XXXVI.—*The Colouring Matter of Drosera Whittakeri.*

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Preliminary Notice.

AMONG the many species of *Drosera* to be found in Australia, one, *Drosera Whittakeri*, which grows plentifully on the hills near Adelaide, is conspicuous in the spring-time by its pretty white flowers, resembling those of the white oxalis. This species is provided with a tuber, one apparently to each plant, which is found attached to a straight stem at a depth of 3 or 4 inches. These tubers invariably consist of an inner solid but soft nucleus, full of reddish sap or juice, and an outer series of easily detached thin and more or less dry layers of an almost black material. Between these layers is to be found small quantities of a brilliant red colouring matter, the amount varying in tubers of different size and age, but apparently more plentiful in the older plants. My attention was drawn to the plant by Professor Tate, of Adelaide University, and on inquiry I found that Mr. Francis, of this city, had extracted the colouring matter by means of carbon bisulphide, found that it was volatile, and that by its means beautiful tints could be produced on silk by the use of various mordants, but beyond that had not continued the investigation.

A preliminary examination having shown that the substance could be obtained in the crystalline condition, it was determined to further investigate it. The plant is easily obtainable in spring, but on the

approach of summer the leaves dry up and disappear. When it is remembered that the yield of colouring matter is very small, that the tubers vary from $\frac{1}{4}$ to $\frac{3}{4}$ inch in diameter, and that to obtain each tuber it is necessary to dig down 4 or 5 inches, often in hard soil, it will be easily understood that a considerable amount of labour is required to collect even a moderate quantity. The time and labour at my disposal being limited, I have only been able to obtain about 4 quarts (weight unfortunately not noted) of the tubers. The crude colouring matter obtained, as described below, from this quantity did not amount to more than 5 or 6 grams at the utmost. The method of extraction was as follows:—

The tubers were well crushed, and repeatedly treated with hot strong alcohol, washed with strong alcohol till the filtrate became almost colourless, and the spirit then distilled off. The residue, still containing a little alcohol, was then mixed with some water, allowed to stand, and filtered. In this way, almost the whole of the colouring matter was obtained as a dark-red mass on the filter-paper. This was dried, and then sublimed. The subliming apparatus consisted of a common saucepan, over the mouth of which was placed an ordinary tinned-iron sand-bath dish, and then inverted over this a large glass funnel, having its neck closed by a cork. The filter-paper with the substance was placed on the tin dish, and the temperature raised till sublimation went on freely, but not to such a point as to cause fusion. A considerable amount of carbonaceous matter always remained behind, but this appeared to consist of a quantity of charred resinous (?) matter extracted by the alcohol, and not to be a product of decomposition, subsequent experiments having shown that sublimation of the purified material could be effected with little or no change.

The sublimate thus obtained was of a brilliant vermilion colour, partly adhering closely to the surface of the glass, and partly in feathery crystals. Three specimens of this apparently pure material were burnt with the following results:—

	I.	II.	III.
Carbon	62·00	61·35	62·46
Hydrogen	4·27	4·84	4·51

These numbers being scarcely satisfactory for a homogeneous material, small quantities of the substance were dissolved in some suitable solvent, a few drops allowed to evaporate, and the residue examined microscopically. This at once revealed the presence of at least two substances, one crystallising in small reddish plates, and the other in longer yellow or reddish-yellow needles, the latter occurring chiefly on the *outer* rim of the evaporated drop, indicating later deposition and therefore greater solubility. After a few trials, it was

found that one of these substances, being much less soluble, could be separated by crystallisation from boiling alcohol or boiling glacial acetic acid. From either of these liquids, the less soluble substance separates on cooling in small, brilliant, red plates, canoe-shaped under the microscope. Below are the results of combustion, the specimens used having been obtained from *different* portions of crude sublimate as follows :—

- I. Crystallised three times from boiling glacial acetic acid.
- II. No. I crystallised once more from the same solvent.
- III. Crystallised first from glacial acetic acid, then twice from boiling alcohol, then twice more from glacial acetic acid.
- IV. Crystallised first from boiling alcohol, then twice from glacial acetic acid.
- V. Crystallised first from boiling alcohol, then three times from glacial acetic acid.

The crystallisation was in each case continued until a drop of the mother-liquid, evaporated on a glass slide, gave no further indication under the microscope of the presence of the reddish-yellow needles above alluded to.

