IV.—*On the Action of the Halogen Compounds of Ethyl and Amyl on some Vegetable Alkaloids.* By Mr HENRY HOW, Assistant to Professor ANDERSON, Glasgow University.

(Read 1st May 1854.)

THE memoir which I have now the honour of presenting to the Society contains part of a continued investigation, of which the first results were published in a paper read, last year, before the Chemical Society of London.* The nature of the materials experimented on is such, and the scope of the subject so large, as to afford nothing more to all I have at present brought to light than the name of a bare and partial outline; yet the facts I have now to adduce, of some interest in themselves, will increase that of those already made known, and prove of additional service in aiding to complete that desirable object, a knowledge of the chemical constitution of the natural bases. In the paper alluded to, I shewed that, by the action of iodide of ethyl and of methyl upon morphia and codeine, the two most prominent alkaloids of opium, new salts are produced, in which the basic molecules appear to assimilate by their chemical characters to the hypothetical metal ammonium, or its oxide rather; so that, in the system of HOFMANN, these peculiar results of natural, and as yet inimitable agencies, would take rank among the nitrile bases. I say as yet inimitable, because it appeared that although one of the new salts possessed precisely the same centesimal composition as the corresponding salt of codeine, the base contained in the artificial product was widely different in appearance and properties from this alkaloid; a fact which seems to militate against a hope of forming the natural bases by this or similar means, and to show that the building up of these bodies is a process peculiarly the function of the *vis vitæ* of the plants producing them; at least that, easy as the transition of morphia into codeine appears to be on a comparison of their respective rational formulæ, and since the adding the required two equivalents of carbon and hydrogen to the former proves of ready performance, the cause of the failure lies deeper than in this difference merely, and that there are peculiarities in the construction of the primary molecules which we are at present as far as ever from being able to imitate. I further remarked, that so far as the amount of basic hydrogen, or compounds supplying its place, is concerned, the fact that it proved the same in these two alkaloids was possibly to be anticipated from their similar origin; and that I intended pursuing the subject with a view of ascertaining if all the bases of the same plant were so far analogous. It will be seen that they do not appear to be

* Quart. Journ. Chem. Soc., vol. vi.

so in reality, my attempts at forming corresponding compounds with some other alkaline principles of opium having been as yet unsuccessful. Another order of plants, however, has furnished me a base, strychnine, which seems in this respect similarly constituted with morphia and codeine, inasmuch as, under the same circumstances, it yielded a new combination, whose stability in the free state, and in some of its salts, caused it to afford more decided results than I was able to obtain with the analogous products from these alkaloids.

This investigation was pursued in the laboratory of Professor ANDERSON, in the University of Glasgow, to whom my cordial thanks are due for the interest he took in its progress, and, among other things, for the facilities he afforded me in placing at my disposal specimens of subjects for experiment.

In describing the individual re-actions, salts, &c., I have preferred giving them, as nearly as is consistent with clearness, in the order in which they were investigated.

Behaviour of Papaverine with Iodide of Ethyl.

Hydriodate of Papaverine.—Next to morphia and codeine, papaverine is the opium alkaloid possessing the most marked characters, and highly basic properties, and as I was acquainted with the beautiful substitution products it yielded to Professor ANDERSON, of which an account has been given to this Society,* I chose it as the subject for further experiment. Accordingly, some of the base, in small crystals, was placed in a tube, spirit of wine poured on it, and iodide of ethyl added; a great part of the crystals was seen to disappear immediately, and when the sealed tube was placed in boiling water, solution became rapidly complete. The clear fluid was allowed to boil about half an hour, but no solid made its appearance, either during the continuance of the heat, or upon the subsequent cooling and standing of the vessel. The solution was distilled finally in a flask to a very small bulk, and the syrup which remained soon solidified into a crystalline mass; this was found to be perfectly soluble in hot water—papaverine itself being insoluble—and in spirit of wine; but, from peculiarities to be mentioned presently, absolute alcohol was preferred as a solvent. From a concentrated hot solution in this menstruum, the new product was obtained, on cooling, in rhombic crystals, a portion of which, as they proved to be an hydriodate, was submitted to analysis in the ordinary way, with the following result:—

$$\left\{ \begin{array}{l} 5.558 \text{ grains, dried in } vacuo, \text{ gave} \\ 2.780 \quad \dots \quad \text{iodide of silver,} \end{array} \right.$$

which gives a percentage of iodine of 27.02, and 27.21 is the theoretical calculation corresponding to the anhydrous hydriodate of papaverine, whose formula is

* Trans. Roy. Soc. Edin., vol. xxi., part i.

I shall shew presently, from an analysis and description of the base obtained from this salt, that there can be no doubt of its real nature; so that, under these circumstances, papaverine behaves in a manner similar to that shewn before* to be the case when hydrated morphia is placed in contact with chloride of amyl, it forms a salt, namely, with the halogen of the ether compound, while no doubt the corresponding alcohol is simultaneously generated by the agency of the elements of water, as in the equation—

this, at least, seems the most obvious explanation of the change when water is present. To determine if the formation of the salt were really due to the agency of water, I repeated the experiment with absolute alcohol in place of rectified spirit, and the papaverine was dried at 212° , to remove accidental moisture, its crystals containing no water of combination. In this case, also, the hydriodate was formed from part of the alkaloid, the rest remaining unaltered. The iodide of ethyl had been distilled from chloride of calcium, and I should think could furnish, at the most, but a minute quantity of water; and it is not easy to see how the reaction is brought about under these circumstances, unless it be assumed that it occurs with the formation of ether. The detection of this substance would not be readily effected upon the small scale upon which I worked, and I therefore only throw out the following equation as a possible explanation of the reaction—

As no account has yet been given of the hydriodate of papaverine, a short description of it may be subjoined. The salt is extremely soluble in boiling water, and the moment the heat is withdrawn from a strong solution, the fluid assumes a milky appearance, and an oil is soon deposited, which, after some hours, passes into the form of stellate colourless needles; it is also soluble in spirits of wine, but in absolute alcohol it dissolves with far less facility, and it requires protracted boiling, when the salt has once taken on the crystalline condition, to obtain perfect solution with this menstruum. The hot liquid deposits the salt rapidly, as it cools, in colourless rhombic crystals. When exposed to a temperature of 212° Fahrenheit, in a dry state, the hydriodate of papaverine assumes a brown tint, loses slightly in weight, and is found to have undergone some decomposition, as it no longer dissolves completely in hot water, but leaves a brown resinous matter.

