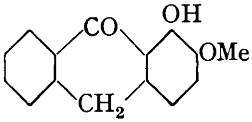
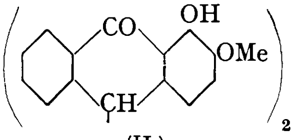
358. *Reduction Products of the Hydroxyanthraquinones. Part XIV.*

By Arthur G. Perkin and (in part) Norman H. Haddock.

It was shown by Attree and Perkin (J., 1931, 144) that when 1-hydroxy-2-methoxyanthrone (I) is oxidised, preferably with iodine in pyridine solution, a colouring matter, $C_{30}H_{18}O_6$ (here termed A), is produced in considerable amount. 1 : 1′-Dihydroxy-2 : 2′-dimethoxydianthrone (II) is (at least in part) a product of this reaction, and as this, when similarly oxidised, also yields (A), a strong probability existed that the latter was 4 : 4′-*dihydroxy*-3 : 3′-*dimethoxyhelianthrone* (III).



(I.)



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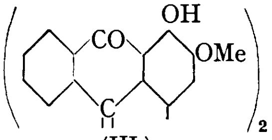

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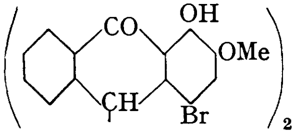

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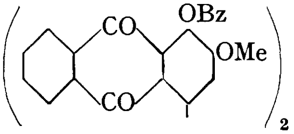
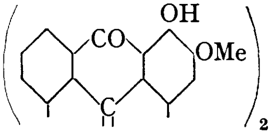


(V.)



(VI.)

The fact that (A) is readily obtained by digesting a boiling pyridine solution of 4-*bromo*-1-*hydroxy*-2-*methoxyanthrone* for a short period appeared to be further evidence for this view, a preliminary formation of the dianthrone (IV) again being assumed to occur.

The view, however, was proved untenable when the helianthrone (III) was synthesised from 4-bromoalizarin 2-methyl ether, preferably in the form of its *benzoyl* compound, by treatment of this in naphthalene solution with copper and ring closure of the resulting *dianthraquinonyl* (V) by Scholl's method (*Ber.*, 1910, **43**, 1734). The product (III) was more soluble than (A) and, unlike this, yielded an *acetyl* compound (with some difficulty).

Demethylation of (III) with a halogen acid gave 3 : 3′ : 4 : 4′-tetrahydroxyhelianthrone, previously synthesised by Eckert and Hampel (*Ber.*, 1927, **60**, 1693) from 3 : 3′ : 4 : 4′-tetra-acetoxydianthracene. There is a remarkable similarity in dyeing properties between this tetrahydroxy-compound (see E. and H.) and the tetrahydroxy-compound obtained either by the demethylation of (A), or directly by the oxidation of 1 : 2-dihydroxyanthrone (*loc. cit.*) with iodine in pyridine solution : both compounds show little or no dyeing affinity towards mordanted calico, and the very similar shades they give on mordanted wool have a poor character. Better results were obtained in this respect by using the sodium sulphonates, for on wool mordanted with tin, aluminium, iron, and oxidised chromium both salts gave deep red-brown, red-violet, black, and slate-blue shades, respectively, which were practically indistinguishable from one another.

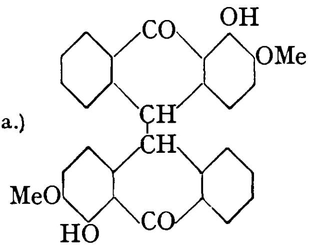
In the hope of isolating some intermediate product of the reaction involved in the formation of (A), the oxidation both of 1-hydroxy-2-methoxyanthrone and of 1 : 1′-dihydroxy-2 : 2′-dimethoxydianthrone with iodine in cold pyridine solution was studied; the crystals that gradually separated in each instance consisted mainly of 4 : 4′-dihydroxy-3 : 3′-dimethoxyhelianthrone (III), only a small amount of (A) being present. This is an excellent method for the preparation of (III) in quantity.

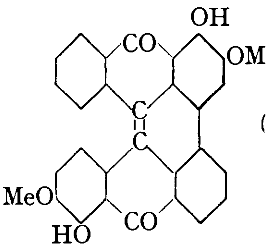
If the pyridine solution of either the anthrone or the dianthrone is allowed to become warm during the addition of the iodine, a mixture consisting of about equal parts of (III) and of (A) is produced, whereas in the boiling solution, though (A) is the main product, some helianthrone (III) is always present. The presence of (III) was not recognised in the early experiments (*loc. cit.*), not only on account of its general similarity to (A), but because, being more soluble, it was in the main eliminated during the recrystallisation process. Both the anthrone and the dianthrone can be thus oxidised by simple aspiration of air through their solutions in boiling pyridine. Here again (A) is the main product, only a trace of 4 : 4′-dihydroxy-3 : 3′-dimethoxyhelianthrone being formed. As a result it appeared possible that in this reaction the latter was the precursor of (A), but numerous trials failed to substantiate this view. The deep colour of (A) indicated that it could hardly be 4 : 4′-dihydroxy-3 : 3′-dimethoxynaphthadianthrone (VI), and experiment supported this.

