

II. *On the Nitrogenated Principles of Vegetables as the Sources of Artificial Alkaloids.*

By Dr. JOHN STENHOUSE, F.R.S.

Received June 13,—Read June 21, 1849.

PART I.

THERE are few departments in organic chemistry which during the last six or seven years have attracted more of the attention of experimenters than the artificial formation of the alkaloids. This perhaps is not to be wondered at when we consider the interesting nature of this class of bodies, both as regards their well-defined chemical properties and the important medical virtues which many of them possess. All attempts to form the natural alkaloids, such as quinine, cinchonine, strychnine, &c., by artificial means have hitherto been unsuccessful, but chemists have been enabled by various processes to procure artificially a considerable number of true alkaloids quite analogous to those which occur in nature. Several of these artificial alkaloids, such as quinoline, narcogenine, cotarnine, &c., are obtained from the natural alkaloids by acting on them by various reagents.

A second group, comprising furfurine, thiosinamine, &c., are formed when ammonia is brought in contact with some of the essential oils, such as oil of mustard.

A third very numerous group, comprising nitraniline, toluidine, cumedine, &c., are obtained by the reducing action of sulphuretted hydrogen or sulphide of ammonium on nitrogenous compounds formed by treating certain hydrocarbons with nitric acid.

I shall conclude this enumeration by noticing a fourth very important group, comprising aniline, picoline, petenine, &c., which are obtained by the distillation of coal or animal substances, as in the case of bone-oil in the preparation of animal charcoal. To this last group I shall especially refer in the course of the present notice.

It is somewhat remarkable therefore, that while so many other sources have been examined, no attempt, so far as I am aware, should hitherto have been made to procure alkaloids from the highly nitrogenated principles, which under the names of vegetable albumen, fibrine, caseine, &c. are found in all plants, in many instances to a very considerable amount. These principles are, as is well known, almost as rich in nitrogen as the corresponding animal compounds, containing on an average about 15 per cent. of that element. What also renders the neglect of these substances by experiments still more singular, is the consideration that among the known sources of the artificial alkaloids coal has been one of the most productive, yielding as it does, in addition to ammonia, four other bases, aniline, quinoline, picoline and pyrrol, and not improbably containing also other organic bases which have hitherto escaped

observation. Now coal is universally admitted to be exclusively of vegetable origin, and to consist of the remains of a variety of vegetables, which, after having undergone putrefactive fermentation, and been subjected to probably enormous compression, have lain for countless ages in the bowels of the earth.

When reflecting therefore on the probable sources of the organic bases in coal, it has for some time past appeared to me highly probable that they are not derived from the woody fibre and other non-nitrogenated vegetable matters from which the coal has been principally formed; but that these bases are exclusively derived from the highly nitrogenated principles, previously enumerated, contained in the plants of the coal-fields. From the energetic agencies to which coal has been subjected, it seemed probable that much of the nitrogen originally present in the vegetables from which it has been formed must have been dissipated, and consequently the amount of bases now obtainable from coal proportionally diminished. It appeared therefore only reasonable to expect, that by acting on the nitrogenated principles of recent vegetables, the same organic bases as those contained in coal, or at any rate a series of analogous bases, would be obtained in proportionally greater abundance. In the sequel it will appear that this latter expectation has not been altogether disappointed.

It is extremely difficult to obtain vegetable albumen, fibrine, or caseine in considerable quantity in a state of purity. And though several chemists have bestowed much attention on the subject, as none of these principles are crystallizable, it is very doubtful if any of them have yet been obtained in a state of absolute purity. Instead therefore of endeavouring to purify these principles, I contented myself with selecting those portions of our commonest plants, usually their seeds, which contain them in the greatest abundance.

