II. "Researches into the Chemical Constitution of Narcotine, and of its Products of Decomposition."—Part IV. By Augustus Matthiessen, F.R.S., Lecturer on Chemistry in St. Bartholomew's Hospital, and C. R. A. Wright, B.Sc. London. Received February 18, 1869.

(Abstract.)

In Section I. of this memoir some new reactions of narcotine are described.

A. When narcotine is submitted to the action of water, either boiling in open vessels or at temperatures above 100° C. in sealed tubes, it splits up into meconin and cotarnine.

$$C_{22}H_{23}NO_7 = C_{10}H_{10}O_4 + C_{12}H_{13}NO_3.$$

The splitting up of narcotine under the influence of heated water may explain the occurrence of meconin in opium-residues, as probably the small amount of meconin always found there is simply due to the partial decomposition of the narcotine during the processes of extraction of morphia.

B. Narcotine heated *per se* to a little above 200° splits up as above into meconin and cotarnine, the latter being immediately decomposed at that temperature.

C. When hydrochlorate of narcotine is heated along with ferric chloride solution, the latter is reduced and the narcotine converted into opianic acid and cotarnine.

$$C_{22}H_{23}NO_7 + O = C_{10}H_{10}O_5 + C_{12}H_{13}NO_3.$$

Section II. treats of the decompositions of the narcotine-bases.

A. Dimethyl-nornarcotine, when heated to above 100° C. with water in sealed tubes, undergoes decomposition: from the corresponding narcotine reaction it would seem that this decomposition might take place in either of two ways:—

$$\underset{\text{Narcotine.}}{C_{19}H_{14}(CH_3)_3NO_7} = \underset{\text{Meconin.}}{C_8H_4(CH_3)_2O_4} + \underset{\text{Cotarnine.}}{C_{11}H_{10}(CH_3)NO_3}.$$

$$\underset{\text{Dimethyl-nornarcotine.}}{C_{19}H_{15}(CH_3)_2NO_7} = \underset{\text{Methyl-normeconin.}}{C_8H_5(CH_3)O_4} + \underset{\text{Cotarnine.}}{C_{11}H_{10}(CH_3)NO_3},$$

or

$$C_{19}H_{15}(CH_3)_2NO_7 = \underset{\text{Meconin.}}{C_8H_4(CH_3)_2O_4} + \underset{\text{Cotarnimide.}}{C_{11}H_{11}NO_3}.$$

Of these the former reaction is apparently the one which thus takes place.

This conclusion is borne out by the fact that, when treated with ferric or platinic chloride, the hydrochlorate of dimethyl-nornarcotine forms methyl-noropianic acid and cotarnine, and not opianic acid and cotarnimide.

$$\underset{\text{Dimethyl-nornarcotine.}}{C_{19}H_{15}(CH_3)_2NO_7} + O = \underset{\text{Methyl-noropianic acid.}}{C_8H_5(CH_3)O_5} + \underset{\text{Cotarnine.}}{C_{11}H_{10}(CH_3)NO_3},$$

and not

$$C_{19}H_{15}(CH_3)_2NO_7 + O = \underset{\text{Opianic acid.}}{C_8H_4(CH_3)_2O_5} + \underset{\text{Cotarnimide.}}{C_{11}H_{11}NO_3}.$$

B. From reasons given in the memoir, the reactions of methyl-nornarcotine and nornarcotine with heated water and oxidizing agents are as follows:—

Methyl-nornarcotine. Normeconin. Cotarnine.
$$C_{19}H_{16}(CH_3)NO_7 = C_8H_6O_4 + C_{11}H_{10}(CH_3)NO_3,$$
and not
Methyl-normeconin. Cotarnimide.
$$C_{19}H_{16}(CH_3)NO_7 = C_8H_5(CH_3)O_4 + C_{11}H_{11}NO_3,$$

Methyl-nornarcotine. Noropianic acid. Cotarnine.
$$C_{19}H_{16}(CH_3)NO_7 + O = C_8H_6O_5 + C_{11}H_{10}(CH_3)NO_3,$$
and not
Methyl-noropianic acid. Cotarnimide.
$$C_{19}H_{16}(CH_3)NO_7 + O = C_8H_5(CH_3)O_5 + C_{11}H_{11}NO_3,$$

Nornarcotine. Normeconin. Cotarnimide.
$$C_{19}H_{17}NO_7 = C_8H_6O_4 + C_{11}H_{11}NO_3,$$
Noropianic acid. Cotarnimide.
$$C_{19}H_{17}NO_7 + O = C_8H_6O_5 + C_{11}H_{11}NO_3.$$

Section III. contains some miscellaneous observations on opianic acid, meconin, and hemipinic acid.

