

LXXIV.—*On Mauveine and Allied Colouring Matters.*

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IN 1864 I gave an account of some experiments I had made on the crystallised colouring matter which had been obtained from the commercial mauve dye or aniline purple (*Proc. R. Soc.*, **12**, 713). I then stated that it contained an organic base having the formula $C_{27}H_{24}N_4$. Since then I have at various times made experiments on this product, and now beg to lay before the Society the principal results I have obtained up to the present time.

When the mauve dye was first prepared on the large scale, aniline made from what is now commercially known as 90 per cent. benzole was employed. It was soon found, however, that by using an aniline containing much larger quantities of toluidine, a colouring matter giving redder shades of purple was produced.* By taking advantage of this, two different products were manufactured, namely, a blue shade of mauve prepared from aniline, containing but little toluidine, and a red shade from an aniline containing large quantities of toluidine. The colouring matter was likewise prepared in two qualities, one being made by precipitating the aqueous solution of the crude colouring matter with sodic hydrate, and a second and purer quality by precipitating it with dilute sulphuric acid. It was noticed that the colouring matter precipitated by sulphuric acid had a satiny aspect, and was evidently crystalline, and this was especially the case with the product obtained from aniline containing considerable quantities of toluidine.

On dissolving this crystalline colouring matter in alcohol, and adding a little sulphuric acid, crystals were deposited, which when washed with alcohol, possessed a green metallic reflection. These consisted of what we now know as the sulphate of mauveine. As this salt is difficultly soluble in alcohol, and unsuitable for the dyer, it was boiled in alcohol with potassic acetate, and thus converted into the soluble acetate of mauveine; alcoholic sodic hydrate was then added in excess, and water added, which caused the mauveine to be entirely precipitated. This was collected, well washed, and dried. This mauveine was then dissolved in boiling alcohol acidulated with acetic acid, rapidly filtered, and allowed to stand to crystallise.

When manufacturing this product, it was always found best to use

* The use of toluidine and other homologues of aniline was claimed in the original patent. No. 1984, Aug. 26, 1856.

colouring matter made from aniline containing large quantities of toluidine, otherwise the crop of crystals was very small, most of the colouring matter remaining in solution. An account of the colouring matter found in the mother-liquors in the preparation of crystalline mauveine will be found described further on in this paper.

After the publication of my paper on "Mauve or Aniline Purple," I was induced to modify the formula of mauveine, and to regard it as containing C_{26} instead of C_{27} . This alteration would only require a difference of '6 per cent. less of carbon, and as my combustions had been made with lead chromate, it was thought that possibly some oxides of nitrogen might have escaped reduction by the copper used. A few numbers were also obtained which seemed to favour this view.

However, a number of careful experiments have since been made, and gave results which I think conclusively settle this point.

The following are combustions of various specimens of the hydrochloride of mauveine dried at $150^{\circ} C.$, and burnt in a boat, oxide of copper and metallic copper being used in the combustion tube:—

| | | |
|-------|-------|---------------------------------------------------|
| I. | ·227 | gram of substance gave |
| | 25·88 | c.c. of nitrogen at $20^{\circ} C.$ and 772·5 mm. |
| II. | ·286 | gram of substance gave |
| | ·7705 | „ of CO_2 , and |
| | ·143 | „ of OH_2 . |
| III. | ·276 | „ of substance gave |
| | ·741 | „ of CO_2 , and |
| | ·14 | „ of OH_2 . |
| IV. | ·293 | „ of substance gave |
| | ·791 | „ of CO_2 , and |
| | ·146 | „ of OH_2 . |
| V. | ·287 | „ of substance gave |
| | ·771 | „ of CO_2 , and |
| | ·145 | „ of OH_2 . |
| VI. | ·2345 | „ of substance gave |
| | ·6310 | „ of CO_2 , and |
| | ·125 | „ of OH_2 . |
| VII. | ·243 | „ of substance gave |
| | ·6535 | „ of CO_2 , and |
| | ·127 | „ of OH_2 . |
| VIII. | ·2705 | „ of substance gave |
| | ·725 | „ of CO_2 , and |
| | ·130 | „ of OH_2 . |

| | Theory for $C_{26}H_{24}N_4$. | Theory for $C_{27}H_{24}N_4$. |
|------------------|--------------------------------|--------------------------------|
| Carbon | 72·81 | 73·55 |
| Hydrogen | 5·83 | 5·67 |
| Nitrogen | 13·06 | 12·73 |

