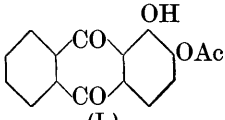
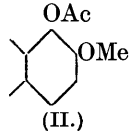
CLXXXI.—*The Migration of the Acyl Group in Partly Acylated Phenolic Compounds. Part II. Synthesis of Anthragallol* 1 : 2- *and* 1 : 3-*Dimethyl Ethers.*

By Arthur George Perkin and Charles William Herbert Story.

In earlier communications (Kubota and Perkin, J., 1925, **127**, 1889; Perkin and Storey, J., 1928, 229), it was shown that when the partly acylated compounds therein described, mainly derivatives of anthraquinone dyes, are methylated with diazomethane, a migration of the acyl group from the 2- to the 1-position occurs; for example, 2-acetylalizarin (I) gives mainly 1-acetylalizarin 2-methyl ether (II), and only a small amount of 2-acetylalizarin 1-methyl ether (III).



(I.)



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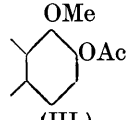
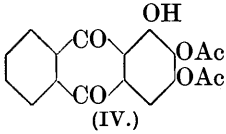


(III.)

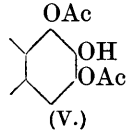
The extent of the migration, which is in no case complete, is dependent, in the instances cited, upon the nature of the acyl group present, being (*a*) with the acetyl group approximately 85%, (*b*) with the ethylcarbonato-group 25%, and (*c*) with the benzoyl group 20% of the possible amount, whereas a wandering of the toluene-*p*-sulphonyl group does not occur.

Many years ago it was shown by Perkin and Hummel (J., 1893, **63**, 1160) that Chay root, *Oldenlandia umbellata*, contains, in addition to alizarin and its glucoside ruberythric acid, anthraquinone derivatives devoid of tinctorial properties, and amongst these alizarin 1-methyl ether, and two anthragallol dimethyl ethers were of special interest. Though the nature of the latter substances has been disputed by Bock (*Monatsh.*, 1902, **23**, 1008), further work has shown (Perkin, J., 1907, **91**, 2066) that his criticism is incorrect, and there can now be no doubt that these compounds are the 1 : 2- and 1 : 3-dimethyl ethers of anthragallol. Owing to the presence in these substances of the 1-methoxy-group, their preparation from anthragallol by ordinary methods of methylation could not be effected, and attention was therefore directed to the use of diazomethane for this purpose, a reagent recently found serviceable for the synthesis of alizarin 1-methyl ether (Kubota and Perkin, *loc. cit.*). By employing this agent, these authors had already obtained from 2 : 3-diacetylanthragallol (IV), 1 : 3-diacetylanthragallol 2-methyl ether (VI), together with a second substance which, judging by

analogy with the behaviour of 2-acetylalizarin under similar conditions (I, II, and III), was thought to be 2 : 3-diacetylanthragallol 1-methyl ether. A further examination of the latter, however, has shown that it is in reality the acetyl derivative of the methyl ether prepared by Bock (*loc. cit.*) from anthragallol 2 : 3-dimethyl ether and by Perkin (*loc. cit.*) from the 1 : 3-dimethyl ether by the action of sulphuric acid, and which, therefore, should contain the methoxy-group in the 3-position. As the formation of 1 : 2-diacetylanthragallol 3-methyl ether from 2 : 3-diacetylanthragallol, was out of harmony with the former results, it was necessary to be certain that the orientation assigned to the anthragallol 3-methyl ether was correct, because, in accordance with the views expressed later, this might prove not to be the case. The preparation of anthragallol 1 : 2-dimethyl ether from 3-aminoalizarin dimethyl ether was accordingly attempted, and after diazotisation in concentrated sulphuric acid solution, the diluted liquid was cautiously heated. In all variations of the process, however, partial demethylation occurred either of the diazonium compound itself, or of the anthragallol 1 : 2-dimethyl ether derived from it, and anthragallol 2-methyl ether, identical with that obtained by Kubota and Perkin (*loc. cit.*) by other methods, was produced. The result, however, clearly indicated that, as the product of the partial demethylation of the 1 : 2-dimethyl ether of anthragallol is the 2-methoxy-compound, and as this is not identical with the product derived by a similar process from partly methylated anthragallol, the latter can only be the 2 : 3-dimethyl ether, and consequently the methyl ether of Bock must contain the methoxy-group in position 3. The action of diazomethane on 2 : 3-diacetylanthragallol (IV) is thus particularly interesting, because during the production of (VII) it seems evident that migration of both acetyl groups has occurred.



(IV.)



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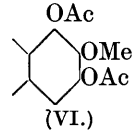
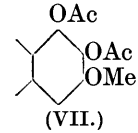


(VI.)



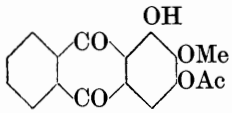
(VII.)

That the formation of the latter can hardly arise from the wandering of the 3-acetyl group to the 1-position appears to be certain, for it has already been shown by Perkin and Storey (*loc. cit.*) that this does not occur when 3-acetylpurpuroxanthin is treated with diazomethane, 3-acetylpurpuroxanthin 1-methyl ether being the sole product (compare also 3 : 7 : 3′ : 4′-tetra-acetylquercetin; Kubota and Perkin, *loc. cit.*). There can be little doubt that 1 : 3-diacetylanthragallol (V) is the first product of the reaction, and is subsequently converted into (VI). Before the methylation of (V) is

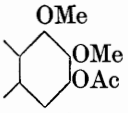
complete, however, a wandering of the acetyl group from the 3- to the 2-position takes place with the eventual formation of (VII).

For the synthesis, through the agency of diazomethane, of the 1 : 2- and 1 : 3-dimethyl ethers that occur naturally in Chay root, monomethyl ethers of monoacylated anthragallols are necessary as a starting point. Many of those employed in the present investigation are novel, and the results of the experiments dealing with these substances are divided into sections.

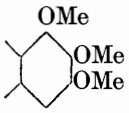
(i) When anthragallol 2-methyl ether was partly acetylated, the 3-*acetyl* compound (VIII) was produced, and from this, by the action of diazomethane, a mixture of 3-*acetylanthragallol* 1 : 2-*dimethyl ether* (IX) and anthragallol trimethyl ether (X) was obtained, no migration of the acetyl group occurring.



(VIII.)



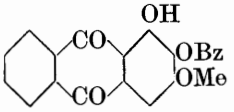
(IX.)



(X.)