Eckert and Hampel (*loc. cit.*) have noted the slow conversion of 3 : 3′ : 4 : 4′-tetrahydroxyhelianthrone into the corresponding naphthadianthrone by the action of light, sulphuric acid being the solvent. It has been ascertained, however, that 3 : 3′ : 4 : 4′-*tetra-acetoxyhelianthrone* is so sensitive to light, more especially in acetone solution, that when crystallised from this solvent in the daytime a considerable amount is converted into the *acetylnaphthadianthrone*.

As the dianthrone (II) yields both (A) and the helianthrone (III) and as the latter is evidently formed according to the scheme anthrone → (possibly 10-iodo-anthrone by the iodine method; compare Barnett, Cook, and Grainger, J., 1922, **121**, 2067) → dianthraquinone → helianthrone, the relationship of these dyes would be clear if (II) reacted in these circumstances both as the 1 : 1′-dihydroxy-2 : 2′-dimethoxy- and also as the 1 : 8′-dihydroxy-2 : 7′-dimethoxy-compound (VIIa). (A), being derived from the latter, would thus be 4 : 5′-dihydroxy-3 : 6′-dimethoxyhelianthrone (VIIb).

(VIIa.)

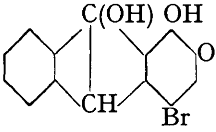




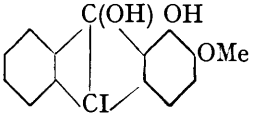
(VIIb.)

Analogy, however, is here lacking and moreover, as experiment showed that when 4-bromo-1-hydroxy-2-methoxyanthrone is kept in cold pyridine suspension (A) only is obtained, it is difficult to bring this fact into line with such a scheme. Indeed, if reaction did occur in the manner indicated, a naphthadianthrone rather than a helianthrone should result.

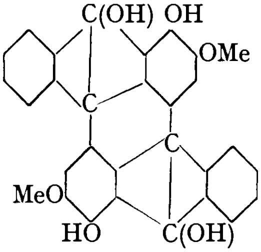
When 4-bromo-1-hydroxy-2-methoxyanthrone is treated with iodine in boiling pyridine solution, the production of the colouring matter does not occur, a dark brown powder being formed. This unexpected result first suggested what is doubtless the correct explanation of the formation of (A). According to this view (A) is 3 : 9-dihydroxy-2 : 8-dimethoxy-5 : 6 : 11 : 12-dibenzperylene-4 : 10-quinone (X), in the formation of which two molecules of the bromo-anthrone are involved. These, under the influence of the pyridine, pass into the anthranol (VIII), from which, by elimination of hydrogen bromide, is produced the leuco- or dihydro-derivative (IX), which is then oxidised to the colouring matter (X).



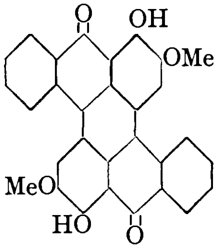
(VIII.)



(XI.)

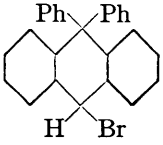


(IX.)

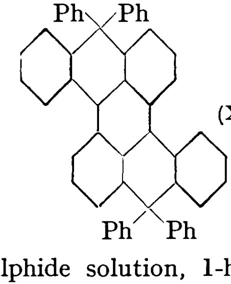


(X.)

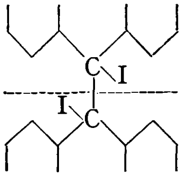
A similar explanation could be given of the formation of (A) (X) by the iodine–pyridine method, if during this process 4-iodo-1-hydroxy-2-methoxyanthrone were produced, for two molecules of this could condense analogously to the bromo-derivative (VIII). Perkin and Story (J., 1931, 2620), who prepared 3-iodo-derivatives from certain hydroxy-anthraquinones by this method, were, however, unable to obtain similar iodo-compounds from the corresponding anthranols. Attempts to isolate 4-iodo-1-hydroxy-2-methoxy-anthrone, or the 4 : 4′-di-iodo-dianthrone, from the iodine–pyridine mixture have also failed, though, owing to the rapidity of colour formation, these cannot be regarded as decisive. It is considered more probable that reaction here proceeds, at least in part, *via* the 10-iodo-anthranol (XI), two molecules of which condense as indicated above, and such a scheme appears to be supported by the work of Liebermann and Lindenbaum (*Ber.*, 1905, **38**, 1799), who found that, when 10-bromo-9 : 9-diphenyl-9 : 10-dihydro-anthracene (XII) is boiled in naphthalene solution, " tetraphenyl heptacyclene " (in reality 4 : 4 : 10 : 10-tetraphenyl-4 : 10-dihydro-5 : 6 : 11 : 12-dibenzperylene, XIII) is produced.



(XII.)



(XIII.)



