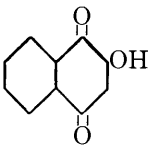
70. *The Colouring Matters of* Drosera Whittakeri. *Part I. The Absorption Spectra and Colour Reactions of Hydroxy-naphthaquinones.*

By A. Killen Macbeth, J. R. Price, and F. L. Winzor.

The insectiverous plant *Drosera Whittakeri*, which is fairly widely distributed in the Adelaide Hills, contains two colouring matters deposited as reddish flakes between the outer sheaths of the small bulb attached to its single root : the bulb itself contains a pale-red sap in which only a negligible concentration of the dye is present. The principal component, $C_{11}H_8O_5$, is isolated as red plates, m. p. 192—193°, from glacial acetic acid; associated with this is a small amount of a more soluble compound, $C_{11}H_8O_4$, consisting of yellow needles, m. p. 178° : traces of the former are removed from the latter only with difficulty. Rennie (J., 1887, **51**, 371; 1893, **63**, 1083) showed that the O_5-compound formed a triacetate and was probably a trihydroxymethylnaphthaquinone : whereas the O_4-compound gave a diacetate and appeared to be a dihydroxymethylnaphthaquinone.

These compounds have now been submitted to further examination and Rennie's suggestions confirmed. For convenience it is proposed to name the O_4-compound *droserone* and the O_5-compound *hydroxydroserone*. In this paper evidence is submitted on which the constitution of the latter may be based. It appears to be 3 : 5 : 8-trihydroxy-2-methyl-1 : 4-naphthaquinone. The amount of droserone available was too small, and its purity too doubtful, to permit of a reliable deduction of its structure by the methods of absorption spectroscopy.

The difference in colour between 1 : 4- and 1 : 2-naphthaquinone (pale yellow and orange-red respectively) led early observers to assign the latter structure to highly coloured derivatives of naphthaquinone such as *iso*lapachol (Hooker, J., 1896, **69**, 1357). As the introduction of hydroxyl groups in many cases brings about a very marked change in the colour of 1 : 4-naphthaquinone, this physical characteristic is much too unreliable a guide on which to base such a conclusion (Fieser and Ames, *J. Amer. Chem. Soc.*, 1927, **49**, 2604), and evidence has since been submitted that the assumption of 1 : 2-naphthaquinone structure was quite unwarranted. Tests such as solubility in sodium bisulphite must also be applied with caution (Fieser, *ibid.*, 1926, **48**, 2925). In the simple naphthaquinones with one hydroxyl group in the quinone nucleus, two tautomeric forms, (I) and (II), may

(I.)  (II.)

exist in equilibrium, and attempts were made to gain some definite idea of the amounts of each present by estimation of the percentages of the respective ethers that could be isolated after etherification (Miller, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 440; 1915, **47**, 1536). The results were later shown to be unreliable, for the particular ether formed was found to depend both on the nature of the alkyl group and on the reactivity of the halogen atom in the alkyl halide employed (Fieser, *loc. cit.*).

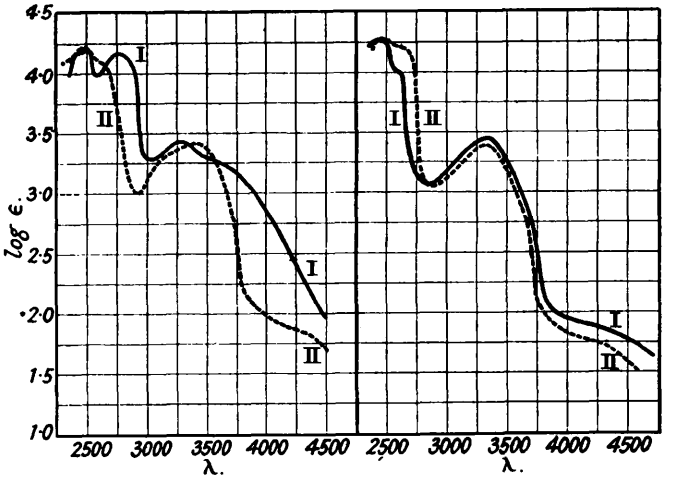
Electrode-potential measurements, on the other hand, have been applied with more success, and the results indicate that the 1 : 2-structure is very unstable (*idem*, *J. Amer. Chem. Soc.*, 1928, **50**, 438). If the constant of the tautomeric equilibrium of the α- and the β-form is defined by the equation $K = [\alpha\text{-form}]/[\beta\text{-form}]$, a simple thermodynamical consideration of the free energies of reduction of the two forms to the common reductant gives an expression dependent on temperature, which at 25° becomes