From (IX), anthragallol 1 : 2-dimethyl ether was obtained by hydrolysis, and this, as its properties and a mixed melting point showed, is identical with the natural product. The replacement of acetyl by methyl, as demonstrated by the formation of (X), the yield of which varied according to the concentration of the diazomethane and the duration of the experiment, had previously been observed by Herzig and Tschatschet (*Ber.*, 1906, **39**, 265), who thus obtained diacetylpyrogallol monomethyl ether from triacetylpyrogallol and *p*-methoxy- and *m*-methoxy-benzoic acids from the corresponding acetoxybenzoic acids.

(ii) By the partial benzoylation of anthragallol 3-methyl ether, 2-*benzoylanthragallol* 3-*methyl ether* (XI) was obtained. This, on treatment with diazomethane, yielded 1-*benzoylanthragallol* 2 : 3-*dimethyl ether* (XII) (80% approx.) and 2-benzoylanthragallol 1 : 3-dimethyl ether (XIII) (16%).



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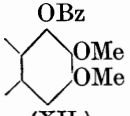
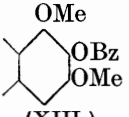


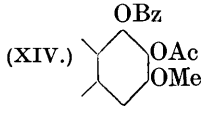
(XII.)



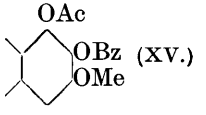
(XIII.)

The anthragallol 1 : 3-dimethyl ether derived from (XIII) by hydrolysis proved to be identical in all respects with that formerly isolated from Chay root, whereas the 2 : 3-dimethyl ether, similarly obtained from (XII), coincided in properties with that prepared by Bock (*loc. cit.*) by the direct methylation of anthragallol with methyl sulphate and alkali in nitrobenzene suspension.

(iii) When 2-benzoylanthragallol 3-methyl ether (XI) was acetylated with acetic anhydride and pyridine at the boiling point, two distinct *acetyl* compounds, A and B (XIV and XV), were produced. A wandering of the benzoyl group occurs, therefore, in part during the acetylation process, a type of change which does not appear to have been previously observed. Which of these formulæ is to be assigned to (A) and which to (B) has not yet been ascertained.

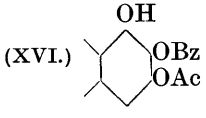


(XIV.)

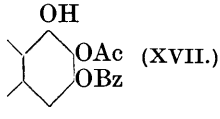


(XV.)

(iv) For the preparation of 2-*benzoylanthragallol* (compare 2-benzoylalizarin; Perkin and Storey, *loc. cit.*) 2 : 3-diacetylanthragallol was cautiously benzoylated in pyridine solution. Here again the result was unexpected, for, in addition to unattacked substance, the product contained two isomeric *monobenzoylmonoacetyl* compounds (C and D). From these, by acetylation, two distinct benzoyldiacetylanthragallols were produced, both of which, on hydrolysis, gave 2-benzoylanthragallol (XVIII). As (C) can also be prepared by the partial acetylation of 2-benzoylanthragallol in the cold, it is evidently the 2-benzoyl-3-acetyl derivative (XVI); and (D), the benzoyl group of which must migrate during hydrolysis, is accordingly either 3-benzoyl- or 1-benzoyl-2-acetylanthragallol. In view of the results obtained by Fischer, Bergmann, and Lipschitz (*Ber.*, 1918, **51**, 45) with the polyhydroxybenzoic acids, which are discussed later, formula (XVII) is tentatively assigned to (D).



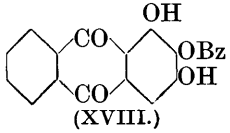
(XVI.)



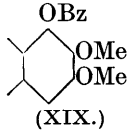
(XVII.)

Such a migration of an acyl group during hydrolysis has not been previously observed during the investigation of acyloxyanthraquinones.

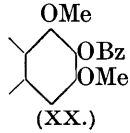
(v) When 2-benzoylanthragallol (XVIII) was treated with diazomethane, three compounds were obtained, *viz.*, 1-benzoylanthragallol 2 : 3-dimethyl ether (60% approx.) (XIX), 2-benzoylanthragallol 1 : 3-dimethyl ether (15·5%) (XX), and 3-benzoylanthragallol 1 : 2-dimethyl ether (13%) (XXI).



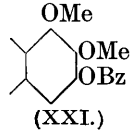
(XVIII.)



(XIX.)



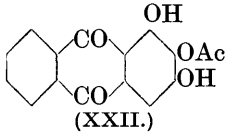
(XX.)



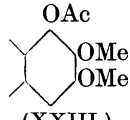
(XXI.)

In this reaction, therefore, the benzoyl group migrates both from the 2- to the 1- and from the 2- to the 3-position, although to a much greater extent in the former than in the latter case.

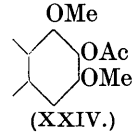
(vi) Although experiments on the direct gentle acetylation of anthragallol have hitherto yielded at once the 2 : 3-diacetyl compound, indicating the very similar basicity of the 2- and the 3-hydroxyl group, it has been shown by Green (J., 1926, 2198) that a monoacetylanthragallol can be prepared from thionylanthragallol by treatment with boiling acetic acid. Considerations of steric hindrance led the author to the conclusion that this substance is 3-acetylanthragallol. As, however, the derivative obtained, m. p. 219—220° (Green gives m. p. 212°), is soluble in cold sodium carbonate solution with a red colour (compare purpuroxanthin) devoid of blue tint (compare alizarin), there can be no doubt that it is in reality 2-acetylanthragallol (XXII). Such a view is also in harmony with its behaviour towards diazomethane, for this is analogous to that shown by 2-benzoylanthragallol (section v) in that it yields 1-acetylanthragallol 2 : 3-dimethyl ether (67%) (XXIII), 2-acetylanthragallol 1 : 3-dimethyl ether (15%) (XXIV), and 3-acetylanthragallol 1 : 2-dimethyl ether (XXV).



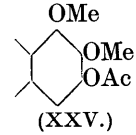
(XXII.)



(XXIII.)



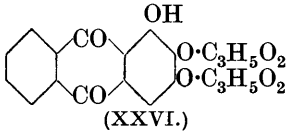
(XXIV.)



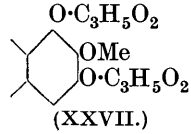
(XXV.)

In these circumstances, therefore, the 2-acetyl group in 2-acetylanthragallol migrates to the 1-position, only slightly more readily than the 2-benzoyl group (section v) : the tendency of the acetyl and the benzoyl group to migrate from the 2- to the 3-position is practically the same in both cases.