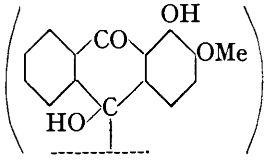
(XIV.)

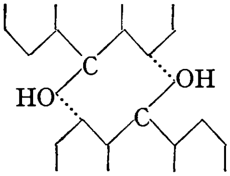
With iodine in carbon disulphide solution, 1-hydroxy-2-methoxyanthrone yielded iodine-like needles of an unstable compound evidently analogous to the substance, $C_{14}H_{10}O,HI,I_2$, which Liebermann and Mamlock (*Ber.*, 1905, **38**, 1784) obtained similarly from anthranol. 1 : 1′-Dihydroxy-2 : 2′-dimethoxyanthrone gave, in the same way, a dark-coloured semi-crystalline product of a similar type. [Both when boiled with pyridine, naturally gave some quantity of (A) (X).] In pyridine solution such compounds could exist but momentarily, and in presence of excess of iodine it seems likely that the 10-iodo-anthrone (XI) is eventually produced.

On the other hand, 1 : 1′-dihydroxy-2 : 2′-dimethoxydianthrone behaves analogously to the anthrone and is most probably the main source of (A) (X). Its conversion into the latter can again be envisaged as proceeding *via* the di-iodo-compound (XIV), and here it is suggested that a production of the free radicals (indicated by the dotted line) then occurs, which subsequently condense to form (X) (compare VIII).

1-Hydroxy-2-methoxyanthrone yields (A) (X) by methods not involving the use of iodine, notably aerial oxidation. Here the dianthrone is, without doubt, produced in quantity and this, it is suggested, passes into the anthrapinacol (XV) at the boiling temperature. The free radicals (XVI) then condense, as above indicated. A formation of the pinacol (XV) in the iodine reaction is indeed also possible.

(XV.)





(XVI.)

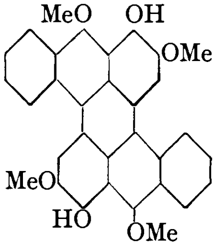
Evidence which supports the suggestions given above has been received from Prof. Heilbron (private communication), who finds that, by heating 4-chloroanthrone at 240°, a purple dye, probably 5 : 6 : 11 : 12-dibenzperylene-4 : 10-quinone, is produced. 4-Chloro-1-hydroxyanthrone reacts in an analogous manner. (Compare also Scholl, Meyer, and Winkler, *Annalen*, 1932, **494**, 201.)

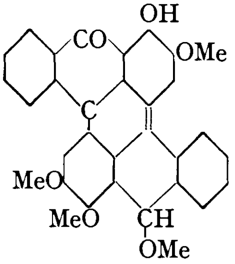
Of interest again in this connexion is the recent patent (E.P. 373139, 1932; I. G. Farbenindustrie A.G.) which describes the preparation of dyes by heating methylene-anthrones with acid condensing agents, *e.g.*, aluminium chloride. These compounds, it is stated, consist probably of 5 : 6 : 11 : 12-dibenzperylene-4 : 10-quinones.

Though the practical results of Attree and Perkin's communication (*loc. cit.*) are unaffected by the present work, it is now certain that the 4 : 4′-dihydroxy-3 : 3′-dimethoxy-helianthrone there referred to is really the isomeric 3 : 9-dihydroxy-2 : 8-dimethoxy-5 : 6 : 11 : 12-dibenzperylene-4 : 10-quinone. So similar are these two compounds in properties, however, that the theoretical points there discussed are applicable to both cases. On the other hand, it has now been ascertained that the colorations given by these compounds with sulphuric acid are respectively malachite-green and blue.

The methylation of (A) (X) by the dry method (D.R.-P. 242379, 1910) gave, as the main product, a *tetramethyl* ether. This separated from benzene as maroon-coloured needles, but crystallised from acetic anhydride in fine scarlet prisms, apparently $C_{32}H_{22}O_6,C_2H_4O_2$, which at 140° passed into the former variety with loss of acetic acid. Cold hydrobromic acid (*d* 1·7) in acetic acid gave a blue solution of the oxonium salt, which soon disappeared, a precipitate, evidently of the dimethyl ether (A) (X), separating: this reaction suggested the demethylation of methoxyls contiguous to the carbonyl groups. With hydrobromic acid at 180° the tetrahydroxy-compound (tetrahydroxydibenzperylenequinone) was obtained. Though the maroon colour of this substance and the fact that it gives, in benzene, a precipitate with alcoholic potash, at first sight suggested that

(XVII.)





(XVIII.)

it is not fully methylated, it may consist of the normal (3 : 9 : 2 : 8-tetramethoxy) compound. On the other hand, it seemed possible that during the preparation of the salt of (A) with alcoholic potash reduction occurred and that the tetramethyl ether derived from this was in reality a dihydro-compound. If such is the case, it will be necessary to assume the presence, in the tetramethyl ether itself, of either the quinol (XVII) or the hydroxyanthranol group (XVIII), though the presence of the latter would be rather unexpected.

