionaldehyde, should be explained with isopelletierine.

The most important reactions used by them for the determination of the structure of pelletierine were the following two[2]:

1) $C_8H_{15}ON$ (pelletierine) $\xrightarrow{H_2NNH_2}$ $C_8H_{17}N_3$ $\xrightarrow{EtONa}$ $C_8H_{17}N$ (coniine)

2) $C_8H_{15}ON$ (pelletierine) $\xrightarrow{H_2NOH}$ $C_8H_{16}ON_2$ $\xrightarrow{PCl_5}$ $C_8H_{14}N_2$ (I) $\xrightarrow{KOH\text{-}EtOH,\ HCl\text{-}EtOH}$ the compound II, assumed to be ethyl 3-(2-piperidyl)-propionate hydrochloride

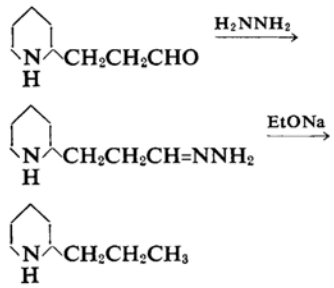
* This work was partly presented at the 12th Annual Meeting of the Chemical Society of Japan, April 4, 1959.

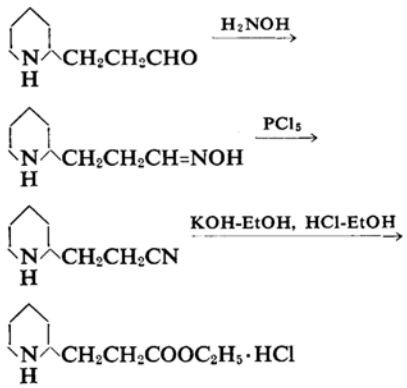
** Immediately before the publication of this paper, the author received a publication of the *J. Am. Chem. Soc.*, in which R. L. Augustine reported the rearrangement of isopelletierine-oxime obtaining the same results; ibid., **81**, 4664 (1959).

1) S. Kuwata, This Bulletin, **33**, 1668 (1960).

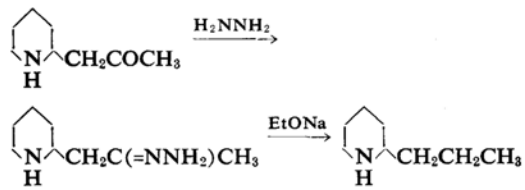
2) K. Hess and A. Eichel, *Ber.*, **50**, 1192 (1917).

Assigning the aldehyde structure to pelletierine, they have explained these reactions as follows:

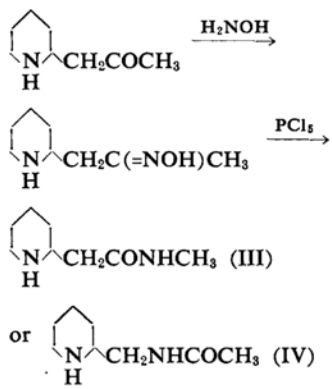
3) 

4) 

In reaction 1, the aldehyde may be replaceable by the ketone (isopelletierine) with the same final reaction product:



But in reaction 2, the product will be entirely different according to the structure of the starting material. Although the production of nitrile is expected from the aldehyde, from the ketone the amide III or IV will be obtainable by the Beckmann rearrangement:



Then, if the compound I is nitrile, as Hess has evaluated, the reaction must involve a skeletal rearrangement which has never been observed hitherto. Or if Hess' evaluation is incorrect, the question as to what structure should be assigned to it remains.

In order to clarify these situations the author has traced reaction 2 using isopelletierine-oxime under the same conditions described by Hess. Thus isopelletierine-oxime was treated with freshly sublimed phosphorus pentachloride in phenetole. The reaction proceeded, as described in the literature[2], with remarkable evolution of heat, and a brown syrupy material was produced, from which, after rectification, the compound which boiled at 104~106°C at 15 mmHg was obtained. When it was purified through picrate, a colorless liquid, boiling at 102~103°C at 10 mmHg, was obtained. This material showed complete agreement with the compound I that Hess and Eichel had obtained from pelletierine-oxime; the comparison between the two is shown in Table I.

