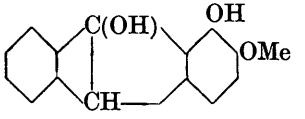
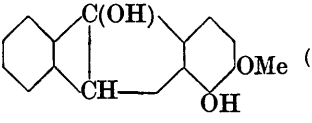
CLXXXI.—*Reduction Products of the Hydroxyanthraquinones. Part VIII.*

By Edwin John Cross and Arthur George Perkin.

When unsymmetrical hydroxyanthraquinones are reduced to hydroxyanthranols, two isomerides can theoretically be obtained; for example, alizarin 2-methyl ether, by treatment with stannous chloride and hydrochloric acid (Miller and Perkin, J., 1925, **127**, 2684), gives both 1-hydroxy-2-methoxy- (I) and 4-hydroxy-3-

(I.) 



(II.)

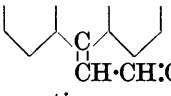
methoxy-anthranol (II), the former in larger amount. As a rule, however, only one isomeride is produced by the reduction; thus 1- and

2-hydroxyanthraquinones yield 1- and 3-hydroxyanthranols, respectively, the theoretically possible isomerides not being produced. The position of the hydroxyl in a hydroxyanthranol therefore cannot be predicted.

The positions of the hydroxyls in the anthranols of anthragallol, anthra-, and flavo-purpurins have now been studied by the method employed by one of us in earlier work and by Miller and Perkin (*loc. cit.*), *viz.*, the conversion of the hydroxyanthranol into the hydroxybenzanthrone, followed by a study of the behaviour of the product when methylated with methyl iodide and alkali. Bistrzycki and Yssel de Schepper (*Ber.*, 1898, **31**, 2790) obtained a 3 : 4 : 7-trimethoxyanthrone (which when oxidised gives flavopurpurin trimethyl ether) by the action of sulphuric acid on 4′ : 5 : 6-trimethoxydiphenylmethanecarboxylic acid, but there is no evidence that this is a methylation product of the hydroxyanthranol derived from flavopurpurin itself (Liebermann, *Ber.*, 1888, **21**, 435).

A drawback to the application of the benzanthrone process (employing glycerol and sulphuric acid) to the hydroxyanthranols is that these are more or less decomposed by the sulphuric acid before the desired reaction occurs, and so the yield of hydroxybenzanthrone is sometimes very small or even infinitesimal. The replacement of sulphuric acid by potassium hydrogen sulphate is sometimes effective. As a rule, more certain results can be obtained by passing hydrogen chloride through a mixture of the hydroxyanthranol and acraldehyde in acetic acid solution. For example, although hydroxybenzanthrones could be prepared in satisfactory amount from the anthranols of anthrapurpurin and anthragallol by all three methods, the acraldehyde method alone was successful in the conversion of flavopurpurin-anthranol into the trihydroxybenzanthrone. 3-Hydroxyanthranol thus gives 2-hydroxybenzanthrone. By this method, however, benzalizarin could not be obtained from 3 : 4-dihydroxy(alizarin)-anthranol.

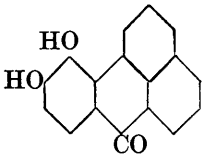
The preparation of hydroxybenzanthrone derivatives by the direct action of acraldehyde in this manner is interesting, because in order that ring formation may take place from the allylanthranol,

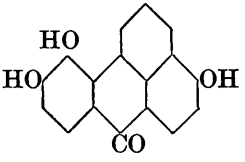


, which is evidently the first product of the reaction, an oxidising agent is necessary. This is presumably supplied by the excess of acraldehyde present, which, as the result, is reduced to allyl alcohol.

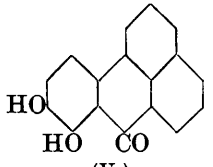
The hydroxybenzanthrone, $C_{17}H_{10}O_4$, derived from anthrapurpurin-anthranol closely resembles benzalizarin (III) in properties. Since it yields a *triacetyl* derivative on acetylation, and with methyl

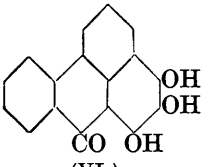
iodide and alkali in theoretical amount a *trimethyl ether*, it is evidently the 2 : 7 : 8-trihydroxy-compound (IV).

