ON

THE PRODUCTS

OF THE

DESTRUCTIVE DISTILLATION OF ANIMAL SUBSTANCES.

PART I.

BY

THOMAS ANDERSON, Esq., M.D.

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On the Products of the Destructive Distillation of Animal Substances. Part I. By THOMAS ANDERSON, Esq., M.D.

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In April 1846, I communicated to the Royal Society a paper on a new organic base, to which I gave the name of Picoline, and which occurs in coal-tar, associated with the Pyrrol, Kyanol, and Leukol of RUNGE. In that paper I pointed out that the properties of picoline resembled, in many respects, those of a base which UNVERDORBEN had previously extracted from DIPPEL's animal oil, and described under the name of Odorine; and more especially mentioned their solubility in water, and property of forming crystallisable salts with chloride of gold, as characters in which these substances approximated very closely to one another. And further, I detailed a few experiments on the odorine of UNVERDORBEN extracted from DIPPEL's oil, with the view of ascertaining whether or not they were actually identical, but on too small a scale to admit of a definite solution of the question.

These observations, coupled with the doubts which had been expressed by some chemists, and more especially by REICHENBACH, as to the existence of the bases described by UNVERDOBBEN, induced me to take up the whole subject of the products of the destructive distillation of animal substances, which has not yet been investigated in a manner suited to the requirements of modern chemistry. In fact, UNVERDORBEN is the only person who has examined them at all, and his experiments, contained in the 8th and 11th volumes of Poggendorf's Annalen, constitute the whole amount of our knowledge on the subject; and his observations, though valuable, and containing perhaps as much as could easily be determined at the time he wrote, are crude and imperfect, when we come to compare them with those which the present state of the science demands. Since his time, the methods of investigation in organic chemistry have undergone an entire change: the simplifications of the process of organic analysis had not then been made, or at least had not come into daily use as the auxiliary of investigation. and UNVERDORBEN, who belonged to the old school, and contented himself with the observation of reactions only, was necessarily led, as I shall afterwards more particularly shew, to confound together substances, the reactions of which approximate so closely that it is impossible, or at least very difficult, to distinguish them by such means alone. The errors, however, lay with the method, and not with the observer; for UNVERDORBEN'S experiments, so far as they go, I have found to

be correct in the main, notwithstanding their having been called in question by REICHENBACH, whose numerous researches on the kindred subject of the products of the destructive distillation of vegetable substances, gave weight to his opinion, and have indeed been the principal cause of the doubts expressed by others on the subject.

The investigation of these products has occupied me pretty continuously since the publication of the paper before alluded to; and my researches have now extended themselves over a large part of the subject, although, from its branching off into so many subdivisions, and embracing the consideration of so large a number of substances belonging to almost every class of organic compounds, some time must still elapse before it is complete in all its parts. It is my intention, therefore, as the subject naturally divides itself into several sections, to take up the consideration of these in a succession of papers, of which the present is the first, and in which I propose to consider the general properties of the crude product employed in my experiments, and those of certain of the organic bases contained in it.

The products of the destructive distillation of animal matters were long since employed in medicine, and were obtained from all parts of the body, and from almost every section of the animal kingdom; but these afterwards entirely gave way to the Oleum Cornu Cervi, which, as hartshorn is entirely free from fatty matters, must necessarily be the pure product of decomposition of the gelatinous The more volatile portions of this oil, separated by distillation with tissues. water, and purified by numerous rectifications, constituted the Oleum Animale Dippellii of the older pharmacopœias. These substances would, in all probability, have been the most convenient crude materials for my experiments; but as they have long since ceased to be employed, and cannot now be obtained except by going through the tedious and disagreeable process for their preparation, I have made use of the bone-oil of commerce, which is prepared on the large scale by the distillation of bones in iron cylinders, and can be had in any quantity from the manufacturers of ivory-black. This oil appears to differ in no respect from the true Oleum Cornu Cervi, and, like it, is the product of decomposition of the gelatinous tissues only; for previous to distillation the bones are boiled in a large quantity of water, by which means both the fatty matters and also a certain proportion of the gelatine are separated. They are then dried, packed in the cylinders, and distilled at a heat which is gradually raised to redness. The oily product of this distillation is separated from the watery portion, and, after rectification, forms the bone-oil of commerce; though in some instances this latter distillation is dispensed with, and the product of the first made use of without any further purification.

