# THE PRODUCTS

OF THE

# DESTRUCTIVE DISTILLATION OF ANIMAL SUBSTANCES.

## PART II.

BY

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XIV.—*On the Products of the Destructive Distillation of Animal Substances.* Part II. By Thomas Anderson, M.D.
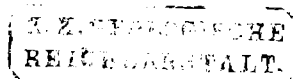
(Read 21st April 1851.)

I propose in the following pages to communicate to the Society the progress of my investigation of the products of the destructive distillation of animal substances, the first part of which was published in the 16th volume of the Transactions. Since that period, partly owing to my numerous avocations, and partly to the inherent difficulties of the subject, less progress has been made than I had hoped or expected, but still I have accumulated some facts of considerable interest, which I think deserving of the attention of the Society.

It may be remembered that, in the paper just referred to, I announced the discovery, among those products, of picoline, which I formerly obtained from coal-tar, and of a new base, to which I gave the name of Petinine; and I entered pretty fully into the method adopted for the preparation of these substances, and of certain other bases, the existence of which I merely indicated, without at the time attempting to characterize them. On proceeding to the more minute investigation of these bases, I soon found that the quantity of material at my disposal was much too small to admit of satisfactory or complete results, although I had employed for their preparation above 300 pounds of bone-oil. I found it necessary, therefore, to begin *ab initio* with the preparation of the bases from another equally large quantity of the oil; and after going through the whole of the tedious processes described in my previous paper, with the expenditure of the labour of some months, I found my object again defeated by deficiency of material. After various experiments, which, though they led to no definite or conclusive results, served to familiarize me with the nature and relations of the products obtained, I made up my mind once more to begin again; and being resolved on this occasion not to be foiled in the same way as before, I used for my new preparation no less than 250 gallons of crude bone-oil, the weight of which was somewhat above a ton. The result of this process, though involving an immense amount of labour, has been satisfactory, not only in supplying me with a large amount of material, but has also enabled me to obtain many substances, some of them possessed of very remarkable properties, which had escaped my observation when operating on a smaller scale.

The employment of so large quantity of material has, as might be expected, led to some modification of the process described in the first part of this paper,

which, though convenient enough on the small scale, was too tedious for the large quantities on which I now operated. The preliminary process of rectifying the oil, which was quite beyond the resources of a laboratory, was effected at a manufactory. The whole oil was introduced at once into a cast-iron retort, furnished with a good condenser, kept cool by an abundant current of ice-cold water. A very gentle heat was applied, and the first twenty gallons which passed over were collected apart; they consisted of about equal bulks of a highly volatile oil, and of water charged with sulphide of ammonium, hydrocyanate and carbonate of ammonia, and a small quantity of very volatile bases. The oil which distilled over after this fraction had been separated was collected in a succession of casks, which were numbered as they were filled.

In the after treatment of the oil, a process was employed similar to that which I had formerly made use of, with this exception, that the watery fluid, which had formerly been rejected, was employed for obtaining any bases which might have been dissolved in it along with the ammonia. For this purpose it was separated from the oil, and dilute sulphuric acid gradually added, when carbonic, hydrocyanic, and hydrosulphuric acids escaped with violent effervescence. When acid enough had been added to communicate a powerfully acid reaction to the fluid, it was put into a large copper boiler and boiled for some time, water being added at intervals, so as to keep up the bulk. After the ebullition had been sufficiently prolonged, the fluid was allowed to cool, and slaked lime added in excess. A copper head was then fitted to the boiler and luted down with clay, a condenser attached, and heat applied. The distillate was collected in a large glass receiver, which, in order to prevent the escape of ammonia and any very volatile products which might be carried along with it, was connected by a doubly-bent tube with a second receiver containing water, through which the gaseous products were allowed to stream. The fluid which distilled was coloured blue by the solution of small quantities of copper from the condenser; it had a powerfully ammoniacal and putrid odour, and when treated with sticks of caustic potass, in the manner described in the first part of this paper, ammonia was rapidly evolved with effervescence, and a small quantity of very volatile and pungent bases collected on the surface of the potash. These bases were separated from the potash fluid, which was preserved along with the ammoniacal solution obtained by the absorption of the gaseous products in the second receiver.

