

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XIX.—*Narcotine, Cotarnine and Hydrocotarnine. Part IV. On Oxynarcotine, a new Opium educt, and its relationships to Narcotine and Narceine.*

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§ 1. *Isolation of Oxynarcotine.*

DURING the preparation and purification of narceine from opium liquors, an indistinctly crystalline mass is often left undissolved on boiling the partially purified narceine with water; a quantity of this material was obligingly given to us for investigation by Messrs. Macfarlan and Co. of Edinburgh, to whom we are further indebted for the narceine used in the experiments subsequently described; the results of our experiments tend to show that this crude product contains a new opium alkaloïd, bearing to narcotine the relationship of benzoic acid to benzoic aldehyde, which new base we therefore propose to term *oxynarcotine*.

The crude material sent yielded to boiling water a large quantity of narceine, but it was found impossible to obtain anything like a complete separation of that substance by this means; the mass was therefore dissolved in just as much hot dilute sulphuric acid of known strength as was required to dissolve all the bases present (about 3—4 equivalents of acid); and the solution, filtered from undissolved humus, &c., was neutralised, whilst still hot, by addition of exactly as much soda-solution as would saturate the acid employed. A thick magma of paper-pulp-like crystals was thus precipitated: after cooling and standing some hours, these crystals were drained and boiled with successive small quantities of water; much narceine was thus dissolved out, whilst sandy crystals of nearly pure oxynarcotine were finally left undissolved; the aqueous liquors thus obtained deposited on cooling crystals resembling paper-pulp, which, on again treating with boiling-water, mostly dissolved, leaving, however, a few more sandy crystals. All the mother-liquors obtained were methodically treated by evaporation, crystallisation and boiling the drained paper-pulp-like crystals with water, until finally an almost complete separation of narceine and oxynarcotine was effected.

These sandy crystals were found to retain minute traces of narceine

capable of being dissolved out by long-continued boiling with alcohol; the alcohol filtered boiling deposited on standing gritty crystals of oxynarcotine with a little of the feathery crystals of narceine, the latter being readily dissolved by hot alcohol, the former only very sparingly. To make sure that no narceine was retained by the sandy crystals, even after this boiling with alcohol, they were dissolved in hydrochloric acid, and the recrystallised hydrochloride precipitated by addition of a small excess of caustic potash to the hot solution; narceine is very readily dissolved by alkalis, oxynarcotine only to a lesser extent. The following numbers were obtained after drying at 100° for several hours.

A. Sandy crystals not purified by alcohol, 0.2850 gram gave 0.6410 CO_2 and 0.1560 H_2O .

B. Sandy crystals boiled several times with alcohol; undissolved portion 0.2940 gave 0.6605 and 0.1605 H_2O .

C. Sandy crystals boiled several times with alcohol; gritty crystals from alcoholic filtrate freed from narceine by several boilings with small quantities of alcohol; 0.2750 gave 0.6140 CO_2 and 0.1430 H_2O .

D. Sample precipitated by potash from hydrochloride, well boiled with alcohol and dried at 110° : 0.3865 gave 0.8700 CO_2 and 0.2060 H_2O ; 0.7790 burnt with soda lime gave 0.1620 platinum.

E. D recrystallised from a large bulk of alcohol and dried at 110° : 0.2580 gave 0.5770 CO_2 and 0.1370.

F. Sample prepared like D from a specimen of hydrochloride that had been recrystallised and pressed: 0.3965 gave 0.8890 CO_2 , and 0.203 H_2O .

These numbers will agree (like those given below for the chloride and the platinum salts) fairly well with either of the three formulæ, $\text{C}_{22}\text{H}_{23}\text{NO}_8$, $\text{C}_{22}\text{H}_{25}\text{NO}_8$ or $\text{C}_{23}\text{H}_{25}\text{NO}_8$, but on the whole they agree best with the first, which is moreover shown to be the true formula by the nature of the decomposition-products of the base (*vide* § 2).