The first substance on which I operated was the seeds of the *Phaseolus communis*, or common horse-bean. This bean contains about 20·8 per cent. of caseine and 1·35 per cent. of albumen, amounting in all to a little more than 22 per cent. nitrogenous matter. The beans were destructively distilled in cast-iron cylinders, about three feet high and eight inches in diameter. The products of the distillation were collected by means of a large condensing LIEBIG's apparatus, kept carefully cool. A great deal of combustible but non-condensable gas was evolved. It had a very disagreeable foetid odour. The liquid which passed into the receiver was strongly alkaline, so much so as to require about a third of its bulk of muriatic acid of ordinary strength to neutralize it. It closely resembled the products of the distillation of bones, flesh and other animal matters, being very complex, and comprising, among other substances, acetone, wood-spirit, acetic acid, empyreumatic oils, tar, a great deal of ammonia, and several organic bases. The crude produce of the distillation was then treated with a considerable excess of muriatic acid, and the clear liquid, after subsidence, was poured off from the tar and other empyreumatic matters which had fallen to the bottom of the vessel. The tarry residue was also repeatedly agitated with small quantities of water, so long as any bases appeared to be dis-

solved. The several liquors were then mixed together, and were boiled for a couple of hours in a copper pan, or still more conveniently in an iron pot lined with enamel. This dissipated the acetone, wood-spirit, and a great deal of the neutral and acid empyreumatic volatile oils contained in the liquid. The boiling also rendered the tar less soluble by converting it and the fixed oils into imperfect resins. The acid liquor was then left at rest till it was quite cold, when it was passed through a cloth filter containing a quantity of pounded charcoal, which retained the greater portion of the resinous matter. The clear liquid was then introduced into a capacious still, and largely supersaturated either with quick-lime in fine powder, or with carbonate of soda, as was found most convenient.

As soon as heat was applied to the still a great deal of ammonia was evolved, and when the liquid boiled a quantity of oily bases began to appear in the ammoniacal liquor which passed into the receiver. Their amount increased as the distillation proceeded. As the first half of the liquid which came over was by much the richest in bases, it was collected separately from the succeeding portions, which contained scarcely any undissolved oil, but consisted chiefly of an aqueous solution of the bases. The distillation was continued however till the liquid which condensed in the receiver had only a slightly alkaline reaction. The mixture of oils which collected on the surface of the first portion of the distillation was drawn off with a pipette and then saturated with muriatic acid, which left any neutral oil which had been mixed with it undissolved. The oil was removed by passing the solution through a wet paper filter. The clear liquid was next supersaturated with carbonate of soda, and rectified in a large glass retort. It was found advantageous to employ a great excess of alkali for this purpose, as these bases are much more soluble in water than in strong alkaline lyes, and therefore distil over more readily from solutions which are strongly alkaline. The bases which passed over into the receiver were drawn off, as before, by means of a pipette from the ammoniacal liquor on which they floated, and were collected in any suitable bottle. The weak alkaline liquors of the previous distillation, which had ceased to yield bases by simple rectification, were again neutralized with muriatic acid, and cautiously concentrated to about half, or even a third, of their bulk, according to their state of dilution. Care should be taken however not to concentrate these liquors, unless in case of necessity, as long-continued boiling has always the effect of destroying a large portion of the bases, which are oxidated and converted into dark-coloured resins. The bases were again rectified with water, which removed much of the resinous matter which had come over with them during the previous distillations. As they still however retained a good deal of ammonia, from which it was necessary to free them, they were washed by being repeatedly agitated with successive portions of a strong solution of potash, which dissolved the ammonia and retained it in solution. The mixture of the lye and the bases was then poured into a long narrow-necked funnel, which was closed at the bottom, and the whole was left for a short time to subside. The bases quickly separated from the

