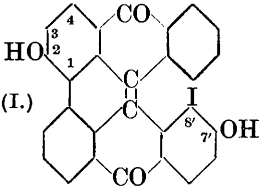
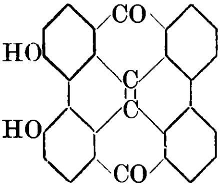
XXV.—*Reduction Products of the Hydroxyanthraquinones. Part X.*

By Richard Walter Hardacre and Arthur George Perkin.

When 3-hydroxyanthranol is gently oxidised, the corresponding dihydroxydianthrone is produced, and from this the dihydroxydianthraquinone and dihydroxyhelianthrone can be successively obtained by similar methods (Haller and Perkin, J., 1924, **125**, 239; Perkin and Yoda, J., 1925, **127**, 1881). The last substance, by iodination in pyridine solution, readily yields a well-characterised monoiodo-derivative, a fact which suggested that the two hydroxyls present are not similarly situated. Therefore, although this compound, judging from its method of formation, could be either a 2 : 2′-, 2 : 7′- or 7 : 7′-dihydroxyhelianthrone, constitution (I) was preferred, the iodine presumably entering position 8′.*



(I.)



(II.)

More recently it has been found that by a more drastic treatment of the dihydroxyhelianthrone with iodine in pyridine solution a di-iodo-compound can be prepared (bromine reacts similarly)—a behaviour which, indicating as it does some resistance to the entry of a second iodine atom, harmonises with the view expressed above. On the other hand, experiment has now definitely shown that the iodine atom in monoiododihydroxyhelianthrone is not in position 8′, because, on exposure of its acetyl derivative in benzene solution to sunlight, the iododiacetoxynaphthadianthrone is produced. Such a reaction could not occur in the case of (I) without elimination of iodine (II) and it is thus evident that the halogen atom or atoms have entered β-positions.

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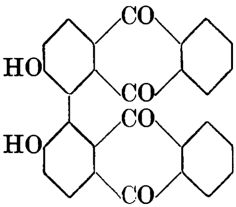
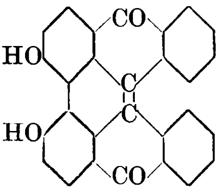
* In the former communication (H. and P., p. 233) this was termed 5′-iodo-3 : 6′-dihydroxyhelianthrone, the orientation employed being that in vogue with anthraquinone derivatives.

When the dihydroxyhelianthrone, preferably in the form of the acetyl derivative, is oxidised with chromic acid (Haller and Perkin, *loc. cit.*), the corresponding dihydroxy-1 : 1′-dianthraquinonyl is obtained. The positions of the hydroxyl groups in this compound have now been studied. Since no change occurred on fusion with alkali at 200—250°, it seemed unlikely that this could be the 2 : 7′- or 7 : 7′-dihydroxy-compound, because if this were so the formation of either a 2 : 7′ : 8′-trihydroxy- or 7 : 8 : 7′ : 8′-tetrahydroxy-derivative, the former containing one, and the latter two alizarin nuclei, was to be expected. 2 : 2′-Dihydroxy-1 : 1′-dianthraquinonyl (III) was therefore synthesised from 1-*bromo*-2-*benzoyloxyanthraquinone* (the 1-*chloro*-compound being much less satisfactory) by the Ullmann method (*Annalen*, 1904, **332**, 28) and subsequent hydrolysis, and proved to be identical in all respects with Haller and Perkin's substance. The helianthrone derived from 3-hydroxyanthranol is therefore the 2 : 2′-dihydroxy-derivative (IV).

(III.)



(IV.)

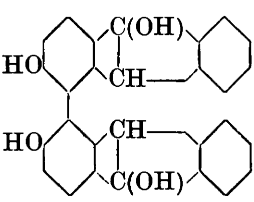


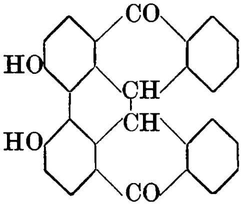
1-*Bromo*-2-*hydroxyanthraquinone* can be obtained, in a similar manner to the 1-chloro-compound (Decker and Laube, *Ber.*, 1906, **39**, 112), from 2-hydroxyanthraquinone and hypobromite in theoretical amount. Excess of the reagent yields 1 : 3-*dibromo*-2-*hydroxyanthraquinone*, and from this, by mild fusion with 40% alkali in an autoclave, 3-bromoalizarin is obtained—a result indicating the more stable character of the β-halogen atom as compared with that in the α-position. 1 : 3-Dibromo-2-hydroxyanthraquinone has been described by Baeyer as the product of the action of sulphuric acid on tetrabromophenolphthalein (*Annalen*, 1880, **202**, 336); the melting points given for this compound, 207—208°, and its acetyl derivative, 189—190°, however, differ from those, 216—217° and 195°, recorded here. Baeyer, again, by the action of 50% alkali in an open dish at 200° for 3 hours, obtained, not 3-bromoalizarin, but alizarin itself. This further discrepancy is no doubt to be accounted for by the fact that during his experiment a considerable concentration of the alkali solution occurred.

