XXVI.—*Researches on Chinoline and its Homologues.*   By C. Greville Williams, Assistant to Dr Anderson, University of Glasgow.

(Read 7th April 1856.)

Twenty-two years have now elapsed, since Runge first published his remark. able experiments on coal naphtha,* and it would, perhaps, be difficult to instance any chemical investigation which has formed the point of departure of a greater number of researches.   When we consider the vast quantity of bodies which have, first and last, been obtained from coal-tar, it might appear that little more remained to be done,—that the mine was exhausted,—but so far from this being the case, the discovery of one substance has only served to pave the way for the isolation of others.

Among the bodies examined by Runge, there was one which apparently possessed comparatively few features of interest; indeed its very name (the first syllable derived from λευκός) was intended to express its supposed inability to produce coloured reactions, a feature which, in the chemistry of the time, militated greatly against its claims to notice.   I have used the expression " supposed inability," because I shall show further on, that this substance is capable, under certain conditions, of affording extremely brilliant colorations.   Eventually, Gerhardt,† by acting on quinine, cinchonine, and strychnine, with hydrate of potash, obtained the same body.   The first chemist who succeeded in procuring any of its compounds in a state of tolerable purity was Hofmann, whose analysis of the platinum salt is very nearly exact.   But, at the time of that analysis, he was of opinion that the products obtained from coal and chinoline were essentially different, an opinion which he subsequently retracted.   In the mean time, the alkaloid, as obtained from cinchonine was examined by Bromeis‡ and Laurent,§ their results, however, not elucidating the composition of the basic fluid obtained in the manner alluded to.

Some time since, I undertook the examination of the bases produced by destructive distillation of the bituminous shale of Dorsetshire, and found them to be identical with those from bone-oil.|| I now began to see the great probability that all processes of destructive distillation of nitrogenous matter at very elevated

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* Poggend. Annäl., Bd. xxxi., p. 65 und 513; und Bd. xxxii., p. 308 und 328.
† Revue Scientif., x., 186.   Compt. Rend. des Trav. de Chim. 1845, p. 30.
‡ Liebig's Annal., Bd. lii., p. 130 ; and Ann. der Chem. u. Pharm. lii., 130.
§ Ann. de Chim. et de Phys. [3] xxx., 368.
|| Quart. Jour. Chem. Soc. Lond., July 1854.

temperatures would result in the formation of the same classes of alkaloids, and subsequent researches* have only tended to confirm this view. In a little paper, " On some of the basic constituents of Coal-Naphtha, and on Chrysène,"† I have given a table, showing the extraordinary similarity of the basic products derived by dry distillation from DIPPEL's oil, coal, the Dorset shale, and cinchonine. The last of these researches was undertaken in the endeavour to throw light upon the discrepancies in the results of the chemists who had previously examined chinoline, the experiments being embodied in a paper which appeared in the Transactions of the Society last year. In that communication,‡ I showed that the fluid usually known as chinoline, and supposed to have the formula $C_{18} H_7 N$, had, in fact, a very complex constitution, and contained in addition to that base, six others. As my chief object at that time, was to demonstrate the real nature of the decomposition which cinchonine undergoes at an elevated temperature in the presence of alkalies, I did not make a minute examination of the chinoline itself, as I conceived it to be sufficient for the purposes of that investigation to show that a base of the formula $C_{18} H_7 N$ did really exist in the fluid. This fact was by no means a matter of course, for the analyses of the chinoline from cinchonine previously published were so conflicting, that it was a difficult matter to derive a formula from them. HOFMANN's analyses were made upon a product from coal-tar, and the formula he gave as the expression of his results, was $C_{18} H_8 N$. But as an even number of atoms of hydrogen in a body containing an equivalent of nitrogen, was incompatible with views now almost universally received of the constitution of organic bodies, $C_{18} H_7 N$ was taken by most chemists as the true formula of the base from coal-tar. But the wide differences in the analyses of the chinoline obtained by distilling cinchonine with potash, induced GERHARDT § to express doubts, as to whether $C_{18} H_7 N$, or $C_{20} H_9 N$ was the correct formula, although he appears to lean towards the latter, for he places it at the head of the section, but, nevertheless, shows that the formula is open to doubt, by annexing a note of interrogation to it. I have shown the cause of the variable nature of the results obtained by other experimenters, and have proved the existence of a homologous series, of which, until I commenced this investigation, only one member was known.

Many circumstances conspire to render a detailed examination of chinoline a problem of interest, for, perhaps, no other body, known for an equal length of time, and investigated by so many hands, is so erroneously described in the manuals of organic chemistry. In fact, there are few things stated regarding it, that are not more or less incorrect.

Chinoline has, however, been invested with an artificial interest, from a supposed intimate connexion between it and quinine, and an equally supposititious parallelism between the action of heat upon the last named alkaloid, and upon the hydrated oxide of tetramethylammonium, while the real points of attraction which it possesses have been neglected, or supposed not to exist.

The first incorrect idea of the connexion between chinoline and quinine, may be very briefly disposed of. It was founded upon the supposition that chinoline was the sole product of the action of hydrate of potash, at a high temperature, upon quinine. In this manner, it was easy to construct an equation by which it was made to appear, that quinine, *minus* a certain number of equivalents of carbon, hydrogen, and oxygen, yielded chinoline.

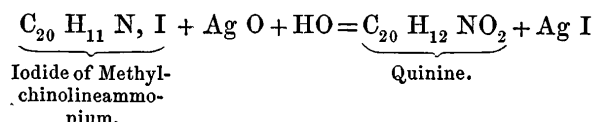Another supposed connexion between the two alkaloids was a very beautiful one, and one that, at the time when $C_{18} H_8 N$ was the received formula for chinoline, could scarcely have failed to suggest itself to the eminent chemist, whose particular train of research led him to examine the action of iodide of methyl upon the natural and artificial alkaloids. It is well known, that iodide of tetrethylammonium, by treatment with oxide of silver, yields hydrated oxide of that base, which is rendered obvious, by a glance at the following equation :—

$$N \begin{Bmatrix} C_4\ H_5 \\ C_4\ H_5 \\ C_4\ H_5 \\ C_4\ H_5 \end{Bmatrix} I + Ag\ O + HO = N \begin{Bmatrix} C_4\ H_5 \\ C_4\ H_5 \\ C_4\ H_5 \\ C_4\ H_5 \end{Bmatrix} O, HO + Ag\ I;$$
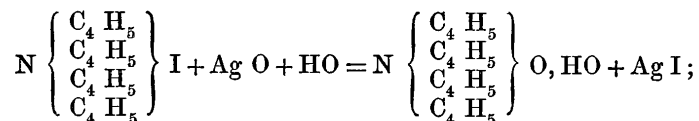
and if we follow out the same equation, substituting iodide of methyl-chinoline-ammonium,* for iodide of tetrethylammonium, we find that at first sight,

$$\underbrace{C_{20}\ H_{11}\ N,\ I}_{\substack{\text{Iodide of Methyl-} \\ \text{chinolineammo-} \\ \text{nium.}}} + Ag\ O + HO = \underbrace{C_{20}\ H_{12}\ NO_2}_{\text{Quinine.}} + Ag\ I$$

appears a reaction likely to take place;† unfortunately, however, there are two reasons why it is impossible, the first being, that iodide of methyl-chinoline-ammonium is represented by $C_{20} H_{10} N, I$, instead of $C_{20} H_{11} N, I$; and the other, that the action of oxide of silver upon the methyl and ethyl compounds of the nitryl bases of this class is more complex than would be supposed from the first equation, and the known success of the reaction with the iodides of the ammonium bases derived from the alcohol radicals alone.

So much has been said about the artificial formation of quinine from the leukol of coal-tar, that I have appended a few reasons for concluding that it is impossible by any analogous process to that previously described. Quinine, accord-
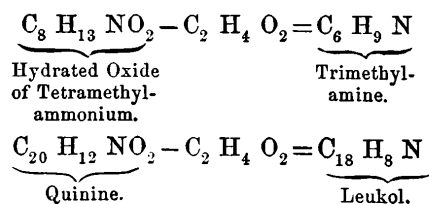
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* Supposing for the moment the old formula for chinoline ($C_{18} H_8 N$) to be correct.