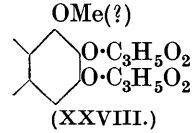
(vii) By the action of diazomethane on 2 : 3-diethylcarbonatoanthragallol (XXVI), Perkin and Storey (*loc. cit.*) obtained two diethylcarbonatoanthragallol methyl ethers, (A) (80%), and (B), of which only 2% was isolated in a pure condition. (A), which was not at the time closely examined, has now been found to consist of 1 : 3-diethylcarbonatoanthragallol 2-methyl ether (XXVII), whereas (B), a sample of which had not been kept, is with little doubt the 2 : 3-diethylcarbonato 1-methyl ether (XXVIII).



(XXVI.)



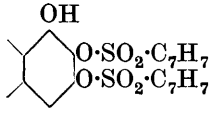
(XXVII.)

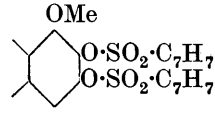


(XXVIII.)

The 2-ethylcarbonato-group in 2 : 3-diethylcarbonatoanthragallol thus migrates five times as readily as the 2-ethylcarbonato-group in 2-ethylcarbonatoalizarin (*loc. cit.*).

(viii) The action of diazomethane on 2 : 3-*ditoluene*-p-*sulphonyl-anthragallol* (XXIX) was now studied in the hope that in this, as in former cases, the toluene-*p*-sulphonyl group would not migrate, and thus permit of the preparation of anthragallol 1-methyl ether, a derivative hitherto unknown. The expectation was realised, since 2 : 3-ditoluene-*p*-sulphonylanthragallol 1-methyl ether (XXX) was the sole product of the reaction.

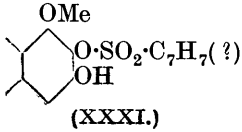
(XXIX.) 



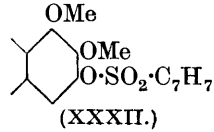
(XXX.)

By the hydrolysis of (XXX), an operation not easily effected, *anthragallol 1-methyl ether* was obtained. This dissolves in alkalis with a bluish-green colour, identical with that given by hystazarin. As a result of the synthesis of this compound, all the possible anthragallol methyl ethers are now known.

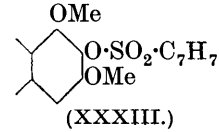
(ix) The resistance to hydrolysis exhibited by (XXIX) has made it possible to prepare therefrom a *monotoluene*-p-*sulphonyl* compound (XXXI ?). With the object of locating the position of the acyl group, this substance was treated with diazomethane; from the product, after hydrolysis, both anthragallol 1 : 2- and 1 : 3-dimethyl ethers were obtained, the latter being the main product. It is clear, therefore, that a mixture of 3-toluene-*p*-sulphonylanthragallol 1 : 2-dimethyl ether (XXXII) and 2-toluene-*p*-sulphonyl-anthragallol 1 : 3-dimethyl ether (XXXIII) had initially been present. It may be reasonably inferred that the toluene-*p*-sulphonyl group in (XXXI) is in position 2, but this is not definitely certain on account of the partial migration of this group during the methylation process, which might have occurred equally well from the 2- to the 3- or from the 3- to the 2-position. Such a migration of the toluene-*p*-sulphonyl group under the influence of diazomethane had not been previously observed, and is of special interest because a wandering of this kind does not occur when (XXIX) is similarly treated.



(XXXI.)

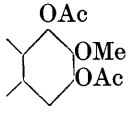


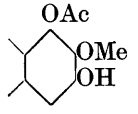
(XXXII.)



(XXXIII.)

(x) Incidentally a study of the partial hydrolysis of 1 : 3-diacetylanthragallol 2-methyl ether (XXXIV) in acetone solution by addition of ammonia has yielded a product which is distinct from the 3-acetyl 2-methyl ether and is doubtless the 1-acetyl compound (XXXV).

(XXXIV.) 

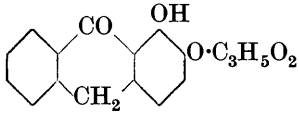


(XXXV.)

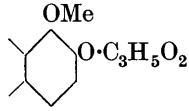
Such a stability of the 1-acyloxy-group in polyacyloxyanthraquinones had not been previously observed, for, as is well known, not only is the hydroxyl in position 1 the least readily acylated, but the 1-acyl group is more readily removed by hydrolysis than that in another position. Diacetylalizarin, for example, yields by gentle hydrolysis the 2-acetyl compound. This result, moreover, is in agreement with the views expressed by Perkin and Storey (*loc. cit.*) on the mechanism of the acyl migration in cases of this kind and is also in harmony with the results of Lesser and Gad (*loc. cit.*) and Bergmann and Dangschat (*Ber.*, 1919, **52**, 371), which are referred to later (p. 1408).

(xi) Hitherto, in the ketonic compounds studied, as, for instance, in the case of alizarin, a hydroxyl vicinal to the carbonyl group has invariably been present, and it appeared of interest to determine whether, in the absence of this group, acyl migration under the influence of diazomethane would occur. In order to test this point, 3-ethylcarbonato-4-hydroxyanthranol suggested itself as a suitable substance for experiment, and it seemed likely that this might be obtained by the reduction of 2-ethylcarbonatoalizarin under the conditions which convert alizarin into 3 : 4-dihydroxyanthranol. Curiously enough, such a result was not produced, the main if not the only product of the reaction being the 2-ethylcarbonato-1-hydroxy-compound (XXXVI). This reaction is evidently analogous to that described by Miller and Perkin (J., 1925, **127**, 2684) who in this way obtained both 1-hydroxy-2-methoxy- and 4-hydroxy-3-methoxy-anthranol, from alizarin 2-methyl ether. Although 1 : 2-dihydroxyanthranol could not be readily obtained by these authors from the 1-hydroxy-2-methoxy-compound by demethylation, this substance may be easily prepared by the hydrolysis of (XXXVI) and it is now shown to possess interesting properties, markedly distinct from those of 3 : 4-dihydroxyanthranol. On treatment with diazomethane, (XXXVI) behaves in the expected manner, the main products (identified by oxidation and subsequent removal of the ethylcarbonato-group as alizarin 1- and 2-methyl ethers, the former in much the larger amount) being evidently 2-ethylcarbonato-

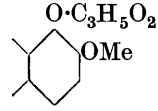
1-methoxyanthranol (XXXVII) and 1-ethylcarbonato-2-methoxyanthranol (XXXVIII).



(XXXVI.)



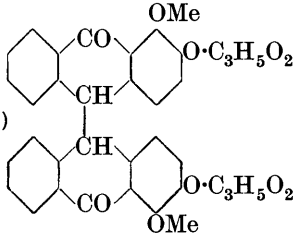
(XXXVII.)

