

α -METHYL-QUINOLINE AS A CONSTITUENT OF THE
SECRETION OF THE ANAL GLANDS OF MEPHITIS
MEPHITICA.

BY THOMAS B. ALDRICH, PH. D.,

AND

WALTER JONES, PH. D.

(From the Laboratory of Physiological Chemistry of the Johns Hopkins University.)

In 1863 Swarts* (in Wöhler's laboratory) noticed in the secretion of the anal glands of *M. mephitica* the presence of a basic body which from its volatility and odor he referred to methyl- or ethyl-amine. Later, in 1879, Loew† stated that the secretion contains a basic body which smells like trimethylamine, and no doubt has a constitution similar to that of neurin. Up to the present time, beyond these conjectures, nothing has been done to characterize or to establish the identity of this body.

As has been stated in a previous communication,‡ the secretion can be readily separated, by distillation, into two sharply defined, nearly equal portions:

1. A more volatile portion, boiling between 100°–130° C., and which for convenience we have designated A.
2. A less volatile portion, left after distilling off A, and which has been called B.

A is a colorless liquid having a neutral reaction, and is further characterized by an unpleasant penetrating odor and by the readiness with which it reacts with mercuric oxide, mercuric cyanide and lead acetate, forming with these reagents for the most part crystalline compounds. It is a mixture of the higher mercaptans, containing among others (still undetermined) normal butyl mercaptan.§

* Liebig's *Annalen*, cxxvii (1862), 266.

† *Aerztliches Intelligenzblatt*, München, June 10, 1879, 252.

‡ T. B. Aldrich, *Journal of Experimental Medicine*, i, 323, 1896.

§ *Journal of Experimental Medicine*, i, 332–336.

The oil B has a dark red color, a neutral reaction, and a less penetrating odor than A. It contains carbon, hydrogen, nitrogen and sulphur, and does not react with the reagents mentioned under A, thus excluding the presence of mercaptans, at least to any considerable extent.

By careful and not too rapid distillation it is possible to separate the mercaptans from B completely,* though to insure a perfect separation it is advisable to shake B with a 50 per cent solution of potassium hydroxide, which not only removes the mercaptans, but also other bodies of acid nature. Accordingly, a small quantity of ether was added to B, and this ethereal solution agitated three successive times with an excess of a 50 per cent potassium hydroxide solution, the alkaline solution removed each time, and finally the ethereal solution washed with successive portions of distilled water until the alkaline reaction disappeared. The resulting oil after this treatment is free from mercaptans and bodies of acid nature, and contains neutral and basic bodies either originally in the secretion or split off by the strong alkali. B after being treated in this manner is a clear fluid, possessing a reddish yellow color; it constituted in one instance 42 per cent of the original secretion; it still contains C, H, N, and S.

It has been stated in a previous communication by one of us† that B contains a basic body either free or combined with some other constituent of the secretion; at that time a small amount of the impure base was isolated and platinic and gold chloride compounds were made.

BASIC BODY ISOLATED FROM B.‡

For the purpose of extracting the basic body from B the latter was shaken three times in succession with an equal volume of a 5 per cent hydrochloric acid solution (ether being added to facilitate the separation) and each acid extract washed once with an excess of ether. By

* This is especially true when working with small quantities.

† T. B. Aldrich, *op. cit.*

‡ B freed of the basic body is a clear, yellowish red, oily looking liquid, having a peculiar sweetish nauseating smell, and constituting about 37 per cent of the original secretion. For convenience we will call it B₁. It contains about 25 per cent of sulphur. We hope in the near future to state something more definite in regard to this portion of the secretion.

evaporating separately each acid extract* so treated it was found that the first contained approximately all of the basic substance, and that it deposited nearly colorless, transparent, needle-like crystals, evidently the hydrochloride of the basic substance, when evaporated nearly to dryness on the water-bath or when placed in a desiccator over sulphuric acid.