potash solution and floated on its surface. The lye was then slowly run off by opening the bottom of the funnel, and when the whole of it was removed the escape of the bases was prevented by again closing the neck of the funnel. This operation was repeated till the whole of the ammonia was removed. A quantity of the bases remained dissolved in the alkaline lye, occasioning a loss, which however was unavoidable. The next step was to free the bases from the water they had absorbed, and which appeared to be nearly equal to that of their own bulk. The water was pretty readily removed by agitating the bases with bits of fused potash, so long as the alkali appeared to be in the least degree moistened. In order to ensure their being perfectly anhydrous, the bases were treated with successive quantities of fresh potash, and were kept in contact with the last portion for nearly a week. The clear liquid was then poured off from the potash into a small glass retort and cautiously rectified. The first two-thirds of the liquid which came over was a colourless transparent oil. The last portions, which distilled at a much higher temperature, had a slightly yellow colour, which increased in depth towards the close of the distillation. The colourless and the coloured portions were therefore collected separately. By repeated rectifications, however, the last portions of the bases were freed from the resinous matter they contained, and rendered as transparent and colourless as the first portion. As it was plain from the great variation in their boiling-points that the liquids were not homogeneous but consisted of a mixture of bases, many attempts were made to obtain them in a separate state by means of fractionated distillation. A thermometer was therefore inserted into the mixture of the bases by means of a perforated cork passed through the tubes of the retort. The mixture began to boil at 108°C. , when a very small portion of a limpid colourless oil, which was collected separately, distilled over. The thermometer rapidly rose to 120°C. , and from that to 130° , at both of which points small portions of oil were also collected. The boiling-point remained stationary for a considerable time between 150° and 155°C. , when a considerable quantity of the oil distilled over, and a second large quantity also came over between 160° and 165°C. The boiling-points of the last portions of the bases ranged between 165°C. and 220°C. The products of these different distillations were again repeatedly rectified, and by this means bases were obtained corresponding more closely with those points at which the thermometer remained longest during the first distillation. Though these various bases differed, as we have just seen, so considerably in their boiling-points, they still exhibited great similarity of character. Thus they formed transparent colourless oils which refracted the light very strongly. They were all lighter than water, and possessed the peculiar, pungent, slightly aromatic smell, so characteristic of this class of compounds. When brought in contact with the hands or with clothes, their odour was very persistent. The smell of the more volatile bases was, as might have been expected, the most pungent. Their taste was hot, and when diluted not disagreeable, reminding one of oil of peppermint. The bases which distilled over at low temperatures were tolerably soluble in water,

at any rate more soluble than those whose boiling-points were high. They all dissolved in every proportion in alcohol and in ether. The bases exhibited strong alkaline reactions with turmeric paper, and restored the blue colour of litmus. They caused abundant fumes when a rod moistened with muriatic acid was held over them, and they neutralized acids perfectly, forming in general crystallizable salt. They formed double salts with the bichlorides of gold, platinum and mercury. These compounds were soluble in water to nearly the same extent as the corresponding ammoniacal salts. The platinum salts crystallized in four-sided prisms arranged in stars. The salts, which the bases with high boiling-points formed, were however often contaminated with a brownish resin, and crystallized but imperfectly. This was the case also with the gold salts. The bases also precipitated the persalts of iron and those of copper just as ammonia does, forming like it a fine blue colour when the bases were in excess. Though kept for a considerable time in loosely-stoppered bottles, which were not unfrequently opened, they remained transparent and colourless; but if exposed to a strong light, especially those of them which had the highest boiling-points, they gradually became of a deep yellow colour. These bases were pretty readily oxidizable. When treated with nitric acid, they were rapidly changed into yellowish resins, but no charbazotic acid was produced. When brought in contact with hypochlorite of lime, they were also changed into brownish resins, but not a trace of aniline could be found, though it was carefully sought for. When the bases were boiled for a few minutes in a retort, they gradually became coloured, though the liquid which distilled over was as colourless as at first. At the close of the distillation a small quantity of resinous matter remained in the retort. I shall now subjoin some very imperfect analytical details, in order to give in the meantime some idea of the nature of these bases. I regret that the difficulty I have hitherto experienced in procuring them in large quantities has prevented me from submitting them to the thorough examination they deserve, and which I hope ere long to accomplish. It is not that beans and other seeds, as we shall presently see, yield smaller quantities of bases than bones and other animal substances; on the contrary, their product in bases is equal to that obtained from the distillation of bones, and, as might have been expected, much greater than that from coal. The difficulty wholly arises from this circumstance, that as both bones and coal are regularly distilled on the largest scale for commercial purposes, the crude oils of both bones and coal may be easily procured in any quantity, and from these their respective series of bases may be readily prepared. In regard to the bases from beans and similar seeds, however, the case is very different, the scientific chemist requiring to distil these substances on purpose, an operation which cannot be conveniently conducted in a laboratory, as the necessary apparatus is so large as to be almost upon a manufacturing scale.

