XII.—*Researches on some of the Crystalline Constituents of Opium.* Second Series.

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(Read 3d January and 1st May 1854.)

In pursuing the investigation of the crystalline constituents of opium, which formed the subject of a previous communication to this Society, I have succeeded in obtaining from the same mother liquor which formed the raw material of my previous researches, a considerable quantity of papaverine, the base recently detected by MERCK, and of meconine, the indifferent crystallizable substance discovered by COUERBE in the year 1830. The former was encountered quite unexpectedly in the precipitate from which narcotine and thebaine were prepared by the process described in the first series of these researches. The latter was only obtained after many fruitless trials, in which I was induced to persevere by the desire of comparing it with the substance discovered by myself among the products of the decomposition of narcotine by nitric acid, and described under the name of opianyl. The composition of that substance, as determined by my analyses, approximates very closely to that of meconine; and though the formula assigned to the former is double that obtained by COUERBE from his analysis of the latter, the sole reason for adopting the higher atomic weight was, that the mode in which opianyl was obtained by the decomposition of narcotine, afforded satisfactory grounds for establishing its true constitution. Nor does their similarity stop here, for it is at once obvious, on a comparison of their properties, that they present many points in common, although even in this respect there are differences which will be afterwards particularly referred to, much too prominent and important to be overlooked. Partly on this account, and partly because my previous investigations of the constituents of opium had shown me that in all other instances the analytical results arrived at by COUERBE were very far from correct, I hesitated to assert their identity until I had had an opportunity of submitting them to an exact comparison, and of repeating the analysis of meconine.

The experiments to be detailed in this paper prove incontestibly that they actually are identical; and while the composition of meconine is confirmed, the necessity for doubling its formula is clearly established. A careful comparison of the properties of the two substances has also shown that they are perfectly alike; but in this respect, and especially as regards the action of various agents on meconine, the statements made by COUERBE require very material correction.

Papaverine.

In the purification of narcotine by repeated crystallizations from boiling alcohol, in the manner described in the paper already referred to, the mother liquors of each successive crystallization had been carefully preserved, and at the conclusion of the investigation they were worked up for the purpose of obtaining the very considerable quantity of narcotine which they obviously still contained. For this purpose the fluids were mixed together, and the greater part of the alcohol separated by distillation. The residue on being left to itself, deposited a considerable quantity of dark-coloured crystals mixed with resinous matters, which were collected on a cloth and expressed, and the fluid which passed through was again concentrated and allowed to crystallize, and this was repeated until it ceased to yield anything on further evaporation. The crystals so obtained were dissolved in the smallest possible quantity of boiling alcohol, from which they were deposited in a tolerably colourless state as the liquid cooled. On further concentrating this mother liquor, and again allowing it to cool, it became filled with crystals of a substance obviously much more soluble in alcohol than narcotine, and differing from it in its general characters. It was particularly observed to restore the blue of reddened litmus, to dissolve readily in acids, and to saturate them completely; properties not possessed by narcotine. Its ready solubility in alcohol led at first to the suspicion that it might be thebaine, which had been already observed accompanying the narcotine, but the difference in its crystalline form, as well as its complete precipitation from its solution in acetic acid, by subacetate of lead, proved it to be different. A very few experiments sufficed to show that the base thus obtained was still contaminated with narcotine, from which it might no doubt have been separated by repeated crystallizations; but as this would have been an extremely tedious process, and have caused the loss of a considerable quantity of material, I preferred a method founded on the marked difference between its basic properties and those of narcotine. The whole of the crystals obtained from the mother liquors, and consisting partly of narcotine and partly of this other base, were reduced to a fine powder, and digested with a limited quantity of acetic acid. The acid was rapidly saturated, and as soon as the fluid had lost its acid reaction it was filtered from the undissolved portion, which was again treated with the acid; and this treatment was cautiously repeated as long as it continued to be thoroughly saturated. The solution was then filtered from the undissolved narcotine, precipitated by ammonia, and the precipitate crystallized from boiling alcohol. The base was now pure, and analysis showed it to be papaverine, with which its characters were found to agree in all respects. A consideration of the properties of papaverine now enabled me to perceive that it must have been present in very large quantity in the mother liquor obtained in the first crystallization of the crude narco-

tine, which had not been mixed with the others, but treated in a different manner for the preparation of thebaine, and it seemed probable that it would be found in abundance in the precipitate produced in that fluid by subacetate of lead. This opinion proved to be perfectly correct, and after a few trials it was found that it might be readily extracted in the following manner. The subacetate of lead precipitate was reduced to fine powder and boiled with alcohol, by which means a very dark fluid was obtained, which deposited a few crystals, apparently of narcotine, on cooling, and on further concentration, a dark-coloured resinous substance was left. After the complete expulsion of the alcohol, the residual mass was treated with dilute hydrochloric acid, which dissolved narcotine and papaverine, and left a quantity of a black resinous matter, which was separated by filtration. The fluid was then concentrated and left to itself. In the course of a few days crystals of the sparingly soluble hydrochlorate of papaverine began to make their appearance, and continued gradually to increase for some time. As soon as they ceased to increase they were removed from the solution, which was found to contain narcotine, and purified by several crystallizations. The base was then separated by ammonia, and obtained in a state of absolute purity, by solution in boiling alcohol, and crystallization.

Papaverine, as thus obtained, is in the form of minute radiated crystals, highly soluble in boiling alcohol; so much so, that a saturated hot solution becomes nearly solid on cooling. It saturates the acids completely, and gives in the most distinct manner the reaction with strong sulphuric acid described by MERCK. Although the formula assigned to papaverine by its discoverer appeared to be correct, an analysis of that obtained by the process just described was made; and as in the course of the investigation it became necessary to ascertain by analysis whether particular specimens were free of narcotine, several additional combustions were obtained, the results of which are also given. The analyses were made with the chromate of lead.

I.	{	4.250 grains of papaverine, dried at 212°, gave	
		11.020 ... carbonic acid, and	
		2.410 ... water.	
II.	{	4.525 grains of papaverine gave	
		11.714 ... carbonic acid, and	
		2.635 ... water.	
III.	{	4.416 grains of papaverine gave	
		11.430 ... carbonic acid, and	
		2.569 ... water.	
	{	8.380 grains of papaverine gave, by PELIGOT's method,	
		0.369 ... nitrogen.	
		8.960 grains of papaverine gave, by PELIGOT's method,	
		0.355 ... nitrogen.	

	Experiment.			Calculation.		
	I.	II.	III.			
Carbon, . .	70.71	70.60	70.58	70.79	C ₄₀	240
Hydrogen, . .	6.29	6.46	6.46	6.20	C ₂₁	21
Nitrogen,* . .	4.40	3.96	...	4.14	N	14
Oxygen, . .	18.60	18.96	...	18.78	O ₈	64
	<hr/> 100.00	<hr/> 100.00		<hr/> 100.00		<hr/> 339

These results correspond completely with the calculated numbers, and were sufficient to show that the base is papaverine, but for further security, a determination of the platinum in its platinum salt was made, with the following results:—

$$\left\{ \begin{array}{l} 5.684 \text{ grains of platinum salt gave} \\ 1.013 \quad \dots \quad \text{platinum} = 17.82 \text{ per cent.} \end{array} \right.$$

This corresponds with calculated result, which gives 18.10 per cent.

