

LXXX.—*The Colouring Matters of Drosera Whittakeri.*

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SINCE the previous paper on this subject (Trans., 1887, **51**, 371) was communicated to the Society, efforts have been made to complete the examination of these colouring matters, but owing to the difficulty and expense of obtaining material and to constant interruptions in the prosecution of the work, the investigation is still far from complete. It is thought better, however, the supply of material having been for the present exhausted, to lay such results as have been obtained before the Society, rather than to wait a considerably longer time before publishing anything more.

The purification of the crude material used in these experiments was effected much in the same way as previously described (*loc. cit.*), but a fatty matter, not before noticed, which is soluble in hot alcohol and separates out on cooling, gave some considerable trouble, necessitating a second, and in some cases a third, sublimation, besides additional crystallisations, before the substance was obtained in a satisfactory condition. The two colouring matters were separated, as before, by crystallisation from glacial acetic acid.

Further examination of the less soluble substance, C₁₁H₈O₅.

In order to fully confirm the preliminary work (*loc. cit.*), three more combustions of the less soluble substance were made after recrystallising it several times. The following are the results.

0.2459	gave	0.5385	CO ₂	and	0.0900	H ₂ O.	C = 59.72; H = 4.06.
0.2588	„	0.5668	„	0.0899	„		C = 59.75; H = 3.86.
0.2320	„	0.5075	„	0.0813	„		C = 59.66; H = 3.89.
C ₁₁ H ₈ O ₅ requires C = 60.00; H = 3.64 per cent.							

All these specimens melted at 192° , the same melting point as that previously found. There can be no doubt, therefore, as to the identity of this substance with that previously prepared.

Molecular Weight.—An attempt to obtain the vapour density by Victor Meyer's method having failed, owing to decomposition of the substance, recourse was had to Raoult's freezing point method, using glacial acetic acid as solvent, with the following results.

	I.	II.
1. Weight of substance taken...	0.117 gram.	0.126 gram.
Weight of solvent.	28.81 grams.	27.27 grams.
Depression of freezing point..	0.065° .	0.08° .

Therefore, using the constant 3860, given by Ostwald for acetic acid,

$$\text{Molecular weight, I} = \frac{3860 \times 0.117}{0.065 \times 28.81} = 241;$$

$$\text{II} = \frac{3860 \times 0.126}{0.08 \times 27.27} = 223.$$

Molecular weight calculated for $\text{C}_{11}\text{H}_8\text{O}_5 = 220$.

These results are fairly close, considering the slight solubility of the substance in cold acetic acid, and the consequent small range of alteration in the freezing point of the solvent.

Acetyl derivative.—Previous experiments having indicated the probable existence of three hydroxyl groups in the substance $\text{C}_{11}\text{H}_8\text{O}_5$, experiments were made to prove this point. Some of the substance was heated in a sealed tube during several hours, at 150 — 160° , with excess of acetic anhydride. On cooling, a yellow substance crystallised out, which was several times recrystallised from benzene after draining off the mother liquors. It melted at 153 — 154° . Another sample, prepared in the same way, gave the same melting point, but the yield was unsatisfactory. Some more of the substance was then boiled for a few minutes with excess of acetic anhydride and a small piece of zinc chloride in an ordinary beaker covered with a watch glass. On cooling, an abundant crop of yellow crystals was obtained, and these, after one or two crystallisations from glacial acetic acid, were found to be pure; the melting point, however, was only 137 — 138° . Several other specimens prepared in the same way, after eight to 10 recrystallisations, gave still the same melting point. There was obviously, therefore, some marked difference between this substance and that prepared by the previous method. Several experiments were therefore made to determine by hydrolysis the nature of the substance of melting point 137 — 138° , the process being carried out in the follow-

ing manner. A weighed quantity was boiled during a few minutes with a solution of caustic soda, then acidified with hydrochloric acid, and, after cooling, the liquid was extracted with ether until colourless. The ethereal extract was then distilled in a tared flask, and the weight of the residue determined. A previous experiment, carried out in a similar way with a weighed quantity of the original substance of the formula $C_{11}H_8O_5$, had shown that the process was very fairly accurate. The following results were obtained, the samples of acetyl derivative *having been all dried at 100°*.