As a by-product of the methylation a little *trimethyl* ether was also produced. This reacted very similarly to the tetramethyl ether with hydrobromic acid. Difficulty was experienced in obtaining consistent methoxy-figures from these compounds by the ordinary Zeisel method. The methylimide process, however, gave better results.

When methylated by the same process, 4 : 4′-dihydroxy-3 : 3′-dimethoxyhelianthrone (III) gave, as the main product, orange-red needles of a compound, apparently 3 : 3′ : 4 : 4′-*tetramethoxyhelianthrone*, less probably a dihydro-derivative of this. With cold hydrobromic acid in acetic acid, partial demethylation occurred, the blue liquid gradually depositing 4 : 4′-dihydroxy-3 : 3′-dimethoxyhelianthrone (III). (Chromic acid oxidation gave yellow crystals evidently of 3 : 3′ : 4 : 4′-tetramethoxy-1 : 1′-dianthraquinonyl.) This did not give an oxonium salt with hydrobromic acid, and in acetic acid was not demethylated even after short boiling with the acid mixture.

As a by-product of the methylation process a brick-red compound was isolated. This again with hydrobromic acid gave 4 : 4′-dihydroxy-3 : 3′-dimethoxyhelianthrone, suggesting it to be the 4-hydroxy-3 : 3′ : 4′-trimethoxy-derivative, though the Zeisel figures agree better with those for a dimethyl ether. The further investigation of this substance is in progress.

1-*Hydroxy*-2-*methylanthrone* (I, with Me for OMe) behaves with iodine in pyridine solution analogously to 1-hydroxy-2-methoxyanthrone (I). At the boiling point, aniline-blue-like plates of a substance $C_{30}H_{18}O_4$ separate, consisting with little doubt of 3 : 9-*dihydroxy*-2 : 8-*dimethyl*-5 : 6 : 11 : 12-*dibenzperylene*-4 : 10-*quinone* (X, with Me for OMe).

Again, with iodine in the cold, though a trace of the preceding quinone is obtained, the main product, green-iridescent needles, is 4 : 4′-*dihydroxy*-3 : 3′-*dimethylhelianthrone* (III with Me for OMe). The *diacetyl* derivative of this compound in acetone solution is converted by the action of light into the diacetyl-naphthadianthrone (as VI, with Me for OMe). Lack of raw material has as yet prevented a closer examination of these compounds.

4-Bromo-1-hydroxy-2-methoxyanthrone is prepared from 4-bromoalizarin 2-methyl ether in boiling acetic acid with stannous chloride–hydrochloric acid. It has no melting point, but gradually passes, on heating, into (A) (X). A second product of the reduction is 4-hydroxy-3-methoxyanthranol, evidently present in the first place as the 1-bromo-compound. The bromine atom, being here contiguous to the carbonyl group, is loosely held and is eliminated by reduction.

1-Hydroxy-2-methylanthrone is similarly obtained from 1-hydroxy-2-methylanthraquinone, in addition to 4-hydroxy-3-methylanthranol. The latter has been previously prepared by the Imperial Chemical Industries Ltd. (private communication). These results further confirm the conclusions of Cross and Perkin (J., 1930, 292).

With the object of obtaining a dibromo-derivative of (A) (X), attempts have been made to prepare 3-*bromoalizarin* 2-*methyl ether* by the partial methylation of 3-bromoalizarin. Merely a trace of this compound was obtained, the main product being 3-*bromoalizarin dimethyl ether*. The partial demethylation of the latter with halogen acid gave better results.

For the analyses given in this paper we are indebted to Dr. A. Schoeller of Berlin.

EXPERIMENTAL.

4-Bromoalizarin 2-methyl ether (33 g.), prepared from alizarin 2-methyl ether (30 g.), boiling acetic acid (750 c.c.), and bromine (24 g.) (D.R.-P. 158,257) with addition of sodium acetate crystals (35 g.), melted at 235—237°. The acetyl compound formed pale yellow needles, m. p. 175—177°.

4-Bromo-1-hydroxy-2-methoxyanthrone.—A mixture of acetyl-4-bromoalizarin 2-methyl ether (5 g.), acetic acid (70 c.c.), and stannous chloride–hydrochloric acid (60 c.c.) was boiled for 1 hour. The orange prismatic needles separating over-night were recrystallised from benzene (Found : C, 56·9; H, 3·6. $C_{15}H_{11}O_3Br$ requires C, 56·4; H, 3·5%).

The filtrate, by treatment with hot water, gave 4-hydroxy-3-methoxyanthranol (2·1 g.), m. p. when pure 198—200°.

4-Bromo-1-acetoxy-2-methoxy-9-anthranyl acetate was obtained by gently warming the anthrone (0·5 g.), acetic anhydride (3·5 c.c.), and pyridine (3 c.c.), pouring the mixture into dilute acid after 12 hours, and washing the product with acetone and crystallising it from alcohol; yellow prisms, m. p. 185—188° (Found : C, 57·1; H, 3·9. $C_{19}H_{15}O_5Br$ requires C, 56·6; H, 3·7%).