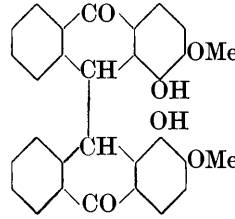


(XXXVIII.)

Curiously enough, some quantity of a sparingly soluble compound, doubtless 2 : 2′-diethylcarbonato-1 : 1′-dimethoxydianthrone (XXXIX), was isolated from the mixture, an indication that oxidation had occurred during the methylation process.

(XXXIX.)



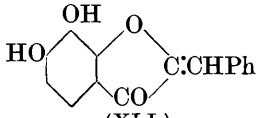


(XL.)

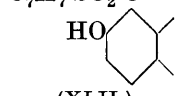
(xii) In view of the failure, just described, to obtain 3-ethylcarbonato-4-hydroxyanthrone, attempts were now made partly to acetylate 3 : 4-dihydroxyanthranol (deoxyalizarin). As, however, these experiments did not yield the desired 3-acetoxy-4-hydroxy-compound, at least in a pure condition, attention was directed to the action of diazomethane on the free anthranol. A considerable amount of a sparingly soluble compound, evidently 4 : 4′-dihydroxy-3 : 3′-dimethoxydianthrone (XL), was present in the methylation product, showing that oxidation had again occurred. From the more soluble fraction, by oxidation, a mixture of alizarin 2-methyl ether and alizarin dimethyl ether was obtained, evidence that the original products of the methylation consisted of 4-hydroxy-3-methoxy- and 3 : 4-dimethoxy-anthranol. It is thus shown that the 3-hydroxy-group of deoxyalizarin is less resistant to methylation than that in the 4-position. The oxidation of methoxyanthranol to dimethoxydianthrone, referred to above (XXXIX and XL), during the interaction with diazomethane appears, from more recent work, to be of fairly general occurrence, and it is indeed probable that the methylation product of 1 : 2 : 3-trihydroxy-(anthragallol) anthranol (Breare and Perkin, J., 1923, **123**, 260), described by these authors as a trimethoxyanthranol, is in fact 1 : 1′ : 2 : 2′ : 3 : 3′-hexamethoxydianthrone. The nature of this oxidation process is under investigation.

(xiii) Finally, with an object similar to that outlined under (xi),

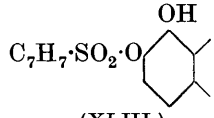
the partial acylation products of 5 : 6-dihydroxy-1-benzylidenecoumaran-2-one (XLI) (Friedländer and Rudt, *Ber.*, 1896, **29**, 879) have been studied. Owing apparently to the very similar basicity of the two hydroxyls, a monoacetyl derivative could not be prepared from this compound. Better results, however, were obtained by the use of toluene-*p*-sulphonyl chloride, two distinct *monotoluene*-p-*sulphonyl* compounds (A and B) being produced, the former being probably (XLII) and the latter (XLIII).



(XLI.)



(XLII.)

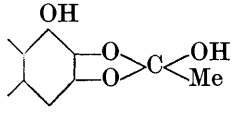


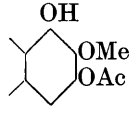
(XLIII.)

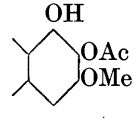
The main product (A) gives fluorescent alkali solutions, whereas those of B are devoid of this property. (B) can also be prepared by the partial hydrolysis of the 5 : 6-*ditoluene*-p-*sulphonyl* compound with alcoholic potash, but there is no evidence that (A) is formed at the same time. When hydrolysed, (A) and (B) both give 5 : 6-dihydroxy-1-benzylidenecoumaran-2-one. It is curious that the latter yields only one *monoethylcarbonato*-derivative. A study of the action of diazomethane on these derivatives is in progress.

In discussing the migration of the acyl group from the 2- to the 1-position in partly acylated hydroxy-ketones under the influence of diazomethane, Perkin and Storey (*loc. cit.*, p. 354) suggested that the main factor determining this change is probably the formation of a compound between diazomethane and the carbonyl oxygen, which is stable so long as the former is present in excess. The co-ordinating effect of the carbonyl on the 1-hydroxyl is thus suppressed, or rendered non-existent, permitting the strongly basic properties of the 1-hydroxyl to come fully into play. The acyl migration so often observed during the present investigation is of the same type and adds support to the above view of the mechanism of the migration process. The suggestion of these authors (*loc. cit.*, p. 233), that the 2-acetyl group in, for example, 2-acetylalizarin attracts to some extent the 1-hydroxyl and thus weakens the chelate ring, appears to be corroborated by experiment. For instance, in order to convert alizarin (0·5 g.), or alizarin 2-methyl ether, into alizarin dimethyl ether, a large excess of diazomethane (nitrosomethylurethane, 4 c.c.) in concentrated acetone solution (15 c.c.) has been found necessary, whereas at most half the amount of this reagent in comparatively dilute solution readily effects the methylation of 2-acetylalizarin and of 2 : 7-diacetylanthrapurpurin. Again, 2-ethylcarbonatoalizarin is more easily methylated than alizarin 2-methyl ether (*loc. cit.*). The effect of the 3-hydroxyl in

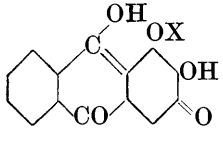
anthragallol, not present in the hydroxyanthraquinones previously examined, on acyl migration, shown in examples (XIX), (XXI), (XXIII) and (XXV), is of much interest, for though the main feature is a change of the acyl group from the 2- to the 1-position, wandering from the 2- to the 3-position also occurs, although to a less extent. There can be little difference in the basicity of the hydroxyls 2 and 3 in anthragallol, since each is meta to one and para to the other carbonyl group, and this evidently explains the difficulty of preparing monoacylanthragallols by direct acylation. Again, whilst anthragallol resembles 2 : 3 : 4-trihydroxybenzoic acid (compare Lesser and Gad, *Ber.*, 1926, **59**, 233) in the fact that acylation of the hydroxyl groups occurs in the order meta, para, ortho, the difference between the reactivity of the 2- and 3-hydroxyls appears to be less pronounced in the case of anthragallol. It is possible that prior to this secondary migration, under the influence of diazomethane, the acyl group may assume a position of equilibrium between the 2- and 3- positions (XLIV) (compare Perkin and Storey, *loc. cit.*, p. 234; Fischer, Bergmann, and Lipschitz, *loc. cit.*) and that this intermediate stage may then break down as follows :—

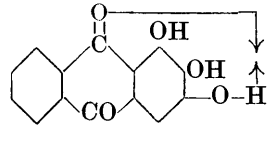
(XLIV.) 



or


There appears to be some evidence that, in anthragallol, the carbonyl vicinal to the 1-hydroxyl group affects not only this hydroxyl group but also, to some extent, that in the 3-position. Pascu (*Ber.*, 1923, **56**, 407) has indeed noticed that in *p*-hydroxybenzoic acids the influence of the carbonyl on the *p*-hydroxyl group is most pronounced. A similar effect may be presumed to exist in anthragallol when the influence of the carbonyl on the adjacent 1-hydroxyl has been suppressed, completely or partly, by the acylation or alkylation of the latter, and there may then arise a tendency for the carbonyl and the 3-hydroxyl to assume a *p*-quinonoid form (XLV) or some type of co-ordination (XLVI).