| | Experiment. | | | |
|----------------|-------------|-------|-------|------|
| | I. | II. | III. | IV. |
| Carbon | — | 73·47 | 73·22 | 73·6 |
| Hydrogen . . . | — | 5·55 | 5·63 | 5·54 |
| Nitrogen .. | 13·15 | — | — | — |

| | Experiment. | | | | Average. |
|------------------|-------------|-------|-------|-------|----------|
| | V. | VI. | VII. | VIII. | |
| Carbon | 73·26 | 73·39 | 73·34 | 73·09 | 73·34 |
| Hydrogen | 5·61 | 5·49 | 5·80 | 5·70 | 5·61 |
| Nitrogen | — | — | — | — | 13·15 |

Experiments were also made to find what quantity of hydrochloric acid a known weight of mauveine would combine with.

The following results were obtained :—

- I. 3·0362 gram of mauveine combined with
 ·2737 „ of HCl.
- II. 3·5869 „ of mauveine combined with
 ·3205 „ of HCl.

| | |
|---------------------------------------------------------------------------------|-------|
| The molecular weight of mauveine calculated from these experiments is | 406·7 |
| The formula $C_{27}H_{24}N_4$ requires | 404·0 |
| „ $C_{26}H_{24}N_4$ „ | 392·0 |

The following fresh analyses of the platinum salt were also made :—

- I. ·550 gram of substance gave
 ·088 „ of platinum.
- II. ·465 „ of substance gave
 ·9085 „ of CO_2 , and
 ·1755 „ of OH_2 .
- III. ·376 „ of substance gave
 ·730 „ of CO_2 , and
 ·144 „ of OH_2 .

| | Theory for $(C_{26}H_{24}N_4)_2H_2PtCl_6$. | Theory for $(C_{27}H_{24}N_4)_2H_2PtCl_6$. |
|--------------------|---------------------------------------------|---------------------------------------------|
| Carbon | 52·15 | 53·09 |
| Hydrogen | 4·34 | 4·09 |
| Platinum | 16·5 | 16·16 |

| | Experiment. | | |
|----------------|-------------|-------|-------|
| | I. | II. | III. |
| Carbon | — | 53·28 | 52·95 |
| Hydrogen | — | 4·19 | 4·25 |
| Platinum | 16·0 | — | — |

These results therefore confirm the original formula, $C_{27}H_{24}N_4$.

The platinum salt of mauveine when heated with water to between 120° and 150° C., gives up hydrochloric acid and hydrochloride of mauveine, which is easily removed by alcohol. From platinum determinations in the residue it appears probable that the decomposition takes place as follows:—



It is well known that mauveine yields different coloured solutions when mixed with acids in various states of concentration: thus, with dilute acids the ordinary purple solutions are obtained, if more concentrated blue solutions, and when very concentrated, as with ordinary sulphuric acid, dirty green solutions.

As it was believed that these colours indicated the existence of different salts, as in the case of rosaniline, attempts were made to prepare one of them.

On adding concentrated hydrochloric acid to a strong alcoholic solution of the acetate of mauveine until it becomes thoroughly blue, a quantity of a crystalline salt possessing a coppery lustre soon separates. This, after being pressed between linen, is found to be blue by transmitted light, but when washed with water or a little alcohol changes to purple, being converted into the ordinary hydrochloride. This salt is believed to be an acid hydrochloride, having the formula—



To prove this an attempt was made to produce the corresponding platinum salt. For this purpose, a somewhat dilute solution of acetate of mauveine was treated with an excess of concentrated hydrochloric acid, so that crystals might not separate; to this a solution of platinic chloride in concentrated hydrochloric acid was added. The dark blue precipitate which formed immediately was collected, washed with concentrated hydrochloric acid, pressed, and then dried by being placed in a bell-jar over caustic lime. It had a coppery aspect. When dry it was powdered and heated in the water-oven until constant. It gave on analysis 23·2 per cent. of platinum, the formula $C_{27}H_{24}N_4 \cdot H_2PtCl_6$ requiring 24·18 per cent. This result, although not very good, is perhaps as near as could be expected. This blue platinum salt, when washed with water, loses platinic chloride and hydrochloric acid.

Mauveine and Sulphuric Acid.