In order to obtain the free base the hydrochloric acid compound was decomposed with sodium hydroxide and the liberated base distilled with steam. By this process an oil was obtained having a light greenish color and a peculiar odor very similar to that of quinoline and its homologues. The water which dissolved the base slightly had a faint alkaline reaction, and fumes were observed when dilute hydrochloric acid was held near the vessel containing the distillate. By this procedure, however, it became evident that we had extracted at least two bodies with the acid solution, one readily volatile with steam and passing over in the first 200 or 300 cc. of the distillate, the other very much less, though still partially, volatile. If the distillation is continued too long the former body becomes mixed with the less volatile and loses to a certain extent its characteristic odor. In order to obtain the former approximately pure the distillation was usually discontinued as soon as the distillate after acidification with hydrochloric acid ceased to give with gold chloride a crystalline precipitate.

Boiling with an excess of pure silver oxide suspended in water decomposes the hydrochloride salt of the base very incompletely. Indeed, after boiling an hour the greater part of the compound was found to be undecomposed, for when sodium hydroxide was added an oil was liberated which was readily carried over with steam and which gave the characteristic odor etc. of the base.

It may be stated in passing that the less volatile body differs from the more volatile in containing sulphur. Whether or not this substance is a mixture of a basic body with some of the portion called B₁ has not been determined. It dissolves, though neither readily nor completely, in dilute hydrochloric acid, and this solution gives with

* The second and third acid extracts left, on evaporation, a reddish oil, possessing properties different from those of the residue of the first.

platinic and gold chloride amorphous yellow precipitates. It seems probable that in shaking B with acid some of B₁ was taken up by the acid; this would explain the presence of sulphur in this body.

The impure basic body after distillation with steam was collected with ether; it constituted about 5 per cent of the original secretion. Further purification can be accomplished by passing the oil through one of its numerous salts. The zinc chloride double salt was used, although others may be employed with equally good results.

PURIFICATION OF THE BASE BY MEANS OF THE ZINC CHLORIDE
DOUBLE SALT.

The base was dissolved in dilute hydrochloric acid and an aqueous solution of zinc chloride added as long as a precipitate was formed. The precipitate was recrystallized from dilute hydrochloric acid, then decomposed with sodium hydroxide, after which the free base was distilled with steam and collected with ether.

Prepared in this manner the base is colorless, has the quinoline odor, and is highly refractive. It is soluble in ether, alcohol, chloroform and acids; slightly soluble in both cold and hot water; insoluble in alkalis. It forms salts with the mineral as well as with the organic acids. The salts of the mineral acids are, as far as investigated, easily soluble in water, or in the respective acid used, and may be obtained in crystalline form by evaporating on the water-bath nearly to dryness, or allowing their solutions to evaporate in a desiccator. The majority of them may be recrystallized from hot alcohol. The hydrochloride salt forms needles, soluble in water and alcohol, insoluble in ether.

The base also forms double salts with platinic and gold chloride, zinc chloride etc., most of which can be obtained in crystalline form.

Among the derivatives which the base forms may be mentioned a bromine and a methyl iodide compound. The base also responds to most of the alkaloidal reagents.

The small quantity of the impure base, not over four or five grammes, which we were able to obtain, necessitated the preparation and analysis of some of the most characteristic salts and derivatives rather than the base itself.

The following pages contain an account of the preparation, properties and analyses of a few of the most characteristic salts and derivatives; we wish to say that while some of these compounds were obtained from the pure base, others were made from the impure product before passing it through the zinc chloride salt.

Platinum Chloride Double Salt ($[\text{C}_{10}\text{H}_9\text{N}.\text{HCl}]_2\text{PtCl}_4$).