(XLV.) 



(XLVI.)

A suggestion of this kind may be used to explain the results of Bergmann and Dangschat (*loc. cit.*), who, by the cautious hydrolysis of 2 : 4-diacetoxybenzoic acid, obtained the 2-acetyl derivative, although, when 2 : 4-dihydroxybenzoic acid is partly acetylated,

the 4-acetyl compound is produced. In the diacetylated acid the influence of the carbonyl group on the 1-acetoxy-group is apparently suppressed, that on the 4-acetoxy-group coming into play, with the result that the latter becomes more lightly bound, and is therefore more readily removed by hydrolysis. Again (Fischer, Bergmann, and Lipschitz, *Ber.*, 1918, **51**, 45) the formation of 3-benzoylgallic acid from 4-benzoyl-3 : 5-diacetylgallic acid by hydrolysis may also be due to the tendency of the carbonyl and the 4-hydroxyl to assume a *p*-quinonoid structure. In anthragallol the effect of the carbonyl on the 3-hydroxyl group appears to be less pronounced than that which exists in the *p*-hydroxybenzoic acids, for experiment shows that when triacetylanthragallol is submitted to careful alkaline hydrolysis the 2 : 3-diacetyl compound is the main product. The existence, however, of some such influence in the case of anthragallol seems to be certain from the fact, shown on p. 1405, that when 1 : 3-diacetylanthragallol 2-methyl ether (XXXIV) is cautiously treated with ammonia, 1-acetylanthragallol 2-methyl ether is produced; and the migration of the benzoyl group in benzoylacetylanthragallol (XVII) during hydrolysis, which resembles that just discussed in the case of certain acyl *p*-hydroxybenzoic acids, appears to arise from a similar cause. Additional support for this view is afforded by the interesting fact that when 1 : 3-diacetoxyanthraquinone (diacetylpurpuroxanthin) is gently hydrolysed, a *monoacetyl* compound, different from that of Perkin and Storey (*loc. cit.*), and doubtless containing the acetoxy-group in the 1-position, is obtained. It is indeed very probable that the formation of two distinct monotoluene-*p*-sulphonyl derivatives of 5 : 6-dihydroxy-1-benzylidenecoumaran-2-one (XLII and XLIII) is to be ascribed to the fact that in preparations of this colouring matter some part is present in the *p*-quinonoid form.

EXPERIMENTAL.

3-Acetylanthragallol 2-Methyl Ether.—Anthragallol 2-methyl ether (Kubota and Perkin, *loc. cit.*) (1·5 g.) was ground into a paste with acetic anhydride (8 c.c.) and treated with powdered potassium acetate (1 g.), and the mixture well stirred and kept over-night. The yellow deposit (1·5 g.), after being washed with alcohol and twice recrystallised from acetone, formed flat orange needles, m. p. 167—169·5° (Found: C, 65·5; H, 3·9; CH_3, 4·8. $C_{17}H_{12}O_6$ requires C, 65·3; H, 3·85; CH_3, 4·8%).

Methylation. 3-Acetylanthragallol 2-methyl ether (1·5 g.), suspended in ether (50 c.c.), was treated with diazomethane (from 6 c.c. of nitrosomethylurethane). After 30 hours, as the suspended product was not of a homogeneous character, a further amount of diazomethane was added (nitrosomethylurethane, 4 c.c.). Little

change having occurred, the mixture of pale and deep yellow needles was collected next day, washed with ether, and extracted with boiling alcohol, which dissolved the paler substance (A). The residue, by recrystallisation from acetone, was obtained as bright yellow needles (0·7 g.), m. p. 177—179°, identical (mixed melting point) with the *acetyl* compound of the anthragallol 1 : 2-dimethyl ether (B) which occurs in Chay root (Found : C, 66·2; H, 4·4. $C_{18}H_{14}O_6$ requires C, 66·3; H, 4·3%).

The methylation mother-liquor and the alcoholic extract (A) were gently evaporated, the viscid residue was dissolved in a little alcohol, the solution treated with a little ammonia, and boiling water added. The precipitate obtained crystallised from alcohol in long, pale greenish-yellow needles, m. p. 167—169°, which were insoluble in alkaline solutions and consisted of anthragallol trimethyl ether (yield, 15% approx.) (Found : C, 68·3; H, 4·7. Calc. for $C_{17}H_{14}O_5$: C, 68·4; H, 4·7%).

The hot ammoniacal filtrate was acidified, causing the gradual separation of long yellow needles, m. p. 230—232°. These, as a mixed melting point showed, consisted of the anthragallol 1 : 2-dimethyl ether of Chay root (Found : C, 67·6; H, 4·3; CH_3, 10·5. Calc. for $C_{16}H_{12}O_5$: C, 67·6; H, 4·2; CH_3, 10·6%).

2-*Benzoylanthragallol*.—To an ice-cold suspension of 2 : 3-diacetylanthragallol (20 g.) in chloroform (500 c.c.) and benzoyl chloride (8 c.c.), pyridine (20 c.c.) was gradually added, rise of temperature, which leads to the formation of dibenzoylanthragallol, being avoided. The solution, after remaining at room temperature for 1 hour, was agitated with dilute sulphuric acid to remove pyridine and with dilute sodium carbonate solution to extract benzoic acid and evaporated to a small bulk. Cautious addition of alcohol then caused the separation of unchanged diacetylanthragallol (6·5 g.), which was removed; from the concentrated filtrate, crystals, m. p. 150—175°, were slowly deposited. These, after extraction with boiling acetone (extract C), yielded a residue which, by recrystallisation from much acetone, was obtained as golden-yellow rectangular plates, m. p. 203—206°, of a *monobenzoylmonoacetylanthragallol*, here termed (A)* (Found : C, 68·7; H, 3·7; C_2H_3O, 11·5. $C_{23}H_{14}O_7$ requires C, 68·6; H, 3·5; C_2H_3O, 10·7%). From the extract (C), on standing, a second compound, mixed with a trace of (A), separated. After removal of the latter by fractional crystallisation, it separated from acetone as yellow needles, m. p. 189—190°, much more readily soluble in acetone and alcohol than (A) and, as a mixed melting point showed, clearly distinct from this compound. Although it is the main product of the benzoylation,

