CCCLXIV.—3-*Iodoalizarin.*

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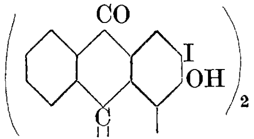
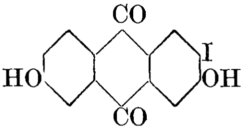
2 : 2′-DIHYDROXYHELIANTHRONE, in boiling pyridine solution, is converted by iodine into the 3 : 3′-di-iodo-derivative (I) in almost quantitative amount (Hardacre and Perkin, J., 1929, 180), and from 2-hydroxyanthraquinone the 3-iodo-compound can be prepared in a similar manner.

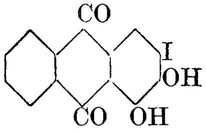
If other hydroxyanthraquinones, containing the β-hydroxyl group and an unsubstituted β-position adjacent thereto, could be thus iodinated, they would be available for the production of hydroxy-2 : 2′-dianthraquinonyls by the Ullmann reaction. With this object the behaviour of alizarin and anthra- and flavo-purpurins towards iodine in these circumstances was studied, with negative



(I.)



(II.)



(III.)

results, and such a failure, at least in the case of the last two compounds, which can be regarded respectively as 2 : 7 : 8- and 2 : 5 : 6-trihydroxyanthraquinone (compare 2-hydroxyanthraquinone) was remarkable. As the result of a long series of experiments, in addition to 2-hydroxyanthraquinone, 2 : 7-dihydroxyanthraquinone proved to be the only other reactive member of this group; and this, which is less readily attacked than the 2-hydroxy-compound, yields, curiously enough, only the 3-*iodo*-derivative (II). The very similar 2 : 6-dihydroxyanthraquinone (anthraflavic acid) could not be thus iodinated.

The reaction in the case of alizarin appears to be inhibited by the presence of the 1-hydroxyl group, for a pyridine solution of alizarin 1-methyl ether gave with iodine a quantitative yield of the 3-iodo-compound. Demethylation with haloid acid at 140° gave 3-*iodoalizarin* (III), and that the iodine was not simultaneously eliminated is a proof that it occupies the position indicated. 3-Iodoalizarin closely resembles alizarin, not only in appearance, but in its general reactions. Like 3-bromoalizarin, it dyes shades which are analogous to, but possess a slightly more yellow tone than, those which are given by alizarin itself.

Though this method is effective for the iodination of alizarin 1-methyl ether, it does not appear to have general application, because, from the analogous anthrapurpurin 1 : 7-dimethyl ether (Perkin and Storey, J., 1928, 229), an iodo-compound could not be obtained.

By the gentle action of alkali on 1 : 3-dibromo-2-hydroxyanthraquinone, Hardacre and Perkin (*loc. cit.*) obtained 3-bromoalizarin, and it appears probable that if 1-bromo-3-iodo-2-hydroxyanthraquinone could be prepared, in similar circumstances it would yield 3-iodoalizarin. However, when 1-bromo-2-hydroxyanthraquinone is gently iodinated in pyridine solution the sole product is 3-iodo-2-hydroxyanthraquinone, and this elimination of the bromine atom, it might be inferred, is to be ascribed to the reducing action of the hydriodic acid which is simultaneously produced. If, however, 1-bromo-2-hydroxyanthraquinone is treated in pyridine solution with much iodine, there is obtained, in addition to 3-iodo-2-hydroxyanthraquinone, a small amount of a sparingly soluble *compound* which crystallises in red prismatic needles. As this in acetic acid solution is very readily reduced by zinc dust or sodium bisulphite to 3-iodo-2-hydroxyanthraquinone, it seems likely that it is a peroxide and contains the group CI·C·O·O·C·CI. The analytical figures given by this red substance, however, are not in harmony with so simple a view of its structure, and though, curiously enough, it so readily passes into 3-iodo-2-hydroxyanthraquinone, it is not reproduced from the latter by the action of iodine. When sufficient material is available, the further examination of this compound will be undertaken.

EXPERIMENTAL.

3-*Iodoalizarin* 1-*Methyl Ether*.—To alizarin 1-methyl ether (prepared from 2-benzoylalizarin and diazomethane; Perkin and Storey, *loc. cit.*) (0·5 g.) in warm pyridine (7 c.c.), iodine (1·1 g.) was added, the mixture boiled for 2 minutes and poured after a short time into acidified sodium bisulphite solution. The yellow product (0·7 g.; calc., 0·75 g.) crystallised from acetone in yellow plates, m. p. 235—237°. It dissolved in sulphuric acid with a brownish red colour, and evolved iodine when strongly heated.