By addition of ammonia to the mother liquors of the salt which had been analysed, a white crystalline precipitate was obtained; this was recrystallized from dilute spirit, and burnt with chromate of lead:—

* Quart. Journ. Chem. Soc., vol. vi.

$\left\{ \begin{array}{l} 3.552 \text{ grains, dried at } 212^{\circ}, \text{ gave} \\ 9.200 \text{ ,, carbonic acid, and} \\ 2.095 \text{ ,, water.} \end{array} \right.$

		Experiment.	Calculation.		
Carbon,	. .	70.63	70.79	C ₄₀	240
Hydrogen,	. .	6.55	6.20	H ₂₁	21
Nitrogen,	. .		4.10	N	14
Oxygen,	. .		18.91	O ₈	64
		<hr/> 100.00	<hr/> 100.00		<hr/> 339

A glance at the result, and the appended calculation of the numbers required by the formula of papaverine, leaves no doubt as to the base of the salt. I was perfectly satisfied as to its nature, from its appearance and some peculiar well marked reactions characteristic of papaverine; thus, with strong sulphuric acid it yielded a splendid purple fluid, at the instant of solution, and when heated with a little nitric acid, became converted into a mass of yellow crystals, which are nitrate of nitropapaverine, described by Dr ANDERSON.*

Behaviour of Narcotine with Iodide of Ethyl.

Hydriodate of Narcotine.—The next alkaloid of opium submitted to examination was narcotine; and the following experiment shews its deportment to be perfectly similar to that of papaverine.

Some narcotine in fine powder was heated in a sealed tube with absolute alcohol and iodide of ethyl; after about ten minutes exposure to a temperature of 212° , the whole of the base disappeared; but to insure complete decomposition, the heat was continued some twenty minutes longer. When the tube had cooled, and stood a short time, groups of four-sided colourless prisms appeared. On opening the vessel, and submitting these to examination, they proved to be unchanged narcotine, while their mother liquor was found to contain an hydriodate. The excess of iodide of ethyl and alcohol was accordingly distilled off, and the remaining syrup tested as to its nature; it was almost entirely soluble in boiling water, leaving only a little narcotine, and the solution contained the hydriodate of that base.

This salt is deposited, from a concentrated fluid, as an oil which does not become crystalline, and when its solution is evaporated, spontaneously or at 212° , an oily mass is also obtained, which does not crystallize from alcohol, or ether, or a mixture of these substances. Owing to its occurring only in this amorphous state, I did not attempt to submit it to analysis; but its solution yielded to ammonia a precipitate easily to be recognised as narcotine, by its characters and chemical reactions; and in order fully to substantiate the nature of the base, the hydriodate was converted into a platinum salt in the following manner:—

* Loc. cit.

An aqueous solution was treated successively with nitrate of silver and hydrochloric acid, and bichloride of platinum was finally added to the clear fluid, care being taken to operate with dilute liquids and in the cold, as the platinum compound of narcotine is very prone to change. An amorphous yellow precipitate resulted, which was quickly collected, washed, and dried; it gave these numbers on ignition,—

$$\begin{cases} 8.375 \text{ grains, dried at } 212^{\circ}, \text{ gave} \\ 1.330 \text{ ,, platinum.} \end{cases}$$

which lead to a percentage of 15.88; and 15.81 is that required by the salt of narcotine, whose formula is

To the nature of the reaction in this case, I would apply the remarks made with reference to papaverine under similar circumstances; but, perhaps, should not permit the subject to pass without drawing attention to the relation my experiment may bear to a fact made known some time since by WERTHEIM.

This chemist announced, in a preliminary notice,* that he had detected in opium two new species of “narcotine,” which, from their composition, he named methylo and propylo-narcotine, while he was led to consider the ordinary alkaloid, hitherto known, as ethylonarcotine: the whole being derived from one fundamental substance. I do not think the detailed account of his experiments has yet been published, but it would certainly be interesting to establish the existence of this series in reality, because, in that case, the ordinary narcotine, with which I worked, would seem to have no longer any replaceable hydrogen, and be the first instance of a natural, or indeed of any compound nitrogenous analogue of ammonium or a metal, unless papaverine be similarly constituted. In the absence of positive proofs, resulting from experiment, nothing can at present be said further as to the nature of these known and unknown bases; but the question seems to me very interesting and worthy of being settled decisively, WERTHEIM’S being an unsupported statement, particularly as, chemically, there is nothing to distinguish narcotine and papaverine from other natural alkaloids, as a class, or to assimilate them to ammonium.

Behaviour of Cotarnine with Iodide of Ethyl.

Hydriodate of Cotarnine.—Cotarnine is a base derived from narcotine by oxidation; some of it was treated exactly in the manner just described. It was found to be completely converted into an hydriodate, which remained, on distilling off the excess of alcohol and iodide of ethyl, as a red-brown oily mass, highly soluble in hot, insoluble in cold, water, and not taking on the crystalline state under any circumstances. This salt was the hydriodate of cotarnine; but being of itself no more

* Journal für Praktische Chemie, vol. liii., p. 431; Chem. Gazette, 1852, p. 36.

fit for analysis than that of narcotine, the composition of the base was ascertained by converting it into a platinum compound, which was a very pale yellow amorphous substance, and gave the following result on analysis:—

$$\begin{cases} 3.265 \text{ grains, dried at } 212^{\circ}, \text{ gave} \\ 0.720 \text{ ,, platinum,} \end{cases}$$

equal to a percentage of 22.38; 22.57 corresponds to the formula of the cotarine salt,

This artificial product then comports itself exactly like the alkaloids papaverine and narcotine; and the reaction is no doubt of the same nature.

The formation of these salts of the alkaloids, in cases where water is present, is possibly brought about by a change, observed by FRANKLAND* to take place between iodide of ethyl and water in a sealed tube at 300° Fahr.; the results of this reaction are, according to this chemist, hydriodic acid and ether. It seems not improbable that the presence of a basic substance may determine this decomposition at a much lower temperature.

On Strychnine.