The salts of papaverine having been already sufficiently investigated by MERCK, I did not think it necessary to extend my experiments in this direction, but proceeded to examine the action of various agents upon the base itself.

Action of Nitric Acid.

Papaverine dissolves in dilute nitric acid without decomposition, and with the formation of a nitrate; but if the solution be mixed with an excess of nitric acid, especially if concentrated, and heat be applied, a brisk action takes place, some red fumes are evolved, the fluid becomes dark red, and orange-coloured crystals begin to make their appearance, and gradually increase in quantity. Nothing can be simpler than the preparation of this substance. The degree of concentration of the acid is immaterial, for the product is sure to be obtained; and if the fluid be sufficiently concentrated, crystals begin to be formed the instant the heat is applied, and soon become so abundant as entirely to fill the fluid. If the solution be more dilute, they appear more slowly, and are then larger, more regularly formed, and much paler coloured. The only precaution necessary is, to avoid the use of too large an excess of nitric acid, as it dissolves the new product much more abundantly than water. The orange-coloured crystals are the nitrate of a new base, to which I give the name of nitropapaverine.

Nitropapaverine — is readily obtained from its nitrate, by dissolving it in boiling water, and precipitating the hot solution by ammonia; but as the salt is very sparingly soluble, even in hot water, it is more convenient to dissolve it in nitric acid, and then to add at once an excess of the alkali. A light yellow flocculent precipitate is immediately deposited, which is collected on a filter, dried,

* MERCK has published only one nitrogen determination of papaverine, giving 4.75 per cent., which greatly exceeds the calculated number. I have observed the same tendency to give an excess, having in one experiment obtained as much as 4.66. The only mode of explaining this anomaly, was by supposing that the base carried down a small quantity of the ammonia which had been used to precipitate it. In order to ascertain whether this opinion was well-founded, a quantity thrown down by potash was analysed, and the results are those of the second determination.

and dissolved in boiling alcohol, from which it is deposited on cooling. Nitropapaverine is thus obtained in pale buff-coloured needles, insoluble in water, but soluble in alcohol and ether. It restores the blue colour of reddened litmus, dissolves in the acids, neutralizes them completely, and forms a series of salts, all of which have a pale buff colour and are sparingly soluble in water. When heated, it undergoes fusion, and at a higher temperature it burns rapidly with a sort of deflagration. Concentrated solution of potash, when boiled with it, causes the evolution of traces of a volatile base. It does not give the purple reaction of papaverine with sulphuric acid. Its analysis gave the following results:—

				5·065 grains of nitropapaverine, dried at 212°, gave			
				11·573 ... carbonic acid, and			
				2·640 ... water.			
				Experiment.		Calculation.	
Carbon,	.	.	.	62·31	62·50	C ₄₀	240
Hydrogen,	.	.	.	5·21	5·20	H ₂₀	20
Nitrogen,	.	.	.	...	7·29	N ₂	28
Oxygen,	.	.	.	...	25·01	O ₁₂	96
				100·00		384	

This corresponds closely with the calculated results for the formula

which is further confirmed by the analysis of the platinum salt given below.

The crystals of the base deposited from alcohol are a hydrate, as indicated by the subjoined experiment.

{ 5·237 grains of nitro-papaverine dried in the air,
lost at 212° 0·14 grains = 2·67 per cent.

One equivalent of water requires 2·29 per cent., so that the crystals have the formula $\text{C}_{40} \text{H}_{20} (\text{NO}_4) \text{O}_8 + \text{HO}$.

Nitrate of Nitropapaverine.—This salt is obtained by the action of nitric acid on papaverine, in the manner already described. It appears in the form of four-sided tables, sometimes of considerable size, and generally of a dark orange colour. By crystallization from boiling alcohol, it is got in a state of absolute purity, and then forms fine yellow crystals of great beauty. It is almost insoluble in cold water, but on boiling it is taken up in somewhat larger quantity, and deposited on cooling in an imperfectly crystalline form. It is much more soluble in water containing nitric or hydrochloric acids, as well as in alcohol and ether. When gently heated it melts, and then deflagrates, leaving a quantity of a nearly black substance, which burns away completely at a higher temperature. Potash and ammonia, when digested on it at ordinary temperatures, rapidly separate the base. The ease with which this substance is formed, and its extreme insolubility render its production a very useful reaction for papaverine, and by means of it I have succeeded in proving that this base also occurred in the fluid from which narco-

tine was separated by precipitation with ammonia. Nitrate of nitropapaverine is anhydrous. Its analysis gave these results:—

$\left\{ \begin{array}{l} 5.497 \text{ grains nitrate of nitropapaverine gave} \\ 10.820 \text{ ... carbonic acid, and} \\ 2.450 \text{ ... water.} \end{array} \right.$						
		Experiment.		Calculation.		
Carbon,	. . .	53.68		53.69	C ₄₀	240
Hydrogen,	. . .	4.95		4.69	H ₂₁	21
Nitrogen,	. . .	...		9.38	N ₃	42
Oxygen,	. . .	...		32.24	O ₁₈	144
				100.00		447

corresponding with the formula

Hydrochlorate of Nitropapaverine—is a sparingly soluble salt, crystallizing in pale yellow needles. It dissolves readily in spirit, and in excess of hydrochloric acid.

Sulphate of Nitropapaverine—is but little soluble in water; it crystallizes in minute prisms.

Platino-Chloride of Nitropapaverine—is thrown down as a pale yellow precipitate, when bichloride of platinum is added to a solution of the hydrochlorate. Its analysis gave the following results,—

$\left\{ \begin{array}{l} 5.555 \text{ grains, dried at } 212^\circ, \text{ gave} \\ 8.245 \text{ ... carbonic acid, and} \\ 1.900 \text{ ... water.} \end{array} \right.$						
$\left\{ \begin{array}{l} 5.579 \text{ grains, dried at } 212^\circ, \text{ gave} \\ 0.924 \text{ ... of platinum.} \end{array} \right.$						
		Experiment.		Calculation.		
Carbon,	. . .	40.47		40.66	C ₄₀	240
Hydrogen,	. . .	3.80		3.55	H ₂₁	21
Nitrogen,	. . .	...		4.72	N ₂	28
Oxygen,	. . .	...		16.26	O ₁₂	96
Chlorine,	. . .	...		18.09	Cl ₃	106.5
Platinum,	. . .	16.56		16.72	Pt	98.7
				100.00		590.2

corresponding completely with the formula

The rest of the salts of nitropapaverine have not been minutely examined.

Action of Bromine on Papaverine.