(1) A solution of 4-bromo-1-hydroxy-2-methoxyanthrone (0·5 g.) in pyridine (20 c.c.), after boiling for 10 minutes, deposited crystals (0·19 g.); from the filtrate, 0·045 g. was isolated (yield, 64·7%). (2) The bromo-anthrone in nitrobenzene was boiled for 15 minutes, or gently heated with sulphuric acid. The products were recrystallised from methyl salicylate and identified as (A) (X) (Found : C, 75·5; H, 3·9. Calc. for $C_{30}H_{18}O_6$: C, 75·9; H, 3·8%).

4-Bromo-1-benzoyloxyalizarin 2-Methyl Ether.—4-Bromoalizarin 2-methyl ether (5 g.), benzoyl chloride (17·5 c.c.), and pyridine (10 c.c.) were heated at 100° for 5 minutes, and alcohol (40 c.c.) added to the cold product. The crystals obtained gave almost colourless plates of the *benzoate* (5 g.), m. p. 207—208°, after recrystallisation from benzene–alcohol (Found : C, 60·3; H, 3·0. $C_{22}H_{13}O_5Br$ requires C, 60·4; H, 3·0%).

4 : *4'-Dibenzoyloxy-*3 : *3'-dimethoxy-*1 : *1'-dianthraquinonyl* (V).—A solution of the preceding benzoate (2 g.) in nitrobenzene (5 c.c.) was boiled for 1½ hours with copper powder (2 g.). The cold crystals were collected, washed with benzene, dissolved in boiling nitrobenzene, decanted from copper, and recrystallised (yellow needles, 1·1 g.). Alternatively, a boiling mixture of the benzoate (9 g.), naphthalene (22 g.), and copper (9 g.) was digested for 1 hour; after removal of naphthalene by means of hot benzene, and recrystallisation, the product weighed 6 g. The *dianthraquinonyl* melted above 360° and dissolved in sulphuric acid with a blood-red tint (Found : C, 73·3; H, 3·6. $C_{44}H_{26}O_{10}$ requires C, 73·6; H, 3·6%).

4 : *4'-Dihydroxy-*3 : *3'-dimethoxy-*1 : *1'-dianthraquinonyl.*—The benzoyl derivative (3 g.) in pyridine (50 c.c.) was boiled with 5% alcoholic potash (20 c.c.) for 15 minutes. After addition of a little water, the solution was acidified; the precipitate was washed with alcohol and crystallised from methyl salicylate. The orange boat-shaped needles dissolved in hot dilute alkali with a violet-red tint, and had not melted at 360° (Found : C, 70·8; H, 3·7. $C_{30}H_{18}O_8$ requires C, 71·1; H, 3·6%). The acetyl derivative, pale yellow needles, m. p. 322—326°, was best prepared with boiling acetic anhydride and a trace of sulphuric acid.

3 : 3' : 4 : *4'-Tetrahydroxy-*1 : *1'-dianthraquinonyl.*—This was obtained by heating the dimethoxy-compound (1 g.) and boric acid (1 g.) in sulphuric acid at 140°. For purification the acetyl compound, m. p. 280—282° after sintering at 275°, was prepared, and this was hydrolysed with hydrochloric acid in the presence of much acetic acid. The small orange-red prismatic needles had the properties described by Eckert and Hampel (*loc. cit.*) (Found : C, 70·1; H, 3·3. Calc. for $C_{28}H_{14}O_8$: C, 70·3; H, 2·9%).

4 : *4'-Dihydroxy-*3 : *3'-dimethoxyhelianthrone* (III).—To 4 : 4'-dihydroxy-3 : 3'-dimethoxy-1 : 1'-dianthraquinonyl (1 g.) in sulphuric acid (20 c.c.) at 140—150°, copper powder was slowly added. After 1 hour, the blue-green liquid was filtered through asbestos into water, and the red precipitate crystallised twice from methyl salicylate; m. p. 335—337° (Found : C, 75·8; H, 3·8. $C_{30}H_{18}O_6$ requires C, 75·9; H, 3·8%). The *helianthrone* (III) separated from pyridine as long, red-brown-green iridescent needles, gave a red powder when ground, was insoluble in alkali solutions, dissolved in sulphuric with a malachite-green tint, and was not reduced by alkali hyposulphite. It was slowly attacked by acetic anhydride and pyridine, more readily, however, by the former and a trace of sulphuric acid. The *diacetate* precipitated by water crystallised from benzene–alcohol in microscopic scarlet needles, m. p. 267—269° (Found : C, 73·1; H, 3·9. $C_{34}H_{22}O_8$ requires C, 73·1; H, 4·0%).

3 : 3' : 4 : 4'-Tetrahydroxyhelianthrone, prepared by heating the dimethoxy-compound with hydrobromic acid (*d* 1·7) at 180—210° for 3 hours, and recrystallised from methyl salicylate, had the properties assigned to it by Eckert and Hampel (*loc. cit.*) (Found : C, 74·6; H, 3·4%).

