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ON THE
CONSTITUTION AND PROPERTIES
OF
PICOLINE,
A NEW ORGANIC BASE FROM COAL-TAR.

BY

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ON THE

CONSTITUTION AND PROPERTIES OF PICOLINE.

The careful study of the products of destructive distillation has enriched organic chemistry with an extensive series of results of unexpected interest and importance. These results have affected, in no inconsiderable degree, the recent progress of the science; and their influence has been of a twofold character, both general and particular, exerted in the former case in the development of some of the more remarkable general doctrines of organic chemistry; in the latter, in the important light thrown by their investigation on the constitution of the substances from which they are derived, and the facilities they have afforded of following out connections, which the examination of the original substance either does not at all present to our view, or, at least, indicates only in an imperfect or dubious manner. Added to this, we have the remarkable fact of the appearance among these products of substances in some cases identical with those occurring in organised beings; and in others, presenting analogies of the very closest character with the actual products of vital affinity, which, taken together, afford abundant reason for pursuing the investigation of substances which have already afforded results of so remarkable a character.

Setting aside altogether those substances, the occurrence of which is so frequent, that they may be called the general products of destructive distillation, such as carbonic acid, light carburetted hydrogen, olefiant gas, acetic acid, &c., it may be laid down as a general rule, that each individual compound produced during such a process, is formed by the destruction of a limited number of substances only, which bear to each other, and to the product, a more or less intimate connection in constitution or chemical relations. In those instances in which we have been enabled to submit to destructive distillation substances of a definite and simple constitution, in a state of chemical purity, and where an uniform temperature has been preserved, the results have been, for the most part, of an exceedingly simple and intelligible character; but in proportion as the atom becomes more complex, so also do the products of its decomposition, and the explanation of the results is found to be proportionately difficult and uncertain. These difficulties and uncertainties are increased in a still higher degree, in the case of a substance such as coal, where we have to deal not merely with one complex atom but with a congeries of several such, and where the process is performed on the large scale, and under a variety of perturbing influences. The distillation of coal is, in fact, attended by the formation of about twenty different substances, the constitution and properties of which have been examined with different degrees of accuracy, and which present among them instances of almost every species of chemical compound. The discovery of six of these substances is due to Runge,* who published, about fourteen years ago, a very interesting memoir containing an account of their general properties. Of these substances, three are possessed of acid properties, and three are bases, to the latter of which he gave the names of Kyanol, Leukol, and Pyrrol, from the peculiar colours developed by the action of certain reagents on their salts. The two former of these substances were afterwards submitted to a detailed examination and analysis by Hoffman,† who arrived at the interesting result, that both are identical with substances which had been independently obtained by the decomposition of certain well known bodies; Kyanol possessing the constitution and properties of the Aniline of Fritsche, and the Benzidam of Zinin; while Leukol is identical with the substance described by Gerhardt under the name of Chinoline, and which was obtained by him as a product of the distillation of quinine, cinchonine, and strychnia, with caustic potass. Hoffman failed, however, entirely in

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* Poggendorf's Annalen, Band 31, u. 32.

† Annalen der Chemie und Pharmacie, vol. xlvii.

obtaining any evidence of the presence of pyrrol in the substance which he examined, and leaves in doubt the existence of such a compound.

Having lately had occasion to examine a quantity of the mixed bases contained in coal-tar, obtained by a method similar to that of Runge, but which, owing to a modification of the process, contained all the more volatile bases formed during the distillation of coal, I was led to try whether or not pyrrol was to be found in it, and I found immediate evidence of its existence, by the characteristic red colour which it gives to fir-wood moistened with hydrochloric acid. The attempt to separate this pyrrol proved that it was present in extremely minute quantity only, but led to the discovery of a new base different from those of Runge, for which I propose the name of Picoline, and the examination of whose properties forms the subject of the present paper.

Preparation of Picoline.