This salt, one of the most characteristic, is deposited in the form of yellow needles when platinic chloride is added to a dilute hydrochloric acid solution of the base. It is obtained as orange-red needles when recrystallized from water or dilute hydrochloric acid. Dried in the air or *in vacuo* over sulphuric acid the salt does not contain water of crystallization, melts under decomposition between 226° – 230° C., and gave on analysis the following results:

I.	0.2479	gramme	substance	gave	0.3155	gramme	CO_2 ,	and	0.0651	gramme	H_2O .
II.	0.2422	"	"	"	0.3059	"	"	and	0.0642	"	"
I.	0.1586	"	"	"	0.0446	"	Pt.				
II.	0.1827	"	"	"	0.0514	"	"				
I.	0.1764	"	"	"	0.2175	"	AgCl.				
II.	0.0643	"	"	"	0.0790	"	"				
I.	0.1971	gr.	substance	gave	6.1	cc.	moist N	at	24°	C.	under a pressure of 764 mm.
II.	0.1977	"	"	"	6.8	"	"	"	22°	"	"

	Calculated for $[\text{C}_{10}\text{H}_9\text{N}.\text{HCl}]_2\text{PtCl}_4$.	Found.	
		I.	II.
C	34.53	34.71	34.44
H	2.88	2.92	2.94
N	4.02	3.94	3.92
Pt	27.93	28.12	28.13
Cl	30.64	31.14	30.47

The platinum compound is further characterized by being very sparingly soluble in cold water, and by giving rise, when decomposed by heating in a dry test tube, to a volatile oil which on cooling deposits transparent colorless needles. These needles are soluble in water, alcohol and dilute hydrochloric acid, insoluble in ether, and are no doubt the hydrochloride salt of the base, the solubilities of which agree with these. The volatility of the base with hydrochloric acid also explains the difficulty experienced in testing qualitatively for nitrogen in this compound. The melting point given above agrees exactly with that of a platinum compound obtained by Fischer and Kuzel* from a basic body which from

* *Ber. d. deutsch. chem., Gesellsch.*, xvi, 165.

444 *α-Methyl-Quinoline in the Anal Glands of M. Mephitica*

analyses they claim to have proved to be identical with Döbner and von Miller's* *α-methyl-quinoline*.

Gold Chloride Double Salt ($C_{10}H_9N \cdot HCl Au Cl_2$).

When an aqueous solution of gold chloride is added to a hydrochloric acid solution of the base a turbidity is produced, giving place in a few minutes to a network of fine slender yellow needles. When recrystallized from dilute hydrochloric acid or water the salt is deposited in the form of glistening yellow needles. Dried *in vacuo* over sulphuric acid the compound melts sharp at 153° C. and gives the following analytical results:

I.	0.2036	gramme	substance	gave	0.1848	gramme	CO ₂ ,	and	0.0409	gramme	H ₂ O.
II.	0.2991	"	"	"	0.2672	"	"	and	0.0580	"	"
I.	0.1261	"	"	"	0.0511	"	Au.				
II.	0.2013	"	"	"	0.0819	"	"				
I.	0.1155	"	"	"	0.1359	"	AgCl.				
II.	0.0848	"	"	"	0.0999	"	"				
I.	0.1939	gr.	substance	gave	4.9	cc.	moist N	at	22°	C.	under a pressure of 764 mm.
II.	0.2023	"	"	"	"	"	"	"	"	"	"

	Calculated for $C_{10}H_9N \cdot HClAuCl_2$.	Found.	
		I.	II.
C	24.87	24.75	24.37
H	2.09	2.23	2.16
N	2.90	2.82	2.76
Au	40.72	40.52	40.68
Cl	29.42	29.18	29.22

The gold chloride compound is characterized by its greater solubility, in both cold and hot dilute hydrochloric acid, than the corresponding platinum compound. It also, on heating in a dry test tube, gives off a volatile body which is deposited in the form of crystals in the cold part of the tube, though this property is not so pronounced as in the case of the platinum compound.

Bichromate Salt [$(C_{10}H_9N)_2 \cdot Cr_2O_7H_2$].

