71. *The Colouring Matters of* Drosera Whittakeri. *Part II.*

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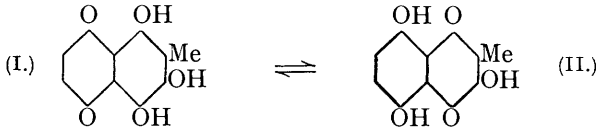
The suggestion (preceding paper) that hydroxydroserone is 3 : 5 : 8-trihydroxy-2-methyl-1 : 4-naphthaquinone is supported by the results obtained with several reagents which detect the positions of hydroxyl groups in quinonoid compounds.

Boroacetic anhydride, which was introduced as a reagent for *peri*-hydroxyl groups by Dimroth *et al.* (*Ber.*, 1921, **54**, 3020; *Annalen*, 1925, **446**, 97), gives a *diboroacetate* with methylnaphthazarin, but only acetylates 2-hydroxy-1 : 4-naphthaquinone. Since hydroxydroserone yields a *diboroacetate*, the presence of two *peri*-hydroxyl groups may be deduced; the third hydroxyl group is acetylated. Droserone, on the other hand, yields a *monoboroacetate*, a fact which suggests that it is probably 3 : 5 (or 3 : 8)-dihydroxy-2-methyl-1 : 4-naphthaquinone. It is difficult to remove all traces of hydroxydroserone from the less oxygenated compound, but Rennie (J., 1893, **63**, 1083) found that partial oxidation of droserone gave a yellow substance, m. p. 178° : since yellow needles of the same m. p. are recovered on decomposition of the boroacetate, it appears that the oxidation referred to merely resulted in the removal of traces of hydroxydroserone present, and that purification may also be effected through the boroacetate.

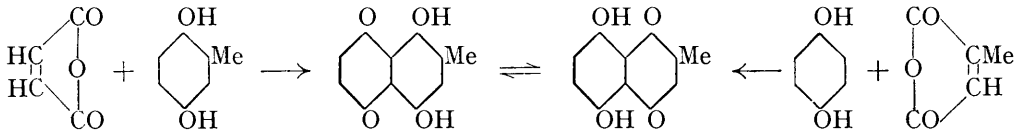
The reaction of stannic chloride and hydroxyanthraquinones (Pfeiffer *et al.*, *Annalen*, 1913, **398**, 137) led to the conclusion that a $SnCl_3$-complex is formed when one *peri*-hydroxyl group is present, whereas with two such groups in the same nucleus a $SnCl_2$-complex is produced, and in no case is a complex formed with a hydroxyl group in another position. On the other hand, Pfeiffer showed that hydroxyl groups in positions other than the *peri*-positions are sufficiently acidic to form pyridine salts. These reactions also held for such hydroxynaphthaquinones as were examined (Pfeiffer, Oberlin, and Segall, *Ber.*, 1927, **60**, 111; Dimroth and Roos, *Annalen*, 1927, **456**, 177). 2-Hydroxy-1 : 4-naphthaquinone, however, combines with one molecule of pyridine and also forms a $SnCl_3$-complex; from which it appears that a 2-hydroxyl group reacts in a similar way to a *peri*-hydroxyl, and stannic chloride is not a specific reagent for the latter. *iso*Naphthazarin, like naphthazarin, forms a $SnCl_2$-complex and, like hystazarin, forms a monopyridine salt. Droserone and hydroxydroserone both give *monopyridine* salts, and so contain at least one hydroxyl in a position other than the *peri*-position : the stannichlorides in these cases were not isolated in a state sufficiently pure to warrant analysis.

Diazomethane combines additively with 1 : 4-benzo- and naphtha-quinones (Pechmann and Seel, *Ber.*, 1899, **32**, 2292; Fieser and Peters, *J. Amer. Chem. Soc.*, 1931, **53**, 4080), but 2-hydroxy- and 2 : 3-dihydroxy-1 : 4-naphthaquinones are methylated, and we have never found addition to occur in these cases even in presence of a large excess of the reagent. Since an alkyl substituent in the quinone ring also appears to inhibit the formation of an additive compound, 2-methyl-1 : 4-naphthaquinone giving negative results, it seemed that the reaction with diazomethane might furnish evidence of the nature of the substitution in hydroxydroserone. This was vigorous and analysis of the product showed that one molecule of diazomethane condensed with a molecule of the quinone, with simultaneous methylation of one hydroxyl group. Work on the reaction of diazomethane and quinones is proceeding, but the present results appear to imply that in hydroxydroserone there are two adjacent unsubstituted positions in the quinone ring. The results therefore point to formula (I) for the compound.