Mauveine may be heated with ordinary concentrated sulphuric acid without undergoing any change, but if fuming acid containing 50 per cent. SO_3 be used, on heating the mixture the mauveine is converted into a soluble sulpho-acid, forming blue-violet salts.

Action of Heat on Mauveine.

I have on a previous occasion mentioned that mauveine, when heated with aniline, produces a blue colouring matter which was believed to be a phenylic derivative of that base.

On heating acetate of mauveine with aniline the reaction takes place pretty readily, but no ammonia is given off. Numerous quantities of this blue product have been prepared and analysed, but no numbers have been obtained corresponding with those required by a phenylated mauveine or a compound of mauveine and aniline.

From experiments I have lately made I am induced to think that aniline plays no part in this reaction, as I find that pure mauveine, if carefully fused, yields a blue product apparently identical with that obtained when aniline is heated with it.

I am still experimenting in this direction, and hope to obtain a clearer insight into this reaction and the nature of the colouring matter produced.

Mauveine and Ethylic Iodide.

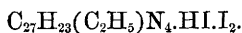
Ethylic iodide acts rapidly upon mauveine at 100°C. , with formation of hydriodide of mauveine and an ethylated derivative. The effect of ethylation, however, is quite different in this instance from that of rosaniline, so far as its influence on the colour of the compound is concerned, as in that case it becomes bluer, whilst in this it becomes redder.

Ethylated mauveine was manufactured commercially and known as "Dahlia." Its colour is between that of a salt of mauveine and rosaniline. As a colouring matter it resists the action of light to about the same extent as mauveine, and can be applied to dyeing and calico-printing in the same manner.

In manufacturing this product, mauveine, prepared from the crystallised acetate, was heated for three or four hours with alcohol and ethylic iodide. It was then allowed to cool thoroughly, and afterwards filtered off from the difficultly soluble hydriodide of mauveine which had been formed. Any free ethylic iodide was then distilled off, and the product diluted with alcohol until of a suitable strength for the consumer.

Sometimes magnificent crystals were deposited from strong solutions of the ethylated mauveine. They were oblique and possessed a golden-green metallic lustre. Their alcoholic solution was of nearly the same colour as the mother-liquor from which they were deposited. When these were formed in any quantity in an operation there was generally a good deal of an almost insoluble blackish-blue product containing iodine found associated with the hydriodate of mauveine.

A great many analyses of these beautiful crystals were made, but the composition of different preparations varied, none of them giving numbers agreeing with the hydriodide of an ethyl-mauveine, the carbon always coming too low. At last it was found that they contained, besides hydriodic acid, combined iodine. This was first discovered on the examination of a specimen which gave exceptionally low carbon determinations, and it was found, on treating it with an alcoholic solution of silver tartrate, that only part of the iodine was precipitated. This specimen was recrystallised from alcohol six times, and gave numbers which are not very far from those required by the formula—



| | Theory. | Experiment. | | |
|---------|---------|-------------|-------|-------|
| | | I. | II. | III. |
| C | 42.75 | 43.85 | 43.77 | 43.85 |
| H | 3.56 | 4.34 | 4.09 | 4.15 |

I have not been able to produce this substance at will, nor do I know the circumstances which most favour its formation. The other specimens of these crystals examined were apparently a mixture of this product and hydriodide of ethyl-mauveine.

To obtain compounds of ethyl-mauveine in a state of tolerable purity the following method was employed.

The crude alcoholic solution of the hydriodide, after being filtered from the hydriodide of mauveine, and heated to remove any excess of ethylic iodide, was diluted with alcohol, and mixed with alcoholic sodic hydrate. It was then gradually added to water to precipitate the colouring matter, which was then collected on a filter and washed. When the saline matter had been removed, and the colouring matter began to dissolve, warm water was used, and the coloured filtrate collected, the washing being continued until it became weak in colour. (From experiments I have lately made, I believe it would be better to boil the washed precipitated colouring matter in water, and then filter off the strongly coloured fluid.) The solution thus obtained was then saturated with sodium chloride, and after standing the colouring matter which had precipitated collected on a filter, and washed until it began to be dissolved. It was then redissolved in a

little boiling water, filtered, and allowed to stand, when it separated out as a crystalline precipitate of a brownish-red colour. This product is the hydrochloride of ethyl-mauveine, and gave the following numbers on analysis:—