Helianthrone can be prepared (Scholl, *Ber.*, 1910, **43**, 1734) from 1 : 1′-dianthraquinonyl by the action of aluminium and sulphuric acid—a reaction involving reduction and subsequent oxidation—

and 4 : 4′-dichlorohelianthrone has been obtained from the corresponding dichlorodianthraquinonyl in a similar manner (Eckert and Tomaschek, *Monatsh.*, 1918, **39**, 839). The conversion of (III) into (IV) was now studied, not only to complete the synthesis of the latter from 1-bromo-2-hydroxyanthraquinone, but with the special object of isolating one or other of the intermediate products of this reaction. This can hardly be accomplished by the aluminium–sulphuric acid method, and when stannous chloride and hydrochloric acid were employed, although indications of the presence of a substance of this character were obtained (Haller and Perkin, *loc. cit.*), its isolation was not found possible. By the action of zinc dust and ammonia on 2 : 2′-dihydroxy-1 : 1′-dianthraquinonyl (III) better results are obtained, for although a partial disruption of the dianthraquinonyl linkage is liable to occur, with eventual production of 3-hydroxyanthranol, the main product of the reaction is without doubt the *dihydroxydianthranolyl* (V).*

(V.)





(VI.)

This compound is extremely prone to oxidation, and by digestion with boiling nitrobenzene changes into 2 : 2′-dihydroxyhelianthrone (IV) ; on this account all attempts to prepare (VI) were unsuccessful.

The fact that 2 : 2′-dihydroxyhelianthrone can be so easily iodinated in pyridine solution (*loc. cit.*) suggested that this method might be used in the case of other hydroxy-compounds, and an account of its application to certain hydroxyanthraquinones will be the subject of a later communication. 2-Hydroxyanthraquinone thus yielded a *monoiodo*-derivative, and as this substance appeared to be of interest in connexion with the present research, the orientation of the halogen atom was determined. Although alcoholic sodium methoxide (Decker and Laube, *loc. cit.*) converts 1-chloro-2-methoxyanthraquinone into a mixture of 1-hydroxy-2-methoxy- and 1 : 2-dimethoxy-anthraquinones, this iodo(methoxy)-compound merely suffered dehalogenation by such treatment, 2-methoxyanthraquinone being produced. Alkali fusion led to the formation of alizarin, suggesting the constitution 1-iodo-2-hydroxyanthraquinone; but this was not conclusive evidence, since 2 : 3-dibromo-

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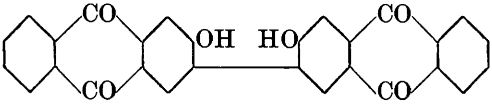
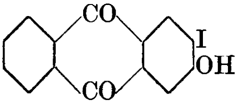
* For (V) without the 2- and 2′-hydroxyls the term *dianthranolyl,* and similarly for (VI) *dianthronyl,* is suggested.

anthraquinone gives a similar result (Battegay and Claudin, *Bull. Soc. Ind. Mulhouse*, 1920, **86**, 632), 2 : 3-dihydroxyanthraquinone (hystazarin) being unstable in these circumstances. By the application, however, of the Ullmann method to the monoiodo-2-hydroxyanthraquinone, a dihydroxydianthraquinonyl was obtained which, being distinct from (III), can only be 3 : 3′-*dihydroxy*-2 : 2′-*dianthraquinonyl* (VII). Accordingly, when 2-hydroxyanthraquinone is treated with iodine in pyridine solution, the iodine enters the 3-position (VIII).



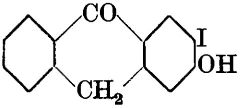
(VII.)



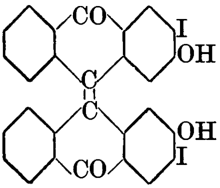
(VIII.)

The conversion of (VIII) into the 3 : 3′-di-iodo-2 : 2′-dihydroxyhelianthrone of Haller and Perkin (*loc. cit.*) was now attempted. Incidentally, the reduction of 1-chloro-2-hydroxyanthraquinone with ammonia and zinc dust, or with stannous chloride and boiling hydrochloric acid, was found to cause elimination of the halogen and formation of 3-hydroxyanthranol (identified as the acetyl derivative, m. p. 157—158°), but with aluminium and sulphuric acid a *chlorohydroxyanthranol* was produced. The orientation of the chloro- and hydroxy-groups present in this compound is under investigation.

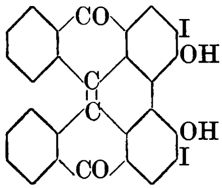
In a similar manner 3-*iodo*-2-*hydroxyanthraquinone* gave but one *anthranol* which experiment indicates has the constitution (X), the isomeric 3-iodo-2-hydroxy-compound being absent. On oxidation with ferric chloride, (X) yielded 2 : 2′-di-iodo-3 : 3′-dihydroxydianthrone, from which the *tetra-acetyl* derivative of *di-iododihydroxydianthranol* was prepared. This differed from the non-halogenated compound (Perkin and Yoda, *loc. cit.*) in that with iodine in pyridine solution the dianthraquinone (XI) was not obtained, and only by a treatment of the di-iododihydroxydianthranol itself with alkaline ferricyanide could this conversion be effected.