† I have vainly searched through the Chemical Journals for any paper by Dr HOFMANN, tending to show the real nature of the action of oxide of silver upon iodide of methylchinoline. This has led me to make the experiments detailed at page 392.

ing to STRECKER's experiments,* takes up only one equivalent of the alcohol radicals, and is therefore concluded with safety to be a nitryl base. Chinoline affords still more complete evidence of belonging to the same class, for not only is it incapable of taking up more than one equivalent, but, by the operation, it becomes converted into a fixed alkaloid. Now, any process for making artificial quinine by means of the reactions mentioned above, would result in the formation of an ammonium base, which must of necessity have a totally different constitution to quinine. It may be worth while, for a moment, to glance at the formidable difficulties by which the artificial formation of such a base as quinine is surrounded. In the first place, in the present state of our information, it appears to consist of three radicals, united and having one equivalent of nitrogen and two of oxygen attached. Now, to acquire a knowledge of the constitution of these three radicals (one of which, in all probability, is oxidized) is a problem involving a new mode of research, the key to which appears, for the present, to be hidden. And even supposing the three radicals known, they have to be formed; and then to combine them with the addition of an equivalent of nitrogen, without destroying the group, presents a task of no ordinary difficulty.

I should not have entered upon this branch of the subject, had it not been for the manner in which the possibility of the formation of quinine, by the method above alluded to, has been accepted as a reality, which is the more remarkable from the manner in which HOFMANN cautioned chemists against placing too much reliance upon the success of the process.

As it is my wish to correct, as far as my information will permit me, the erroneous views which have been formed of the relations between chinoline and quinine, I return to the supposed similarity between the action of heat upon quinine and the hydrated oxide of tetramethylammonium. This part of the subject is the more interesting, as it appears to have formed one of the links in the chain of reasoning, which led to a belief in the possibility of converting leukol into quinine, by the successive actions of iodide of methyl and oxide of silver. As the fixed base, hydrated oxide of tetramethylammonium, by heating yields trimethylamine, the difference being $C_2 H_4 O_2$, so quinine, less $C_2 H_4 O_2$ yields the old formula of leukol† thus,—

$$\underbrace{C_8 H_{13} NO_2}_{\substack{\text{Hydrated Oxide}\\\text{of Tetramethyl-}\\\text{ammonium.}}} - C_2 H_4 O_2 = \underbrace{C_6 H_9 N}_{\substack{\text{Trimethyl-}\\\text{amine.}}}$$

$$\underbrace{C_{20} H_{12} NO_2}_{\text{Quinine.}} - C_2 H_4 O_2 = \underbrace{C_{18} H_8 N}_{\text{Leukol.}}$$

The identity in kind of the above equations presupposes two conditions, neither

* Researches in Organic Chemistry, by ADOLPH STRECKER. Compt. Rend. xxxi. 49. Chem. Soc., Quart. Jour. 1854, vol. vii., p. 278.

† Quart. Jour. Chem. Soc., vol. iv., p. 328.

of which exist, the first being the correctness of the old formula for chinoline (or leukol), the second, its being the sole basic product in the distillate, from the cinchona alkaloids.

The next prevalent error with regard to chinoline is, that its salts have less tendency to crystallize than the generality of nitryl bases; whereas, in fact, the reverse (with some exceptions) is the truth. I have seldom seen salts more easy to crystallize than the nitrate, oxalate, and bichromate of chinoline, while its double salts, with platinum, gold, palladium, uranium, and cadmium, are beautiful substances, the same may be said of the iodides of the methyl, ethyl, and amyl compounds. The erroneous idea alluded to arose from previous experimenters, working on an impure substance.

The only means for determining the constitution of chinoline up to the present time, has been Dr HOFMANN'S analysis of the platinum salt, from a base extracted from coal-tar; for the combustions of the base itself yet made, are very unsatisfactory. Annexed are the results as yet obtained.[*]

		HOFMANN.			BROMEIS.		$C_{18}H_7N$	$C_{20}H_9N$
Carbon, . . .		82·67	82·88	82·34	82·74	82·78	83·70	83·91
Hydrogen, . .		6·56	6·25	6·10	6·11	5·88	5·41	6·29
Nitrogen, . .		11·28	...	...	...	...	10·89	9·80
							100·00	100·00

A glance at the above numbers shows that no conclusion can be drawn from them; and when it is considered, that chinoline and lepidine only differ by ·21 in their percentage of carbon, it becomes evident, that careful analyses of the salts of these bases are the only means by which their history and composition can be rendered certain. The platinum salt of chinoline possesses characters which render it peculiarly well adapted for this purpose, inasmuch as it differs totally from the corresponding compound from the Dippel and aniline series, in its great insolubility. I therefore selected this compound as a means of ascertaining the purity of the various fractions obtained in the course of the investigation, and which were intended for conversion into the various salts described further on; sometimes I was contented with merely a platinum determination, at others, I ascertained by combustion with chromate of lead, the percentage of carbon and hydrogen, and in this manner, the analyses quoted below were obtained. In my former paper, I gave the result of three combustions of the platinum salt of chinoline, and three platinum determinations; the salts analysed were obtained from fractions boiling at a somewhat lower temperature than those the details of the analyses of which are given below. The following analyses were made with salts obtained from fractions boiling about 460°, which is, probably, very nearly the boiling point of chinoline.

* GERHARDT, Traité, troisième partie, p. 149.

I. {
8·900 grains of platinum-salt of chinoline from fractions boiling between
450° and 460° F. gave
10·559 ... carbonic acid and
2·191 ... water, and
6·235 ... platinum salt of chinoline, gave
1·827 ... platinum.
}

II. {
6·057 ... platinum-salt of chinoline gave
1·772 ... platinum.
}

III. {
5·907 ... platinum-salt of chinoline gave
1·731 ... platinum.
}

or, per cent.—

		I.	II.	III.	Mean.
Carbon,	.	32·36	...	...	32·36
Hydrogen,	.	2·74	...	...	2·74
Nitrogen,	.	...	...	...	...
Chlorine,	.	...	...	...	...
Platinum,	.	29·30	29·26	29·30	29·29

In the following table, the result of all my analyses (including those in the former paper) is compared with the numbers required by theory; the analysis just quoted being the fourth in the series :—

	I.	II.	III.	IV.	V.	VI.	Mean.	Theory.
Carbon, .	31·93	32·24	32·52	32·36	...	...	32·26	32·19
Hydrogen,	3·09	2·62	2·58	2·74	...	...	2·76	2·39
Nitrogen,.	...	...	...	...	...	...	...	4·17
Chlorine,.	...	...	...	...	...	...	...	31·74
Platinum,	29·44	29·30	29·60	29·30	29·40	29·26	29·38	29·51

100·00

It will be seen that there is a slight excess both in the carbon and hydrogen of these analyses. This arises from the presence of a small quantity of lepidine, the platinum salt of the two bases being too nearly of the same degree of solubility to allow of separation by fractional crystallization. This source of error is much lessened in the other salts, their formation, in most cases, being a process of purification. Platinochloride of chinoline is very sparingly soluble in cold water, requiring 893 parts for solution at 60° F.

It is to be remembered, that all the chinoline compounds mentioned in this paper were made from a base procured by distillation of cinchonine with potash, the coal-chinoline requiring a tedious series of purifications, in addition to the fractional distillations, before it could be obtained pure enough for conversion into compounds fit for analysis. The platinum-salt is, however, more easily obtained in a pure state from the coal bases, than most other compounds of this alkaloid.

In the following table, the mean result of my analyses of the platinum-salt of chinoline is compared with those obtained by other observers,* whose numbers have been recalculated according to the present atomic weight of carbon.

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* GERHARDT, loc. cit.