A. Opianic acid treated with sulphuric acid and dilute solution of bichromate of potassium becomes oxidized to hemipinic acid.

$$C_{10}H_{10}O_5 + O = C_{10}H_{10}O_6.$$

When heated a few degrees above its melting-point, opianic acid loses water and yields a substance crystallizable from hot alcohol, differing in properties from opianic acid, and apparently containing $C_{40}H_{38}O_{19}$, being formed thus:—

$$4C_{10}H_{10}O_5 = H_2O + C_{40}H_{38}O_{19}.$$

B. All attempts to oxidize meconin to opianic or hemipinic acid were failures.

Nitrous acid gas passed into melted meconin caused the formation of nitromeconin, identical with that got by the action of nitric acid, each sample, however, giving rather different qualitative reactions from those usually ascribed to this substance.

C. Hemipinic acid, when heated to 170°, loses water and becomes an anhydride, $C_{10}H_8O_5$, which may be crystallized unaltered from absolute alcohol, but when treated with ordinary spirit of 90 per cent. alcohol forms ethyl-hemipinic acid, $C_{10}H_9(C_2H_5)O_6$.

Résumé of results obtained in the four portions of this research.*

(1) It has been shown from the analyses of various samples of narcotine derived from various sources, that narcotine has always the same composition, viz. $C_{22}H_{23}NO_7$ (vol. xii. p. 501).

* Parts I. & II. by Professor G. C. Foster and one of us, Proc. Roy. Soc. vol. xi. p. 55; xii. p. 501; xvi. p. 39. Part III. Proc. Roy. Soc. vol. xvii. p. 337. Part. IV. vol. xvii. p. 340.

(2) As stated by former observers, narcotine under the influence of oxidizing agents splits up into opianic acid and cotarnine.

$$C_{22}H_{23}NO_7 + O = C_{10}H_{10}O_5 + C_{12}H_{13}NO_3.$$

(3) When heated to a little above 200° *per se*, or for a considerable time in contact with water, narcotine splits up into meconin and cotarnine (vol. xvii. p. 340).

$$C_{22}H_{23}NO_7 = C_{10}H_{10}O_4 + C_{12}H_{13}NO_3.$$

(4) When narcotine is heated with excess of hydrochloric acid for a short time (about two hours), chloride of methyl is formed, and one atom of H substituted for CH_3 in the narcotine; if heated for a long time (some days), two atoms of H are substituted for two of CH_3; when heated with fuming hydriodic acid, iodide of methyl is formed in such quantities as to prove that three atoms of H are substituted for three of CH_3. A series of homologous bases is thus formed, whose decompositions are analogous to those of narcotine.

(5) Cotarnine has been shown to have the formula $C_{12}H_{13}NO_3$, and not $C_{13}H_{13}NO_3$, and is capable of crystallizing with half a molecule, and with a whole molecule, of water of crystallization.

(6) When cotarnine is heated with dilute nitric acid, under certain not clearly understood circumstances, cotarnic acid and methylamine is produced,

$$C_{12}H_{13}NO_3 + 2H_2O = C_{11}H_{12}O_5 + CH_5N;$$

with strong nitric acid, as stated by previous observers, apophyllic acid is produced; other oxidizing agents give no definite results (vol. xi. p. 59).

(7) When cotarnine is heated with strong hydrochloric acid, chloride of methyl is formed, and hydrochlorate of cotarnamic acid.

$$C_{12}H_{13}NO_3 + H_2O + 2HCl = CH_3Cl + C_{11}H_{13}NO_4, HCl.$$

Hydriodic acid produces a similar reaction, only *one* equivalent of CH_3 being removed for one of cotarnine (vol. xii. p. 503).