When bromine water is added, drop by drop, to a solution of hydrochlorate of papaverine, a precipitate is obtained which at first immediately redissolves, but on the further addition of bromine water, at length becomes permanent. It is the hydrobromate of a derivative base, bromopapaverine.

Bromopapaverine itself is easily obtained from this substance, by digesting it with ammonia, and dissolving the product in boiling alcohol. It is deposited, on cooling, in minute white needles, insoluble in water, but readily soluble both in alcohol and ether. It dissolves in the acids and forms salts, the greater number of which are characterized by their sparing solubility. Its crystals were anhydrous, and gave on analysis the subjoined results,—

{	5.168 grains bromopapaverine gave
	10.845 ... carbonic acid, and
	2.335 ... water.
{	4.780 grains, dried at 212°, gave
	2.185 ... bromide of silver.

These results correspond with the formula $C_{40}H_{20}BrNO_8$, as is obvious from the calculation given below.

Experiment.				Calculation.		
Carbon,	.	.	57.23	57.41	C_{40}	240
Hydrogen,	.	.	5.02	4.78	H_{20}	20
Nitrogen,	.	.	...	3.34	N	14
Oxygen,	.	.	...	15.34	O_8	64
Bromine,	.	.	19.45	19.13	Br	80
				100.00		4.18

Hydrobromate of Bromopapaverine.—This salt is obtained, as already mentioned, by the addition of bromine water to a solution of hydrochlorate of papaverine. It varies somewhat in its appearance, according to the degree of concentration of the solution from which it is obtained. If concentrated, it is deposited with a more or less yellow colour, and is apt to form resinous lumps, particularly if the bromine water is added rapidly; but when the solutions are more dilute, it appears in the form of a perfectly white powder. It is well washed with water, dissolved in boiling spirit, and on cooling is deposited in a state of purity in the form of a crystalline powder, insoluble in water, and sparingly soluble in alcohol. When gently heated it melts, and is decomposed. When digested with potash or ammonia, it is decomposed, with separation of the base. Its crystals are anhydrous, and gave the following results on analysis:—

{	5.647 grains, dried at 212°, gave
	10.015 ... carbonic acid, and
	2.215 ... water.
{	6.398 grains, dried at 212°, gave
	4.883 ... bromide of silver.

Experiment.				Calculation.		
Carbon,	.	.	48.36	48.09	C_{40}	240
Hydrogen,	.	.	4.35	4.20	H_{21}	21
Nitrogen,	.	.	...	2.80	N	14
Oxygen,	.	.	...	12.85	O_8	64
Bromine,	.	.	32.48	32.06	Br_2	160
				100.00		499

corresponding with the formula

Hydrochlorate of Bromopapaverine — is soluble in water, though sparingly. The rest of its salts have not been examined.

Action of Chlorine on Papaverine.

When a current of chlorine is passed through a solution of hydrochlorate of papaverine, the fluid becomes brown, and after a time a dirty gray precipitate makes its appearance, which is insoluble, or nearly so, in water, but dissolves in boiling alcohol, and gives a resinous deposit as the solution cools. When treated with ammonia, hydrochloric acid is separated, and a powder is obtained which is obviously chlorine base. It dissolves in the acids, and is reprecipitated by ammonia. Alcohol takes it up, and deposits it in an amorphous form on cooling or by spontaneous evaporation. The properties of this substance proving unsatisfactory, I then tried the action of chlorate of potass added in small successive portions to a solution of papaverine in excess of hydrochloric acid, but the same amorphous gray powder being produced, I did not pursue the subject further; for although one or more derivative bases are unquestionably produced, their properties are not sufficiently well marked to admit of their proper purification.

Action of Iodine on Papaverine.

When an alcoholic solution of papaverine is mixed with tincture of iodine, and the solution is left to itself for some hours, small crystals are slowly deposited, and by further evaporation of the fluid from which they have been removed, another substance is obtained.

Teriodide of Papaverine.—To the crystals first separated I give this name. They are purified by solution in boiling alcohol, from which they are slowly deposited in small rectangular prisms. Their colour is purple by reflected, and dark red by transmitted light. They are insoluble in water, but soluble in alcohol. It is not acted upon by dilute acids, but ammonia and potash rapidly decompose it, removing iodine, and leaving papaverine. From this fact it is clear that it is not the salt of a substitution base, but corresponds in constitution with the teriodide of codeine, which I described in a former paper.* Analysis gave the subjoined results:—

$$\left\{ \begin{array}{l} 7.065 \text{ grains teriodide of papaverine, dried at } 212^\circ, \text{ gave} \\ 8.550 \quad \dots \quad \text{carbonic acid, and} \\ 2.045 \quad \dots \quad \text{water.} \end{array} \right.$$

$$\left\{ \begin{array}{l} 7.650 \text{ grains teriodide of papaverine gave} \\ 7.489 \quad \dots \quad \text{iodide of silver.} \end{array} \right.$$

* Edinburgh New Philosophical Journal, vol. 1., p. 103.

				Experiment.	Calculation.		
Carbon,	.	.	.	33·02	33·47	C ₄₀	240
Hydrogen,	.	.	.	3·21	2·92	H ₂₁	21
Nitrogen,	.	.	.	...	1·95	N	14
Oxygen,	.	.	.	...	8·95	O ₈	64
Iodine,	.	.	.	52·90	52·71	I ₃	378
					100·00		717

The formula of the substance is therefore

Pentiodide of Papaverine.—By evaporating the mother liquor of the teriodide this compound is deposited, and is purified from excess of iodine by crystallization from alcohol. It then forms slender needles, with an orange colour by transmitted light, and a reddish-bronze surface colour. It is much more soluble in alcohol than the teriodide, but is insoluble in water. It loses iodine by the application of a moderate heat, although perfectly stable at 212°. It is insoluble in acids, and is rapidly decomposed by ammonia. Its composition was:—

{	5·502	grains	pentiodide of papaverine	gave
{	5·000	...	carbonic acid,	and
{	1·283	...	water.	
{	3·902	grains	pentiodide	gave
{	4·665	...	iodide of silver.	

				Experiment.	Calculation.		
Carbon,	.	.	.	24·78	24·76	C ₄₀	240
Hydrogen,	.	.	.	2·59	2·16	H ₂₁	21
Nitrogen,	.	.	.	...	1·44	N	14
Oxygen,	.	.	.	...	6·63	O ₈	64
Iodine,	.	.	.	64·60	65·01	I ₅	630
					100·00		969

These results give the formula

It is difficult to form a rational conception of the constitution of these substances. The formulæ given above seem to be on the whole the most probable; but it is clear that the analyses admit of a different interpretation, and we may assume these compounds to be hydriodates with excess of iodine, and represent their constitution by the formulæ

the additional atom of hydrogen making too small a difference to be important. We have, however, no experiments to enable us to decide between these two views, which could only be done by an extended investigation of the similar compounds of the other bases; and in the absence of further information, I have

chosen to represent them as iodides, simply because it involves less hypothesis, and sufficiently expresses their constitution.