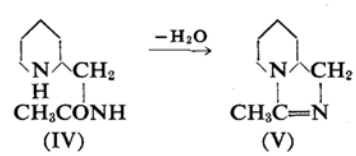
Table I. The properties of the compounds obtained from the reaction of oxime and rhosphorus pentoxide

Oxime	Molecular formula	B. p., °C (mmHg)	M. p. of picrate, °C
Isopelletierine-oxime	$C_8H_{14}N_2$	104~106(15) 102~103(10)*	174~175
Pelletierine-oxime[2]	$C_8H_{14}N_2$	105~108(15) 104~106(15)*	175~176

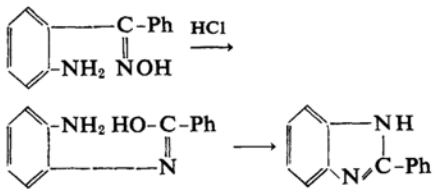
* Purified through picrate.

Thus it was ascertained that the reaction is reproducible with isopelletierine.

This compound I cannot be nitrile, for its infrared spectrum shows no absorption between 4.0 μ and 5.0 μ. It is also certain from analytical data that this compound I is neither the amide III nor IV, though the most probable reaction in this case may be the Beckmann rearrangement. On comparing the two formulae, $C_8H_{14}N_2$ of the compound I, and $C_8H_{16}ON_2$ of the amide, it will be easily seen that the difference is just one molecule of water. This fact may allow one to suppose that the compound I may be producible by intramolecular dehydration of the amide, produced by the Beckmann rearrangement of the keto-oxime. Such a dehydration is difficult sterically with formula III, but with formula IV, the following ring closure may be brought on:

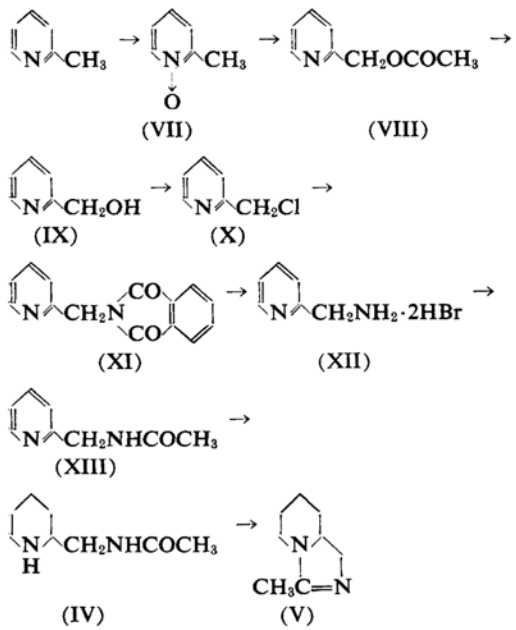


An analogous dehydration has been illustrated, in fact, with *o*-aminobenzophenoneoxime, which provides benzenylphenyleneamidine by the Beckmann rearrangement according to the following scheme[3]:



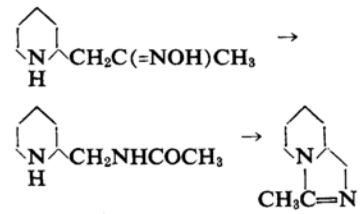
For the purpose of confirming the correctness of this assumption, 2-acetamidomethylpiperidine (IV) was synthesized by another route, and its dehydrative cyclization was attempted by treating it with phosphorus oxychloride, according to the method of Bower[4] (Eq. 1).

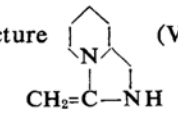
Eq. 1

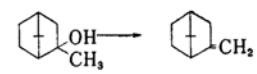


The compound V thus obtained boiled at 103～106°C at 11 mmHg and its picrate melted at 174～175°C. This was never depressed when it was mixed with the picrate of I. The identity of both picrates was also confirmed by the Debye-Scherrer diagram.