(8) Opianic acid under the influence of nascent hydrogen (as when treated with sodium-amalgam or zinc and sulphuric acid) is reduced to meconin (vol. xii. p. 503).

$$C_{10}H_{10}O_5 + H_2 = H_2O + C_{10}H_{10}O_4.$$

(9) Opianic acid heated with bichromate of potassium and dilute sulphuric acid becomes oxidized to hemipinic acid (vol. xvii. p. 341).

$$C_{10}H_{10}O_5 + O = C_{10}H_{10}O_6.$$

(10) Opianic acid heated with caustic potash splits up into meconin and hemipinic acid (vol. xi. p. 57).

$$2C_{10}H_{10}O_5 = C_{10}H_{10}O_4 + C_{10}H_{10}O_6.$$

(11) Opianic acid heated with excess of hydrochloric acid forms chloride of methyl, hydrogen being substituted for CH_3 in the opianic acid: it appears probable that two distinct substances are thus produced, noropianic acid and methyl-noropianic acid—the former by substitution of H_2 for

$(CH_3)_2$, and the latter by substitution of H for CH_3; only the latter has been isolated in a pure state, the former decomposing spontaneously.

$$C_{10}H_{10}O_5 + 2HCl = 2CH_3Cl + C_8H_6O_5,$$
$$C_{10}H_{10}O_5 + HCl = CH_3Cl + C_9H_8O_5.$$

Hydriodic acid apparently produces similar decompositions.

Like opianic acid, methyl-noropianic acid is monobasic (vol. xvi. p. 39).

(12) All experiments to oxidize meconin to opianic acid or hemipinic acid or any other product have proved failures.

(13) Meconin treated with excess of hydrochloric or hydriodic acid forms chloride or iodide of methyl, and a body derived from meconin by substitution of H for CH_3, methyl-normeconin.

$$C_{10}H_{10}O_4 + HCl = CH_3Cl + C_9H_8O_4.$$

Attempts to procure (hypothetical) normeconin by substituting H_2 for $(CH_3)_2$ did not yield anything capable of isolation in a pure state (vol. xvi. p. 39).

(14) Hemipinic acid treated with various reducing agents has in no case been reduced to opianic acid or meconin; nor have experiments to form opianic acid by the union of hemipinic acid and meconin been successful; nor has hemipinic acid been oxidized to any other compound.

(15) When hemipinic acid is heated with excess of hydrochloric acid, chloride of methyl and carbonic acid are formed, together with a new acid, methyl-hypogallic acid, in accordance with the following equation:—

$$C_{10}H_{10}O_6 + HCl = CH_3Cl + CO_2 + C_8H_8O_4.$$

When heated with hydriodic acid, hypogallic acid is found, together with iodide of methyl and carbonic acid: thus,

$$C_{10}H_{10}O_6 + 2HI = 2CH_3I + CO_2 + C_7H_6O_4$$ (vol. xvi. p. 40).

(16) The observations of Anderson, that hemipinic acid is bibasic, have been confirmed, and an anhydride obtained by simple desiccation (vol. xvii. p. 341).

$$C_{10}H_{10}O_6 = H_2O + C_{10}H_8O_5.$$

Methyl-hypogallic acid, however, is monobasic (vol. xvi. p. 40).

(17) Hemipinic acid is capable of crystallizing with different amounts of water of crystallization, crystals with half a molecule, with a whole molecule, and with two molecules of water having been obtained (vol. xvi. p. 40).

(18) All the reactions of narcotine and of its products of decomposition may be satisfactorily accounted for by the following rational formula:—

$$\left.\begin{matrix} CH_3 \\ (C_{11}H_9O_2)'' \end{matrix}\right\} N,$$
$$\left.\begin{matrix} (C_8H_4O)'''' \end{matrix}\right\} O_3,$$
$$\left.\begin{matrix} (CH_3)_2H \end{matrix}\right\} O_3.$$