	Calculated.		Found.						Mean.
			A.	B.	C.	D.	E.	F.	
C_{22}	264	61.54	61.34	61.27	60.89	61.38	60.99	61.15	61.17
H_{23}	23	5.36	6.08	6.07	5.78	5.92	5.90	5.68	5.90
N	14	3.26	—	—	—	2.95	—	—	2.95
O_8	128	29.84	—	—	—	—	—	—	*29.98
$\text{C}_{22}\text{H}_{23}\text{NO}_8$..	429	100.00							100.00

When oxynarcotine is dissolved in hot water containing 4 to 5 equivalents of hydrochloric acid, pulpy crystals form on cooling, containing (after well pressing in filter paper) $\text{C}_{22}\text{H}_{23}\text{NO}_8 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$.

1.0700 gram of crystals dried in filter paper lost at 100° 0.0885 gram = 8.27 per cent.

* By difference

0.8820 gram of crystals dried in filter paper lost at 100° 0.0770 gram = 8.73 per cent.

Calculated for the above formula, 7.17 per cent.

0.3115 gram of salt dried at 100° gave 0.6490 CO₂ (H₂O lost).

0.2930 " " " 0.6140 CO₂ and 0.1515 H₂O.

0.9805 " " " 0.2970 AgCl.

1.3170 " " " 0.4025 "

	Calculated.		Found.	
C ₂₂	264	56.72	56.82	57.15
H ₂₄	24	5.15	—	5.74
Cl	35.5	7.63	7.50	7.56
N	14	3.01	—	—
O ₈	128	27.49	—	—
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C ₂₂ H ₂₃ NO ₈ .HCl	465.5	100.00		

The platinum salt, dried at 100°, gave the following numbers :—

From sample D : 0.4780 gram gave 0.7365 CO₂ and 0.1900 H₂O.

" A : 0.3730 " 0.5760 " 0.1540 "

" D : 0.9445 " 0.1450 Pt.

" E : 0.6820 " 0.1050 Pt.

	Calculated.	Found.	
Carbon	41.55	42.03	42.11
Hydrogen	3.78	4.42	4.58
Platinum	15.55	15.35	15.40

Oxynarcotine forms minute, micaceous, sandy crystals, very sparingly soluble in water and in alcohol, even when boiling, and crystallisable without changing in gritty crystals from large bulks of either menstruum; both kinds of crystals are very dissimilar from those of narceine, but are not at all unlike those of narcotine prepared by precipitation from a hot solution of the hydrochloride, and by crystallisation from alcohol respectively. It differs from narcotine in being partially dissolved by boiling water, and in being but sparingly soluble in boiling alcohol, and practically insoluble in benzene, ether, and chloroform. Fixed alkalis and their carbonates added to concentrated solutions of its salts precipitate it, but with more dilute solutions no precipitate is formed till after standing some time, whilst the base appears to be somewhat soluble in alkalis.

Like narcotine and narceine hydrochlorides, oxynarcotine hydrochloride breaks up in contact with hot water into hydrochloric acid and more basic salts; thus, a specimen of the hydrochloride examined above, when recrystallised from 50 parts of hot water, gave feathery crystals, of which 0.8540 gram dried at 100° gave 0.0570 AgCl. Cl = 1.65 per cent.

On recrystallising these from boiling water, sandy crystals were left undissolved, whilst the second crop of crystals gave these numbers.

0.7170 gram dried at 100° gave 0.0315 AgCl. Cl = 1.08 per cent. $5C_{22}H_{23}NO_8 \cdot HCl$ and $7C_{22}H_{23}NO_8 \cdot HCl$, require respectively 1.63 and 1.16 per cent. of Cl.

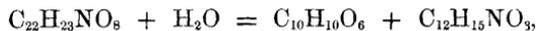
The crude product obtained by Messrs. Macfarlan and Co., and examined by us as above described, was examined some few years ago by Herr Ludwig Mayer (Proceedings of the *Phil. Soc., Glasgow*, 1871), who, however, does not appear to have succeeded in obtaining the new base present in a state of perfect purity, to judge from his analytical figures, and his statement that his product, though virtually insoluble in ether, communicated to it a blue fluorescence; Mayer found in the free base: carbon, 59.46, 59.72; hydrogen, 5.95, 5.98; nitrogen, 2.79; and in the platinum salt: carbon, 39.93, and hydrogen, 4.62, the percentage of platinum not being determined: from these numbers Mayer deduced the formula, $C_{25}H_{29}NO_{10}$, the platinum salt dried at 100° being viewed as $(C_{25}H_{29}NO_{10}, HCl)_2PtCl_4 \cdot 4H_2O$ (!). Without doubt this substance was simply oxynarcotine, retaining some narceine and a trace of resinous decomposition-products, &c., giving the fluorescent property.

