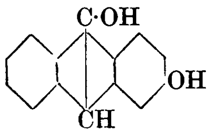
# XXII.—*Reduction Products of the Hydroxyanthraquinones. Part XII.*

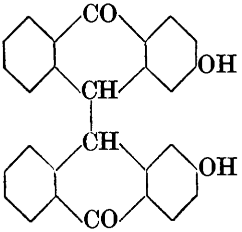
By Gordon Frederick Attree and Arthur George Perkin.

By the oxidation of 3-hydroxyanthranol (I) Perkin and Whattam (J., 1922, **121**, 289) obtained 3 : 3′-dihydroxydianthrone (II), and from this by the action of alkaline ferricyanide 2 : 2′-dihydroxyhelianthrone (IV) was prepared by Haller and Perkin (J., 1924, **125**, 231).

The intermediate product 3 : 3′-dihydroxydianthraquinone (III) is readily produced (Perkin and Yoda, J., 1925, **127**, 1884) by the action of iodine in pyridine solution on 3 : 3′-diacetoxy-9 : 9′-dianthranyl diacetate. It could not thus be obtained from 3 : 3′-diacetoxydianthrone, evidence that in the conversion of (II) into (III) the enolisation of the former is first essential.

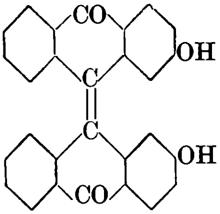
(I.)

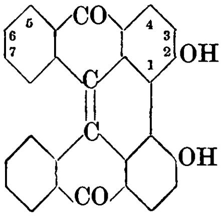




(II.)

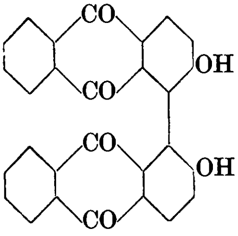
(III.)





(IV.)

Proof of the constitution of (IV) was afforded (Perkin and Hardacre, J., 1927, 181) by its oxidation with chromic acid to 2 : 2′-dihydroxydianthraquinonyl (V), which was synthesised by the Ullmann method from 1-bromo-2-hydroxyanthraquinone.



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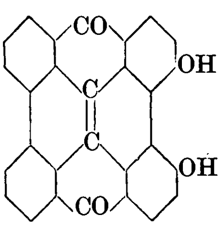
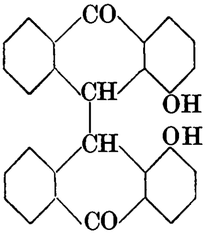


(VI.)

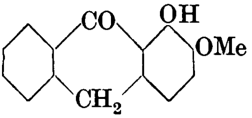


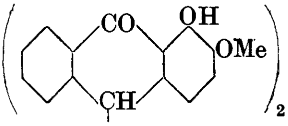
(VII.)

From (IV), by further oxidation, 2 : 2′-dihydroxynaphthadianthrone (VI) was obtained. Attempts were made to obtain from 3 : 4-dihydroxyanthranol (deoxyalizarin) and 3 : 4 : 6-trihydroxyanthranol (deoxyanthrapurpurin) respectively, by similar methods, 7 : 7′ : 8 : 8′-tetrahydroxy- and 2 : 2′ : 7 : 7′ : 8 : 8′-hexahydroxy-helianthrones, because such compounds, it was anticipated, would possess tinctorial properties of interest. Although in each case the production, from these anthranols, of the corresponding hydroxydianthrones could be readily effected, attempts to convert the latter into hydroxyhelianthrones were unsuccessful (Goodall, Macmaster, and Perkin, J., 1924, **125**, 476; 1927, 1306). It is shown in the sequel that 4 : 4′-*dihydroxydianthrone* (VII) is also unreactive in this respect. The reason for these failures is now, at least in part, clear, because, by the methods of oxidation here cited, the production of the 1 : 1′-dianthraquinonyl linkage, which is essential for the conversion of hydroxydianthraquinone into hydroxyhelianthrone (compare III and IV), only occurs between the hydroxylated rings. Obviously, therefore, in the case discussed above (compare VII) helianthrone formation is not possible from hydroxydianthrones which contain a hydroxyl group in position 4. Such an explanation, however, is incomplete in that it affords no reason for the non-production from these 4-hydroxy-compounds of the corresponding dianthraquinones (compare III) and indeed, as shown later, this reaction is also inhibited by the presence of hydroxyl groups other than that in this position.

In continuation of experiments with the desire of preparing mordant dyes of the helianthrone group 1-hydroxy-2-methoxyanthrone (VIII) (Miller and Perkin, J., 1925, **127**, 2684) was now studied with a more satisfactory result. From it, by air oxidation in alcoholic potassium hydroxide solution, 1 : 1′-*dihydroxy*-2 : 2′-*dimethoxydianthrone* (IX) was obtained, and this, by treatment with iodine in hot pyridine solution, gave 4 : 4′-*dihydroxy*-3 : 3′-*dimethoxyhelianthrone* (XI) in excellent yield.

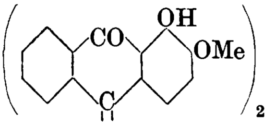
(VIII.)

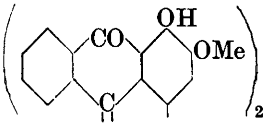




(IX.)

(X.)



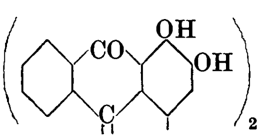


(XI.)

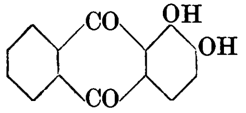
Later experiments have shown that for this purpose the isolation of (IX) is unnecessary, and that from (VIII), by means of iodine or arsenic acid in pyridine solution, the production of (XI) can be effected just as well in one operation. 4 : 4′-Dihydroxy-3 : 3′-dimethoxyhelianthrone is again produced (yield, 40%) when a nitrobenzene solution of (VIII) is boiled for thirty minutes, and indeed to a minor extent when the latter is heated beyond its melting point at about 250°. Although 1 : 1′-dihydroxy-2 : 2′-dimethoxydianthraquinone (X) is evidently an intermediate product in these reactions, so readily does it pass into (XI) that its satisfactory isolation has not yet been effected. When, however, a pyridine solution of (VIII) is boiled for a long period there is formed, in addition to (XI), a trace of a second compound, as yet only prepared in an impure condition, which very probably consists of (X).

Some doubt arose as to the correctness of the constitution assigned to (XI) in that the corresponding naphthadianthrone (compare VI) could not be prepared by exposing its solution in nitrobenzene to light even for many weeks, and in that the corresponding dianthraquinonyl could not be produced by oxidation with chromic acid. That (XI) consists of 4 : 4′-dihydroxy-3 : 3′-dimethoxyhelianthrone, however, has been proved by its synthesis from 4-bromo-1-hydroxy-2-methoxyanthraquinone as the result of experiments carried out by Mr. N. H. Haddock and one of us (A. G. P.), an account of which will be shortly communicated to the Society.

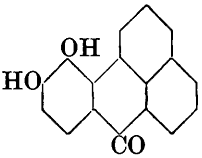
By the demethylation of (XI) with haloid acid 3 : 3′ : 4 : 4′-*tetrahydroxyhelianthrone* (XII) is obtained as maroon-coloured needles



(XII.)

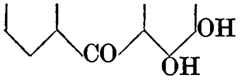


(XIII.)



(XIV.)

giving blue solutions in alkalis. More simply it can be prepared from 1 : 2-dihydroxyanthrone Cross and Perkin, J., 1930, 296) or from the 1 : 1′ : 2 : 2′-*tetrahydroxydianthrone* derived from it by the methods described above as serviceable for the preparation of (XI) from 1-hydroxy-2-methoxyanthrone. Although reaction occurs more rapidly with 1 : 2-dihydroxyanthrone than with the 1-hydroxy-2-methoxy-compound, the yield is poorer in the former case, and secondary products of an indefinite character are produced in considerable amount.

3 : 3′ : 4 : 4′-Tetrahydroxyhelianthrone does not dye mordanted calico even in the colloidal condition, and though it shows tinctorial property towards wool prepared with tin, aluminium, iron, and chromium, the shades obtained, especially as regards the first two mordants,* are weak and of a poor character. This appears at first sight peculiar, because there is present in both nuclei of (XII) the group  (A) which is present in alizarin (XIII) itself and to which the powerful dyeing property of the latter is usually ascribed. On the other hand, it has been pointed out by Miller and Perkin (J., 1925, **127**, 2686) and Cross and Perkin (*loc. cit.*) that, though in the hydroxybenzanthrone series the group (A) does confer tinctorial property, as, for instance, on 3 : 4 (or 4 : 5)-dihydroxy- and 2 : 4 : 5-trihydroxy-benzanthrones (*iso*benzalizarin and

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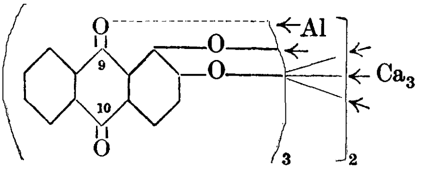
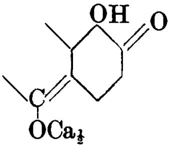
* The sodium salt of 3 : 3′ : 4 : 4′-tetrahydroxyhelianthronedisulphonic acid, evidently the 2 : 2′-compound, is, however, a powerful dye.