Action of Soda Lime on Papaverine.

Papaverine was mixed with about four times its weight of a soda lime, composed of equal weights of its constituents, and the mixture heated in the oil bath. At 250° traces of a volatile base began to appear, which increased in abundance when the temperature rose to 300°. After the heat had been continued for some hours, a small quantity of a pungent base was collected in the receiver. It gave white fumes with hydrochloric acid, and with bichloride of platinum a highly soluble salt, precipitated by alcohol and ether in shining plates. A determination of the platinum in this compound gave the following results :—

$$\left\{ \begin{array}{l} 5.197 \text{ grains platinum, dried at } 212^{\circ}, \text{ gave} \\ 1.882 \quad \dots \quad \text{platinum.} \end{array} \right.$$

This corresponds to 36.21 per cent. of platinum, and lies almost exactly between the numbers required for propylamine and ethylamine, the calculated number for the former being 37.21, for the latter 35.34. It is probable that the substance analysed actually contained both bases, but from the small scale on which it was necessary for me to work, I was precluded from any attempts to substantiate this opinion.

Meconine.

In preparing narceine by the process described in the first series of these researches, I expected to have obtained it mixed with meconine, in the same way as it had been previously found by COUERBE and other observers. Much to my disappointment, however, the narceine proved to be remarkably pure; and even after one crystallization, ether extracted from it only a minute trace of a resinous matter, but no meconine. As it could not be doubted that meconine, if present at all, must still remain in the mother liquor from which the crystals of narceine had been separated, the fluid was concentrated and left to itself for some time, but no meconine made its appearance. On further concentration, and standing for some months, granular crystals were abundantly deposited, which proved to be nothing but muriate of ammonia, mixed with a resinous matter. Attempts were then made to remove the amorphous residual matters which abounded in the fluid, and appeared to prevent the crystallization of meconine, and a variety of methods were tried to make it deposit crystals, but without success.

After many abortive trials, which it is unnecessary to detail, I found that meconine might be easily separated by agitating the fluid with ether. For this purpose the concentrated fluid was poured into large bottles in which it was mixed with about a fifth of its bulk of ether. The bottles were tightly corked, set in a warm place where their temperature was kept at about 80° Fahr., and frequently shaken.

After standing for 24 hours, the ether, which had acquired a brown colour, was drawn off with a syphon and a new supply added ; and this process was repeated as long as it continued to extract any considerable quantity. The ether was then distilled off in the water-bath, and left behind a dark amber-coloured or brown syrupy fluid. The first extracts remained thick and syrupy, even after 24 or 48 hours ; but those obtained after the agitation with ether had been several times repeated, occasionally, though not always, became filled with crystals on standing. On the addition of water, a quantity of a thick resinoid substance, not unlike turpentine, separated and remained for some time in a semifluid form at the bottom of the fluid. When hydrochloric acid was dropped into it, part of the resinoid matter dissolved, and the rest solidified into a dark-gray crystalline powder, which was separated by filtration. The hydrochloric solution gave with alkalis a dirty gray precipitate which soon became resinous on standing, with bichloride of platinum a yellow, and with corrosive sublimate a dirty white precipitate. It contained therefore an alkaloid, which was thrown down by ammonia, and purified by solution in alcohol, in which it was highly soluble, and by boiling with animal charcoal. It was deposited on cooling in irregular needles, which nearly filled the fluid, and was shown to be papaverine, by its giving a blue colour with concentrated sulphuric acid and orange crystals of nitrate of nitropapaverine with nitric acid.* The granular precipitate was impure meconine. It was purified by solution in boiling water, which left a small quantity of an indifferent resin, and the fluid on cooling deposited an abundance of needle-shaped crystals, still retaining a yellowish shade of colour, which was easily removed by animal charcoal.

Composition of Meconine.

Meconine has been already analysed by its discoverer COUERBE, and by REGNAULT. The earlier analyses of the former† of which the details are not given in the original memoir, led to the formula $C_{18}H_9O_8$; but as these are admitted to have been erroneous, it is unnecessary to refer to them further. The results contained in his second memoir,‡ and those of REGNAULT,§ are collected in the following table, in which all are recalculated according to the atomic weight of carbon now in use.

* Although the salts of papaverine are highly crystallizable and sparingly soluble, the presence of resinous impurities in the opium fluid has a remarkable tendency to prevent their separating in the crystalline form ; and we see that in this instance a certain quantity of the base had even resisted precipitation by ammonia. It is probably the same peculiarity which prevents its appearing as an impurity in the hydrochlorate of morphia, prepared by the process of ROBERTSON and GREGORY. The hydrochlorate of papaverine is less soluble than the hydrochlorate of morphia, and *a priori* we should expect it to be the first substance to deposit from the concentrated fluid, yet the commercial hydrochlorate of morphia does not contain a trace of it, the whole being retained in the mother liquor.

† *Annales de Chimie et de Physique*, 2d Series, vol. l., p. 347.

‡ *Ibid.*, vol. lix., p. 140.

§ *Ibid.*, vol. lviii., p. 157.

	COUERBE.				REGNAULT.		
Carbon, . . .	60·87	61·03	60·86	61·63	61·36	61·22	61·51
Hydrogen, . . .	5·11	5·54	5·09	5·22	5·40	5·33	5·34
Oxygen, . . .	34·02	33·43	34·05	33·15	33·24	33·45	33·15
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

numbers which agree very well with the formula $C_{10} H_5 O_4$, given for meconine in the same paper. My own analyses completely confirm these results. The details are as follows:—

- I. { 5·405 grains of meconine, dried at 212°, gave
 12·170 ... carbonic acid, and
 2·495 ... water.
- II. { 5·445 grains of meconine, dried at 212°, gave
 12·280 ... carbonic acid, and
 2·515 ... water.

	Experiment.		Calculation.		
	I.	II.			
Carbon, . . .	61·40	61·50	61·85	C_{20}	120
Hydrogen, . . .	5·12	5·13	5·15	H_{10}	10
Oxygen, . . .	33·48	33·37	33·00	O_8	64
	100·00	100·00	100·00		194

In the calculated numbers, I have assumed its formula to be the same as that of opianyl, and it will be immediately shown that the true constitution of both substances is actually so represented.

Properties of Meconine.