I. 0.298 grm. of the base, boiling between 150° and 155° C., when analysed gave 0.815 carbonic acid and 0.222 water.

II. 0.270 grm. gave 0.7405 CO_2 and 0.189 water.

			I.	II.
10 C	750.0	74.98	74.60	74.78
6 H	75.0	7.49	8.18	7.77
1 N	175.2	17.53		
	<hr/> 1000.0	<hr/> 100.00		

When the anhydrous base combined with muriatic acid much heat was evolved. The muriate was very soluble in water, but when sufficiently concentrated it crystallized in slender prisms. With sulphuric and nitric acids the base also formed similar compounds. The platinum double salt was readily procured by adding bichloride of platinum to a pretty concentrated solution of the base in muriatic acid. This salt crystallized in four-sided prisms, arranged in stars of a deep yellow colour. It was rather less soluble in water than the corresponding ammoniacal compound. It was purified by a second crystallization out of water, which freed it from a little resinous matter it was apt to contain at the first. The formula of this salt was $C_{10}H_6N, HCl, PtCl_2$, and the calculated quantity of platinum 34.50 per cent.

I. 0.7314 grm. salt, dried *in vacuo*, gave 0.254 Pl=34.72 per cent.

II. 0.3150 grm. salt gave 0.109 Pl=34.60 per cent.

When chloride of gold was added to a solution of this base in muriatic acid, a double salt was immediately formed. It crystallized very readily in pale yellow needles, which were very soluble in hot water, and were again deposited on the cooling of the liquid.

It is evident that this base, the probable formula of which is $C_{10}H_6N$, approaches very closely in its composition to nicotine, and in its characters to picoline, the base discovered by Dr. ANDERSON in coal-tar. The formula of nicotine is $C_{10}H_7N$. The boiling-point of the new base is higher than that of picoline, and its solubility in water is much less. Dr. ANDERSON says that picoline is soluble in water in every proportion, while this base requires at least six or seven times its bulk of water to dissolve it. The new base was lighter than water. Its smell was peculiar and slightly aromatic. Its taste was hot, reminding one of peppermint. It dissolved in every proportion, both in alcohol and in ether. It remained colourless, though kept in an imperfectly stoppered bottle, if not exposed to a strong light. It caught fire readily, and burnt with a bright smoky flame.

In order to obtain an approximative idea of the per-centage composition of the other bases with which this was accompanied, three of them were subjected to analysis.

I. 0.2632 grm. of the base, or not improbably mixture of bases, boiling between 160° and $165^\circ C.$, gave 0.715 carbonic acid and 0.191 water.

II. 0.239 grm. of the liquid, boiling between 165° and $170^\circ C.$, gave 0.661 carbonic acid and 0.1835 water.

III. 0.197 grm., boiling between 200° and $210^\circ C.$, gave 0.547 Co^2 and 0.155 water.

	I.	II.	III.
C	74.08	75.42	75.63
H	8.06	8.52	8.73

It is rather singular that the amount of carbon and hydrogen does not vary more, while the boiling-points of these bases, or not improbably mixture of bases, are so exceedingly different. They all form double salts with chlorides of gold and platinum. Those with the highest boiling-points do not crystallize so readily as the less volatile bases, and are apt to be contaminated with resinous matter. As the height of their boiling-points rises, the solubility of the bases in water diminishes. They all appear to possess equally strong basic properties. Their detailed examination must however be reserved for a future communication.