Having examined the action of the alcohol iodides on a number of bases with only one equivalent of nitrogen, I was anxious to ascertain the deportment of a base containing, like strychnine, two atoms of this element, in the hope of throwing some light on the function of the second equivalent. The researches of Hofmann, on a great variety of alkaloids, have shewn us that the volatile bases starting from the original type ammonia, and passing upwards to the most complicated substances, may be viewed as nitrogen attached to basic hydrogen alone, or to it in combination with hydrocarbons performing its functions, or finally to hydrocarbons occupying the entire hydrogen part of the molecule. In the fixed vegetable alkaloids, we see oxygen also included in the system; and if, as I have attempted to prove in the case of some of these, they are comparable with nitrile bases, the hydrogen part of the compounds must contain oxygenized hydrocarbons acting as hydrogen. In the case of a base containing two atoms of nitrogen, it is possible that this element performs as it were two parts; one may be referable to the function of that in any ammonia, amidogen, or nitrile base, while the other may be more analogous to that property in virtue of which, in combination with oxygen, as NO₂, it replaces an atom of hydrogen in the carbohydrogen forming part of the compound molecule. The

* Gerhardt Suite de Berzelius, ii., p. 323.

possibility of the latter being the case, as regards one of the atoms of nitrogen in an alkaloid containing two, was thrown out as a speculative suggestion some few years ago by FRESSENIUS.

In the hope of arriving at some conclusions regarding these points, I proceeded to examine the deportment of strychnine with reagents suited to my purpose. The decision of the whole question seems to devolve upon the reactions of two classes of agents; the amount of basic hydrogen would be learned by the quantity of hydrocarbons or alcohol radicals the base is capable of taking up from their halogen compounds, while reducing agents should remove oxygen from any oxidized combination of nitrogen; if it be as NO_2 , that the second atom of this element exists, sulphuretted hydrogen should, as in other compounds of this class, remove the four equivalents of oxygen, and permit two additional atoms of hydrogen to enter into the new product.

The first part of the question is gone into in some detail in the present memoir, while, without being in a position to give anything decisive at present with regard to the second, I may mention that strychnine undergoes a curious decomposition in contact with sulphide of ammonium, which results in the formation of hyposulphite of the base itself,—a very beautiful and stable salt,—and the production of another substance I am still engaged in studying. The description of the properties and composition of these products I must reserve till I am able to shew the complete history of the change, and how far the real constitution of strychnine is determined by the experiments; but I may state that, from what I have as yet learned, the decomposition does not appear to be of the nature just spoken of.

Action of Iodide of Ethyl on Strychnine.

Hydriodate of Ethylstrychnine.—Strychnine, in a state of fine powder, is readily attacked by iodide of ethyl; even when these two substances are boiled together in water, a perceptible quantity of iodine is found in the solution, precipitable by silver salts; the insolubility of the alkaloid, however, no doubt interferes with the reaction, for the change is much more easily effected when spirit of wine is used as a medium. The most successful method I found to be that employed before, viz., to operate with alcohol and iodide of ethyl on the powdered base in sealed tubes; at the temperature of boiling water the change is complete in about twenty minutes. A heavy crystalline powder is formed, differing in appearance from strychnine; but solution is not at any time during the experiment complete, no change being perceptible beyond the more definitely crystallized nature of the solid contents of the tube, the complete solubility of which in boiling water announces the completion of the reaction.

A boiling aqueous solution of the new substance having deposited, upon cooling, masses of silky white crystals, which proved to consist of an hydriodate, they

were collected, washed, and dried, and a portion of them was submitted to analysis in the ordinary way.

$$\left\{ \begin{array}{ll} 4.325 \text{ grains, dried at } 212^{\circ}, \text{ gave} \\ 8.925 \text{ ,, carbonic acid, and} \\ 2.180 \text{ ,, water.} \\ 4.565 \text{ ,, dried at } 212^{\circ}, \text{ gave} \\ 2.195 \text{ ,, iodide of silver.} \end{array} \right.$$

	Experiment.	Calculation.		
Carbon, . . .	56.27	56.31	C ₄₆	276
Hydrogen, . . .	5.60	5.50	H ₂₇	27
Nitrogen, . . .		5.71	N ₂	28
Oxygen, . . .		6.55	O ₄	32
Iodine, . . .	25.98	25.93	I ⁴	127.1
	<hr/> 100.00	<hr/> 100.00		<hr/> 490.1

A comparison of the above results and appended calculation will shew that a replacement of hydrogen by ethyl in, or an attachment of iodide of ethyl to, the alkaloid has taken place, according to the equation,

The salt crystallizes without water, and whatever constitution subsequent experiment may assign to it, it will be now described as an hydriodate, and its base as ethylostrychnine.

Hydriodate of ethylostrychnine is soluble in about 50 or 60 parts boiling water, and in about 170 of water at 60°; a tolerably dilute fluid deposits the salt in very fine white four-sided prisms of considerable lustre, which they retain in the dry state; it is also soluble in rectified spirit, and comes out of that menstruum in short prismatic crystals. It is unaltered in the air; at 212° it loses no weight, but acquires a slight shade of colour; at a higher temperature it fuses and blackens, affording thick vapours of an alkaline reaction, and disagreeable odour; and a yellowish sublimate, rather oily in appearance, forms on the sides of the vessel; no vapours of iodine are to be observed during the process of heating.

This salt gives no base with potass or ammonia, but is less soluble in these alkaline fluids than in water, and is consequently precipitated, on their addition, in strong solutions; strong potass throws it down at once in the cold, and when ammonia is added to a concentrated boiling aqueous solution, the unchanged salt deposits immediately in fine needles. It is readily decomposed by oxide of silver, and the hydrated base may be obtained in the crystalline state. These reactions assimilate the salt to an iodide rather than to an hydriodate, and the characters of the base, when isolated as far as it can be, being those of an analogue of ammonium oxide, its salts would perhaps be more correctly called

iodide, chloride, &c.; and in the following pages I make use of these terms, without, however, making any alteration in the conventional nomenclature for the base.

The salts of ethylostrychnine, generally, are characterized by their beautifully crystalline nature, and the facility with which they may be obtained pure. I have analysed a few, as affording a favourable opportunity of examining the combinations of one of these derivatives from a natural fixed alkaloid.