*iso*benzflavopurpurin), these are scarcely strong colouring matters and therefore show some analogy in this respect to 3 : 3′ : 4 : 4′-tetrahydroxyhelianthrone. There can be no doubt that in the dye lakes given by alizarin (and other hydroxyanthraquinone dyes) there is present a co-ordinated (chelate) metallic complex as expressed in the formula of Morgan for Turkey-red lake (XV) (J., 1922, **121**, 161), which is based on the analytical results of Mohlau (*Ber.*, 1913, **46**, 483), though a modification of this can be suggested as possible. It would thus appear that the distinction between the dyeing properties both of the hydroxybenzanthrones cited and of 3 : 3′ : 4 : 4′-tetrahydroxyhelianthrone and those possessed by alizarin arises from the fact that in the latter an additional carbonyl group is present in position 10. This, however, can hardly be the entire explanation, because 7 : 8-dihydroxybenzanthrone (XIV) dyes full shades very similar to those produced by alizarin, though possibly of a less permanent character. That the carbonyl group strongly influences a hydroxyl when this is in the para-position thereto has been discussed in earlier papers (*loc. cit.*), and it is now suggested that such a group, which is present in both alizarin and benzalizarin and is absent from the hydroxybenzanthrones above cited and from 3 : 3′ : 4 : 4′-tetrahydroxyhelianthrone, is essential for the development of strong tinctorial property in mordant dyes. As co-ordination between the *p*-hydroxyl and carbonyl groups is hardly to be anticipated, it suggests itself that in the dye lakes concerned these groups are involved in the formation of a *p*-quinonoid complex. For the satisfactory dyeing of adjective dyes, more especially with iron and aluminium mordants, the presence of a calcium salt is necessary, which, without doubt, reacts, as in the case of alizarin, in the first place with the 2-hydroxyl, or with that present in other colouring matters in the *p*-position to the carbonyl group, and indeed (J., 1899, **75**, 433) a crystalline 2-monocalcium salt of alizarin has been prepared. That such a compound is produced in the dye-bath hardly explains its service in the dyeing operation, and this, it is now considered, arises from the fact that such calcium salts tend to take up a *p*-quinonoid form if this is not present in the original dye. With alizarin this change may be represented as (XVI), and such a scheme can without difficulty be embodied in Morgan's formula (XV) for Turkey-red lake. That a chelate group is present

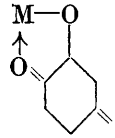
(XV.)



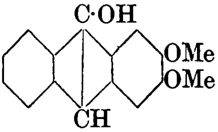
(XVI.)



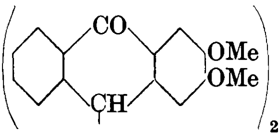
in phenolic dye lakes in general and is not confined only to those derived from colouring matters, mainly hydroxyanthraquinones, in which a hydroxyl adjacent to a carbonyl group is present, seems certain, owing to the general similarity in property of such pigments. How the presence of such a linkage in the dye lakes of colouring matters of the type of benzalizarin (XIV) is to be represented does not appear to have been previously discussed. However, if these contain, as is suggested, a *p*-quinonoid group, the chelation can evidently be expressed as follows, M representing the metal involved. Among other dyes of importance are hæmatein and brazilein, which undoubtedly are *p*-quinonoid (Engels, Perkin, and Robinson, J., 1908, **93**, 1140) and it is difficult to see how the chelation which exists in their colour lakes is to be otherwise represented. When acetylated even at 200°, 3 : 3′ : 4 : 4′-tetrahydroxyhelianthrone gives only the 4 : 4′-dihydroxy-3 : 3′-diacetoxy-compound, being analogous in this respect to the hydroxybenzanthrones previously cited, in which the α-hydroxyl group has a similarly inert character. The chelate linkage in these compounds is, therefore, of an extremely stable character, whereas in comparison that present in alizarin is much weaker, for the α-hydroxyl of the latter can even be acetylated in the cold if the mixture is kept for several days (Perkin, *loc. cit.*). It seems possible, therefore, that the presence of a stable chelate group in such colouring matters may adversely influence their power of lake formation in the dyeing operation.



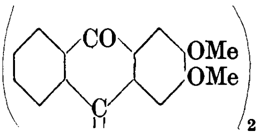
Although 2 : 3 - dihydroxy(hystazarin)anthranol is readily oxidised to 2 : 2′ : 3 : 3′-*tetrahydroxydianthrone*, attempts to convert the latter into the corresponding dianthraquinone have failed. On the other hand, 2 : 2′ : 3 : 3′-*tetramethoxydianthrone* (XVIII) (from 2 : 3-*dimethoxyanthranol*, XVII) does react with alkaline persulphate to yield 2 : 2′ : 3 : 3′-tetramethoxydianthraquinone (XIX). By the prolonged action of light on the latter in benzene–alcohol solution 2 : 2′ : 3 : 3′-*tetramethoxyhelianthrone* (XX), together with a little of the corresponding naphthadianthrone, is produced.



(XVII.)

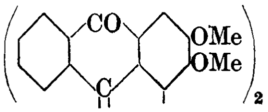


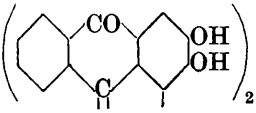
(XVIII.)



(XIX.)

(XX.)

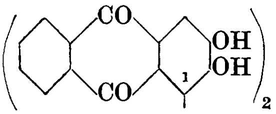




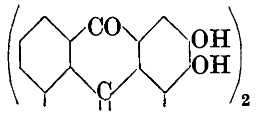
(XXI.)

Haloid acid converts (XX) into 2 : 2′ : 3 : 3′-*tetrahydroxyhelianthrone*. This compound is specially interesting because, unlike the 3 : 3′ : 4 : 4′-tetrahydroxyhelianthrone just discussed, it strongly dyes both mordanted wool and calico, if applied thereto either in the colloidal condition or in dilute ammoniacal solution. As the hydroxyl groups in 2 : 2′ : 3 : 3′-tetrahydroxyhelianthrone are in analogous positions to those present in hystazarin (2 : 3-dihydroxyanthraquinone), which it is known is but a feeble dye, this was hardly to be anticipated, and it thus appears that the tinctorial effect resulting from the positions of the hydroxyl groups in the helianthrone molecule differs markedly from that due to the position of hydroxyl in the anthraquinone group.

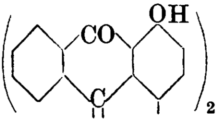
When (XXI) as acetyl compound is oxidised with chromic acid, 2 : 2′ : 3 : 3′ - *tetrahydroxy*-1 : 1′ - *dianthraquinonyl* (XXII) (dihystazarin), a compound closely resembling hystazarin itself, is produced. Unlike hystazarin again, however, this compound



(XXII.)



(XXIII.)



(XXIV.)

(XXII) dyes well both with mordanted wool and with calico and it is evident, therefore, that the tinctorial properties of both this compound and the tetrahydroxyhelianthrone (XXI), from which it is derived, are largely influenced by the 1 : 1′-dianthraquinonyl linkage, a group which is obviously absent from hystazarin itself. On the other hand, 2 : 2′ : 3 : 3′-tetrahydroxynaphthadianthrone (XXIII) dyes feeble shades, which in their intensity resemble those given by hystazarin. Thus, whereas the presence in (XXII) of the 1 : 1′-dianthraquinonyl linkage enhances the tinctorial effect, this is nullified by the introduction of a similar group in the 8 : 8′-position. No explanation of this influence of the latter can at present be suggested.

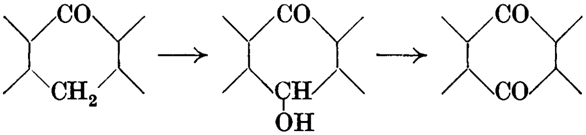
Attempts to prepare 1 : 1′-dihydroxydianthrone from 1-hydroxyanthrone have hitherto been unsuccessful, though 1 : 1′-*dimethoxydianthrone* is readily produced by the air oxidation of 1-*methoxyanthrone* in alcoholic potash solution. More drastic treatment of the latter in the same manner, or, alternatively, the action of iodine on the former compound, gives 1 : 1′-*dimethoxydianthraquinone* and from this, by illumination and subsequent demethylation, 4 : 4′-*dihydroxyhelianthrone* (XXIV) and 4 : 4′-*dihydroxynaphthadianthrone* are obtained. These two substances, though closely resembling the 2 : 2′-dihydroxy-compounds of Haller and Perkin (*loc. cit.*), are not only insoluble in alkaline solutions but also resistant to acetylation, and afford a further instance of the stability of the chelate linkage which is present in α-hydroxyhelianthrones and naphthadianthrones.

Although 3-hydroxyanthranol yields the dianthrone (*loc. cit.*) in almost quantitative amount, 3-methoxyanthranol gives but a trifling yield of 3 : 3′-*dimethoxydianthrone*. From this compound, 3 : 3′-dimethoxydianthraquinone, the related helianthrone and naphthadianthrone, compounds previously prepared by Perkin and Yoda (*loc. cit.*) by other methods, are readily produced, and the last, which was only cursorily examined by those authors, has been isolated in quantity.

In attempts, which have proceeded over a long period, to prepare hydroxyhelianthrones other than those described above, numerous hydroxyanthranols have been used, but in all cases with negative results : though hydroxydianthrones could usually be prepared from them, their conversion into hydroxydianthraquinones could not be effected. Similar failures were experienced when the hydroxyls present in these compounds were either partly or entirely replaced by methoxyl groups, though care was taken to effect, as far as possible, the conversion of the methoxydianthrone into dianthranol either previous to or during the oxidation process. It is puzzling that the presence of hydroxyl groups in various positions in dianthrone (which itself yields dianthraquinone) should inhibit this reaction, and that whereas 3 : 3′-dihydroxydianthrone readily suffers this change, such compounds as 3 : 3′ : 7 : 7′-tetrahydroxy-, 3 : 3′ : 7 : 7′-tetramethoxy- and 3 : 3′-dihydroxy-7 : 7′-dimethoxydianthrones do not.

For the preparation of hydroxyanthranols or anthrones from hydroxyanthraquinones, boiling stannous chloride and hydrochloric acid (Goodall and Perkin, *loc. cit.*) has proved to be the most effective reducing agent. Methoxyanthraquinones, however, are often demethylated during the process. Although this defect can be avoided by the use of copper or aluminium and sulphuric acid at 40° as the reducing agent, the procedure here generally adopted has been to add stannous chloride–hydrochloric acid to the methoxyanthraquinone in hot acetic acid and allow the mixture to cool. On the other hand, the partial demethylation of a polyhydroxyanthraquinone, if desired, may be effected by boiling such a mixture, usually for about one hour. As the partly methylated anthranol or anthrone thus obtained (preferably acetylated) can be readily oxidised to the hydroxymethoxyanthraquinone, a method is available for the preparation of compounds of this type which are usually difficult to obtain by other methods. Again it is curious that when symmetrical dimethoxyanthraquinones, as, for instance, the 2 : 7-, 1 : 8-, and 1 : 5-compounds, are thus reduced and yield, as they do respectively, the 2-hydroxy-7-methoxy-, 1-hydroxy-8-methoxy-, and 1-hydroxy-5-methoxy-anthranols, one methyl group only is eliminated and not both.