§ 2. Action of Oxidising Agents on Oxynarcotine.

When narcotine is treated with oxidising agents, the first decomposition takes place (Part I of these researches, this *Journal*, 1875, 573) in accordance with the reaction:—



opianic acid and hydrocotarnine resulting, and the latter becoming oxidised to cotarnine, $C_{12}H_{13}NO_3$, whilst still nascent; by a parallel reaction it might be anticipated that oxynarcotine would split up, forming ultimately either opianic acid and an oxycotarnine, $C_{12}H_{13}NO_4$, or hemipinic acid and cotarnine; of these the latter is the final change taking place, the equation—



consequently representing the first change that occurs.

In order to make sure that the hemipinic acid thus produced did not result from the oxidation of opianic acid first formed, an oxidizer was necessary, which, although capable of splitting up narcotine and oxidising hydrocotarnine, should yet be incapable of oxidising opianic acid to hemipinic acid: ferric chloride has been shown by Matthiessen and Wright (*Phil. Trans.*, 1869, 667) to be such an agent, but

to make sure that no appreciable quantity of hemipinic acid is really formed by the action of this body on narcotine, the experiments of Matthiessen and Wright were repeated. Narcotine hydrochloride was boiled with ferric chloride for about 12 hours, and the cooled liquid well shaken with ether; on evaporation the ether left a large quantity of opianic acid, which was recrystallised from boiling water: after drying at 100° , 0.2520 gram gave 0.5285 CO_2 and 0.1080 H_2O .

	Calculated.		Found.
C_{10}	120	57.14	57.19
H_{10}	10	4.76	4.76
O_5	80	38.10	—
$\text{C}_{10}\text{H}_{10}\text{O}_5$	210	100.00	

The mother-liquors of the sparingly soluble opianic acid were neutralised with ammonia, filtered, and evaporated down to dryness on the water-bath; water then took up from the residue of opiammonia only a very minute amount of an ammonium salt, capable of precipitating ferric chloride, silver nitrate, and lead acetate: the amount of this substance only just sufficed to give these qualitative reactions on watch-glasses, and the hemipinic acid present (if that acid were actually present), certainly did not amount to anything like 1 per cent. of the opianic acid formed. It may hence be fairly concluded that narcotine does not form any considerable quantity of hemipinic acid by oxidation with ferric chloride, and *a fortiori*, that opianic acid when not nascent is not appreciably oxidised by that agent; whilst, as Matthiessen and Wright have shown, narcotine forms practically the theoretical quantity of opianic acid on long-continued boiling with ferric chloride.

On carrying out the same experiment with oxynarcotine, nothing but hemipinic acid could be isolated from the ethereal extract; the acid extracted yielded, on neutralisation with sodium carbonate, a sodium salt, which was precipitated by lead acetate; the filtrate yielded no trace of opianic acid on treatment with sulphuretted hydrogen and agitation of the acidulated fluid with ether; from the lead precipitate there was obtained, by means of sulphuretted hydrogen, an acid resembling hemipinic acid in all respects, giving the same qualitative reactions, fusing with loss of water at 180° — 181° (water of crystallisation having been previously expelled at 100°), and forming proto-catechuic acid on fusion with potash and methyl-norhemipinic acid on boiling with hydriodic acid. (Part III.) The silver-salt gave these numbers—

$$0.4085 \text{ gram gave } 0.2025 \text{ Ag} = 49.57 \text{ per cent.}$$

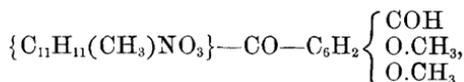
$$\text{Calculated for } \text{C}_{10}\text{H}_{18}\text{Ag}_2\text{O}_6 = 49.09 \quad ,,$$