Bone-oil, as supplied by the manufacturer, has a dark-brown, almost black colour, with a somewhat greenish shade, and perfectly opaque in the mass; but when spread in a thin layer on a glass plate, it is seen to be brown by transmitted light. Its specific gravity is about 0.970. Its smell is peculiarly disagreeable, and is mixed with that of ammonia, which is always present, though sometimes in so small quantity that its odour is disguised by that of the oil itself, and is only rendered apparent by distillation. A piece of fir-wood moistened with hydrochloric acid, and held over the mouth of a vessel containing it, rapidly acquires the dark reddish-purple colour which is characteristic of the pyrrol of RUNGE. Acids agitated with the oil acquire a brown colour, especially on standing, and extract the bases contained in it; but if the quantity of the acid be large, and in a pretty concentrated state, a nonbasic oil is also dissolved, which, on standing for some time, and more rapidly if heated, undergoes decomposition, and the fluid becomes filled with orange-yellow flocks of a resinous substance, which acquires a dark colour by exposure to the air; this change is produced by the stronger vegetable as well as the mineral acids. Alkalies extract an acid oil, and a considerable quantity of hydrocyanic acid, which, on the addition of an acid to the alkaline solution, and distillation, can be distinguished in the product by its smell, as well as by its reaction with the salts of iron.

Previous to the separation of the bases, the crude oil was again rectified in portions of about fifteen pounds each, in an iron retort,-an operation attended with some trouble, as the fluid is apt to froth up and boil over in the early part of the process, so that the retort must not be more than half full, and the heat requires to be applied in a very gradual manner. At first a watery fluid distils, containing in solution ammonia, and a small quantity of the most volatile bases. This is accompanied by an oil of a pale yellow colour, limpid and very volatile, which after a time comes over without water, and with an increased though by no means dark colour. The distillation proceeds in a perfectly steady and gradual manner, until about two-fifths of the oil have passed over, when a point is attained at which the temperature requires to be considerably raised, in order that the distillation may continue uniformly, and the product becomes much thicker and more oily in its appearance. At this point the receiver was changed for the purpose of collecting the less volatile portion apart, and the distillation continued until the bottom of the retort reached a red heat. The latter portions of these products were obviously altered during the distillation, for a bulky porous charcoal remained in the retort; the oil which passed over smelt strongly of ammonia, crystals of carbonate of ammonia made their appearance in the neck of the retort, and a certain quantity of water collected in the receiver. The oil also became gradually darker in colour, and more viscid in its consistence. By collecting in a succession of receivers, I had an opportunity of observing a great number of curious optical phenomena at different epochs of the distillation. The oils frequently presented well-marked appearances of epipolic dispersion, and the very last portion exhibited a curious species of dichroism, its colour being dark reddish.

brown by transmitted, and green, with the effect of opacity, by reflected light. All these appearances, however, were very evanescent, and are only seen in the newly distilled oil, for after a few days it becomes very dark coloured, and they are then no longer visible.

Both the more and the less volatile oils contain a variety of bases, and were separately treated for their extraction. In neither, however, is the quantity large. I obtained from the more volatile portion of three hundred pounds of bone-oil less than two pounds of the mixed bases; but as, in the course of the various processes to which it was submitted, some small portions were lost, the whole may perhaps amount to about three-fourths per cent. of the total quantity of oil. The less volatile portion yields a larger quantity, which may be estimated at two or three per cent. of the crude oil. These, of course, are only rough estimates, but they may serve to give an idea of the quantity of the products.

Preparation of the Bases.