When hydroxyanthranols are converted into hydroxydianthrones the yields obtained are variable and frequently poor, even when different methods of oxidation are employed, owing to the simultaneous production of hydroxyanthraquinone. This poverty of yield may arise to some extent from the easier solubility of certain of these compounds in the solvent employed (usually acetic acid) and their consequent liability to further attack by the oxidising agent, but it is more probably due to the fact that in the circumstances of the experiment a mixture of both hydroxyanthranol and hydroxyanthrone is present and that, whereas the former is oxidised to the dianthrone, the latter yields the anthraquinone according to the following scheme :



## EXPERIMENTAL.

To 2-methoxyanthraquinone (10 g.) in sulphuric acid (160 c.c.), copper powder was gradually added, with good stirring, and the mixture was kept at 140° for 1 hour. After filtration through asbestos to remove copper, the liquid was poured on ice, and the precipitate collected and dried on tile. A suspension of the product in acetic anhydride (25 c.c.) was treated with pyridine (20 c.c.) and the solution kept over-night. The crystalline deposit, after being washed with alcohol, was recrystallised from carbon disulphide, giving sulphur-yellow plates (7·5 g.) of 3-*methoxy*-9-*anthranyl acetate*, m. p. 152—154° (Found : C, 76·7 ; H, 5·4. $C_{17}H_{14}O_3$ requires C, 76·7 ; H, 5·3%).

For hydrolysis, hydrochloric acid (5 pts.) was gradually added to the acetyl compound (1 pt.) in boiling acetic acid (15 pts.). Cautious addition of boiling water caused the separation of 3-*methoxy*-9-*anthranol* as fine needles, m. p. 108—109°, after recrystallisation from alcohol (Found : C, 80·2 ; H, 5·5. $C_{15}H_{12}O_2$ requires C, 80·5 ; H, 5·3%).

3 : 3′-*Dimethoxydianthrone* was prepared from 3-methoxy-9-anthranol (1 pt.), acetic acid (5 pts.), alcohol (5 pts.), and ferric chloride solution [commercial ferric chloride (1 pt.) in acetic acid

(2 pts.)] * by gentle evaporation on the water-bath. After one hour, dilution with alcohol caused the gradual deposition of crystals (0·3 pt.), which separated from benzene (charcoal) as small colourless prisms, m. p. 215—217° to a green liquid; these dissolved in sulphuric acid with a pale yellow tint (Found: C, 80·6; H, 5·3. $C_{30}H_{22}O_4$ requires C, 80·7; H, 4·9%).

From the acetic acid filtrate, water precipitated a product which by fractional crystallisation from benzene gave 2-methoxyanthraquinone, m. p. 195—197°, as the main constituent.

3 : 3′-*Dimethoxydianthranyl* 9 : 9′-*diacetate*, obtained with acetic anhydride and pyridine in the usual manner, crystallised in hair-like needles, m. p. 228—230°, soluble in sulphuric acid with a violet-red tint (Found: C, 77·3; H, 5·2. $C_{34}H_{26}O_6$ requires C, 77·0; H, 4·9%).

3 : 3′-*Dimethoxydianthraquinone.*—To the diacetyl compound (0·5 g.) in pyridine (5 c.c.), iodine (0·5 g.) was added and the liquid was kept at 80° for 1½ hours, and poured into acidified sodium bisulphite solution. The yellow precipitate after exhaustion with acetone separated from nitrobenzene as small yellow plates, m. p. 294—295° (Found: C, 80·4; H, 4·8. Calc. for $C_{30}H_{20}O_4$: C, 81·0; H, 4·5%). Perkin and Yoda (*loc. cit.*), who prepared this compound by the methylation of 3 : 3′-dihydroxydianthraquinone, give m. p. 297—299°.

2 : 2′-*Dimethoxynaphthadianthrone*, previously obtained in an impure condition by Perkin and Yoda, is readily prepared by exposing a solution of 3 : 3′-dimethoxydianthraquinone (0·4 g.) in pyridine (55 c.c.) to light for a fortnight. Recrystallised from nitrobenzene, it consists of orange-red needles which do not melt below 340° and dissolve in sulphuric acid with a red tint (Found: C, 81·5; H, 4·1. $C_{30}H_{16}O_4$ requires C, 81·8; H, 3·6%).

3 : 6-*Dihydroxy*-9-(iso*anthraflavic acid*)-*anthranol.*—*iso*Anthraflavic acid, prepared in bulk by the method of Hall and Perkin (J., 1923, **123**, 2036), was dissolved (160 g.) in pyridine (250 c.c.), the solution filtered and treated with twice its volume of boiling water, and hydrochloric acid added until precipitation was complete. The pale yellow needles were practically pure. To obtain the anthranol previously described by Roemer and Schwarzer (*Ber.*, 1882, **15**, 1041), who employed zinc dust and ammonia as the reducing agent, *iso*anthraflavic acid (8 g.), suspended in stannous chloride–hydrochloric acid solution [stannous chloride (2 pts.), hydrochloric acid (5 pts.)],† was digested at the boiling point for 4 hours. From the pale grey, crystalline product (7·5 g.), which was

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* Referred to throughout this paper as ferric chloride solution.

† Referred to throughout this paper as stannous chloride–hydrochloric acid.

sufficiently pure for further work, the acetyl compound was prepared. This melted at 183—184°, and not at 173° as stated by Roemer and Schwarzer.

3 : 3′ : 6 : 6′-*Tetrahydroxydianthrone*.—To *iso*anthraflavic acid-anthranol (1 g.) in acetic acid (10 c.c.), ferric chloride solution (2 c.c.) was added, and the mixture boiled for 15 minutes. The crystals (0·4 g.) were collected and washed with water and with alcohol. By using, however, the anthranol (1 g.), acetic acid (5 c.c.), alcohol (25 c.c.), and ferric chloride solution (2 c.c.), a purer product (0·42 g.) was obtained. The 3 : 3′ : 6 : 6′-*tetra-acetoxy*-9 : 9′-*dianthranyl diacetate*, prepared with acetic anhydride and pyridine, separated from alcohol–acetic acid in small, pale yellow plates, m. p. 280—282°, which dissolved in sulphuric acid with a scarlet tint (Found : C, 68·2; H, 4·3. $C_{40}H_{30}O_{12}$ requires C, 68·3; H, 4·2%).

For hydrolysis, 0·5 g. in acetic acid (15 c.c.) was digested at the boiling point with hydrochloric acid (5 c.c.). The crystalline deposit contained a greenish-blue impurity, giving a blue solution in alcohol, evidently derived from the dianthrone by the action of hydrochloric acid [compare 3 : 4 : 6 : 3′ : 4′ : 6′-hexahydroxy(anthrapurpurin)dianthrone; J., 1929, 192]. Thus obtained, 3 : 3′ : 6 : 6′-*tetrahydroxydianthrone* forms small, pale yellow prisms which darken at 270°, become green at about 300°, and do not appear to have a definite melting point (Found : C, 74·6; H, 4·0. $C_{28}H_{18}O_6$ requires C, 74·6; H, 4·0%).

When a solution of the hexa-acetyldianthranol in pyridine was boiled with the addition of iodine, dianthraquinone formation did not occur and the main bulk of the original compound was recovered unaltered. The behaviour of the dianthrone (as sodium dianthranoxide) with alkaline ferricyanide or hypobromite was also studied with a negative result.

iso*Anthraflavic acid dimethyl ether*, prepared from *iso*anthraflavic acid in sodium hydroxide solution (10%) and methyl sulphate in the usual manner, separated from acetic acid as yellow needles, m. p. 215—217° (Found : C, 71·5; H, 4·4. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·4%).

3 : 6-*Dimethoxy*-9-*anthranol* was prepared from this dimethyl ether (7 g.) by means of sulphuric acid (100 c.c.) and copper powder (14 g.) (see 3-methoxyanthranol, above). The product was acetylated in the cold, pyridine (10 c.c.) and acetic anhydride (12 g.) being used, and crystallised from alcohol–acetic acid or carbon disulphide, 3 : 6-*dimethoxy*-9-*anthranyl acetate* being obtained in pale yellow, prismatic needles, m. p. 180—181°, soluble in sulphuric acid with a transient red colour, a yellowish-green fluorescent solution being

eventually produced (Found : C, 74·0; H, 5·3. $C_{18}H_{16}O_4$ requires C, 72·9; H, 5·4%).

Hydrolysis with hydrochloric acid in the usual manner gave colourless leaflets of 3 : 6-dimethoxy-9-anthranol resembling phenanthrene in appearance; after recrystallisation, these melted at 158—160° (Found : C, 75·5; H, 5·5. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%).

3 : 3′ : 6 : 6′-*Tetramethoxy*-9 : 9′-*dianthrone*.—The anthranol (1·2 g.) in acetic acid (12 c.c.) was heated at 85°, and ferric chloride solution (3·5 c.c.) added. After 1½ hours, alcohol (1·5 pts.) was added, and the product (0·95 g.) collected and recrystallised both from alcohol and from benzene. The faintly fluorescent, colourless needles, m. p. 242—243°, dissolved in sulphuric acid with a pale yellow tint (Found : C, 76·0; H, 5·2. $C_{32}H_{26}O_6$ requires C, 75·9; H, 5·1%).

In the acetic acid mother-liquor the presence of *iso*anthraflavic acid dimethyl ether, m. p. 215—217°, was detected.

3 : 3′ : 6 : 6′-Tetramethoxy-9 : 9′-dianthranyl diacetate, prepared with acetic anhydride and pyridine and crystallised from alcohol–acetic acid, formed yellow prisms, m. p. 255—256°, soluble in sulphuric acid with a red coloration. Digested at 80° with a solution of iodine (1 pt.) in pyridine (5 pts.) for 1 hour, it remained unattacked, no dianthraquinone formation being observed. Negative results were also obtained when the dianthrone itself (*a*) rendered colloidal by solution in sulphuric acid and reprecipitation with water, was gently warmed with alkaline ferricyanide solution, and (*b*) was digested with boiling alcoholic potash, and the liquid poured into dilute aqueous ammonium persulphate.

6-*Hydroxy*-3-*methoxyanthranol*.—A mixture of *iso*-anthraflavic acid dimethyl ether (2·5 g.), acetic acid (30 c.c.), and stannous chloride–hydrochloric acid (30 c.c.) was boiled for 1 hour, the solution poured into water, and the precipitate washed and dried. After extraction with benzene to remove *iso*anthraflavic acid dimethyl ether anthranol (isolated as leaflets, m. p. 156—158°), the product was acetylated; the 3-*methoxy*-6-*acetoxy*-9-*anthranyl acetate* crystallised from alcohol–acetic acid in colourless needles, m. p. 197—199°, and gave with sulphuric acid a bluish-red coloration which quickly became yellow (Found : C, 70·7; H, 5·0. $C_{19}H_{16}O_5$ requires C, 70·4; H, 4·9%).