$$\log K = [E_0^{\beta} - E_0^{\alpha}]/0{\cdot}0296,$$

where E_0^{α} and E_0^{β} are the normal reduction potentials of the two forms. Working values may be obtained by examining the ethers instead of the parent hydroxy-quinones (the β-form being unstable), and since E_0^{α} for 2-methoxy-1 : 4-naphthaquinone is 0·353 volt and E_0^{β} for 4-methoxy-1 : 2-naphthaquinone under the same conditions is 0·433 volt, the difference (0·08 volt) substituted in the equation leads to a value of $K = 502$. In other words, in the solvent in question (37% alcohol), only 0·2% of the β-form is present in the equilibrium mixture. It is therefore very unlikely that a hydroxy-naphthaquinone with the group as a substituent in the quinone ring will exist in other than the 1 : 4-form : since hydroxydroserone contains such a group, the α-structure is thus rendered very probable, a conclusion which is supported by the absorption spectra now examined.

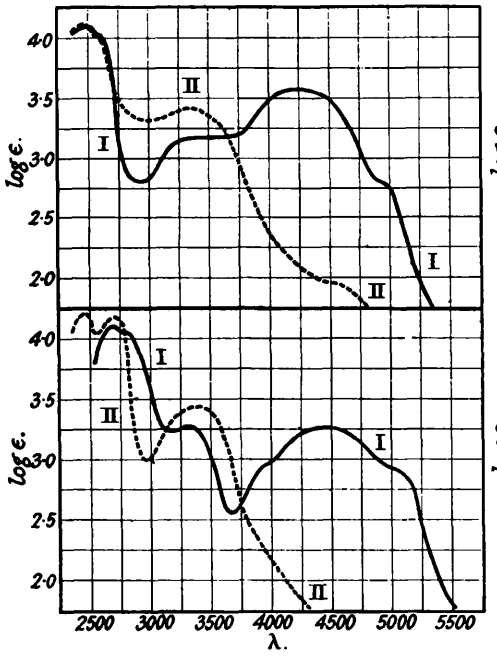
The spectra of representative hydroxy-naphthaquinones are reproduced in the figs. which show that the introduction of hydroxyl groups in most cases modifies the absorption of 1 : 4-naphthaquinone and 2-methyl-1 : 4-naphthaquinone which may be regarded as typical of the 1 : 4-structure : the curves of the acetates, however, revert to a form which closely resembles the simple type. On the other hand, the absorption of 1 : 2-naphthaquinone examined by Goldschmidt and Graef (*Ber.*, 1928, **61**, 1862) is markedly similar to that of 4-methoxy-1 : 2-naphthaquinone now described. One band in the spectra of these substances is not found in the case of the 1 : 4-naphthaquinone type, and may be

regarded as a criterion for the 1 : 2-structure. Since acetylated hydroxydroserone does not show such a band, but on the contrary generally resembles the 1 : 4-type, it seems

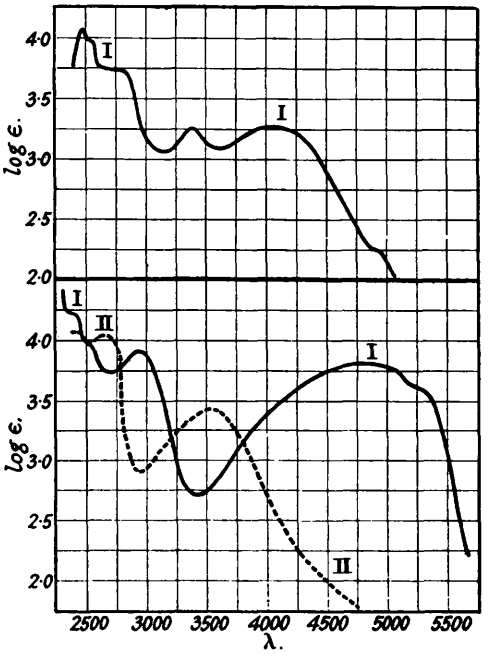


I = 2-*Hydroxy*-1 : 4-*naphthaquinone*. II = 2-*Acetoxy*-1 : 4-*naphthaquinone*.

I = 1 : 4-*Naphthaquinone*. II = 2-*Methyl*-1 : 4-*naphthaquinone*.



Upper curves I = *Juglone*.
II = *Juglone acetate*.
Lower curves I = iso*Naphthazarin*.
II = iso*Naphthazarin diacetate*.