The treatment of the oil was conducted in a manner very similar to that already described, and as I desired to have only the more volatile products, I employed the first half of the oil only. It was agitated with dilute sulphuric acid in casks about half full, and after two or three days, during which the agitation was frequently repeated, more water was added, and the solution of the bases separated from the oil. To this fluid acid was added, so as to have a distinct excess; and it was then boiled for the separation of RUNGE's pyrrol, to which reference

has been made in the first part of this paper. As, however, I observed that a very powerful and pungent odour was evolved when the fluid began to boil, and the vapours presented the characteristic reaction of pyrrol in a very high degree, the head of the boiler was luted on, and the condenser attached, for the purpose of endeavouring to obtain that substance, which in my previous experiments I had not done. The fluid which distilled over carried with it a small quantity of oil, which, at the moment of distillation, was perfectly colourless, but soon acquired a reddish shade, and in the course of a few days became almost black. The greater part of this oil passed over with the first portion of water; but the last traces adhered with great obstinacy to the acid fluid, and could only be separated by very protracted distillation. The substance thus obtained proved to be a mixture of an oil insoluble in acids, and which appeared to be merely a small quantity of the crude oil, mechanically mixed with the fluid, and of a series of bases of very remarkable properties, and obviously related to one another, to which I shall afterwards refer under the provisional name of *pyrrol bases.*

When these substances had entirely distilled, the fluid was allowed to cool, excess of slaked lime added, and the distillation again commenced, in order to obtain the bases which had been retained by the sulphuric acid. The separation of these was conducted in a manner in all respects similar to that employed in the former preparations, solid caustic potash being added in sufficient quantity to cause the separation of the bases held in solution in the water. The potash fluid, however, retained a certain proportion of ammonia, another gaseous base, and of the most volatile bases, which could be separated only by a very large excess of potash. The fluid was therefore distilled in glass vessels, and the product collected in a succession of three receivers, the first of which was kept cold by water, the second by a freezing mixture, and the third contained hydrochloric acid, for the purpose of condensing the gaseous products. The first receiver now contained the bases dissolved in a small quantity of water, from which they were readily separated by potash; the second receiver contained only a drop or two of liquid; but in the third the hydrochloric acid was rapidly saturated, and required repeated renewal during the progress of the distillation.

The hydrochloric solution thus obtained contained a very large quantity of chloride of ammonium, along with a small proportion of another base, in order to obtain which the fluid was slowly evaporated, allowed to cool at intervals, and the sal-ammoniac which deposited was separated by straining through cloth and expression. After the separation of several crops of crystals, a dark-brown mother liquor was left, which refused to crystallize by evaporation on the water-bath, but on cooling solidified into a mass of long foliated crystals, which soon deliquesced in moist air. These crystals still contained traces of sal-ammoniac, for the separation of which they were evaporated to complete dryness on the water-bath, and dissolved in the smallest possible quantity of absolute alcohol,

with the aid of heat. The filtered fluid, on cooling, deposited a few tabular crystals mixed with a little sal-ammoniac, which was got rid of by a second filtration: and the filtrate, when treated with animal charcoal and further concentrated, solidified, on cooling, into a mass of large foliated crystals.

These crystals are long, transparent, and colourless plates, entirely without odour, and with a pungent and bitter taste. In moist air they deliquesce rapidly. Solid potash added to their concentrated solution causes the immediate escape of a gaseous base resembling ammonia, but distinguished by its peculiar putrid odour. This gas dissolves readily in water, and gives a powerfully alkaline solution. It gives with corrosive sublimate a fine white precipitate, soluble in hot water or spirit, and deposited on cooling in fine silvery plates; and its hydrochlorate gives, with bichloride of platinum, a soluble salt, depositing from its hot saturated solutions in beautiful golden-yellow scales. I selected this salt as a means of determining the constitution of its base.

I. $\left\{\begin{array}{l}\text{6·885 grains of the platinochloride, dried at 212°, gave}\\ \text{1·243 ... of carbonic acid, and}\\ \text{1·648 ... of water.}\end{array}\right.$

II. $\left\{\begin{array}{l}\text{6·189 grains of the salt gave}\\ \text{2·565 ... of platinum.}\end{array}\right.$

III. $\left\{\begin{array}{l}\text{11·531 grains of another preparation gave}\\ \text{4·764 ... of platinum.}\end{array}\right.$

|  | Experiment. |  | Calculation. |  |  |
|---|---|---|---|---|---|
| Carbon, | 4·92 | ... | 5·06 | $C_2$ | 12 |
| Hydrogen, | 2·67 | ... | 2·52 | $H_6$ | 6 |
| Nitrogen, | ... | ... | 5·92 | N | 14 |
| Chlorine, | ... | ... | 44·89 | $Cl_3$ | 106·5 |
| Platinum, | 41·31 | 41·44 | 41·61 | Pt | 98·7 |
|  |  |  | 100·00 |  | 237·2 |

These analyses, then, correspond exactly with the formula $C_2 H_5 N \, HCl \, Pt \, Cl_2$; and the base is consequently methylamine, with which it and its salts agree in all respects.