Fieser's deduction of the structure of naphthapurpurin, based on a study of the reduction potentials of hydroxynaphthaquinones (*J. Amer. Chem. Soc.*, 1928, **50**, 439), indicates that the form containing three hydroxyl groups in the same nucleus is unstable, and can

exist only in extremely small amount in the equilibrium mixture of the two forms. In accordance with this view formula (II) would better represent the structure of hydroxydroserone. This formula is also in accord with the colour reactions and absorption spectra (preceding paper), and to account for the reaction with diazomethane it is only necessary to assume tautomerisation to the alternative structure in the presence of a suitable reagent. That tautomerisation of this type readily occurs is seen in the case of methylnaphthazarin, which is synthesised either by the condensation of (*a*) maleic anhydride and toluquinol or (*b*) citraconic anhydride and quinol (this vol., p. 333) :



Experimental.

Boroacetates.—The boroacetates were formed by warming the colouring matter with acetic anhydride in the presence of boric acid. If the boroacetate did not separate on cooling, the excess of anhydride was removed under reduced pressure. In the analysis of the compounds the following estimations were carried out : (*a*) the acetyl value of the product, which was determined by a slight modification of Perkin's method, the ethyl acetate being distilled into a known volume of standard alcoholic potassium hydroxide and the alkali consumption measured by the addition of excess of hydrochloric acid, the surplus being found (after boiling to expel carbon dioxide) by titration with baryta in the presence of neutral-red; (*b*) the percentage residue after hydrolysis of the boroacetate by cold water; (*c*) the acetyl value of this residue; (*d*) the total acidity of the filtrate from (*b*) by titration with baryta and phenolphthalein, after the addition of mannitol; (*e*) the percentage of boron in the boroacetate, which is calculated from the boric acid value $d-(a-c)$.

Methylnaphthazarin diboroacetate. Boric acid (0·4 g.) in acetic anhydride (10 c.c.) was added to a solution of the quinone (1 g.) in acetic anhydride (10 c.c.) at 50—60°. The *boroacetate* crystallised in reddish-violet plates on cooling, and was washed with acetic anhydride and with ether (dried over sodium) [Found : (*a*) 36·6; (*b*) 44·0; (*c*) nil; (*d*) 0·2451 g. required 7·5 c.c. of baryta (0·429*N*), calc., 7·45 c.c.; (*e*) 5·0. $C_{11}H_6O_4B_2(OAc)_4$ requires (*a*) 37·4; (*b*) 44·3; (*e*) 4·8%].

Hydroxydroserone diboroacetate. Finely powdered hydroxydroserone (1 g.) was slowly added to warm acetic anhydride (50 c.c. at 50—60°) containing boric acid (0·6 g.). The solution was filtered hot through fritted glass and concentrated under reduced pressure to 15 c.c.; on standing in a closed flask in the ice-chest, the *diboroacetate* separated as a red crystalline powder which was treated as in the preceding case [Found : (*a*) 41·1; (*b*) 50·8; (*d*) 0·2050 g. required 5·0 c.c. of baryta (0·459*N*), calc., 5·17 c.c.; (*e*) 4·2. $C_{11}H_5O_4B_2(OAc)_5$ requires (*a*) 41·5; (*b*) 50·6; (*e*) 4·2%. Found : (*c*) 15·6. Calc. for $C_{11}H_7O_4(OAc)$: 16·4%].

Hydroxydroserone 3-monoacetate obtained on hydrolysis of the boroacetate by cold water had m. p. 151—156° when thrice recrystallised from benzene. When heated with acetic anhydride and a little zinc chloride, it yielded the triacetate, m. p. 156°, identical with that prepared directly from hydroxydroserone.

Droserone boroacetate. Only a small amount of material was available, but analysis of the product isolated in the usual way indicated that a *monoboroacetate* mainly is formed, but the second hydroxyl group undergoes partial acetylation [Found : (*a*) 27·2; (*b*) 63·1; (*c*) traces; (*d*) 0·1025 g. required 2·4 c.c. of baryta (0·382*N*), calc., 2·42 c.c.; (*e*) 3·1. $C_{11}H_7O_4B(OAc)_2$ requires (*a*) 25·8; (*b*) 61·5; (*e*) 3·3%].

The residue after hydrolysis of the boroacetate by cold water melted at *ca.* 170°, but after warming with sodium hydroxide, reprecipitation by acid, and crystallisation from alcohol was isolated as yellow needles of pure droserone, m. p. 178°.