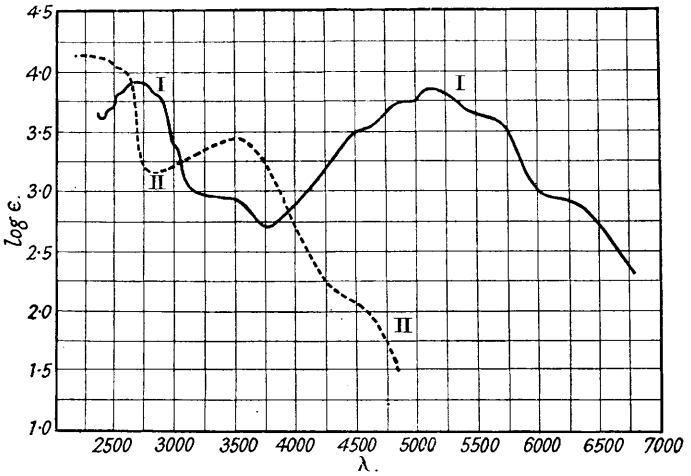
Upper curve I = *Methoxy*-1 : 2-*naphthaquinone*.
Lower curves I = *Hydroxydroserone*.
II = *Hydroxydroserone triacetate*.

justifiable to infer that it possesses the latter structure : the question, however, will be discussed more fully later.

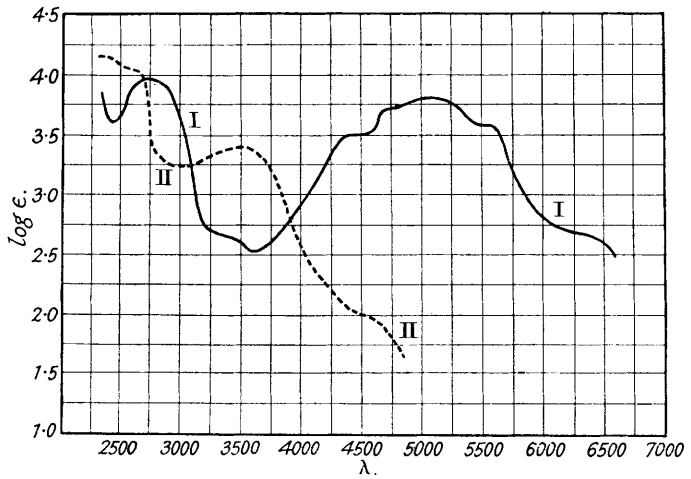
For purposes of comparison, the absorption maxima observed may be grouped into several spectral regions, and these are summarised in the tables below : the numbers

italicised indicate that an inflexion occurs at that particular wave-length instead of a band.

Baly and Stewart (J., 1906, **89**, 502, 618), as a result of a qualitative examination of a number of substituted benzoquinones, found that considerable modification in the characteristic absorption of the parent quinone occurred on substitution, and in the case of highly substituted compounds points of similarity had almost or entirely disappeared. They concluded that the effects could be explained by assuming that the substituted quinones



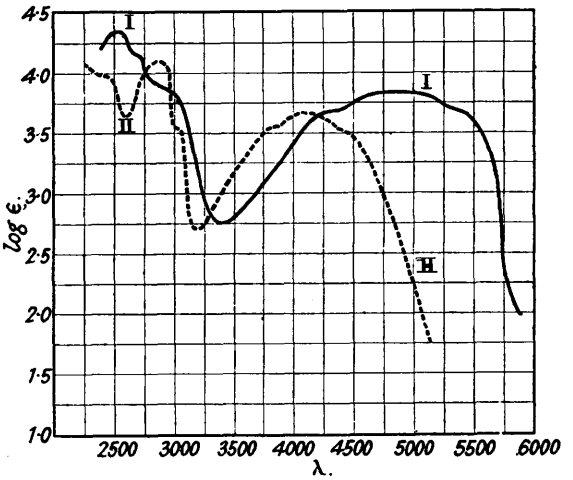
I = *Naphthazarin.* II = *Naphthazarin diacetate.*



I = *Methylnaphthazarin.* II = *Methylnaphthazarin diacetate.*

were definitely of a more benzenoid character. The further suggestion, that the increasing difficulty experienced in oxime formation as substitution increases might be accounted for on this basis rather than by steric hindrance as suggested by Kehrmann (*Ber.*, 1888, **21**, 3315; *J. pr. Chem.*, 1889, **39**, 399; **40**, 257), is not altogether free from objection, but in view of Baly and Stewart's work it was thought desirable to compare the wave-lengths of the bands or inflexions in the spectra of the hydroxynaphthaquinones with the bands recorded for naphthalene and the alkylnaphthalenes by Morton and de Gouveia (J., 1934, 927) and attributed by them to the absorptive centre C_6H_5—C=C—. The naphthalene maxima are included in Table I, and although there is some apparent agreement it is