For the crude substance employed in the preparation of picoline, I am indebted to the kindness of Mr Astley of the Bonnington Chemical Works, and it was obtained by the following modification of Runge's process. In the preparation of naphtha from coal-tar, the first product of distillation is agitated with sulphuric acid for the purpose of separating any naphthaline which may be present, as well as a variety of substances in extremely minute quantity, which communicate to the crude naphtha the property of becoming dark-coloured by exposure to the air ; among these substances, of course, are all the basic compounds contained in the oil. The sulphuric acid which had been used for this purpose was neutralised by impure ammonia obtained by a single distillation of the watery fluid of the gas-works. On the addition of the ammonia there was no separation of any oil in quantity appreciable to the eye ; but upon distillation, the bases, which had been dissolved in the fluid, passed over with the first portions of the water, and collected in a separate layer in the receiver. This oil, when it came into my hands, possessed a very dark brown colour, a somewhat viscid consistence, and a peculiar pungent and disagreeable odour. It was heavier than water, a layer of which, containing a small proportion of oil in solution, floated on the surface. The examination of this oil proved it to consist, in addition to picoline, of a mixture of pyrrol, aniline, an oily base possessing the general properties of leukol, and a thick heavy oil destitute of basic properties.

In order to separate picoline, the oil, along with the water which floated on its surface, was introduced into a retort and carefully distilled. At first, water, accompanied by a little oil, passed over, and then an oil by itself, which dissolved completely in the watery fluid contained in the receiver.* As the distillation proceeded, another oil made its appearance, which collected in a layer on the surface of the fluid which had previously distilled. When about three-fourths of the oil had passed over, the process was stopped, by which means the oil, destitute of basic properties, which requires a very high temperature for its distillation, was left behind in the retort. The fluid in the receiver was now supersaturated with sulphuric acid diluted with water, care being taken to obtain a powerfully acid reaction. The peculiar odour which the fluid possessed, was by this process entirely changed, but not destroyed; and, on distillation, the water which passed over, carried with it all the pyrrol contained in the solution, while the other bases were retained by the sulphuric acid. Caustic potass was then added to the residue in the retort until an alkaline reaction was manifest, and it was again distilled; the water which passed over carried with it the oily bases, partly dissolved, partly floating on the surface of the solution, exactly as in the first distillation. A few sticks of fused potass were introduced into the product, and the whole was left in repose; as the potass dissolved, the oil, which is entirely insoluble in solutions of the fixed alkalis, rose to the surface and there collected in the form of a pale yellow layer, still containing a considerable quantity of water, which may amount to 30 or 40 per cent. of the bulk of the oil. The oil was separated from the watery fluid by means of a pipette and pieces of fused potass added so long as they continued to become moist. The dry oil was then introduced into a retort and distilled. A transparent and colourless oil passed over, which was tested at intervals by allowing a drop of it to fall into a solution of chloride of lime. So soon as the reaction of aniline made its appearance the receiver was changed. The first portion was now picoline in a state approaching to purity; that which immediately followed consisted of a mixture of picoline and aniline. The first portion was again digested with fused potass and rectified; that which distilled at 272° was collected apart, and constituted pure picoline.

Constitution of Picoline.

The general analogy in properties which picoline bears to aniline and the other oleaginous bases, permitted the assumption that it, like these substances, was free from oxygen; I proceeded, therefore, in its analysis, upon this hypothesis, and neglected the determination of the nitrogen. The following are the results of the analyses :—

Analysis I. { 5·630 grains of picoline gave
15·954 ... carbonic acid,
3·944 ... water.

... II. { 5·347 grains of picoline gave
15·100 ... carbonic acid,
3·670 ... water.