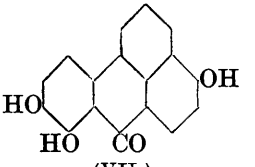
(III.) 

 (IV.)

This substance, which we have named *benzanthrapurpurin*, gives a crimson oxonium salt, $C_{17}H_{10}O_4,H_2SO_4$, and dyes shades similar to, although slightly yellower than, those given by anthrapurpurin itself. On the other hand, iso*benzanthragallol*, $C_{17}H_{10}O_4$, obtained in a similar manner from anthragallol-anthranol, crystallises in yellow needles and differs markedly from anthragallol in properties. On acetylation, a *diacetyl* compound only is obtained, and the substance is not methylated by treatment with methyl iodide or with methyl sulphate and alkali. With diazomethane, however, a *dimethyl ether* is produced. This is unattacked by prolonged boiling with acetic anhydride and pyridine, but gives with alcoholic potash a *potassium* salt, and it is thus evident that of the three hydroxyls present in this compound one, evidently adjacent to a carbonyl group, is remarkably resistant both to methylation and to acetylation. A somewhat similar difficulty was experienced in the case of *iso*benzalizarin (V) (*loc. cit.*). *iso*Benzanthragallol is consequently either a 2 : 3 : 4- (VI) or a 5 : 6 : 7-trihydroxybenzanthrone. For reasons given later, the first of these constitutions appears to be preferable.

 (V.)

 (VI.)

 (VII.)

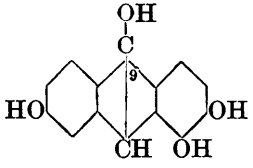
The substance dyes shades distinct from and weaker than those given by anthragallol.

Crude deoxyflavopurpurin from commercial flavopurpurin gives an amorphous acetyl derivative (compare Liebermann, *loc. cit.*; Graebe and Thode, and Bernhard, *Annalen*, 1906, **349**, 207, 222), and cannot be purified in the same way as anthrapurpurin-anthranol (Goodall and Perkin, J., 1924, **125**, 470). A crystalline acetyl compound of the pure substance has also not been described. It is now found that if crude flavopurpurin, crystallised from nitrobenzene, is reduced to the anthranol, and the product is partly

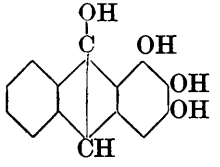
acetylated in the cold, a crude *diacetyl* derivative is obtained which can be freed by recrystallisation from the acetyldeoxyanthraflavic acid which is present. The pure diacetyl compound thus obtained is converted by Fischer and Bergmann's method of acetylation (*Ber.*, 1918, **51**, 1797) into *tetra-acetyldeoxyflavopurpurin*, which is readily obtained pure in pale yellow plates. Hydrolysis of this yields deoxyflavopurpurin, which crystallises in deep yellow plates.

iso*Benzflavopurpurin*, $C_{17}H_{10}O_4$, was obtained from flavopurpurin-anthranol by the acraldehyde method. By methylation, only a *dimethyl ether* could be obtained, although the formation from the latter of a *potassium* salt was evidence of the presence of a third hydroxyl group. Acetylation in the ordinary manner gave a *diacetyl* compound, and only by prolonged treatment in boiling solution could a mixture of di- and tri-acetyl derivatives be produced. *iso*Benzflavopurpurin is thus either 2 : 5 : 6- (VII) or 3 : 4 : 7-trihydroxybenzanthrone, and of these the former constitution is to be preferred.

These results therefore indicate that the hydroxyl groups in anthrapurpurin-, anthragallol-, and flavopurpurin-anthranols are present respectively in the 3 : 4 : 6 (VIII), 1 : 2 : 3 (IX), and 1 : 2 : 6 (X) positions.



(VIII.)



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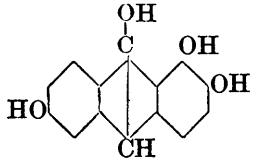

(X.)