Among the salts of quinoline and its homologues none are more characteristic than those of the bichromates. This compound of the base is precipitated as a yellow-red oil, crystallizing almost immediately when an aqueous solution of potassium bichromate is added to the hydrochloric acid solution of the base. It crystallizes from hot water in the form of yellow-red needles, which in their color and crystalline form are hardly to be distinguished from the platinum double salt. Dried in a desiccator

* *Ber. d. deutsch. chem. Gesellsch.*, xv, 3075.

it melts under decomposition at 130°–140° C. When heated rapidly, like the corresponding salt of quinoline, it decomposes suddenly. It is with difficulty soluble in cold, readily in hot water.

Incineration of the salt gave the following result:

0.1694 gramme substance gave 0.0508 gramme Cr_2O_3 .

	Calculated for $[\text{C}_{10}\text{H}_9\text{N}]_2 \cdot \text{Cr}_2\text{O}_7 \cdot \text{H}_2\text{O}$	Found.
Cr	20.76	20.58

Picrate Salt $[\text{C}_{10}\text{H}_9\text{N} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}]$.

The picrate is precipitated as an insoluble yellow cloud, changing almost immediately into yellow crystals whenever a saturated aqueous solution of picric acid is added to a hydrochloric acid solution of the base. Recrystallized from a saturated alcoholic solution it is deposited as glittering yellow needles; from a dilute solution it forms well-defined prisms. Dried *in vacuo* over sulphuric acid it melts when heated rapidly at 177° C.; when heated gradually it melts between 193° and 194° C.

A nitrogen determination gave the following results:

- I. 0.1953 gramme substance gave 25.6 cc. moist N at 22° C. under a pressure of 764.5 mm.
- II. 0.1957 gramme substance gave 26 cc. moist N at 20° C. under a pressure of 764.5 mm.

	Calculated for $\text{C}_{10}\text{H}_9\text{N} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}$	Found.	
		I.	II.
N	15.05	14.93	15.27

This salt is sparingly soluble in cold water or alcohol, readily soluble in hot alcohol.

Owing to the very limited amount of material at our disposal the following salts and derivatives were not obtained in sufficient quantity for analysis.

Zinc Chloride Double Salt $[(\text{C}_{10}\text{H}_9\text{N} \cdot \text{HCl})_2 \cdot \text{ZnCl}_2]$.

As has already been stated, under purification of the base, this salt is formed when an aqueous solution of zinc chloride is added to the hydrochloric acid solution of the base. It is of especial importance from the fact that it is suitable for the purification of the base, being readily soluble in hot water, quite insoluble in cold. From its hot alcoholic and from its dilute aqueous solution it crystallizes in transparent colorless monoclinic crystals which in general appearance might be mistaken for gypsum crystals, although twin crystals have not been observed. It is insoluble in ether, sparingly soluble in cold alcohol and water, readily soluble in hot alcohol, water and dilute acids. Recrystallized from

446 *α-Methyl-Quinoline in the Anal Glands of M. Mephitica*

water and dried in the air the salt melts under decomposition between 230°–240° C.

Hydroferrocyanic Acid Salt $[(C_{10}H_9N)_2 \cdot H_4Fe(CN)_6]$.

This salt is formed whenever an aqueous solution of potassium ferrocyanide is added to the acid solution of the base. It can be readily obtained in the form of transparent prisms from hot dilute acids. It is decomposed readily by alkalies, and may thus be used to advantage in purifying the base.

Silver Nitrate Salt $[(C_{10}H_9N)_2AgNO_3]$.

This salt is obtained when an aqueous solution of silver nitrate is added to an alcoholic solution of the base. It is obtained from alcohol in transparent colorless needles.

Methyl Iodide Addition Product $[C_{10}H_9N \cdot CH_3I]$.

If equal parts by weight of methyl iodide and the base are brought together and warmed gently on the water-bath (using a reflex condenser) reaction takes place, and yellow needle-shaped crystals are soon deposited. This compound is very soluble in alcohol and water, insoluble in ether; and though characteristic in appearance, has nevertheless been difficult to obtain.

Bromine Addition Product.