improbable that this is due to the quinone existing in the bimolecular, aroxyl, or peroxide form which is necessary to provide the $C_6H_5—C{=}C—$ chromophore. The aroxyl and peroxide forms cannot be reconciled with the behaviour of the hydroxynaphthaquinones which contain hydroxyl groups in *peri*-positions to the quinone oxygens: and Goldschmidt and Graef (*loc. cit.*) have shown that in *o*-benzoquinone the amount present in the aroxyl form can only be very small indeed, and in *p*-benzoquinone even smaller. Further, comparison of the log ε values disclosed the fact that these are consistently higher for the hydroxynaphthaquinone bands than for the corresponding naphthalene bands: and the contention that the maxima of the former are connected with a naphthenoid structure cannot therefore be sustained.



I = *Naphthapurpurin*. II = *Hydroxyjuglone*.

It seems more probable that the bands in Tables I and II may be correlated with the maxima observed by Morton, Hassan, and Calloway (J., 1934, 883) in the curves of benzaldehyde, acetophenone, and other aromatic aldehydes and ketones. These workers showed that the $C_6H_5{\cdot}CO$ group gives rise to three distinct bands; the first, of low persistence, at λ 310—320 mμ, they attributed to the $C{=}\overset{*}{O}$ group, the second at λ 280 mμ to the carbonyl group influenced by phenyl $C_6H_5—C{=}\overset{*}{O}$, and the third at λ 242 mμ to the phenyl group influenced by carbonyl $\overset{*}{C_6}H_5—C{=}O$. Since the $C_6H_5{\cdot}CO$ group is present

TABLE I.

λ 250—300 mμ.

Substance.	$\lambda_{max.}$	log ε.	Naphthalene. $\lambda_{max.}$	Naphthalene. log ε.
2 : 5-Dihydroxy-1 : 4-naphthaquinone (Hydroxyjuglone)	*301*	3·56	302	2·54
5 : 8-Dihydroxy-1 : 4-naphthaquinone (Naphthazarin)	*298*	3·52	297	2·60
2 : 5 : 8-Trihydroxy-1 : 4-naphthaquinone (Naphthapurpurin)	*289*	3·92	286	3·74
Hydroxyjuglone	286	4·12		
2 : 3-Dihydroxy-1 : 4-naphthaquinone (*iso*Naphthazarin)	*282*	4·05	283	3·74
Naphthazarin	*284*	3·84		
2-Hydroxy-1 : 4-naphthaquinone	276	4·20	275	3·90
5 : 8-Dihydroxy-2-methyl-1 : 4-naphthaquinone (2-Methylnaphthazarin)	275	3·98		
*iso*Naphthazarin	270	4·12	273	3·90
Naphthazarin	270	3·92		
Naphthapurpurin	*268*	4·20	265	3·78
2 : 3-Diacetoxy-1 : 4-naphthaquinone (*iso*Naphthazarin diacetate)	268	4·15		
2-Acetoxy-1 : 4-naphthaquinone	*262*	4·14		
5-Hydroxy-1 : 4-naphthaquinone (Juglone)	*262*	4·00		
5 : 8-Diacetoxy-2-methyl-1 : 4-naphthaquinone (2-Methylnaphthazarin diacetate)	*256*	4·09	256	3·70
5 : 8-Diacetoxy-1 : 4-naphthaquinone (Naphthazarin diacetate)	*256*	4·05		
5-Acetoxy-1 : 4-naphthaquinone (Juglone acetate)	*255*	4·05		
Naphthazarin	*254*	3·82		
Naphthapurpurin	252	4·36		
1 : 4-Naphthaquinone	*256*	4·13		
2-Methyl-1 : 4-naphthaquinone	*259*	4·23		
3 : 5 : 8-Trihydroxy-2-methyl-1 : 4-naphthaquinone (Hydroxydroserone)	298	3·92	297	2·60
Hydroxydroserone	*255*	3·95	256	3·70
3 : 5 : 8-Triacetoxy-2-methyl-1 : 4-naphthaquinone (Hydroxydroserone triacetate)	*265*	4·06	265	3·78

in the naphthaquinones, it would seem more satisfactory to attribute the maxima recorded above to similar vibrations rather than to postulate a naphthenoid structure.

TABLE II.

λ 240—250 mμ.