In order to prove that cotarnine was also formed during the action of ferric chloride on oxynarcotine, the liquors left after treatment with ether were precipitated by excess of sodium carbonate, and the filtrate acidified with hydrochloric acid and kept in contact with zinc for a couple of days, so as to transform any cotarnine present into hydrocotarnine; finally, ammonia in excess was added, and the whole agitated with ether, which dissolved out a base resembling hydrocotarnine in all respects: the crude base left on evaporation of the ether did not crystallise readily; but on conversion into hydrochloride, crystallisation and expression of the latter, and finally treatment of the pressed crystals with ammonia and ether, pure hydrocotarnine was obtained, crystallising from ether in the characteristic way, the crystals melting at 54°. The platinum salt gave these numbers—

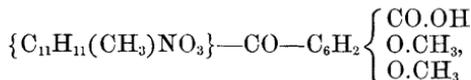
$$\begin{array}{l} 0.2475 \text{ gram gave } 0.0555 \text{ Pt} \quad \quad \quad = 22.42 \text{ per cent.} \\ \text{Calculated for } (\text{C}_{12}\text{H}_{15}\text{NO}_3 \cdot \text{HCl})_2\text{PtCl}_4 = 23.11 \quad \quad \quad ,, \end{array}$$

On heating with sulphuric acid, the base gave the series of colours characteristic of hydrocotarnine.

It may be inferred from these results that if the structural formula of narcotine be



that of oxynarcotine must be



i.e., narcotine is the aldehyde of oxynarcotine, which possesses a complex character, being both carboxyl acid and ammonia-base at the same time, the basic characters, however, considerably predominating. It hence seems highly probable that oxynarcotine may be, not a proximate constituent of opium, but only an alteration-product of narcotine, formed by atmospheric oxidation during the process of morphine extraction.

By the action of other oxidising agents on oxynarcotine, a similar result appears to be produced; thus manganese dioxide and sulphuric acid form hemipinic acid, isolable by extraction with ether and washing the ammonia salt with a little alcohol. On heating oxynarcotine to 140°—150° in a sealed tube with water for 15—20 hours, the base became much charred and decomposed; no trace of either meconin, opianic acid, or hemipinic acid, and no solid alkaloid soluble in ether could be obtained from the product: hence it would seem that, under the influence of water alone, oxynarcotine does not break up as readily as narcotine, the latter forming in this way hydrocotarnine and opianic

acid (Part I), which latter becomes reduced to meconin by the action of the products formed by the further partial decomposition of the hydrocotarnine.

§ 3. *Action of Oxidising Agents on Narceine.*

The peculiar instability in presence of hot water of the salts of narcotine, oxynarcotine, and narceine, seems to indicate an analogy between the structures of the three bases, which is further confirmed by an observation made by us some time ago, that on fusing narceine with caustic potash, protocatechuic acid is formed (*vide* § 4). The solubility of narceine in water, and especially in alkaline solutions, tends to show that this base rather approximates to oxynarcotine than to narcotine in structure, a view completely borne out by the following experiments :—

(A.) *Action of Sulphuric Acid and Potassium Dichromate on Narceine.*

When narceine is dissolved in about 100 parts of boiling water and potassium dichromate is added, little or no action ensues, and no appreciable reduction of the latter takes place ; but if sulphuric acid be also added in sufficient quantity to saturate the oxides of potassium and chromium formed by the reduction of the dichromate, a large amount of reduction is at once manifest (the liquid being hot), and carbon dioxide escapes ; when rather more than two parts of dichromate to one of narceine are used (about 10 equivalents of available oxygen to 1 of alkaloid), and the whole boiled, after addition of the sulphuric acid, for half-an-hour, a green liquid is obtained from which ether extracts an acid identical with the *hemipinic acid* obtainable from narcotine and from oxynarcotine by oxidation ; the yield of this acid is about 10 per cent. of the alkaloid used (56 per cent. should be obtained if the reaction were such that one proportion of narceine gives one of hemipinic acid), or about 18 per cent. of the theoretical quantity. The acid was obtained pure by distilling off the ether from the extract, converting the residue into ammonia salt, evaporating this to dryness, and washing the crystalline salt with alcohol, whereby some tarry impurities were washed away, and finally shaking the acidified salt solution with ether ; by spontaneous evaporation crystals formed, of which, when dry—

0.7870 gram lost at 100° 0.1085 gram = 13.78 per cent.