3 : 3' : 4 : *4'-Tetra-acetoxynaphthadianthrone.*—The tetrahydroxyhelianthrone was boiled with acetic anhydride and pyridine for 2 hours, the liquid poured into water, and the precipitate crystallised from benzene. When it was boiled with acetone, pale yellow, fine needles

of 3 : 3′ : 4 : 4′-*tetra-acetoxynaphthadianthrone* remained undissolved (filtrate A). These, recrystallised from benzene, appeared to melt at about 360° and dissolved in sulphuric acid with a red-violet tint (Found : C, 70·1; H, 3·4. $C_{36}H_{20}O_{10}$ requires C, 70·5; H, 3·2%).

Filtrate (A), when partially concentrated, deposited some of the same compound; on further evaporation, orange needles of 3 : 3′ : 4 : 4′-*tetra-acetoxyhelianthrone separated.* These, possibly containing a trace of the acetylnaphthadianthrone, melted at 282—286° and dissolved in sulphuric acid with a green-blue tint (Found : C, 70·3; H, 3·7. $C_{36}H_{22}O_{10}$ requires C, 70·3; H, 3·6%)

Sulphonation.—3 : 3′ : 4 : 4′-Tetrahydroxyhelianthrone (0·5 g.) in fuming (20%) sulphuric acid was heated at 100° for 1 hour, and the solution poured into water. After addition of sodium chloride and boiling, the sodium sulphonate separated; it was collected when cold, washed with brine during 3 days, and dried. It dissolved in water with a claret colour, passing to violet-blue on addition of alkali. In similar circumstances the sodium sulphonate prepared from the tetrahydroxy-compound derived from (A) (X) yielded a pure blue tint.

Iodine Oxidation of 1-*Hydroxy*-2-*methoxyanthrone.*—(a) A solution of the anthrone (1 g.) in hot pyridine (5 c.c.) was cooled, and to the semi-solid mass iodine (1 g.) in pyridine (3 c.c.) was slowly added, with good cooling. From the clear liquid, crystals slowly separated, 0·65 g. being obtained after 5 days. Extraction with boiling pyridine left a residue (0·1 g.) which, recrystallised from methyl salicylate, had the properties of (A) (X). The pyridine filtrate, on concentration, gave reddish-brown iridescent needles of 4 : 4′-dihydroxy-3 : 3′-dimethoxyhelianthrone, m. p. 335—337° (Found : C, 75·6; H, 3·7%). The acetyl compound obtained from it had m. p. 267—269°.

(b) 1 : 1′-Dihydroxy-2 : 2′-dimethoxydianthrone (III) (3 g.), pyridine (15 c.c.), and iodine (3 g.) in pyridine (9 c.c.) were employed, also in the cold. The crystals which had separated after 4 days contained 4 : 4′-dihydroxy-3 : 3′-dimethoxyhelianthrone (1·5 g.) and (A) (X) (0·5 g.).

(c) Iodine (20 g.) was gradually added to 1-hydroxy-2-methoxyanthrone (10 g.) in pyridine (200 c.c.), and the mixture boiled for 20 minutes. The product gave (A) (X) (6·6 g.), which was recrystallised from nitrobenzene (Found: C, 75·7; H, 3·8; CH_3, 5·8. Calc. for $C_{30}H_{18}O_6$: C, 75·9; H, 3·8; CH_3, 6·3%), and 4 : 4′-dihydroxy-3 : 3′-dimethoxyhelianthrone (III) (2·2 g.).

Air Oxidation.—Through a solution of 1-hydroxy-2-methoxyanthrone (4 g.) in boiling pyridine (100 c.c.) contained in a distilling flask with attached condenser, air was aspirated for 90 minutes, the distillate being returned when necessary. The crystals were collected from time to time to minimise bumping. They weighed 1·92 g. (yield, 48%) and consisted approximately of 1·67 g. of (A) (X) and 0·25 g. of 4 : 4′-dihydroxy-3 : 3′-dimethoxyhelianthrone. The pyridine filtrate contained a dull red powder from which nothing definite could be isolated.

4-*Bromo*-1-*hydroxy*-2-*methoxyanthrone and Cold Pyridine.*—The powdered anthrone (1 g.) was repeatedly shaken with pyridine (15 c.c.) and filtered off. The filtrate slowly darkened and the crystals (0·1 g.) were collected after 4 days. The residual bromoanthrone, similarly treated with pyridine (15 c.c.), gave crystals (0·17 g.). The product, crystallised from methyl salicylate, consisted entirely of (A) (X).