For the preparation of the bases precisely the same processes were followed throughout for both portions into which the oil was separated by distillation; and as the bases to be described in the present paper were contained in the more volatile portion, I shall detail the steps followed in reference to that quantity only. The oil was mixed in a cask with sulphuric acid diluted with about ten times its weight of water, and the fluids left in contact for a week or two, during which time they were frequently agitated. More water was then added, and the whole drawn off, and the process repeated with fresh quantities of sulphuric acid as long as any bases were extracted. The solution, which had a reddish and sometimes very dark brown colour, contained the bases, along with a quantity of nonbasic oil and of pyrrol. It was mixed with an additional quantity of sulphuric acid, introduced into a glass distilling apparatus, and heat applied. As the fluid approached the boiling point, a quantity of the red resinous matter before alluded to began to separate, and occasioned succussions of so violent a character as to endanger the safety of the vessel, and render it necessary to interrupt the process for the purpose of filtering it off, after which the distillation proceeded without difficulty. A small quantity of oil distilled over, and the water which accompanied it had exactly the smell of the water in a gas-meter, and contained pyrrol.* which continued to pass over for a long time, during the whole of which the distillation was continued. This distillation I had recourse to at first, from a suspicion that some of the bases were separated from the acid, and volatilised during the process; but so soon as I had ascertained that this was not the case it was

^{*} These odours were so exactly alike, that I was induced to seek for pyrrol in the water of gasmeters, and I found that when mixed with sulphuric acid and distilled, the product gave the characteristic reaction of pyrrol with fir-wood. Ammonia remained in combination with the sulphuric acid.

dispensed with, and the fluid boiled down in porcelain or copper evaporating basins, water being added, and the distillation continued until, by taking a small quantity of the fluid and distilling off a few drops in a retort, they were found to be free from pyrrol. Even this precaution soon became unnecessary, for a little experience enabled me to know when the evaporation had been sufficiently prolonged.

The dark-brown fluid which remained in the basins was once more strained, in order to get rid of such resinous matters as might have separated during the evaporation, and then distilled in a large glass balloon connected with a condenser, after the acid had been previously supersaturated by a base. For this purpose, potass, soda, and lime were indifferently made use of: the latter answers extremely well, but, owing to the large quantity of sulphate of lime separated, the distillation requires to be carried on in the chloride of calcium or oil bath. When the alkali is added in sufficient quantity, an oil floats up to the surface of the fluid, and a strong pungent odour is given off, in which that of ammonia is apparent, along with another which can be compared to nothing but the smell of stink-At the first part of the distillation a transparent and colourless ing lobsters. watery fluid passed over, which contained the bases in solution; but after this had continued for some time, an oil made its appearance running in globules down the tube of the condenser, and dissolving immediately in the fluid which had already distilled. When the bases ceased to distil in quantity, the receiver was changed, and a small quantity of oil heavier than water was obtained by continuing the distillation for some time. At the end of the process an oil remained floating upon the concentrated fluid in the balloon, the quantity of which is very variable, and depends on the distillation of the crude bone-oil, having been continued too long before changing the receiver. In fact, it contains some of the bases of the less volatile oil, and will come to be considered in an after part of the investigation.

To the product of the distillation sticks of caustic potass were added, and, as these dissolved, the oily bases separated from the fluid in a manner exactly similar to that which was observed in the preparation of picoline, as detailed in the paper to which reference has already been made. The alkaline solution was drawn off by means of a siphon, and more potass added as long as water was separated. In this way the greater part of the base was obtained, but a small quantity of the most volatile of all still remains in the alkaline solution, and cannot be separated except by the addition of a very large quantity of potass. It was, however, readily obtained by distilling the fluid, and collecting only the first portion of the product, from which it was separated by a comparatively small expenditure of potass. The small quantity so obtained was preserved separately from the large mass.

The product of this operation was found to be extremely complex, and to consist of a mixture of four or five different bases, exclusive of ammonia. For the purpose of obtaining these in a separate state a great variety of processes was attempted, but none were found to answer so well as fractionated distillation, although it is an extremely tedious method of separation, and occasions a considerable loss of substance, which is very annoying when the quantities obtained are so small. When the mixed bases were distilled with a thermometer, ammonia began to escape at a very low temperature; but at 160° Fahr. the fluid entered into steady ebullition, and a perfectly transparent and limpid oil began to distil. A small quantity of oil passed over between this temperature and 212°, which was received by itself, and the after products collected in a succession of receivers, which were changed at every ten degrees which the thermometer rose. The fluid continued in steady and rapid ebullition, and the thermometer ascended rapidly to 240°; and between that and 250° a considerable quantity was collected. then again went up pretty rapidly, and another large quantity was obtained between 270° and 280°; after which the distillation proceeded more slowly until the temperature rose to 305°, at which point the characters of the products underwent a complete change. All the substances obtained at lower temperatures dissolved instantaneously in water; but that which now distilled floated on the surface, and only dissolved on agitation with a considerable quantity of water. Distillation now continued with somewhat greater rapidity, till the thermometer rose to about 355°, when a drop of the product allowed to fall into a solution of chloride of lime immediately gave the reaction of aniline. When this was observed, the whole remaining products, which formed only a small fraction of the whole, were collected together. They consisted chiefly of aniline.