As the *Phaseolis communis* was selected as the representative of that numerous tribe of plants, the Leguminosæ, of which the various kinds of beans, peas, lentils, &c. are the most familiar examples, the next substance subjected to distillation was oil-cake, or the dried seeds of *Linum usitatissimum*, from which the fat oil had been expressed. Oil-cake was selected as the type of the numerous class of plants in which the starch of the Gramineæ is replaced by oil. Of these, the poppy, rape, mustard, &c. are the best known. They are all very rich in vegetable albumen. The oil-cake was broken into moderate-sized pieces and distilled in the same cylinders as were employed for the beans. The quantity on which I operated was about two hundred weight. It yielded, as might have been expected, a smaller amount of liquid products than the beans. Their odour was peculiarly offensive. They consisted of acetone, acetic acid, a great deal of tar and empyreumatic oils. The quantity of ammonia was also exceedingly great. I was however disappointed to find that the organic bases were much less than in the case of the beans, amounting to not more than a third of what they yielded. The only way in which I can account for this different result, is from the greatly higher temperature at which the oil-cake was distilled, the heat not being mitigated, as in the case of the beans, by the presence of much moisture. Now, as all these volatile alkaloids are when highly heated resolved into ammonia, I think there is every reason to conclude, that in this, as in many other instances, a large portion of the bases which would have been generated at a lower temperature, were either not formed at all, or were destroyed immediately after their formation. The large amount of ammonia and the deficiency of the other bases is thus very naturally accounted for. The bases from oil-cake were separated and purified by similar methods to those employed for the preceding bases. They also formed a different series from either the coal or the bone bases, as they contained neither aniline nor quinoline. Their odour also differed considerably from that of the bases from beans, which however they closely resembled in other respects; their basic properties were equally decided, and they also formed similar salts. It appears probable enough therefore that some of the bases in both series are identical. But on this subject I expect to be able to speak more decidedly in a future paper.

Wheat.

A considerable quantity of the flour of *Triticum hybernum*, or common wheat, was also destructively distilled. Wheat was selected as a type of the Gramineæ, a most important order of plants, of which barley, oats, maize, &c. are those with which we are most familiar.

The liquid which the wheat-flour yielded, unlike that of the two preceding substances, was strongly acid from the large quantity of acetic acid it contained, derived from the starchy matters of the grain. The amount of acetone and wood-spirit was also very considerable. The empyreumatic products had a much less offensive odour than those from either oil-cake or from beans. The amount of ammonia was by no means inconsiderable, but the quantity of organic bases was less than I expected. They amounted however to pretty nearly the same quantity as those yielded by oil-cake. They did not contain either aniline or quinoline, and closely resembled the two preceding series in their general characters. They seemed however to be more volatile, distilling over at a lower temperature. At present I shall confine myself to the statement, that wheat, and most probably the other Gramineæ when distinctly distilled, also yield organic bases. As the starch in wheat, the quantity of which is so considerable, only forms acetic acid and other non-nitrogenated products, I intend in repeating this experiment to employ the gluten from the starch-makers, which contains almost the whole of the nitrogen in the wheat, and being a refuse product can be had for a trifle.

Peat.

A quantity of peat from the moors in the neighbourhood of Glasgow was also destructively distilled. I selected for this purpose the densest peat I could find. It had a deep black colour, and was very free from earthy matters. The products of its distillation were very nearly neutral to test-paper, owing to the formation of a considerable amount of acetic acid. Acetone and wood-spirit were also present in considerable quantity. The crude liquor was saturated with muriatic acid and gently boiled for some time to drive off the acetone, wood-spirit, &c., by which much of the tarry matter was held in solution. On the cooling of the liquid, the tar readily solidified and formed a soft crust on the surface, which was easily removed. The clear liquid was then supersaturated with carbonate of soda and distilled. The ammoniacal liquor which passed into the receiver contained a considerable amount of bases, which floated in it as a light oil. These were freed from ammonia and purified by the same means as in the preceding instances. The bases from peat bore a much larger proportion to the amount of ammonia than was the case with oil-cake. I ascribe this result chiefly to the porous nature of peat which conducts heat but slowly, and also to the greater degree of moisture contained in it. The bases therefore being distilled at a much lower temperature, a smaller amount of them was resolved into ammonia than in the instance of oil-cake. I expected to have found

aniline among the bases, but they appeared to contain neither it nor quinoline. They resembled the preceding series pretty closely therefore, but whether they will prove identical with them or not I am at present unable to say.

Distillation of Wood.

