334. *The Colouring Matters of* Drosera Whittakeri. *Part V. The Constitution of Droserone.*

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The structure—2 : 5(or 2 : 8)-dihydroxy-1 : 4-naphthaquinone—proposed for droserone has now been supported by the measurement of its normal reduction potential. This is in good agreement with values calculated from data previously obtained (J., 1936, 1457) and shows the close relationship to hydroxyjuglone on the one hand and phthiocol on the other.

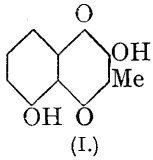
The 1 : 4-naphthaquinone structure of droserone is shown by the characteristic absorption spectrum of its acetate, and its relationship to hydroxyjuglone is further shown by the similarity of the spectra of the colouring matters and their acetates. The absorption spectra of phthiocol and naphthapurpurin and their acetates are also discussed, showing their relationship to lawsone and hydroxydroserone respectively.

The isolation of pure droserone from the natural source is described.

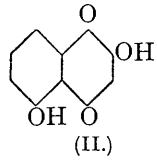
In previous papers (J., 1935, 325, 334) it was shown that hydroxydroserone, one of the colouring matters of *Drosera Whittakeri*, was 3 : 5 : 8-trihydroxy-2-methyl-1 : 4-naphthaquinone; a fact which was verified by synthesis (*ibid.*, p. 336). The associated dye, droserone, was considered to be the corresponding 3 : 5(or 3 : 8)-dihydroxy-compound, as it formed only a monoboroacetate and gave a pyridine salt. Droserone of sufficient purity for the examination of its reduction potential and the study of its absorption spectrum has now been prepared.

The reduction potentials of a large number of naphthaquinones were measured by Lugg, Macbeth, and Winzor (J., 1936, 1457), and from the data recorded a value of the normal reduction potential of droserone may be derived. On the assumption that the hydroxyl groups in droserone (I) occupy the same relative positions as in hydroxyjuglone (II), the value of the normal reduction potential of the former is obtained by adding the effect of the substituted 2-methyl group (— 0·0628 volt) to the observed reduction potential of the latter (0·3149 volt). This gives a calculated value of 0·2521 volt, but the method makes no allowance for any effect the substituent methyl group may exert on the tautomerism, if any, of the hydroxyjuglone system.

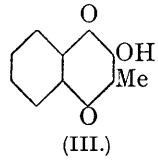
An alternative result may be derived by considering the effect of introducing a 5-hydroxyl group (— 0·0373 volt) into phthiocol (III) (0·2992 volt). The resultant value, 0·2619 volt, does not differentiate between the 2 : 5- and the 2 : 8-isomeride, and the actual value may also be influenced by tautomeric changes consequent on the introduction of a second hydroxyl group.



(I.)



(II.)



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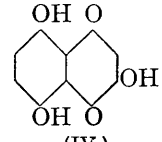


(IV.)

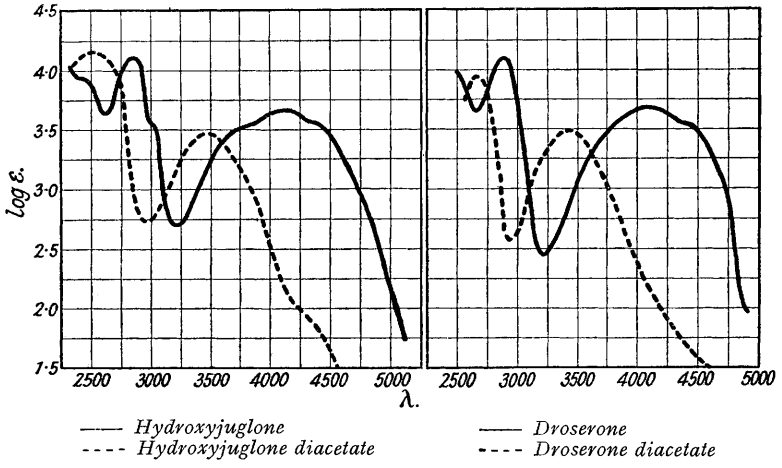
The experimental values of the normal reduction potential of droserone obtained by three different titration methods (0·2576, 0·2585, 0·2598 volt) are in good agreement with the calculated values, showing a maximum difference of some 8 millivolts only : and the proposed structure of the colouring matter thus derives considerable support.

Macbeth, Price, and Winzor (J., 1935, 325) showed that, although the introduction of hydroxyl groups in most cases modifies the typical spectrum of 1 : 4-naphthaquinone, the curves of the acetates revert to a form which closely resembles the simple 1 : 4-naphthaquinone type. The examination of the acetoxy-derivatives therefore provides a method for detecting this particular structure, and the absorption spectrum of droserone diacetate conforms to the 1 : 4-naphthaquinone type.

The close relationship between the structures of droserone and hydroxyjuglone is further

shown by the similarity in the absorption spectra of the compounds and their acetates. The colouring matters themselves show two well-marked bands and a well-defined inflexion, which are at similar locations and are of corresponding intensities. The same holds good

FIG 1. FIG. 2.