Which give the following results per cent. :—

	I.	II.
Carbon	77·16	77·18
Hydrogen	7·77	7·62
Nitrogen	15·20	15·20
	100·00	100·00

These results correspond closely with the formula $C_{12} H_7 N$; the calculated result of which is—

		Theory.	Mean.
C_{12}	900·0	77·29	77·17
H_7	87·5	7·43	7·69
N	177·0	15·28	15·14
	1164·5	100·00	100·00

This formula is precisely the same as that of aniline, along with which picoline occurs in coal-tar. In order to ascertain whether the atomic weights of these substances were also identical, I prepared the platinum salt of picoline, and determined the amount of platinum contained in it. The salt was obtained by adding bichloride of platinum to a solution of picoline in excess of hydrochloric acid: no immediate precipitation took place unless the solutions were very concentrated, but in the course of twenty-four hours the salt was deposited in fine orange-yellow needles. When dried at 212°, it gave the following results:—

I. { 9·670 grains of chloride of picoline and platinum gave
3·147 ... platinum = 32·544 per cent.

II. { 10·844 grains of chloride of platinum and picoline gave
3·517 ... platinum = 32·522 per cent.

From these analyses are deduced the following atomic weights:—

I.	II.
1211·1	1213·7

These agree sufficiently well with the theoretical atomic weight, which is 1164·5. They correspond also precisely with the results of the analysis of the aniline salts. The identity of these results is shewn by the following table of the analyses by Fritsche, Zinin, and Hoffman, of aniline from its different sources, and of picoline, as well as of the platinum salts of these substances:—

	Aniline.*	Benzidam.*	Cyanol.	Picoline.	Theory.
C =	77·73	77·32	76·67	77·17	77·29
H =	7·60	7·50	7·72	7·69	7·43
N =	14·98	14·84	15·62	15·14	15·28
	100·31	99·66	100·00	100·00	100·00

The following are the results for the platinum salts:—

	Benzidam.	Kyanol.	Picoline.	Theory.
Mean platinum, per cent.	32·501	32·886	32·533	32·94
Atomic weight .	1216·1	1170·5	1212·4	1164·5

The results of all these analyses agree perfectly with one another; but the properties possessed by picoline differ from

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* Not having the original papers of Fritsche and Zinin at hand, I extract these two results from Berzelius' Arsberättelse, 1844, p. 454, where they are calculated according to C=75·12, the rest are with C=75, but the difference is so small as not to affect the comparison.

those of aniline, which, whether obtained from coal-tar, indigo, or nitrobenzid, presents a perfect identity in its chemical characters.

Properties of Picoline.

Picoline is a perfectly colourless, transparent, limpid fluid, extremely mobile, and destitute of viscidity. It possesses a powerful, penetrating, and somewhat aromatic smell, which, when very dilute, is replaced by a peculiar rancid odour, adhering pertinaciously to the hands and clothes. Its taste is acrid and burning when concentrated; but when very dilute, as, for instance, when its vapour is sucked into the mouth, it is powerfully bitter, as are also the solutions of its salts. It is not changed by exposure to a cold of 0°. Picoline is extremely volatile, and evaporates rapidly in the air. It boils at the temperature of 272°, and the thermometer remains perfectly stationary during the whole period of the ebullition; it is therefore much more volatile than aniline, which, according to Hoffman, boils at 359°. It may be preserved for a long time in a bottle containing only a small quantity of it, and which is frequently opened, without becoming manifestly coloured; whereas aniline becomes rapidly brown, and, indeed, cannot easily be obtained colourless, except by distillation in a current of hydrogen. The specific gravity of picoline is less than that of water. I found it to be 0·955 at 50°, while, according to Hoffman, that of aniline is 1·020 at 68°.

Picoline mixes with water in all proportions, and forms a transparent and colourless solution. It is insoluble, however, in solution of potass, as well as in most alkaline salts, the addition of which causes its immediate separation from the water. It dissolves also readily in alcohol, ether, pyroxylic spirit, and the fixed and volatile oils. It is a powerful alkaline base: a rod dipped in hydrochloric acid, and held over it, is immediately surrounded by a copious white cloud of hydrochlorate of picoline. It restores the blue colour of reddened litmus, but does not affect the colouring matter of red cabbage. It does not coagulate the white of eggs as aniline does.