- I. ·277 gram of substance gave
 ·749 „ of CO₂ and
 ·157 „ of OH₂.
- II. ·239 „ of substance gave
 23·37 c.c. of N at 17° and 764 mm.
- III. ·207 gram of substance gave
 20·75 c.c. of N at 16° and 774 mm.

| Theory for C ₂₇ H ₂₃ (C ₂ H ₅)N ₄ HCl. | Experiment. | | |
|------------------------------------------------------------------------------------------------|-------------|-------|-------|
| | I. | II. | III. |
| Carbon 74·27 | 73·74 | — | — |
| Hydrogen 6·19 | 6·37 | — | — |
| Nitrogen 11·95 | — | 11·82 | 11·90 |

The hydrochloride of ethyl-mauveine is very soluble in alcohol, forming a beautifully clear red-purple solution, which cuts off the green and most of the yellow from the spectrum, as in the case of a salt of mauveine. It is also moderately soluble in water; from this solution potassic hydrate separates the colouring matter as a purple-brown powder. Silver oxide also removes the colouring matter as a precipitate, silver chloride being formed at the same time.

Alcoholic potassic hydrate added to an alcoholic solution of the hydrochloride of ethyl-mauveine has but little influence upon its colour. Silver oxide renders it a trifle bluer in shade.

It dissolves in concentrated sulphuric acid, forming a dirty yellowish-green solution, changing to blue, and then to purple as it is diluted. With concentrated hydrochloric acid it forms a beautiful blue solution.

Platinum Salt.—An alcoholic solution of the hydrochloride of ethyl-mauveine, when mixed with platonic chloride also in alcoholic solution, gives a crystalline precipitate with a beautiful golden-green metallic reflection. When viewed under the microscope, this is seen to consist of oblique crystals, which appear like golden spangles by reflected light. This compound is only slightly soluble in alcohol. On analysis it gave the following numbers:—

- I. ·491 gram of substance gave
 ·07425 „ of platinum.
- II. ·471 „ of substance gave
 ·0710 „ of platinum.

| | | |
|-------|-------|--------------------------|
| III. | ·4902 | gram of substance gave |
| | ·0757 | „ of platinum. |
| IV. | ·3927 | „ of substance gave |
| | ·0607 | „ of platinum. |
| V. | ·408 | „ of substance gave |
| | ·0613 | „ of platinum. |
| VI. | ·2756 | „ of substance gave |
| | ·0430 | „ of platinum. |
| VII. | ·2905 | „ of substance gave |
| | ·5825 | „ of CO ₂ and |
| | ·1314 | „ of OH ₂ . |
| VIII. | ·3067 | „ of substance gave |
| | ·6144 | „ of CO ₂ and |
| | ·1377 | „ of OH ₂ . |
| IX. | ·4324 | „ of substance gave |
| | ·0670 | „ of platinum. |
| X. | ·3166 | „ of substance gave |
| | ·6313 | „ of CO ₂ and |
| | ·1438 | „ of OH ₂ . |
| XI. | ·4344 | „ of substance gave |
| | ·0657 | „ of platinum. |
| XII. | ·1710 | „ of substance gave |
| | ·3440 | „ of CO ₂ and |
| | ·0768 | „ of OH ₂ . |

| Theory for $2[\text{C}_{27}\text{H}_{23}(\text{C}_2\text{H}_5\text{N}_4)]_2\cdot\text{H}_2\text{PtCl}_6$. | Experiment. | | | |
|---------------------------------------------------------------------------------------------------------------|-------------|-------|-------|-------|
| | I. | II. | III. | IV. |
| Carbon | 54·52 | — | — | — |
| Hydrogen .. | 4·54 | — | — | — |
| Platinum .. | 15·45 | 15·12 | 15·08 | 15·44 |
| | | | 15·44 | 15·45 |

| | Experiment. | | | | |
|----------------|-------------|-------|-------|-------|-------|
| | V. | VI. | VII. | VIII. | IX. |
| Carbon | — | — | 54·66 | 54·68 | — |
| Hydrogen .. | — | — | 5·02 | 4·98 | — |
| Platinum .. | 15·02 | 15·60 | — | — | 15·49 |

| | Experiment. | | | Average. |
|----------------|-------------|-------|-------|----------|
| | X. | XI. | XII. | |
| Carbon | 54·38 | — | 54·85 | 54·64 |
| Hydrogen .. | 5·04 | — | 4·97 | 5·00 |
| Platinum .. | — | 15·12 | — | 15·26 |

The nitrate of ethyl-mauveine crystallises in beautiful crystals with a golden-green reflection.