	HOFMANN.		GERHARDT.			BROMEIS.			GREV. WILLIAMS. Mean.	Calcul.
Carbon, .	32·06	...	32·99	32·46	32·51	33·31	33·42	33.33	32·26	32·19
Hydrogen,	2·58	...	3·14	3·14	3·28	2·71	2·83	2·68	2·76	2·39
Nitrogen,	...	...	4·42	...	...	3·98	4·21	4·00 ···	...	4·17
Chlorine,	30·96	...	...	...	...	...	...	...	...	31·74
Platinum,	29·27	29·11	27·80	28·08	27·69	28·23	28·34	28·81	29·38	29·51
										100·00

Only the first of these analyses was made from a base extracted from coal-tar; all the others were obtained from chinoline, produced by destructive distillation of cinchonine with potash.

LAURENT, by mixing hot alcoholic solutions of hydrochlorate of chinoline and bichloride of platinum, obtained, after twenty-four hours, fine yellow needles ; but, on examination under the lens, it was found not to be a homogeneous crystallization, for a small quantity of little grains had also deposited.* I have not found that any observer, except myself, has subjected the bases produced from cinchonine to a systematic fractionation, before forming the platinum salt. The fraction analysed by me had been rectified fourteen times, and was nearly constant between 460° and 470°.

Aurochloride of Chinoline.—The only account of this beautiful salt I have been able to find is in Dr HOFMANN's paper, on the bases of coal-tar, where he merely states, that it corresponds in colour and other properties with the gold salt of aniline, but the latter appears† to be a yellow precipitate which rapidly becomes brown in the air, and, therefore, differs considerably from the chinoline salt, which is quite permanent under the same circumstances. As obtained by me from a specimen of chinoline of considerable purity, it was in the form of slender canary-yellow needles, sparingly soluble in cold water, and precipitating instantly on the addition of a solution of terchloride of gold, to a moderately strong solution of hydrochlorate of chinoline.

{ 3·883 grains of aurochloride of chinoline dried at 212° gave, on ignition,
{ 1·625 ... of gold.

or, per cent.—

Experiment.	Theory. $(C_{18} H_7 N, HCl + Au Cl_3)$
41·85	42·00

Palladiochloride of Chinoline.—Dr HOFMANN describes this salt in his paper, previously quoted, as resembling that from aniline, but M. MÜLLER‡ states the latter to be *yellow* ; I found, however, that when moderately concentrated solutions of chloride of palladium and hydrochlorate of chinoline are mixed, a copious

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* GERHARDT, loc. cit., and LAURENT, Ann. de Chim. et de Phys. [3] xxx., 368.
† GERHARDT, Traité, tome troisième, p. 86.   ‡ Ann. der Ch. u. Pharm. lxxxvi., 368.

deposit of *chestnut-brown* crystals takes place. This salt is moderately soluble in water. It requires a very strong heat to give pure metallic palladium.

$\left\{\begin{array}{l} 3\cdot423 \text{ grains of palladiochloride of chinoline gave, on powerful ignition in a porcelain capsule,} \\ \cdot725 \quad \ldots \quad \text{palladium.} \end{array}\right.$

or, per cent.—

<div align="center">

Experiment.   Theory.

$(C_{18} H_7 N, HCl, + Pd Cl$

21·18   20·96

</div>

Cadmium Salt Chinoline.—The experiments of CROFT, and more especially VON HAUER, have shown that cadmium forms well-defined crystalline salts, with the chlorides of the alkalies, alkaline earths, and the chloride of ammonium. Before I became acquainted with the results of the latter chemist, I had been engaged in a series of experiments made with a view of extending our knowledge of the double salts formed by the hydrochlorates of the alkaloids with metallic chlorides. The information at present in our possession on this subject is very limited. The only salts of the class alluded to which have been analysed, are those formed with platinum, gold, palladium, and mercury. Now the salts of the latter metal vary greatly in constitution, and are, moreover, somewhat troublesome to analyse. I have, therefore, made a few experiments with a view to ascertain what other metals than those mentioned above, yield chlorides capable of combining with the alkaloids, to form well crystallized double salts. In the present communication, however, I only notice those formed by the chlorides of cadmium and uranyl with chinoline.

When moderately concentrated solutions of hydrochlorate of chinoline and chloride of cadmium are mixed, the fluid solidifies with rise of temperature to a snow-white mass of crystals. If the solutions are not too strong, they are obtained in the form of needles occupying a great bulk when in the mother liquor, but shrinking very much when pressed. They are less soluble in alcohol; I therefore used that fluid to wash them. The alcoholic washings, when kept for some time, deposit needles, often an inch long, but so silky and fragile as to be preserved of their original size with difficulty. They retain their colour perfectly, and, with the exception of losing two equivalents of water of crystallization, are quite unaltered by drying for a few hours at 212°. The salt volatilizes at a considerably higher temperature, without residue. The quantity at my disposal was very limited, and being, therefore, obliged to work on small quantities, I found it inconvenient to estimate the cadmium as oxide by the usual process, as the carbonate of cadmium, when precipitated from solutions containing chinoline at the boiling heat, not only has a strong tendency to pass through the filter, but adheres to the paper so strongly as to cause a loss of metal by reduction and volatilization during incineration. The precipitate was too light to be collected by decantation.

I obtained, however, an accurate result by precipitating with sulphuretted hydrogen, and collecting the sulphide of cadmium on a weighed filter.

I. $\begin{cases} 7\cdot911 \text{ grains of cadmium salt, dried at } 212°, \text{ gave} \\ 8\cdot976 \quad \cdots \quad \text{carbonic acid, and} \\ 1\cdot765 \quad \cdots \quad \text{water.} \end{cases}$

II. $\begin{cases} 8\cdot875 \quad \cdots \quad \text{cadmium salt, dried at } 212°, \text{ gave} \\ 10\cdot053 \quad \cdots \quad \text{carbonic acid, and} \\ 2\cdot060 \quad \cdots \quad \text{water.} \end{cases}$

III. $\begin{cases} 10\cdot534 \quad \cdots \quad \text{cadmium salt, dried at } 212°, \text{ treated by } \text{PELIGOT's process, gave} \\ \cdot42295 \quad \cdots \quad \text{nitrogen.} \end{cases}$

IV. $\begin{cases} 6\cdot997 \quad \cdots \quad \text{cadmium salt chinoline, dried at } 212°, \text{ gave} \\ 2\cdot885 \quad \cdots \quad \text{sulphide cadmium.} \end{cases}$

	I.	II.	III.	IV.	Mean.	Calculation.		
Carbon, .	30·94	30·89	...	...	30·92	30·99	C_{18}	108
Hydrogen, .	2·48	2·58	...	...	2·53	2·29	H_8	8
Nitrogen, .	...	...	4·02	...	4·02	4·02	N	14
Chlorine, .	...	...	...	...	...	30·56	Cl_3	106·5
Cadmium, .	...	...	...	32·07	32·07	32·14	Cd_2	112
						100·00		348·5

It is evident, therefore, that the formula for the salt dried at 212° is—

$$C_{18} H_7 N, H Cl + 2 Cd Cl.$$
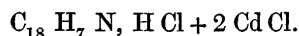
Several examples of salts of the same constitution occur in inorganic chemistry, some of which have been examined by M. VON HAUER, who terms them chlorobicadmiates. The chinoline salt, if merely dried by exposure to the air, contains two equivalents of water, for at 212° it loses 5·41 per cent.; theory requires 4·91. The excess arises from a little moisture adhering somewhat tenaciously to the crystals.

Hydrochlorate of Chinoline and Chloride of Uranyl.—If double carbonate of uranium and ammonia, dissolved in hydrochloric acid, is added to a strong solution of hydrochlorate of chinoline, the fluid rapidly becomes filled with short, brilliant, yellow needles, and in a few minutes the whole fluid solidifies, so that the vessel may be inverted without the contents escaping. From more dilute solutions, prismatic crystals are deposited, sometimes of considerable size. The salt is of a rich yellow colour, and is very soluble in water. It was quite free from any trace of ammonia. The mother liquid was removed by washing with alcohol. The quantity at my disposal was too small to allow of a complete examination of all its properties.