The reactions which it produces with other substances are also quite distinct from those presented by aniline. When brought in contact with the solution of chloride of lime, it does not produce, in the least degree, the violet colour which is so characteristic of aniline; on the contrary, the solution remains perfectly colourless, unless, indeed, the picoline has not been well separated from pyrrol; in which case, a slight brown makes its appearance, but no violet. Picoline is also incapable of producing the yellow colour in fir wood and the pith of the elder, which is so readily obtained with aniline. When treated with chromic acid, even when very concentrated, and after boiling, no change takes place in the colour of the solution, and only a small quantity of a yellow powder is deposited; while aniline gives an abundant precipitate, which has, according to the degree of concentration of the fluid, a green, blue, or black colour.

Picoline precipitates from solutions of chloride of copper a portion of the oxide of copper, while the remaider forms a pale blue solution, which, when evaporated to a small bulk, deposits a congeries of prismatic crystals, which seem to be a double salt. No blackening of the solution takes place, as is the case with aniline. When an excess of hydrochloric acid is present, there is obtained, on evaporation, another double salt in large crystals, apparently derived from the rhombohedral system. Picoline produces also double compounds with the chlorides of mercury, platinum, gold, tin, and antimony. With chloride of gold it gives an exceedingly characteristic compound, in the form of a fine lemon-yellow precipitate, which is soluble in a considerable quantity of boiling water, and is deposited, on cooling, in delicate yellow needles. Aniline, under similar circumstances, gives a reddish-brown precipitate, resembling the ferrocyanide of copper. It gives, with infusion of nut-galls, a copious curdy precipitate of a pale-yellow colour, which dissolves in hot water, and is deposited again on cooling. It does not precipitate the solutions of nitrate of silver, chlorides of barium and strontium, or sulphate of magnesia.

The properties of picoline, as now detailed, are obviously different from those of aniline. They recalled, however, strongly to my mind those of a base called Odorin, obtained by Unverdorben* from Dippel's animal oil. According to this chemist, Dippel's oil, which is obtained by several successive distillations of the oleum cornu cervi, is a mixture of four different bases, to which he gives the names of Odorin, Animin, Olanin, and Ammolin. Of these, the two first constitute nineteen twentieths of the whole oil, and the odorin, which resembles picoline in its solubility in water, is obtained by simply distilling the oil, and collecting the product as long as it dissolves. These results, however, have been called in question by subsequent observers; Reichenbach, especially, asserts that he was unable to separate any basic compounds, and considers the substances obtained by Unverdorben to be mixtures of empyreumatic oil with ammonia. As, however, the properties which Unverdorben has attributed to odorin, approximate in some respects to those of picoline, I thought it desirable to ascertain the existence of this substance, and whether or not it is identical with picoline. In order to prepare odorin, I rectified the oleum cornu cervi, and then distilled the product; but on allowing the first drops of oil to fall into water, they were not dissolved, as Unverdorben has asserted, but floated unchanged upon the surface. Finding this process unsuccessful, I agitated the crude oil with dilute sulphuric acid; the acid fluid immediately acquired a very deep reddish-brown colour, and when separated from the oil, and supersaturated with potass, a semisolid viscid mass separated from the fluid. This, when distilled with water, yielded a mixture of several oily bases, while a dark-coloured resinous substance, probably Unverdorben's Fuscin, was left in the retort. The mixed bases which I thus obtained, formed an exceedingly small fraction of the oil employed. They were purified by several successive rectifications, and generally in a method similar to that employed for picoline, and the first portions of the product collected apart. It then constituted a colourless oil, which became brown in the air, dissolved readily in water, and presented an odour similar to, though not quite the same as, that of picoline. It gave, with chloride of gold, a dirty-yellow precipitate, which dissolved in hot

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* Poggendorf's Annalen, vol. xi.

water, and deposited, on cooling, in the pulverulent form, and with bichloride of platinum, a compound in red wart-like crystals. By an accident in the laboratory, the small quantity of this substance which I had prepared for analysis was destroyed, so that the evidence of their identity cannot be considered as sufficient. The characters of odorin, as given by Unverdorben, are not perfectly identical, either with those of picoline or the base which I obtained. Odorin, according to Unverdorben, boils at about 212°, and its salts are oleaginous compounds which distil in the form of an oily fluid, whereas those of picoline are mostly crystallizable. I am at present engaged with the examination of these substances.