Miller and Perkin (*loc. cit.*) suggested that the reduction of a hydroxyanthraquinone to its anthranol or anthrone will take place in such a way that any β-hydroxyl in the former will preferably occupy a para-position with respect to the anthranol hydroxyl (9) or anthrone carbonyl group in the latter. Although the conditions dealt with in the present communication differ from those discussed on the former occasion, because two β-hydroxyls are present in all the hydroxyanthraquinones now studied, it will be observed, on examining the formulæ of the hydroxyanthranols given above, that this suggestion still holds good in the case of one β-hydroxyl group at least. The presence of such a hydroxyl in a hydroxyanthraquinone seems, therefore, to be a determining factor in the orientation of the hydroxyls of the anthranol derived from it by reduction. Moreover, it is now suggested as likely that in all cases where the β-hydroxyl is present in the anthranol in the 3- or 6-position, and the contiguous α-position is free, the benz-

anthrone condensation will take place at the latter point; for instance, 3-hydroxyanthranol gives 2-hydroxybenzanthrone, and anthrapurpurin(3 : 4 : 6-trihydroxy)-anthranol gives 2 : 7 : 8-trihydroxybenzanthrone. It is therefore considered probable that the trihydroxybenzanthrones derived from anthragallol- (IX) and flavopurpurin- (X) anthranols will be represented by the formulæ (VI) and (VII).

Interesting again is the fact that 3-hydroxyanthranol, on treatment with alkali and glucose (Bradshaw and Perkin, J., 1922, **121**, 911), yields 2-hydroxybenzanthronecarboxylic acid.

Benzalizarin (III) and benzanthrapurpurin (IV) are red substances and their dyeing properties resemble those of alizarin and anthrapurpurin, respectively. *iso*Benzflavopurpurin (VII) dyes yellow shades of a similar character to those of *iso*benzalizarin (V) and differs markedly from flavopurpurin in this respect. According to the quinonoid theory, (III) and (IV) can only be represented as *p*-quinonoid and (V) and (VII) as *o*-quinonoid dyes, and, as suggested in a previous communication (*loc. cit.*), the very distinct shades of red and yellow given by these colouring matters respectively are explainable on the assumption that they possess such configurations. On the other hand, *iso*benzanthragallol (VI), as its formula suggests, may be represented as either a *p*- or an *o*-quinonoid dye, though its somewhat feeble tinctorial property favours the latter view.

Experimental.

Benzanthrapurpurin.—A mixture of anthrapurpurin-anthranol (4 g.; prepared by hydrolysis of pure acetylanthrapurpurin-anthranol: Goodall and Perkin, *loc. cit.*), sulphuric acid (47 c.c.), water (23 c.c.), and glycerol (8 g.) was slowly heated to 125—130° with constant stirring and kept at that temperature for 1 hour. The dark red solution, when cold, was poured into water, the precipitate was collected, washed, dried, and repeatedly extracted with boiling alcohol, and the extracts were concentrated and poured into much ether. The solution was filtered, well washed, and evaporated, and the dark brown residue (3·1 g.) was digested with acetic anhydride and a trace of pyridine. The product, after repeated crystallisation from acetic acid (charcoal), was obtained in yellow plates (1·9 g.), m. p. 245—246° (Found: C, 68·3; H, 4·2; $C_2H_4O_2$, 44·7. $C_{23}H_{16}O_7$ requires C, 68·3; H, 4·0; $C_2H_4O_2$, 44·55%).

This compound, evidently *triacetylbenzanthrapurpurin*, gave with sulphuric acid a deep red solution, which gradually deposited crimson, microscopic needles of *benzanthrapurpurin sulphate*. These were collected, washed with glacial acetic acid, and dried

at 100° (Found: $C_{17}H_{10}O_4$, 73·75. $C_{17}H_{10}O_4,H_2SO_4$ requires $C_{17}H_{10}O_4$, 73·9%).

The *benzanthrapurpurin* obtained from this salt by the action of boiling water crystallised from dilute alcohol in microscopic, orange needles which did not melt below 340° and dissolved in caustic soda solution with a violet coloration. It produced light brown, orange, dull maroon, and dark brown shades on wool mordanted with aluminium, tin, chromium, and iron respectively.