$C_{10}H_{10}O_6, 2H_2O$ requires 13.74 „

0.3145 gram of dried product gave 0.616 CO_2 and 0.1340 H_2O .

	Calculated.		Found.
C ₁₀	120	53.10	53.42
H ₁₀	10	4.42	4.73
O ₆	96	42.48	—
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C ₁₀ H ₁₀ O ₆	226	100.00	

Of the silver salt prepared by precipitation and washing—

0.5585 gram gave 0.2740 Ag Ag = 49.06 per cent.
 Calculated for C₁₀H₈Ag₂O₆ 49.09 „

After drying at 100°, the acid fused completely at 182°—183°, evolving water in so doing (the same temperature was found for a specimen of pure acid from narcotine examined simultaneously). When heated to 180° for some time, 0.4505 gram of acid dried at 100°, lost 0.0360, and the residue, after crystallisation from absolute alcohol, corresponded absolutely in all properties with hemipinic anhydride from narcotine; 0.1990 gram gave 0.4220 CO₂ and 0.0730 H₂O.

Loss at 180° calculated for the reaction—

C₁₀H₁₀O₆ = H₂O + C₁₀H₈O₅ = 7.97 per cent.
 Observed loss 7.99 „

	Calculated.		Found.
C ₁₀	120	57.69	57.83
H ₈	8	3.85	4.07
O ₅	80	38.46	—
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C ₁₀ H ₈ O ₅	208	100.00	

This hemipinic anhydride from narceine melted at 166°—167°, exactly at the same temperature as that observed with a specimen from narcotine, examined simultaneously.

The hemipinic acid from narceine, when heated with hydriodic acid, gave rise to a product which, like methyl-norhemipinic acid (this Journal, xxi, 262), gave a blue coloration with ferric chloride; when fused with caustic potash at 230°—240°, it gave rise to protocatechuic acid; its ammonia-salt precipitated lead, silver, and ferric solutions in just the same way as that from narcotine.

The chromic liquors from which the hemipinic acid had been extracted by ether, were precipitated by potassium carbonate; the filtrate was distilled with caustic potash, whereby a volatile base was expelled; this was received in hydrochloric acid, and the solution obtained was evaporated to dryness and treated with absolute alcohol; methylamine hydrochloride dissolved, the platinum-salt of which

(after several further treatments of the hydrochloride with alcohol to separate ammonium chloride), gave these numbers—

$$\begin{array}{rcl} 0.7530 \text{ gram gave } 0.3120 \text{ Pt} & = & 41.44 \text{ per cent.} \\ \text{Calculated for } (\text{CH}_3\text{NH}_2\text{HCl})_2\text{PtCl}_4 & 41.60 & ,, \end{array}$$

Nothing fit for analysis could be obtained from the potash-solution left after distilling off the volatile bases, and no organic substance was present in the precipitated chromic oxide.

This formation of methylamine, as well as hemipinic acid, possibly points to the existence of *three* methyl-groups in narceine (as in narcotine), the third being on the nitrogenous side of the compound, and the other two being connected with the benzene nucleus.

(B.) *Action of Ferric Chloride on Narceine.*

On treating this alkaloid in the same way as the narcotine and oxynarcotine above described, *no discernible trace of opianic acid was formed, but instead, a considerable proportion of hemipinic acid, the ferric chloride being simultaneously reduced.* The absence of opianic acid was proved by the fact that, after precipitating as lead salt the hemipinic acid from the liquid obtained by extracting with ether, evaporation, and neutralisation with soda, the filtrate yielded nothing to ether after freeing from lead by sulphuretted hydrogen and acidulation. (Opianate of lead is soluble in water.)

