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### THE IODIDES OF NARCEINE.

BY G. B. FRANKFORTER.

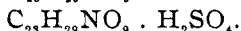
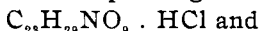
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THE alkaloid narceine when treated with iodine forms a characteristic blue substance analogous in many respects to the blue substance formed by the action of iodine on starch. This blue substance was first observed by Stein<sup>1</sup> in the early history of the alkaloid who regarded it as a periodide of narceine; but as pure narceine was then unknown, and as no definite formula was given for the substance, due allowance must be made in accepting his work.

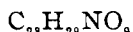
The isolation of pure narceine and the determination of the new empirical formula, as well as the synthetic structure,<sup>2</sup> has made it necessary to repeat all of the early investigations. So far, at present, as this repetition has been carried out, different conclusions have been reached. This fact explains in a degree the variations and contradictions of the early investigators. The formula of narceine was finally fixed by Anderson<sup>3</sup> as



and salts were prepared corresponding to



Later work on the alkaloids shows that both the chloride and sulphates are not salts of the base



but of a base containing one molecule of water less,



<sup>1</sup> Fresenius' *Zeitschrift für analytische Chemie*, 9, 390.

<sup>2</sup> Frankforter, "Beitrag zur Kenntniss des Narceins." Inaug. Dis., Berlin.

<sup>3</sup> Anderson, *Liebig's Annalen d. Chemie. and Pharmacie.*, 86, 182.

In like manner the iodides of narceine were found to be derivatives, not of the Anderson formula, but the same less one molecule of water.

*The Blue Iodide.*  $((C_{23}H_{27}NO_3)_3 I_2 + 3H_2O)$  When narceine is treated with a water solution of iodine the blue iodide is formed, varying in color from a gray to an indigo blue, according to the amount of iodine used. By treating crystals of narceine direct with iodine, indigo-blue crystals are formed which still retain the same crystal form of narceine. By heating they change from long fine prismatic needles to short irregular ones. The blue crystals are slightly soluble in water, soluble with difficulty in alcohol, and quite insoluble in ether and chloroform.

On treating with dilute sodium hydroxide the blue color disappears, and when excess is avoided fine felt-like crystals of narceine are formed. By treating the blue crystals suspended in water with silver nitrate in the presence of nitric acid, beautiful hexagonal columns are formed which are now in process of analysis. The blue crystals contain three molecules of water which may be removed at  $100^\circ C$ .

0.3836 gram of the iodide lost 0.0118 gram at  $100^\circ$ .

Found,  $3H_2O$ .  
3.07 per cent.

Calculated for,  
 $(C_{23}H_{27}NO_3)_3 I_2 + 3H_2O$ .  
3.29 per cent.

#### ANALYSES:

- I. 0.2020 gram iodide gave 0.4050 gram  $CO_2$ , 0.1107 gram  $H_2O$ .  
 II. 0.2632 " " " 0.5294 " " 0.1424 " "  
 III. 0.3109 " " " 0.0912 " AgI.

	I.	Found, II.	III.	Calculated for, $(C_{23}H_{27}NO_3)_3 I_2$ .
C	54.65 per cent.	54.82 per cent.		54.63 per cent.
H	6.08 " "	6.00 " "		5.10 " "
I			15.95 per cent.	16.01 " "

Dried at  $120^\circ$ – $130^\circ$  the blue color changes to a brownish, but changes back to the blue on cooling. The dried substance melts at  $176^\circ$ – $177^\circ C$ . If heated rapidly a melting point of  $180^\circ$ – $181^\circ$  may be obtained.

*The Red Iodide.*  $(C_{23}H_{27}NO_3)_3 I$ . It was found that by treating narceine with an alcoholic solution of iodine a grayish-blue substance was formed which proved to have different properties

from the blue iodide. On standing in the air, or by gently heating, it changes to a red color and loses its well-defined crystal form. Dried at  $110^{\circ}$ – $120^{\circ}$  it becomes brick red and changes slightly to the blue on standing some days in the air. It melts at  $181^{\circ}$  and is insoluble in water, alcohol, and ether. It contains three molecules of water which may be removed by drying at  $90^{\circ}$ – $100^{\circ}$ .

0.2209 gram iodide dried at  $100^{\circ}$ – $110^{\circ}$  lost 0.0092  $\text{H}_2\text{O}$ .

Found, $3\text{H}_2\text{O}$ .	Calculated for,
4.12 per cent.	$(\text{C}_{23}\text{H}_{27}\text{NO}_8)_3\text{I} + 3\text{H}_2\text{O}$ .
	3.56 per cent.

Analyses gave numbers which correspond best to the above formula.

## ANALYSES:

- I. 0.1826 gram iodide gave 0.3770 gram  $\text{CO}_2$ , 0.1025 gram  $\text{H}_2\text{O}$ .  
 II. 0.3763 " " " 0.0546 " AgI.

Found,		Calculated for,
I	II	$(\text{C}_{23}\text{H}_{27}\text{NO}_8)_3\text{I}$ .
C 56.35 per cent.		56.63 per cent.
H 6.23 " "		5.54 " "
I	7.84 per cent.	8.00 " "

Like the blue iodide it is transformed into narceine by carefully neutralizing with sodium hydroxide. In the presence of an alkali no iodide is formed. By treating with silver nitrate, slightly acidulated with nitric acid, fine long hexagonal columns crystallize out, on standing some hours in a cool place. The crystals are soluble in water and alcohol and melt at  $110^{\circ}$ – $112^{\circ}$ . They are in process of analysis. It will be observed that the analyses give the per cent. of hydrogen too high. This was also observed in a great many analyses made in determining the new formula for narceine. In all these analyses, some of which were made by professional analysts, the hydrogen ran too high. So that it is barely possible that the formula for narceine may be changed from  $\text{C}_{23}\text{H}_{27}\text{NO}_8$  to  $\text{C}_{23}\text{H}_{28}\text{NO}_8$ . This would raise the per cent. of hydrogen to 6.24, while the average of ten analyses made by four analysts gave an average of 6.4 per cent. This work was begun in the University of Nebraska, and for many favors received there, I wish to thank Prof. H. H. Nicholson.

UNIVERSITY OF MINNESOTA.