I. $\begin{cases} 6\cdot760 \text{ grains of uranium salt of chinoline, dried at } 212°, \text{ gave} \\ 7\cdot900 \quad \cdots \quad \text{carbonic acid, and} \\ 1\cdot686 \quad \cdots \quad \text{water.} \end{cases}$

II. $\begin{cases} 5\cdot135 \quad \cdots \quad \text{uranium salt, dried at } 212°, \text{ gave} \\ 4\cdot352 \quad \cdots \quad \text{chloride of silver.} \end{cases}$

				Experiment.		Calculation.		
				I.	II.			
Carbon,	.	.	.	31·87	...	32·05	C_{18}	108
Hydrogen,	.	,	.	2·77	...	2·37	H_8	8
Nitrogen,	.	.	.	...	...	4·15	N	14
Chlorine,	.	.	.	...	20·97	21·07	Cl_2	71
Uranium,	.	.	.	...	...	35·61	Ur_2	120
Oxygen,	.	.	.	...	...	4·75	O_2	16
						100·00		337

The formula—

$$C_{18} \, H_7 \, N, \, H \, Cl, \, + \, (Ur_2 \, O_2) \, Cl,$$
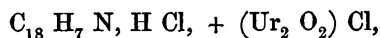
appears, therefore, to be the correct expression of the analysis, and it agrees in constitution with the anhydrous ammoniochloride of uranyl of PELIGOT. It is my intention to examine the double compounds of uranium with other organic bases.

Binoxalate of Chinoline.—The great discrepancy in the results of RUNGE and HOFMANN with regard to the oxalate of chinoline, made me desirous of ascertaining the nature of this salt. According to the former chemist, leukol (chinoline) has such a great tendency to form a crystalline oxalate, that this property is its marked characteristic; HOFMANN, on the other hand, could only obtain it in the form of a confused, radiated, glutinous mass, deposited when the solution had reached a certain state of concentration. I found, however, that if 24·3 parts of chinoline are added to 16·5 parts dry oxalic acid, dissolved in a small quantity of water, the whole solidifies to a white crystalline mass, of the consistence of soft cheese. The salt cannot be obtained pure by a random admixture of the ingredients, as, although the chief tendency appears to be to form the binoxalate, yet other compounds are also formed in sufficient quantity to prevent constant analytical results from being obtained, unless the above proportions are used. The salt, before being employed for analysis, must be recrystallized from alcohol once or twice, when it forms fine silky needles. It is partially decomposed by exposure for two days to 212°, with evolution of chinoline, a salt being formed intermediate in composition between the binoxalate and quadroxalate. It is necessary, therefore, to dry it for analysis *in vacuo* over sulphuric acid.

$$\left\{ \begin{array}{lll} 6·995 & \text{grains of binoxalate of chinoline, dried } in \ vacuo, \text{ gave} \\ 15,407 & ... & \text{carbonic acid, and} \\ 2,798 & ... & \text{water.} \end{array} \right.$$

				Experiment.	Calculation.		
Carbon,	.	.	.	60·07	60·27	C_{22}	132
Hydrogen,	.	.	.	4·44	4·11	H_9	9
Nitrogen,	.	.	.	...	6·39	N	14
Oxygen,	.	.	.	...	29·23	O_8	64
					100·00		219

Nitrate of Chinoline.—In some respects my experiments on this salt tally with those of Dr HOFMANN, in others they differ considerably. It was obtained by the last-named chemist by allowing a mixture of leukol and dilute nitric acid to rest under a bell-jar; after some time the salt crystallized in confused concentric needles, which were obtained white and dry by pressure between folds of filtering paper. He does not appear to have analysed it. I found that if, after an excess of nitric acid slightly diluted was added to chinoline, the fluid was evaporated on the water-bath, a pasty mass was obtained, which solidified on cooling. From a hot alcoholic solution fine white needles soon deposited, which were infusible at 212°, and unalterable in the air. Dr HOFMANN, on the contrary, found his salt to fuse on moderate heating, and to rapidly become blood-red by exposure to the air; these are, evidently, the characters of an impure substance. The nitrate of chinoline was burnt with oxide of copper, a long column of copper turnings being placed in the front of the tube.

$$\begin{cases} 6{\cdot}590 \text{ grains of nitrate of chinoline, dried at } 212°, \text{ gave} \\ 13{\cdot}516 \quad \ldots \quad \text{carbonic acid, and} \\ 2{\cdot}530 \quad \ldots \quad \text{water.} \end{cases}$$

				Experiment.	Calculation.		
Carbon,	.	.	.	55·94	56·25	C_{18}	108
Hydrogen,	.	.	.	4·27	4·17	H_8	8
Nitrogen,	.	.	.	…	14·58	N_2	28
Oxygen,	.	.	.	…	25·00	O_6	48
					100·00		192

Chinoline gives a very marked reaction with strong fuming nitric acid, and which also shows its great stability. If a few drops of the base are allowed to trickle down the side of a test-tube, and a small excess of the acid is added, the two combine with violence, the portion of alkaloid adhering to the sides is converted by the fumes of the acid into long needles, and, when cold, the whole fluid solidifies to a beautifully white crystalline mass of pure nitrate. No nitrochinoline, or any other decomposition product, is formed, if the base be free from impurities.

Bichromate of Chinoline.—GERHARDT, in describing this salt,* merely states, that chromic acid in solution gives, with pure chinoline, an orange-yellow crystalline precipitate, and that the dry acid decomposes the base with inflammation, Dr HOFMANN, in his paper on the coal bases, previously referred to, states that, a short time after he had commenced the investigation of leukol, he was inclined to consider it the same as that GERHARDT obtained by the action of hydrate of potash on quinine, cinchonine, and strychnine. He says, however, that he soon convinced himself that they were totally distinct, their behaviour towards a

* Traité de Chimie Organique, troisième partie, p. 150.

solution of chromic acid being quite dissimilar, for while chinoline and its salts gave a beautiful orange-yellow crystalline precipitate, leukol was oxidized and converted into a black resinous oil. Subsequently,[*] LIEBIG announced, upon the authority of experiments made by HOFMANN, that perfectly pure leukol gave the same crystalline precipitate with chromic acid. I have not been so successful as M. HOFMANN; for, although the chinoline and lepidine procured by destructive distillation from cinchonine have, in my hands, given salts of extreme beauty and purity with chromic acid, I have failed to obtain the same result with either the chinoline or lepidine from coal-tar. I have also boiled the bases from the latter source with dilute chromic acid, to destroy impurities, and then separated them by distillation with potash, but they merely gave an oily precipitate with chromic acid. When dissolved in hydrochloric acid, and bichromate of potash is added, the same result occurs. I even took a platinum salt of coal-lepidine, which yielded, on combustion, the numbers detailed in Analysis I., p. 398; and, after having reobtained the base by distillation with potash, endeavoured to procure from it a crystalline chromate, but in vain, a red oil being the only product. It is true, that when I added dilute chromic acid to chinoline from coal-tar, the sides of the tube acquired a coating of very minute brilliant points, which reflected light with a peculiar satin-like lustre; but the lens resolved them into oily globules. The following experiments were, therefore, made upon chinoline from cinchonine. Neither GERHARDT nor HOFMANN have analysed the salt.

The beauty of the bichromate of lepidine described in my last paper,[†] induced me to ascertain the composition and properties of the homologue next below it, in the anticipation that its outward appearance would be equally striking. But there are some slight differences in the two bodies; bichromate of chinoline is still less soluble than the other salt, and this prevents the crystals from being readily procured of so large a size. When dry, it is much more violently decomposed by heat than the lepidine compound. The fixed product is, however, the same, namely, green oxide of chromium and carbonaceous matter. If the dry salt be placed in a capsule, and heat be very gradually applied, no change at first takes place, but suddenly it takes fire with explosive violence, and the greater part of the green oxide and carbon is projected. I prepared the salt for analysis by adding dilute chromic acid in excess to pure chinoline; at first the product is somewhat resinous, but immediately it is touched with a glass rod, it becomes gritty and crystalline. The solid is then filtered off, the mass slightly washed, dissolved in boiling water, filtered to remove traces of an oily impurity, and, on cooling, the fluid becomes filled with brilliant yellow needles arranged in groups. It may be dried at 212° with safety, provided adhering moisture has been removed as much as possible by pressure between folds of filtering paper. If the

* Chem. Gaz., vol. iii.. p. 251 (1845). Proc. of Chem. Soc., April 7, 1845.
† Trans. Roy. Soc. Edin., vol. xxi. part ii.

salt is previously moistened with hydrochloric acid, it may be ignited without explosion, and the green oxide estimated with accuracy. The combustion was made with oxide of copper.