(X.)



(XI.)



(XII.)

Although 2 : 2′-di-iodo-3 : 3′-dihydroxydianthranol could be oxidised to the helianthrone by ferricyanide in excess, better results were obtained with alkaline persulphate (compare Eckert and Tomaschek, *loc. cit.*). The 3 : 3′-di-iodo-2 : 2′-dihydroxyhelianthrone (XII) produced was identical with the iodination product of 2 : 2′-dihydroxyhelianthrone described above, and this, on further treatment with persulphate, yielded a compound which was not closely examined but was doubtless the corresponding naphthadianthrone.

Whereas 3 : 4-dihydroxyanthranol (deoxyalizarin) is readily oxidised to 3 : 4 : 3′ : 4′-tetrahydroxydianthrone, the conversion of the latter into the corresponding tetrahydroxydianthraquinone and tetrahydroxyhelianthrone could not be effected (Goodall and Perkin, J., 1924, **125**, 470). Owing to the presence of hydroxy-groups in the positions indicated, such compounds should be of tinctorial interest and attention was accordingly directed to 3 : 4 : 6-trihydroxyanthranol (deoxyanthrapurpurin; Cross and Perkin, J., 1927, 1297) in the hope that the 6-hydroxyl group of this substance, in that it may be considered analogous to that of 3-hydroxyanthranol itself, would favour these reactions. By using ferric chloride, the dianthrone can be obtained, but this is tedious to purify owing to the simultaneous production of an amorphous blue compound, and better results are obtained with hydrogen peroxide. The conversion of 3 : 4 : 6 : 3′ : 4′ : 6′-hexahydroxydianthrone into the corresponding dianthraquinone and helianthrone could not be effected owing, evidently, to its preferential oxidation to anthrapurpurin. Even by digestion with boiling acetone this colouring matter is produced, and all processes of mild oxidation give a similar result. It seems evident that other methods for the synthesis of dianthraquinones and helianthrones of this type must be discovered, and experiments in this direction are now in progress.

EXPERIMENTAL.

3 : 3′-*Di-iodo*-2 : 2′-*dihydroxyhelianthrone* (XII).—A solution of 2 : 2′-diacetoxyhelianthrone (1 g.) and iodine (3 g.) in pyridine (15 c.c.) was boiled for 10 minutes and poured into acidified sodium bisulphite solution. The maroon precipitate was again treated with iodine (3 g.) in pyridine (15 c.c.) as above. The yield was 1·288 g. (calc. for a di-iodo-compound, 1·33 g.). Acetylation in pyridine caused the rapid separation of 3 : 3′-*di-iodo*-2 : 2′-*diacetoxyhelianthrone* as small orange prisms, m. p. 268—270° (decomp.) after recrystallisation from much acetone; these dissolved in sulphuric acid with a green coloration, quickly changing to blue (Found : I, 32·8. $C_{32}H_{16}O_6I_2$ requires I, 33·6%). Hydrolysis with sulphuric acid in the presence of acetic acid gave the di-iododihydroxy-compound as minute maroon needles. When, however, the acetyl derivative in boiling pyridine was treated with a little diethylamine,

and the solution diluted with an equal bulk of acetic acid and treated with hydrochloric acid, the di-iododihydroxyhelianthrone was deposited in fair-sized leaflets having a beetle-green iridescence; these were sparingly soluble in the usual solvents and gave a blue solution in sulphuric acid. (The 3-iodo-2 : 2′-dihydroxyhelianthrone of Haller and Perkin, *loc. cit.*, can be crystallised in a similar manner.) With hydrosulphite and alkali a green vat is produced.

3 : 3′-*Dibromo*-2 : 2′-*dihydroxyhelianthrone*.—To 2 : 2′-diacetoxyhelianthrone (1 g.) in ice-cold pyridine (15 c.c.), bromine (1 g.) was slowly added. After 12 hours, the solution, when added to acidified sodium bisulphite, gave a brick-red precipitate (1·18 g. Calc. for a dibromo-derivative, 1·15 g.). 3 : 3′-Dibromo-2 : 2′-diacetoxyhelianthrone crystallises from acetic anhydride in orange-red prismatic needles, m. p. 293—296°, which dissolve in sulphuric acid with a pure blue coloration.

3-*Iodo*-2 : 2′-*diacetoxynaphthadianthrone*.—3-Iodo-2 : 2′-diacetoxyhelianthrone (1 g.) in benzene (1500 c.c.) was exposed to light for 3 weeks. Pale yellow, almost colourless needles separated, the fluorescence of the solution gradually disappearing. The product, m. p. above 340°, which gave a red solution in sulphuric acid and evolved iodine when strongly heated, without doubt had the above-stated constitution.