From these results, the author thinks that the real structure of the compound I, to which Hess and Eichel assigned 3-(2-piperidyl)-propionitrile, should be represented by V, and the reaction should be explained as shown in the following scheme:



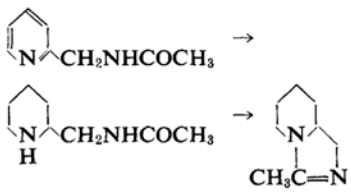
An alternative structure  (VI), however, may also be assumable for the compound I, because such a structure, having the terminal vinyl group, can be seen in some cases as α-fenchene from methyl-α-fenchocamphorol by intramolecular dehydration[5]:



However, on treating the compound I with ozone, no formaldehyde can be detected, so structure V, and not VI, should be assigned to this compound. The fact that its near infrared spectrum shows no absorption at ca. 1640 mμ and ca. 2130 mμ corresponding to $CH_2=C\langle$[6], may also support this conclusion.

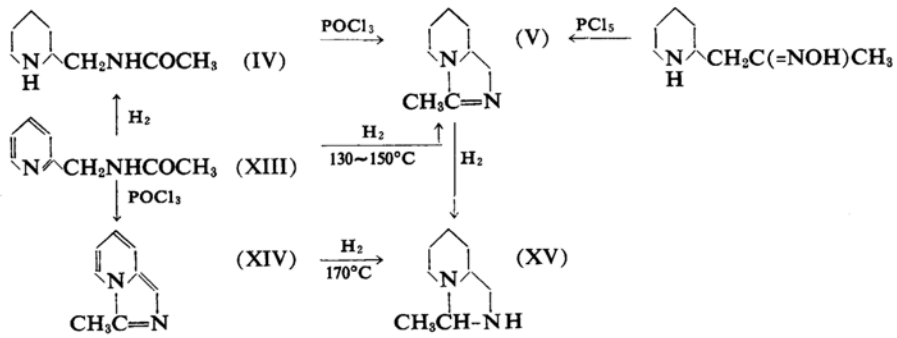
Another proof of structure V for this substance was also found in another way. When this compound was reduced catalytically, a colorless liquid, b. $p._{14}$ 85～100°C, which gave crystalline styphnate of m. p. 183～185°C, was obtained. This compound proved identical, by the mixed melting point of both the styphnates, with 2-methyl-1, 3-diazabicyclo[4 : 3 : 0]-nonane obtained by reducing 3-methyl-2 ; 3a-diazaindene catalytically.

The compound V was also found to be producible when 2-acetamidomethylpyridine was hydrogenated in ethanol at 130～150°C over Raney nickel, the reaction of which would probably be represented by the scheme:



This fact may be a proof that *N*-acetamidomethylpiperidine can be easily cyclized into the bicyclic compound V. The relationship among these bicyclic compounds will be shown diagramatically as follows.

3) J. Meisenheimer and H. Meis, *Ber.*, **57**, 289 (1924).
4) J. D. Bower and R. G. Ramage, *J. Chem. Soc.*, **1955**, 2834.
5) J. L. Simonsen, "The Terpenes", Vol. II, Cambridge University Press (1949), p. 540.
6) Private communication from Mr. M. Nishikawa of the Research Laboratory, Takeda Pharmaceutical Industries, Ltd.; cf. R. H. Holman, *Anal. Chem.*, **28**, 1533 (1956); W. Kaye, *Spectrochimica Acta*, **6**, 257 (1954).



Hess and Eichel treated their "nitrile", the compound I, with alcoholic potash, then with alcoholic hydrochloric acid, and obtained the compound II, which they believed to be ethyl 3-(2-piperidyl)-propionate hydrochloride on the basis of its analytical data and the comparison of the melting points of both the compounds as well as their gold salts. On re-examining their description, one will see that these evidences have some weak points. It is true that analytical data given by them, C, 54.39; H, 9.10, agree well with those for the ester hydrochloride (C, 54.10; H, 9.08), but, those of N and Cl are not given by them. The comparison between the melting points is also not decisive, because it is not dependent on the mixed melting point method. From these situations it seems necessary to re-examine the nature of the hydrolysis product obtained by Hess and Eichel from their "nitrile".