The products of these different distillations were repeatedly rectified, and by this means bases were obtained, corresponding to the points at which the thermometer was found to remain longest in the first distillation. Of these I have as yet examined only the most volatile, and that which boiled at about 270°.

Petinine.

The most volatile portion of the bases obtained by the fractionated distillation, was mixed with the small portion which was separated with difficulty from the potash solution, and had been kept separate from the large quantity. The mixed fluid still contained a large quantity of ammonia, for the separation of which it was again rectified several times in succession, and fractionated in a small retort, the receiver being kept carefully cool. After this process has been repeated until it is properly purified, it constitutes the base to which I give the name of Petinine (from $\pi erenvos$, *volatilis*), in allusion to its volatility, which is greater than that of any base yet known, with the exception, of course, of ammonia. The quantity of this substance contained in the bone-oil is excessively small, as I obtained from

three hundred pounds no more than was sufficient for the determination of its constitution, and the leading characters of a few of its compounds. It is probable, however, that some loss was incurred in the preliminary processes, as, from not anticipating the presence of so volatile a base, I did not take any precautions for producing complete condensation of the products, by means of freezing mixtures or otherwise; and a considerable quantity was also lost owing to my anxiety to expel completely the ammonia which it might retain.

Constitution of Petinine.

The petinine employed for analysis was very carefully dried over caustic potass, the fluid poured off after some days' contact, and distilled in the waterbath at a very gentle heat; a precaution which is rendered necessary by its dissolving a certain quantity of potass. I did not possess a sufficient quantity to make a determination of the nitrogen, but took it for granted that oxygen was absent; an assumption which is justified by the analogy of all the other volatile bases, as well as by the perfect coincidence of the experimental results with the calculated formulæ. It was analysed with oxide of copper in a very long tube, and gave the following results:

ſ	6.663	grains	of petinine gave	
ł	16 ·286		carbonic acid, an	ıd
l	8.382		water;	

corresponding exactly with the formula $C_8 H_{10} N$, as is shewn by the following comparison :

			F	Experiment.		Calculation.			
Carbon,		•	•	66.66	66.66	C ₈	600.0		
Hydrogen,	•			13·97	13.88	H_{10}	125.0		
Nitrogen,		•	•	19.37	19.44	N	175.0		
				100.00	100.00		<u>900∙0</u>		

In order to ascertain the atomic weight of petinine, I prepared its compound with chloride of platinum, and made the following determinations of the platinum contained in it:

I. { 6.351 grains of chloride of platinum and petinine gave 2.245 ... platinum = 35.34 per cent.
II. { 3.860 grains of chloride of platinum and petinine gave 1.372 ... platinum = 35.54 per cent.
III. { 2.844 grains of chloride of platinum and petinine gave platinum = 35.51 per cent.

The atomic weights deduced from which agree very closely with the calculated results:

I. Atomic weight, by experiment,									
II.	• •••	•••			•	891·2			
III.						894.2			
Mean,	•		•	•		898 ·5			
Calculation,		•				900 ∙0			

The mode in which this base is formed during the decomposition of gelatine, it is, of course, impossible at present to perceive. In its chemical relations it is, however, in all probability, related to the butyric series; and it is even possible that we may obtain it by artificial processes. Some time since, KOLBE* published some researches on the galvanic decomposition of valerianic acid, among the products of which he discovered a carbo-hydrogen, having the formula $C_8 H_9$. Now, by treating this substance in the same manner as benzine is acted upon for the preparation of aniline, we ought to obtain from it, if not petinine, at least an isomeric compound, as may be easily seen by comparing the formulæ of the different substances:

I have not yet had an opportunity of determining whether the change which theory would lead us to expect actually takes place, but there is every reason to suppose that it would.