I have already drawn attention to the existence of a second colouring matter in the mauve dye, differing from mauveine in its great solubility in alcohol. I have also mentioned that this is produced in the largest quantities when aniline of low boiling point is used. It is very difficult to free it from mauveine, as its solutions seem to act as solvents for the compounds of this colouring matter. I have made many experiments on this subject, and give an example of the processes used for its isolation.

A strong solution of the commercial mauve dye was first made by dissolving the dried paste in about three times its weight of boiling alcohol slightly acidulated, to this a small quantity of concentrated sulphuric acid was added, and the mixture allowed to stand two or three days. It was then filtered off from the sulphate of mauveine which had crystallised out. To the strong bronze-looking filtrate ether equal to about twice its bulk was gradually added, and after standing for a day or two the liquid was filtered off from deposited colouring matter, ether was again added, and after standing the solution filtered. A large excess of ether was then used, and the product set aside for some days. It was afterwards filtered, and the excess of the ether separated by distillation. The remaining purple solution was mixed with alcoholic potassic hydrate, added to boiling water, and heated until free from alcohol. The colouring matter which separated as a plastic mass was collected, washed, dried, and then dissolved in hot concentrated sulphuric acid to decompose or render soluble any impurities. The resulting green solution was diluted, and the precipitated colouring matter washed until the washings were but feebly acid and of a clear purple colour. It was then dissolved in boiling water, filtered, precipitated by the addition of sulphuric acid, and allowed to stand until cold; the precipitate was washed, redissolved, filtered, and again precipitated with sulphuric acid; when washed it was boiled with caustic potash, and, after removal of the alkali with water, dried. The black product was then dissolved in alcohol, with addition of a little potassic hydrate, and the solution filtered and evaporated to dryness. The resulting mass was ground with water, and was undoubtedly crystalline, as it gave the liquid a satiny aspect; it was finally well washed and dried. The following analyses were made with different specimens dried at 150° C. :—

- | | | |
|-----|--------|--------------------------|
| I. | .3640 | gram of substance gave |
| | 1.0569 | „ of CO ₂ . |
| II. | .1900 | „ of substance gave |
| | .5520 | „ of CO ₂ and |
| | .1000 | „ of OH ₂ . |

| | | |
|------|-------|--------------------------|
| III. | ·2608 | gram of substance gave |
| | ·7516 | „ of CO ₂ and |
| | ·1270 | „ of OH ₂ . |

These numbers give percentages agreeing with the formula



| Theory. | Experiment. | | |
|--------------------|-------------|-------|-------|
| | I. | II. | III. |
| Carbon | 79·12 | 79·18 | 78·59 |
| Hydrogen | 5·49 | — | 5·85 |

This base, which I propose to call *pseudo-mauveine*, differs from mauveine in being much more soluble in alcohol and in forming salts, which are also extremely soluble in that fluid. It is, however, like mauveine in being a very powerful base, and the combining with carbonic acid; it also dyes silk a shade of colour nearly identical with that produced with mauveine; and with concentrated sulphuric acid it forms a green solution, passing into blue and then purple on dilution. When heated it fuses, and yields a blue colouring matter.

Hydrochloride of Pseudo-mauveine.

This was prepared by dissolving the base in water very slightly acidulated with hydrochloric acid, filtering the purple solution, and precipitating by adding an excess of hydrochloric acid. The hydrochloride thus obtained was collected, washed, and dried. It was then dissolved in cold alcohol, filtered, and the solution evaporated to dryness. Thus obtained it has a greenish-golden reflection. It is more soluble in water than the hydrochloride of mauveine, and in alcohol it dissolves so freely that its solution may be obtained like a syrup with a bronze surface. Specimens of various preparations were examined, and gave the following numbers:—

| | | |
|------|-------|--------------------------|
| I. | ·3651 | gram of substance gave |
| | ·9674 | „ of CO ₂ and |
| | ·1728 | „ of OH ₂ . |
| II. | ·3774 | „ of substance gave |
| | ·9930 | „ of CO ₂ and |
| | ·1778 | „ of OH ₂ . |
| III. | ·3130 | „ of substance gave |
| | ·8281 | „ of CO ₂ and |
| | ·1577 | „ of OH ₂ . |
| IV. | ·2221 | „ of substance gave |
| | ·5868 | „ of CO ₂ and |
| | ·1143 | „ of OH ₂ . |