	Substance.	CO ₂ .	H ₂ O.
I.....	0.2109	0.4655	0.076
II.....	0.2026	0.444	0.0715
III.....	0.2116	0.4639	0.0764
IV.....	0.2240	0.4895	0.0818
V.....	0.2723	0.5974	0.0985

	Calculated for C ₁₁ H ₈ O ₅ .	Found.				
		I.	II.	III.	IV.	V.
C	60.00	60.19	59.77	59.93	60.00	59.83
H*.....	3.64	4.00	3.92	4.01	4.05	4.01
O	36.36	—	—	—	—	—
	<hr/> 100.00					

It is easily seen that the numbers agree fairly well with those required by the formula C₁₁H₈O₅, which may represent a *trihydroxy-methylnaphthaquinone*. The reactions to be subsequently described seem to confirm this view.

The crystals are anhydrous, and when dry are magnificently brilliant in sunlight. All the specimens described above melted at or very near to 192—193°. The substance is soluble, although with some diffi-

* It was found afterwards that a slight defect in the drying apparatus was the probable cause of the rather high results for hydrogen.

culty, in boiling strong alcohol or glacial acetic acid, very sparingly soluble in the cold liquids, and almost completely precipitated by water, in which, however, it dissolves to a small extent on boiling. It dissolves more easily in ether, and less readily in benzene and carbon bisulphide. It is soluble in solutions of the caustic alkalis and ammonia, with production of a splendid deep violet-red colour, and is immediately precipitated by acids, or gradually by carbon dioxide. On mixing boiling dilute solutions of potash and this substance in strong alcohol, and cooling, a dark-coloured compound crystallised out, but the quantity obtained was too small to purify for analysis.

In order to get some proof of the nature of this material, attempts were made to discover the presence of hydroxyl-groups, but so far unsuccessfully—this, however, is probably due to the fact that want of material has prevented the repetition of experiments under proper conditions.

A small quantity of material heated with benzoic chloride at 180° in a sealed tube for several hours yielded only a tarry uninviting mass.

One gram of substance was heated with methyl alcohol, methyl iodide, and caustic potash in suitable proportions in a flask attached to a reflux condenser, but the resulting liquid, on acidification, yielded only the unchanged substance.

Oxidation.—The substance is easily and rapidly oxidised by nitric acid, chromic acid, alkaline permanganate or alkaline ferricyanide. In order to examine the products, one gram was heated in a flask (attached to reversed condenser) with a mixture of potassium dichromate and sulphuric acid containing about 5 per cent. of the former: carbon dioxide came off in abundance. As soon as action had ceased, the liquid was distilled nearly to dryness, the retort filled up with distilled water, the contents again distilled off, and this process repeated. The mixed distillates were neutralised with pure barium carbonate, filtered, evaporated in a platinum dish, the residue taken up in a small quantity of water, filtered, and again evaporated in a weighed dish and dried. The residue was crystalline, and answered to the qualitative tests for barium acetate.

Weight of barium acetate found = 0.602 gram = 0.2833 gram acetic acid = 28.33 per cent. Theoretically a *trihydroxymethylnaphthaquinone* should yield 27.27 per cent. of acetic acid on oxidation.

The salt gave on analysis 53 per cent. of barium instead of 53.72 per cent. as required by theory, so that it was not quite pure. This result, therefore, so far confirms the view expressed above as to the nature of the substance. Oxalic acid appears to be a product of oxidation by nitric acid, but this was not confirmed.

Reduction.—So far as preliminary experiments on a small scale in test-tubes are evidence, reduction is not easily effected by sodium

amalgam, by zinc and hydrochloric acid, by iron and acetic acid, or by sulphurous acid. When, however, a boiling alcoholic (or acetic acid) solution is poured carefully into a boiling solution of stannous chloride in a mixture of alcohol (or acetic acid) with hydrochloric acid, the deep red colour of the solution rapidly passes into pale yellow, and on cooling a yellow substance crystallises out in brilliant scales, canoe-shaped under the microscope. Once or twice, when alcoholic solutions were used, the liquid on boiling for some time longer became green, and then violet-red; but as this change did not occur with acetic acid solutions, it was probably due to the formation of a small quantity of colouring matter caused by the alcohol or some contained impurity, especially as a specimen of substance which crystallised out green instead of yellow had the same melting point as the yellow material, and on recrystallisation from a mixture of alcohol and water regained its yellow colour. The crystals were filtered off, washed with water, and then dried in a vacuum over sulphuric acid. Two specimens thus prepared melted at 215–217°.