Hydrolysis with hydrochloric acid in acetic acid gave the free *anthranol*, which separated from alcohol in almost colourless prisms apparently containing alcohol of crystallisation, as when heated these became opaque, subsequently melting at 234—236°. It dissolved in dilute alkali with a yellow colour, and in sulphuric acid gave a yellow solution with a green fluorescence (Found : C, 74·8; H, 5·1. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5%).

iso*Anthraflavic Acid Monomethyl Ether.*—3-Methoxy-6-acetoxy-9-anthranyl acetate in acetic acid was oxidised with chromic acid; addition of hot water then precipitated yellow needles of *acetyl*iso*anthraflavic acid monomethyl ether*, which, after recrystallisation from alcohol, melted at 194—196° and dissolved in sulphuric acid with a crimson coloration (Found : C, 68·5; H, 4·1. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4%).

Hydrolysis with hydrochloric acid gave the free *monomethyl* ether, which separated from acetic acid as fine yellow needles, m. p. 283—285° (Found : C, 70·7; H, 4·2. $C_{15}H_{10}O_4$ requires C, 70·9; H, 3·9%).

*iso*Anthraflavic acid monomethyl ether is also obtained in trifling amount when *iso*anthraflavic acid is methylated with methyl sulphate and alkali, and can be isolated from the crude dimethyl ether by extraction with dilute aqueous ammonia. It is also produced when *iso*anthraflavic acid monomethyl ether anthranol in alcoholic solution is exposed to light : the liquid gradually darkens during about 3 days and on dilution with water yields a precipitate, from which the pure compound is obtained by crystallisation from alcohol–acetic acid.

6 : 6′-*Dihydroxy*-3 : 3′-*dimethoxydianthrone.*—To acetyl*iso*anthraflavic acid monomethyl ether anthranol (0·3 g.) in acetic acid (2 c.c.), ferric chloride solution (0·6 c.c.) was added, and the mixture, after being kept at 70° for ½ hour, was diluted with alcohol and gently evaporated. The crystals (0·05 g.) obtained (filtrate A) were washed with alcohol and converted into the acetyl compound, which crystallised from alcohol in pale yellow, prismatic needles, m. p. 229—231°, and dissolved in sulphuric acid with a scarlet coloration. From filtrate A, by dilution with water, a precipitate consisting almost entirely of *iso*anthraflavic acid monomethyl ether was isolated.

On dissolution of the acetyl compound in boiling dilute alcoholic potassium hydroxide, acidification, and cautious addition of boiling water, the *dianthrone* separated as fine colourless needles. After being washed with alcohol, these commenced to darken at about 250° and melted at 292—295° (Found: C, 75·4; H, 4·9. $C_{30}H_{22}O_6$ requires C, 75·3; H, 4·6%). 3 : 3′-Dimethoxy-6 : 6′-diacetoxydianthranyl diacetate in boiling pyridine solution is not oxidised by iodine to the corresponding dianthraquinone, and the action of ammonium persulphate on the dianthrone itself was similarly ineffective.

3 : 7-Dihydroxy-9-anthranol was readily prepared from anthraflavic acid by the stannous chloride–hydrochloric acid method

(Goodall and Perkin, *loc. cit.*) in a condition sufficiently pure for experiment. Only 5 g. of this compound were available.

3 : 3′ : 7 : 7′-*Tetrahydroxydianthrone*.—A mixture of the anthranol (1 g.), acetic acid (10 c.c.), and ferric chloride solution (2 c.c.) was digested at the boiling point for 15 minutes. The anthranol without apparent solution passed into the *dianthrone*, which was washed with alcohol. It darkened at 290°, melted at about 315—318°, and dissolved in sulphuric acid with an orange-yellow colour (Found : C, 74·4 ; H, 4·0. $C_{28}H_{18}O_6$ requires C, 74·6 ; H, 4·0%). Owing to its sparingly soluble character it is somewhat slowly attacked by boiling acetic anhydride and pyridine.

3 : 3′ : 7 : 7′-*Tetra-acetoxy*-9 : 9′-*dianthranyl diacetate* separated from hot nitrobenzene on dilution with alcohol in colourless needles, which darkened at about 290° and did not appear to have a definite melting point. Sulphuric acid dissolved it with a scarlet colour, which passed through brown to green on keeping (Found : C, 68·3 ; H, 4·4. $C_{40}H_{30}O_{12}$ requires C, 68·3 ; H, 4·2%). Neither from this compound nor from the free dianthrone could the corresponding dianthraquinone be produced.

*Hystazarin*.—For the isolation of this colouring matter from the product obtained by the condensation of pyrocatechol with phthalic anhydride in the presence of aluminium chloride, the following modification of D.R.-P. By. 298,345 was employed. The mass, thoroughly exhausted with boiling hydrochloric acid and with boiling water, was extracted with hot dilute aqueous ammonia, and the extract acidified. The pale brown product (A) was acetylated and the acetyl hystazarin, after purification, was hydrolysed in the usual manner. (The brownish-black product of the reaction, insoluble in ammonia and formed in considerable amount, has vat-dyeing property : a suspension in dilute alkali solution readily dissolves on the addition of sodium hyposulphite, giving a clear solution from which cotton can be dyed in deep brown shades. These, though fast to soap, show little permanence in contact with dilute alkaline hypochlorite solution.)

Hystazarin (2 : 3-dihydroxy)anthranol was prepared from hystazarin by Schrobsdorff (*Ber.*, 1903, **36**, 2938) by the aid of zinc dust and ammonia. It can be obtained in almost quantitative yield by digesting hystazarin with boiling stannous chloride–hydrochloric acid solution for 4 hours.

2 : 2′ : 3 : 3′-Tetrahydroxydianthrone separated when a mixture of acetyl hystazarin anthranol (1 g.), acetic acid (4 c.c.), and ferric chloride solution (2 c.c.) was heated at 85° for 1 hour ; yield (0·5 g.). 2 : 2′ : 3 : 3′-*Tetra-acetoxy*-9 : 9′-*dianthrone*, prepared by digesting the dianthrone with boiling acetic anhydride for 2 hours, crystallised

from alcohol–acetic acid in pale yellow prisms, which darkened at about 230°, melted at 274—277°, and dissolved in sulphuric acid with an orange colour (Found: C, 69·7; H, 4·2. $C_{36}H_{26}O_{10}$ requires C, 69·9; H, 4·2%). When pyridine, however, is present during the acetylation process, 2 : 2′ : 3 : 3′-*tetra-acetoxy*-9 : 9′-*dianthranyl diacetate* is produced and this is deposited from alcohol–acetic acid in small colourless prisms which darken at about 250° and melt at 293—295°. Sulphuric acid dissolves it with a red coloration, which passes through green, and eventually develops a brown tint (Found: C, 68·5; H, 4·4. $C_{40}H_{30}O_{12}$ requires C, 68·4; H, 4·2%). Heated with iodine in pyridine solution at 80° for 1 hour, it was unaffected and could be recovered unchanged, and from neither this compound nor the free dianthrone could the corresponding dianthraquinone be obtained.

For the preparation of hystazarin dimethyl ether the crude hystazarin (A) was employed and the methylation product was prepared in a similar manner to 1-methoxyanthraquinone (*loc. cit.*) and crystallised from benzene (yield, 60%). The mother-liquor contained a more soluble substance, probably alizarin dimethyl ether.

2 : 3-*Dimethoxyanthranol*.—Hystazarin dimethyl ether (3 g.) was dissolved in boiling acetic acid (55 c.c.), the solution slightly cooled, and stannous chloride–hydrochloric acid solution (35 c.c.) added. The greenish-yellow liquid was kept over-night and poured into much water, and when the viscid mass had solidified it was collected, dried on tile, and acetylated (3 g.) with acetic anhydride and pyridine. 2 : 3-*Dimethoxy*-9-*anthranyl acetate* separated from alcohol in silky needles, m. p. 169—171°, soluble in sulphuric acid with an orange colour (Found: C, 72·85; H, 5·6. $C_{18}H_{16}O_4$ requires C, 72·9; H, 5·4%).

For hydrolysis, boiling dilute potassium hydroxide solution was employed, and the product recrystallised from alcohol. The *anthranol* was thus obtained as pale yellow, prismatic needles, m. p. 143—146°, giving with sulphuric acid a brown solution (Found: C, 74·9; H, 5·6. $C_{16}H_{14}O_3$ requires C, 75·5; H, 5·5%).

2 : 2′ : 3 : 3′-*Tetramethoxydianthrone*.—A mixture of the anthranol (1 g.), acetic acid (10 c.c.), and ferric chloride solution (2 c.c.) was boiled for 30 minutes. Methyl alcohol (35 c.c.) was now added, the clear liquid was evaporated to one-fourth of its bulk, and the crystals which separated were recrystallised from alcohol and from benzene. The small colourless needles obtained melted at 243—245° and dissolved in sulphuric acid with an orange-red colour (Found: C, 76·3; H, 5·6. $C_{32}H_{28}O_6$ requires C, 75·9; H, 5·1%).

2 : 2′ : 3 : 3′-Tetramethoxy-9 : 9′-dianthranyl diacetate, prepared

in the usual manner, was recrystallised from alcohol–acetic acid and obtained in hair-like needles, m. p. 194—196°.

2 : 2′ : 3 : 3′ - *Tetramethoxydianthraquinone.*—2 : 2′ : 3 : 3′ - Tetra-methoxydianthrone (1 g.), suspended in alcohol (10 c.c.), was boiled with the addition of 5% alcoholic potassium hydroxide (10 c.c.), and the clear liquid stirred into 4% ammonium persulphate solution (25 c.c.). The yellow product was collected after some time, washed with water and with alcohol, and dissolved in much benzene (charcoal), and the solution evaporated to crystallisation. The product, recrystallised from the same solvent, consisted of pale yellow needles (0·8 g.) which darkened at 285°, melted at 290—291°, and gave with sulphuric acid a dull red-violet coloration, quickly passing to blackish-brown. It dissolved in boiling benzene with a deep green tint, which faded on keeping, a property evidently characteristic of dianthraquinone and its compounds (Found: C, 76·3; H, 4·7. $C_{32}H_{24}O_6$ requires C, 76·2; H, 4·7%).