Substance.	$\lambda_{max.}$	log ε.	Substance.	$\lambda_{max.}$	log ε.
Methylnaphthazarin diacetate	*240*	4·17	Naphthazarin.....	*247*	3·73
Hydroxyjuglone	*240*	3·96	2-Methyl-1 : 4-naphthaquinone ...	248	4·27
2-Hydroxy-1 : 4-naphthaquinone...	*244*	4·20	2-Acetoxy-1 : 4-naphthaquinone...	248	4·26
Naphthazarin diacetate.....	*244*	4·16	Juglone	249	4·12
Juglone acetate	245	4·16	2-Hydroxy-1 : 4-naphthaquinone	249	4·24
*iso*Naphthazarin diacetate	246	4·21	Hydroxydroserone	*239*	4·27
1 : 4-Naphthaquinone	246	4·28	Hydroxydroserone triacetate	*241*	4·09

Some other characteristics shown by the curves are set down in Table III. An absorption in the region λ 330 mμ occurs in all the quinones and their acetates, except those containing hydroxyl groups in the *peri*-positions. In the latter case the band is either missing or modified to an inflexion, but in the acetates of such compounds a definite band is present; and it is significant that when two *peri*-acetoxyl groups are found in the compound the maximum is at λ 351 mμ.

It is probable that the absorption in this region is due to the chromophore C=C—C=C, and Morton, Hassan, and Calloway (*loc. cit.*) are of the opinion that in a chromophore of this type the absorbing electron is in the C=C linkage when the molecular extinction coefficients are of the order 10^3—10^5 as is the case in the naphthaquinones. The log ε values are remarkably constant for the substances examined, apart from the inflexions already mentioned in the quinones containing two *peri*-hydroxyl groups.

TABLE III.

Substance.	$\lambda_{max.}$	log ε.	
1 : 4-Naphthaquinone	334	(3·44)	
2-Methyl-1 : 4-naphthaquinone	333	(3·37)	
2-Hydroxy-1 : 4-naphthaquinone.....	331	(3·45)	
2-Acetoxy-1 : 4-naphthaquinone	333	(3·41)	
Naphthazarin	*338*	(2·95),	*450* (3·50), *485* (3·75), 513 (3·85) *
Naphthazarin diacetate.....	352	(3·42)	
Methylnaphthazarin	*331*	(2·72),	*454* (3·60), *481* (3·75), 510 (3·81) *
Methylnaphthazarin diacetate	352	(3·38)	
Juglone	*339*	(3·18)	
Juglone acetate	338	(3·41)	
*iso*Naphthazarin.....	335	(3·31)	
*iso*Naphthazarin diacetate	338	(3·42)	
Hydroxyjuglone	—	—	
Naphthapurpurin	—	—	*440* (3·71), 485 (3·85), *523* (3·70) †
Hydroxydroserone	—	—	— — 488 (3·83), 518 (3·71) †
Hydroxydroserone triacetate	351	(3·43)	

Also inflexions in the region λ 410—440 mμ (1·78—2·15) in the case of simple 1 : 4-naphthaquinones and their acetates; but these are absent in derivatives with two substituents (acetoxyl or methyl) in the quinone ring.

* Two *peri*-OH-groups. † Two *peri*-OH-groups and OH in the quinone ring.

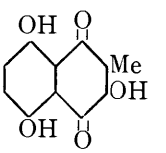
4-*Methoxy*-1 : 2-*naphthaquinone*.—The curves for 1 : 2-naphthaquinone recorded by Goldschmidt and Graef (*loc. cit.*) show maxima in alcoholic solution in close agreement with those now found in the case of 4-methoxy-1 : 2-naphthaquinone :

1 : 2-Naphthaquinone.		4-Methoxy-1 : 2-naphthaquinone.	
$\lambda_{max.}$	log ε.	$\lambda_{max.}$	log ε.
500	2·00	*490*	2·20
400	3·40	403	3·29
340	3·40	339	3·26
—	—	*273*	3·78
—	—	*254*	4·01
250	4·35	250	4·07

The definite maximum in the region λ 400 mμ, and the inflexion in the region 490—500 mμ, are without parallel in the absorption characteristic of the 1 : 4-naphthaquinone

type, and may reasonably be applied as a criterion to distinguish between the **1** : 2- and the 1 : 4-structure. Qualitative examination of the absorption of 7-hydroxy-**1** : 4-naphthaquinone showed that, as in the case of the **1** : 4-compounds, the introduction of the hydroxyl group modifies the characteristic curves of the simple substances : a sample of the acetate was not available, but it is to be expected that further work will show that acetylation will in such cases also cause a reversion to the standard type.