Nitrate of Ethylostrychnine.—This compound is readily formed by double decomposition from the preceding, by use of nitrate of silver in warm dilute solutions. It is easily soluble in boiling water, but of extremely sparing solubility in this menstruum when cold; so much so, that I have used this property as a test of the existence of the base on many occasions; a solution containing it, even when tolerably dilute, depositing, on the addition of a little nitric acid, in a short time, very fine four-sided prismatic crystals; in more concentrated fluids their appearance is immediate. The salt, in a pure state, is in colourless prisms of high refractive power, which may be obtained of great beauty from dilute aqueous fluids. Its analysis gave the following results:—

		$\left\{ \begin{array}{ll} 4.555 \text{ grains, dried at } 212^{\circ}, \text{ gave} \\ 10.790 \quad \dots \quad \text{carbonic acid, and} \\ 2.680 \quad \dots \quad \text{water.} \end{array} \right.$	
	Found.	Calculation.	
Carbon, . . .	64.60	64.94	C ₄₆ 276
Hydrogen, . .	6.53	6.35	H ₂₇ 27
Nitrogen, . . .		9.88	N ₃ 42
Oxygen, . . .		18.83	O ₁₀ 80
	<hr/> 100.00	<hr/> 100.00	<hr/> 425

which agree precisely with the formula—

Its crystals contain no water.

Chromates of Ethylostrychnine.—Both neutral and acid chromate of potass yield precipitates with salts of the base; the former giving, even in dilute fluids, short prismatic yellow crystals, and the latter tufts of silky needles. As the number of bichromates, of whose analysis we are in possession, is in reality very small, being limited, I believe, to those of potass and ammonia, whose constitution is peculiar, I examined the salt in the present instance, to see if it were quite analogous to these compounds, which it does not appear to be.

Bichromate of ethylostrychnine is deposited from strong mixed solutions of the appropriate salts in very beautiful transparent plates of a golden yellow colour: it falls, as just mentioned, from more dilute fluids, in tufts of needles; it is readily

soluble in boiling water, but when cold, this liquid dissolves but little of the salt. The following is the analysis :—

I.	{	5.173 grains, dried at 212°, gave
		10.840 ... carbonic acid, and
		2.755 ... water.
		5.885 ... dried at 212°, gave, on ignition,
		0.938 ... sesquioxide of chromium.
II.	{	4.480 ... dried at 212°, when ignited, gave
		0.715 ... sesquioxide of chromium.

	Experiment.		Calculation.		
	I.	II.			
Carbon,	57.15		57.33	C ₄₆	276
Hydrogen, . . .	5.91		5.81	H ₂₈	28
Nitrogen, . . .			5.81	N ₂	28
Oxygen,			29.99	O ₆	48
Chromic acid, . . .	20.86	20.88	21.06	2(CrO ₃)	101.4
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00		<hr/> 481.4

which gives results according satisfactorily with a formula which contains an atom of water more than those of the corresponding potass and ammonia salts, and may be thus written :—

The failure of the analogy here, with the peculiar combinations of potass and ammonia, is worthy of attention; of course, it readily admits of explanation, if the one atom of water be assumed as retained from the water of crystallization of the new salt. The loss sustained by exposing the crystals to heat was as follows:—

I.	$\left\{ \begin{array}{l} 4.660 \text{ grains, lost at } 212^{\circ}, \\ 0.160 \quad \dots \quad \text{water} \end{array} \right.$	
II.	$\left\{ \begin{array}{l} 11.510 \quad \dots \quad \text{lost at } 212^{\circ}, \\ 0.435 \quad \dots \quad \text{water} \end{array} \right.$	
Percentage of water,	I. 3.43	II. 3.77

and 3.60 is the calculated percentage corresponding to a loss of two atoms of water by a salt of the formula,—

Platinum Salt of Ethylostrychnine.—By the successive addition of nitrate of silver and hydrochloric acid to a warm solution of the iodide, and that of bichloride of platinum to the clear fluid, this salt fell as a curdy yellow precipitate, which became crystalline after some hours; from more dilute liquids it crystallizes at once in a very beautiful form, namely, in groups of stars, of which the individual

rays resemble, on being magnified, the fronds of some species of ferns. The platinum alone, in this compound, was determined,—

$$\begin{cases} 3.390 \text{ grains, dried at } 212^{\circ}, \text{ gave} \\ 0.592 \text{ ... platinum.} \end{cases}$$

The percentage resulting from this experiment is 17.46; and 17.37 is that corresponding with the formula,—

The salt is anhydrous when crystallized.

The substitution of terchloride of gold for the platinum solution gives, by the same process, a yellowish curdy precipitate, soluble in boiling water; and this fluid deposits colourless brilliant prisms of splendid appearance, of the corresponding gold compound.

The chloride is a very soluble salt, crystallizing in needles; the sulphate is less soluble, an acid fluid furnishing groups of pearly needles and plates, possibly a bisulphate; the oxalate, prepared in a similar manner, has much the same appearance; the acetate remains as a gummy transparent mass when a proper solution is evaporated to dryness at 212° ; the chloride gives, with mercuric chloride, a curdy white precipitate, crystallizable from hot water in white needles.

Carbonates of Ethylostrychnine.—Having observed, in the course of experiments to be detailed presently, which were made for the purpose of obtaining the ethylostrychnine in an isolated state for analysis, the tendency of the base, when free and in solution, to absorb carbonic acid, it occurred to me to attempt the production of any carbonates of determinate composition it might be capable of forming. I shall be able to shew that the base enters readily into combination with this acid, forming at least two salts, of which while the one, the monocarbonate, cannot be obtained in the dry state, the other, a bicarbonate,—into which, with the occurrence of some other product of decomposition, the first appears to have a great tendency to pass,—may be readily procured in the solid form, of determinate composition, and even as a very beautiful crystalline substance.

It was found that when moist carbonate of silver is added to iodide of ethylostrychnine, covered with a little water, double decomposition ensues, and is complete in a few minutes, when the vessel containing the mixture is well shaken: iodide of silver, of course, remaining undissolved, while the fluid contains a carbonate of extreme solubility. When, without employing heat, the process is quickly performed, so as to occupy only a few minutes of time, a perfectly colourless liquid is obtained; but with a longer contact of the excess of carbonate of silver, or the application of heat, the fluid assumes a light claret colour, which, by the continued action of either of the above causes, may be deepened almost indefinitely, and seems to be the result of oxidation. This solution shews all the characters of a

carbonate in its reactions, and when saturated with dilute nitric acid, becomes filled, almost before the cessation of effervescence, with the characteristic crystals of the nitrate of ethylostrychnine; when evaporated to dryness, however, either *in vacuo* or at 212° Fahr., it is found to have undergone a singular decomposition. The residue obtained in both cases is crystalline, and in part colourless, with claret-coloured spots pervading its mass; on adding water to this, the great bulk dissolves to a deep claret-coloured fluid, which contains carbonic acid and ethylostrychnine, while an amorphous substance, in whitish flocks, remains in appreciable quantity.