0.3318 gram	gave	0.1880 $C_{11}H_8O_5$	=	56.6	per cent.
0.4495	„	0.2575	„	=	57.3 „
0.2383	„	0.1345	„	=	56.4 „
0.2187	„	0.1240	„	=	56.7 „

As a triacetyl derivative should yield 63.6 per cent. of $C_{11}H_8O_5$, these figures were obviously unsatisfactory, but on further examination the difficulty disappeared. It was found that the substance melting at 137—138° very slowly lost weight at 100°, and much more rapidly at 120—130°, finally, however, ceasing to lose weight, and then *melting at 153—154°*. An experiment with a sample treated in this way, and melting at 153—154°, gave a much more satisfactory result, 0.2812 gram yielding 0.1772 $C_{11}H_8O_5$ = 63.01 per cent.

The figures obtained in the previous experiments leave little doubt that the substance melting at 137—138° is a compound of the triacetyl derivative melting at 153—154° with 1 mol. of acetic acid (acetic acid of crystallisation?). Such a compound should yield 54.18 per cent. of $C_{11}H_8O_5$ on hydrolysis. That the figures actually obtained are from 2 to 3 per cent. higher than this is doubtless due to the fact that the samples used had been dried during some time at 100°, and therefore had lost some acetic acid. In fact, by simply keeping during several weeks in the air, a considerable part of the acetic acid was given off. A direct determination of the loss at 120—130° gave the following results.

0.448 gram substance lost 0.069 gram = 15.4 per cent.

$C_{11}H_8O_5(C_2H_3O)_3 + C_2H_4O_2$ requires = 14.77 „

That the loss of weight was due to the escape of acetic acid, and not of water, was pretty obvious from the method of preparation, and from the fact that in the process of heating the yellow colour did not change, as it would have done in the presence of water from partial hydrolysis. In order to remove any doubt, however, a direct experiment was made which showed that acetic acid was actually given off.

Metallic Derivatives.—It was mentioned in the previous paper (*loc. cit.*) that a small quantity of crystalline substance had been obtained which appeared to be a potassium derivative. Further

experiments have shown that some metallic derivatives are comparatively easily obtained. On boiling the substance with sodium carbonate and a little water, complete dissolution was effected, carbonic anhydride was evolved, and, on cooling, a mass of crystals of a rich brown colour separated. Under the microscope, they appeared as short, dark, reddish-brown needles; they were recrystallised from water and heated to 100° ; they did not, however, become anhydrous at 100° , but gave off more water when heated at 130 – 140° .

0.405 gram substance lost (at 130 – 140°) $0.0522 \text{ H}_2\text{O} = 12.88$.

0.3039 ,, (dried at 100°) gave $0.0782 \text{ gram Na}_2\text{SO}_4$,
 $\text{Na} = 8.33$.

$\text{C}_{11}\text{H}_7\text{O}_5\text{Na}_2 \cdot 2\text{H}_2\text{O}$ requires $\text{Na} = 8.27$; $\text{H}_2\text{O} = 12.95$ per cent.

This compound is therefore a monosodium derivative retaining 2 mols. of water at 100° .

On adding a solution of the monosodium derivative to a solution of calcium chloride, a crystalline precipitate of a rich, dark-brown colour was formed, which, like the monosodium derivative, is not anhydrous at 100° .

0.225 gram, dried at 100° , lost (at 130 – 140°) $0.0235 \text{ H}_2\text{O} = 10.44$,
 and yielded 0.0605 CaSO_4 . $\text{Ca} = 7.9$ per cent.

$(\text{C}_{11}\text{H}_7\text{O}_5)_2\text{Ca} \cdot 3\text{H}_2\text{O}$ requires $\text{Ca} = 7.52$; $\text{H}_2\text{O} = 10.15$.