* Referred to as C in the introduction (iv).

it was difficult to isolate it in a pure condition, and of this second *monobenzoylmonoacetylanthragallol* (B) * but 2 g. were obtained (Found: C, 68·6; H, 3·65; C_2H_3O, 10·8%). To eliminate the acetyl group from (B) a solution of the latter (0·5 g.) in acetic acid (10 c.c.) and hydrochloric acid (1·5 c.c.) was kept at 100° for 1½ hours. The long orange needles of *2-benzoylanthragallol* which separated gave a red solution in dilute aqueous sodium carbonate, and after recrystallisation from alcohol or tetrachloroethane melted at 241—243° (Found: C, 70·0; H, 3·5. $C_{21}H_{12}O_6$ requires C, 70·0; H, 3·3%). (A), when hydrolysed in a similar manner, gave orange needles, m. p. 241—243°, which also consisted of 2-benzoylanthragallol (mixed m. p.).

By acetylation with boiling acetic anhydride and pyridine, the benzoyl group of 2-benzoylanthragallol is replaced and triacetylanthragallol obtained. 2-Benzoyl-1 : 3-diacetylanthragallol is obtained, however, by adding acetic anhydride (0·4 c.c.) to a solution of 2-benzoylanthragallol (0·2 g.) in ice-cold pyridine (0·6 c.c.). Crystals are rapidly deposited, which separate from acetone–alcohol as pale yellow needles, m. p. 211—213° [depressed by admixture of either 2 : 3-diacetylanthragallol or the monobenzoylmonoacetyl compound (A)].

For the partial acetylation of 2-benzoylanthragallol (0·075 g.) in acetic anhydride (0·5 c.c.), a trace of potassium acetate was added and the mixture kept over-night. The product crystallised from acetone in yellow plates, m. p. 203—206°, identical with (A) (mixed melting point)—a proof that this compound is 2-benzoyl-3-acetylanthragallol. (A), when fully acetylated, yielded the 2-benzoyl-1 : 3-diacetylanthragallol, m. p. 210—212°, described above.

On the other hand, when (B) was fully acetylated in the same manner as (A), yellow needles of a *benzoyldiacetylanthragallol* were obtained. Although these melted at the same temperature (203—205°) as (A), a mixed melting-point determination proved that the two compounds were not identical. Accordingly, when from (B), which consists of either 1-benzoyl-2-acetyl- or 3-benzoyl-2-acetylanthragallol, the acetyl group is removed by hydrolysis, a wandering of the benzoyl group from the 1- to the 2- or from the 3- to the 2-position occurs.

Methylation. 2-Benzoylanthragallol (1 g.) in acetone (50 c.c.) was treated with ethereal diazomethane (from nitrosomethylurethane, 4 c.c.). After 2 days, the liquid was concentrated and the deposit (filtrate A) recrystallised from acetone, giving pale greenish-yellow needles of *1-benzoylanthragallol 2 : 3-dimethyl ether*, m. p. 216—218° (Found: C, 71·0; H, 4·3. $C_{23}H_{16}O_6$ requires

* Referred to as D in the introduction (iv).

C, 71·1; H, 4·1%). Treatment of this with boiling 1% methyl-alcoholic potassium hydroxide and subsequent dilution with water gave anthragallol 2 : 3-dimethyl ether, which crystallised from alcohol in long yellow needles, m. p. 160—162° (identified by mixed melting point, and also by the melting point of the acetyl compound, 165—167°). The sample of the latter necessary for purposes of comparison was prepared from anthragallol by Bock's method (*loc. cit.*).

The methylation filtrate (A), after dilution with alcohol and fractional evaporation, gave deposits of indefinite melting point. These were hydrolysed by alcoholic potash and, after acidification, the mixed dimethyl ethers produced were collected. To a concentrated solution of the ethers in boiling alcohol, a little ammonia was added (compare Perkin and Hummel, *loc. cit.*), causing the deposition of purple plates of an ammonium salt mixed with yellow needles of the 2 : 3-dimethyl ether. These were collected (filtrate B). The ammonium salt was removed by solution in water, and the liquid acidified. The yellow needles, after recrystallisation, melted at 218—220° and, as a mixed melting point showed, were identical with the anthragallol 1 : 3-dimethyl ether (A) which is present in Chay root.

The filtrate (B), when concentrated, deposited yellow needles, which were collected and extracted with dilute ammonia solution, a small amount of anthragallol 2 : 3-dimethyl ether remaining undissolved. The liquid, on acidification, yielded a precipitate (0·12 g.) which crystallised from alcohol, in yellow needles, m. p. 230° after sintering at 222°. These consisted of almost pure anthragallol 1 : 2-dimethyl ether (B) (mixed m. p.). These results indicated that when 2-benzoylanthragallol is methylated with diazomethane, 60, 15·5, and 13%, respectively, of the benzoyl derivatives of anthragallol 2 : 3-, 1 : 2-, and 1 : 3-dimethyl ethers are obtained.

Anthragallol 3-Methyl Ether.—Anthragallol 2 : 3-dimethyl ether (5 g.) in sulphuric acid solution (100 c.c.) was heated at 100° for 1 hour. When the product was poured into water, brown flocks separated; these, repeatedly crystallised from acetone, gave red needles (2·5 g.), m. p. 242—243° (Bock gives m. p. 235°) (Found : C, 66·4; H, 3·8; CH_3, 5·5. Calc. for $C_{15}H_{10}O_5$: C, 66·6; H, 3·7; CH_3, 5·5%). The acetyl compound was obtained as greenish-yellow flat needles, m. p. 204—206° (Bock gives m. p. 184°) (Found : C, 64·6; H, 4·1. Calc. for $C_{19}H_{14}O_7$: C, 66·4; H, 3·9%).

Anthragallol 3-methyl ether, as already indicated, is identical with the presumed 1-methyl ether which Kubota and Perkin (*loc. cit.*) obtained by the action of diazomethane on 2 : 3-diacetylanthragallol, and this was confirmed by a repetition of their experiment.

The melting point given by the latter authors for their compound is 237—241°, and for its acetyl derivative 203—205°.