Meconine crystallizes from its solution in water in brilliantly white and very beautiful needles, which are arranged in branched tufts, in a highly characteristic manner. Its taste is slightly but distinctly bitter. It is soluble in water, alcohol, and ether, and its saturated hot solution in the first menstruum becomes filled, on cooling, with a net-work of crystals, which occupies the whole of the fluid. It requires for solution 22 times its weight of boiling water, and upwards of 700 times its weight of water at 60°. These numbers differ considerably from those of COUERBE, who finds it to be soluble in 18·5 parts of hot, and 265 of cold water. Three careful determinations on solutions made by boiling with excess of meconine, allowing the fluid to cool, and filtering from the deposited crystals, concurred in giving the former result; and in this respect meconine completely agrees with opianyl, which also requires 700 parts of cold water for solution. When dry meconine melts at 230°, and not at 194°, as stated by COUERBE. It fuses under water at a temperature of 170°, and it is possible that COUERBE may have been misled by this appearance, and determined its fusing point by heating it in water; but

there is no statement to this effect in the paper, nor does he mention how that employed for analysis was dried, so that it is impossible to ascertain how he made his experiment. When heated to a higher temperature it volatilizes completely, and is deposited on cooling in fine crystals. If the quantity be large, and the heat carelessly applied, a trifling carbonaceous residue is left. Meconine does not appear to dissolve more abundantly in the alkalies than water, and gives no compounds with the metallic oxides. Its effect on subacetate of lead was particularly examined, but no precipitate could be obtained by any mode of operating. COUERBE states that he obtained and analysed such a precipitate; but his description of the whole reaction is extremely unsatisfactory, his two analyses differ immensely, and there can be little doubt, that the substance he obtained was not a true chemical compound, but due to some impurity contained in the meconine he employed. Nitric acid, chlorine, bromine, and iodine, act upon meconine with the production of particular compounds, to be afterwards described. When treated in the cold with concentrated sulphuric acid, it forms a colourless solution, but on gently heating, a faint purple makes its appearance, which gradually increases in depth, as the temperature rises, until it becomes so intense, that a stratum of a quarter of an inch thick is quite opaque; and at length, if the temperature becomes too high, sulphurous acid is evolved, and the substance charred. When the purple solution is diluted with water, a dark-brown precipitate is thrown down, and a brown fluid obtained. The precipitate dissolves in alkalies, with a fine red colour, and appears to be a true colouring matter. Exactly the same phenomena are observed when opianyl is treated in the same manner. COUERBE obtained with meconine, a green colour, but I have never seen this when it was pure; although, if it be taken after its first crystallization, and while still yellow, I have found it to produce a dirty greenish purple colour, and COUERBE's results are no doubt to be attributed to the presence of some impurity.

The observations just made are sufficient to show that meconine and opianyl are actually identical; and if further proof be required, it is to be found in the properties of the substitution products of both substances, to be immediately described. It is clear, also, that the discrepancies in the characters of the former substance as described by myself, and those attributed to meconine, such as its melting point, precipitation of subacetate of lead and green colour with sulphuric acid, which caused me to hesitate in asserting their identity, are due to erroneous observations on the part of COUERBE.

In what follows, I propose to make use of the name of opianyl, which appears much more suited to the substance than that of meconine. For some reasons, perhaps, the name proposed by the original discoverer ought to be retained; but having been applied to it as an isolated substance, it must be considered as in some sense as a provisional name, and ought to give way to another, which points out its relation to opianic acid, and through it to narcotine, from which it can also

be obtained. I shall only employ the word meconine to distinguish that got directly from opium from that produced by the decomposition of narcotine.

Action of Nitric Acid on Opianyl.

The relation in formulæ of opianyl and opianic acid led me to anticipate the easy conversion of the one into the other; but this anticipation has not been confirmed by experiment. I had immediate recourse to nitric acid, as the readiest means of effecting the expected change; but in place of opianic acid there was formed a substitution product corresponding with COUERBE's hyponitro-meconic acid, although neither its properties nor the mode of its preparation agree with his description.

Nitropianyl.—Opianyl dissolves abundantly in cold concentrated nitric acid, and a few red fumes are given off when heat is applied. On dilution the fluid becomes filled with bulky crystals, which are obtained pure by washing and solution in boiling spirit. Nitropianyl is obtained in fine white needles and prisms, sometimes of considerable length. It is very sparingly soluble in cold water, more so in boiling, and the solution on cooling deposits it in minute crystals. It is much more soluble in boiling alcohol, and is also dissolved by ether. All these solutions are perfectly colourless, and absolutely neutral to test-paper. It melts at 320° into a transparent fluid, which solidifies on cooling into a crystalline mass. Heated in small quantity on a platinum knife, it volatilizes almost completely, leaving only a trifling carbonaceous residue; but in a test-tube it decomposes suddenly, when the temperature rises to a certain point, leaving a bulky, porous charcoal. It is not precipitated by metallic salts, and possesses no acid properties. It does not dissolve in cold potash or ammonia more abundantly than in water; but on boiling, a larger quantity is taken up, the fluid becomes yellow, but nothing is deposited on cooling or on the addition of hydrochloric acid, and the nitropianyl obviously undergoes some change, which deficiency of material has prevented me from examining. Nitropianyl is insoluble in hydrochloric acid; strong nitric acid dissolves it readily in the cold, and deposits it in crystalline flocks on dilution. When treated with concentrated sulphuric acid the crystals immediately become yellow, and on the application of heat they dissolve with a red colour, which becomes more and more intense as the temperature rises. On dilution with water, the fluid acquires a dirty red colour, which is rendered darker by ammonia. The analysis of nitropianyl gave the following results:—

				$\left\{ \begin{array}{l} 5.170 \text{ grains of nitropianyl, dried at } 212^{\circ}, \text{ gave} \\ 9.500 \quad \dots \text{ carbonic acid, and} \\ 1.840 \quad \dots \text{ water.} \end{array} \right.$			
				Experiment.		Calculation.	
				Carbon,	. . . 50.11	50.20	C ₂₀ 120
				Hydrogen,	. . . 3.92	3.76	H ₉ 9
				Nitrogen,		5.85	N 14
				Oxygen,		40.19	O ₁₂ 96
						100.00	239

This leads to the formula $C_{20}H_9(NO_4)O_8$, which is exactly the same as that of the substance described by COUERBE under the name of hyponitromeconic acid. This substance, according to COUERBE, is an acid capable of combining with the alkalis, and yielding precipitates with the salts of iron and copper. It occurs in long yellow needles, gives yellow solutions with water and alcohol, but not with ether, and dissolves in the alkalis with a dark yellow, almost red colour, and is precipitated by acids. It is said to melt at 302° . These characters, though differing very remarkably from those of nitropianyl, approximate so closely in other respects that there can be no doubt about the identity of the two substances, although the discrepancies are somewhat puzzling. Some of them may, no doubt, be explained on the supposition that COUERBE's substance was impure; but others scarcely admit of any such explanation. This particularly applies to his description of the mode in which it was obtained. He says that nitric acid is to be boiled with meconine, and the fluid evaporated to complete expulsion of the acid, and the residue, on treatment with water, gives hyponitromeconic acid. I found, on the contrary, that the residue, which represented only a small quantity of the opianyl or meconine employed, was highly soluble in water, and the solution gave, on evaporation, an amorphous mass which dissolved in almost all proportions in alcohol and ether. In one instance only in which this process was tried, a small quantity of a crystalline matter was obtained. The soluble substance was not examined, as its properties were not such as to admit of easy purification. It is probably a further substitution product.

Action of Chlorine on Opianyl.