| | | |
|-----|-------|--------------------------|
| V. | ·3280 | gram of substance gave |
| | ·8648 | „ of CO ₂ and |
| | ·1718 | „ of OH ₂ . |
| VI. | ·2426 | „ of substance gave |
| | ·6456 | „ of CO ₂ and |
| | ·1205 | „ of OH ₂ . |

| | | Experiment. | | |
|-----------------------------------------------------------------|-------|-------------|-------|----------|
| | | I. | II. | III. |
| Theory for C ₂₄ H ₂₀ N ₄ .HCl. | | | | |
| Carbon | 71·91 | 72·26 | 71·75 | 72·15 |
| Hydrogen .. | 5·24 | 5·25 | 5·25 | 5·59 |
| | IV. | V. | VI. | Average. |
| Carbon | 72·05 | 71·90 | 72·57 | 72·11 |
| Hydrogen .. | 5·71 | 5·82 | 5·51 | 5·52 |

The hydrochloride of pseudo-mauveine, when dissolved in alcohol and mixed with an alcoholic solution of platinic chloride, yields a platinum salt in the form of a black non-crystalline powder. On analysis it gave the following numbers :—

| | |
|-------|---------------------------------|
| ·2152 | gram of substance gave |
| ·0372 | „ of platinum = 17·05 per cent. |

The formula (C₂₄H₂₀N₄)₂H₂PtCl₆ requires 17·29 per cent.

From the analysis of pseudo-mauveine and its hydrochloride, it is evident that it cannot be regarded as a homologue of mauveine, as it contains two atoms of hydrogen too many for such a compound.

I have found that pure aniline obtained from benzene prepared from benzoic acid yields when oxidised a purple colouring matter, having apparently all the properties of pseudo-mauveine; as, therefore, this colouring matter contains twenty-four atoms of carbon, it appears probable that it is a derivative of aniline.* Of course one naturally hesitates in speaking too decidedly about the formula of such a substance as pseudo-mauveine, on account of not being able to prepare it in a definitely crystalline condition; still from the large number of analyses made of different preparations, it is difficult to see how it can be incorrect.

Some experiments have been made to show, if possible, the compounds from which ordinary mauveine is derived. From what has already been stated about its preparation, there could be no doubt that it was a derivative of aniline and toluidine, but the question unanswered was, is it para- or ortho-toluidine?

* It has already been mentioned that aniline containing but little toluidine yields a colouring matter of a bluer shade than that containing much toluidine. This blueness is due to the presence of some secondary products which are precipitated by ether in the purification of pseudo-mauveine.

Experiments were first made upon the oxidation of the sulphates of these two toluidines alone, and then in combination with aniline.

A mixture of solutions of the sulphate of paratoluidine and potassic bichromate, when allowed to stand, deposits a large quantity of a brown precipitate; this was collected, washed, and dried. On digesting it with benzene it gives to it a rich orange-red colour. This benzoic extract when distilled to a small bulk, deposits beautiful garnet-red crystals of a new azo-derivative, having the percentage composition of azotoluene, but possessing different properties. This substance is now under investigation. The residue left by the benzene, when digested with alcohol, yielded no colouring matter.

The sulphate of orthotoluidine treated in a similar manner gives a purple benzoic extract. This, when agitated with hydrochloric acid, gives up its colouring matter as a precipitate which dissolves in alcohol, with a dirty green colour, becoming indigo-blue on the addition of potassic hydrate.

The residue left after treatment with benzene gives a purple colour to alcohol; the amount of colouring matter, however, is small, and of a much redder shade than mauveine, even when purified.

A mixture of sulphates of aniline and paratoluidine in molecular proportions gives when oxidised a brownish-black precipitate. This gives to benzene a brown extract, but the residue treated with alcohol yields considerable quantities of mauveine, which can be obtained in a crystalline condition.

A mixture of sulphate of aniline and orthotoluidine in molecular proportions yields a very black precipitate, yielding to benzene a purple-brown colour. The residue gives up colouring matter to alcohol, but the amount is comparatively small, and the product of a very red shade of purple not at all like that of a mauveine salt.

Judging from these results it would appear that mauveine is derived from aniline and paratoluidine.