It is obvious that, with the observation of this decomposition, all hope of analysing the expected residue of pure monocarbonate of ethylostrychnine was at an end; nevertheless, as I was curious to know the actual amount of carbonic acid retained, a certain weight of the residue, obtained by evaporation *in vacuo*, was treated with cold water, and to the filtered solution was added a mixture of chloride of barium and caustic ammonia, which had been suffered to remain in contact for some time; the precipitate produced would contain all the carbonic acid, and when collected and washed with the proper precautions, it was ignited; the resulting percentage, calculated on the amount of residue employed, was almost that of the bicarbonate to be described immediately.

The flocky matter remaining undissolved by the water appears to be a new base; it does not effervesce with acids, but dissolves tranquilly and completely, and is again thrown down by ammonia in white flocks; with nitric acid, it yields no crystalline salt, as ethylostrychnine does; it dissolves with the greatest ease in spirits of wine, but is not to be obtained from this menstruum in a crystalline state; the solution, which is, or soon becomes, of a fine pink colour, deposits no crystals on standing for weeks even, but red transparent drops appear at the sides and bottom of the vessel, and an amorphous residue remains on evaporating the fluid to dryness; these characters evidently separate the product widely from strychnine and ethylostrychnine, and must cause it to be considered a peculiar base. It would be an interesting decomposition to follow out, but I had far too little substance at my command to do more than observe the above facts at the time, and the consumption of material necessary for its investigation is an obstacle to the research.

Bicarbonate of Ethylostrychnine.—The preceding experiment having shewn the tendency of the base to accumulate carbonic acid, I proceeded to seek a higher carbonate, by passing a stream of the washed acid gas into the solution, obtained by the double decomposition just mentioned. During this process, a very slight turbidity ensued, and after the gas had passed through the fluid a considerable time, this was filtered and obtained perfectly colourless; it proved to admit of evaporation to dryness, *in vacuo* or at 212°, with similar results as to the properties and composition of the residue. In the former case, a white crystalline mass,

—having, however, here and there, faintly claret-coloured spots—remains, which, by continued drying, becomes a white enamel-like substance; the latter process yields a crystalline residue of a reddish-yellow colour; these products are the bicarbonate. The salt undergoes in a very slight degree the decomposition before spoken of, but this is scarcely perceptible when evaporation is quickly performed; the flocky base produced, at 212° especially, being exceedingly minute in quantity.

The aqueous solution of the bicarbonate, and, though not deliquescent, the salt is extremely soluble in water, has a powerful alkaline reaction, and proves a ready means of forming the compounds too soluble to be got by double decomposition. The dry salt dissolves completely in a little absolute alcohol; the addition of good ether to this fluid causes in a little time the deposition of bicarbonate in very fine colourless prismatic crystals, of great refractive power. In the analyses which follow, the carbonic acid was estimated as before mentioned, and the specimens were of different preparation:—

I.	{ 4.525 grains, dried <i>in vacuo</i> , gave
	{ 2.150 ... carbonate of baryta.
II.	{ 4.990 ... dried at 212° Fahr., gave
	{ 2.330 ... carbonate of baryta.

	Experiment.		Calculation.		
	I.	II.			
Carbon, . . .			65.09	C ₄₆	276
Hydrogen, . . .			6.60	H ₂₈	28
Nitrogen, . . .			6.60	N ₂	28
Oxygen, . . .			11.34	O ₆	48
Carbonic Acid, . .	10.62	10.44	10.37	2(CO ₂)	44
			100.00		424

These numbers agree perfectly with those required theoretically by a salt of the base analogous to bicarbonate of potass, as expressed in the formula—

This salt is somewhat interesting, inasmuch as it is, I think, the first combination of one of the artificial ammonium bases with carbonic acid which has proved definite by analysis. While on the subject, it will not be out of place to mention some experiments made with the natural alkaloids, for the purpose of preparing, if possible, similar salts with these bodies, as it gives the opportunity of correcting an error to be found in the manuals. Thus, it is stated in LIEBIG'S *Traité*,* that a carbonate of strychnine is obtained both by precipitation of its salts with carbonated alkalies and solution of the base itself in water, through which a stream

* LIEBIG. *Traité de Chimie Organique*, par Gerhardt ii., p. 630.

of carbonic acid gas is passed, it being deposited in this case in beautiful crystals. I have carefully gone over those experiments, and satisfied myself that the substance in both cases is the pure base. A carbonate is certainly obtained by double decomposition, between hydrochlorate of strychnine and carbonate of silver, but it exists only for a short time, even in solution, as the gas escapes on standing, and the pure alkaloid is deposited in fine, though small, crystals.

I could obtain no dry carbonates of morphia, codeine, papaverine, or narcotine; they behave like strychnine under the same circumstances. While these experiments were in progress, my attention was called to the production of a definite carbonate of quinine by LANGLOIS,* and I gave up the idea I had entertained of extending the observations to the vegetable alkaloids generally, as it is possible the subject will be gone into at greater length by this chemist.

Hydrate of Ethylostrychnine.—I have mentioned already that potass and ammonia fail to separate this base from its iodine combination, which is thrown down unaltered from its aqueous solution by strong potass, and is also less soluble in ammoniacal than in pure water. Oxide of silver readily effects the elimination of the iodine; in fact, when the solid salt is covered by moist oxide of silver, a few minutes' contact, in the cold, suffices to complete the change, iodide of silver remaining undissolved, and a fluid of a red purple colour being formed, which contains all the base. When this is suffered to evaporate to dryness spontaneously, a crystalline purplish mass results, which contains some carbonic acid, and dissolves in a small quantity of cold water; leaving, however, constantly, a minute residue of the nature before spoken of in describing the monocarbonate. Evaporation *in vacuo* over sulphuric acid produces a less crystalline residue, of a similar colour, which is found to be completely soluble in hot absolute alcohol to a purple fluid; a concentrated solution of this kind deposited, on cooling, a substance in colourless, small, prismatic crystals. These were collected on a filter, washed from the coloured mother liquor with a little absolute alcohol and ether, and finally dried out of contact of air. Tests, to be mentioned presently, having shewn the deposit to be, as nearly as it is possible to be procured, the pure base, it was retained *in vacuo* till it ceased to lose weight, and then gave these results on analysis:—

		{ 4.643 grains, dried <i>in vacuo</i> , gave		
		{ 11.600 ... carbonic acid, and		
		{ 3.425 ... water.		
Experiment.		Calculation.		
Carbon, . . .	68.13	67.81	C ₄₆	276
Hydrogen, . .	8.19	7.61	H ₃₁	31
Nitrogen, . .		6.87	N ₂	28
Oxygen, . . .		17.71	O ₉	72
		100.00		407

* Chemical Gazette, 1853, p. 470.