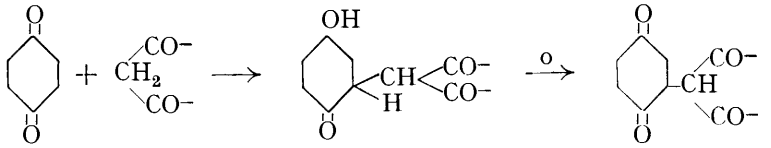
Hydroxydroserone.—A comparison of the curves of simple **1** : 4-naphthaquinones and the acetates of hydroxy-**1** : 4-naphthaquinones shows that hydroxydroserone triacetate conforms closely to the general type : and a **1** : 4-structure may therefore be inferred. It is also evident that hydroxydroserone itself more closely resembles those derivatives such as naphthazarin, methylnaphthazarin, and naphthapurpurin in which two hydroxyl groups are *peri* to the quinone oxygen atoms. Thus, in the region λ 330—350 mμ, the values for the acetates of naphthazarin, methylnaphthazarin, and hydroxydroserone are practically identical (a sample of the acetate of naphthapurpurin was not available) and are considerably higher than those for the other acetates examined. In the region λ 240—250 mμ, 1 : 4-naphthaquinone, 2-methyl-**1** : 4-naphthaquinone, 2-acetoxy-**1** : 4-naphthaquinone, and *iso*naphthazarin diacetate have almost the same $\lambda_{max.}$ (246—248 mμ), whilst the value for juglone acetate is somewhat lower (245 mμ), and those for the acetates of naphthazarin, methylnaphthazarin, and hydroxydroserone are still lower (240—244 mμ). The log ε values for the first four substances are also higher. In the region λ 250—300 mμ, the log ε values for the same four compounds lie close together, and are lower than those of the other substances under discussion. These facts indicate that hydroxydroserone contains at least one, but more probably two, hydroxyl groups in *peri*-positions.



(III.)

Inspection of the curves also shows that substitution in the quinone ring expresses itself in the region λ 240—280 mμ : in this region hydroxydroserone triacetate shows points of similarity to *iso*naphthazarin diacetate, and it may thus be inferred that the quinone ring is fully substituted : and the absence of inflexions at λ 410—440 mμ in these two cases is a further point of agreement. Since the presence of two *peri*-hydroxyl groups has already been suggested, the introduction of the methyl group and the remaining hydroxyl into the quinone ring leads to the structure (III) for hydroxydroserone. This has been confirmed by a study of the reactivity of the compound (see following paper).

Colour Reactions of Naphthaquinones (with A. B. Beck).—Ionescu (*Bull. Soc. chim.*, 1927, **41**, 1094) showed that certain quinones react with substances containing an active methylene group, and formulated the change as a two-stage reaction involving the methylene group :



Later, Kesting (*Z. angew. Chem.*, 1928, **41**, 358, 745) described the colour reactions of naphthaquinones and malononitrile, and in a further paper (*Ber.*, 1929, **62**, 1422) discussed those of quinones and compounds of the structure –(E)·C·CH_2·C·(E)–, where E is a multivalent element. *p*-Benzoquinone and **1** : 2- and **1** : 4-naphthaquinones gave colours with such substances as malononitrile, ethyl cyanoacetate, cyanoacetamide, acetyl- and benzoylacetone, and ethyl aceto- and benzoyl-acetate. In cases where the p_H of the quinone was less than that of the solvent, colours were obtained without the further addition of alkali, but otherwise the addition of ammonia or other base was essential. We have examined the series of naphthaquinones now available, and find that on treatment in alcoholic-solution with ethyl cyanoacetate and ammonia colorations are given by juglone, naphthazarin and methylnaphthazarin : the acetates of these compounds gave similar colorations, but the rate of development was considerably reduced. The following **1** : 4-naphthaquinones and such of their acetates as were available gave no colorations apart

from the colour of their ammonium salts : 2-hydroxy-, 2 : 3-dihydroxy-, 2 : 5-dihydroxy-, 2 : 5 : 8-trihydroxy-. For such hydroxy-quinones as gave coloured ammonium salts, a Hellige colorimeter was used throughout to detect intensity changes, if any, on the addition of the cyanoacetate.

From the results, it appears that introduction of even one hydroxy group in the quinone nucleus is sufficient to inhibit colour production, although the hydrogen atom required by the formulations of Ionescu and Kesting is still available. Since neither hydroxydroserone nor its acetate gave any positive test, this behaviour may be taken as additional evidence that a hydroxyl group is present in the quinone ring.

The behaviour of a further series of $-(E)\text{:}C\cdot CH_2\cdot C\text{:}(E)-$ compounds with 1 : 4-naphthaquinone was studied in order to supplement the results of previous workers. Colorations were obtained in all cases, except with tribenzoylmethane. In view of the fact that Craven (J., **1931**, 1606) is examining the constitutions of such derivatives, we did not extend work in this direction.