1 : 3-*Dibromo*-2-*hydroxyanthraquinone*.—To 2-hydroxyanthraquinone (2 g.) in boiling 1% sodium hydroxide solution (220 c.c.), sodium hypobromite (prepared from bromine, 4 g., and sodium hydroxide solution, 10 c.c.) was gradually added, and the digestion continued for 1 hour. The cold liquid, when poured into acidified sodium bisulphite solution, gave a precipitate which, after repeated crystallisation from alcohol, formed microscopic yellow needles, m. p. 216—217° (Found: C, 44·2; H, 1·7. $C_{14}H_6O_3Br_2$ requires C, 43·8; H, 1·8%).

1 : 3-*Dibromo*-2-*acetoxyanthraquinone* crystallises from acetic acid in yellow needles, m. p. 195° (Found: Br, 37·9. $C_{16}H_8O_4Br_2$ requires Br, 37·7%).

1 : 3-*Dibromo*-2-*methoxyanthraquinone*, prepared by means of methyl sulphate and alkali, separates from benzene in pale yellow, hair-like needles, m. p. 226—227° (Found: CH_3, 3·8. $C_{15}H_8O_3Br_2$ requires CH_3, 3·8%).

3-*Bromoalizarin*.—1 : 3-Dibromo-2-hydroxyanthraquinone (0·5 g.) was mixed with sodium hydroxide (7 g.) in water (10 c.c.) and heated in a small iron autoclave at 200° for 6 hours; the melt was then diluted with water, and the violet solution neutralised with acid. The dull yellow product was dried and extracted with boiling solvent naphtha, the extract agitated with dilute sodium hydroxide solution, and the alkaline liquid acidified. By acetylating the bright orange powder produced, an acetyl compound was obtained in needles, m. p. 201—202°. That this compound was diacetyl-3-bromoalizarin was evident from a mixed melting-point determination, the 3-bromoalizarin required for this purpose being prepared by the action of bromine on alizarin-3-sulphonic acid (Ger. Pat. 77179, 1905; Friedländer's "Fortschritte," IV, 330; compare Baeyer, *loc. cit.*).

1-*Bromo*-2-*acetoxyanthraquinone.*—To 2-hydroxyanthraquinone (1 g.) in 1% caustic soda solution (100 c.c.), bromine (0·7 g.) in 10% caustic soda solution (20 c.c.) was gradually added, and the liquid was slowly raised to its boiling point, allowed to cool, and neutralised with hydrochloric acid. The product (1·29 g.) was converted into the *acetyl* compound, which crystallised from acetone in yellow rods, m. p. 182—183° (Found : C, 55·4; H, 2·6; Br, 23·5. $C_{16}H_9O_4Br$ requires C, 55·6; H, 2·6; Br, 23·2%).

1-*Bromo*-2-*hydroxyanthraquinone*, obtained by the hydrolysis of the acetyl compound with hydrochloric acid in the usual manner, separated from alcohol in small yellow cubes, m. p. 185—187° (Found : C, 55·4; H, 2·3. $C_{14}H_7O_3Br$ requires C, 55·4; H, 2·3%).

1-*Bromo*-2-*methoxyanthraquinone*, obtained by the action of methyl sulphate and alkali, consisted of hair-like needles, m. p. 247° (Found : CH_3, 4·7. $C_{15}H_9O_3Br$ requires CH_3, 4·7%).

1-*Bromo*-2-*benzoyloxyanthraquinone.*—To 1-bromo-2-hydroxyanthraquinone (1 g.), suspended in chloroform (5 c.c.) and benzoyl chloride (2 c.c.), pyridine (1·5 c.c.) was added with good stirring. Reaction occurred without apparent solution, and after 24 hours the product was washed with alcohol (yield, 1·25 g.) and recrystallised from benzene, giving yellow needles, m. p. 229—230° (Found : C, 61·9; H, 2·75. $C_{21}H_{11}O_4Br$ requires C, 61·9; H, 2·7%).

2 : 2′-*Dihydroxy*-1 : 1′-*dianthraquinonyl* (III).—A solution of 1-bromo-2-benzoyloxyanthraquinone (0·3 g.) in naphthalene (0·8 g.) was boiled with copper powder (0·3 g.) for 2 hours. The product, freed from naphthalene by extraction with boiling alcohol, was digested with boiling 1% methyl-alcoholic potash and the crimson liquid was filtered, diluted with water, and acidified. The yellow deposit, acetylated with acetic anhydride and pyridine, yielded yellow plates which, after recrystallisation from acetic anhydride, melted at 278—279°, gave in sulphuric acid a scarlet solution slowly changing to black, and were identified, by a mixed melting-point determination, with the 2 : 2′-diacetoxy-1 : 1′-dianthraquinonyl which is obtained by the oxidation of 2 : 2′-diacetoxyhelianthrone with chromic acid in presence of acetic acid.