When a current of chlorine is passed into a cold saturated solution of opianyl in water, crystals soon begin to make their appearance, and gradually fill the whole fluid. In preparing this substance in large quantity, it is convenient to employ a warm solution, so that the bulk of the fluid may be smaller; but in this case care must be taken to stop the process before it has gone too far, as the crystals are apt to diminish, or even disappear, apparently owing to the formation of a farther product of decomposition, and the same precaution is necessary, though to a less degree, with the cold solution. The crystals are purified by solution in boiling alcohol. Chloropianyl may also be obtained by passing dry chlorine over fused opianyl. The gas is rapidly absorbed, hydrochloric acid is evolved, and the mass becomes gradually less and less fusible, so that the temperature of the oil-bath in which the tube is immersed must be slightly raised. After the action has gone on for some time, the current of gas must be stopped and the heat removed. If the action has been properly managed, the mass is highly crystalline, and on solution in boiling alcohol gives crystals identical with those obtained in the wet way. In this case, also, care must be taken to stop the action at the proper point, for if it be continued too long, no crystals are obtained, and the fluid solidifies into a resinous mass like Canada balsam.

Chloropianyl as obtained by either of these processes is in the form of transparent colourless needles, scarcely soluble in cold water, rather more so in boiling. Alcohol and ether dissolve it much more abundantly, and deposit it in fine crystals. It is not more soluble in the alkalis than in water, and they do not remove chlorine from it. Nitric acid dissolves it with a red colour, and on heating it is decomposed. It is soluble in cold oil of vitriol, and on heating, a fine greenish-blue solution is obtained, from which water throws down brown flocks, soluble in the alkalis with a red colour. Chloropianyl melts at 347° , and sublimes unchanged at a higher temperature. The properties of specimens prepared from opianyl and from meconine extracted directly from opium, were compared, and found to be perfectly identical. Of the following analyses, the first two were made with chloropianyl obtained from meconine in the dry way, and the third was from opianyl, and prepared in the wet way.

I.	{ 5.095 grains of chloropianyl, dried at 212° , gave		
	9.790	...	carbonic acid, and
	1.985	...	water.
II.	{ 3.352 grains of chloropianyl gave		
	6.435	...	carbonic acid, and
	1.280	...	water.
III.	{ 4.285 grains of chloropianyl gave		
	8.265	...	carbonic acid, and
	1.620	...	water.
{ 4.950 grains of chloropianyl gave			
{ 3.039			
...			
chloride of silver.			

	Experiment.			Calculation.		
	I.	II.	III.			
Carbon, . . .	52.40	52.35	52.60	52.51	C_{20}	120
Hydrogen, . . .	4.32	4.21	4.20	3.93	H_9	9
Chlorine, . . .	15.17	...	...	15.53	Cl	35.5
Oxygen, . . .	28.11	...	...	28.03	O_8	64
	100.00			100.00		228.5

This corresponds with the formula $C_{20} H_9 Cl O_8$.

The action of chlorine upon meconine has been examined by COUERBE, but his results differ entirely from those just described, and his statements are very loose, unsatisfactory, and in some points absolutely conflicting. He passed chlorine into fused meconine, and obtained a product containing 25.75 per cent. of chlorine, and consisting of crystals mixed with a resinous matter. The greater part of the chlorine exists in the latter, the former containing only 5.43 per cent., which is removed by oxide of silver, or by potash. The product is said to crystallize from alcohol in short prisms, to contain no chlorine, but to have a powerfully acid reaction, and to precipitate the salts of lead and copper. COUERBE designates it mechloic acid, and assigns to it the formula $C_{14} H_7 O_{10}$, which obviously bears no relation to that of the original substance, and is in itself impro-

bable. The alleged absence of chlorine must also be considered as in the highest degree questionable; indeed COUERBE appears to have relied entirely on the action of oxide of silver in removing the chlorine he found in the crude substance, and does not appear to have tested by heating with lime, and hence has overlooked the substitution chlorine which his substance undoubtedly contained. Nor is this surprising, for his paper was written at a time when the law of substitution was unknown, and little attention had been paid to the organic chlorine compounds.

I have already mentioned that if the current of chlorine is passed through fused opianyl for too long a time, no crystals are deposited, and a substance resembling Canada balsam is obtained, which is no doubt identical with the resinous matter which COUERBE got mixed with the crystals of his mechloic acid. This substance is insoluble in water, but highly soluble in alcohol and ether, and deposited in an amorphous condition when these menstrua are evaporated. When treated with potash it dissolves, and the fluid on saturation with an acid yields a pulverulent precipitate, soluble in alcohol, and giving irregular crystals on evaporation. This substance I at first suspected might be mechloic acid, but it is entirely different, contains abundance of chlorine, and is obviously a further substitution product, although it was not obtained of definite constitution. A single analysis gave—

$\left\{ \begin{array}{ll} 4.540 \text{ grains, dried at } 212^{\circ}, \text{ gave} \\ 8.295 \quad \dots \quad \text{carbonic acid, and} \\ 1.535 \quad \dots \quad \text{water.} \end{array} \right.$			
Carbon,	.	.	45.82
Hydrogen,	.	.	3.75

This lies nearly half-way between the numbers of chloropianyl and those required for a product containing two equivalents of chlorine.

COUERBE gives for his resinous substance the formula $C_{10} H_5 O_8$; but if we assume it to have contained chlorine, his analysis would agree pretty well with the formula $C_{20} H_8 Cl_2 O_8$. His numbers, recalculated with the correct atomic weight of carbon, are given below, and compared with that formula.

COUERBE.					Calculation.		
Carbon,	.	.	46.93	45.53	45.63	C_{20}	120
Hydrogen,	.	.	3.72	3.83	3.04	H_8	8
Chlorine,	.	.	...	...	26.99	Cl_2	71
Oxygen,	.	.	...	...	24.34	O_8	64
					100.00		268

It is highly probable that this substance actually did contain chlorine, but the approximation to the formula is possibly only fortuitous.

Action of Bromine on Opianyl.

When bromine water is dropped into an aqueous solution of opianyl, crystal-

line flocks of bromopianyl are immediately deposited, which are purified by solution in boiling spirit. Bromopianyl is thus obtained in colourless transparent needles, very sparingly soluble in water, much more so in alcohol and ether. It is rather more fusible than chloropianyl, its melting point being 332° ; but in its general characters and relations to acids and bases it is so similar to that substance that the same words may serve to describe both. Its analysis gave—

$$\left\{ \begin{array}{l} 5.105 \text{ grains of bromopianyl, dried at } 212^{\circ}, \text{ gave} \\ 8.202 \quad \dots \quad \text{carbonic acid, and} \\ 1.565 \quad \dots \quad \text{water.} \end{array} \right.$$

$$\left\{ \begin{array}{l} 4.200 \text{ grains of bromopianyl gave} \\ 2.883 \quad \dots \quad \text{bromide of silver.} \end{array} \right.$$

					Experiment.			Calculation.		
Carbon,	.	.	.	.	43.81			43.95	C ₂₀	120
Hydrogen,	.	.	.	.	3.40			3.29	H ₉	9
Bromine,	.	.	.	.	29.21			29.30	Br	80
Oxygen,	.	,	,	.	23.58			23.46	O ₈	64
					100.00			100.00		273

corresponding with the formula C₂₀ H₉ Br O₈.