The oily bases which had been separated from their solution in water by means of potass, were dried by the addition of successive portions of that substance, as long as it continued to become moist. The dry oil, which was very dark coloured, was then introduced into a large retort, furnished with a thermometer and a tubulated receiver kept cold by ice, and connected first with a U tube immersed in a freezing mixture, and then with a large vessel of water, in order to collect the gaseous bases which began to escape with effervescence almost as soon as heat had been applied. At a temperature under 150° Fahr. drops began to condense in the neck of the retort, and the fluid entered into rapid ebullition. At 212° the receiver was changed, and the oil distilling above that temperature was collected in receivers, which were changed at every ten degrees.

The quantity of bases which distilled under 212° was much less than I had anti-

cipated, and proportionably much smaller than that obtained when operating on a much smaller scale before; and I consequently found myself compelled to proceed very carefully, so as to avoid loss in the purification. By distilling the product which boiled under 212°, I collected fractions nearly equal in bulk at every five degrees, all very similar in their general properties. They were all limpid and colourless fluids, with high refractive power, and pungent odour, remarkably similar to that of ammonia in the lower fractions. They fumed strongly when a rod moistened with hydrochloric acid was brought near them, and presented all the properties of powerful bases. Exposed in the anhydrous state to a mixture of snow and salt, they remain perfectly fluid, but if a small quantity of water be added, beautiful white crystals of a hydrate are deposited. I attempted, by several successive distillations, to obtain fixed boiling points; but the quantity I had to work with was too small for an operation involving so much loss of material, and I therefore converted portions of the fractions which I had reason to suspect corresponded with particular bases into platinum salts. I selected, in the first place, the lowest fraction of all, that, namely, which boiled under 150°. It was dissolved in water, saturated with hydrochloric acid, and evaporated to dryness on the water-bath. The highly crystalline residue obtained was dissolved in water, and mixed with a solution of bichloride of platinum, when a yellow crystalline salt was slowly deposited, which dissolved readily in water even in the cold, and still more abundantly on boiling; and the solution on cooling deposited fine golden scales, scarcely to be distinguished in their appearance from those of methylamine or of petinine. These crystals were separated, and as the salt was highly soluble, and much remained in the mother liquor, a mixture of alcohol and ether was added, when the fluid rapidly filled with small shining scales. The analysis of this salt dried at 212° gave the following results:—

$$\begin{cases} 6\cdot970 \text{ grains of platinochloride gave} \\ 3\cdot392 \quad \ldots \quad \text{of carbonic acid, and} \\ 2\cdot434 \quad \ldots \quad \text{of water.} \end{cases}$$

6·475 grains of the salt gave 2·422 grains platinum.
8·257     …     …     3·047     …

|  | | Experiment. | | Calculation. | | |
|---|---|---|---|---|---|---|
| Carbon, | . | 13·27 | … | 13·57 | $C_6$ | 36 |
| Hydrogen, | . | 3·88 | … | 3·77 | $H_{10}$ | 10 |
| Nitrogen, | . | … | … | 5·27 | N | 14 |
| Chlorine, | . | … | … | 40·18 | $Cl_3$ | 106·5 |
| Platinum, | . | 37·56 | … | 37·21 | Pt | 98·7 |
|  | | | | 100·00 | | 265·2 |

From these results we arrive at the formula $C_6H_9N \, HCl \, Pt \, Cl_2$, which is that of the platinum salt of a base $C_6H_9N$. The base is therefore the substance I have

before described* as a product of the action of alkalies upon codeine, under the name of Metacetamine, but which I now prefer calling Propylamine, in accordance with the name now usually applied to the acid with which it corresponds. Unfortunately the quantity of propylamine obtained was too small to admit of my examining either its compounds or itself with accuracy. It is, however, a perfectly limpid and colourless fluid, with a strong pungent odour resembling that of petinine, but more ammoniacal. It gives an abundant white cloud when a rod dipped in hydrochloric acid is brought near it, and unites with the concentrated acids, with the evolution of much heat. Its hydrochlorate crystallizes in large plates closely similar to those of methylamine and petinine.