2 : 2′ : 3 : 3′-*Tetramethoxyhelianthrone.*—A solution of the dianthraquinone (2 g.) in benzene (400 c.c.) and alcohol (100 c.c.) was exposed to light during 20 days. The highly fluorescent, orange-red liquid produced contained in suspension crystals of 2 : 2′ : 3 : 3′-tetramethoxynaphthadianthrone (see below); these (0·1 g.) were removed and the liquid was evaporated to a small bulk. On addition of alcohol and further evaporation, scarlet crystals separated (1·5 g.) (filtrate A), which were washed with alcohol and fractionally recrystallised in the same manner, a little tetramethoxynaphthadianthrone being thus eliminated. Finally, the product was dissolved in pyridine, and the solution treated with hot alcohol; alternatively, it was recrystallised from nitrobenzene. The prismatic needles, m. p. 287—288, dissolved in sulphuric acid with a deep indigo-blue colour (Found: C, 76·1; H, 4·4. $C_{32}H_{22}O_6$ requires C, 76·4; H, 4·4%).

The filtrate (A) contained a little tetramethoxydianthraquinone. 2 : 2′ : 3 : 3′-*Tetramethoxyhelianthrone* dissolves sparingly in boiling benzene to give a yellow solution with an intensely green fluorescence. It is not readily reduced by warm alkaline hyposulphite and the green vat is quickly oxidised by air to the original substance.

2 : 2′ : 3 : 3′-*Tetrahydroxyhelianthrone.*—The finely ground tetramethoxy-compound (0·5 g.) in a mixture of acetic acid (5 c.c.) and hydrochloric acid (*d* 1·16) (5 c.c.) was heated in a sealed tube at 190° for 3 hours. The product, which consisted of crystals suspended in a deep maroon-coloured liquid, the latter evidently containing the oxonium salt in solution, was poured into water, yielding a dull red mass of prismatic needles. These could be recrystallised by solution in boiling alcoholic ammonia and acidification, and thus separated as iridescent metallic leaflets.

Owing to its sparing solubility in the usual solvents this compound could not be recrystallised in the usual manner. Analyses have not given concordant results, though no difficulty has been experienced in this respect with either its tetramethoxy- or tetra-acetyl derivative. Possibly the compound retains water of crystallisation tenaciously. The point will be further investigated. Very dilute alkali solutions dissolve the compound with a dull violet-red tint, whereas with stronger solutions an almost black liquid is produced. With dilute solutions of ammonia and sodium bicarbonate a dull crimson coloration is obtained. Rendered colloidal by solution in dilute alkali and reprecipitation with acid, 2 : 2′ : 3 : 3′-tetrahydroxyhelianthrone dyes mordanted calico, though preferably it is dissolved in the minimum of dilute aqueous ammonia before being added to the dye-bath. Such a solution, just neutralised with acetic acid, behaves equally well. By applying in this manner 2% of colouring matter to woollen cloth, mordanted with tin, aluminium, iron, and chromium, maroon, deep brown-maroon, deep black, and blackish-brown shades are obtained respectively. These are of the anthragallol type but bluer in tone. Hystazarin applied to wool in the same manner gave with the same mordants pale dull orange, pale dull pink, pale brown-purple, and weak maroon colours.

2 : 2′ : 3 : 3′-Tetrahydroxyhelianthrone, finely powdered, was digested with boiling acetic anhydride and pyridine. Ochre prisms separated during the digestion and these were dissolved in boiling benzene (charcoal), and the intensely fluorescent solution was diluted with alcohol and partly evaporated; the orange leaflets of 2 : 2′ : 3 : 3′-*tetra-acetoxyhelianthrone*, after recrystallisation in similar manner, melted at 295—297° (Found : C, 70·5; H, 3·5. $C_{36}H_{22}O_{10}$ requires C, 70·3; H, 3·5%).

2 : 2′ : 3 : 3′-*Tetra-acetoxy*-1 : 1′-*dianthraquinonyl*.—To 2 : 2′ : 3 : 3′-tetra-acetoxyhelianthrone (0·2 g.) in boiling acetic acid (12 c.c.), chromic acid (0·25 g.) in 50% acetic was slowly added. Cautious addition of boiling water gave pale yellow crystals, which were dissolved in much acetone and the solution concentrated. The plates or leaflets congealed together at about 200°, resolidified, and melted at 268—270°. When, however, the melting-point tube was plunged into a bath at 200°, complete fusion of the substance occurred, followed by rapid solidification. Sulphuric acid dissolved the *compound*, giving a red-brown solution (Found: C, 66·5; H, 3·3. $C_{36}H_{22}O_{12}$ requires C, 66·8; H, 3·4%).

Hydrolysis with hydrochloric acid in the presence of acetic acid caused the gradual deposition of 2 : 2′ : 3 : 3′-*tetrahydroxydianthraquinonyl* as minute prisms or prismatic needles, which in their dull yellow colour resembled hystazarin itself. It is very sparingly soluble in the usual solvents, does not melt below 360°, and forms green-blue solutions in alkalis and a brick-red solution in sulphuric acid (Found: C, 69·9; H, 3·0. $C_{28}H_{14}O_8$ requires C, 70·2; H, 3·0%). It dyes tin-, aluminium-, iron-, and chromium-mordanted calico when applied thereto by the methods found serviceable with 2 : 2′ : 3 : 3′-tetrahydroxyhelianthrone for this purpose, producing bright orange, dull red-purple, purple, and dull brown shades.

2 : 2′ : 3 : 3′-*Tetramethoxynaphthadianthrone*, obtained in small amount during the preparation of the helianthrone (above), formed the sole product when 2 : 2′ : 3 : 3′-tetramethoxydianthraquinone (1 g.) in benzene (200 c.c.) and alcohol (100 c.c.) was exposed to light for 6 weeks. The deposit separated from much nitrobenzene as orange-coloured silky needles (Found: C, 76·4; H, 4·0. $C_{32}H_{20}O_6$ requires C, 76·8; H, 4·0%).

2 : 2′ : 3 : 3′-Tetrahydroxynaphthadianthrone, prepared by heating the tetramethoxy-compound with a mixture of hydrochloric acid (*d* 1·16) (3 pts.) and acetic acid (1 pt.) at 215° for 1 hour and subsequently at 200° for 3 hours, formed a glistening scarlet mass of fine needles, very sparingly soluble in all solvents, soluble in sulphuric acid with a violet-red coloration. It dissolves in sodium hydroxide solution (10%) with a red-brown colour, and in dilute aqueous ammonia with a crimson colour, which changes to red-brown on dilution, whereas with dilute sodium carbonate solution a crimson colour is produced. It possesses little affinity for mordanted calico, and is a poor dye also towards wool mordanted with tin, aluminium, iron, or chromium. The shades (2%) given on the latter are respectively dull pink, pale pink drab, brown-black, and somewhat pale olive-brown.

2 : 2′ : 3 : 3′-*Tetra-acetoxynaphthadianthrone*.—When the tetrahydroxy-compound was acetylated in boiling solution, the crystals did not appear to dissolve but were gradually replaced by fine yellow needles. These, after recrystallisation from much nitrobenzene, darkened and sintered at about 350°, but had not melted at 360° (Found: C, 70·3; H, 3·0. $C_{36}H_{20}O_{10}$ requires C, 70·5; H, 3·1%).

4 : 4′-*Dihydroxydianthrone*.—To 4-hydroxyanthranol (Cross and Perkin, *loc. cit.*) (2 g.) in acetic acid (20 c.c.) and alcohol (20 c.c.), ferric chloride solution (4 c.c.) was added, and the mixture gently evaporated at 100° to one-third of the original bulk. Crystals commenced to separate almost immediately; at the end of the operation these (1·1 g.) were collected hot and washed with boiling alcohol. From the filtrate, 1-hydroxyanthraquinone separated. The almost colourless, thin plates or leaflets dissolved in sulphuric

acid with an orange-red colour, and when heated darkened at about 240° and melted at 256—258° (Found : C, 80·0; H, 4·3. Calc. for $C_{28}H_{18}O_4$ : C, 80·3; H, 4·3%).

4 : 4′-*Diacetoxy*-9 : 9′-*dianthranyl diacetate*, obtained in the usual manner, crystallised from acetic anhydride in colourless prisms, m. p. 265—267° after previous blackening (Found : C, 76·4; H, 4·5. $C_{32}H_{22}O_6$ requires C, 76·5; H, 4·3%). Neither from this compound nor from the dianthrone itself could the corresponding dihydroxydianthraquinone be prepared.

## *Section II.*

1-Hydroxyanthrone (1 g.) in acetic acid (3 c.c.) was unaffected when, after addition of ferric chloride solution (1 c.c.), the mixture was heated at 100° for 1 hour. Other experiments, at various temperatures and with different oxidising agents, gave no indication of the production of a dianthrone from this compound.

For the preparation of 1-methoxyanthraquinone advantage was taken of the German patent (D.R.-P. 242379, 1910; Friedländer's "Fortschritte," X, 592) specially designed for the methylation of the α-hydroxyl group when present in hydroxyanthraquinones. A mixture of potassium 1-hydroxyanthraquinone (10 g.), methyl sulphate (60 g.), and sodium carbonate (25 g.) was heated at 140°. After crystallisation from alcohol the product melted at 168—169°.

1-*Methoxyanthrone*.—1-Methoxyanthraquinone (10 g.) in sulphuric acid (140 c.c.) was treated with copper powder (12 g.) at 40—45° and stirred for 3 hours, the procedure being identical with that given (*op. cit.*) for the preparation of 2-methoxyanthranol. A mixture of the product (9 g.), acetic anhydride (15 c.c.), and pyridine (12 c.c.), after being kept, was run into dilute sulphuric acid, and the viscid precipitate air-dried. This consisted of 1-*methoxyanthrone*, formation of the acetyl anthranol not having occurred : other instances which are given in this paper and the results of experiments which are in progress appear to indicate that this is a general property of anthrones containing an α-methoxyl or α-hydroxyl group, and that enolisation of anthrone to anthranol does not occur in these circumstances. By crystallisation from carbon disulphide, the product was obtained in large prismatic needles, m. p. 129—131° (Found : C, 80·4; H, 5·4. $C_{15}H_{12}O_2$ requires C, 80·35; H, 5·35%). Graebe and Bernhard (*Annalen*, 1906, **349**, 229) describe 1-methoxyanthrone, which they prepared by the direct methylation of 1-hydroxyanthrone, as melting at 105°. It is likely, however, that their compound, judging from its method of formation, is 1-methoxy-9-anthranyl methyl ether.