I must mention that the complete desiccation of this substance was extremely tedious, occupying above a fortnight, and that in the state in which it was burned, it was a very light and bulky powder, highly electrical and hygroscopic, so that the high percentage of hydrogen is not remarkable. The numerical results of the above analysis admit of translation into the formula, which, in analogy with the corresponding combination of potassa, the assumed congener of ethylostrychnine, may be thus written :—

and this hydrate of oxide of ethylostrychnine differs from the known crystallized hydrate of potassa, in containing an atom of water less.

The substance as analysed was not deliquescent; it dissolved immediately on being covered with cold water, furnishing a red fluid, and leaving only a minute flocky residue, which seemed to increase on application of heat; the solution, made in the cold, became filled, almost immediately on the addition of a little nitric acid, with the crystalline salt before spoken of as characteristic of the base, and no effervescence was perceptible.

When the hydrate, carefully dried *in vacuo*, is dissolved in a quantity of absolute alcohol, sufficient to prevent a deposit on cooling, the addition of some ether causes the formation of a tremulous jelly, which renders the whole fluid semi-solid. On stirring for some time with a glass rod, this jelly gradually changes into a crystalline substance; by management of the respective amounts of alcohol and ether, very beautiful small crystals, perfectly colourless, may be obtained at once, or on standing. To effect this result the hydrate must be well dried, or it falls in purple, oily drops.

The hydrate cannot be freed of its water of crystallization by exposure to 212° , as at this temperature it undergoes decomposition in a much greater degree; a portion so heated was found to effervesce in a lively manner with acids, and though it yielded plenty of the crystalline nitrate, yet when treated with cold water it left a considerable residue of the character already described. I made an analysis of a part of the substance giving these reactions with a view of ascertaining how far decomposition had proceeded, and give it with the understanding of its approximative value :—

		$\left\{ \begin{array}{l} 4.925 \text{ grains, dried at } 212^\circ, \text{ gave} \\ 12.600 \quad \dots \quad \text{carbonic acid, and} \\ 3.480 \quad \dots \quad \text{water.} \end{array} \right.$			
		Found.	Calculation.		
Carbon, . . .	69.77	69.34	C_{46}	276	
Hydrogen, . .	7.85	7.53	H_{30}	30	
Nitrogen, . .		7.05	N_2	28	
Oxygen, . . .		16.08	O_8	64	
		100.00		398	

These numbers agree closely with those corresponding to a formula containing an atom of water less than the preceding,

and it is just possible that the errors occasioned by the presence of carbonic acid and the basic product of decomposition, both of which, after all, bear but a small proportion to the whole substance, may counterbalance each other; I leave the fact of the analysis, since it is some sort of control over that immediately preceding.

A freshly prepared solution of the base, by action of oxide of silver on the iodide, has a red purple colour and an extremely bitter taste; its reaction is highly alkaline. It yields no immediate precipitate with solutions of barium and calcium chlorides, but causes partial precipitation on application of heat; it throws down from sulphate of magnesia, in the cold, a flocky precipitate, and also gives with solutions of the heavy metallic oxides, and with alumina, immediate deposits; but I had not material sufficient to determine its solvent power in particular cases. On being boiled, it evolves the odour of a volatile base. With chlorine, bromine, and iodine, it yields products. When it, or its carbonate, is treated with hydrosulphuric acid, and suffered to stand, a hyposulphite is found to result, which may be obtained crystalline by evaporation, and is soluble in alcohol. This base gives the same reaction as strychnine with sulphuric acid and chromate of potass.

When iodide of ethylostrychnine is heated in a retort with excess of soda-lime, a heavy oil distills over which is partly basic and partly insoluble in acids: the hydrochloric solution of the soluble portion gave with bichloride of platinum an uncrystalline salt, but I had not sufficient to determine if, in this decomposition, the ethyl molecule attaches itself to the volatile base, which is no doubt either leucoline or ethyleucoline.

Action of Iodide of Ethyl on Ethylostrychnine.—This reaction appears to result in the formation of iodide of ethylostrychnine and some other product. I employed for the experiment the mother liquor of the hydrate which was analysed; this alcoholic fluid was sealed up in a tube with iodide of ethyl, and the whole was heated for half-an-hour in boiling water. The liquid remained clear while hot, but soon became turbid on cooling, and finally deposited some rounded transparent yellowish grains. These proved, when separated from the mother liquor by decantation, to be completely soluble in hot water; their solution deposited a little flocky matter, and when filtered from this and evaporated, groups of stellate crystals. These crystals agreed in characters with iodide of ethylostrychnine, and furnished with oxide of silver a caustic yellow liquor, which became filled with prismatic crystals on the addition of a little nitric acid. The alkaline solution

had not, it is true, the rich red-purple afforded in former instances, but in all other characters was quite the same.

The mother liquor of the grains, when distilled to a syrup, and, after the addition of some water, finally evaporated to dryness, left a red and green resinous residue, which dissolved incompletely in hot water; the aqueous solution again left a resin, only partially soluble, on evaporation; there exists in this solution a base—partially, at least—precipitable by ammonia, as an iodine compound. It is possible this secondary product may somewhat affect the characters of the iodide of ethylostrychnine, which, I think, is certainly formed, as might have been expected.

Action of Chloride of Amyl upon Strychnine.

Chloride of Amylostrychnine.—Strychnine, placed in contact with chloride of amyl, is found to undergo, very slowly, a change quite analogous to that with iodide of ethyl under the same circumstances. About eighty grains of the finely powdered alkaloid being sealed up in a strong tube with two fluid drachms of chloride of amyl, and some ten of absolute alcohol, the vessel was placed in boiling water, and retained at the same temperature for a long time. Complete solution took place in about fifty hours, and the heat was continued nearly forty-eight hours longer. The rather oily liquid deposited nothing on cooling, and left, on distillation to a syrup, a thick mass which finally dried up to a crystalline residue. This proved to be the chlorine salt of a base generally analogous to the ethyl product; it was very soluble in hot water, and crystallizable from a very strong boiling solution on cooling, or a more dilute one by evaporation, in fine colourless prisms.