Attempts to prepare 2 : 2′-dibenzoyloxy-1 : 1′-dianthraquinonyl as described above, but with tetralin instead of naphthalene as solvent, were unsuccessful because the tetralin caused elimination of the halogen; the sole product was 2-benzoyloxyanthraquinone.

1-Chloro-2-methoxyanthraquinone, prepared from the 1-chloro-2-hydroxy-compound, methyl sulphate, and alkali in the usual manner, separated from alcohol in yellow needles, m. p. 223—224°. After being heated (0·3 g.) with copper powder (0·3 g.) in boiling nitrobenzene (3 c.c.) for 2 hours, it was recovered unchanged.

1-*Chloro-2-benzoyloxyanthraquinone.*—To 1-chloro-2-hydroxyanthraquinone (1·2 g.), suspended in a mixture of chloroform (6 c.c.) and benzoyl chloride (3 c.c.), pyridine (2 c.c.) was gradually added, and after 24 hours the product was collected, washed with alcohol (yield, 1·5 g.), and recrystallised from benzene, giving yellow needles, m. p. 228—230°. A mixture of this compound (0·4 g.), naphthalene (0·5 g.), and copper powder (0·3 g.) was boiled for 6 hours and the product was isolated and hydrolysed by the methods previously described. On acetylation, small plates of 2 : 2′-diacetoxy-1 : 1′-dianthraquinonyl, m. p. 274°, were obtained in trifling amount.

2 : 2′-*Dihydroxy*-1 : 1′-*dianthranolyl* (V).—A solution of 2 : 2′-dihydroxy-1 : 1′-dianthraquinonyl (1 g.) in concentrated ammonia (20 c.c.) and water (50 c.c.) was boiled, and zinc dust (3 g.) gradually added, access of air being prevented. After 15 minutes the greenish-yellow liquid was filtered into dilute hydrochloric acid and the pale yellow precipitate dried. Acetylation with acetic anhydride and pyridine gave a product which could be readily separated by extraction with boiling alcohol into two fractions, A remaining practically undissolved, and B passing into solution. From the extract, on cooling, B separated in colourless needles which, after removal in the same manner of a trace of A, melted at 157—158° and consisted, without doubt, of 3 : 9-*diacetoxyanthracene* (Found : C, 73·2; H, 4·9. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·7%). A, recrystallised from alcohol–acetic acid, formed yellow prisms, m. p. 267—268°, which were somewhat sparingly soluble in sulphuric acid, giving a pale yellow solution (Found : C, 73·45; H, 4·5; $CH_3{\cdot}CO_2H$, 41·2. $C_{36}H_{28}O_8$ requires C, 73·7; H, 4·4; $CH_3{\cdot}CO_2H$, 40·9%).

This *tetra-acetyl* derivative of 2 : 2′-dihydroxy-1 : 1′-dianthranolyl was readily oxidised by chromic acid in the presence of acetic acid, yellow plates of 2 : 2′-diacetoxy-1 : 1′-dianthraquinonyl, m. p. 275—277°, being obtained. Hydrolysis with hydrochloric acid then gave 2 : 2′-*dihydroxy*-1 : 1′-*dianthranolyl* (V) as yellow cubes, which blackened at 270° and melted indefinitely at about 290° (Found : C, 80·2; H, 4·4. $C_{28}H_{18}O_4$ requires C, 80·3; H, 4·4%). It was almost insoluble in the usual solvents but gave yellow solutions in alkalis. Boiling nitrobenzene dissolved it readily, but oxidation simultaneously occurred, a red powder separating. This with acetic anhydride and pyridine gave an acetyl compound in yellow needles, m. p. 277°, soluble in sulphuric acid with a violet coloration, which, as its properties and a mixed melting-point determination indicated, was 2 : 2′-diacetoxyhelianthrone.

Further experiments on the reduction of 2 : 2′-dihydroxy-1 : 1′-dianthraquinonyl with ammonia and zinc dust have shown that, if the latter is added all at once, the formation of 3-hydroxyanthranol can, with care, be avoided. By this method, 2 g. of the dianthraquinonyl gave 1·87 g. of dihydroxydianthranolyl (calc., 1·87 g.), from which a pure acetyl compound was at once obtained on acetylation in the usual manner. Boiling with stannous chloride and hydrochloric acid for 15 minutes gave dihydroxydianthranolyl mixed with some dihydroxyhelianthrone (and probably 3-hydroxyanthranol).