The hemipinic acid obtained from the lead precipitate melted at 180° — 181° , gave the reactions of hemipinic acid, and formed a silver salt, of which—

$$\begin{array}{rcl} 0.5105 \text{ gram gave } 0.2505 \text{ Ag} & = & 49.07 \text{ per cent.} \\ \text{Calculated for } \text{C}_{10}\text{H}_8\text{Ag}_2\text{O}_6 & = & 49.09 \quad ,, \end{array}$$

(C.) *Action of other Oxidisers and of Water on Narceine.*

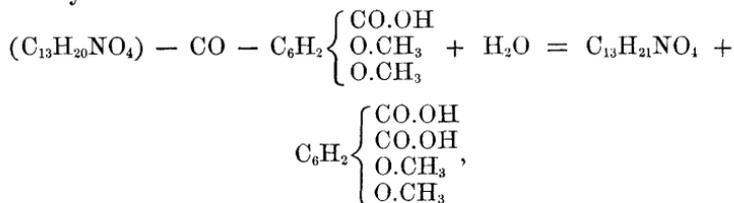
When narceine is boiled with manganese dioxide and sulphuric acid, hemipinic acid is formed, but only in small quantity; after conversion into ammonium salt and washing with alcohol, a silver salt was obtained, of which—

$$\begin{array}{rcl} 0.2180 \text{ gram gave } 0.1080 \text{ Ag} & = & 49.54 \text{ per cent.} \\ \text{Calculated for } \text{C}_{10}\text{H}_8\text{Ag}_2\text{O}_6 & = & 49.09 \quad ,, \end{array}$$

When an aqueous solution of narceine is mixed with potassium permanganate, the latter is more or less rapidly decolorised according to the temperature, and a brown manganese hydrate falls; the filtrate, when acidified and agitated with ether, yields some tarry non-crystalline matter, with a little hemipinic acid, recognised by its qualitative reactions.

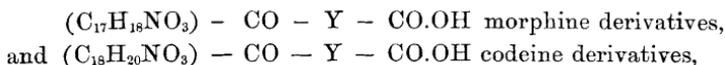
When narceine is heated to 140° — 150° for 15—20 hours with water in a sealed tube, it chars and becomes decomposed, but does not form either meconin, opianic acid, or hemipinic acid, nor any solid base soluble in ether; a trace of methylamine, however, is thus formed.

The foregoing results are readily symbolised if to narceine be attributed the structural formula $(C_{13}H_{20}NO_4) - CO - C_6H_2$ $\left\{ \begin{array}{l} CO.OH \\ O.CH_3, \text{ dif.} \\ O.CH_3 \end{array} \right.$ differing from that of oxynarcotine only in the character of the nitrogenous radicle; the formation of hemipinic acid and the non-formation of opianic acid from it by oxidation can thus readily be accounted for. All attempts to trace out what becomes of the nitrogen of the narceine during oxidation have proved failures; the base, $C_{13}H_{21}NO_4$, which may be supposed to be the hydrocotarnine correlative in the narceine series, and which, together with hemipinic acid, is doubtless first produced by the reaction—



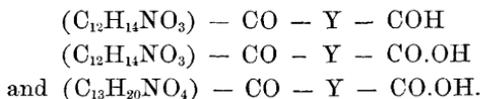
apparently much more readily resinized and otherwise altered than hydrocotarnine, so that as yet we have not succeeded in obtaining either it or its alteration-products in a fit state for analysis; no base analogous either to cotarnine or to hydrocotarnine could be obtained from the product of the oxidation of narceine by manganese dioxide, and sulphuric acid, the only substance obtainable in a state of sufficient purity for examination being a small quantity of unchanged narceine.