Methylation. To a boiling mixture of acetylbenzanthrapurpurin (2 g.), methyl alcohol (30 c.c.), and methyl iodide (12 c.c.), a solution of caustic potash (2 g.*) in methyl alcohol was gradually added during 12 hours. The excess of methyl iodide was distilled off, the deep reddish-brown liquid was kept over-night, and the crystals that separated were washed with water and dried. The light brown product (0·98 g.) was dissolved in benzene, and a small amount of alcoholic potash added to precipitate any dimethyl ether present as potassium salt. The filtered and concentrated solution deposited crystals over-night, which, by recrystallisation from benzene (charcoal), were obtained in golden-yellow needles (0·45 g.), m. p. 185—185·5° (Found: C, 74·9; H, 4·9; CH_3, 13·7. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0; CH_3, 14·1%).

This compound, *benzanthrapurpurin trimethyl ether*, could also be obtained by methylating benzanthrapurpurin with methyl sulphate in the usual manner.

To demethylate this compound completely, it was necessary to perform the Zeisel determination twice on the same material, as was the case with benzalizarin dimethyl ether (Perkin, J., 1920, **117**, 696).

iso*Benzanthragallol.*—A mixture of anthragallol-anthranol (2 g.), glycerol (50 g.), and powdered anhydrous potassium hydrogen sulphate (20 g.), made into a smooth paste, was gradually heated, with stirring, to 190—200°; the solution was maintained at this temperature for ½ hour, a light brown powder separating. The mixture was cooled somewhat and poured into water, and the precipitate thus produced was washed by decantation, dried, and extracted two or three times with cold alcohol to remove resinous impurities. The product was acetylated, and the crystals that separated (0·9 g.) were recrystallised repeatedly from acetic acid, giving yellow needles of *diacetyl*iso*benzanthragallol*, m. p. 232—233° (Found: C, 69·5; H, 4·0; $C_2H_4O_2$, 32·75. $C_{21}H_{14}O_6$ requires C, 69·6; H, 3·9; $C_2H_4O_2$, 33·15%).

This diacetyl compound, when hydrolysed with hydrochloric

* Commercial stick. Theory requires 1·66 g. KOH for hydrolysis and methylation.

and acetic acids, gave 77·06% of iso*benzanthragallol* (calc., 76·8%). The latter crystallised from nitrobenzene in yellow needles, m. p. 319—321° (decomp.), sparingly soluble in alcohol, ether, benzene, or acetic acid (Found : C, 73·3; H, 3·8. $C_{17}H_{10}O_4$ requires C, 73·4; H, 3·6%).

*iso*Benzanthragallol becomes blood-red, without apparently dissolving, on treatment with caustic soda solution, and dyes mordanted woollen cloth shades which are distinct from those given by anthragallol. Pale brown, yellow, light brown, and olive shades are obtained on aluminium, tin, chromium, and iron mordants, respectively.

By prolonged digestion (27 hours) with acetic anhydride and a trace of pyridine, the diacetyl derivative only could be obtained. Acetylation in the cold by Fischer and Bergmann's method (*loc. cit.*) yielded, at least mainly, the diacetyl derivative, without apparent solution of the *iso*benzanthragallol.

iso*Benzanthragallol Dimethyl Ether*.—As experiment showed that methylation of *iso*benzanthragallol could not be effected with methyl iodide or methyl sulphate in the usual way, a suspension of *iso*benzanthragallol (1·5 g.) in dry ether (120 c.c.) was treated with diazomethane (generated from 6 c.c. of nitrosomethylurethane) and kept over-night. The excess of diazomethane was then removed, the solution filtered from unchanged *iso*benzanthragallol (0·8 g.), the filtrate evaporated to dryness, and the residue washed with a little acetone to remove resinous matter. There was thus obtained a yellow, crystalline powder (0·22 g.), and a further small amount (0·03 g.) was deposited from the acetone washings after concentration. By repeated crystallisation from benzene (animal charcoal), yellow needles of iso*benzanthragallol dimethyl ether*, m. p. 152—153°, were obtained (Found : C, 74·5; H, 4·7; CH_3, 9·8. $C_{19}H_{14}O_4$ requires C, 74·5; H, 4·6; CH_3, 9·8%). The final acetone filtrate contained much resinous matter from which nothing definite could be isolated.