1 : 1′-*Dimethoxydianthrone*.—To 1-methoxy-9-anthrone (1 g.) in

acetic acid (4 c.c.), ferric chloride solution (1 c.c.) was added, and the mixture heated at 60° for 1 hour. Addition of alcohol caused crystals of the dianthrone (0·2 g.) to separate, and these were washed with hot alcohol (filtrate A). Preferably, methyl-alcoholic potassium hydroxide (20%) (2·5 c.c.) was added to 1-methoxyanthrone (1 g.) in methyl alcohol (35 c.c.), and air aspirated through the boiling solution. From the resulting dull orange liquid, crystals of the dianthrone soon separated, and after ½ hour these were collected hot (0·33 g.) and washed with alcohol. From this filtrate and also from filtrate (A), on cooling, crystals of 1-methoxyanthraquinone were deposited, which, after purification, melted at 169°. 1 : 1′-*Dimethoxydianthrone* is deposited from much acetone as minute, pale yellow, prismatic needles which darken at about 200° and do not appear to have melted at 330° (Found: C, 81·1; H, 5·1. $C_{30}H_{22}O_4$ requires C, 80·7; H, 4·9%).

The 1 : 1′-*dimethoxy*-9 : 9′-*dianthranyl diacetate* obtained by acetylation in presence of boiling pyridine crystallised from alcohol–acetic acid in pale yellow prisms, m. p. 290—291° (Found: C, 76·9; H, 4·9. $C_{34}H_{26}O_6$ requires C, 76·9; H, 4·9%). The crimson solution in sulphuric acid became violet and then blue on keeping.

1 : 1′-*Dimethoxydianthraquinone*.—If during the oxidation of 1-methoxyanthrone with air in the presence of methyl-alcoholic potassium hydroxide much methyl alcohol is employed, a crystalline deposit is obtained which separates more slowly, dissolves in sulphuric acid with an indigo-blue coloration, and consists mainly of the dianthraquinone. Alternatively, a mixture of 1 : 1′-dimethoxydianthrone (1 g.), pyridine (30 c.c.), and iodine (1 g.) was kept at 60° for 1½ hours. The liquid, diluted with alcohol, gave a crystalline deposit (0·7 g.), which was washed with alcohol and dissolved in hot nitrobenzene and the solution was cautiously diluted with boiling alcohol. The pale yellow needles obtained darkened at 280°, became black at 300°, and melted at about 315—316° (Found: C, 81·1; H, 4·7. $C_{30}H_{24}O_4$ requires C, 81·1; H, 4·5%).

4 : 4′-*Dimethoxyhelianthrone and* 4 : 4′-*Dimethoxynaphthadianthrone*.—1 : 1′-Dimethoxydianthraquinone, rendered colloidal by solution in sulphuric acid and precipitation with water, was gently warmed with alkaline potassium ferricyanide solution (compare Haller and Perkin, *loc. cit.*), but without effect. When, however, 1 : 1′-dimethoxydianthraquinone (0·5 g.) in the minimum of acetone (1 litre approx.) was exposed to light, crystals slowly separated; after 1 month these (0·35 g.) were collected and recrystallised from nitrobenzene (filtrate A). The long orange-red needles, which consisted of 4 4′-*dimethoxynaphthadianthrone*, did not melt below 360°

and gave with sulphuric acid a highly fluorescent, crimson solution (Found : C, 81·6 ; H, 3·7. $C_{30}H_{16}O_4$ requires C, 81·8 ; H, 3·6%).

This compound, added to hydrobromic acid (40%) (3 pts.) and acetic acid (1 pt.), became violet and in part dissolved, evidently owing to the formation of an oxonium hydrobromide. The mixture, heated at 180° for 3 hours, gave a salmon-red deposit of 4 : 4′-*dihydroxynaphthadianthrone* which, recrystallised from much nitrobenzene, formed scarlet hair-like needles, which did not melt below 360° (Found : C, 80·7 ; H, 3·1. $C_{28}H_{12}O_4$ requires C, 81·5 ; H, 2·9%).

4 : 4′-Dihydroxynaphthadianthrone is not dissolved by alkali solutions, does not suffer reduction with alkali hyposulphite, and is unattacked by digestion with boiling acetic anhydride and pyridine for several hours. Sulphuric acid dissolves it with a red tint.

The hot nitrobenzene filtrate (A), treated with much boiling alcohol, deposited minute needles of 4 : 4′-*dimethoxyhelianthrone*. Recrystallisation from nitrobenzene gave a salmon-coloured mass, which did not melt below 360° and gave with sulphuric acid a violet solution (Found : C, 80·7 ; H, 4·1. $C_{30}H_{18}O_4$ requires C, 81·4 ; H, 4·1%).

For the demethylation of this compound, carried out as in the case of 4 : 4′-dimethoxynaphthadianthrone, only a trace of 4 : 4′-dimethoxyhelianthrone was available. The 4 : 4′-dihydroxyhelianthrone, obtained as orange-red needles, was insoluble in alkaline solutions and did not appear to yield an acetyl compound by ordinary methods.

Anthrarufin(1 : 5-dihydroxy)anthrone, previously obtained by Pleuss (*Ber.*, 1902, **35**, 2928) by the action of hydriodic acid and phosphorus on anthrarufin, is more conveniently prepared in quantity by digesting the latter, finely powdered, with boiling stannous chloride–hydrochloric acid solution. Reduction occurs somewhat slowly, and the digestion should occupy about 40 hours. The product was acetylated and the acetyl compound, m. p. 184—185° after recrystallisation from alcohol–acetic acid (compare Pleuss), was hydrolysed with hydrochloric acid in the usual manner. The yellow leaflets of the anthranol became black at about 220° and had not melted at 300°. Pleuss gives 200° as the decomposition point. From neither 1 : 5-dihydroxy-9-anthrone nor its acetyl compound could a dianthrone be obtained by the action of ferric chloride.

Anthrarufin dimethyl ether according to D.R.-P. 77818 is obtained, in conjunction with chrysazin dimethyl ether, by the action of methyl-alcoholic sodium hydroxide on crude dinitroanthraquinone. For the purpose of this investigation it was prepared, however, from potassium anthrarufin (10 g.) and methyl sulphate (50 g.) in the presence of sodium carbonate (25 g.) at 140° (compare D.R.-P. 242379). It melted at 236—238°, whereas, according to the former patent, the melting point is 230°.

1 : 5-*Dimethoxyanthrone.*—To anthrarufin dimethyl ether (5 g.) in acetic acid (150 c.c.) at 100°, stannous chloride–hydrochloric acid (125 c.c.) was added, and the mixture kept for 10 minutes without further heating. The pale green crystals (3 g.) were collected (filtrate A), washed with hydrochloric acid and with water, and recrystallised from acetic acid, 1 : 5-*dimethoxyanthrone* being obtained in brown-red leaflets, m. p. 181—182°, which gave in sulphuric acid a red solution quickly changing to green-blue (Found: C, 75·6; H, 5·6; $CH_3$, 11·5. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5; $CH_3$, 11·6%).

From filtrate (A), by addition of hot water, yellow crystals of anthrarufin anthranol monomethyl ether (see below) separated.

1 : 5-*Dimethoxy*-9-*anthranyl acetate*, obtained in the usual manner, crystallised from alcohol–acetic acid in pale yellow needles, m. p. 169—171° (Found: C, 72·7; H, 5·3. $C_{18}H_{16}O_4$ requires C, 72·9; H, 5·4%).

1 : 1′ : 5 : 5′-*Tetramethoxydianthrone* was prepared from the anthrone (1 g.) in acetic acid (10 c.c.) with ferric chloride solution (3 c.c.) at 85°. Crystals soon commenced to separate and after 1 hour the mixture was diluted with alcohol. The *dianthrone* separated from much benzene in small colourless needles, m. p. 305—307°, giving in sulphuric acid a transient deep red-brown solution changing through green to blue (Found: C, 75·7; H, 5·2. $C_{32}H_{26}O_6$ requires C, 75·9; H, 5·1%). The dianthrone was not attacked by boiling acetic anhydride and pyridine, and on treatment by the iodine and persulphate methods no evidence of dianthraquinone formation was observed.

10-*Hydroxy*-1 : 5-*dimethoxyanthrone.*—Anthrarufin dimethyl ether (2 g.) in acetic acid (40 c.c.) was treated with stannous chloride–hydrochloric acid (40 c.c.), and the mixture kept at 65° for 3 hours. The green precipitate gradually became crystalline and after being washed with hydrochloric acid and with water and recrystallised from acetic acid (charcoal) gave long violet needles, m. p. 153—155°, soluble in sulphuric acid with a pure blue colour (Found: C, 71·0; H, 5·2; $CH_3$, 10·95. $C_{16}H_{14}O_4$ requires C, 71·0; H, 5·2; $CH_3$, 11·1%).

1-*Hydroxy*-5-*methoxyanthrone.*—To anthrarufin dimethyl ether (5 g.) in acetic acid (100 c.c.), stannous chloride–hydrochloric acid (125 c.c.) was added, and the mixture boiled for 1 hour. The liquid, diluted with hot hydrochloric acid, deposited pale yellow needles;

after cooling, these were collected (4·2 g.) and recrystallised from alcohol. The product, m. p. 131—133°, dissolved in sulphuric acid with a pale yellow colour. 1-*Acetoxy*-5-*methoxy*-9-*anthranyl acetate*, prepared from the anthrone in the usual manner, separated from alcohol in stout yellow needles, m. p. 161—163°. The alcoholic solution has a strong blue fluorescence (Found : C, 70·5; H, 5·0. $C_{19}H_{16}O_5$ requires C, 70·4; H, 4·9%).

1 : 1′-*Dihydroxy*-5 : 5′-*dimethoxydianthrone*.—A mixture of the anthrone (0·5 g.), acetic acid (5 c.c.), alcohol (5 c.c.), and ferric chloride solution (1·5 c.c.) was kept at 85° for 1 hour and the crystals formed (0·4 g.) were then collected and washed with alcohol. Unless alcohol is present during the oxidation process an almost black product results. Recrystallisation from much acetic acid gave pale yellow prisms, m. p. 287—289°, soluble in sulphuric acid with an orange-yellow colour which quickly passes to greenish-blue (Found : C, 75·4; H, 4·6. $C_{30}H_{22}O_6$ requires C, 75·3; H, 4·6%).