Chlorohydroxyanthranol.—To 1-chloro-2-hydroxyanthraquinone (3 g.) in sulphuric acid (60 c.c.) at 30—40°, aluminium powder (1 g.) was slowly added. After 1 hour, the yellow solution was poured into water (500 c.c.), the mixture slowly heated to boiling, and the precipitate collected (2·6 g.). Acetylation in pyridine gave *chlorodiacetoxyanthracene*, which crystallised from alcohol–acetic acid in light yellow cubes, m. p. 167—168° (Found : C, 65·7; H, 3·9; Cl, 10·9; $CH_3{\cdot}CO_2H$, 36·9. $C_{18}H_{13}O_4Cl$ requires C, 65·7; H, 3·95; Cl, 10·8; $CH_3{\cdot}CO_2H$, 36·5%). Hydrolysis with hydrochloric acid gave the *chlorohydroxyanthranol* as a greenish-yellow precipitate, which separated from acetic acid in prisms, m. p. 230° (Found : C, 68·7; H, 3·8. $C_{14}H_9O_2Cl$ requires C, 68·7; H, 3·7%).

3-*Iodo*-2-*hydroxyanthraquinone.*—Iodine (1·5 g.) was added to a solution of 2-hydroxyanthraquinone (0·6 g.) in pyridine (5 c.c.), and the mixture boiled for 15 minutes. On keeping, crystals separated which were collected (the mother-liquor being employed for a second operation) and washed with acidified sodium bisulphite solution (yield, 0·75 g.). The *acetyl* compound, obtained with acetic anhydride and pyridine, crystallised from acetic acid in large yellow needles, m. p. 224—225° (Found: C, 48·8; H, 2·4; I, 32·0. $C_{16}H_9O_4I$ requires C, 48·9; H, 2·3; I, 32·4%). On hydrolysis with hydrochloric acid it gave yellow needles of 3-*iodo*-2-*hydroxyanthraquinone*, m. p. 278—279° after recrystallisation from alcohol, in almost theoretical yield (Found: C, 47·8; H, 2·1. $C_{14}H_7O_3I$ requires C, 48·0; H, 2·0%). This resembled 2-hydroxyanthraquinone in general properties and when fused with alkali at 200° yielded alizarin (identified as the acetyl compound).

3-*Iodo*-2-*methoxyanthraquinone*, prepared from the iodohydroxycompound, alkali, and methyl sulphate, separated from benzene in pale yellow needles, m. p. 228—229° (Found: C, 49·2; H, 2·3; CH_3, 4·2. $C_{15}H_9O_3I$ requires C, 49·4; H, 2·5; CH_3, 4·1%). Owing to the sparing solubility of this substance in hydriodic acid, two treatments with the latter were necessary to ensure complete demethylation.

With the object of substituting a methoxy-group for the iodine in 3-iodo-2-methoxyanthraquinone (compare Decker and Laube, *loc. cit.*) and thus ascertaining its exact position, 0·6 g. was heated with sodium methoxide (sodium, 3 g., in alcohol, 9 c.c.) at 110° in a sealed tube for 12 hours. The product was treated with water, and the undissolved residue crystallised from alcohol. The pale yellow needles obtained melted at 196°, and, as a mixed melting point showed, consisted of 2-methoxyanthraquinone.

3-*Amino-2-hydroxyanthraquinone* (?).—3-Iodo-2-hydroxyanthraquinone (1 g.) in concentrated ammonia (10 c.c.) and a trace of copper were heated at 160—180° in a small autoclave for 8 hours. The violet liquid was acidified, and the red precipitate crystallised by solution in much alcohol and concentration to a small bulk. The reddish-brown leaflets, which possessed a metallic iridescence, had no definite melting point (decomposing above 300°) and gave a yellow solution in sulphuric acid (Found: N, 5·9. $C_{14}H_9O_2N$ requires N, 5·85%). Attempts to prepare a dihydroxyanthraquinone from this compound by the diazotisation process (so as to establish the position of the iodo-group in the iodo-2-hydroxyanthraquinone) failed, and it is likely that the yellow product obtained by means of sodium nitrite and concentrated sulphuric acid is rather a diazo-oxide than a diazonium sulphate.

3-*Iodo-2-benzoyloxyanthraquinone.*—3-Iodo-2-hydroxyanthraquinone (1 g.) in chloroform (5 c.c.) and benzoyl chloride (2 c.c.) was treated with pyridine (1 c.c.). From the clear liquid on keeping, crystals separated, which, by recrystallisation from benzene, were obtained as yellow plates, m. p. 185° (Found: C, 55·3; H, 2·3. $C_{21}H_{11}O_4I$ requires C, 55·5; H, 2·4%).

3 : 3′-*Dihydroxy*-2 : 2′-*dianthraquinonyl* (VII).—A mixture of 3-iodo-2-benzoyloxyanthraquinone (1 g.), naphthalene (1·5 g.), and copper powder (0·5 g.) was boiled for 5 hours, and the product was worked up and finally acetylated as described on p. 186. The acetyl derivative obtained separated from benzene in colourless needles, m. p. 315° (Found: C, 72·15; H, 3·6. $C_{32}H_{18}O_8$ requires C, 72·45; H, 3·4%). This compound is therefore distinct from the 2 : 2′-diacetoxy-1 : 1′-dianthraquinonyl of Haller and Perkin (*loc. cit.*), which melts at 278—279°. The former, again, is soluble in sulphuric acid with an orange colour, whereas the latter thus yields

a crimson liquid which slowly changes to violet-black. The present compound is therefore 3 : 3′-*diacetoxy*-2 : 2′-*dianthraquinonyl.*