It is obvious, from the observations contained in Hoffman's[*] paper, that picoline must have been present along with aniline and chinoline in the substance which he examined. He mentions, especially, that his aniline, as obtained by distillation only, possessed a peculiar pungent and disagreeable odour, which was got rid of only by several successive crystallizations of its oxalate from alcohol, and that the impure aniline has a specific gravity less than that of water. He observes also, that the quantity of the substance present must have been excessively minute, as it did not affect the results of the analysis, a phenomenon, the cause of which is sufficiently explained by the identity in constitution of the two substances. Hoffman did not obtain picoline in the separate state, simply because the bases employed by him were obtained from the less volatile portions of coal-tar, which necessarily contain it only in minute proportion.

Combinations of Picoline.

Picoline forms a series of compounds which are generally closely analogous to those of aniline, but present in a less marked degree the regularity and facility of crystallization which are so characteristic of the salts of the latter base. It forms, however, with the greater number of acids, salts which can be obtained in a crystalline form. These are all highly soluble in water, and some of them are even deliquescent;

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[*] Liebig's Annalen, vol. xlvii.

they are also for the most part readily soluble in alcohol, even in the cold. They are most readily obtained by evaporating their aqueous solutions at 212°, and not by adding an acid to the etherial solution of the base; as in the latter case the presence of even a minute proportion of water causes them to precipitate in the form of a semifluid mass. Picoline forms a number of acid salts, in which respect it differs from aniline. Its salts are less readily decomposed in the air than the corresponding aniline compounds, but they do eventually become brown, although without presenting any of the rose-red colour which the latter salts assume.

Sulphate of Picoline.—I obtained this salt by supersaturating sulphuric acid with picoline. The solution obtained was perfectly colourless, and when evaporated in the water-bath, it evolved picoline in abundance, and formed a thick oily fluid, which, on cooling, concreted into a tough mass of transparent and colourless crystals, apparently of a tabular form. Exposed to the air, it deliquesces rapidly into a transparent and colourless oil, which, after a time, acquires a slight brownish colour. It is insoluble in ether, but readily in alcohol, both hot and cold. It is not deposited in crystals by allowing the hot alcoholic solution to cool. I analysed this salt by evaporating to dryness in the water-bath, in a weighed platinum crucible, and allowing it to cool under an exsiccator. It was then rapidly weighed, dissolved in water, and precipitated by chloride of barium:—

4·364 grains of sulphate of picoline gave
5·230 ... sulphate of baryta=41·20 per cent. of anhydrous sulphuric acid.

This result corresponds with the formula $C_{12}H_7N + 2HO, SO_3$, as is shewn by the following calculation:—

		Theory.	Experiment.
2 Eq. Sulphuric acid	1000·0	41·84	41·20
1 ... Picoline	1164·5	48·74	...
2 ... Water	225·0	9·42	...
	2389·5	100·00	

The sulphate of aniline dried at 212° has a different constitution; it gives 28·67 per cent. of sulphuric acid, which corresponds to the formula $C_{12}H_7N, HO, SO_3$.

Oxalate of Picoline.—This salt is obtained by mixing oxalic acid and picoline in excess, and evaporating the solution over quicklime. When the solution is reduced to a very small bulk, it is deposited in the form of short prisms radiating from a centre; and on further evaporation, the whole concretes into a solid mass. The crystals evolve the odour of picoline in the air; they are highly soluble in water and alcohol, both absolute and hydrated. When heated to 212° it fuses and evolves abundance of picoline vapours, and on cooling it forms a thick fluid which slowly deposits crystals in the form of fine needles. These are probably an acid salt. I did not obtain the oxalate in a state of sufficient purity for analysis.

Nitrate of Picoline is obtained as a white crystalline mass, when a mixture of picoline and dilute nitric acid is evaporated to dryness at a moderate heat. At a higher temperature it sublimes in white feathery crystals.