I must mention that, in the first place, the whole of the product was dissolved in hot water, and the fluid evaporated to crystallization; the resulting crystals have their composition represented in analysis I. below, and must have contained any strychnine salt, or a great part of it, had any been originally present, as this is less soluble than the new one.

The entire mother liquor of these crystals was super-saturated by ammonia, no precipitate appeared for some time; on stirring, however, a certain quantity of a crystalline deposit fell, which presented the characters of strychnine. The ammoniacal fluid was suffered to stand two hours or so, and then filtered and evaporated to dryness at 212°. The residue was found to be completely soluble in hot water, or left but a little insoluble strychnine, and was made to crystallize like the first product. These are the crystals employed in analysis II., and could contain no strychnine.

The identity of the analytical results furnished by these two salts, and the appearance of the strychnine, caused me to make direct experiments with ammonia, to be described presently; in the meantime, the analyses of the salts, obtained as

above, are given ; the chlorine was determined in a specimen different from either of the others :—

I.	{		4.505 grains, dried at 212°, gave
	{		11.425 ... carbonic acid, and
	{		3.165 ... water.
II.	{		4.213 ... dried at 212°, gave
	{		10.750 ... carbonic acid, and
	{		2.990 ... water.
III.	{		4.140 ... dried at 212°, gave
	{		1.345 ... chloride of silver.

	Found.				Calculation.		
	I.	II.	III.	Mean.			
Carbon, . . .	69.16	69.58		69.37	69.41	C ₅₂	312
Hydrogen, . .	7.80	7.88		7.84	7.56	H ₃₄	34
Nitrogen, . .					6.22	N ₂	28
Oxygen, . . .					8.92	O ₅	40
Chlorine, . . .			8.03	8.03	7.89	Cl	35.5
					100.00		449.5

These numbers indicate a change quite analogous to that before seen to obtain with iodide of ethyl, and it may be expressed thus :—

but the salt, as deposited from water, retains an equivalent of the same at 212°, and is, according to the above analysis—

while, in the air-dry state, the crystals contain in addition seven atoms, which they readily part with, as these numbers shew :—

$$\begin{cases} 8.170 \text{ grains, air-dry, lost at } 212^\circ \\ 1.025 \text{ ... water;} \end{cases}$$

which give a percentage of 12.54; and 12.29 is that required by a loss of seven atoms of water in a salt of the formula,—

The hydrated chloride of amylostrychnine crystallizes from water in fine, thick, colourless, oblique rhombic prisms, which have a peculiar greasy appearance when dry; it is very soluble in alcohol. Its aqueous solution is not affected by dilute potass, or by ammonia, except when left long in contact; but is immediately precipitated by strong potass, the salt being thrown down unchanged. Oxide of silver eliminates the chlorine, leaving the base dissolved. When heated, the dry salt

fuses and gives off, first water, then acid vapours, and finally, with intumescence and blackening, alkaline fumes of a very nauseous odour, which also affect the throat most unpleasantly.

Its aqueous solution gives, with that of mercuric chloride, a heavy white precipitate, which is difficultly soluble in boiling water, and is deposited in the cold in very small and separate crystals; these seem, when magnified, to be prisms and octahedra; it furnishes, with chloride of gold, an insoluble amorphous yellow precipitate. With bichloride of platinum a pale yellow uncrystalline precipitate is obtained, but this could not, in three trials, be obtained of constant composition; the platinum came always much too high, even above that of the strychnine salt itself, in two cases, by 0·3 to 0·7 per cent.

Bichromate of Amylostrychnine.—This salt was obtained from the mother liquor of salt II. above, by addition of bichromate of potass; it fell as a crystalline yellow salt, soluble in boiling water; when ignited, it gave the following result:—

$\left\{ \begin{array}{l} 6\cdot418 \text{ grains, dried at } 212^{\circ}, \text{ gave} \\ 0\cdot965 \quad \dots \quad \text{sesquioxide of chromium.} \end{array} \right.$

The percentage of anhydrous chromic acid corresponding to this number is 19·63; and 19·37 is that required by a salt, analogous to that of the ethyl base, of the formula—

There exists also a crystalline chromate.

Nitrate of Amylostrychnine.—This was prepared from the crystals of the chloride I., by double decomposition with nitrate of silver in warm liquids. It is more soluble than the corresponding salt of ethylostrychnine; but it is by no means of great solubility in cold water, though readily taken up in the heat. It crystallizes from hot water in very beautiful radiated groups of colourless needles; the analysis of these gave the numbers which follow:—

$\left\{ \begin{array}{l} 3\cdot695 \text{ grains, dried at } 212^{\circ}, \text{ gave} \\ 8\cdot850 \quad \dots \quad \text{carbonic acid, and} \\ 2\cdot415 \quad \dots \quad \text{water.} \end{array} \right.$

Found.		Calculation.		
Carbon, . . .	65·32	65·54	C_{52}	312
Hydrogen, . .	7·26	7·14	H_{34}	34
Nitrogen, . . .		8·82	N_3	42
Oxygen, . . .		18·50	O_{11}	88
		100·00		476

and it appears that this salt is also not anhydrous at 212°, its formula being—

The air-dried crystals contain, in addition, ten atoms of water:—

$$\begin{cases} 4.390 \text{ grains air-dry salt, lost at } 212^\circ \\ 0.685 \text{ ... water.} \end{cases}$$

This number leads to a percentage of 15.60; and 15.90 is that corresponding to a loss of ten aq. by a salt of the composition—

The aqueous solution of the nitrate gives, with that of mercurous nitrate, a crystalline deposit in the form of colourless needles; these are no doubt a double salt.

Hydrate of Amylostrychnine.—The chloride furnishes, with oxide of silver in water, a rich red purple fluid of a highly alkaline nature, which agrees most strikingly in its characters with the solution of ethylostrychnine; indeed, the two might be readily mistaken for each other; their deportment with metallic salts, and on evaporation, *in vacuo* or at 212° , is precisely the same. The flocky basic product by evaporation in the case of each, bears possibly the same relation to its congener which the parent bases mutually possess.