The barium derivative separated from the solution as a thick jelly which could not be obtained in a crystalline state. The silver derivative could not be precipitated by adding the monosodium salt to a solution of silver nitrate.

On adding to the monosodium derivative a quantity of *pure* caustic soda (very slightly in excess of that required to form a disodium derivative) dissolved in a small quantity of water, the mass, which was at first quite thin and watery, soon became almost solid, and exhibited a distinct green *sheen* like that possessed by rosaniline salts. A little cold water having been added, the mass was filtered under reduced pressure, washed with a little cold water, and then left *in vacuo* over sulphuric acid during several hours. Under the microscope, it appeared as a homogeneous mass of needles.

0.2305 gram, heated at 100° , lost 0.0115 gram , and, on further heating at 120 – 140° , lost nothing more; loss = 4.99 per cent.

Theory for $\text{C}_{11}\text{H}_6\text{O}_5\text{Na}_2 \cdot \text{H}_2\text{O}$ is 6.38 per cent.

Possibly the substance had lost some water *in vacuo*, but it is obviously different from the monosodium derivative.

0.219 gram dry substance gave $0.1205 \text{ gram Na}_2\text{SO}_4$. $\text{Na} = 17.82$.

$\text{C}_{11}\text{H}_6\text{O}_5\text{Na}_2$ requires $\text{Na} = 17$.

Other samples were made in a similar way, but had a less satisfactory appearance, and did not show the green *sheen* so well as the first sample; they gave respectively $\text{Na} = 16.4$ and 16.77 . These figures are not so satisfactory as could be wished, but they indicate the existence of a disodium derivative. Further experiments could not be undertaken for want of material.

Oxidation.—It was previously shown that the substance $\text{C}_{11}\text{H}_8\text{O}_5$, when oxidised by dichromate mixture, yields acetic acid. Attempts to obtain an intermediate oxidation product by other oxidising agents have so far failed. Nitric acid oxidises it completely and easily to oxalic acid.

Attempts to prepare an Acetyl Derivative of the Reduction Product $\text{C}_{11}\text{H}_{10}\text{O}_5$.—The reduction product, $\text{C}_{11}\text{H}_{10}\text{O}_5$, mentioned in the previous paper, was boiled with excess of acetic anhydride and a fragment of zinc chloride; a white, crystalline substance was obtained, but only in small quantity, and was difficult to purify (at least with the small amount in hand). Sufficient material could not be obtained for a proper examination. One sample melted at 204 — 205° .

Further Examination of the Substance $\text{C}_{11}\text{H}_8\text{O}_4$.

A fresh quantity of the more soluble substance $\text{C}_{11}\text{H}_8\text{O}_4$ was prepared from the mother liquor after crystallisation of the less soluble substance, much in the same way as previously described, but instead of attempting to purify it more thoroughly by further crystallisation, it was boiled during a few minutes with acetic anhydride and a fragment of zinc chloride. On adding water to the product, a mass of yellow crystals soon formed, which proved to be a mixture of a small quantity of the acetyl derivative of the compound $\text{C}_{11}\text{H}_8\text{O}_5$ with a larger quantity of the acetyl derivative of the compound $\text{C}_{11}\text{H}_8\text{O}_4$. The two substances could, however, be separated with comparative ease by crystallisation, the former being much the less soluble. On hydrolysing the latter with caustic soda and acidifying with hydrochloric acid, the original substance, $\text{C}_{11}\text{H}_8\text{O}_4$, was obtained. This was recrystallised from a large quantity of water containing a trace of acid. Various samples obtained in this way melted at temperatures varying from 170° to 175° , and after two crystallisations from alcohol, at 174 — 175° . A specimen on combustion gave the following result, confirming the formula originally given.

0.2004 gave 0.4734 CO_2 and 0.0755 H_2O . $\text{C} = 64.42$; $\text{H} = 4.18$.

$\text{C}_{11}\text{H}_8\text{O}_4$ requires $\text{C} = 64.70$; $\text{H} = 3.92$ per cent.

There is reason to doubt, however, whether the substance thus obtained is pure. (See under *Oxidation*.)