I. $\left\{\begin{array}{l} 6\cdot827 \text{ grains of bichromate of chinoline, dried at 212° gave} \\ 11\cdot284 \quad \ldots \quad \text{carbonic acid, and} \\ 2\cdot146 \quad \ldots \quad \text{water.} \end{array}\right.$

II. $\left\{\begin{array}{l} 6\cdot381 \quad \ldots \quad \text{bichromate of chinoline, dried at 212°, gave, on ignition,} \\ 2\cdot072 \quad \ldots \quad \text{green oxide of chromium.} \end{array}\right.$

III. $\left\{\begin{array}{l} 5\cdot534 \quad \ldots \quad \text{bichromate of chinoline, dried at 212°, gave, on ignition,} \\ 1\cdot787 \quad \ldots \quad \text{green oxide of chromium.} \end{array}\right.$

	Experiment.			Calculation.		
	I.	II.	III.			
Carbon, . .	45·08	...	...	45·11	C_{18}	108
Hydrogen, . .	3·49	...	...	3·34	H_8	8
Nitrogen, . .	...	...	...	5·85	N	14
Chromium, . .	...	22·40	22·28	22·31	Cr_2	53·4
Oxygen, . .	...	...	...	23·39	O_7	56·0
				100·00		239·4

Density of the Vapour of Chinoline.—In Dr HOFMANN'S paper on the coal bases, he states that a determination of the density of the vapour of leukol (chinoline) failed, owing to its leaving a yellow residue on distillation. I have not found this circumstance to operate sufficiently in the case of chinoline from cinchonine, to cause more error than is usually found in determining the vapour densities of bodies obtained by fractional distillation, and having so high a boiling point. The specimen used, boiled in the fourteenth rectification between 460° and 470° F.

Temperature of air,	.	.	13° centigrade.
... vapour,	.	.	277° ...
Pressure,	. . .	.	751 millimetres.
Capacity of balloon,	.	.	330 cent. cub.
Residual air,	. .	.	17·5 ...
Excess of weight of balloon,		.	0·4980 grammes.

The formula
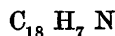
$$C_{18} H_7 N$$

requires

18 volumes carbon vapour,	.	.	0·829 . 18 = 14·922
14 ... hydrogen,	.	.	0·0692 . 14 = ·9688
2 ... nitrogen,	.	.	0·9713 . 2 = 1·9426

$$\frac{17\cdot8334}{4} = 4\cdot4583$$

Experiment.	Theory.
	$C_{18} H_7 N = 4$ volumes.
4·5190	4·4583

Action of Iodide of Methyl on Chinoline.

Hydriodate of Methyl-Chinoline.—When an excess of iodide of methyl is added to chinoline, and the mixture, inclosed in a pressure tube, is heated for

ten minutes to 212', combination is perfectly effected, a finely crystallized hy-driodate resulting. If this salt, which is perhaps more correctly called iodide of methyl-chinoline-ammonium, is treated in the cold with excess of oxide of silver, a strongly alkaline solution is obtained, containing the hydrated oxide of the am-monium base. The solution possesses little stability; on heating with potash, an excessively pungent odour is evolved, acting strongly on the eyes and mucous membrane of the nose. The solution reddens turmeric paper as powerfully as solution of caustic potash, and instantly restores the colour of reddened litmus. The reactions of this base, generally, are the same as those of the ethyl compound next to be described. The smell of a volatile base, a product of the decomposition of methyl-chinoline, is evolved from the moment of its formation; it appears to be methylamine.

By alternate precipitation of the hydriodate by nitrate of silver, hydrochloric acid, and bichloride of platinum, after removal of the chloride of silver, a sparingly soluble platinum salt was obtained. The following is the result of its ana-lysis:—

I. $\begin{cases} 8\cdot930 \\ 11\cdot350 \\ 2\cdot496 \end{cases}$ grains of platinochloride of methyl-chinoline, gave
     ...   carbonic acid, and
     ...   water.

II. $\begin{cases} 8\cdot515 \\ 10\cdot777 \\ 2\cdot303 \end{cases}$ ...   platinochloride of methyl-chinoline gave
     ...   carbonic acid, and
     ...   water.

III. $\begin{cases} 7\cdot861 \\ 2\cdot217 \end{cases}$ ...   platinochloride of methyl-chinoline gave
     ...   platinum.

IV. $\begin{cases} 5\cdot165 \\ 1\cdot456 \end{cases}$ ...   platinochloride of methyl-chinoline gave
     ...   platinum.

	Experiment.				Mean.	Calculation.		
	I.	II.	III.	IV.				
Carbon,	34·66	34·52	...	...	34·59	34·33	C_{20}	120
Hydrogen,	3·11	3·00	...	...	3·06	2·86	H_{10}	10
Nitrogen,	...	...	...	...	...	4·01	N	14
Chlorine,	...	...	...	...	...	30·47	Cl_3	106·5
Platinum,	...	...	28·20	28·19	28·20	28·33	Pt	99
						100·00		349·5

Methyl-chinoline is, therefore, isomeric with lepidine, but has no other point of resemblance. The decompositions of the hydriodate almost exactly resemble those of the ethyl base, and, as the atomic weight of the latter, being higher, gave it an advantage for experiment, I selected it for the purpose.

Action of Iodide of Ethyl on Chinoline.

Hydriodate of Ethyl-Chinoline.—No action takes place on the mere addition of excess of iodide of ethyl to chinoline, but if the tube containing the mixture be sealed and exposed for some hours to a temperature of 212°, the whole becomes a

mass of crystals. When this is the case, and the tube cools, the end may be cut off, a tube bent twice at right angles attached by means of a cork, and, the pressure-tube being immersed in the water-bath, the excess of iodide of ethyl distilled over. The crystals are then dissolved out in a small quantity of hot alcohol, and the solution allowed to cool. The first crop is of a rich yellow colour, becoming of a pale lemon tint on recrystallization. In the state in which the salt is thus obtained it possesses the property of becoming a deep blood-red at 212°, and regaining its normal tint on cooling; this peculiarity becomes much lessened by a repetition of the process. The crystals appear to be cubic, and are easily obtained of considerable size. They dissolve more readily in water than alcohol, but the latter is the best solvent for the purposes of crystallization.

I. $\begin{cases} 6\cdot336 & \text{grains of hydriodate of ethyl-chinoline, dried at 212°, gave} \\ 10\cdot810 & \text{...} \quad \text{carbonic acid, and} \\ 2\cdot513 & \text{...} \quad \text{water.} \end{cases}$

II. $\begin{cases} 6\cdot684 & \text{...} \quad \text{hydriodate of ethyl-chinoline, dried at 212°, gave} \\ 5\cdot457 & \text{...} \quad \text{iodide of silver.} \end{cases}$

	Experiment.		Calculation.		
	I.	II.			
Carbon,	46·53	...	46·32	C_{22}	132
Hydrogen,	4·41	...	4·21	H_{12}	12
Nitrogen,	...	...	4·91	N	14
Iodine	...	44·12	44·56	I	127
			100·00		285

Platinum Salt of Ethyl-Chinoline.—After adding nitrate of silver to a solution of hydriodate of ethyl-chinoline, as in making the iodine determination last mentioned, the excess of silver was removed by the addition of hydrochloric acid, the liquid filtered, and evaporated to a moderate bulk, on the addition of bichloride of platinum, a rich golden-yellow precipitate of sparing solubility was obtained; it was first washed with a little water, and afterwards with alcohol.