The residue left *in vacuo* dissolves to a very rich purple fluid in hot absolute alcohol, and ether causes in this solution an abundant and quickly appearing deposition of radiated white needles. I have not as yet analysed these, but I apprehend they must bear a close analogy to the hydrate of ethylostrychnine.

The chloride of amylostrychnine seeming to have a tendency to decompose in contact with ammonia, some solutions of the salt were supersaturated with this alkali; in no instance did any immediate precipitate occur; but in all, after the lapse of a shorter or longer period, crystalline deposits were formed, while the fluids assumed a reddish-brown colour; in some cases the product was but microscopic at the end of a fortnight, while other specimens furnished within this time quite a decided crystallization on the sides of the vessels. These crystals had the qualitative characters of strychnine; and it is easy to imagine a decomposition taking place in which this alkaloid should be regenerated with the formation of amylamine; thus—

I have not as yet been able to verify this equation; for there has remained much of the amylostrychnine undecomposed in those cases where I tried to prove the existence of amylamine.

In the hope of hastening the decomposition, some of the mother liquor of the chloride was sealed in a tube with strong ammonia; the vessel was kept in boiling water for many days; a rather dark-coloured deposit gradually formed, while the liquid itself became brown and rather mucilaginous. At the end of a

week the tube was opened, but I could gain nothing decisive as to the evident decomposition which had taken place, and which seems of a more complex nature than had been anticipated.

The brown deposit was for the most part soluble in hydrochloric acid, but did not present the characters of pure strychnine when reprecipitated by ammonia. Its mother liquor, from the tube, was evaporated to dryness at 212° to expel the excess of ammonia, and it left a residue which had a most remarkable resemblance to common glue in appearance and odour: this contained the chlorine salt of some base, and when dissolved in water, and decomposed by nitrate of silver in excess, the fluid, filtered from the chloride of silver, gave in a few minutes a brilliant metallic mirror, but no crystalline salt.

These decompositions, at both temperatures, seem worthy of study. I may mention that chloride of ethylostrychnine, in contact with aqueous ammonia in the cold, also yields, after the lapse of some days, a small deposit of most minute crystals.

I have not at present experimented further with these substances, but hope to be able to render their history more complete, and, if possible, to clear up some points touched upon in this paper, by studying their especial products of decomposition in these cases. I have the intention also of submitting some of the other alkaloids, yet unexamined, to a similar investigation.

With regard to what has been actually brought forward in the present communication, I would draw the following inferences:—

That the new basic products, ethylo and amylo-strychnine are analogous to the compound ammonium bases of Hofmann, and quite distinct from the natural fixed alkaloids. In their resemblance to metallic oxides, and the combinations they form with water and acids, they shew, in common with these, general family features, while special distinctions exist as individual characteristics, and are to be paralleled in many saline compounds.

That the already complex molecule in the vegetable alkaloids is rendered more susceptible of change by association with additional hydrocarbons.

That as regards the constitution of strychnine, this alkaloid appears to be made up of a complicated molecule, in which the one atom of nitrogen, as in ammonia, etc., is associated with a nitrogenous aggregate of elements, whose function is that of three atoms of hydrogen, and whose nitrogen is in a distinct form of combination, as yet undetermined, from that of the first, generic atom. The expression of such a composition may be attempted thus:—

And the association of this molecule with any alcohol hydrocarbon occasions the production of an ammonium congener, which, as it exists in combination with some electronegative element, may be written thus :—

In conclusion, I give a tabular view of the new compounds mentioned in the preceding pages ; and, in doing so, I have adopted the termination “ ium ” for the bases, in analogy with the name ammonium ; strychnia, the old name of the alkaloid in English, being, it seems to me, the more appropriate designation for the analogue of ammonia ; and it would be but consistent with the ammonium theory, to look upon the alkaloid in entering into combination, with hydrochloric acid for instance, as undergoing the same process as the volatile type, and to speak of the new salt as chloride of strychnium. The products of this investigation, then, are the following :—

Hydriodate of Papaverine, . . .		$\text{C}_{40} \text{H}_{21} \text{NO}_8 \text{HI}.$
Iodide of Ethylostrychnium, . . .		$\text{C}_{46} \text{H}_{27} \text{N}_2 \text{O}_4 \text{I}.$
Hydrated oxide of do., . . .	crystallized	$\text{C}_{46} \text{H}_{27} \text{N}_2 \text{O}_4 \text{O}, \text{HO}, + 3 \text{ aq.}$
Nitrate of do., . . .	”	$\text{C}_{46} \text{H}_{27} \text{N}_2 \text{O}_4 \text{NO}_6$
Bichromate, . . .	dried at 212°	$\text{C}_{46} \text{H}_{27} \text{N}_2 \text{O}_4 \text{CrO}_4, \text{HCrO}_4.$
” . . .	crystallized	$\text{C}_{46} \text{H}_{27} \text{N}_2 \text{O}_4 \text{CrO}_4, \text{HCrO}_4 + 2 \text{ aq.}$
Bicarbonate, . . .	dry	$\text{C}_{46} \text{H}_{27} \text{N}_2 \text{O}_4 \text{CO}_3, \text{HCO}_3.$
Platinum compound, . . .	crystallized	$\text{C}_{46} \text{H}_{27} \text{N}_2 \text{O}_4 \text{Cl}, \text{PtCl}_2.$
Chloride of Amylostrychnium, . . .	dried at 212°	$\text{C}_{52} \text{H}_{33} \text{N}_2 \text{O}_4 \text{Cl}, \text{HO}.$
” ” ” . . .	crystallized	$\text{C}_{52} \text{H}_{33} \text{N}_2 \text{O}_4 \text{Cl}, \text{HO} + 7 \text{ aq.}$
Nitrate of Oxide, . . .	dried at 212°	$\text{C}_{52} \text{H}_{33} \text{N}_2 \text{O}_4 \text{NO}_6, \text{HO}.$
” ” . . .	crystallized	$\text{C}_{52} \text{H}_{33} \text{N}_2 \text{O}_4 \text{NO}_6, \text{HO} + 10 \text{ aq.}$
Bichromate, . . .	dried at 212°	$\text{C}_{52} \text{H}_{33} \text{N}_2 \text{O}_4 \text{CrO}_4, \text{HCrO}_4.$