Oxidation of Mauveine.

When the commercial mauve dye is oxidised, it is converted, amongst other products, into a beautiful red colouring matter. It was first observed as a bye-product in the preparation of this colouring matter, but afterwards was manufactured in sufficient quantities to send into the market. It was, however, an expensive product. Originally it was called "aniline pink," but afterwards "safranine," a name which has since been applied to a similar colouring matter obtained from orthotoluidine.

To prepare this substance, the mauve dye was dissolved in water acidulated with acetic acid, the solution kept boiling, freshly precipi-

tated peroxide of lead was then thrown in little by little, until the oxidation had proceeded far enough; sodic hydrate was afterwards added in slight excess, and the product filtered. The red filtrate was next boiled for a short time with a little powdered zinc and carbonate of lime, again filtered, and then slightly acidified with hydrochloric acid, the precipitation of the colouring matter being rendered complete by the addition of sodic chloride. It was thus obtained as a red-brown precipitate, dissolving in water or alcohol with a splendid red colour.

I commenced the investigation of this substance several years since, and found that it consisted of the hydrochloride of an organic base, which I now propose to call *parasafranine*. To purify it for analysis it was dissolved in boiling water and rendered somewhat strongly alkaline with caustic alkali filtered from a small quantity of a purple colouring matter which had been precipitated and then thrown down by neutralising with hydrochloric acid and saturating the liquid with common salt. This process was repeated until all the purple-colouring matter had been separated. The product is the hydrochloride of *parasafranine*. If other salts are required I found it convenient in many cases to dissolve this hydrochloride in boiling water, render it alkaline with caustic alkali, and then acidify with the desired acid, and if necessary saturate the solution with a soluble salt of the acid used. The precipitated compound is then collected, washed, and crystallised. The oxalate prepared in this manner may be obtained in needles of a dark-green metallic aspect simply by adding oxalic acid and allowing the solution to stand. The nitrate also comes down readily on the addition of nitric acid.

In my earliest experiments I worked with the hydriodide of this colouring matter, because it was less soluble in alcohol than the hydrochloride, and thinking that perhaps it was a feeble base a little hydriodic acid was added each time it was crystallised. On analysis it was found that the more frequently it was recrystallised the lower the percentage of carbon came. At last a product was obtained which appeared to be definite, and gave numbers agreeing with the formula $C_{18}H_{18}N_4HI$. They are as follows:—

| Theory. | Experiment. | | | |
|----------------|-------------|-------|-------|-------|
| | I. | II. | III. | |
| Carbon | 51·6 | 51·64 | 51·65 | 51·51 |
| Hydrogen .. | 4·5 | 4·57 | 4·51 | 4·39 |

After this, however, I obtained a specimen containing still less carbon, and this led me to discontinue working with this salt. I have not examined carefully into the cause of this change of composition, but it appears probable that it was due to the combination of the

hydriodide with free iodine from the oxidation of the hydriodic acid used.

I then examined other salts. A specimen of the hydrochloride of parasafarine was crystallised from alcohol, in which it was very soluble: it was obtained in a confused crystalline condition. It gave the following numbers on analysis:—

| | | |
|-----|-------|--------------------------|
| I. | ·2605 | gram of substance gave |
| | ·6492 | „ of CO ₂ and |
| | ·1305 | „ of OH ₂ . |
| II. | ·6265 | „ of substance gave |
| | ·2586 | „ of AgCl. |

These give percentages agreeing with the formula C₂₀H₁₈N₄.HCl.

| Theory. | Experiment. | |
|--------------------|-------------|-------|
| | I. | II. |
| Carbon | 68·44 | 67·96 |
| Hydrogen | 5·42 | 5·56 |
| Chlorine | 10·41 | — |
| | | 10·21 |

Nitrate of Parasafarine.—This salt crystallises beautifully from alcohol in long needles with a dark-green metallic reflection, and when seen by strong transmitted light they appear of a dark garnet-red colour. It is rather difficultly soluble in cold water and only moderately so in boiling water. It is not very soluble in cold, but freely so in boiling alcohol. Specimens dried at 140—150° gave the following numbers:—

| | | |
|-----|-------|--------------------------|
| I. | ·3005 | gram of substance gave |
| | ·7016 | „ of CO ₂ and |
| | ·1400 | „ of OH ₂ . |
| II. | ·2284 | „ of substance gave |
| | ·5320 | „ of CO ₂ and |
| | ·1104 | „ of OH ₂ . |

| Theory for C ₂₀ H ₁₈ N ₄ .HNO ₃ . | Experiment. | |
|-------------------------------------------------------------------------------|-------------|-------|
| | I. | II. |
| Carbon | 63·6 | 63·67 |
| Hydrogen | 5·04 | 5·15 |
| | | 5·37 |

The results of the analysis of these salts coincide with those lately published by Messrs. Dale and Schorlemmer in this Journal (p. 682).