Action of Chloride of Iodine on Opianyl.

Iodine, whether in solution in alcohol or in the solid form, is entirely without action on opianyl. I therefore tried whether the ingenious process described by Mr BROWN for causing the substitution of iodine for hydrogen would succeed in this case, and the experiment proved completely successful, although the change was very slowly effected. When chloride of iodine was added to an aqueous solution of opianyl, no crystals were deposited at first, and the fluid retained its colour. It was placed upon the sand-bath, in a moderately warm place, where it was left for several days, at the end of which time crystals of an inch in length, and mixed with some iodine had deposited. The crystals were separated, and dissolved in boiling alcohol, which deposited them pure and colourless.

Iodopianyl is obtained in colourless needles of considerable size and great beauty, which are scarcely soluble in water, but dissolve in alcohol and ether. At 234° it fuses to a colourless liquid, which soon becomes brown, and at a higher temperature it is decomposed and iodine evolved. Nitric acid destroys it, with separation of iodine. Sulphuric acid dissolves it, and on heating a dark colour is produced. Its analysis gave—

$$\left\{ \begin{array}{l} 6.993 \text{ grains of iodopianyl gave} \\ 9.530 \quad \dots \quad \text{carbonic acid, and} \\ 1.865 \quad \dots \quad \text{water.} \end{array} \right.$$

$$\left\{ \begin{array}{l} 4.735 \text{ grains of iodopianyl gave} \\ 3.460 \quad \dots \quad \text{iodide of silver.} \end{array} \right.$$

	Experiment.	Calculation.			
Carbon,	37·16	37·48	C ₂₀	120	
Hydrogen,	2·96	2·81	H ₉	9	
Iodine,	39·48	39·70	I	127·1	
Oxygen,	20·40	20·01	O ₈	64	
	100·00	100·00		320·1	

The formula is therefore C₂₀ H₉ I O₈.

Action of Peroxide of Lead and Sulphuric Acid on Opianyl.

I had fully expected that either opianic or hemipinic acids would have been produced by the action of nitric acid on opianyl; but having failed to obtain them, I had recourse to peroxide of lead as a convenient oxidizing agent. When opianyl is heated very gently along with that substance and sulphuric acid, an action takes place, carbonic acid is evolved, and an amorphous substance obtained in solution. Deficiency of material, however, prevented the extension of my experiments in this direction as far as was desirable; but having recently contrived a process by means of which opianyl may be obtained with great certainty from narcotine, I hope to return to the subject in a future paper. There can, I think, be no doubt that by the use of an oxidizing agent incapable of producing a substitution product, one or other of these acids must be obtained.

The preceding experiments having established the identity of meconine with a decomposition product of narcotine, it seemed natural to suppose that the former was not an original constituent of opium, but had been produced by the decomposition of the latter, either during the process of inspissation, or in the chemical treatment to which it had been submitted; and in that case, the mother liquors from which it was extracted ought also to contain cotarnine. As that base is not precipitated by ammonia, the probability was, that if present at all, it must have existed in the fluid along with opianyl, and ought to have been extracted from it by ether, but no satisfactory evidence of its presence could be obtained, the only basic substance contained in the ether, being the small quantity of papaverine which was separated in the manner already described. Nor can this excite surprise, for the difficulty there is in making cotarnine crystallize under any circumstances, and the extent to which its properties are masked by the presence of other substances, are such as almost to preclude the hope of extracting it from the large mass of indeterminate amorphous substances with which it must be mixed. Resinous matters possessed of basic properties, and giving precipitates with bichloride of platinum, and corrosive sublimate, were found along with thebaine, and abound in all parts of the opium mother liquor; but no special attention was paid to these, very few trials having shown that their purification would have been attended with great difficulties. It is possible that cotarnine may exist in some of them.

The relationship thus brought out between two substances which have been long described as isolated constituents of opium is entitled to much consideration, and is the first step towards the simplification of the chemistry of a substance so remarkable for its complexity. As a matter of speculation, the opinion has long been entertained, that when several well-defined substances exist in the same plant, they must bear some relation to one another, and it has not unfrequently happened that this idea has been borne out by the formulæ assigned to them. Quinine and cinchonine, which were once supposed to differ only in the proportion of oxygen they contain, may be cited as striking instances; and it was commonly believed that these two substances must be related in the same manner as two different oxides of a metal, and by the proper use of oxidizing and reducing agents must be mutually convertible. But neither in this nor in any similar instance has the anticipated conversion been realized, except with harmaline and harmine, the two bases of the *Peganum harmala*, and it is somewhat remarkable, that the former is converted into the latter by the oxidation of two equivalents of hydrogen, exactly as I have found to occur with narcotine, excepting that there is no splitting up into two products, as with the latter substance.

But although the conversion of other alkaloids has not hitherto been successful, there cannot be a doubt that the close approximation in the formulæ of substances occurring in the same plant, indicates some natural connexion, and it is important that all such relations, where they exist, should be kept distinctly in view. For this reason, I propose to direct attention to those which have been brought out by the investigation of the compounds of opium.

Between the two best known of these alkaloids, morphia, and codeine, a very simple relation subsists. Their formulæ are,

and their relation is that of the two immediately adjoining members of a homologous series. Yet there is little, if anything, except their formulæ, to bear out the opinion that they actually are homologous. They show but little of that close similarity in properties, which frequently renders the separation and distinction of such substances so difficult; and especially in their relations to solvents, there are very marked differences. Still the connexion is worthy of mention; the more especially, as the experiments of Mr How* lead to the opinion that they are both nitryl bases.

Thebaine and codeine are likewise somewhat closely connected,—

* Quarterly Journal of Chemical Society, vol. vi., p. 125.

The difference is here only two equivalents of carbon ; but at present we know too little regarding the former base, to permit more than a simple reference to this difference. Again, comparing thebaine with papaverine,—

we find them to differ by the elements of two equivalents of carbonic oxide.

Passing from these, which may be considered as forming a group of substances closely allied, at least in formulæ, to one another, we come to other bases nearly related among themselves, but which cannot be connected in any simple way with those just mentioned. Narcotine and narceine deserve the first notice.

They differ, therefore, by four equivalents of water only, and narceine might be considered as a hydrate of narcotine. It appeared to me that it must be easy to ascertain whether the molecular condition of narceine admits of this construction ; for in that case, it might be expected to undergo decompositions similar to those of narcotine. I accordingly tried the action of nitric acid upon it, but there was no production of opianyl or cotarnine, and though the decomposition was not followed up, enough was seen to lead me to the inference that most probably a substitution base was produced.