The discovery of methylamine and propylamine among these products naturally directed my attention to the probable presence of ethylamine, the intermediate term of the same series; but as I had not employed any very particular precautions in condensing the more volatile products during the successive rectifications to which I had subjected the crude oil, almost the whole of it appears to have escaped. By collecting, however, the first few drops passing over in the rectification of the portion boiling under 150° in hydrochloric acid, and forming a platinum salt, I obtained the following result:—

<div align="center">6·930 grains of platinochloride gave 2·649 grains platinum.</div>

This corresponds to 38·22 per cent. Now the per-centage of platinum in the ethylamine salt is 39·60, and the result obtained, which is much too high for the propylamine salt, shows that I must have had a mixture of the two, which might have been separated had I possessed a sufficient quantity of the salt. It will readily be understood that a result of this kind could not in general be produced as evidence of the existence of ethylamine, but under the particular circumstances of the case, the next term of the same series on either side of it having been detected, it may be considered as sufficiently conclusive of its presence.

The occurrence of these bases enables us to establish, on satisfactory grounds, the constitution of petinine. In the first part of this paper, an analysis of that base is given, which agrees in the most perfect manner with the formula $C_8 H_{10} N$, which was also confirmed by that of its platinum salt. It cannot, however, for a moment be doubted that it is homologous with the bases with which I have now shewn it to be associated, that its true formula is $C_8 H_{11} N$, and that it is really butylamine, the corresponding base of the butyric group. The analysis of the platinum salt given in my former paper agrees equally well with this formula, and though that of the base differs from it to some extent, much less reliance is to be placed upon it, as it is scarcely possible, when operating upon so small a scale as that upon which I was compelled to work, to subject the bases to a sufficient number of distillations to effect their complete separation.

I have thus then established the existence, among the products of destructive distillation, of ammonia, and the first four members of the series of bases homologous with it.   I have every reason, however, to believe that the series does not end with petinine, for the fraction boiling about 200° yields a platinum salt in fine scales, and having all the characters of the salts of the same series of bases, and in all probability contains valeramine.   I am not without hope also of obtaining caprylamine; but this I expect will be the last of the series, for when we reach the temperature of about 240°, the character of the bases changes, and we enter upon an entirely different series.

In the separation of the bases boiling above 240°, I have encountered very great difficulties.   After the trial of many different processes, such as converting them into salts, exposing them to cold, partial saturation, and every other plan which appeared likely to answer, I have been compelled to return to fractionated distillation, as the method most likely to answer the end I had in view.   But even with this process the difficulties are great, and I have been by no means so successful in obtaining fixed boiling points as I was when operating on a smaller scale in my former preparations.   I subjected the whole of the oils boiling above 212° to a systematic course of fractionation, each fraction being distilled alone, and the product collected in a fresh series of bottles, and the receivers changed at every ten degrees.   In the earlier rectifications each fraction spread itself over a very large number of degrees, and shewed little tendency towards concentration to fixed points.   The distillations were repeated no less than fourteen times, but even after all this the indications of boiling points were extremely indistinct.   Sometimes in one distillation certain fractions appeared larger than others, but their pre-eminence disappeared again in succeeding rectifications.   Still a certain improvement was manifest, some of the fractions being confined more nearly to the range of degrees within which they had boiled at the previous rectification.   It was obvious, from the whole phenomena of the distillation, that the separation of the different bases was going on, although with extreme slowness; and at this point I endeavoured, by the examination of the platinum salts obtained at different temperatures, to determine the constitution of the bases which these fractions contained; and as I knew from previous experiment, that the quantity boiling between 270° and 280° consisted of picoline, I had from this fact indications of the temperatures at which bases were likely to be found, and I have thus been enabled to determine the existence of two substances belonging to the same homologous series with that substance.