—— *Hydroxyjuglone*
---- *Hydroxyjuglone diacetate*

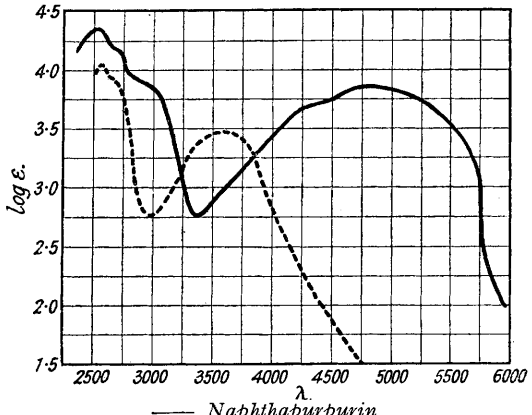
—— *Droserone*
---- *Droserone diacetate*

	$\lambda_{max.}$, A.	log ε.	$\lambda_{max.}$, A.	log ε.	$\lambda_{max.}$, A.	log ε.
Droserone	4100	3·7	2880	4·1	*ca. 2500*	4·0
Hydroxyjuglone	4080	3·66	2860	4·12	*ca. 2400*	3·96
Droserone diacetate	3440	3·5	2675	3·96		
Hydroxyjuglone diacetate	3460	3·48	2500	4·06		

in the case of the acetates, which show two similarly placed maxima, one of which in the case of hydroxyjuglone diacetate, however, covers a wider region than the corresponding band of droserone diacetate (Figs. 1 and 2).

Macbeth, Price, and Winzor (*loc. cit.*) directed attention to the fact that the acetates of naphthazarin, methylnaphthazarin, and hydroxydroserone all showed a maximum at λ3520 A. of like intensities. The presence of the *peri*-hydroxyl groups in hydroxydroserone was deduced on such grounds, and further data on this point are now available in the case of naphthapurpurin (IV) and its acetate (Fig. 3). The structures of naphthapurpurin and hydroxydroserone are closely related, and this is reflected in the spectra of the compounds and their acetates (table below).

FIG. 3.



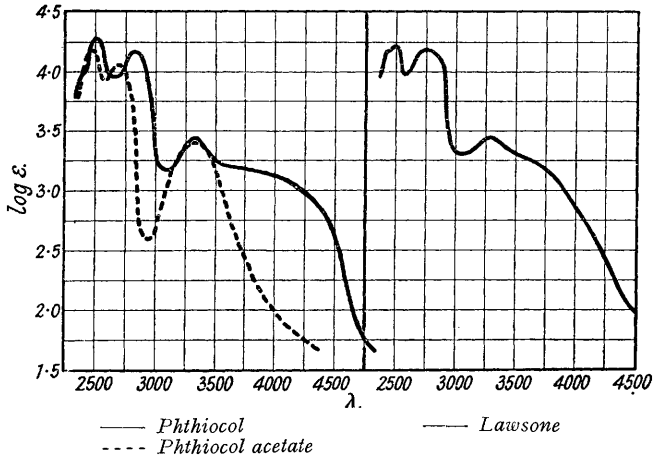
—— *Naphthapurpurin*
---- *Naphthapurpurin triacetate*

The absorption spectrum of phthiocol closely resembles that of lawsone (2-hydroxy-1 : 4-naphthaquinone), the effect of the substituent methyl group expressing itself as a slight increase in the general absorption in the regions of longer wavelength. Similar maxima are found in the case of the two acetates, an inflexion in the

	$\lambda_{max.}$, A.	log ε.	$\lambda_{max.}$, A.	log ε.	$\lambda_{max.}$, A.	log ε.
Naphthapurpurin	4860	3·86	*ca. 2900*	3·9	2530	4·3
Hydroxydroserone	4880	3·83	2980	3·92	*ca. 2550*	3·95
Naphthapurpurin triacetate	3550	3·48	2540	4·06		
Hydroxydroserone triacetate	3510	3·43	2600	4·06		

absorption curve of lawsone acetate being magnified into a definite band, similarly located, in the spectrum of phthiocol acetate (Fig. 4).

FIG. 4.



	$\lambda_{max.}$, A.	log ϵ.	$\lambda_{max.}$, A.	log ϵ.	$\lambda_{max.}$, A.	log ϵ.
Phthiocol	2500	4·28	2810	4·18	3310	3·44
Lawsone	2490	4·24	2760	4·2	3310	3·45
Phthiocol acetate	2480	4·18	2670	4·06	3330	3·4
Lawsone acetate	2480	4·26	*ca. 2620*	4·14	3330	3·41

EXPERIMENTAL.