Methylation of 4 : 4′-*Dihydroxy*-3 : 3′-*dimethoxyhelianthrone.*—The powdered substance (5 g.) was digested with boiling 20% alcoholic potash (25 c.c.), the liquid evaporated, and the residue finely ground and added to a mixture of methyl sulphate (30 g.) and anhydrous sodium carbonate (12·5 g.) at 90°. The whole was heated to 140°, and the product lixiviated with water, dried, and extracted with benzene. Addition of alcoholic potash to the liquid precipitated a potassium salt (B), which was removed, and the solution, after being washed with water, was evaporated to dryness. The residue separated from acetone mainly as a semi-solid mass of hair-like orange needles. These, in contact with the solvent during some weeks, gradually changed to fine scarlet prisms, m. p. 263—265°, soluble in sulphuric acid with a malachite-green colour (Found : C, 76·5; H, 4·9; CH_3, 11·2. $C_{32}H_{22}O_6$ requires C, 76·5; H, 4·4; CH_3, 11·8%).

3 ; 3′ : 4 : 4′-*Tetramethoxyhelianthrone* gave in benzene a yellow fluorescent solution. The 4 : 4′-dihydroxy-3 : 3′-dimethoxyhelianthrone prepared from it with cold hydrobromic acid (*d* 1·7) in acetic acid, after recrystallisation from pyridine, melted at 335—337°.

The potassium salt (B) was neutralised with dilute acid, and the product crystallised twice from benzene (charcoal), in which it gave a yellow fluorescent solution. The glistening scarlet needles, m. p. 285—287°, obtained were insoluble in dilute alkali solution and dissolved in sulphuric acid with a malachite-green tint (Found : C, 76·2; H, 4·3; CH_3, 6·8. $C_{31}H_{20}O_6$ requires C, 76·2; H, 4·1; CH_3, 9·2%. $C_{30}H_{18}O_6$ requires C, 75·9; H, 3·8; CH_3, 6·5%). 4 : 4′-Dihydroxy-3 : 3′-dimethoxyhelianthrone obtained from this compound with cold hydrobromic acid (*d* 1·7) and acetic acid melted at 335—337° after purification. To a boiling solution of the tetramethyl ether in acetic acid, chromic acid was added until a green liquid was obtained. The 3 : 3′ : 4 : 4′-tetramethoxy-1 : 1′-dianthraquinonyl isolated by addition of water, separated from nitrobenzene–alcohol as small yellow prisms, m. p. 335—336°, soluble in sulphuric acid with a red-brown tint.

Methylation of 3 : 9-*Dihydroxy*-2 : 8-*dimethoxy*-5 : 6 : 11 : 12-*dibenzperylene*-4 : 10-*quinone* (*A*).—The potassium salt from 5 g. of the substance was prepared and then methylated according to the preceding method. The product, after lixiviation with water, was extracted with boiling pyridine, leaving 1 g. of residue. The crystals which separated on cooling (2·5 g.) (filtrate C) were dissolved in hot benzene, alcoholic potash added, and the potassium salt collected and decomposed with acid. The *tetramethyl* ether separated from benzene (charcoal) in maroon needles, m. p. 317—319° (Found : C, 76·4; H, 4·0; CH_3, 11·6%). From hot acetic anhydride, maroon needles first separated. These were removed and small scarlet prisms were then deposited. They became maroon-coloured at 140° and melted at 314—315° with loss of acetic acid (Found in air-dried material: C, 71·7; H, 24·5; CH_3, 10·4; $C_2H_4O_2$, 11·2, 10·8. $C_{32}H_{22}O_6,C_2H_4O_2$ requires C, 72·5; H, 4·6; CH_3, 10·7; $C_2H_4O_2$, 10·7%. Found in material dried at 140° : C, 76·8; H, 4·35; CH_3, 11·6. $C_{32}H_{22}O_6$ requires C, 76·5; H, 4·4; CH_3, 12·0%). This tetramethyl ether was insoluble in dilute alkali, gave in pyridine a yellow fluorescent solution, with sulphuric acid a green-blue liquid, and did not appear to be capable of acetylation. The product given by hydrobromic acid (*d* 1·7) in cold acetic acid crystallised from nitrobenzene in iridescent needles, was insoluble in dilute alkali, and had the properties of 3 : 9-dihydroxy-2 : 8-dimethoxydibenzoperylenequinone (A) (X). The substance obtained by heating the crystalline product at 190° with hydrobromic acid (*d* 1·75) in acetic acid dissolved in alkali with a deep blue colour, and yielded the acetyl compound of the tetrahydroxydibenzperylenequinone previously described. Oxidation with chromic acid in acetic acid solution gave water-soluble products only.

The trimethyl ether. The pyridine filtrate (C above) was poured into acid, and the precipitate collected and dissolved in boiling benzene. The glistening red needles obtained closely resembled the analogous substance described above, as obtained from (III), and melted at 289—290° (Found : C, 75·85; H, 4·3; CH_3, 8·7. $C_{31}H_{20}O_6$ requires C, 76·2; H, 4·1; CH_3, 9·2%). The ether was insoluble in dilute alkali, dissolved in sulphuric acid with a green-blue tint, and gave yellow fluorescent solutions. The precipitate obtained by means of cold hydrobromic acid in acetic acid separated from nitrobenzene as needles, was insoluble in alkali, and closely resembled 3 : 9-dihydroxy-2 : 8-dimethoxy-5 : 6 : 11 : 12-dibenzperylene-4 : 10-quinone (A) (X).