2-Benzoylanthragallol 3-Methyl Ether.—Anthragallol 3-methyl ether (5 g.) in chloroform (35 c.c.) and benzoyl chloride (2·3 g.) was slowly treated with a solution of pyridine (5 c.c.) in chloroform (45 c.c.), the whole being cooled with ice. After 1¼ hours, alcohol was added and the crystals were collected; unattacked 3-methyl ether could be recovered from the mother-liquor. By recrystallisation from acetone, the *monobenzoyl* derivative was obtained as orange needles (3·5 g.), m. p. 221—223° (Found: C, 70·5; H, 4·0; CH_3, 4·0. $C_{22}H_{14}O_6$ requires C, 70·6; H, 3·7; CH_3, 4·0%).

Acetylation. 2-Benzoylanthragallol 3-methyl ether was digested with boiling acetic anhydride and pyridine for 1 hour. The crystals which separated on cooling evidently consisted of two substances, the main product (A) being pale yellow, whereas the other substance (B) had a deep yellow colour and was more soluble in acetone than (A). (A) separated from acetone in microscopic leaflets, m. p. 195—196°, and was evidently a *benzoylacetylanthragallol 3-methyl ether* (Found: C, 69·2; H, 3·9. $C_{24}H_{16}O_7$ requires C, 69·2; H, 3·8%). (B), which was also a *benzoylacetylanthragallol monomethyl ether*, was obtained by recrystallisation from acetone as deep greenish-yellow, rectangular plates, m. p. 214—217° (Found: C, 69·4; H, 4·1%); as a mixed melting point showed it was not (A) in a purer form.

Methylation. 2-Benzoylanthragallol 3-methyl ether (3 g.) in acetone (100 c.c.) was treated with ethereal diazomethane (from nitrosomethylurethane, 12 c.c.). The suspension became red and gradually changed into yellow crystals; after 3 days, these were collected (A) and the mother-liquor (B) was freed from ether by evaporation. (A) (1·18 g.) and the crystals which separated from (B) on keeping (0·6 g.) (filtrate C) were recrystallised from acetone, greenish-yellow prisms, m. p. 216—218°, of 1-benzoylanthragallol 2 : 3-dimethyl ether, identical with that produced by the methylation of 2-benzoylanthragallol (above), being obtained (Found: CH_3, 7·6. $C_{23}H_{16}O_6$ requires CH_3, 7·7%). Hydrolysis with 1% methyl-alcoholic potash gave anthragallol 2 : 3-dimethyl ether, m. p. 161—162°.

A second crop of crystals, deposited by (C) on keeping (0·78 g.) (filtrate E), melted at 150—175°, and these, being obviously a mixture, were debenzoylated with methyl-alcoholic potash. From the boiling liquid, purple-black leaflets separated (filtrate D), which were collected, washed with methyl alcohol, and dissolved in water; acidification yielded flocks (0·22 g.), m. p. 212—213°, which crystallised from alcohol in yellow needles of the anthragallol 1 : 3-dimethyl

ether (A) which is present in Chay root (Found: C, 67·8; H, 4·3; CH_3, 10·5. Calc. for $C_{16}H_{12}O_5$: C, 67·6; H, 4·2; CH_3, 10·5%). The acetyl compound, prepared in the usual manner, melted at 218—220° (Perkin and Hummel, *loc. cit.*, give 213—215°) (Found: C, 66·2; H, 4·0; CH_3, 9·0. Calc. for $C_{18}H_{14}O_6$: C, 66·25; H, 4·3; CH_3, 9·2%). The filtrate (D) was diluted with water and acidified, and from the yellow product, by maceration with ammonia, a further amount of anthragallol 2 : 3-dimethyl ether (0·4 g.) was isolated. The ammoniacal extract on acidification yielded 0·06 g. of crude anthragallol 1 : 3-dimethyl ether, m. p. 202—206°. The final methylation mother-liquor (E) on evaporation gave a residue, from which, by hydrolysis with alcoholic potash, 0·09 g. of anthragallol 1 : 3-dimethyl ether was obtained. Thus the total yield of this ether (0·3 g.), reckoned as benzoyl compound, from 3 g. of 2-benzoylanthragallol 3-methyl ether was 15%. The remainder is 1-benzoylanthragallol 2 : 3-dimethyl ether, of which 76% is accounted for above.

2-*Acetylanthragallol.*—2 : 3-Thionylanthragallol (Green, *loc. cit.*) was digested with boiling acetic acid, and the acetyl compound (yield, 35%) isolated, according to the directions of this author. After repeated crystallisation from toluene it melted at 219—220° (Found: C, 64·6; H, 3·3. Calc. for $C_{16}H_{10}O_5$: C, 64·4; H, 3·4%).

Methylation. 2-Acetylanthragallol (2 g.) in acetone (50 c.c.) was treated with diazomethane (from nitrosomethylurethane, 8 c.c.) and after 12 hours, the ether was removed and the pale yellow needles, which slowly separated (A) (0·8 g.), m. p. 158—165°, were collected. Addition of alcohol to the filtrate and fractional concentration gave crystals, (B), m. p. 145—156°, and (C), m. p. 147—170°. The final mother-liquor is termed (D).

(A) after recrystallisation from alcohol melted at 160—175° and consisted mainly of 1-acetylanthragallol 2 : 3-dimethyl ether, as hydrolysis showed. The alcoholic mother-liquor from the above, by treatment with boiling 1% methyl-alcoholic potash, acidification, and dilution with water, gave needles (0·15 g.), m. p. 158—161°, which were insoluble in ammonia and evidently consisted of anthragallol 2 : 3-dimethyl ether. From (B) by a similar treatment, 0·3 g. of this ether was obtained. (C), when hydrolysed, gave a product almost entirely soluble in ammonia, whereas that given by (D) was but partly soluble and 0·15 g. of the 2 : 3-dimethyl ether was isolated therefrom. The yield of this ether, taking into account that obtained from (A) (0·65 g.), corresponds to a total yield of anthragallol 2 : 3-dimethyl ether (as acetyl compound) of 69%.

The ammoniacal extracts were acidified; the precipitate, crystallised from alcohol, gave yellow needles (0·22 g.), m. p. 228—231°,

of anthragallol 1 : 2-dimethyl ether. From the filtrate, anthragallol 1 : 3-dimethyl ether (0·22 g.), m. p. 212—213°, was isolated by means of its ammonium salt.