Through the kindness of Mr. TURNBULL, an extensive manufacturer of pyroligneous acid in this city, I was enabled to examine considerable quantities of the crude acid liquor obtained from the destructive distillation of beech, oak, ash and other hard woods. The stems and the larger branches of these trees are alone employed for this purpose. I was astonished to find that these liquors contained scarcely a trace of ammonia or any other organic bases. The woody portions therefore of the stems and trunks of trees appear to be almost entirely devoid of nitrogenous matter, in which respect they exhibit a remarkable contrast to peat.

This circumstance appears to me as perhaps calculated to throw some light upon a question of great interest to geologists, viz. the origin of the coal-beds. Whether therefore have the coal-beds been formed by the submersion of whole forrests and the floating of uprooted timber into estuaries and lakes, or whether are they due to the submersion of beds of peat? Now irrespective of all other considerations which might be urged in favour of the latter opinion, I would remark that the amount of nitrogen in coal, and consequently the quantity of ammonia and other bases which it yields when destructively distilled, are very considerable, constituting in fact an extensive branch of chemical manufacture. Wood, however, as we have just seen, appears to be quite incapable of furnishing the amount of nitrogen which we find existing in coal. Peat, on the other hand, from the quantity of ammonia and other bases which it yields when destructively distilled, is capable of furnishing more than the required amount of ammonia. This circumstance appears therefore highly confirmatory of the opinion, that the true source of coal is only to be sought for in peat.

As was already observed, I expected to have been able to procure from peat, in addition to ammonia, aniline, quinoline, picoline and the other coal bases. I did not find these however, but merely an analogous series of bases. I can only account for this result on the assumption that the different genera of plants, when destructively distilled, yield different series of organic bases. This we already know to be the case in several instances; for when indigo or any of the indigoferæ are destructively distilled, they yield ammonia and aniline; tobacco leaves, when similarly treated, yield ammonia and nicotine; the different species of the Peruvian bark, quinoline, and beans, wheat, oil-cake, &c., as we have already seen, do not yield aniline and quinoline, but are analogous series of bases. I am induced to believe therefore that the reason why modern peat does not yield the identical bases found in coal is, because the peat beds of primitive times, which in the course of ages have been converted into coal, were formed from the decaying remains of quite different plants than the various species of *Erica* and those other vegetables which constitute the peat

mosses of the present day. Had the plants in both cases been the same, I see no reason for doubting that when distilled they would have yielded identical bases.

Formation of Organic Bases from the nitrogenous Principles of Vegetables and Animals otherwise than by destructive Distillation.

1. *By treating them with alkaline lyes.*—From the facts which have been previously stated, I think we are warranted to conclude, that when ammonia is produced in large quantities by the destructive distillation of either vegetable or animal substances, it is always accompanied by the formation of organic bases. Now as ammonia is known to be procurable from these substances by several other methods, it seemed by no means improbable that on these occasions organic bases would also be produced. It has long been known that ammonia is largely generated when the nitrogenous portions of either plants or animals are boiled with strong alkaline lyes. A quantity of beans was therefore introduced into the body of a large still, and was boiled with a strong solution of caustic soda. The beans were speedily disintegrated, being converted into a slimy, dark-coloured pulp. The greatest difficulty attending the operation was caused by the frothing up of the pasty mixture, which, unless the still was very capacious and the fire kept moderate, was very apt to boil over and choke up the worm of the distilling apparatus. By cautiously rectifying the product of the distillation, a clear, strongly alkaline liquid was procured. It contained a large amount of ammonia, a little of a very agreeably smelling aromatic oil, and a considerable quantity of organic bases. The liquid was neutralized with muriatic acid, and the aromatic oil separated by means of a moist filter. On supersaturating with caustic soda and redistilling it, a strongly ammoniacal liquid passed into the receiver. It contained a considerable quantity of oily bases, partly in solution and partly floating on the liquid. These bases closely resemble those obtained by destructively distilling the beans, but whether they will prove identical with them or not I am at present unable to say.

Oil-cake was also distilled with a strong soda lye. It also yielded ammonia and similar organic bases. I should therefore expect that the same results will be obtained with the corresponding nitrogenous portions of most other plants.

PART II.