It is scarcely necessary to refer to the constitution of narcotine, and its relation to opianyl, further than to observe, that in my former memoir I have assumed it to be produced by coupling cotarnine with a substance, $C_{20} H_{12} O_8$, to which I have given the name of hydruret of opianyl. I recur to it here, because I am inclined to think that opianine is similarly constituted, although it must be admitted, that the unsatisfactory and incomplete information we at present possess regarding that base gives the opinion I am now about to hazard a somewhat speculative character.

HINTERBERGER,* in his preliminary notice announcing the discovery of opianine, assigned to it the formula $C_{66} H_{36} NO_{23}$, which is altered in the published paper† to $C_{66} H_{36} N_2 O_{21}$. The difference between these two statements is attributed by HINTERBERGER to his having at first employed VARRENTRAP and WILL's method of determining nitrogen, by which only half of that element is separated in the form of ammonia, and he consequently obtained only 2.22 per cent. of nitrogen ; but in subsequently repeating its determination by DUMAS's method, he obtained

* Annalen der Chemie und Pharmacie, vol. lxxvii., p. 207.

† Ibid., vol. lxxxii., p. 320.

twice that quantity. If this be the case, opianine must be a base entirely unique in its properties; for in all the fixed alkaloids hitherto examined, the whole of the nitrogen is converted into ammonia with the utmost facility by ignition with soda lime. On this ground alone I should be inclined to question the accuracy of HINTERBERGER'S results; and these doubts are increased by a more minute examination of his analyses. In two determinations by DUMAS'S method, he obtains 4.12 and 4.41 per cent. of nitrogen, while the calculation for his formula requires 4.45. Now it is a familiar fact, that, owing to the impossibility of removing the last traces of atmospheric air from the tube, the determination of nitrogen as gas invariably gives a larger quantity than theory requires, so much so that an excess of a half per cent. is not uncommonly met with, even in the hands of the most careful experimenters. But in both of HINTERBERGER'S experiments, the quantity falls short of theory, and in one of them to the extent of about 0.4 per cent. Partly on this account, and partly because his formula is at variance with the law of the divisibility of formulæ, I incline to the opinion that it cannot be correct, and that in all probability his first nitrogen determinations are more accurate, and to them I shall adhere. The details which HINTERBERGER has supplied us with regard to opianine and its salts are extremely meagre, and do not afford very decided grounds on which to found a formula; but weighing them all, the constitution of opianine appears to be best represented by $C_{66}H_{37}NO_{22}$. That this formula would agree almost as well with HINTERBERGER'S experiments as that he has himself given, is at once obvious from the following comparison, in which all his results excepting the nitrogen determinations are contained.

Opianine.

				Experiment.		Calculation.	
						$C_{66}H_{36}N_2O_{21}$	$C_{66}H_{37}NO_{22}$
Carbon,	.	.	.	62.99		63.06	63.56
Hydrogen,	.	.	.	5.69		5.73	5.93
Nitrogen,	.	.	.	...		4.45	2.24
Oxygen,	.	.	.	...		27.76	28.27
						100.00	100.00

Mercury Compound of Opianine.

				Experiment.		Calculation.	
						$C_{66}H_{36}N_2O_{21}$	$C_{66}H_{37}NO_{22}$
Carbon,	.	.	.	49.14		49.50	49.81
Hydrogen,	.	.	.	4.60		4.63	4.77
Nitrogen,	.	.	.	...		3.50	1.76
Oxygen,	.	.	.	...		21.00	22.16
Chlorine,	.	.	.	9.31		8.87	8.93
Mercury,	.	.	.	12.28		12.50	12.57
						100.00	100.00

Now if this be its formula, we have only to subtract from it an equivalent of hydruret of opianyl to have narcotine.

And pursuing this point, we should develop a remarkable relation between these two bases and narcogenine, for all these would be compounds of cotarnine and hydruret of opianyl in different proportions, as thus represented:—

The possibility of representing narcotine and narcogenine in this manner has been already suggested by WERTHEIM,* and derives great support from the researches contained in this and the previous paper; and should the view I have taken of the constitution of opianine be confirmed, these three will form a very remarkable and important group of bases. I have had no opportunity of examining Egyptian opium, from which alone opianine is obtained, and have been unable to submit my view to the test of experiment, but I have thrown it out as deserving the attention of any one who may have occasion to re-examine that substance.

The following is a table of the compounds analyzed in this paper:—

Papaverine,		$\text{C}_{40} \text{H}_{21} \text{NO}_8$
Nitropapaverine,		$\text{C}_{40} \text{H}_{20} (\text{NO}_4) \text{NO}_8$
Nitrate of Nitropapaverine,		$\text{C}_{40} \text{H}_{20} (\text{NO}_4) \text{NO}_8 + \text{HO NO}_5$
Platinum salt of papaverine,		$\text{C}_{40} \text{H}_{20} (\text{NO}_4) \text{NO}_8 \text{H Cl Pt} + \text{Cl}_2$
Bromopapaverine,		$\text{C}_{40} \text{H}_{20} \text{Br NO}_8$
Hydrobromate of bromopapaverine,		$\text{C}_{40} \text{H}_{20} \text{Br NO}_8 + \text{H Br}$
Teriodide of papaverine,		$\text{C}_{40} \text{H}_{21} \text{NO}_8 + \text{I}_3$
Pentiodide of papaverine,		$\text{C}_{40} \text{H}_{21} \text{NO}_8 + \text{I}_5$
Opianyl (meconine),		$\text{C}_{20} \text{H}_{10} \text{O}_8$
Nitropianyl,		$\text{C}_{20} \text{H}_9 (\text{NO}_4) \text{O}_8$
Chloropianyl,		$\text{C}_{20} \text{H}_9 \text{Cl O}_8$
Bromopianyl,		$\text{C}_{20} \text{H}_9 \text{Br O}_8$
Iodopianyl,		$\text{C}_{20} \text{H}_9 \text{IO}_8$

In conclusion, I may state that in pursuing the investigation of the compounds of opium, I have ascertained that by treatment with sulphuric acid, opianic acid is converted into a true colouring matter capable of giving, with iron and alum mordants, all the colours produced by madder; and taking into consideration that the formula of alizarine, $\text{C}_{20} \text{H}_6 \text{O}_6$, differs from that of opianic acid by the elements of four equivalents of water only, I think it is not impossible that the new colouring matter may actually prove identical with it. Should it do so,

* Annalen der Chemie und Pharmacie, vol. lxx., p. 71.

a very important and remarkable relation would be brought out between madder and opium. At the same time I must mention that my experiments are not as yet sufficiently advanced to enable me to speak with any degree of certainty on this point. I have also ascertained that apophyllic acid is an acid methyllamide corresponding in its constitution with oxamic and tartramic acids, but containing methylamine in union with a non-nitrogenous acid. I have likewise contrived a process by which opianyl can be obtained from narcotine by a different decomposition from that described in my former paper, and with absolute certainty.

The full details of these and other matters required to complete the history of these compounds, I must reserve for a future paper.