Properties of Petinine.

Petinine is a transparent colourless fluid, limpid as ether, and possessing a high refracting power. It has an excessively pungent odour resembling that of ammonia, and yet quite distinct, for when the effect of its pungency has gone off, or it is smelt in a dilute state, its smell is disagreeable, and somewhat similar to that of decayed apples. Its taste is hot and very pungent. It boils at a temperature of about 175° F.; but the quantity which I possessed was too small to admit of an accurate determination either of this point, or of its specific gravity, although the latter is certainly less than that of water. Petinine is a very powerful base, and immediately restores the blue colour of reddened litmus, and gives abundant fumes, when a rod dipped in hydrochloric acid is held over it. It unites with the concentrated acids, with the evolution of much heat. It dissolves in all proportions in water, alcohol, ether, and the oils; and is also soluble in dilute solution of potass, but not in concentrated. Petinine gives double salts with bichloride of

* Memoirs of the Chemical Society of London, Part xxi.

platinum and corrosive sublimate, both of which are soluble in water. With chloride of gold it gives a pale yellow precipitate, which does not dissolve on boiling the solution, and is not deposited in crystals. Petinine throws down peroxide of iron from its compounds. It also precipitates salts of copper, and the oxide thrown down dissolves in excess of the base with a fine blue colour.

These properties agree with those of none of the bases described by UNVER-DORBEN; and, in fact, it is certain that petinine could not have been present in the mixture to which he applies the name of odorine, for he expressly states that it commenced boiling at 212°. And it is easy to see why he did not obtain it, because, in separating the bases from the acid by which they were extracted from the crude oil, he took care to add a quantity of potass just so great that the oily bases were liberated, and not the ammonia; and as his object in doing so was to get rid of the latter substance, and there being no means of doing this exactly, it is probable that he did not fully separate the bases, but the most volatile, which is also the most powerful, remained in combination with the acid along with the ammonia.

Compounds of Petinine.

The minute quantity of petinine which I obtained has necessitated a very cursory examination of its salts, which are interesting, both from the facility with which they crystallise, and their great stability. None of them undergo change in the air, but may be left exposed for any length of time without acquiring colour. They are all soluble in water, and those with the volatile acids sublime without decomposing, and are deposited in crystals upon cold surfaces.

Sulphate of Petinine, is obtained by adding petinine to dilute sulphuric acid until the fluid is neutral. On evaporating, petinine is given off, and the solution, when concentrated to a syrup, concretes on cooling into a foliated mass of crystals of an acid sulphate. These crystals are strongly acid to test-paper, extremely soluble in water, and slightly deliquescent in moist air.

Nitrate of Petinine.—The solution of petinine in nitric acid, evaporated to dryness, and gently heated on the sand-bath, gives a sublimate of the nitrate in fine woolly crystals.

Hydrochlorate of Petinine.—Hydrochloric acid combines with dry petinine, with the evolution of much heat, and the formation of a salt which is extremely soluble in water, and sublimes in fine needle-shaped crystals.

Chloride of Platinum and Petinine.—If bichloride of platinum be added to a dilute solution of hydrochlorate of petinine, the salt formed remains in solution; but when both substances are concentrated, it falls as a pale yellow precipitate, which was purified by crystallisation from hot water. On cooling, the fluid, if sufficiently concentrated, becomes entirely filled with exceedingly beautiful golden-yellow plates, resembling those of crystallised iodide of lead. It is pretty soluble

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in cold water, extremely so in hot, and is not decomposed by boiling the solution. It is also soluble in alcohol.

	•	chloride of platinum and petinine gave
		carbonic acid, and
Į	3.593	water.

By three determinations of platinum, the details of which have been already given, the mean per-centage of platinum was found to be = 35.46.