In the Zeisel determination, it was found necessary to submit the substance to a second distillation with hydriodic acid. The residue, after treatment with bisulphite solution, consisted of *iso*benzanthragallol.

*iso*Benzanthragallol dimethyl ether did not yield an acetyl derivative even by prolonged digestion (5 hours) with acetic anhydride and pyridine. It was soluble with difficulty in absolute alcohol, yielding a faintly yellow solution which, on the addition of alcoholic potash, became of a somewhat deeper colour. On keeping, pale yellow, hair-like, silky needles separated which were washed with alcohol and dried. They darkened at 130°, melted at 235—240°

to form a black liquid, gave ash on ignition, and evidently consisted of the monopotassium salt of *iso*benzanthragallol dimethyl ether. A suspension in absolute alcohol to which a trace of phenolphthalein was added showed no red coloration, but on addition of water this was observed owing to decomposition of the potassium salt.

Methylation. To a boiling suspension of *iso*benzanthragallol dimethyl ether (0·5 g.) in methyl alcohol (10 c.c.) and methyl iodide (3 c.c.), a solution of caustic potash (0·12 g.*) in methyl alcohol was gradually added during 11 hours, and the digestion was continued for 2—3 hours longer. The excess of methyl iodide was removed, and after 12 hours the crystals were collected, washed with methyl alcohol and with water, and dried. The yellow, microscopic needles (0·45 g.), m. p. 152—153°, were shown to consist entirely of unchanged *iso*benzanthragallol dimethyl ether by a mixed m.-p. determination.

Flavopurpurin-anthranol.—Commercial flavopurpurin (10 g.), partly purified by crystallisation from nitrobenzene, was treated for 1 hour with a boiling solution of stannous chloride (10 parts) in hydrochloric acid (50 parts). When cold, the product was collected, washed with hydrochloric acid and with water, and dried. The light brown powder (8·7 g.), on treatment with acetic anhydride and potassium acetate in the cold, slowly dissolved, but after a short time crystals separated; after 12 hours, these were collected and washed with alcohol (yield, 4·3 g.). By repeated crystallisation from acetic acid (charcoal), this *acetyl* derivative was obtained in yellow plates (2·2 g.), m. p. 209—212° (Found : C, 66·2; H, 4·4; $C_2H_4O_2$, 36·6. $C_{18}H_{14}O_6$ requires C, 66·25; H, 4·3; $C_2H_4O_2$, 36·8%).

This substance, *diacetylflavopurpurin-anthranol*, was hydrolysed with hydrochloric acid in acetic acid solution in the usual way. The product, by recrystallisation from dilute alcohol, was obtained in deep yellow, rectangular plates which darkened at 200° and melted at 231—233° when slowly heated. If the m.-p. tube, however, was introduced into a bath at 235°, the substance melted at 243—245° (Found : C, 69·4; H, 4·3. Calc. for $C_{14}H_{10}O_4$: C, 69·4; H, 4·1%). Graebe and Thode (*loc. cit.*) described it as a crystalline powder, m. p. 258°. Flavopurpurin-anthranol dissolves in caustic soda solution with an orange-red colour which in air rapidly develops the purple tint characteristic of the alkaline solution of flavopurpurin.

By acetylating diacetylflavopurpurin-anthranol by Fischer and Bergmann's method (*loc. cit.*), *tetra-acetylflavopurpurin-anthranol*

* Commercial stick. Theory requires 0·09 g. KOH.

was obtained, which, after repeated crystallisation from methyl alcohol, was isolated in very pale yellow, rectangular plates, m. p. 181—182°, sparingly soluble in methyl alcohol with formation of a blue fluorescent solution (Found: C, 64·2; H, 4·5; $C_2H_4O_2$, 58·3. $C_{22}H_{18}O_8$ requires C, 64·4; H, 4·4; $C_2H_4O_2$, 58·5%).