### Pyridine.

The first of these bases, to which I give the name of pyridine, occurs in the fraction boiling about 240°.   This fraction has an odour precisely similar to that of picoline, but more powerful and pungent.   It is perfectly transparent and colour-

less, and does not become coloured by exposure to the air. It dissolves in water in all proportions, and is also readily soluble both in the fixed and volatile oils. It dissolves in the concentrated acids, with the evolution of much heat, and the formation of highly soluble salts. When bichloride of platinum is added to a solution of its hydrochlorate, a double salt is slowly deposited in flattened prisms, which are tolerably soluble in boiling water, less so in alcohol, and entirely insoluble in ether. When these crystals are boiled for a considerable time in water, they appear to undergo decomposition, with the formation of a platinum salt, crystallizing in golden scales. Two analyses of this salt were made, one upon the substance simply precipitated from the hydrochlorate; the other was the same salt redissolved in hot water, so as to leave a considerable proportion undissolved. In the last analysis the salt was mixed with the chromate of lead when still rather hot, and it immediately evolved a strong smell of the base, which accounts for the loss of carbon obtained in the experiment.

I. $\begin{cases} 8\cdot234 \text{ grains of the platinochloride gave} \\ 6\cdot486 \quad \ldots \text{ of carbonic acid, and} \\ 1\cdot705 \quad \ldots \text{ of water.} \end{cases}$

II. $\begin{cases} 5\cdot396 \text{ grains of the platinochloride gave} \\ 4\cdot015 \quad \ldots \text{ of carbonic acid, and} \\ 1\cdot091 \quad \ldots \text{ of water.} \end{cases}$

8·138 grains platinochloride gave 2·792 grains platinum.
4·956 ... ... 1·703 ...

|  |  | Experiment. | | Calculation. | | |
|---|---|---|---|---|---|---|
| Carbon, | . . | 21·48 | 20·29 | 21·03 | $C_{10}$ | 60 |
| Hydrogen, | . . | 2·30 | 2·24 | 2·10 | $H_6$ | 6 |
| Nitrogen, | . . | ... | ... | 4·93 | N | 14 |
| Chlorine, | . . | ... | ... | 37·34 | $Cl_3$ | 106·5 |
| Platinum, | . . | 34·30 | 34·56 | 34·60 | Pt | 98·7 |
|  |  |  |  | 100·00 |  | 285·2 |

The formula $C_{10} H_5 N, HCl, Pt Cl_2$ agrees very closely with these analyses; and the salt is consequently that of a base having the formula $C_{10} H_5 N$, which forms a term of the picoline series. I have not as yet directed further attention to this base, as the phenomena observed in the examination of the next base served to shew that, notwithstanding the correspondence of the salt with theory, much difficulty would be experienced in obtaining the base itself in a state of purity.

## *Lutidine.*

In the fraction boiling about 310°, a base occurs which possesses precisely the constitution of toluidine, and to which I give the name of lutidine. When in the distillation of the mixed bases the temperature rises to about 305° to 310°, more distinct indications of a fixed boiling point are obtained than at any other temperature, and the base which distils presents sufficiently distinct characters from those obtained at lower points. The product is now much less soluble in water;

when dropped into a small quantity of that fluid it floats on the surface, and is only slowly dissolved on agitation. It possesses the remarkable property of immediately separating from its solution on the application of a gentle heat, and collecting on the surface in the form of an oily layer which dissolves again as the temperature falls. Its smell is less pungent and more aromatic than that of picoline, and it is also more oily in its characters. It unites with the acids and forms salts, all of which are highly soluble.

Analyses were made of the different portions of oil boiling about the temperature of 310°, with the following results :—

I. $\begin{cases} 3\cdot840 \text{ grains of the base, boiling between } 310° \text{ and } 315°, \text{ gave} \\ 11\cdot007 \quad \ldots \quad \text{of carbonic acid, and} \\ 3\cdot060 \quad \ldots \quad \text{of water.} \end{cases}$

II. $\begin{cases} 4\cdot012 \text{ grains of the base, boiling between } 315° \text{ and } 320°, \text{ gave} \\ 11\cdot516 \quad \ldots \quad \text{of carbonic acid, and} \\ 3\cdot160 \quad \ldots \quad \text{of water.} \end{cases}$

III. $\begin{cases} 4\cdot319 \text{ grains of the base, boiling between } 316° \text{ and } 320°, \text{ gave} \\ 12\cdot430 \quad \ldots \quad \text{of carbonic acid, and} \\ 3\cdot576 \quad \ldots \quad \text{of water.} \end{cases}$