Brissemoret and Coombes (*J. Pharm. Chim.*, 1907, **25**, 53) found that nickel acetate formed co-ordination compounds with hydroxynaphthaquinones, the reaction being indicated by the formation of blue, or violet-blue, colorations when dilute solutions of the reagents were mixed. Examination of the hydroxynaphthaquinones now available shows that colours other than those stated are produced in some cases, and since *iso*naphthazarin gives an intense blue colour, the reaction is not inhibited by two hydroxyl groups in the quinone ring.

Experimental.

2-Hydroxy-1 : 4-naphthaquinone prepared by Fieser's method (*loc. cit.*) had m. p. 189° (decomp.). Methylation by diazomethane gave the 2-methoxy-derivative, which after crystallisation from water had m. p. 183·5°. The 2-acetoxy-derivative was prepared by direct acetylation with acetic anhydride and zinc chloride, and had m. p. 131°.

2-Methyl-1 : 4-naphthaquinone was prepared by adding 2-methylnaphthalene in glacial acetic acid to a cold solution of chromic acid in 80% acetic acid (Madinaveitia and de Buruaga, *Anal. Soc. Fís. Quím.*, 1929, **27**, 647); yellow needles from glacial acetic acid, m. p. 106°.

4-Methoxy-1 : 2-naphthaquinone was prepared by the alkylation of the silver salt of 2-hydroxy-1 : 4-naphthaquinone (Fieser, *loc. cit.*); orange-red needles from benzene, m. p. 190°.

5-Hydroxy-1 : 4-naphthaquinone (juglone), prepared from 1 : 5-dihydroxynaphthalene by Willstätter and Wheeler's method (*Ber.*, 1914, **47**, 2796), after recrystallisation from light petroleum had m. p. 150—151° in a bath preheated to 140°. The acetate (Bernthsen and Semper, *Ber.*, 1885, **18**, 206), pale yellow needles from alcohol, had m. p. 154—154·5°.

2 : 5-Dihydroxy-1 : 4-naphthaquinone (oxyjuglone), prepared by Mylius's method (*Ber.*, 1885, **18**, 469) by the oxidation of hydrojuglone (Willstätter and Wheeler, *loc. cit.*), had m. p. 210° (decomp.).

2 : 3-Dihydroxy-1 : 4-naphthaquinone (*iso*naphthazarin) was an I.-G. product which was repeatedly recrystallised from glacial acetic acid. The diacetyl derivative, prepared by the continued action of acetyl chloride (Wheeler and Edwards, *J. Amer. Chem. Soc.*, 1917, **39**, 2465), after recrystallisation from glacial acetic acid had m. p. 191°. We found methods involving the use of acetic anhydride unsatisfactory (Zincke and Schmidt, *Annalen*, 1895, **286**, 36; Thiele and Winther, *ibid.*, 1900, **311**, 348), the product repeatedly recrystallised from alcohol having m. p. 134°.

2 : 5 : 8-Trihydroxy-1 : 4-naphthaquinone (naphthapurpurin) is difficult to prepare in the pure state (Fieser, *J. Amer. Chem. Soc.*, 1928, **50**, 460; Thiele and Winther, *loc. cit.*; Dimroth and Roos, *Annalen*, 1927, **456**, 191). A pure sample, in poor yield, was obtained by condensing maleic anhydride (2 g.) with 1 : 2 : 4-trihydroxybenzene (1 g.), the mixture being added to a melt of aluminium chloride (20 g.) and sodium chloride (4 g.) at 180°; the temperature rose to about 200° and was maintained there for some 5 mins. The melt was then heated to 220°, and the pasty mass removed from the crucible before solidification, dissolved in water, and after the addition of an equal volume of concentrated hydrochloric acid the solution was heated till the colour of the aluminium chloride complex changed to dull-red. After cooling in ice, the solid was filtered off, and the filtrate extracted with chloroform. The dried solid was also repeatedly extracted with chloroform, and the combined extracts shaken with sodium hydroxide solution. The solid precipitated from the alkaline extract on the addition of concentrated hydrochloric acid was dried and extracted (Soxhlet) with light petroleum for several days;

a small amount of very pure crystalline material then collected in the flask. Sufficient was not available to form the triacetate, which is not described in the literature.

Methylnaphthazarin (5 : 8-dihydroxy-2-methyl-1 : 4-naphthaquinone) was prepared (*a*) by condensing maleic anhydride with toluquinol and (*b*) by condensing citraconic anhydride with quinol. The two products were identical. The procedure followed closely that described in the preceding case, but the product was crystallised from alcohol. In appearance, it closely resembles naphthazarin, having the same brilliant green sheen; m. p. 173° (Found : C, 64·7; H, 4·0. $C_{11}H_8O_4$ requires C, 64·7; H, 3·8%).