$\begin{cases} 6\cdot813 & \text{grains of platinochloride of ethyl-chinoline gave} \\ 1\cdot847 & \text{...} \quad \text{platinum.} \end{cases}$

Agreeing with the formula

$$C_{22} H_{11} N, H Cl + Pt Cl_2.$$
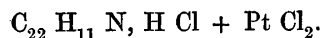
	Experiment.	Calculation.		
Carbon,	...	36·31	C_{22}	132
Hydrogen,	...	3·30	H_{12}	12
Nitrogen,	...	3·85	N	14
Chlorine,	...	29·30	Cl_3	106·5
Platinum,	27·11	27·24	Pt	99
		100·00		363·5

It is evident that ethyl-chinoline is isomeric with cryptidine, the new base to be described further on.

Action of Oxide of Silver on Iodide of Ethyl-Chinoline.

Hydrated Oxide of Ethyl-Chinoline-Ammonium.—A solution of iodide of ethyl-chinoline is decomposed with ease by oxide of silver, even in the cold, a colourless strongly alkaline fluid being formed, containing the fixed base corresponding to the hydrated oxide of tetrethylammonium. The solution instantly reddens turmeric paper, and restores the colour of reddened litmus. It precipitates solutions of sulphate of copper, sesquichloride of iron, acetate of lead, and corrosive sublimate. The addition of a small quantity to a red solution of bichromate of potash renders it yellow, by neutralizing the second equivalent of chromic acid. The solution of the base decomposes chloride of ammonium, liberating the ammonia freely.

The heat of a water-bath decomposes the solution of the hydrated oxide, with production of a splendid crimson colour, the sides of the basin where the liquid has dried becoming a brilliant emerald green, passing in a few seconds to a blue of great beauty and intensity. These colours, like those to be mentioned presently, evidently depend upon oxidation, and would require a very large amount of material to follow out in detail. When the solution of hydriodate of ethyl-chinoline is heated on the water-bath with excess of oxide of silver, a volatile product is evolved, acting strongly upon the eyes.

Action of Sulphate of Silver upon Hydriodate of Ethyl-Chinoline.

If hot solutions of sulphate of silver and hydriodate of ethyl-chinoline are mixed, double decomposition ensues, without any further action taking place, the solution of sulphate of ethyl-chinoline remaining colourless, and the iodide of silver separated being of the normal tint; but, if it be attempted to concentrate the solution by evaporation on the water bath, it undergoes a curious metamorphosis, the sides of the dish, where the solution has dried, become a deep pure blue, but, as the evaporation proceeds, the solution becomes crimson, and when dry, the mass is so deep in tint, as to be nearly black. The dry substance has a slight coppery lustre, like that which indigo possesses when rubbed. It dissolves in water, the solution being of the most gorgeous crimson, becoming rose-coloured by addition of ammonia, while hydrochloric or nitric acids convert it to a scarlet. The colour is tolerably stable, requiring a considerable excess of bromine water to decompose it, the fluid then becoming reddish-brown.

The crimson liquid undoubtedly contains the sulphate of a new base, apparently a product of oxidation of ethyl-chinoline. The reactions upon which this supposition is founded, are the following:—If solution of potash be added to the crimson solution, the colouring matter is almost entirely precipitated, and, if the experi-

ment be successful, the solution merely retains a slight blue tinge. This precipitate appears to be the new base, although probably in a very impure state. When first thrown down, it has a beautiful reddish-violet colour, like that of the crystallized sesquichloride of chromium. It may be washed with water on a filter, being sparingly soluble; it dissolves readily in alcohol, forming a fine crimson fluid, which precipitates a spirituous solution of chloride of mercury. The base dissolves readily in hydrochloric acid, the solution giving a voluminous precipitate with bichloride of platinum. The platinum salt, after well washing with water, was burnt for the percentage of metal, to ascertain whether its atomic weight was higher or lower than that of ethyl-chinoline.

$$\left\{ \begin{array}{l} 2\cdot081 \text{ grains of platinum salt gave} \\ \cdot492 \quad \ldots \quad \text{platinum.} \end{array} \right.$$

212·2   157·0

Atomic weight of new base.   Atomic weight of ethyl-chinoline.

The atomic weight which is derived from this experiment is so excessively high, that no simple relation is apparent between the red product and ethyl-chinoline. The single platinum determination, although carefully made, is evidently insufficient to enable any speculation to be made as to the nature of the decomposition.

It is known that most nitryl bases (those composed solely of the alcohol radicals being the chief exceptions) yield colours by the action of oxide of silver on the ammonium compounds formed with methyl, ethyl, and amyl, but I think none yet worked on yield such magnificent tints as those mentioned in this paper. The subject has another and much greater point of interest than the mere formation of coloured reactions, however beautiful they may be, inasmuch as the careful following out of the decompositions on the large scale promises to assist us in acquiring a knowledge of the constitution of alkaloids of this class. I have therefore promised myself to examine the matter more fully, when the other investigations with which I am now occupied are concluded.

Action of Iodide of Amyl on Chinoline.

Hydriodate of Amyl-Chinoline.—Iodide of amyl reacts with comparative slowness upon chinoline. It is necessary to keep the materials in a pressure-tube for some hours at 212° to effect combination. The iodide crystallizes from alcohol with extreme readiness, and when evaporated slowly upon flat surfaces presents under the lens very peculiar and beautiful forms. On one occasion, after dissolving the iodide in alcohol in a beaker, the fluid was poured into another vessel, and the solution remaining on the sides crystallized in the manner I have endeavoured to illustrate in the annexed sketch. The figure represents the forms about four times the natural size.

The hydriodate of amyl chinoline gave, in a determination of the percentage of iodine, the following numbers.

$\left\{\begin{array}{l} 9 \cdot 882 \text{ grains hydriodate amyl-chinoline gave} \\ 7 \cdot 086 \quad \ldots \quad \text{iodide silver.} \end{array}\right.$

				Experiment.	Calculation.		
Carbon,	.	.	...		51·38	C_{28}	168
Hydrogen,	.	.	...		5·50	H_{18}	18
Nitrogen,	.	.	...		4·28	N	14
Iodine,	.	.		38·75	38·84	I	127
					100·00		327

The fluid from which the iodine had been precipitated was treated with hydrochloric acid in excess, the chloride of silver removed by filtration, and the fluid evaporated to a moderate bulk, excess of bichloride of platinum was then added, and the precipitated platinum salt washed, first with a little water, and then with a mixture of alcohol and ether. The platinochloride of amyl-chinoline is only sparingly soluble in water, it was dried at 212°, and burnt with chromate of lead and copper turnings.

$\left\{\begin{array}{l} 6 \cdot 756 \text{ grains of platino-chloride of amyl-chinoline, gave} \\ 10 \cdot 233 \quad \ldots \quad \text{carbonic acid, and} \\ 2 \cdot 813 \quad \ldots \quad \text{water} \\ 7 \cdot 150 \quad \ldots \quad \text{platinochloride of amyl-chinoline gave} \\ 1 \cdot 733 \quad \ldots \quad \text{platinum.} \end{array}\right.$

			Experiment.	Calculation.		
Carbon,	.	.	41·31	41·43	C_{28}	168
Hydrogen,	.	.	4·63	4·44	H_{18}	18
Nitrogen,	.	.	...	3·45	N	14
Chlorine,	.	.	...	26·26	Cl_3	106·5
Platinum,	.	.	24·24	24·42	Pt	99
				100·00		405·5

Action of Chlorine on Chinoline.—According to GERHARDT,[*] chlorine converts chinoline into a black resin, but my experiments show that it acts in a very different manner, if care be taken to prevent rise of temperature. On dropping chinoline into a large glass vessel of the gas, and leaving it for twelve or fourteen hours, a yellow oil is produced, which, on treatment with water, leaves a white insoluble matter, which I have not yet had an opportunity of studying more in detail.

Action of Chloride of Acetyl on Chinoline.—Chloride of acetyl on being added

[*] Traité, troisième partie, p. 150.

to chinoline, develops much heat, and on evaporation at 212°, a crystalline mass was obtained, but so deliquescent, as to be unfit for examination.

On the Chinoline Series as it occurs in Coal-Tar.