IV. $\begin{cases} 4\cdot430 \text{ grains of the base, boiling between } 320° \text{ and } 324°, \text{ gave} \\ 12\cdot812 \quad \ldots \quad \text{of carbonic acid, and} \\ 3\cdot405 \quad \ldots \quad \text{water.} \end{cases}$

|  | I. | II. | III. | IV. |
|---|---|---|---|---|
| Carbon, | 78·17 | 78·28 | 78·48 | 78·87 |
| Hydrogen, | 8·85 | 8·75 | 9·10 | 8·54 |
| Nitrogen, | 12·98 | 12·97 | 12·42 | 12·59 |
|  | 100·00 | 100·00 | 100·00 | 100·00 |

These results agree very closely with the formula $C_{14} H_9 N$, as is shewn by the following comparison of the mean experimental and calculated numbers.

|  | Mean. | Calculation. | | |
|---|---|---|---|---|
| Carbon, | 78·45 | 78·50 | $C_{14}$ | 84 |
| Hydrogen, | 8·81 | 8·41 | $H_9$ | 9 |
| Nitrogen, | 12·54 | 13·09 | $N$ | 14 |
|  | 100·00 | 100·00 | | 107 |

Notwithstanding the close correspondence of these results, however, further experiment shewed that some of the fractions, especially those of lower boiling points, contained appreciable quantities of picoline, the presence of which was established by the analysis of the platinum salts. When, for instance, a portion of any of these fractions was saturated with dilute hydrochloric acid and bichloride of platinum added, fine prismatic crystals were slowly deposited, which, as the result of numerous experiments, were found to contain about 32·8 per cent. of platinum, which is exactly the quantity present in the picoline salt, of which the theoretical per-centage is 32·92. On evaporation of the mother liquor, crystals were deposited which gave quantities of platinum varying from 32·5 to 32·0 per

cent., and which were obviously mixtures of the picoline and lutidine salts. When the last mother liquor, however, was evaporated to a small bulk, and alcohol and ether added, another salt altogether distinct from that of picoline, and crystallizing in flattened tables, was deposited, which analysis proved to have the constitution of the lutidine salt.

This platinum salt crystallizes from its solutions in square tables, sometimes very distinct, at other times confused and irregular. It dissolves very readily in cold water, and still more abundantly in boiling, and appears also to be very easily soluble in excess of hydrochloric acid. Numerous analyses of this salt were made, of which the following are the results :—

No. 1. This was the analysis of the salt prepared from the oil distilling between 315° and 325° in the seventh rectification.

$$\begin{cases} 6\cdot377 \text{ grains of the platinochloride gave} \\ 6\cdot187 \quad \dots \quad \text{of carbonic acid, and} \\ 1\cdot915 \quad \dots \quad \text{of water.} \end{cases}$$

6·810 grains platinochloride gave 2·146 grains platinum.
6·476 ... ... 2·051 ...

No. 2. Portion of the oil distilling between 295° and 300° in the fourteenth rectification ; the platinum salt of picoline was separated by crystallization, and the salt analysed precipitated by alcohol and ether.

7·906 grains gave 2·491 grains platinum.
7·835 ... of the salt recrystallized gave
2·470 ... of platinum.

No. 3. Another preparation from the same portion of oil.

$$\begin{cases} 7\cdot330 \text{ grains of platinochloride gave} \\ 7\cdot070 \quad \dots \quad \text{of carbonic acid, and} \\ 2\cdot090 \quad \dots \quad \text{of water.} \end{cases}$$

6·830 grains gave 2·155 grains platinum.

No. 4. Portion of the oil boiling between 300° and 305° in the thirteenth rectification.

7·401 grains gave 2·328 grains platinum.

No. 5. Portion boiling between 325° and 335° in the seventh rectification.

7·194 grains gave 2·256 grains platinum.

| | I. | | II. | | III. | IV. | V. |
|---|---|---|---|---|---|---|---|
| Carbon, | 26·41 | ... | ... | ... | 26·30 | ... | ... |
| Hydrogen, | 3·33 | ... | ... | ... | 3·16 | ... | ... |
| Platinum, | 31·51 | 31·67 | 31·50 | 31·52 | 31·55 | 31·45 | 31·35 |

These results correspond very closely with the formula $C_{14} H_9 N HCl Pt Cl_2$, of which the following is the calculated result compared with the mean of experiment.