3-*Iodoalizarin*.—The methyl ether (0·1 g.), suspended in a mixture of acetic acid (2 c.c.) and hydrobromic acid (3 c.c.), was heated at 140° for 2 hours. The crystalline product was acetylated, and the *acetyl* 3-*iodoalizarin* isolated as yellow needles, m. p. 205—207° after recrystallisation from alcohol (Found: C, 47·9; H, 2·4. $C_{18}H_{11}O_6I$ requires C, 48·0; H, 2·4%). The acetyl compound, by hydrolysis with hydrochloric acid in the presence of acetic acid, gave orange-red needles of 3-*iodoalizarin*, which became more scarlet after recrystallisation from *m*-xylene and melted at 227—229° (Found: C, 46·3; H, 2·0. $C_{14}H_7O_4I$ requires C, 46·0; H, 1·9%). It dissolves in sulphuric acid with a dull orange-red colour, very similar to that given by 3-bromoalizarin, whereas alizarin thus gives a deep maroon-coloured liquid. In dilute potassium carbonate it is soluble with a violet-blue tint, slightly bluer than that given by both alizarin and 3-bromoalizarin in similar circumstances, but on the other hand it is deposited from its hot alkali solution by acid as a yellow precipitate, that yielded by alizarin being orange-coloured.

Comparative dyeing experiments, carried out with alizarin and 3-iodoalizarin on woollen cloth mordanted with chromium, aluminium, tin, and iron, showed that except in the case of the iron mordant, iodoalizarin dyes more yellow shades than alizarin. These, however, are hardly so yellow as those given by 3-bromoalizarin.

	Cr.	Al.	Sn.	Fe.
Alizarin	Deep maroon	Red	Red-orange	Purple-black
Iodoalizarin	Red maroon	Scarlet	Orange	Deep black

3-*Iodo*-2 : 7-*dihydroxyanthraquinone.*—A solution of *iso*anthraflavic acid (1 g.) and iodine (1·5 g.) in pyridine (7 c.c.) was boiled for 30 minutes. The mixture, poured into acidified sodium bisulphite, gave 1·35 g. of product (calc., 1·52 g.), indicating that reaction was hardly complete. This was acetylated, and the *acetyl* compound repeatedly crystallised from benzene until the melting point was constant (filtrate A) (Found : C, 48·3 ; H, 2·5. $C_{18}H_{11}O_6I$ requires C, 48·0 ; H, 2·4%). The almost colourless prisms melted at 218—221° and dissolved in sulphuric acid with a deep red colour.

Hydrolysis of the acetyl compound with hydrochloric acid in the presence of acetic acid gave orange-yellow needles of 3-*iodo*iso-*anthraflavic acid* (somewhat redder in tone than those of *iso*anthraflavic acid regenerated from its acetyl derivative), which became darker in colour at about 300° and melted at 305—307° to a black liquid (Found : C, 46·5 ; H, 1·9. $C_{14}H_7O_4I$ requires C, 46·0 ; H, 1·9%).

Filtrate A, by evaporation, gave pale yellow needles, the more soluble fraction of which, after recrystallisation from alcohol–benzene and acetic acid, melted at 195—205°. As destructive distillation gave but a trace of iodine, this product evidently consisted, at least in the main, of acetyl*iso*anthraflavic acid.

Iodination of 1-*Bromo*-2-*hydroxyanthraquinone.*—To 1-bromo-2-hydroxyanthraquinone (0·6 g.) in pyridine (7 c.c.), iodine (1·5 g.) was added, and the solution boiled for 15 minutes. The dull red product was isolated in the usual manner and acetylated, and the crude acetyl derivative extracted with much boiling benzene, a trace of a black impurity remaining undissolved. The concentrated extract deposited crystals and these, after recrystallisation from the same solvent, consisted of yellow prismatic needles, m. p. 225—228° (Found : C, 49·0 ; H, 2·4. Calc. for $C_{16}H_9O_4I$: C, 49·0 ; H, 2·3%). Hydrolysis gave fine yellow needles, m. p. 278—280°, evidently consisting of 3-iodo-2-hydroxyanthraquinone (Found : C, 48·1 ; H, 1·9. Calc. for $C_{14}H_7O_3I$: C, 48·0 ; H, 2·0%).

A solution of 1-bromo-2-hydroxyanthraquinone (0·6 g.) in pyridine (7 c.c.) was treated with iodine (1·5 g.), and the mixture boiled for 15 minutes. The deposit which separated on cooling was collected, washed with alcohol, and treated with boiling acetic anhydride and a trace of pyridine. The reddish-brown product was repeatedly extracted with acetone (residue B), the extract concentrated, and the dull yellow needles obtained, which were contaminated with red specks evidently of B, again extracted with acetone; the crystals, m. p. 225—227°, consisted of 3-iodo-2-acetoxyanthraquinone. The residue B was recrystallised twice from acetic acid and obtained in red prismatic needles which melted at 289—290° to a black liquid, and appeared to contain acetic acid of crystallisation, two different samples heated at 160° losing respectively 14 and 12·4% by weight (Found in material dried at 100°; C, 51·8; H, 3·0%. Found in material dried at 160°: C, 52·8, 52·9; H, 2·4, 2·45; I, 35·9%). The *compound* dissolves in sulphuric acid with a yellow colour, is insoluble in hot sodium hydroxide solution, and does not contain an acetyl group in that it is unaffected by treatment with hydrochloric acid in the presence of boiling acetic acid. A hot solution in acetic acid becomes immediately pale yellow on addition of a trace of zinc dust or sodium bisulphite, and from the liquid water precipitates yellow flocks of 3-iodo-2-hydroxyanthraquinone, identified by means of the acetyl compound, m. p. 225—227°.

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