Preparation of Pure Droserone.—The air-dried bulbs of *Drosera Whittakeri* were repeatedly extracted with boiling alcohol until the extract was practically colourless. After hot filtration fatty substance settled on cooling, and after decantation and removal of the bulk of alcohol the crude colouring matters were precipitated by pouring the residue into water. After drying, the crude dyes were sublimed, the process being repeated if necessary. On fractional crystallisation from glacial acetic acid the droserone was retained in the mother-liquors, and the crude material obtained by precipitation with water was, after drying, acetylated by short refluxing with acetic anhydride and anhydrous zinc chloride. Hydroxydroserone triacetate was recovered by fractional crystallisation of the acetates, first from glacial and then from dilute acetic acid. The crude product obtained by pouring the mother-liquors into water was hydrolysed by boiling with dilute sodium hydroxide solution, and after crystallisation from acetic acid was reacetylated as before. An equal volume of glacial acetic acid was added to the hot acetic anhydride solution; on cooling, a further yield of impure hydroxydroserone triacetate crystals separated. The mother-liquors were poured into water and the product after deacetylation by dilute alkali was obtained in light red needles, m. p. 174°, on recrystallisation from dilute alcohol. The crystals were suspended in water, and dioxan was added until at the boiling point the substance was practically all dissolved. A few drops of 5% sulphuric acid–dichromate solution were added to oxidise traces of hydroxydroserone, and boiling was continued for a few minutes. Dull yellow needles separated on cooling, and the product gave, after recrystallisation from acetic acid (norit), pale yellow needles, m. p. 181°.

Droserone diacetate was prepared by heating droserone with acetic anhydride and a little anhydrous zinc chloride. It separated in pale yellow needles, m. p. 119°, from methyl alcohol (Found: C, 62·35; H, 4·1. $C_{15}H_{12}O_6$ requires C, 62·5; H, 4·15%).

Reduction Potential of Droserone.—The solubility and the normal reduction potentials of droserone were determined at 25° by the method and in the solvent (50% aqueous alcohol containing 0·1*M*-hydrogen chloride and 0·2*M*-lithium chloride) described in the previous work (*loc. cit.*). The reduction of the droserone for electrometric titration could not be effected without the aid of the platinum–platinum oxide catalyst, and the usual quinone destruction was encountered—ranging from 13 to 22% in the various titrations. The potentials were established quickly and were well poised. The normal reduction potentials, recorded in reference to the

hydrogen electrode at 760 mm. Hg total pressure of hydrogen and solvent vapour, were 0·2576 volt (titration with benzoquinone, ΔE_1 19·7 mv.; ΔE_2 20 mv.), 0·2585 volt (titration with juglone, ΔE_1 18·4 mv.; ΔE_2 19·4 mv.), and 0·2598 volt (titration with 1 : 4-naphthaquinone, ΔE_1 18·1 mv.; ΔE_2 19·3 mv.). The solubility of droserone in the experimental solvent was 5·1 millimols. per l.

Naphthapurpurin was obtained in better yield by substituting for the 1 : 2 : 4-trihydroxybenzene used in the previous preparation (Macbeth, Price, and Winzor, *loc. cit.*) the trimethyl ether prepared by treating hydroxyquinol triacetate in methyl alcohol with sodium hydroxide and a large excess of methyl sulphate. The naphthapurpurin was crystallised from benzene.

Naphthapurpurin triacetate is difficult to obtain pure, as the reaction mixture readily becomes a tarry mass, and the acetate is extremely susceptible to slight hydrolysis with consequent deepening in colour. It was isolated on treatment of pure naphthapurpurin with acetic anhydride and a *small* fragment of anhydrous zinc chloride. It crystallised from methyl alcohol in brownish-orange needles, m. p. 164° (Found: C, 57·6; H, 3·9. $C_{16}H_{12}O_8$ requires C, 57·8; H, 3·6%).

Phthiocol was prepared from 2-methyl-1 : 4-naphthaquinone through 1 : 4-diketo-2-methyltetrahydronaphthalene-2 : 3-oxide (Madinareita, *Anal. Fís. Quím.*, 1933, **31**, 750). The oxide itself was best prepared by treating a solution of 2-methyl-1 : 4-naphthaquinone (3·4 g.) in methyl alcohol with 30% hydrogen peroxide (13 c.c.) and 2*N*-sodium hydroxide (20 c.c.). The mixture, which became warm, was kept for 15 minutes, diluted slightly with water, and neutralised with dilute sulphuric acid. The oxide separated in fine white needles, m. p. 102° after recrystallisation from ethyl alcohol.

Phthiocol acetate, obtained by acetylation of phthiocol with acetic anhydride and zinc chloride, crystallised from dilute methyl alcohol in almost white needles, m. p. 106°.

Hydroxyjuglone diacetate was obtained by refluxing for a few minutes hydroxyjuglone with acetic anhydride (4 parts) and a fragment of anhydrous zinc chloride. On cooling, the mixture was poured into water; the acetate, recrystallised from methyl alcohol, formed pale yellow needles, m. p. 137° (Found: C, 61·0; H, 3·85. $C_{14}H_{10}O_6$ requires C, 61·3; H, 3·65%).

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