This compound is most conveniently prepared in a chloroform solution. The base was dissolved in chloroform and a corresponding solution of bromine added until the color persisted. Upon the addition of ether a crystalline compound was precipitated which, when filtered and washed with ether, became nearly colorless. The body is obtained as beautiful colorless prisms when recrystallized from alcohol containing ether, or when dissolved in chloroform and precipitated with ether. The compound may also be prepared in glacial acetic acid solution and precipitated with water. It is readily soluble in hot alcohol, also in chloroform and glacial acetic acid; insoluble in ether and water.

Quinaldine Yellow $[C_{10}H_9N \cdot (CO_2)C_6H_4]$.*

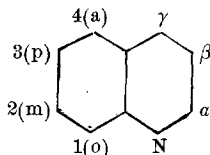
Equivalent weights of the base, phthalic anhydride and anhydrous zinc chloride were heated together in a bath at 200° C. from three to four hours. The resulting product was dissolved in concentrated sulphuric acid at water-bath temperature and then poured into twenty times its volume of water, with the result that a reddish brown flocculent body was

* *Ber. d. deutsch. chem. Gesellsch.*, xvi, 1602.

precipitated. Filtered and recrystallized, first from glacial acetic acid and then twice from hot 98 per cent alcohol, beautiful, fine, lustrous yellow needles were obtained. Dried in the air the body melts without decomposition between 235°–240° C. to a cherry-red liquid. The compound is very soluble in glacial acetic acid, readily in hot alcohol and concentrated sulphuric acid; insoluble in water, ether and dilute acids; sparingly soluble in cold alcohol.

The analytical data given on the preceding pages agree with those of a base having the empirical formula $C_{10}H_9N$. This body is therefore identical or isomeric with the naphthylamines ($C_{10}H_7NH_2$) or the methyl-quinolines ($C_9H_8CH_3N$). Since, however, the former are solids at ordinary temperatures, the base can be referred only to the latter. Indeed, the whole deportment of the base—odor, similarity of salts etc.—stamps it as a quinoline homologue.

Of the seven normal monomethyl-quinolines in which the methyl group occupies either the α , β , γ , 1(o), 2(m), 3(p), or 4(a), position in the following structural formula,



the base agrees perfectly, as far as investigated, with the α -compound.

The following considerations lead to this conclusion:

1. The platinum double salt of the base contains no water of crystallization; all of the platinum double salts of the seven normal monomethyl-quinolines, with the exception of the α -compound, contain one or two molecules of water of crystallization.*
2. The platinum double salt of the base melts, similarly to that of α -methyl-quinoline, between 226°–230° C.† under decomposition.
3. The crystalline form, color, solubilities and melting points of the

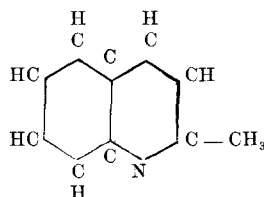
* Of the seven possible isomethyl-quinolines, only three, as far as the literature is known to us, have been prepared. The platinum compounds of two of these contain water of crystallization; the platinum salt of the third melts at 253.5° C. These bases are therefore not identical with the basic body in the secretion. The normal anamethyl-quinoline is excluded through its picrate with m. pt. 208°–209° C.

† E. Fischer u. Kuzel, *Ber. d. deutsch. chem. Gesellsch.*, xvi, 165.

other salts and derivatives of the base, as far as prepared, agree very closely, and in most instances exactly, with those of *α*-methyl-quinoline.

4. Quinoline yellow,* formed by the action of phthalic anhydride and zinc chloride on *α*-methyl-quinoline, departs itself precisely like the corresponding compound of the base.

These points of resemblance, when considered together with the properties of the base itself (odor, volatility, solubilities etc.), would seem to afford evidence sufficient to warrant the assertion that the base is identical with *α*-methyl-quinoline, and consequently has the well known structural formula,



For purposes of comparison *α*-methyl-quinoline was prepared synthetically,† and its salts and derivatives compared with those of the base.

Synthetic Preparation of α-Methyl-quinoline.

The base was prepared by heating together for four or five hours on the water-bath a mixture of 1½ parts of paraldehyde, 2 parts of concentrated hydrochloric acid, and 1 part of aniline.