In my paper " On some of the Basic Constituents of Coal-Naphtha and on Chrysène," I ventured to express a belief, that chinoline was not the only member of the group to which it belongs present in coal-tar ; and feeling assured that other homologues remained to be discovered, I was desirous of testing the accuracy of the supposition. Owing to the kindness of Mr GEORGE MILLER of Dalmarnock, I was enabled to obtain fifty gallons of coal-oil of a very high boiling point, and of a density greater than that of water. It was shaken with sulphuric acid to extract the alkaloids, and the acid fluid after dilution with water was treated with excess of lime, and distilled as long as any came over. As the amount of bases of the Dippel series present, was not large, the product being of such a high boiling point, I did not add potash to separate the more soluble portion, but only collected that part which, from its density and insolubility, sank to the bottom of the fluid accompanying it in the distillation. By means of a tap funnel, the basic-oil was separated from the chief part of the water accompanying it, which contained some of the pyridine series in solution. The bases thus obtained are exceedingly impure, and contain aniline and some non-basic substances. It being probable, that toluidine and even other members of the same series might be present, I thought that as apparently insurmountable difficulties prevented their separation from the chinoline series by means of oxalic acid, or similar methods, their presence might nevertheless be made manifest through their products of decomposition. With this view, I treated the mixed bases with nitrite of potash and hydrochloric acid, in the manner indicated by HUNT,* and by this means effectually decomposed all traces of the aniline group present. But the amount of oil heavier than water containing the hydrates of phenyl and cresyl was too small to allow of my further examining them. I propose, however, to return to the subject at a future time.

The acid fluid, after decantation from the heavy oil last alluded to, was then placed in a retort, and a jet of steam sent through the tubulature to the bottom of the liquid ; by this means, many non-basic impurities were removed, and amongst them a white crystalline solid distilled over with the steam, and which eventually proved to be naphthaline. The acid fluid in the retort, after being filtered through pulverized charcoal, to separate resinous matters not volatilized, was treated with potash, to liberate the base, which was then separated by a tap funnel, and completely dried by digestion with sticks of potash. It is proper to

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* SILLIMAN's Journal 1849 ; Chem. Gaz., Jan. 1850 ; GERHARDT, Traité, tome 3me, p. 83 ; HOFMANN, Quart. Jour. Chem. Soc.

mention, that by this treatment, the boiling point of the bases was considerably raised, the aniline being removed, which boils 100° below chinoline.

The bases, as purified by the above method yield, on distillation, fractions from 350° to 525°, Considerably more than one hundred distillations were made before sufficient separation had taken place, to justify me in making any analyses.

Chinoline having already been proved to exist in coal-tar, I began the experiments by searching for lepidine. This base, which was discovered by me* among the volatile alkaloids procured by distilling cinchonine with potash, has the formula,

$$C_{20} H_9 N,$$
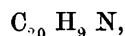
which was established by analyses of the platinum salt, nitrate, hydrochlorate, and bichromate, confirmed also by a determination of its vapour density.

As obtained from coal-tar, lepidine is in the form of an oil, having an odour almost exactly the same as that from cinchonine. But it is impossible by distillation alone, even after the treatment of the crude base with nitrous acid, to procure it in the same state as from the source where it was first found. Coal-lepidine, therefore, yields salts which, for the most part, crystallize with incomparably greater difficulty than that from cinchonine. When dissolved in an acid, although the solution is perfect, there is always an after-odour evolved, somewhat like naphthaline, unless the base has been purified with great care. I was unable, by any means at at my disposal, to obtain the bichromate in a crystalline state, whereas the lepidine from cinchonine yields a beautiful salt, in brilliant yellow needles half-an-inch long. Even when coal-lepidine is boiled with diluted chromic acid for an hour, the base, when separated and redistilled, gives an oily precipitate with chromic acid; moreover, the same occurs if the base be dissolved in hydrochloric acid, and a solution of bichromate of potash is added, as has been previously mentioned in describing the bichromate of chinoline. The red oil obtained in this manner from coal-lepidine may be kept for weeks without showing any tendency either to crystallize or decompose; even the base obtained from a platinum salt of considerable purity, behaved in the same way. On the other hand, coal-lepidine reacts with nitric acid and some other re-agents, like that from cinchonine.

If it were not for the decisive manner in which the fact of Dr HOFMANN's having obtained the crystalline precipitate with leukol and chromic acid has been announced, I should have felt justified in asserting that the bases derived from the two sources were isomeric but not identical; but as the last-named chemist's well-known accuracy prevents me from entertaining a belief in the possibility of an error of experiment, I can only express my regret, that I am ignorant of the method of

* Trans. Royal Soc. Edin., vol. xxi., pt. 27.

purification adopted by him. The most satisfactory mode of explanation of the differences in the properties of the coal and cinchonine series, as obtained by me, is that they are in a peculiar molecular condition, analogous in some respects to the phenomena known in the cases of quinine, the amylic alcohol, and many other bodies, instances of which are daily becoming more numerous. Chemists are aware that even variations in the density and boiling point of the same fluid, when in different states, have been observed; and I may mention, as corroborative of this, that with bases distilled the same number of times, lepidine as pure as I could procure it from both sources differed in boiling point by 25° F.; for the lowest fraction of coal-lepidine that gave correct results on analysis distilled between 485° and 495°, whereas the lowest fraction of the same base from cinchonine, boiled between 510° and 520° F. Another fact which seems corroborative of the supposition that Dr HOFMANN obtained the chinoline from coal-tar in the state in which I procured it from cinchonine, is found in the circumstance that the density of chinoline from coal-tar was ascertained by him to be 1·081, or very near the same number as in my determination of the density of the same base from cinchonine, viz., 1·085. But the coal bases examined by me were lighter than this; for even the lepidine from the the last source had a density of only 1·072 at 60° F., being actually lighter than the homologue, one step below from cinchonine.

I have observed with the pyridine series, as obtained from bone-oil, coal-naphtha, and bituminous shale, that considerable differences are found in their power of forming crystalline salts, and it is, therefore, most probable that the same distinctions exist between them that are met with in the case of the bases from coal and cinchonine. I trust eventually to be able to elucidate some of these points, by subjecting chinoline from both the above substances to the action of polarized light.

The lepidine platinum salt, from cinchonine, precipitates at once in a pulverulent state; but from coal it is for a few seconds soft and resinous, but soon becomes hard and crystalline. The following are my analyses of it from the latter source:—

I. { 9·216 grains crystallized platinochloride of lepidine from fraction boiling 485°-95° 14th rectification, dried at 212°, gave
11·652 ... carbonic acid, and
2·466 ... water.

II. { 5·954 ... platinochloride lepidine from fraction 485°-95°, gave
1·673 .. platinum.

III. { 8·754 ... platinochloride lepidine from fraction 495°-505°, 14th rectification, gave
11·101 ... carbonic acid, and
2·452 ... water.

IV. { 5·554 ... platinochloride lepidine, same as last, gave
1·575 ... platinum.

V. { 5·047 ... platinum salt, 485°-95° crystallized, gave
1·417 ... platinum.

	Experiment.					Mean.	Calculation.		
	I.	II.	III.	IV.	V.				
Carbon,	34·48	...	34·58	...	...	34·53	34·33	C_{20}	120
Hydrogen,	2·97	...	3·11	...	...	3·04	2·86	H_{10}	10
Nitrogen,	...	...	...	...	...	...	4·01	N	14
Chlorine,	...	...	...	...	...	...	30·47	Cl_3	106·5
Platinum	...	28·09	...	28·36	28·08	28·17	28·33	Pt	99
							100·00		349·5

In the following table, the mean of these results is compared with my analyses of the platinum salt from the cinchonine bases.

	Coal-Tar. Mean.	Cinchonine. Mean.	Theory.
Carbon, . . .	34·53	34·04	34·33
Hydrogen, . . .	3·04	2·95	2·86
Nitrogen, . . .	...	...	4·01
Chlorine, . . .	...	...	30·47
Platinum, . . .	28·17	28·13	28·33

Action of Iodide of Ethyl on Lepidine.

Hydriodate of Ethyl-Lepidine.—As it was evident that the process for preparing this compound, and from it the platinum salt, was one of purification, I thought that I should, by this means, obtain nearer results on analysis than was the case with the experiments last quoted; and the following may be considered as confirming the truth of the supposition.