On combustion the following numbers were obtained:—

	Substance.	CO ₂ .	H ₂ O.
I.	0.2095	0.4558	0.093
II.	0.2183	0.4760	0.096

	Calculated for C ₁₁ H ₁₀ O ₅ .	Found.	
		I.	II.
C	59.46	59.33	59.42
H	4.50	4.93	4.88
O	36.04	—	—
	<hr/> 100.00		

The numbers, therefore, agree fairly well with those required for the corresponding hydroquinone. When dry, this substance is stable in the air, but if left in contact with alcohol or water it soon becomes red. This change, evidently due to reoxidation, is much more rapid in alkaline solution, especially on heating, when the deep violet-red colour characteristic of a solution of the original substance in alkali appears almost immediately. Oxidation occurs also when an attempt is made to sublime the reduced product in presence of air. It is easily soluble in alcohol and ether, less readily in benzene or carbon bisulphide.

Examination of the Mother-liquor after Separation of the first described Substance.—The mother-liquor, whether acetic or alcoholic, deposited on standing (in a covered beaker) a further small quantity of crystalline substance, which, however, proved to be the same as that already described.

On pouring off the clear liquid and adding water, a copious crystalline precipitate formed. This was filtered off, dried, and then boiled with ordinary strong acetic acid (not glacial) in such quantity as only to dissolve part of it, leaving perhaps about three-fourths undissolved, and the liquid filtered. The residue was then boiled again with the same solvent, this time in sufficient quantity to dissolve all but a very small portion, the latter filtered off and the liquid allowed to crystallise, and this operation then repeated, the object of the method of treatment being—first, to get rid of any more soluble matter; and, secondly, to remove any of the less soluble substance which might yet remain. The crystals thus obtained were *needles* quite different in appearance from the red plates above described, although to the eye of much the same colour. Under the microscope the single crystals seemed yellow, but wherever they overlapped the colour became deep orange to red, and the material was apparently homogeneous.

The quantity in hand was small, and did not allow of many recrystallisations to make sure of purity, but the melting point was fairly constant, several *different* specimens melting at 164–165°; one, however, melted at 170°. The numbers obtained on combustion agree fairly well among themselves and with those required for the formula $C_{11}H_8O_4$.

	Substance.	CO ₂ .	H ₂ O.
I.	0.2213	0.5194	0.0871
II.	0.2195	0.5136	0.0839
III.	0.2031	0.4780	0.0788

	Calculated for $C_{11}H_8O_4$.	Found.		
		I.	II.	III.
C	64.70	64.01	63.81	64.18
H	3.92	4.38	4.24	4.31
O	31.38	—	—	—
	<hr/> 100.00			

This substance is considerably more soluble than the other in all solvents tried. Its solution in caustic alkalis has simply a deep-red colour without any trace of violet, and this corresponds with a marked difference in the absorption spectrum as shown below.

Material was wanting for a study of the oxidation and reduction products in this case; but oxidation is readily effected as in the other case, and the deep-red solution becomes pale-yellow on treatment with stannous chloride as described above, but no crystals separate (at least in the experiment tried) indicating a much greater solubility of the reduced product.

In all probability, therefore, this second substance is also a derivative

of methylnaphthaquinone, but contains one hydroxyl-group less than the first.

Absorption Spectra.—The following are approximate representations of the absorption spectra of these two substances when dissolved in alcoholic potash, the upper dotted curve representing the less soluble substance $C_{11}H_8O_5$, whilst the lower represents the more soluble $C_{11}H_8O_4$.

Possibly there is still a third substance present, for the mother-liquor from the crystallisation of the second substance, when diluted, gives a precipitate, and this, when treated with boiling ordinary acetic acid, leaving a small quantity undissolved, yields a crop of crystals of lower melting point; if this process is repeated, the melting point becomes still lower. Whether this is due to some more soluble impurity which increases in proportion at each crystallisation, or to the presence of a third substance of lower melting point, I am at present unable to say, the quantity of material at my disposal being altogether insufficient.

There can be little doubt from the preliminary experiments that these colouring matters are derivatives of a methylnaphthaquinone. Possibly the red substance referred to at the outset as occurring between the outer layers of the tubers is the less soluble and more highly oxidised of the two, the soft juicy interior of the tubers containing the other, but this point must be left for further examination. I hope next spring to be able to secure a much larger quantity of material, and to follow up these results by a closer investigation.