Bases from Flesh by the Action of Caustic Lyes.

An ox-liver was cut into moderate sized pieces, and introduced into the body of a capacious still containing a quantity of tolerably strong caustic soda. The liver, speedily dissolved, formed a brownish and very liquid jelly, which frothed up exceedingly. A strongly ammoniacal liquid distilled over accompanied by an aromatic oil, very similar to that obtained from the beans. The ammoniacal liquid was neutralized with muriatic acid and concentrated. During this operation the aromatic

oil was converted into a brownish resin. The concentrated liquid was then supersaturated with carbonate of soda and redistilled. The ammoniacal solution which came over contained a considerable quantity of oily bases. I am at present unable to state what these bases are, but hope to do so in the course of a few weeks. One advantage in operating with caustic lyes is, that the bases are immediately obtained quite free from empyreumatic oils or resins.

2. *Formation of Bases by means of Sulphuric Acid.*—A quantity of beans was also digested with sulphuric acid, diluted with three or four times its bulk of water. The beans, as in the previous instance, were speedily disintegrated. Care was taken to prevent the action proceeding so far as to decompose the sulphuric acid and to generate sulphurous acid. The strongly acid liquid, after being filtered, was supersaturated with carbonate of soda and distilled. The ammoniacal liquid which passed into the receiver was, on examination, found also to contain organic bases. I think it may be inferred, therefore, that when other vegetable and animal substances are similarly treated they will also yield analogous results.

3. *Bases by Putrefaction.*—Putrefaction is the only other method I at present recollect by which ammonia is procurable, in quantity, from animal and vegetable substances. I have not at the moment an opportunity of ascertaining whether in these cases also the ammonia is accompanied with the formation of organic bases, though I feel strongly inclined to believe that it is. The peculiarly disagreeable odour of the ammoniacal liquors, derived from putrid substances, appears to indicate the presence of such bases. And I should not be at all surprised, if, from the very gentle nature of the process, putrefaction should prove to be the most advantageous method of preparing the volatile alkaloids on a large scale.

Guano.

Since the above was written, I distilled an aqueous solution of a quantity of Peruvian guano with an excess of quick-lime. The guano had a pale yellow colour, was very dry, and emitted a comparatively feeble odour. The strong ammoniacal liquid which distilled over was neutralized with muriatic acid, and concentrated to about a third of its bulk. It was then supersaturated with carbonate of soda and redistilled. The liquid which passed into the receiver contained a small, but very appreciable quantity of a basic oil, similar to that obtained from the preceding substances. Muriatic acid dissolved it very readily, forming a transparent solution, from which it was precipitated by alkalis. It was considerably more soluble in water than any of the bases previously described. Its amount was less than I expected, though guano cannot be regarded as a favourable example of the usual effects of putrefaction on a complex nitrogenous substance, as the chief portion of the nitrogen contained in it existed from the first in the state of ammoniacal salts. Guano, however, in addition to ammonia, also contains a quantity of volatile organic bases.

From the facts which have been now stated, I think it may be pretty safely

MDCCCL.

assumed, that "*whenever ammonia is generated in large quantity from complex, either animal or vegetable substances, it is always accompanied by the formation of a larger or smaller amount of volatile organic bases.*" If therefore researches similar to the present are actively prosecuted, and if the seeds and leaves of the various genera of plants especially are subjected to these or similar processes, it seems not unreasonable to expect that the number of the volatile organic alkaloids will ere long be considerably increased.

Another inference which we think may be fairly deduced from these experiments is, that the nitrogenous principles of plants, viz. vegetable albumen, caseine, fibrine, &c., though very analogous, are not identical with the corresponding principles of the animal kingdom, otherwise the products of their decomposition would have been the same. The same series of bases would therefore have been obtained from both beans and bones, and so also from the other animal and vegetable substances. This, as we have seen, however, is not the case; I should therefore be disposed to conclude that animal and vegetable fibrine, caseine, &c., though very analogous, are not identical substances, as has hitherto been supposed by some eminent chemists.