2-*Iodo*-3-*hydroxyanthranol* (X).—3-Iodo-2-acetoxyanthraquinone (5 g.) in sulphuric acid (130 c.c.) was gradually treated with aluminium powder (1·5 g.) at 35—40°. The pale yellow liquid was poured into water (1000 c.c.), and the mixture heated to boiling in order to granulate the precipitate (yield, 4·1 g.). Treatment with acetic anhydride and pyridine then gave the *diacetyl* compound, which crystallised from alcohol–acetic acid in colourless needles, m. p. 196° (Found: C, 51·5; H, 3·15; I, 30·6; $CH_3{\cdot}CO_2H$, 29·2. $C_{18}H_{13}O_4I$ requires C, 51·4; H, 3·1; I, 30·6; $CH_3{\cdot}CO_2H$, 28·6%). 2-*Iodo*-3-*hydroxyanthranol*, prepared by the hydrolysis of the acetyl compound with hydrochloric acid, crystallised from acetone in small plates, m. p. 239—240° (Found: C, 49·8; H, 2·8. $C_{14}H_9O_2I$ requires C, 50·0; H, 2·7%).

2 : 2′-*Di-iodo*-3 : 3′-*dihydroxydianthrone.*—To the diacetylanthranol (5·35 g.) in acetic acid (29 c.c.), ferric chloride (7·2 g.) in acetic acid (9·6 c.c.) was added, and the mixture was heated to boiling and then kept at 100° for 45 minutes. Yellow leaflets separated which, after cooling, were collected and washed with alcohol. The yield was 3·95 g. (74%; calc., 79·7%).

2 : 2′-*Di-iodo*-3 : 3′-*diacetoxydianthrone* can be prepared by the addition of a trace of sulphuric acid to a suspension of the dianthrone in acetic anhydride and boiling for a few seconds. It crystallises from acetic anhydride in plates, m. p. 227—228° after darkening at about 215°, which give a yellow solution in sulphuric acid (Found: C, 50·7; H, 3·0. $C_{32}H_{20}O_6I_2$ requires C, 50·9; H, 2·6%). With boiling acetic anhydride and pyridine, the *tetra-acetyl* derivative of 2 : 2′-di-iodo-3 : 3′-dihydroxydianthranol is produced, which separates from acetone in yellow prisms containing two molecules of acetone of crystallisation (Found: C, 53·0; H, 3·55. $C_{36}H_{24}O_8I_2,2C_3H_6O$ requires C, 42·8; H, 3·7%). When heated, it melts between 200° and 220°, resolidifies at about 260°, and melts again at 290°. Kept at 160° until constant in weight, it loses 12·1% of acetone (theory requires 12·2%) and then melts at 290°. Again, when alcohol is added to a solution of the tetra-acetyl derivative in acetic anhydride, the deposited crystals contain approximately one molecule of alcohol of crystallisation (Found: loss at 160°, 4·1. Theory requires loss, 5·2%). It separates, however, solvent-free from acetic anhydride and then melts at 293—295° (Found: C, 51·4; H, 3·0; $CH_3{\cdot}CO_2H$, 29·1. $C_{36}H_{24}O_8I_2$ requires C, 51·55; H, 2·8; $CH_3{\cdot}CO_2H$, 28·6%). Sulphuric acid dissolves it with a magenta coloration. Hydrolysis gave 2 : 2′-*di-iodo*-3 : 3′-*dihydroxydianthrone* as yellow needles, which darkened at 255° and melted at 267—268° (Found :

C, 50·5; H, 2·5. $C_{28}H_{16}O_4I_2$ requires C, 50·15; H, 2·4%). The property of the tetra-acetyldi-iodoanthranol, which is apparently not possessed by the diacetyldianthrone, to separate from acetone with solvent of crystallisation which is retained with some tenacity is analogous to that of the unhalogenated tetra-acetyl compound (Perkin and Whattam, J., 1922, **121**, 293). The latter indeed it has now been found crystallises from benzene in brown prisms, $C_{36}H_{26}O_8,C_6H_6$, m. p. 175—177°, and from chloroform in prisms, probably $C_{36}H_{26}O_8,CHCl_3$, melting at 161° when quickly heated.

2 : 2′-*Di-iodo*-3 : 3′-*dihydroxydianthraquinone* (XI).—Attempts to prepare this compound by the action of iodine upon the tetra-acetyldi-iododianthranol in pyridine solution having failed (compare Perkin and Yoda), 2 : 2′-di-iodo-3 : 3′-dihydroxydianthrone (2 g.) was dissolved in 10% sodium hydroxide solution (100 c.c.), the liquid well boiled, and, after cooling, 8% potassium ferricyanide solution (25 c.c.) slowly added. After 2 hours the suspension was neutralised by hydrochloric acid, the dull yellow precipitate collected (1·97 g.), and acetylated in pyridine. Without apparent solution, pale yellow plates, m. p. 306—308°, of 2 : 2′-di-iodo-3 : 3′-diacetoxydianthraquinone were obtained. These dissolved in sulphuric acid with a crimson colour passing to brown-black—a property of dianthraquinone itself and its 3 : 3′-dihydroxy-compound (*loc. cit.*).