2-Hydroxy-1 : 4-naphthaquinone gave no boroacetate even on concentration of the reaction mixture. The solid precipitated by water was 2-acetoxy-1 : 4-naphthaquinone, m. p. 131° after crystallisation from alcohol. Had a boroacetate been formed, the hydroxyquinone itself, m. p. 190°, would have been recovered.

Stannichloride Compounds and Pyridine Salts.—In the preparation of the stannichloride compounds, solutions of the hydroxyquinone and stannic chloride in hot anhydrous benzene were

mixed and heated under reflux for several hours. The tin complex which separated was quickly filtered off, washed free from hydrochloric acid and excess of stannic chloride with dry benzene, and stored in a desiccator over phosphoric oxide. The stannichlorides isolated contain a molecule of benzene, and are contaminated with traces of adhering benzene which it is difficult to remove completely : this, although affecting the percentage composition, does not alter the tin–chlorine ratio. The tin complex on hydrolysis on the water-bath with a mixture of water (25 c.c.) and saturated ammonium nitrate solution (25 c.c.) gives a precipitate, which is ignited and weighed as SnO_2. Chloride in the filtrate, acidified with nitric acid, is estimated gravimetrically as silver chloride.

2-*Hydroxy*-1 : 4-*naphthaquinone*. To the quinone (0·4 g.) dissolved in anhydrous benzene (50 c.c.), stannic chloride (0·5 c.c.) in the same solvent was added, and the mixture refluxed on the water-bath for 2 days. The yellow-brown precipitate was analysed directly after preparation (Found : Sn, 22·5, 22·6; Cl, 19·9, 21·1; Sn : Cl = I : 2·95, 2·97. $C_{10}H_5O_3SnCl_3 + C_6H_6$ requires Sn, 25·0; Cl, 22·35%). The *pyridine* salt crystallised as orange-red needles from a solution of the quinone in hot pyridine, and all the pyridine was lost on heating at 110° (Found : pyridine, 31·1. $C_{10}H_6O_3Py$ requires Py, 31·2%).

2 : 3-*Dihydroxy*-1 : 4-*naphthaquinone*. The *tin complex* separated as a green powder when a solution of the quinone (0·4 g.) in anhydrous benzene (50 c.c.) containing stannic chloride (1 c.c.) was refluxed for 6 hours and cooled (Found : Sn, 23·6, 23·9; Cl, 14·2, 14·3; Sn : Cl = 1 : 1·98, 2·03. $C_{10}H_4O_4SnCl_2 + C_6H_6$ requires Sn, 26·1; Cl, 15·6%). The *pyridine* salt, which is very soluble, was obtained by the addition of excess of light petroleum to a solution of the quinone in pyridine. After filtration and quick washing with light petroleum, the salt was pressed between filter-papers and stored in a desiccator over phosphoric oxide for 2 hours (Found : Py, completely removed at 110°, 29·8. $C_{10}H_6O_4Py$ requires Py, 29·4%).

Hydroxydroserone. The stannichloride was not isolated in a pure state, but the *pyridine* salt separated as bright red needles when a hot pyridine solution of the quinone was cooled (Found : Py lost at 110°, 26·4. $C_{11}H_8O_5Py$ requires Py, 26·4%).

Droserone gave a *pyridine* salt which separated as needles of a somewhat more orange tint than the preceding compound (Found : Py, 27·7. $C_{11}H_8O_4Py$ requires Py, 27·9%).

Action of Diazomethane.—(I) On addition of an ethereal solution of diazomethane to 2-hydroxy-1 : 4-naphthaquinone suspended in ether, the quinone dissolved, but the methyl ether soon separated as small, pale yellow crystals, m. p. 183° after recrystallisation from alcohol, identical with 2-methoxy-1 : 4-naphthaquinone prepared by the action of acid methyl alcohol on the quinone (Fieser, *J. Amer. Chem. Soc.*, 1926, **48**, 2932).

(2) *iso*Naphthazarin dimethyl ether, yellow needles, m. p. 115°, was obtained in a similar way (compare Fieser, *ibid.*, 1928, **50**, 461).

(3) There was a vigorous reaction on the addition of an ethereal solution of diazomethane to a suspension of hydroxydroserone in dry ether, and after previous solution a product was precipitated in brown needles, m. p. 189° after crystallisation from alcohol and from glacial acetic acid [Found : N, 10·9; OMe, 10·9. $C_{12}H_7O_4N_2(OMe)$ requires N, 10·2; OMe, 11·3%].

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