Tetra-acetylflavopurpurin-anthranol, on oxidation with chromic acid in acetic acid solution, gave yellow needles of triacetylflavopurpurin, m. p. 208—211° (Frobenius and Hepp, *Ber.*, 1907, **40**, 1049, give m. p. 202—203°).

iso*Benzflavopurpurin*.—Attempts to prepare this substance by the glycerol–sulphuric acid method were unsuccessful, and the following procedure was therefore adopted. Hydrogen chloride was passed into a mixture of diacetylflavopurpurin-anthranol (1 g.), acraldehyde (3 c.c. of a solution of 1 part of acraldehyde in 5 parts of glacial acetic acid), and glacial acetic acid (10 c.c.), and the mixture was heated to the b. p. during ¼ hour and boiled for ¼ hour. The yellow solution became orange as the boiling point was reached, and brown at the end of the operation. The solution, poured into boiling water (150 c.c.), gave a resinous precipitate. This, which solidified when cold, was ground with water, washed, and digested with boiling acetic anhydride and a trace of pyridine. The crystals (0·4 g.) of *diacetyliso*benzflavopurpurin thus obtained separated from acetic acid (charcoal) in yellow needles (0·23 g.), which sintered at 233° and melted at 236° (Found: C, 69·4; H, 3·9; $C_2H_4O_2$, 33·01. $C_{21}H_{14}O_6$ requires C, 69·6; H, 3·9; $C_2H_4O_2$, 33·15%).

Benzanthrapurpurin, *iso*benzanthragallol, and 2-hydroxybenzanthrone, prepared in about 30% yield from anthrapurpurin- and anthragallol-anthranols and 3-hydroxyanthranol, respectively, by this acraldehyde method, were identified by the melting points of their acetyl derivatives.

Diacetyl*iso*benzflavopurpurin, hydrolysed with hydrochloric acid in presence of acetic acid, gave iso*benzflavopurpurin*, which is soluble in alkaline solutions with a yellow colour. It is sparingly soluble in acetic acid, and crystallises therefrom in long, light brown needles containing one molecule of acetic acid of crystallisation (Found: $C_{17}H_{10}O_4$, 82·1. $C_{17}H_{10}O_4+C_2H_4O_2$ requires $C_{17}H_{10}O_4$, 82·25%). These crystals, although stable at 100°, are converted at 160° with loss of acetic acid into dull yellow needles, m. p. 293—295° (decomp.) (Found: C, 73·2; H, 3·7. $C_{17}H_{10}O_4$ requires C, 73·4; H, 3·6%).

*iso*Benzflavopurpurin dyes shades which are quite distinct from those yielded by flavopurpurin. On wool mordanted with aluminium, tin, chromium, and iron, yellow, pale yellow, yellowish-brown, and brown shades are respectively obtained.

By treatment for 5 hours with boiling acetic anhydride and

pyridine, *iso*benzflavopurpurin gave a product which melted at 217—221° and consisted of yellow needles, probably of the triacetyl derivative, mixed with clusters of microscopic needles of the diacetyl compound. Even after further prolonged boiling, some diacetyl derivative still remained.

Methylation. A mixture of diacetyl*iso*benzflavopurpurin (1 g.), methyl alcohol (15 c.c.), and methyl iodide (6 c.c.) was boiled for 16 hours, a solution of caustic potash (0·9 g.*) in methyl alcohol being gradually added. From the clear solution at first obtained, a yellow precipitate of the potassium compound of the methyl ether slowly separated, and this was collected, washed with water, and dried. This compound, which did not melt below 300° and gave an ash on ignition, was ground with dilute hydrochloric acid (1 : 4), the mixture boiled, and the precipitate collected (yield, 0·65 g.). The product, now ash-free, crystallised from alcohol–acetic acid in long, light brown needles, m. p. 199—200° (Found : C, 74·3; H, 4·8; CH_3, 9·7. $C_{19}H_{14}O_4$ requires C, 74·5; H, 4·6; CH_3, 9·8%).

iso*Benzflavopurpurin dimethyl ether* was completely demethylated only after the finely divided substance had been boiled with hydriodic acid for 12 hours.

A solution of the dimethyl ether in absolute alcohol, on addition of alcoholic potash, gave an immediate crystalline precipitate of the monopotassium salt.

We are much indebted to the British Alizarine Co., Ltd., for the commercial anthra- and flavo-purpurin necessary for this investigation.

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