Hydrochlorate of Picoline may be prepared by mixing picoline and hydrochloric acid, and evaporating on the water-bath. On cooling, the thick fluid which remains consolidates into a mass of prismatic crystals. When heated to a high temperature, it sublimes easily, and deposits itself on the sides of the vessel in transparent crystals, which deliquesce rapidly in the air.

Chloride of Platinum and Picoline.—This salt is easily obtained by adding picoline to a solution of bichloride of platinum, containing an excess of hydrochloric acid; it deposits itself immediately, if the solution be concentrated, but when moderately diluted, it makes its appearance only after the lapse of some time. The crystals which are deposited are rather liable to retain an excess of picoline, which renders it advisable to redissolve them in a dilute solution of chloride of platinum with a little hydrochloric acid. From this solution it is deposited pure, on cooling, in the form of fine orange-yellow needles, which can easily be obtained half an inch long even when operating on very small quantities. It is much more soluble both in water and alcohol than the aniline salt, and indeed than the platinum salts of the organic bases generally. It requires only about four times its weight of boiling water for solution.

The crystals of this salt, after washing with alcohol and ether, and drying at 212°, gave the following results of analysis:—

10·032 grains of chloride of platinum and picoline gave
8·862 ... carbonic acid, and
2·760 ... water.

The determination of the platinum, as formerly mentioned, gave in two different trials 32·544 and 32·522 per cent., the mean of which is 32·533. The analysis corresponds with the formula $C_{12}\ H_7\ N,\ H\ Cl,\ Pt\ Cl_2$.

		Theory.	Experiment.
C_{12}	= 900·0	24·07	24·09
H_8	= 100·0	2·67	3·05
N	= 177·0	4·73	...
Cl_3	= 1330·4	35·59	...
Pt	= 1232·0	32·94	32·533
	3739·4	100·00	

Chloride of Picoline and Mercury.—When picoline is added to a concentrated solution of bichloride of mercury, a white curdy precipitate immediately falls. If, however, the solution be dilute, it is not precipitated for some time, and then appears in the form of radiated silky needles. It is sparingly soluble in cold water, more readily in hot. It dissolves pretty abundantly in boiling alcohol, and the solution, on cooling, deposits it, sometimes in prismatic, sometimes in feathery crystals. It dissolves readily in dilute hydrochloric acid, with the formation of a peculiar compound which I have not particularly examined. Boiled with water it is decomposed, picoline being evolved, and a white powder being deposited.

In the analysis of this compound I interposed, between the combustion tube and the chloride of calcium apparatus, a small tube in which the mercury and water were condensed, and at the conclusion of the process, a current of dry air, heated to 212°, was drawn through the tube, by means of which the water was conveyed into the chloride of calcium apparatus. The salt was dried simply by exposure to the air, as it loses picoline when heated; when analysed it still smelt of picoline, which accounts for the excess of carbon obtained.

The following are the results of the analysis :—

10·962 grains chloride of mercury and picoline gave
8·245 ... carbonic acid,
2·168 ... water.

This corresponds to the formula $C_{12} H_7 N + Hg Cl_2$, which gives the following results :—

		Theory.	Experiment.
C_{12} =	900·0	19·63	20.51
H_7 =	87·5	1·90	2·19
N =	177·0	3·86	...
Cl_2 =	887·0	19·35	...
Hg =	2531·6	55·26	...
	4583·1	100·00	

This salt differs in constitution from the aniline salt, which is represented by the formula $2 (C_{12} H_7 N) + 3 Hg Cl_2$; it tallies, however, perfectly with the compound of chinoline and bichloride of mercury, which is $C_{18} H_8 N + Hg Cl_2$.

I have not particularly examined the other compounds of picoline.

Products of Decomposition of Picoline.

The small quantity of picoline at my disposal has hitherto prevented my examining particularly the products of its decomposition, a branch of the subject which presents numerous points of interest. Such results, however, as I have obtained, indicate a striking difference between the products afforded by it and aniline.