3 : 3′-*Di-iodo*-2 : 2′-*dihydroxyhelianthrone* (XII).—A solution of 2 : 2′-di-iodo-3 : 3′-dihydroxydianthrone (0·5 g.) in 5% sodium hydroxide solution (25 c.c.) was boiled and then filtered into a solution of potassium persulphate (1·5 g.) in water (50 c.c.), a brown deposit separating. The mixture was acidified and the crude helianthrone collected and dried (yield, 0·4 g.). The *diacetyl* compound, obtained in the usual manner and recrystallised from much acetone, consisted of orange prisms, m. p. 268—270°, which gave in sulphuric acid a green solution rapidly becoming blue (Found: C, 51·2; H, 2·9. $C_{32}H_{16}O_6I_2$ requires C, 51·2; H, 2·1%). A comparison of this compound with the acetylation product of the di-iododihydroxyhelianthrone obtained by the direct iodination of 2 : 2′-dihydroxyhelianthrone (*loc. cit.*) indicated that they were identical.

3 : 4 : 6 : 3′ : 4′ : 6′-*Hexahydroxydianthrone*.—To acetylanthrapurpurinanthranol (0·4 g.) in acetic acid (2 c.c.), ferric chloride (0·6 g.) in acetic acid (1 c.c.) was added and the mixture was boiled for 2 minutes and then kept at 100° for 1 hour. The green deposit (0·25 g.), which consisted of a yellow product mixed with a blue amorphous compound, was acetylated with acetic anhydride. The latter impurity, being unattacked, was removed by hot filtration,

and addition of alcohol to the filtrate caused the separation of 3 : 4 : 6 : 3′ : 4′ : 6′-*hexa-acetoxydianthrone* as colourless needles, m. p. 250—251° after recrystallisation from acetone (Found : C, 65·15; H, 4·2; $CH_3·CO_2H$, 50·1. $C_{40}H_{30}O_{14}$ requires C, 65·4; H, 4·1; $CH_3·CO_2H$, 49·0%).

The nature of the blue compound has not yet been ascertained. It is insoluble in the usual solvents, dissolves in sulphuric acid with a yellow coloration, and, as prepared above, contains iron, which is evidently in combination, as it is not removed by the action of boiling hydrochloric acid. Apparently the same substance, in this case iron-free, is in part produced when the hexa-acetyldianthrone is digested with boiling alcoholic sulphuric acid; this product will be further examined in due course. Subsequent experiments have shown that by oxidising anthrapurpurinanthranol (5 g.) in alcohol (20 c.c.) and 10% caustic soda solution (10 c.c.) (boiling to effect solution and subsequently well cooling) with 100-volume hydrogen peroxide (10 c.c.), the dianthrone can be produced without admixture with this blue substance. After 5 hours the liquid was diluted with water and acidified with sulphuric acid and the dianthrone (4·8 g.) was washed with acetone and with ether. It was thus obtained as a pale green, amorphous powder which darkened at about 140° and blackened at 240°, but had no definite melting point. Although when acetylated it gives the crystalline acetyl compound referred to above, it has not itself been obtained in a crystalline condition, and indeed separates as a green powder when the acetyl compound is hydrolysed with hydrochloric acid in presence of acetic acid.

When 3 : 4 : 6 : 9-tetra-acetoxyanthracene (5 g.) in acetic acid (250 c.c.) was exposed to sunlight, colourless prisms slowly separated and the liquid, at first pale yellow, developed a green tint. After 5 weeks, the crystals (1·7 g.), which evidently consisted of 3 : 4 : 6 : 9 : 3′ : 4′ : 6′ : 9′-*octa-acetoxydianthranol*, were collected; after recrystallisation from acetic acid, they melted at 239—240° (Found : C, 64·7; H, 2·0. $C_{44}H_{34}O_{16}$ requires C, 64·6; H, 4·2%).

3 : 4 : 6 : 3′ : 4′ : 6′-Hexahydroxydianthrone is very susceptible to oxidation and its yellow solution in acetone, when boiled, gradually develops a red colour owing to the formation of anthrapurpurin, for the residue obtained on removal of the acetone gave on acetylation triacetylanthrapurpurin, m. p. 227°. Attempts to prepare the corresponding hexahydroxydianthraquinone and helianthrone from this dianthrone have failed, all gentle methods of oxidation giving anthrapurpurin. When the dianthrone (2 g.), suspended in ether (50 c.c.), was treated with diazomethane (nitrosomethylurethane, 8 c.c.), and the crude product crystallised from alcohol,

colourless needles of a methyl ether, m. p. 215—216°, were obtained. This compound has not yet been further investigated.

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