Acetylation in boiling solution in presence of pyridine gave 1 : 1′-*diacetoxy*-5 : 5′-*dimethoxy*-9 : 9′-*dianthranyl diacetate*, which separated from acetic acid (charcoal) as pale yellow needles. These darkened at about 230° and appeared to melt at 250—252° (Found : C, 70·8; H, 4·7. $C_{38}H_{30}O_{10}$ requires C, 70·6; H, 4·6%).

Experiments by the methods previously indicated failed to produce the corresponding dianthraquinone either from this compound or from 1 : 1′-dihydroxy-5 : 5′-dimethoxydianthrone.

1 : 8-*Dimethoxyanthrone*.—Chrysazin dimethyl ether (D.R.-P. 77818), m. p. 217—219°, was prepared similarly to anthrarufin dimethyl ether (above). For reduction, 10 g., rendered colloidal by solution in sulphuric acid and precipitation by ice-water, were digested with boiling 10% aqueous ammonia (250 c.c.), and zinc dust (25 g.) gradually added during 8 hours. When cold, the product was collected, washed, dried, and extracted with boiling acetic acid. The crystals of zinc acetate which separated on cooling were removed, and the filtrate was concentrated. The yellow hair-like needles of the *anthrone* thus obtained, after recrystallisation from acetic acid, melted at 196—197° and dissolved in sulphuric acid with an orange coloration (Found : C, 75·7; H, 5·6; $CH_3$, 11·7. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5; $CH_3$, 11·8%).

1 : 1′ : 8 : 8′-*Tetramethoxydianthrone*.—To 1 : 8-dimethoxy-9-anthrone (1 g.) in alcohol (70 c.c.), 20% alcoholic potassium hydroxide (2·5 c.c.) was added, and air aspirated through the boiling solution for 20 minutes. The liquid became orange-brown and deposited crystals (0·5 g.), which were dissolved in pyridine (charcoal) and the solution was cautiously diluted with hot water. Colourless prisms separated which darkened at about 250°, did not melt below

340°, and dissolved in sulphuric acid with a red-brown colour which rapidly changed to dull green (Found: C, 75·9; H, 5·2. $C_{32}H_{24}O_6$ requires C, 75·9; H, 5·1%).

Prolonged digestion with boiling acetic anhydride and pyridine failed to yield the corresponding acetyldianthranol, the dianthrone being unaffected, and the methods of oxidation usually serviceable for the purpose failed to convert it into a dianthraquinone.

1-*Hydroxy*-8-*methoxyanthrone*.—A solution of chrysazin dimethyl ether (10 g.) in boiling acetic acid (400 c.c.) was cooled to 40°; when crystallisation commenced, stannous chloride–hydrochloric acid solution (250 c.c.) was added. After being kept over-night, the clear solution was diluted with hot water (500 c.c.), and when cold the yellow amorphous precipitate was collected and washed with hydrochloric acid and with water (yield, 8 g.). By repeated crystallisation from acetic acid it was obtained as pale yellow needles, m. p. 183—185°, soluble in sulphuric acid with an orange-yellow colour, which gradually changed to dull green (Found: C, 75·3; H, 5·1; $CH_3$, 6·6. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0; $CH_3$, 6·25%).

Acetylation in pyridine gave 1-*acetoxy*-8-*methoxy*-9-*anthranyl acetate*. This separated from alcohol–acetic acid as needles, m. p. 164—165° (Found: C, 70·2; H, 4·9. $C_{19}H_{16}O_5$ requires C, 70·3; H, 4·9%).

1 : 1′-*Dihydroxy*-8 : 8′-*dimethoxydianthrone*.—To the anthrone (1 g.) in acetic acid (10 c.c.) and alcohol (5 c.c.), ferric chloride solution (3 c.c.) was added, and the mixture kept at 80° for 1 hour. The separated product (0·6 g.) crystallised from acetic acid (charcoal) in pale yellow prisms which did not melt below 330° (Found: C, 75·5; H, 4·7. $C_{30}H_{22}O_6$ requires C, 75·3; H, 4·6%).

The acetyl compound, prepared as usual, separated from acetic acid in almost colourless needles, m. p. 284—287°, which dissolved in sulphuric acid with a red coloration. It was not found possible to obtain a dianthraquinone from either this compound or the dianthrone itself.

1-*Hydroxy*-2-*methoxyanthrone*.—In the preparation of this compound from alizarin 2-methyl ether by the action of boiling stannous chloride–hydrochloric acid (Miller and Perkin, *loc. cit.*) the yield is poor and much viscid matter is produced as a result of over-reduction. The following process gives better results. A solution of alizarin 2-methyl ether (20 g.) in boiling acetic acid (500 c.c.) is slightly cooled, some crystallisation occurring, and stannous chloride–hydrochloric acid (320 c.c.) added. On keeping, a clear liquid is produced, from which long needles of 1-hydroxy-2-methoxyanthrone gradually separate. After 2 days, hot water (150 c.c.) is slowly added and, when cold, the crystals (18 g.) are collected. By fractional crystallisation from alcohol the more soluble 4-hydroxy-3-methoxyanthranol is removed from the mixture and the pure 1-hydroxy-2-methoxy-compound (11·5 g. approx.) obtained.

1 : 1′-*Dihydroxy*-2 : 2′-*dimethoxydianthrone.*—To 1-hydroxy-2-methoxyanthrone (1 g.) in boiling methyl alcohol (40 c.c.), concentrated aqueous ammonia (20 drops) was added and air aspirated through the solution. After 15 minutes the crystals (0·9 g.) were collected and recrystallised from benzene. The yellow prisms obtained, m. p. 195—197°, dissolved in sulphuric acid with a red colour which passed to violet on keeping. Alternatively, the anthrone in boiling alcohol was treated with a little concentrated alkaline hypoiodite solution. The separated crystals, evidently of a sodium salt of the dianthrone, were collected and digested with boiling dilute hydrochloric acid, and the product crystallised from benzene. In a third process, ferric chloride solution (1 c.c.) was added to 1-hydroxy-2-methoxyanthrone (0·5 g.) in acetic acid (5 c.c.) and alcohol (5 c.c.), and the mixture gently evaporated. The crystalline deposit of the *dianthrone* was collected hot; the filtrate contained much alizarin 2-methyl ether (Found: C, 75·5; H, 4·4. $C_{30}H_{22}O_6$ requires C, 75·3; H, 4·6%).

On account of the formation of some 4 : 4′-dihydroxy-3 : 3′-dimethoxyhelianthrone when 1 : 1′-dihydroxy-2 : 2′-dimethoxydianthrone was acetylated in boiling solution, a solution of the latter (1 g.) in pyridine (4 c.c.) and acetic anhydride (5 c.c.) was gently warmed for a few seconds and kept over-night. The 1 : 1′-*diacetoxy*-2 : 2′-*dimethoxy*-9 : 9′-*dianthranyl diacetate* obtained crystallised in colourless needles, m. p. 242—245° (Found: C, 72·1; H, 4·7. $C_{34}H_{26}O_8$ requires C, 72·6; H, 4·9%).

1 : 1′-Dihydroxy-2 : 2′-dimethoxydianthrone was also produced when a solution of 1-hydroxy-2-methoxyanthrone (0·5 g.) in nitrobenzene (2 c.c.) was boiled; it was isolated by the addition of alcohol. Again, it was obtained in almost quantitative amount when the hydroxymethoxyanthrone (2 g.) in acetone (50 c.c.) was treated with diazomethane (nitrosomethylurethrane, 8 c.c.) (compare the similar behaviour of 3 : 4-dihydroxyanthranol; Perkin and Story, J., 1929, 1406).

4 : 4′-*Dihydroxy*-3 : 3′-*dimethoxyhelianthrone.*—To a boiling solution of 1-hydroxy-2-methoxyanthrone (2 g.) in pyridine, iodine (4 g.) is gradually added during ½ hour. A red colour soon develops and needles of the helianthrone separate. After dilution with alcohol, and keeping, the crystals (1·7 g.) are collected and washed with a trace of pyridine and then with alcohol. The filtrate is poured into acidified bisulphite solution, and the maroon precipitate dried

and redissolved in a minimum of boiling pyridine. A further amount of the helianthrone (0·075 g.) separates on cooling. In the final mother-liquor the presence of a substance soluble in sulphuric acid with a violet, and in dilute alkali with a red colour, possibly alizarin 2-methyl ether, can be detected. Reaction also occurred when the mixture, above described, was heated at 90° for 2 hours, the helianthrone being deposited as iridescent magenta-like leaflets, but the yield (75%) was lower. The maroon-coloured needles, though apparently pure, were recrystallised from much nitrobenzene, in which they dissolved sparingly at the boiling point to give a highly fluorescent solution. The helianthrone does not melt below 330°, and dissolves in sulphuric acid with an intense greenish-blue colour (Found: C, 75·8; H, 3·8. $C_{30}H_{18}O_6$ requires C, 75·9; H, 3·8%).

4 : 4′-*Dihydroxy*-3 : 3′-*dimethoxyhelianthrone* is also formed when 1-hydroxy-2-methoxyanthrone in pyridine is boiled with the gradual addition of a solution of arsenic acid in the same solvent. It can again be obtained, though in small amount, by merely boiling a pyridine solution of the anthrone: 1-hydroxy-2-methoxyanthrone (0·5 g.) in pyridine (5 c.c.), boiled for 6 hours, gave, after dilution with alcohol, 4 : 4′-dihydroxy-3 : 3′-dimethoxyhelianthrone (0·09 g.). The red filtrate was poured into dilute hydrochloric acid, and the precipitate washed, drained on tile, and added to a little boiling acetone. Dull orange needles separated in trifling amount and these dissolved in sulphuric acid with a violet tint, passing to dark brown on keeping, a colour reaction suggesting that they consisted of 1 : 1′-dihydroxy-2 : 2′-dimethoxydianthraquinone. The conversion of 1-hydroxy-2-methoxyanthrone (1 g.) into the helianthrone could also be effected by digesting it in boiling nitrobenzene (5 c.c.) for 1½ hours (yield, 0·4 g.).