Thus the author wanted to trace their experiments as accurately as possible, but their description of the reaction conditions is not so definite. They state, "Das Nitril wurde mit einer 5-prozentigen alkoholischen Kaliumhydroxydlösung kurze Zeit auf dem Wasserbade erwärmt" and "1 Stunde mit alkoholischer Salzsäure gekocht." In alkali treatment, the volume of alkali solution, the temperature and the reaction time, and in acid treatment the concentration of hydrochloric acid and its volume, are not definite. Thus the reaction was carried out by varying the conditions, and various results were obtained, which are summarized in Table II. Unfortunately in all these cases no crystalline product corresponding to Hess' "ethyl 3 (2-piperidyl)-propionate hydrochloride" could be isolated, but in one case yellow crystalline gold salt (m. p. about 90~95°C, C, 18.51; H, 3.00; Au, 48.40) was obtained from the semisolid hydrolyzate. On recrystallization it gave red needles (m. p. about 120°C, C, 22.30; H, 3.34; Au, 47.05), which seemed to resemble the gold salt of ethyl 3-(2-piperidyl)-propionate hydrochloride (m. p. 128°C, C, 22.87; H, 3.84), as far as the melting point and contents of C and H were concerned, but it was quite apparent from the difference in color (the authentic sample of the gold salt of ethyl 3-(2-piperidyl)-propionate hydrochloride is yellow) as well as from the Au-contents that the two compounds were not identical. Though it is impossible to decide, however, whether the gold salt obtained here was the same compound as Hess and Eichel have isolated, because they have never reported the nature of their compound except its melting point, it may be said at least that by treating the compound I according to their method, a gold salt resembling the one reported by them is obtainable.

On the grounds which have been described hitherto, the author believes that he can deduce the conclusion that pelletierine, to which Hess and Eichel have assigned the structure 3-(2-piperidyl)-propionaldehyde, is nothing but isopelletierine, 1-(2-piperidyl)-2-propanone. By this conclusion can easily be solved many conflicts, arising from the assumption that pelletierine is 3-(2-piperidyl)-propionaldehyde, e. g. a confilict that pelletierine is stable against oxidation, and can not be oxidized into 3-(2-piperidyl)-propionic acid with chromic acid, or a conflct that it can be isolable without any special care, though 3-(2-piperidyl)-propionaldehyde can not be synthesized by any method on account of its extreme instability. The reaction of pelletierine that Hess and Eichel used for the determination of the structure is also easily explainable with isopelletierine, when 3-(2-piperidyl)-propionitrile is replaced by 2-methyl-1, 3-diazabicyclo[4 : 3 : 0]-2-nonene (V) with the same molecular formula. This conclusion also agrees with the finding by Wibaut and Hollstein[7] that 3-(2-piperidyl)-propionaldehyde has no anthelmintic activity, while 1-(2-piperidyl)-2-propanone (isopelletierine) is strongly anthelmintic.

7) J. P. Wibaut and U. Hollstein, *Koninel. Ned. Akad. Wetenschap., Proc. Ser.*, **B59**, 426 (1956); *Chem. Abstr.*, **51**, 11364*i* (1957).

Experimental

Isopelletierine-oxime.—To the solution of $NH_2OH \cdot HCl$ (20 g.) and NaOAc (20 g.) in water (40 cc.) was added isopelletierine (16 g.) in methanol (18 cc.). After standing at room temperature overnight, the solution was made alkaline with sodium hydroxide and was extracted with ether. After drying and distilling off the solvent, the residue (colorless needle crystals, m. p. 97~99°C) was distilled under reduced pressure; b. $p._{10}$ 148~152°C (lit.[8] b. $p._{2.5}$ 134°C, b. $p._{5.6}$ 146°C). The yield was 12.5 g. After boiling the viscous distillate with petroleum ether and cooling, needle crystals were separated; m. p. 105~106°C (from ether). (As to the melting points for the two isomers, Mortimer et al.[8] have reported 105.5°C and 90°C, while Hess and Eichel[2] have reported 96~97°C and 80°C for pelletierine-oxime. The author used the higher melting isomer for the next reaction because it was also the higher one that Hess and Eichel had used for the reaction with phosphorus pentachloride).