The best result was obtained by making the hydrochloride of aniline first and then adding the paraldehyde in small portions, avoiding excessive heating, and finally finishing on the water-bath. At the end of this time a current of steam was passed through the mixture, thus removing a small quantity of oil. The whole mass was then made strongly alkaline, the receiver changed and the distillation continued. A light green oil passed over, which was collected with ether. The base was freed of aniline by dissolving the oil in dilute hydrochloric acid and adding an excess of an aqueous solution of zinc chloride. The crystalline precipitate was recrystallized once from dilute hydrochloric acid and treated as heretofore explained for the purification of the base. Since aniline does not form an insoluble zinc salt it is possible in this manner to separate the two bases.

* *Ber. d. deutsch. chem. Gesellsch.*, xvi, 2602.

† Döbner u. von Miller, *op. cit.*, xvi, 2465.

The base so prepared is colorless, highly refractive, possesses the quinoline odor, and boils between 230°–240° C.

In the following table some of the derivatives of the basic body from the secretion and those of *α*-methyl-quinoline are compared.

α-Methyl-Quinoline (from *M. mephitica*). B. Pt. —.*

When pure the base is a highly refractive, colorless oil, having a faint quinoline odor (very pronounced on warming). It is readily volatile with steam, gives fumes when hydrochloric acid is held near it, is readily soluble in ether, chloroform, alcohol and mineral acids; insoluble in alkalies, sparingly soluble in both hot and cold water.

SALTS AND DERIVATIVES.

	Soluble in	Insoluble in	M. Pt.	Form.	Color.	Water of crystallization.
Platinum.	H ₂ O, dil. HCl, alcohol.	ether.	226°–230° C. (decomposition).	cryst. (needles).	orange-red.	none.
Gold.	H ₂ O, dil. HCl, alcohol.	ether.	153° C. (decomposition).	cryst. (needles).	yellow.	none.
Picrate.	hot alcohol.	H ₂ O, ether.	193°–194° C. (decomposition).	cryst. (needles or prisms).	yellow.	none.
Bichromate.	hot H ₂ O.	cold H ₂ O, ether.	130°–140° C. (decomposition).	cryst. (needles).	orange-red.	none.
Quinaldine yellow.	glac. acetic acid, hot alcohol, con. H ₂ SO ₄ .	H ₂ O, ether, dil. acids.	235°–240° C. (red liq'd, solidifies).	cryst. (needles).	golden yellow.	—
Zinc.	hot H ₂ O, hot alcohol, " dil. acids.	ether, sparingly sol. in alcohol & cold H ₂ O.	230°–240° C. (decomposition).	cryst. (monoclinic).	colorless.	—
Methyl iodide.	H ₂ O, alcohol.	ether.	—	cryst. (needles).	yellow.	—
Bromine.	chloroform, glac. acetic acid, hot alcohol.	ether, H ₂ O.	—	cryst. (prisms).	colorless.	—

* The small quantity of the base prevented the determination of the b. pt.

450 *α-Methyl-Quinoline in the Anal Glands of M. Mephitica**α-Methyl-quinoline (Synthetic). B. Pt. 235°–240° C.**

When pure *α*-methyl-quinoline is a highly refractive, colorless oil, having a faint quinoline odor, very pronounced on warming. It is readily volatile with steam, gives fumes when hydrochloric acid is held near it, is readily soluble in ether, chloroform, alcohol and mineral acids; insoluble in alkalis, sparingly soluble in both hot and cold water.

SALTS AND DERIVATIVES.