It may be noticed in passing that the formulæ attributed to narcotine, oxynarcotine, and narceine in these papers bear a close relationship to those of the unnamed products obtained by us, by acting on morphine and codeine with bibasic acids, *e.g.*, succinic and camphoric acids. (This Journal, 1875, 689.) Employing the empirical formulæ of morphine and codeine for simplicity's sake, these new bases may be written :—

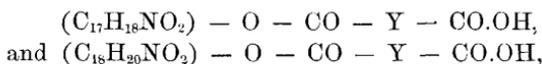


Y standing for the bivalent radicles C_2H_4 and C_6H_{14} , in succinic acid $C_2H_4(CO.OH)_2$, and camphoric acid $C_6H_{14}(CO.OH)_2$ respectively. Writing Y also for the bivalent radicle $C_6H_2(O.CH_3)_2$ of opianic acid,

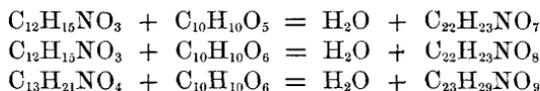
$C_6H_2(O.CH_3)_2 \left\{ \begin{array}{l} COH \\ CO.OH \end{array} \right.$ and hemipinic acid, $C_6H_2(O.CH_3)_2(CO.OH)_2$
narcotine, oxynarcotine, and narceine will be respectively written :—



There is, however, this difference between the morphine and codeine derivatives referred to, and the three opium-bases narcotine, oxynarcotine, and narceine, that, whilst the formulæ of the former may be still further dissected (in accordance with the reactions whereby the bodies are generated), thus :—



there is no evidence as yet that such further dissection is appropriate in the case of the latter three bases; *i.e.*, there is no evidence that a linking O-symbol may be interpolated between the nitrogenous radicle and the CO—Y— group in the case of these three substances; and hence it does not necessarily follow that narcotine, oxynarcotine, and narceine should be capable of synthesis from hydrocotarnine and opianic acid, hydrocotarnine and hemipinic acid, or the as yet not isolated base $C_{13}H_{21}NO_4$ and hemipinic acid, by the reactions—



although it is by no means improbable that such may be the case under suitable conditions. Experiments with a view to such syntheses are now being commenced.

§ 4. *Action of Potash on Narceine.*

In the hope of possibly obtaining the hypothetical base $C_{13}H_{21}NO_4$ from narceine by the action of alkaline solutions (just as the morphine and codeine derivatives above alluded to reproduce these bases together with succinic or camphoric acid when subjected to similar treatment), narceine was boiled for varying periods with very dilute caustic potash, and potassium carbonate solutions: the desired end was not attained, but a minute quantity of a new body was obtained apparently closely related to narceine. Ammonia and methylated ammonia were expelled during the boiling, and were collected by reception in dilute hydrochloric acid, and separated by absolute alcohol after evaporation

to dryness. In this way platinum salts were finally obtained, giving the following numbers:—

Ammonia platinum salt from hydrochloride insoluble in alcohol
0.2040 gram gave 0.900 Pt = 44.11 per cent.

Calculated for $(\text{NH}_4\text{Cl})_2\text{PtCl}_4$ 44.24 „

Trimethylamine platinum salt from one experiment 0.7580 gram
gave 0.2860 Pt = 37.73 per cent.

Calculated for $\{\text{N}(\text{CH}_3)_3\text{HCl}\}_2\text{PtCl}_4$ = 37.24 per cent.

Dimethylamine platinum salt from another experiment 0.3775 gram
gave 0.1320 CO_2 , and 0.1120.

0.6980 gram gave 0.2750 Pt.

Calculated for $\{\text{N}(\text{CH}_3)_2\text{H}_2\text{Cl}\}_2\text{PtCl}_4$.	Found.
Carbon..... 9.55	9.54
Hydrogen 3.18	3.29
Platinum..... 39.32	39.39

From these figures it results that no pyridine or other analogous volatile bases were formed. The production of trimethylamine seems to confirm the notion arrived at in § 3 (A), that narceine, like narcotire, contains *three* CH_3 groups, and hence that the hypothetical base $\text{C}_{13}\text{H}_{21}\text{NO}_4$ will be found to possess the formula $\text{C}_{12}\text{H}_{18}(\text{CH}_3)\text{NO}_4$ analogous to hydrocotarnine, $\text{C}_{11}\text{H}_{12}(\text{CH}_3)\text{NO}_3$.