Methylnaphthazarin diacetate is best prepared by refluxing methylnaphthazarin with excess acetyl chloride for several days, or until the red colour disappears. After addition of glacial acetic acid, the acetyl chloride is distilled off and the diacetate crystallises on cooling. After two crystallisations from benzene–light petroleum, it has m. p. 168° (Found : C, 62·7; H, 4·4. $C_{15}H_{12}O_6$ requires C, 62·5; H, 4·2%).

*Derivatives of Naphthalene-*1 : 5-*disulphonyl Chloride.*—In the preparation of naphthalene-1 : 5-disulphonic acid required in the synthesis of juglone (Bernthsen and Semper, *Ber.*, 1887, **20**, 924), a copious white precipitate was obtained when the reaction mixture of naphthalene and chlorosulphonic acid was poured into water. It was identified as naphthalene-1 : 5-disulphonyl chloride, white prisms, m. p. 179°, from ether, benzene, acetone, or carbon tetrachloride (cf. 183°; Armstrong, *Ber.*, 1882, **15**, 205). Naphthalene-1 : 5-disulphonamide was obtained on treating the dichloride with a little alcohol and large excess of aqueous ammonia, boiling, and filtering. Unchanged dichloride was extracted from the residue by acetone. The diamide was slightly soluble in aniline, but practically insoluble in other organic solvents and had no sharp m. p. Naphthalene-1 : 5-bisdimethylsulphonamide was prepared (*a*) by methylating the amide with methyl sulphate and alkali and (*b*) by warming the dichloride with sodium hydroxide and dimethylamine hydrochloride. After recrystallisation from acetone, both samples had m. p. 241—242°. Phenyl naphthalene-1 : 5-disulphonate was obtained on the addition of the dichloride in acetone to sodium phenoxide. On addition of water after evaporation of part of the acetone a precipitate of the crude ester was thrown down, which separated as faintly pink prisms, m. p. 173—174° from acetone.

Naphthalene-1 : 5-disulphinic acid, sparingly soluble in water, m. p. 162—163°, was obtained on boiling the dichloride with aqueous sodium sulphite. The disulphinic acid crystallised on cooling the hot filtrate acidified with sulphuric acid. It responds to Smiles's test (concentrated sulphuric acid and anisole, blue colour) for aromatic sulphinic acids.

Colorations with –(E)·C·CH_2·C·(E)– *Compounds.*—In the cases tabulated below 1 : 4-naphthaquinone was taken as a standard test quinone, and gave the range of colours recorded (Mulliken's charts) when treated with alcoholic solutions of the reagents listed. The rate of colour change varied from case to case. Tests with juglone and naphthazarin gave a similar range of colours, and in all cases 0·1 g. of the reagent was added to 5 ml. of an *M*/1000-alcoholic solution of the quinone, and 3 ml. of a mixture of equal parts of alcohol and ammonia (*d*, 0·880) added.

Reagent.	Colour change (—→).		
Ethyl malonate	Blue.	Violet.	Brn.†
*iso*Amyl malonate	Blue.	Bkn Violet.	Brn.
Ethyl ethylmalonate	Blue.	Bkn Violet.	Brn.
Ethyl diethylmalonate	Pale Bkn Blue.*		Brn.
Ethyl cyanoacetate	Violet-blue.	Green.	Brn.
Ethyl acetoacetate	Blue-violet.	Violet-red.	Brn.
Acetylacetone	Red-violet.	Violet-red.	
Benzoylacetone	Blue-violet.	Violet.	Violet-red.
Dibenzoylmethane	Blue-violet.	Violet.	
Tribenzoylmethane	Yellow (very faint).		

* Colour due to traces of ethyl ethylmalonate.

† Brn denotes an indefinite range between Bkn Red and Bkn Yellow.

Colorations with Nickel Acetate.

Reagent.	Colour.	Reagent.	Colour.
2-Hydroxy-1 : 4-naphthaquinone	Yellow-orange	Naphthazarin	Blue
Juglone	Violet-red	*iso*Naphthazarin	,,
Lapachol	,,	Hydroxyjuglone	Red
Hydroxyhydrolapachol	,,	Naphthapurpurin	Red-violet
Dihydroxyhydrolapachol	,,		

JOHNSON CHEMICAL LABORATORIES, UNIVERSITY OF ADELAIDE. [*Received, December 28th*, 1934.]