The Reaction of Isopelletierine-oxime with Phosphorus Pentachloride.—According to a method just the same as Hess and Eichel's[2], isopelletierine-oxime (m. p. 105~106°C) (4.4 g.) was dissolved into freshly rectified anhydrous hot phenetole (10 cc.) and cooled to about 35~40°C, and this solution was added dropwise into a phenetole (30 cc.) solution of freshly sublimed phosphorus pentachloride (9 g.). At the beginning, the oxime precipitated gelatinously, but after some time it turned into a dark brown mass with violent evolution of heat and hydrochloric acid gas, and precipitated to the bottom. After several hours, phenetole was distilled off under reduced pressure at the temperature of 70~85°C, and the residue was dissolved in water while cooling. After the removal of residual phenetole by extraction with ether, the solution was made alkaline with sodium hydroxide and extracted with ether. The ether extract was dried with potassium hydroxide, freed from ether and distilled under diminished pressure. Thus the fraction boiling at 104~106°C at 15 mmHg was gathered. The yield was 1.2 g. After being converted into picrate, recrystallized and regenerated by sodium hydroxide the purified sample was obtained, boiling at 102~103°C at 10 mmHg; n_D^{25} 1.4973.

Found: C, 68.83; H, 10.14; N, 19.17. Calcd. for $C_8H_{14}N_2$: C, 69.52; H, 10.21; N, 20.27%.

The error of the analysis would probably be attributable to the hygroscopicity of this material.

Picrate: yellow needles, m. p. 174~175°C (from ethanol).

Found: C, 45.82; H, 4.72; N, 18.88. Calcd. for $C_{14}H_{17}O_7N_5$: C, 45.77; H, 4.67; N, 19.07%.

2-Picoline *N*-Oxide (VII).—The compound VII was obtained in 90% yield from the reaction of 2-picoline and hydrogen peroxide in acetic acid by the method of Boekelheide[9]; b. $p._{25}$ 146~148°C (lit.[9] b. $p._{15}$ 123~124°C).

2-Pyridylmethanol Acetate (VIII).—The compound VII was converted into VIII in 79% yield by the action of acetic anhydride according to Boekelheide[9]; b. $p._{18}$ 117~119°C (lit.[9] b. $p._{22}$ 115~118°C).

2-Pyridylmethanol (IX).—The acetate VIII was hydrolyzed with 10% hydrochloric acid in 70% yield according to Kobayashi[9]; b. $p._{17}$ 118~121°C (lit[10] b. $p._{16}$ 111~115°C); picrate, m. p. 160~161°C (lit.[9] m. p. 160.5~161°C).

2-Pyridylmethylchloride (X).—According to Itai[11], X was obtained by the reaction of the alcohol IX and phosphorus trichloride in 60% yield; b. $p._{21}$ 87°C (lit.[11] b. $p._5$ 70~80°C).

2-Pyridylmethylamine Hydrobromide (XII).—The chloride X (35 g.), potassium phthalimide (50 g.) and dimethylformamide (300 cc.) were heated at 90~100°C for about 5 hr. in water bath. When water was added to the reaction product after removal of the solvent under reduced pressure, all the contents of the vessel solidified (solid XI weighed 72 g.) After washing thoroughly with water and dilute sodium carbonate solution, the solid was boiled for 2 hr. with 48% HBr (300 cc.) in oil-bath, and phthalic acid, which separated on cooling, was filtered off. Being decolorized and condensing the filtrate, 60 g. of the crude XII was obtained. From 10 g. of this salt, after treating with sodium hydroxide, extracting with chloroform and distilling the extract, 2.5 g. of the free amine, boiling at 81°C at 5 mmHg, was obtained (lit.[4] b. $p._{20}$ 95~98°C).

2-Acetamidomethylpyridine (XIII).—To the mixture of XII (30 g.) and 30% sodium hydroxide solution (240 cc.), acetyl chloride (30 cc.) was added gradually with stirring, keeping the temperature below 20°C. The reaction product was extracted with chloroform, dried with sodium sulfate and distilled under diminished pressure; b. $p._3$ 145~149°C (lit.[4] b. $p._5$ 160~163°C), n_D^{25} 1.5430; picrate, m. p. 169~170°C (Found: N, 18.14%).