|  | Mean. | Calculation. | | |
|---|---|---|---|---|
| Carbon, . | 26·35 | 26·81 | $C_{14}$ | 84 |
| Hydrogen, | 3·23 | 3·19 | $H_{10}$ | 10 |
| Nitrogen, . | ... | 4·49 | N | 14 |
| Chlorine, . | ... | 34·00 | $Cl_3$ | 106·5 |
| Platinum, . | 31·50 | 31·51 | Pt | 98·7 |
|  |  | 100·00 |  | 313·2 |

It is clear, from these analyses, that the salt obtained is that of the base of which the analysis is given above; but it is equally evident, from the presence of small quantities of picoline, that the base itself was not obtained in a state of absolute purity, notwithstanding the close approximation of the experimental results with those required by theory. I have been struck throughout the whole course of the investigation by the fact, that when the fraction corresponding to the boiling point of any particular base has been analysed, results very nearly correct were obtained, even when the substance was very far from being pure. I found, for instance, in the earlier part of the investigation, that the fraction boiling between 270° and 280°, after one or two rectifications, gives precisely the results obtained from pure picoline, although on further rectification the fluid will begin to boil about 250°, and a small portion will still remain in the retort when the thermometer has risen to 300°. It is, however, readily intelligible, that this should be the case when we have to deal with a series of homologous bases, in which the per-centage of carbon goes on increasing as the boiling point rises, so that, as in this particular case, we have the excess of carbon in the less volatile base exactly counterbalancing the deficiency in the more volatile. Thus lutidine, containing 78·5 per cent. of carbon, and pyridine only 75·9, and each successive rectification removing equal quantities of the more and less volatile substances of which the boiling points are equidistant from that of the intermediate member of the series, must always leave a substance in which the quantities of the two impurities must be exactly sufficient to counterbalance the error which each will occasion.

*Hydrargo-chloride of Lutidine.*—I directed my attention to this compound, which is sparingly soluble and crystallizable, in hopes that it might be adapted to the purification of the base itself. I soon, however, abandoned it, as it turned out that it was not possible, in repeating its preparation, to obtain invariably the same substance, each base appearing, like aniline, to form different compounds with corrosive sublimate. When a solution of corrosive sublimate in alcohol is added to an alcoholic solution of lutidine, a curdy white precipitate falls immediately, unless the solutions be highly dilute, in which case it is slowly deposited in groups of radiated crystals. This salt dissolves in boiling water, with partial decomposition; it is still more soluble in spirit, and is deposited unchanged as the solution cools. The following analysis corresponds exactly with the formula $2\,Hg\,Cl + C_{14}\,H_9\,N.$

$$\left\{\begin{array}{l} 7\cdot850 \text{ grains dried } in \text{ } vacuo \text{ gave} \\ 6\cdot373 \quad \ldots \quad \text{of carbonic acid, and} \\ 1\cdot905 \quad \ldots \quad \text{of water.} \end{array}\right.$$

3·112 grains gave 2·32   grains of chloride of silver.
7·684          gave 4·090 grains mercury.

|              |   | Experiment. | Calculation. |          |     |
|--------------|---|-------------|--------------|----------|-----|
| Carbon,      | . | 22·14       | 22·05        | $C_{14}$ | 84  |
| Hydrogen,    | . | 2·69        | 2·36         | $H_9$    | 9   |
| Nitrogen,    | . | ...         | 3·69         | $N$      | 14  |
| Chlorine,    | . | 18·43       | 18·64        | $Cl_2$   | 71  |
| Mercury,     | . | 53·22       | 53·26        | $Hg_2$   | 202 |
|              |   |             | 100·00       |          | 380 |

On another occasion results were obtained more nearly corresponding with the formula $3\,Hg\,Cl + C_{14}\,H_9\,N$; and intermediate results were also obtained, but as the existence of these different compounds appeared to me to be fatal to their employment as a means of purifying the base, I did not attempt to pursue the subject further.   The separation of lutidine from the other bases was also attempted by forming other salts, but none were found to answer, all being highly soluble except the carbazotate, which crystallizes in beautiful, long, yellow needles, a property which, however, is unfortunately possessed by the carbazotates of all the other bases.

From all these experiments, it appears that I have been able to substantiate the existence of two bases, pyridine and lutidine, although it has been as yet impossible to obtain the bases themselves in a state of satisfactory purity.   I am inclined, however, to think that the platinum salts, from their greater stability, and the ease and regularity with which they crystallize, will afford means of purification, but I have been hitherto deterred from trying this method on the large scale by the enormous quantity of platinum which would be requisite for the purpose.