1-*Hydroxy*-2-*methylanthrone* (as I).—To commercial 1-hydroxy-2-methylanthraquinone (recrystallised from benzene; 3 g.) in hot acetic acid, stannous chloride–hydrochloric acid was added, and the mixture boiled for ½ hour. The crystals separating over-night (filtrate) were recrystallised from methyl alcohol, giving pale yellow needles, m. p. 136—138°, which dissolved in sulphuric acid with a pale orange tint (Found : C, 80·0; H, 5·4. $C_{15}H_{12}O_2$ requires C, 80·3; H, 5·3%). Occasionally 1-*hydroxy*-2-*methylanthrone* separated from this solvent in leaflets, more soluble than the needle variety but having the same m. p. (Found : C, 79·9; H, 5·4%). The filtrate (above) contained 4-hydroxy-3-methylanthranol, m. p. 197°. 1-Acetoxy-2-methyl-9-anthranyl acetate, prepared from the anthrone, formed prisms (alcohol), m. p. 180—182°.

3 : 9-*Dihydroxy*-2 : 8-*dimethyl*-5 : 6 : 11 : 12-*dibenzperylene*-4 : 10-*quinone* (as X).—To 1-hydroxy-2-methylanthrone (0·5 g.) in boiling pyridine (7·5 c.c.), iodine (1·2 g.) was added, giving first a green and then a red liquid. Leaflets separated and these were slowly deposited from methyl salicylate in rectangular plates (0·3 g.) resembling aniline-blue. The *compound* was insoluble in dilute alkali solution, soluble in sulphuric acid with a blue-green tint, was with difficulty reduced in alkaline solution with sodium hyposulphite, forming a green liquid, and appeared to be incapable of acetylation (Found : C, 81·0; H, 4·0. $C_{30}H_{18}O_4$ requires C, 81·4; H, 4·1%).

4 : 4′-*Dihydroxy*-3 : 3′-*dimethylhelianthrone* (as III).—1-Hydroxy-2-methylanthrone (1 g.) in cold pyridine (15 c.c.) was treated with iodine (1 g.) in pyridine (2 c.c.) with good cooling. After 4 days, the collected deposit was extracted with boiling pyridine, a small part, evidently consisting of the dibenzperylenequinone derivative, being insoluble. The concentrated red fluorescent solution deposited green-iridescent, red, prismatic needles (0·2 g.), soluble in sulphuric acid with a blue tint, changing to violet (Found : C 81·3; H, 4·1. $C_{30}H_{18}O_4$ requires C, 81·4; H, 4·1%).

For acetylation in the usual manner, boiling for some hours is necessary. On keeping, yellow needles separated in small amount, soluble in sulphuric acid with a magenta tint, consisting evidently of 4 : 4'-diacetoxy-3 : 3'-dimethylnaphthadianthrone (as VI). The filtrate, added to water, gave an orange deposit, which was dissolved in benzene. The concentrated liquid on addition of alcohol, deposited fine orange needles of 4 : 4'-*diacetoxy*-3 : 3'-*dimethylhelianthrone*, m. p. 297—300° after darkening at about 280° (Found : C, 77·7; H, 4·2. $C_{34}H_{22}O_6$ requires C, 77·6; H, 4·2%).

3-*Bromoalizarin*.—This was prepared, from alizarin (30 g.), acetic acid (400 c.c.), bromine (22 g.), and anhydrous sodium acetate (20 g.) (compare Dimroth, *Ber.*, 1920, **53**, 3025), in a yield of 28 g., m. p. 260—261°.

3-*Bromoalizarin Dimethyl Ether*.—3-Bromoalizarin (15 g.) was added to alcoholic potash (KOH, 9 g.), the product dried and stirred into a mixture of methyl sulphate (140 g.) and anhydrous sodium carbonate (60 g.), and the whole heated to 140°. The lixiviated product was dissolved in benzene, a little alcoholic potash added, and the potassio-3-bromoalizarin 2-methyl ether removed. From the concentrated filtrate, yellow needles of the *dimethyl* ether were deposited, m. p. 136—137° (Found : C, 55·3; H, 3·1; Br, 23·0. $C_{16}H_{11}O_4Br$ requires C, 55·4; H, 3·1; Br, 23·0%).

3-*Bromoalizarin* 2-*Methyl Ether*.—The dimethyl ether (1 g.) was heated with hydrochloric acid (33%) (10 c.c.) at 135—140° for 90 minutes. The *product*, freed from dimethyl ether (see above), crystallised in orange-yellow needles, m. p. 186—187° (Found : C, 54·05; H, 2·7. $C_{15}H_9O_4Br$ requires C, 54·2; H, 2·8%). The *acetyl* compound separated from alcohol as almost colourless needles, m. p. 150—151° (Found : C, 54·5; H, 2·9. $C_{17}H_{11}O_5Br$ requires C, 54·4; H, 2·9%).

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