The salts of parasafarine differ in solubility and crystallise better

than those of the safranine examined by Hofmann and Geyger. I find, however, that commercial safranine also contains a little parasafraanine. The specimen I examined was made about four years since and obtained from Messrs. Guinon and Co. of Lyons. Some of this product was dissolved in a large quantity of boiling water and rendered strongly alkaline with caustic alkali; this caused most of the colouring matter to precipitate, but on filtration a strong red solution was obtained. The solution was acidified with nitric acid, and when cold the precipitate was collected, washed, and further purified by crystallisation from alcohol. On analysis it gave the following numbers:—

·2339 gram of substance gave
 ·5450 ,, of CO₂ and
 ·1132 ,, of OH₂.

These represent carbon 63·54 per cent. and hydrogen 5·37 per cent., and agree closely with those required by the formula C₂₀H₁₈N₄.HNO₃.

Silk dyed with this product was of the same shade as when dyed with the colouring matter from mauveine.

The safranine which had been precipitated with caustic alkali was dissolved in boiling water acidulated with acetic acid, filtered and precipitated with nitric acid; the nitrate thus obtained was crystallised from alcohol, and on analysis gave the following numbers:—

·2480 gram of substance gave
 ·5830 ,, of CO₂ and
 ·1240 ,, of OH₂.

These give percentages agreeing with the formula C₂₁H₂₀N₄.HNO₃.

| | Theory. | Experiment. |
|--------------------|---------|-------------|
| Carbon | 64·45 | 64·11 |
| Hydrogen | 5·37 | 5·55 |

Safranine salts differ from those of parasafraanine in the colour they dye silk, yielding shades which are somewhat more scarlet.

Pseudo-mauveine, when oxidised, yields a colouring matter similar to parasafraanine. This is probably present in the product obtained by oxidising the commercial mauve dye, but lost in the after processes of purification.

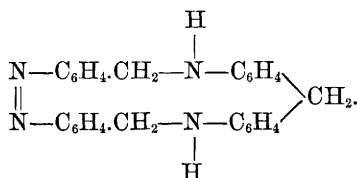
Up to the present very little is known of the constitution of mauveine, but there can be no doubt it is derived from aniline and paratoluidine.

Hofmann has shown that safranine is derived from 3 molecules of orthotoluidine; now as parasafraanine contains one atom less of carbon than this compound, and is derived from mauveine, it is more than pro-

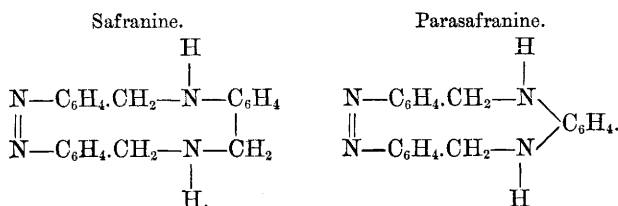
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bable that it is formed from 2 molecules of paratoluidine and 1 molecule of aniline; and as mauveine contains 7 atoms more carbon, it would be a derivative of 3 molecules of paratoluidine and 1 molecule of aniline; this would also be gathered from its containing 27 atoms of carbon.

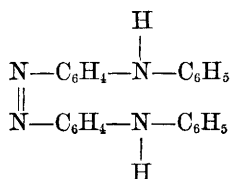
Now, as aniline and also paratoluidine yield azo-derivatives when oxidised, it is very probable that mauveine may belong to that class of compounds, and, if so, might perhaps be represented thus:—



Safranine and parasafrafranine might also be represented in a somewhat similar manner:—



And pseudo-mauveine as—



I bring these forward merely as suggestions; experiment alone can settle the true constitution of these bodies. I am at present making some experiments upon the acetylic replacement-derivatives of mauveine and safranine, which I hope may throw a little additional light upon the matter.