	Soluble in	Insoluble in	M. Pt.	Form.	Color.	Water of crystallization.
Platinum.	H ₂ O, dil. HCl, alcohol.	ether.	226°–230° C. (decomposition).	cryst. (needles).	orange-red.	none.
Gold.	H ₂ O, dil. HCl, alcohol.	ether.	153° C. (decomposition).	cryst. (needles).	yellow.	none.
Picrate.	hot alcohol.	H ₂ O, ether.	193°–194° C. (decomposition).	cryst. (needles or prisms).	yellow.	none.
Bichromate.	hot H ₂ O.	cold H ₂ O, ether.	130°–140° C. (decomposition).	cryst. (needles).	orange-red.	none.
Quinaldine yellow.	glac. acetic acid, hot alcohol, con. H ₂ SO ₄ .	ether, dil. acids, H ₂ O.	235° C. (red liq'd, solidifies).	cryst. (needles).	golden yellow.	—
Zinc.	hot alcohol, " water. " dil. acids.	ether, sparingly sol. in cold H ₂ O & alcohol.	230°–240° C. (decomposition).	cryst. (monoclinic).	colorless.	—
Methyl iodide.	H ₂ O, alcohol.	ether.	195° C.	cryst. (needles).	yellow.	—
Bromine.	glac. acetic acid, chloroform, hot alcohol.	ether, H ₂ O.	—	cryst. (prisms).	colorless.	—

* Döbner u. von Miller (op. cit., xvi, 2464) gave 238°–239° C. Others give from 240°–247° C.

The presence of α -methyl-quinoline in the animal organism deserves more than passing notice. This is the first time its natural occurrence has been demonstrated either in the vegetable or animal kingdom. It is true that a few of the methyl-quinolines, together with related bases, have been found among the products resulting from the destructive distillation of nitrogenous organic matter, but up to the present time they have never been demonstrated as products other than of laboratory methods. Thus Jacobsen and Reimer* found α -methyl-quinoline in coal-tar, while Williams† obtained γ -methyl-quinoline (lepidine) by distilling cinchonine with potash. Furthermore, it is to be observed that quinoline and its homologues are confined, for the most part, to the vegetable world.

When we consider the number of nitrogenous organic bodies that are found in the tissues and fluids of the body, or when we consider the diversity of the products formed through the activity of the living cells, it does not seem strange that α -methyl-quinoline should be found among these products. Indeed, the isolation of kynurenic acid (oxy-quinolin-carboxylic acid) from the dog's urine, first by Liebig,‡ and later by different methods by Hoffmeister,§ Brieger,|| Schmiedeberg and Schultzen,¶ proved the presence of quinoline in the animal organism. There is no doubt but that these quinoline compounds have their origin in the proteid molecule, for, according to Baumann,** the amount of kynurenic acid in the urine under ordinary conditions is dependent upon the nature of the food supplied to the animal, being greatest under a proteid diet. It is interesting to note also in this connection that the food of the skunk consists exclusively of proteid matter.

The indications are that α -methyl-quinoline is free, that is, not combined with any other substance in the secretion, for it can be partially extracted from B, or the original secretion, by shaking persist-

* *Ber. d. deutsch. chem. Gesellsch.*, xvi, 1082.

† *Jahresber. f. Chem.*, 1855, 550.

‡ *Liebig's Annalen*, lxxxvi (1853), 125; cviii (1858), 354.

§ *Zeit. f. Phys. Chem.*, v, 67.

|| *Zeit. f. Phys. Chem.*, iv, 89.

¶ *Liebig's Annalen*, clxiv (1872), 155.

** *Zeit. f. Phys. Chem.*, x (1886), 131.

ently with an excess of water. Furthermore, the compounds thus far isolated from the secretion do not, so far as is known, combine with α -methyl-quinoline.

The fact that α -methyl-quinoline is destroyed when injected subcutaneously* into dogs, supports the view that the cells of the anal glands are directly concerned in the elaboration of this compound. This presumption is furthermore substantiated by the fact that the base has never been found in the blood or in any other tissue of the animal body. We can safely assume that these particular cells, and no others, are concerned in the elaboration of this compound.

In conclusion, we desire to express our thanks to Dr. C. Hart Merriam, Chief of Division of Ornithology and Mammalogy, Washington, D. C., who has kindly furnished us with part of the material used in this investigation.

* R. Cohn, *Zeit. f. Phys. Chem.*, xx, 210.