The only product that could be obtained in a fit state for examination from the potash-liquors was a kind of weak acid; this was separated by acidulating and agitating with ether; on agitating the ethereal extract with potash, and adding hydrochloric acid to the alkaline liquid thus obtained, tarry flakes were precipitated; after recrystallisation from boiling alcohol two or three times, this substance formed minute white crystals fusing at 210° with slight decomposition in a capillary tube; if kept at 200° — 205° for a few minutes it became darker in colour, and melted some degrees below 210° ; it was sparingly soluble in cold and hot water and in cold alcohol, tolerably readily in hot alcohol and in ether; the solution had an acid reaction; the following numbers were obtained:—

0.3035 gram dried at 100° gave 0.6990 CO_2 and 0.1430 H_2O .

0.1930 „ „ „ 0.4375 „ „ 0.0920 „

0.2580 „ „ „ 0.5865 „ „ 0.1240 „

0.6300 burnt with soda-lime gave 0.1140 Pt.

	Calculated.		Found.			Mean
C_{23}	276	62.58	62.82	61.81	62.00	62.21
H_{23}	23	5.22	5.24	5.30	5.34	5.29
N	14	3.17	—	2.57	—	2.57
O_8	128	29.03	—	—	—	—
$\text{C}_{22}\text{H}_{23}\text{NO}_8$..	441	100.00				

These numbers agree better with the formula $C_{23}H_{23}NO_3$ than with any other equally probable formula; a result borne out by the following values obtained with the lead and mercuric salts precipitated by adding lead acetate and mercuric chloride respectively to a weak alcoholic solution of the acid.

0·1240 gram of lead salt gave 0·0415 PbO.	Pb = 31·05 per cent.
Calculated for $C_{23}H_{21}PbNO_3$	32·04 ,,
0·5900 gram gave 0·2210 HgS	Hg = 32·29 ,,
Calculated for $C_{23}H_{21}HgNO_3$	31·29 ,,

The yield of this substance from narceine was very small; only enough for the above analyses was obtained from about 100 grams of alkaloid; and as this was worked up in several different portions, the crystals ultimately obtained in each case were probably not absolutely pure owing to the small quantities dealt with. Admitting the above formula to be correct, this acid may be regarded as formed from narceine by the removal of the elements of water and of hydrogen:—



Concerning its actual structure no clue was obtained, except that by fusion with caustic potash it yielded a small amount of an acid giving all the reactions of *protocatechuic acid*; on treating narceine in the same way, keeping the semi-fused alkaloid well stirred up with the potash at a temperature of 230°—240°, a somewhat larger amount of this acid was obtained; after extraction by ether from the acidulated fused mass, and crystallisation from water (after decolorisation by animal charcoal) the following numbers were obtained:—

0·4530 gram lost at 100°	0·0480 gram = 10·59 per cent.
Calculated for $C_7H_6O_4, H_2O$	10·47 ,,

0·2735 gram of substance dried at 100° gave 0·5455 CO_2 and 0·1035 H_2O .

	Calculated.		Found.
C_7	84	54·54	54·39
H_6	6	3·90	4·20
O_4	64	41·56	—
$C_7H_6O_4$	154	100·00	

The dried substance melted at 197° (corrected), and on heating with pumice stone furnished a distillate of pyrocatechin, which, after crystallisation from benzene fused at 100°, gave the qualitative reactions of pyrocatechin, and gave the following numbers:—

0·1290 gram gave 0·3085 CO_2 and 0·073 H_2O .

	Calculated.		Found.
C ₆	72	65·45	65·22
H ₆	6	5·46	6·29
O ₂	32	29·09	—
<hr/>			
C ₆ H ₆ O ₂	110	100·00	

It deserves special notice that this production of protocatechuic acid from narceine by fusing potash is not visibly preceded by the formation of methyl-normeconin, as is the case with narcotine (Part III). Various experiments at lower temperatures made with a view to obtain the substance proved fruitless. This negative result is precisely what ought to be found if narcotine and narceine differ in that the one contains COH as a lateral benzene radicle, and the second CO.OH in the same position: narcotine first forms opianic acid, the aldehydic character of which allows of the formation of meconin, and hence of methyl normeconin, which finally becomes converted into protocatechuic acid; whilst narceine first forms hemipinic acid, which cannot be reduced to opianic acid or to meconin, and hence can form no methyl-normeconin, although by the continued action of potash it becomes converted into protocatechuic acid.