Coal-lepidine, sealed in a tube with excess of iodide of ethyl, and exposed for some hours to 212°, yields a mass of brown needles, which, on recrystallization from alcohol, are of a brilliant canary yellow. They have the same property of becoming red at 212° as the corresponding salt of chinoline, although scarcely to the same degree.

$\begin{cases} 7\text{·}111 \text{ grains iodide ethyl-lepidine gave} \\ 5\text{·}595 \quad ... \quad \text{iodide silver.} \end{cases}$

or per cent.—

	Experiment.	Calculation.		
Carbon, ...		48·16	C_{24}	144
Hydrogen, ...		4·68	H_{14}	14
Nitrogen, ...		4·68	N	14
Iodine, . .	42·52	42·48	I	127
		100·00		299

Platinum Salt of Ethyl-Lepidine.—This salt was obtained in the same manner as the corresponding one of ethyl-chinoline. It is, at the first moment of precipitation, somewhat soft, but soon becomes hard and crystallized. It was pulverized and well washed with a mixture of alcohol and ether previous to analysis.

I. $\begin{cases} 8\cdot374 \text{ grains platinochloride ethyl-lepidine gave} \\ 11\cdot667 \quad \ldots \quad \text{carbonic acid, and} \\ 2\cdot880 \quad \ldots \quad \text{water.} \end{cases}$

II. $\begin{cases} 6\cdot377 \quad \ldots \quad \text{platinochloride ethyl-lepidine gave} \\ 1\cdot688 \quad \ldots \quad \text{platinum.} \end{cases}$

III. $\begin{cases} 4\cdot952 \quad \ldots \quad \text{platinochloride ethyl-lepidine gave} \\ 1\cdot317 \quad \ldots \quad \text{platinum.} \end{cases}$

	Experiment.			Calculation.		
	I.	II.	III.			
Carbon, . .	38·00	...	...	38·14	C_{24}	144
Hydrogen, . .	3·82	...	...	3.71	H_{14}	14
Nitrogen, . .	...	...	...	3·71	N	14
Chlorine, . .	...	...	...	28·21	Cl_3	106·5
Platinum, . .	...	26·47	26·60	26·23	Pt	99
				100·00		377·5

Density of Vapour of Lepidine.—In my former paper on the chinoline bases, I gave 5·14 as the density of the vapour of lepidine, as found by experiment, and I was desirous of ascertaining that of the same base, as extracted from coal-tar, in order to serve as a comparison. It is remarkable to observe the difference which an increment of $C_2 H_2$ has in modifying the power of substances to resist the decomposing influence of heat. While, in taking the density of chinoline at 531° F., being 71° above its boiling point, the fluid condensed in the balloon was almost colourless, lepidine after exposure under the same circumstances to only 523° F., or 28° above its boiling point, had become nearly black; this darkening, caused by separation of carbon, prevented me from making the experiment at a temperature as much above the boiling point as in the case of chinoline, and the two sources of error have the effect of making the density come out somewhat too high.

Temperature of air, . .	15° centigrade.
... vapour, .	273° ...
Pressure, ...	755 millimetres.
Capacity of balloon . .	331 cent. cub.
Excess of weight of balloon, .	·6745 grammes.
Residual air, . . .	6 cent. cub.
Density, . . .	5·15

The formula

$$C_{20} H_9 N$$
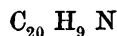
requires the following numbers:—

20 volumes carbon vapour, . .	$=0\cdot8290 \,.\, 20 = 16\cdot580$
18 ... hydrogen, . . .	$=0\cdot0692\,.\,18 = 1\cdot2456$
2 ... nitrogen, . . .	$=0\cdot9713\,.\,2 = 1\cdot9426$

$$\frac{19\cdot7682}{4} = 4\cdot94205$$

Density of vapour of lepidine from cinchonine.	Density of vapour of lepidine from coal.	Theory.
5·14	5·15	$C_{20} H_9 N = 4$ volumes.
		4·94

On Cryptidine, a new Volatile Alkaloid homologous with Chinoline.

In examining the highest fractions of the bases from coal-tar, I have ascertained the presence of a new volatile base, to which I have given the above name.* The quantity at my disposal was so exceedingly small, that the platinum salt is the only compound I have been able to obtain in a state of tolerable purity; but the analyses of this substance leave no doubt whatever of the constitution of this the third homologue of the chinoline series.

If a solution of bichloride of platinum be added to a solution in hydrochloric acid of the fraction boiling about 525°, a pasty yellow mass precipitates, and, on stirring, adheres to the rod. In a few seconds the precipitate becomes crystalline, and is no longer adhesive, and, if it is now dissolved in boiling water, it separates on cooling in groups of yellow needles, sparingly soluble in cold water. Two specimens of salt prepared in this manner, and well washed, first with water, and after with a mixture of alcohol and ether, yielded on combustion the numbers following :—

I. $\begin{cases} 8\cdot018 \text{ grains platinochloride cryptidine, dried at } 212°, \text{ gave} \\ 10\cdot535 \quad \ldots \quad \text{carbonic acid, and} \\ 2\cdot493 \quad \ldots \quad \text{water.} \end{cases}$

II. $\begin{cases} 6\cdot066 \quad \ldots \quad \text{platinochloride of cryptidine, gave} \\ 1\cdot645 \quad \ldots \quad \text{platinum.} \end{cases}$

III. $\begin{cases} 8\cdot958 \quad \ldots \quad \text{platinochloride of cryptidine (another preparation), gave} \\ 11\cdot807 \quad \ldots \quad \text{carbonic acid, and} \\ 2\cdot647 \quad \ldots \quad \text{water.} \end{cases}$

IV. $\begin{cases} 5\cdot990 \quad \ldots \quad \text{platinochloride of cryptidine, gave} \\ 1\cdot631 \quad \ldots \quad \text{platinum.} \end{cases}$

	Experiment.				Mean.	Calculation.		
	I.	II.	III.	IV.				
Carbon, . . .	35·83	...	35·95	...	35·89	36·31	C_{22}	132
Hydrogen, . .	3·45	...	3·28	...	3·37	3·30	H_{12}	12
Nitrogen, . .	...	...	...	...	...	3·85	N	14
Chlorine, . .	...	...	...	...	...	29·30	Cl_3	106·5
Platinum, . .	...	27·12	...	27·23	27·18	27·24	Pt	99·0
						100·00		363·5

If the fraction boiling at 515°-25° is treated with ordinary nitric acid, it dissolves with a purple coloration, and, if the solution is evaporated to dryness, and redissolved in water, an insoluble yellow powder becomes apparent. To the filtered solution bichloride of platinum being added, an adhesive precipitate is formed, having the properties previously assigned to the platinochloride of cryptidine, as obtained from coal-tar. On solution in boiling water and subsequent cooling, a fine crop of orange-yellow needles was obtained, which, on combustion with chromate of lead and copper turnings, gave the result annexed.

* From κρυπτός.

I. $\begin{cases} 7\cdot921 \text{ grains platinochloride of cryptidine, after treatment with nitric} \\ \qquad\qquad \text{acid, \&c., dried at 212°, gave} \\ 10\cdot603 \quad \dots \quad \text{carbonic acid, and} \\ 2\cdot453 \quad \dots \quad \text{water.} \end{cases}$

II. $\begin{cases} 5\cdot108 \quad \dots \quad \text{platinochloride of cryptidine, same as last, gave} \\ 1\cdot392 \quad \dots \quad \text{platinum.} \end{cases}$

			I. & II.	Calculation.
Carbon,	.	.	36·51	36·31
Hydrogen,	.	.	3·44	3·30
Nitrogen,	.	.	...	3·85
Chlorine,	.	.	...	29·30
Platinum,	.	.	27·25	27·24
				100·00

A very perceptible increase in the carbon is, therefore, obtained by the removal of the impurity rendered insoluble by means of nitric acid.

Chinoline is, therefore, the first of a series of homologous nitryl bases, of which three members are now known, viz. :—

Chinoline,	.	.	$C_{18} H_7 N$
Lepidine,	.	.	$C_{20} H_9 N$
Cryptidine,	.	.	$C_{22} H_{11} N$

And of which a greater number might possibly be obtained by an extension of the inquiry.