4 : 4′-Dihydroxy-3 : 3′-dimethoxyhelianthrone is unattacked when boiled with acetic anhydride and pyridine during many hours, though digestion with alcoholic potassium hydroxide solution gives evidence of the formation of a potassium salt. It is not reduced by stannous chloride–hydrochloric acid, or by warming with alkali hyposulphite, does not suffer conversion into the corresponding naphthadianthrone when its solution in much nitrobenzene is exposed to light for 1 month, and does not appear to yield a tetrahydroxydianthraquinonyl when oxidised with chromic acid in much glacial acetic acid solution, owing, possibly, to the presence of the unprotected 4-hydroxyl group.

3 : 3′ : 4 : 4′-*Tetrahydroxyhelianthrone* is readily prepared by heating the 4 : 4′-dihydroxy-3 : 3′-dimethoxy-compound with a mixture of hydrochloric acid (*d* 1·16) (3 pts.) and acetic acid (1 pt.)

at 180° for 3 hours. The voluminous maroon-coloured needles, consisting apparently in part of hydrochloride, are collected; after being washed with alcohol, they have a coppery lustre (Found : C, 75·4; H, 3·2. $C_{28}H_{14}O_6$ requires C, 75·3; H, 3·1%).

The *tetrahydroxyhelianthrone* does not melt below 360°. It is soluble in sulphuric acid with a green-blue tint, and in dilute alkalis with a deep blue colour, which is not discharged on addition of sodium hyposulphite. It dissolves in aqueous ammonia with a violet colour. When rendered colloidal by solution in alkali and reprecipitation with acid, it does not dye mordanted calico. However, it shows tinctorial property, though of a weak character, towards wool prepared with tin, aluminium, iron, and chromium mordants, giving dull pink, pale dull red-violet, dull brown-purple, and dull violet shades respectively. For dyeing purposes it is preferably applied to the material as a solution obtained by dissolving the colloidal substance in the minimum of dilute aqueous ammonia, the dye-bath being subsequently rendered faintly acid with acetic acid.

3 : 3′ : 4 : 4′-Tetrahydroxyhelianthrone (0·5 g.) in acetic anhydride (75 c.c.) and pyridine (2 c.c.) was digested at the boiling point for 3 hours. The 4 : 4′-*dihydroxy*-3 : 3′-*diacetoxyhelianthrone* (0·4 g.) thus obtained was recrystallised from nitrobenzene in which, at the boiling point, it gives a scarlet fluorescent solution. It consists of iridescent chocolate-coloured needles, m. p. about 325° (Found : C, 72·2; H, 3·4. $C_{32}H_{18}O_8$ requires C, 72·4; H, 3·4%).

A solution of 3 : 3′ : 4 : 4′-tetrahydroxyhelianthrone (0·5 g.) in fuming (20%) sulphuric acid (5 c.c.) was heated at 100° for 1 hour, and the product diluted with water. To the boiling suspension, sodium chloride was added, and the sodium sulphonate collected, washed with salt solution, drained, and dried. It dissolved in boiling water, the magenta solution being turned blue by alkali. It is a powerful dye, giving on wool mordanted with tin, aluminium, iron, and oxidised chromium, respectively, deep red-brown, red-violet, black, and slate-blue shades.

1 : 1′ : 2 : 2′-*Tetrahydroxydianthrone*.—To a solution of 1 : 2-dihydroxyanthrone (0·5 g.) in acetic acid (5 c.c.) and alcohol (5 c.c.), ferric chloride solution (1 c.c.) was added, and the mixture gently concentrated by heating at 90°. The pale yellow needles which separated (0·45 g.) were washed with methyl alcohol, with water, and with boiling acetone; they then darkened at about 210° and melted at 226—228°. When recrystallised from benzene, they developed an orange tint and melted at 240—241°. The compound is soluble in sulphuric acid with an orange-red, and in dilute alkali

with a crimson colour (Found : C, 74·8; H, 3·9. $C_{28}H_{18}O_6$ requires C, 74·7; H, 4·0%).

1 : 1′ : 2 : 2′-*Tetrahydroxydianthrone* (0·4 g.) in pyridine (1 c.c.) was treated in the cold with acetic anhydride (1·3 c.c.). The solution gradually deposited crystals and, after keeping, these were collected and recrystallised from benzene (charcoal). The colourless leaflets of 1 : 1′ : 2 : 2′-*tetra-acetoxy*-9 : 9′-*dianthrone* melted at 245—247° and dissolved in sulphuric acid with an orange-red colour (Found : C, 70·4; H, 3·8. $C_{36}H_{26}O_{10}$ requires C, 69·9; H, 4·2%).

1:1′:2:2′-Tetrahydroxydianthrone is also obtained when a solution of 1 : 2-dihydroxyanthrone in the minimum of nitrobenzene is boiled for a few seconds and allowed to cool. The fine orange crystals produced, washed with benzene and recrystallised from the same solvent, melted finally at 240—241°.

To 1 : 2-dihydroxyanthrone (2 g.) in pyridine (20 c.c.), iodine (4 g.) was added. On warming, an energetic action occurred and in 5 minutes a thick crystalline suspension was obtained. This was collected (filtrate A) and washed with alcohol, and the crude product was stirred with pyridine, again collected, and washed with alcohol. The yield of pure 3 : 3′ : 4 : 4′-tetrahydroxyhelianthrone thus obtained was 0·8 g. approximately. Addition of much boiling alcohol to filtrate (A) caused the deposition of a dark brown powder (B), soluble in sulphuric acid with a deep blue-black and in dilute alkali with a violet colour. This is probably a mixture and has not been further studied. A solution of 1 : 2-dihydroxyanthrone (1 g.) in boiling nitrobenzene (15 c.c.) soon commenced to deposit crystals of 3 : 3′ : 4 : 4′-tetrahydroxyhelianthrone and after 20 minutes reaction was complete (yield, 0·4 g.). The deep-coloured filtrate, diluted with much alcohol, gave a product closely resembling that described above (B).

3 : 3′ : 4 : 4′-Tetrahydroxyhelianthrone (0·5 g.) in sulphuric acid (2 c.c.) was heated at 160° for 2 hours, the liquid poured into water, and the precipitate collected and repeatedly extracted with alcohol and with water. The small residue was digested with acetic anhydride and pyridine; orange-red needles of an acetyl compound separated in trifling amount, which did not melt below 360°, dissolved in sulphuric acid with a red-violet colour, and presumably consisted of 4 : 4′-dihydroxy-3 : 3′-diacetoxynaphthadianthrone.

*Purpuroxanthin dimethyl ether*, obtained as a by-product of the methylation of purpuroxanthin with methyl sulphate and alkali (Graebe and Bernhard, *Annalen*, 1906, **349**, 222), is more readily prepared in quantity from the dry potassium salt and methyl sulphate in the presence of sodium carbonate (compare chrysazin dimethyl ether). It crystallises from benzene in needles containing benzene of crystallisation, m. p. 164—165° (Found: C, 71·4; H, 4·6%). Graebe and Bernhard give m. p. 150—153°.

Attempts to prepare the corresponding anthrone from purpuroxanthin dimethyl ether by reduction with copper and sulphuric acid, or zinc dust and ammonia, in aqueous suspension or in pyridine solution (compare alizarin dimethyl ether), failed in each case, the unattacked substance being mainly recovered. In the latter instance, however, crystallisation of the product from benzene gave as a more soluble fraction red prismatic needles, m. p. 156—158°, which consisted, very probably, of *10-hydroxy-1 : 3-dimethoxyanthranol* (Found: C, 71·0; H, 4·8. $C_{16}H_{14}O_4$ requires C, 71·0; H, 5·2%).

When stannous chloride–hydrochloric acid (25 c.c.) was added to purpuroxanthin dimethyl ether (1 g.) in hot acetic acid (20 c.c.), the liquid became red and deposited crystals, apparently of the above-described compound, which slowly dissolved on boiling. After dilution with water, the product was collected, washed, dried, and acetylated in the usual manner. The acetyl compound, which crystallised from alcohol in yellow prismatic needles, m. p. 154—155°, and dissolved in sulphuric acid with an evanescent yellow colour, was evidently *triacetylpurpuroxanthinanthranol*, demethylation having occurred during the reduction process (Found: C, 67·8; H, 4·6. $C_{20}H_{16}O_6$ requires C, 68·1; H, 4·5%).

Hydrolysis with hydrochloric acid in the presence of acetic acid gave pale brown leaflets of 1 : 3-dihydroxy(purpuroxanthin) anthrone, m. p. 217—219°. Experiment showed that the latter is also obtained by digesting purpuroxanthin with boiling stannous chloride–hydrochloric acid for 4 hours. By acetylating the product, the acetyl compound, m. p. 154—155°, was obtained. Attempts to convert purpuroxanthinanthrone into the corresponding dianthrone have hitherto failed.

A solution of alizarin dimethyl ether in hot acetic acid was slightly cooled, and stannous chloride–hydrochloric acid (30 c.c.) added. After being kept over-night, the product, isolated by dilution with water, gave on crystallisation from alcohol needles consisting evidently of 3 : 4-dimethoxyanthranol (compare Graebe and Thode, *Annalen*, 1906, **349**, 207). This by acetylation in boiling solution in the usual manner gave *3 : 4-dimethoxy-9-anthranyl acetate*, which separated from alcohol in yellow plates, m. p. 146—148° (Found: C, 73·1; H, 5·4. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·3%).

When 3 : 4-dihydroxyanthranol (deoxyalizarin) is methylated with methyl sulphate and alkali (Graebe and Thode, *loc. cit.*), the yield of

3 : 4-dimethoxyanthrone obtained is variable owing to the production of 3 : 4-*dimethoxy*-9-*anthranyl methyl ether*. If the methylation process is continued until a colour change does not occur on the addition of alkali, the methyl ether is the sole product of the reaction. It crystallises from alcohol in yellow prisms, m. p. 116—118° (Found : C, 76·1 ; H, 4·6. $C_{17}H_{16}O_3$ requires C, 76·1 ; H, 6·0%).

Though Graebe and Thode prepared 3 : 4-dimethoxyanthrone from alizarin dimethyl ether in aqueous suspension by reduction with zinc dust and ammonia, the method is tedious, and experiment has shown that reaction takes place much more readily in the presence of pyridine. To alizarin dimethyl ether in boiling commercial pyridine (20 pts.), zinc dust is added, and concentrated aqueous ammonia drop by drop during 30 minutes. After cooling, the cautious addition of boiling water causes the separation of the dimethoxy-compound in almost quantitative yield. By recrystallisation from carbon disulphide it is obtained as colourless needles, m. p. 162° (Found : C, 75·6 ; H, 5·8%). Graebe and Thode describe it as yellow and give its melting point as 150°.

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