Acetyl Derivative.—The acetyl derivative was obtained by adding water to the mother liquor left after separation of the acetyl derivative of $C_{11}H_8O_6$, as described above, and further purifying the precipitate by dissolving again in acetic acid (not so strong as commercial glacial acid), and fractionally precipitating by addition of water, rejecting the earlier portions of the precipitate. It was then again crystallised from acetic acid. All the samples so prepared consisted of yellow needles melting at $109-110^\circ$. On combustion of the substance dried at 100° the following results were obtained.

0.1050 gave 0.2425 CO_2 and 0.0455 H_2O . C = 62.98; H = 4.81.

0.2117 „ 0.4867 „ 0.0877 „ C = 62.70; H = 4.65.

$C_{11}H_8O_4(C_2H_5O)_2$ requires C = 62.50; H = 4.16 per cent.

On hydrolysing exactly in the manner described in the earlier part of the paper, the following results were obtained.

0.4100 gave 0.2845 $C_{11}H_8O_4$ = 69.4.

0.5435 „ 0.3805 „ = 70.0.

$C_{11}H_8O_4(C_2H_5O)_2$ requires 70.83 per cent.

A diacetyl derivative is therefore formed.

A small specimen made from the purest specimen of $C_{11}H_8O_4$, obtained as above described, melted at 110° , but as it is doubtful, for reasons to be presently stated, whether the original substance was pure, the purity of the acetyl derivative is equally doubtful.

Metallic Derivatives.—The substance readily dissolves in a solution of sodium carbonate, but the sodium salt is so soluble that it has not yet been obtained in a form suitable for analysis.

Oxidation.—About 0.5 gram of the substance was boiled during some time, in a reflux apparatus, with a dichromate mixture containing about 5 per cent. of $K_2Cr_2O_7$ and 10 per cent. H_2SO_4 . The liquid was then distilled to a small bulk, water added, and again distilled. The strongly acid distillate was neutralised with barium carbonate, and the barium salt purified in the usual manner. It behaved as an acetate, and a barium determination gave the following result.

0.2582 gave 0.2362 $BaSO_4$. Ba = 54.22.

Barium acetate requires Ba = 53.72 per cent.

The residual liquid in the flask after the distillation yielded to ether a very small quantity of a crystalline substance, not sufficient in quantity for examination.

An attempt to moderate the oxidation, and so obtain an intermediate product, led to a curious and unexpected result. About 0.7 gram of the substance $C_{11}H_8O_4$ was introduced into a flask with a quantity of water and carbon tetrachloride, and the flask attached to a reversed

condenser. The mixture was heated to boiling, and, by means of a tap funnel passing through the cork, about 47 c.c. of an oxidising solution of the same strength as mentioned above was slowly run in, the object being to ensure, as far as possible, an excess of the oxidisable substance during the operation, the quantity of dichromate being insufficient for complete oxidation. On cooling and standing, a small quantity of *yellow* crystals separated, both from the aqueous solution and from the carbon tetrachloride. These crystals, after washing and drying, melted at about 178° , and gave the qualitative reactions of the original substance, but the quantity was not large enough for complete examination. If this be the substance $C_{11}H_8O_4$ in a purified condition (the colour of all samples hitherto prepared being red), and it seems at least probable that it is, it follows that the less soluble substance, $C_{11}H_8O_5$, must adhere very obstinately in small quantity to its companion. It would also follow, of course, that the substance $C_{11}H_8O_5$ is the more easily oxidisable, at any rate by chromic acid. Without further investigation it is, perhaps, too early to assume that this interpretation is correct, but, if it is so, it has struck the writer that this result may have some bearing on Dr. Armstrong's contention that the colours of certain substances, which he believed should be colourless, are due to small quantities of obstinately adhering impurities.

Conclusion.—Material is wanting at present for a continuation of this investigation, but more is being accumulated with a view to an attempt at its completion. The experiments above described, however, so far as they go, fully bear out the opinion previously expressed, that these substances are hydroxy-derivatives of a methylnaphthaquinone.