2-Acetamidomethylpiperidine (IV).—The amide XIII (5 g.) in dioxane (30 cc.) was hydrogenated over Raney nickel with hydrogen of initial pressure of 70 kg./cm² for 2 hr.; b. $p._{14}$ 158~165°C, n_D^{25} 1.5205. This was proved to be a mixture of XIII and IV, because from this distillate two picrates were obtained. One was hardly soluble in ethanol and melted at 169~170°C and was confirmed as the picrate of unreacted XIII by mixed melting point determination. Another, the picrate of IV, was easily soluble in ethanol and melted at 153~155°C.

Anal. of picrate of IV. Found: N, 17.85. Calcd. for $C_{14}H_{19}O_8N_5$: N, 18.18%.

The distillate was used for the next reaction without further separation.

Cyclization of IV by Phosphoryl Chloride.—A mixture of IV (5.6 g.) and phosphoryl chloride (20 cc.) in benzene (50 cc.) was refluxed for 3 hr. in water bath. Benzene was distilled off, and the residue was dissolved in water, made alkaline with sodium hydroxide and extracted with chloroform.

8) P. I. Mortimer and S. Wilkinson, *J. Chem. Soc.*, 1957, 3967.

9) V. Boekelheide and W. J. Linn, *J. Am. Chem. Soc.*, 76, 1286 (1954); cf. G. Kobayashi and S. Furukawa, *Pharm. Bull. (Japan)*, 1, 347 (1953).

10) W. M. Edwards and P. C. Teague, *J. Am. Chem. Soc.*, 71, 3548 (1949).

11) T. Itai and H. Ogura, *J. Pharm. Soc. Japan (Yakugaku Zasshi)*, 75, 296 (1955).

The extract, dried with sodium sulfate and after removal of the solvent, was distilled under diminished pressure, and was obtained the fraction of b. p.$_{11}$ 103~106°C, n_D^{25} 1.5011. The yield was 0.5 g. Its picrate melted at 174~175°C, and showed no depression of the melting point when mixed with the picrate of the reaction product of isopelletierine-oxime and phosphorus pentachloride. Both picrates showed identical Debye-Scherrer diagram.

Anal. of picrate. Found: C, 45.66; H, 4.64. Calcd. for $C_{14}H_{17}O_7N_5$: C, 45.77; H, 4.67%.

Cyclization of XIII to 3-Methyl-2; 3a-diazaindene (XIV) with Phosphoryl Chloride. — According to Bower and Ramage[4], the compound XIII (4 g.) and phosphoryl chloride (8 cc.) in benzene (24 cc.) were heated under gentle reflux for 4 hr. After distilling off benzene and the remaining phosphoryl chloride under reduced pressure, water was added to the residue, which was made alkaline and extracted with chloroform. After removal of solvent, the residue was distilled under reduced pressure; b. p.$_7$ 120~134°C (mainly distilled at b. p.$_7$ 134°C) (lit.[4] b. p.$_4$ 112~117°C); n_D^{25} 1.5951. The yield was 2.5 g.

Picrate: yellow amorphous crystals, m. p. 210°C (darkened over 200°C) (lit.[4] m. p. 221°C (decomp.)).

Found: C, 46.31; H, 3.46. Calcd. for $C_{14}H_{11}O_7N_5$: C, 46.54; H, 3.07%.

Reduction of 2-Methyl-1,3-diazabicyclo[4:3:0]-2-nonene (V) to 2-Methyl-1,3-diazabicyclo[4:3:0]-nonane (XV).—V was hydrogenated over Raney nickel in ethanol with hydrogen having an initial pressure of 95 kg./cm^2 at 150°C for 3.15 hr. After removal of the catalyst and solvent, the reduction product was distilled under diminished pressure; b. p.$_{14}$ 85~100°C. Styphnate: amorphous yellow crystals, m.p. 183~185°C.

Anal. of styphnate. Found: C, 43.52; H, 5.06. Calcd. for $C_{14}H_{19}O_8N_5$: C, 43.64; H, 4.97%.

Reduction of XIV to XV.—The compound XIV was hydrogenated over Raney nickel in ethanol with hydrogen having an initial pressure of 95 kg./cm^2 at 170°C for 4 hr. After removal of the catalyst and solvent, the reduction product was distilled under reduced pressure; b. p.$_{12}$ 96~98°C, n_D^{25} 1.4600. Styphnate: amorphous yellow crystals, m. p. 183~185°C. This styphnate was identical with the one of XV derived from V, which was confirmed by mixed melting point determination and the comparison of their IR spectra.