When treated with nitric acid of specific gravity 1·5, picoline is immediately dissolved, but without communicating to the fluid the fine indigo-blue colour which aniline produces under similar circumstances. On the application of heat there is produced an extremely slow evolution of nitrous fumes, which contrasts strikingly with the tumultuous action which aniline produces. After very long-continued treatment with nitric acid, the fluid was evaporated to a very small bulk, when it deposited large crystals in the form of rhomboidal tables. These crystals, on being treated with potass, evolved picoline unchanged. The potass solution was red, but it contained no carbazotic acid, at least no carbazotate of potass was deposited on evaporation.

An excess of bromine water added to picoline causes an immediate and abundant precipitate of a reddish colour, which, on standing during the night, deposited itself in the form of a transparent reddish oil. This substance is destitute of basic properties, and is readily soluble in alcohol and ether, but not in water. Aniline, when treated in the same manner, gives, as is well known, the bromaniloid of Fritsche, which is solid, and crystallises in silky needles, fusible at 232°. It seems probable that the oily fluid obtained from picoline may possess a constitution similar to that of bromaniloid, in which case it would have the formula $C_{12}(H_4Br_3)N$, and would receive the name of bromopicoloid. I had not enough of it for analysis.

The action of chlorine on picoline is remarkably analogous to that which it produces on aniline. When passed into anhydrous picoline it is rapidly absorbed, and colourless crystals, apparently of hydrochlorate of picoline, are deposited. In a short time, however, the fluid becomes dark brown, and is finally converted into a resin. This resin was mixed with water, and a current of chlorine passed through it for some hours. The fluid was then introduced into a retort, and distilled, a crystalline substance passed over along with the water, and after all the water had passed, another substance made its appearance, while a large quantity of carbon was left in the retort. The quantity in which I obtained these substances was far too small to admit of their particular examination, but it appeared to me that the odour of the latter substance was different from that of chlorophenesic acid, which is produced by the action of chlorine on aniline.

The preceding investigation is sufficient to establish the identity, in constitution and difference, in properties of picoline and aniline. These substances are then isomeric, in the strict sense of the term, possessing the same composition per cent., and the same atomic weight.

Although isomerism has been recognised in a great variety of different classes of compounds, I believe the present to be the first instance in which it has been satisfactorily proved among organic bases. Two instances, indeed, have been previously described, but in neither can the evidence be considered absolutely conclusive. One of these cases is that of two bases discovered by Pelletier and Couerbe* in the husks of the Cocculus Indicus, to which they have given the names of Menispermin and Paramenispermin. The characters which they have assigned to these substances are sufficiently distinct, but their analyses of both lead to the formula $C_{18} H_{12} N O_2$. This result, however, is unsupported by any determination of their atomic weights, without which the isomerism cannot be admitted as proved. The other instance is that of bebeerine, which, according to the analyses of Dr D. Maclagan,† is isomeric with morphia, both being represented by the formula $C_{35} H_{20} N O_6$; and as this result is supported by the analysis of the platinum compound, the probability of their isomerism is much higher than in the former case. Unfortunately, however, another source of fallacy enters into the question in the amorphous condition of bebeerine, which renders it impossible to determine with certainty its freedom from impurity; even the constitution of morphia, by far the most definite of the two substances, can scarcely be considered as fixed, Gerhardt, for instance, representing it by the formula $C_{36} H_{19} N O_6$, and not by that formerly given.

With aniline and picoline, however, these uncertainties disappear. Both substances are possessed of definite boiling points widely different from one another, and of all the other physical characters of pure substances. The lowness of their atomic weight also precludes any possibility of doubt regarding the true formula, and enables us to speak with certainty as to the identity of their constitution. The isomerism of these substances is, moreover, of much higher interest in a theoretical point of view. Menispermin and morphia are isolated substances, entirely unconnected, in constitution or general relations, with any other substance. Aniline, on the other hand, is a member of one of the most extensive, widely distributed, and interesting groups of substances, with which the recent discoveries of organic chemistry have made us

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* Annales de Chimie et de Physique, vol. liv.