	Experiment.				Calculation.			
Carbon, .	•		•	16.93	17.26		600·0	
Hydrogen,			•	4.17	3.96	\mathbf{H}_{11}	137.5	
Nitrogen,					5.04	N	$175 \cdot 0$	
Chlorine,		•			38.29	Cl_3	1330·4	
Platinum,			•	35.46	35.45	Pt	1232.0	
					100.0		3474.9	

These results correspond with the formula $C_8 H_{10} N$, H Cl, Pt Cl₂.

Chloride of Mercury and Petinine.—A solution of petinine in water, added to a solution of corrosive sublimate, gives a white precipitate, which dissolves in a considerable quantity of hot water, from which it is again deposited in crystals. It is much more soluble in alcohol; and the boiling solution gives a deposit of beautiful silvery plates on cooling. It is decomposed by boiling its watery solution, petinine being driven off, and a white powder deposited. It is readily soluble in the cold in dilute hydrochloric acid, probably with the formation of another double salt.

Products of Decomposition of Petinine.

The want of substance, which prevented the full investigation of the salts, has likewise curtailed this branch of the subject to a very few observations, which is the more to be regretted, as the general properties and low atomic weight of petinine give promise of definite products, which might enable us fully to determine its position in the chemical system.

When treated with concentrated nitric acid, it dissolves without any remarkable phenomena, and, on boiling, a feeble evolution of nitrous fumes takes place; but the petinine is attacked only to a very small extent, for, after being kept boiling for a long time, and then supersaturated with potass, it evolved the smell of the base apparently unchanged. Solution of chloride of lime immediately acts upon it in the cold, and developes a highly irritating odour, and some compound is manifestly produced; the solution remains colourless. Bromine water dropped into an aqueous solution of petinine occasions the precipitation of a yellow oil heavier than water, and insoluble in acids,—the solution contained hydrobromate of petinine. From the analogy of the other volatile bases, we should expect this to be tribromopetinine, $C_8 H_7 Br_3 N$. My material being exhausted, I was not able to extend these observations further.

Picoline.

Having determined the properties of petinine, I next turned my attention to that portion of the mixed bases which boiled between 270° and 280° , where I had every reason to expect the presence of picoline. After several rectifications, in each of which the first and last portions of the product were separated, I obtained a fine colourless transparent oil, possessed of all the properties of that substance. It dissolved readily in water : gave, with chloride of gold, a fine yellow compound depositing in needles from the hot solution, and with bichloride of platinum, a salt crystallizing in orange-yellow needles, analogous in all its properties to that of picoline. This identity was confirmed by analysis, which gave the following results:

	{	5.648 (15.990 3.998			rains of picol carbo wate			
Carbon,					77.21	77.41	C_{12}	900 ·0
Hydrogen,						7.53	H_7	8 7 ·5
Nitrogen,	•	•	•		14.93	15.06	Ν	175.0
					100.00	100.00		1162.5

For still further security, a determination of the platinum in its double salt with the chloride was made :

 $\begin{cases} 12.784 \text{ grains of chloride of platinum and picoline gave} \\ 4.204 & \text{platinum.} \end{cases}$

This corresponds to 32.88 per cent., and the calculation gives 32.94.

The suspicion, then, of the occurrence of picoline in the odorine of UNVER-DORBEN turns out to be perfectly correct; at the same time my experiments have clearly shewn, that odorine is a mixture of picoline, with at least one other base, the properties of which will be detailed in the second part of this investigation. The quantity of picoline contained in bone-oil is considerable, and it can be more readily prepared from that substance than from coal-tar naphtha; in fact, I obtained from three hundred pounds of bone-oil a larger quantity of picoline than that employed in my examination of it, which was obtained from some hundred gallons of coaltar naphtha; and by means of it, I shall be enabled to trace out the products of its decomposition, which I was unable to pursue in my former communication

12 DR ANDERSON ON THE DISTILLATION OF ANIMAL SUBSTANCES.

The presence of aniline in bone-oil I have already alluded to, and its quantity, though small, is by no means inconsiderable, when compared with that of the other bases. I did not think it necessary to take any further means for its identification than its highly characteristic reactions with chloride of lime and nitric acid.

The investigation of the other bases is not yet in a sufficiently advanced state for publication. The sparingly soluble one has been especially troublesome, and its purification is attended by difficulties which I have not yet fully overcome. The consideration of these will be taken up in the second part of this investigation.