Reduction of XIII in Ethanol.—The amide XIII (16 g.) in ethanol (20 cc.) was hydrogenated over Raney nickel (ca. 1 g.) with hydrogen having an initial pressure of 130 kg./cm^2 for 4 hr. at 130~150°C. Distilling the reaction product, after removal of solvent, the following distillates were obtained.

(A) b. p.$_{11}$ ~91°C, 4.1 g.

(B) b. p.$_{11}$ 91°C~b. p.$_{12}$ 158°C, very little.

(C) b. p.$_{12}$ 158~163°C (mainly distilled at 162~163°C), 5.6 g.; n_D^{25} 1.5196.

A portion boiling at 102~108°C at 11 mmHg (n_D^{25} 1.4975) in the fraction B formed the picrate, m. p. 174~175°C (needle crystals from ethanol), and this picrate showed no depression of melting point when mixed with the picrate of V, prepared by the action of phosphorus pentachloride upon isopelletierine-oxime. The identitly of both the picrates was also confirmed by the Debye-Scherrer diagram.

Anal. of the picrate. Found: C, 46.02; H, 4.79. Calcd. for $C_{14}H_{17}O_7N_5$: C, 45.77; H, 4.67%.

Treating the fraction C with phosphoryl chloride in benzene as mentioned previously, liquid of b. p.$_{11}$ 103~106°C and n_D^{25} 1.4985 was obtained, the picrate of which melted at 174~175°C and showed no depression of melting point when mixed with the picrate of V. From the residue, after removal of the liquid (b. p.$_{11}$ 103~106°C), the picrate of m. p. 200°C (decomp.) was obtained and showed no depression of melting point when mixed with the picrate of XIV.

Fraction A mainly distilled at 80~83°C at 13 mmHg on redistillation; n_D^{25} 1.4628, d_4^{25} 0.9142. Styphnate melted at 123~125°C (Found: C, 43.69; H, 5.65%).

Treatment of the Compound V, Obtained from the Reaction of Isopelletierine-oxime with Phosphorus Pentachloride, with Alcoholic Potassium Hydroxide and Alcoholic Hydrochloric Acid.—V was heated in waterbath with 5% alcoholic potassium hydroxide and the solution was evaporated to

Table II. Conditions and results of alcoholic potassium hydroxide and alcoholic hydrochloric acid treatment of V

Exp. No.	V g.	KOH g.	EtOH cc.	Time	HCl	EtOH cc.	Time	Product
1	0.8	1.5	30	reflux 2 hr.	saturate	30	reflux 1 hr.	Syrupy, hygroscopic, insoluble in hot acetone; crystalline gold salt could not obtained.
2	0.5*	0.5	10	reflux 0.5 hr.	bubbling	10	reflux 1 hr.	Needle crystals separated on standing, insoluble in hot acetone, m. p. 190~192°C.
3	1.2	1	20	warm ca. 60°C 30 min.	conc. HCl 5 cc.	15	reflux 1 hr.	Syrupy, soluble in hot acetone; gold salt formed into red needles** (from H_2O), m. p. ca. 120°C.

* Purified material through picrate.

** By adding $AuCl_3$ solution to the syrupy material dissolved in water, yellow amorphous gold salt was obtained, m. p. 90~95°C (Found: C, 18.51; H, 3.00; Au, 48.40%). By recrystallization of this salt from $AuCl_3$ solution, yellow needles were obtained, but from water, there obtained red needles melting at about 120°C (Found: C, 22.30; H, 3.34; Au, 47.05%).

dryness after acidifying with concentrated hydrochloric acid. The dried crystallinematter was extracted with ethanol. After removal of the solvent the extract was refluxed with an alcoholic hydrochloric acid. After 1 hr.'s refluxing, the solution was evaporated under reduced pressure. A part of the residue was dissolved in water and the aqueous gold chloride was added. The conditions of the experiments and the properties of the residues or gold salts were listed in Table II.

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