In conducting the destructive distillation of animal and vegetable substances, the chief point to be attended to is to operate at as low a temperature as possible, for I have not unfrequently found that when the heat had been inadvertently raised too high the organic bases were almost entirely destroyed, and ammonia was consequently almost the only alkaline product. I strongly suspect, therefore, that in many cases a considerable portion of the ammonia obtained from the distillation of animal and vegetable substances is really derived from the destruction of organic bases. This will appear still more probable when we consider that the organic bases are more complex in their structure than ammonia, and that if we pass even the most stable of them once or twice through a tube filled with red-hot charcoal, they are almost entirely resolved into that alkali. And even when organic bases are strongly heated in contact with potash or soda, or when their aqueous solutions are simply boiled for any length of time, they always undergo partial decomposition, ammonia being an invariable product.

I must again apologize for the imperfect state of this paper. It is however merely the first of a series, and will, I trust, be regarded as only preliminary to more mature investigations.

Glasgow, 11th June, 1849.

Addendum to the paper on the Nitrogenous principles of Vegetables as the sources of artificial Alkaloids.

Since the preceding paper was written several additional experiments have been made, some of the results of which I now beg leave to subjoin.

Bases by putrefaction.

A quantity of horse-flesh which had been cut into small pieces and the juice extracted by long-continued boiling, was moistened with water and was placed in a warm situation for nearly a month. It became very putrid and was full of maggots. It was then supersaturated with muriatic acid, and repeatedly agitated with water so long as anything was dissolved. The acid liquor was superfluous, concentrated to a moderate bulk, and filtered to remove the flocculent and albuminous matters collected in it. The clear liquid was next supersaturated with carbonate of soda and subjected to distillation. A highly alkaline liquor came over, consisting chiefly of carbonate of ammonia, but mixed with small quantities of organic bases. By repeated rectifications with caustic soda, a quantity of a light oily fluid consisting of one or more bases was separated. It had a pleasant aromatic odour, and was exceedingly soluble in water, from which however it separated, when sufficiently concentrated, as a transparent colourless oil, which was strongly alkaline, saturating acids and forming salts similar to those of the preceding bases. I was surprised however to find that it did not contain any aniline. The quantity of organic bases obtained by this experiment, though very appreciable in amount, was not nearly so great as I had anticipated; as, instead of yielding more than was obtained by destructive distillation, it gave a great deal less. Had however the superfluous putrefaction been carried far enough, and the whole of the flesh been decomposed, it is not improbable that as large or even a greater amount of bases would have been obtained as by destructive distillation; but a great deal of time would have been required to have effected the complete decomposition of the flesh by simple putrefaction. The present experiment however sufficiently proves that putrefaction forms no exception to the law I have ventured to lay down in a preceding part of this paper, viz. "that whenever ammonia is generated in quantity from a complex organic substance, it is always accompanied by the production of a larger or smaller amount of organic bases." It is also remarkable that the putrefaction of flesh in this instance yielded no aniline, which is a constant and considerable product when either flesh or bones are destructively distilled. The nature of the organic bases obtainable from the decomposition of nitrogenous substances appears to be dependent therefore on the processes to which they are subjected.

Bases from Lycopodium.

A quantity of lycopodium (pollen) was boiled with some strong soda-lye, and then evaporated to dryness. It was next destructively distilled in an iron retort, and the

products collected in the way already so frequently described. Besides much ammonia they contained a considerable quantity of a basic oil but slightly soluble in water, of a very peculiar and penetrating odour resembling that of the borage plant. It neutralized acids perfectly, and was evidently quite distinct from any of the bases previously met with. A quantity of lycopodium destructively distilled *per se* also yielded this base, but towards the close of the distillation it was mixed with other bases resembling those previously described. Lycopodium therefore affords us another proof that different tribes of vegetables, when destructively distilled, furnish a diversity of volatile organic bases.

Bases from the Common Fern (Pteris aquilina).

A quantity of the stems and leaves of the fern *Pteris aquilina* were also destructively distilled. They yielded a very alkaline liquid, containing much ammonia and a considerable quantity of oily bases similar in character to those obtained from beans, oil-cake, &c. ; but I am at present unable to determine their nature individually.