† Proceedings of the Royal Society of Edinburgh, No. 26.

acquainted, the Indigo Salicyl and Benzoil series. The members of this large group already present a variety of instances both of isomeric and polymeric compounds, a few of which I have here brought together in the form of a table, which does not pretend to any scientific arrangement, its sole object being to point out the remarkable relations of aniline and picoline to the group.

Indigogene,	$C_{16} H_6 N O_2$	Indine.
Indigo,	$C_{16} H_5 N O_2$	...
Isatine,	$C_{16} H_5 N O_4$	...
Anthranilic acid,	$C_{14} H_7 N O_4$	...
Salicylic acid,	$C_{14} H_6 O_6$	?*
Nitrosalicylic acid,	$C_{14} H_5 (N O_4) O_6$	...
Benzoic acid,	$C_{14} H_6 O_4$	Salicylous acid.
Nitrobenzoic acid,	$C_{14} H_5 (N O_4) O_4$	Nitrosalicylous acid.
Chlorobenzoic acid,	$C_{14} H_5 Cl O_4$	Chlorosalicylous acid.
Hydruret of benzoil,	$C_{14} H_6 O_2$	Benzoine.
Benzonitril,	$C_{14} H_5 N$	Azotide of Benzoil.
Stilbene,	$C_{14} H_6$	...
Phenol,	$C_{12} H_6 O_2$	...
Aniline,	$C_{12} H_7 N$	Picoline.
Tribromaniline,	$C_{12} H_4 Br_3 N$	Tribromopicoline ?
Benzin,	$C_{12} H_6$	?
Nitrobenzid,	$C_{12} H_5 (N O_4)$	...

The facility with which aniline can be obtained by the decomposition of different members of this group, renders it by no means impossible to anticipate the artificial production of picoline also.

As we can start from benzoic acid, and convert it into benzin, benzin into nitrobenzid, and that finally into aniline, by the action of sulphuretted hydrogen, it seems by no means improbable that salicylous acid, the isomeric of benzoic acid, may be made to undergo a similar series of changes, the final result of which would be the formation either of picoline, or of some other compound isomeric with it and aniline. In order to subject this hypothesis to the test of experiment, I mixed salicylous acid with equal weights of slaked lime and caustic baryta, and distilled in the oil bath, with the view of

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* Gerhardt has observed (Precis de Chimie Organique, tom. ii., p. 21), that benzoic acid, when fused with hydrate of potass, evolves hydrogen, and gives the potass salt of a new acid. This may possibly be isomeric with salicylic acid.

obtaining a substance which should be isomeric with benzin. The greater part of the salicylous acid, however, passed over unchanged; but by agitation with solution of potass, there was left undissolved an excessively minute quantity of a solid crystalline substance. Finding this mode of operating unsuccessful, I passed salicylous acid over spongy platinum heated to a very low red heat in a glass-tube. A dark viscid oily fluid passed over into the recipient, of which the greater quantity dissolved in caustic potass, but left behind a larger quantity of the solid substance than was yielded by the first experiment. By distillation with water this substance passed into the receiver in the form of oily drops, which solidified on cooling, and formed a crystalline mass in which minute needles could be detected. It had a peculiar pleasant smell which resembled that of benzin; but the quantity which I obtained was much too minute to admit of its analysis, or of any attempt to convert it into picoline.

Postscript.

Although the analogy existing between picoline and the other oleaginous bases is perfectly sufficient to warrant the assumption of the absence of oxygen in that substance, I have thought it advisable to append here an experimental determination of the nitrogen. As the volatile bases cannot be readily analysed by Varrentrap and Will's method, I made a combustion of the platinum salt, and determined the proportion by volume of the carbonic acid and nitrogen in four tubes, which gave the following results:—

I.	94	volumes gave	8·	nitrogen.
II.	240	...	18·	...
III.	84	...	6·5	...
IV.	421	...	35·	...
	839		67·5	

These results give the gases in the proportion of 11½ to 1; in other words, they shew a slight excess over the theoretical result, according to which they should be in the proportion of 12 to 1. They confirm perfectly, however, the absence of oxygen.