It appears, then, that DIPPEL's oil contains two series of bases, one that is homologous with ammonia, the other a series peculiar to that oil, homologous with one another, and remarkable for their isomerism with the series of which aniline is the type.   Thus we have—

|           |   |              |   |   |           |
|-----------|---|--------------|---|---|-----------|
| Pyridine, | . | $C_{10}\,H_5\,N$ |   |   |           |
| Picoline, | . | $C_{12}\,H_7\,N$ | . | . | Aniline.  |
| Lutidine, | . | $C_{14}\,H_9\,N$ | . | . | Toluidine.|

And it is probable that the series existing in DIPPEL's oil does not cease here, as I have found that the bases, with higher boiling points, give a steadily decreasing per-centage of platinum.   It is impossible, in the present state of the investigation, to give any opinion as to the intimate constitution and relations of these two groups of what I may call isohomologous bases.   The most obvious explanation, however, would be to suppose the new bases to be imidogen or nitrile bases,

which would enable us to understand why they differ from the aniline series, which we know to be amidogen bases. If, however, they belong to either of these classes, they must differ remarkably from any of those hitherto examined, all already formed being extremely unstable, and decomposed even by very feeble affinities, while picoline and its congeners are extremely stable, and resist even the action of nitric acid. Into these points, however, I shall not now enter, but reserve their discussion for a future part of this paper.

### Pyrrol Bases.

I have already referred, at the commencement of this paper, to another series of bases, to which I have given the provisional name of pyrrol bases, and which distil away from the acid fluid by which the others are retained. They are obtained in the form of an oil, which is transparent and colourless at the moment of distillation, but rapidly acquires first a rose, then a reddish-brown, and finally an almost black colour, and the mixture gives, with hydrochloric acid and a piece of fir wood, the purple-red colour which RUNGE describes as characteristic of pyrrol. In fact, I imagined that I had at length obtained this substance, which had escaped me in my previous experiments, but I soon found that the product was really a mixture of several different bases. When distilled with the thermo-meter it began to boil at about 212°, and the temperature gradually rose to above 370°, and during the whole of the distillation pretty large fractions were obtained at every ten degrees, but those between 280° and 310° were decidedly larger than the others. These oils were all bases, with a peculiar and disgusting odour, quite different from, and much more disagreeable than, that of the picoline series of bases. They all acquire colour on standing, although more slowly than the crude oil. These substances dissolve easily in a small quantity of hydrochloric acid, and give, with bichloride of platinum, a precipitate which is at first yellow, but is rapidly converted into a black substance. When dissolved in an excess of acid, and heated along with it, they present a very remarkable character; the solution at a certain temperature becomes filled with red flocks, so abundant and bulky, that, if not too dilute, the fluid becomes perfectly solid, and the vessel can be inverted without anything escaping. The same change takes place, though more slowly, in the cold, and the substance deposited is then of a pale orange-colour, but becomes darker by boiling or exposure to the air. When this substance is collected on a filter, washed, and dried, it forms a reddish-brown and very light and porous mass. It is insoluble in water, acids, and alkalies, but soluble in alcohol, and the solution on evaporation leaves a dark resinous mass. When subjected to dry distillation, it leaves a bulky charcoal, while an exceedingly dis-gusting oil distils.

The acid fluid which has been separated from this substance by filtration, when supersaturated by an alkali, evolves the odour of the bases of the *picoline*

series.   These pyrrol bases I conceive, therefore, to be substances formed by the coupling of the picoline series with some substance which yields the red matter to which I have alluded.   I have not as yet, however, pursued the investigation of these bases, but shall communicate the result of their examination in a future paper.

### The Non-basic Constituents of Bone Oil.

I have as yet directed very little attention to this branch of the subject.   I have found, however, that when the most volatile part of the oil, after separation of the bases, is repeatedly rectified, it improves in odour, and at length there is obtained a substance which, when acted upon by nitric acid, and then by sulphide of ammonium, gives the reaction of aniline,—indicative of the presence of benzine in the oil.   It is probable, therefore, that this series of homologous carbohydrogens forms a part of the oil, but not the whole of it, for I have found that when the oil is boiled for some time with potass, ammonia is evolved, and on supersaturating the potash solution with sulphuric acid, the odour of butyric acid, or at all events of one of the fatty acids, becomes apparent; from which phenomena I draw the conclusion that it also contains the nitriles of these acids.