1-*Acetylanthragallol 2-Methyl Ether.*—To 1 : 3-diacetylanthragallol 2-methyl ether, in boiling acetone, an excess of ammonia was added. The red liquid was acidified with acetic acid and partly evaporated; yellow needles separated, m. p. 205—208° after recrystallisation from acetone (Found: C, 65·4; H, 3·9. $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·8%). Hydrolysis with hydrochloric acid in the usual manner gave anthragallol 2-methyl ether, m. p. 218—220°.

Methylation. 1-Acetylanthragallol 2-methyl ether (0·08 g.) in acetone (5 c.c.) was treated with diazomethane (from nitrosomethylurethane, 0·5 c.c.). After 3 days, yellow plates, m. p. 168—170°, of 1-acetylanthragallol 2 : 3-dimethyl ether had separated. From the mother-liquor, by evaporation, and treatment of the residue with alcoholic potash, only anthragallol 2 : 3-dimethyl ether, m. p. 160—162°, could be isolated.

1-*Acetylpurpuroxanthin.*—To a solution of triacetylpurpuroxanthin (0·5 g.) in boiling acetone (10 c.c.), concentrated aqueous ammonia (2 c.c.) was added; the red liquid was kept for a few seconds, cooled, and neutralised with hydrochloric acid. Cautious dilution with water caused the separation of crystals which, recrystallised from methyl alcohol (charcoal), gave pale orange-yellow needles of 1-*acetylpurpuroxanthin*, m. p. 231—235°, readily soluble in acetone (Found: C, 68·2; H, 3·7. $C_{16}H_{10}O_5$ requires C, 68·1; H, 3·5%). Hydrolysis with hydrochloric acid in the usual manner gave purpuroxanthin, m. p. 268—270° (Plath, *Ber.*, 1876, **9**, 1204, gives m. p. 262—263°). 3-Acetylpurpuroxanthin, which is obtained by gently acetylating purpuroxanthin, melts at 144° (Perkin and Storey, *loc. cit.*).

In preparing purpuroxanthin from commercial purpurin (by the sodium hyposulphite method), it has been found preferable to crystallise the latter, before reduction, from pentachloroethane, rather than solvent naphtha as previously advocated (*loc. cit.*). The crude purpuroxanthin is readily purified by crystallisation from 10 parts of pyridine.

1 : 3-*Diacetylpurpurin.*—Triacetylpurpurin (0·5 g.) in sufficient boiling acetone was partly cooled, aqueous ammonia (2 c.c.) added, the red liquid neutralised, and the product crystallised from acetic acid. The orange-yellow needles obtained, m. p. 203—205°, were, as the acetyl determination indicates, perhaps slightly impure (Found: C, 63·9; H, 3·9; $C_{14}H_8O_5$, 76·2. $C_{18}H_{12}O_7$ requires C, 63·5; H, 3·5; $C_{14}H_8O_5$, 75·3%). When triacetylanthragallol is

similarly treated and the operation is rapidly performed, 2 : 3-diacetylanthragallol, m. p. 223—224°, is obtained.

3-*Nitroalizarin Dimethyl Ether*.—Finely powdered, commercial 3-nitroalizarin (25 g.) was treated with potassium hydroxide (2 mols.) in alcohol, and the product dried at 100°. To ensure complete formation of potassium salt, the mass was again ground with alcohol and dried. The product (37 g.), mixed with anhydrous sodium carbonate (95 g.), was stirred into methyl sulphate (155 c.c.), the whole gradually heated to 140° and, when cold, lixiviated with water. By extracting the residue with benzene and concentrating the solution, long yellow needles were obtained which, after recrystallisation, melted at 168—171° (yield, 16 g.) (Found: C, 61·3; H, 3·6; N, 4·5. $C_{16}H_{11}O_6N$ requires C, 61·35; H, 3·5; N, 4·5%).

3-*Aminoalizarin Dimethyl Ether*.—The nitro-compound (5 g.) was stirred into a solution of sodium sulphide (10 g.) in a little water. The mixture was added to 1 litre of hot water containing excess of ammonium chloride, the latter being employed to reduce the alkalinity, and the suspension boiled for 15 minutes. The product (5 g.) crystallised from benzene (200 c.c.) in red prisms, m. p. 203—205° (Found: C, 68·1; H, 4·7; N, 5·0. $C_{16}H_{13}O_4N$ requires C, 68·0; H, 4·6; N, 4·9%).

3-Acetamidoalizarin dimethyl ether, prepared from the amino-compound by boiling with acetic acid containing a little acetic anhydride, crystallised from alcohol in yellow rhombic plates, m. p. 237—240°.

To 3-aminoalizarin dimethyl ether (2 g.) in sulphuric acid (80 c.c.) cooled in ice, a slight excess of sodium nitrite was added; the mixture was subsequently well stirred at room temperature for 4 hours. The liquid, after the addition of a little urea, was treated as follows: (*a*) It was diluted with a little water, heated to 130°, cooled to 110°, and maintained there for 15 minutes. When cold, the greenish-yellow precipitate was collected and extracted with boiling benzene, and the deposit obtained by concentrating the extract was acetylated: the product, after recrystallisation, melted at 146—150° and had all the properties of 1 : 3-diacetylanthragallol 2-methyl ether (Perkin and Storey, *loc. cit.*). (*b*) In the hope of avoiding hydrolysis of the 1-methoxy-group, the acid solution, before boiling, was partly neutralised with sodium acetate. As a result, however, no well-defined product could be obtained. (*c*) The acid liquid was heated at 100°, the viscid product dissolved in alcohol, the solution poured into ether, the clear liquid decanted from deposited tarry matter, the ether removed, and the residue dissolved in alcohol. Addition of lead acetate caused the deposition of anthragallol 2-methyl ether as lead salt; in the filtrate, the

presence of a small amount of alizarin dimethyl ether only could be detected.

2 : 3-*Ditoluene*-p-*sulphonylanthragallol*.—To anthragallol (4 g.) in pyridine (40 c.c.) cooled by ice, toluene-*p*-sulphonyl chloride (8 g.) was added. The mixture was well stirred during ½ hour, and kept for a similar period at room temperature; alcohol was then added. The deposit (5 g.) crystallised from a little pyridine in yellow plates, m. p. 196—198° (Found: C, 59·5; H, 3·6. $C_{28}H_{22}O_9S_2$ requires C, 59·4; H, 3·8%). Acetylation by Fischer's method gave the acetyl compound as yellow prisms, m. p. 212—215°.

Anthragallol 1-*Methyl Ether*.—2 : 3-Ditoluene-*p*-sulphonylanthragallol (2·5 g.) in acetone (30 c.c.) was treated with diazomethane (from nitrosomethylurethane, 10 c.c.), and the product kept overnight. The deposited pale yellow needles (1·7 g.), m. p. 210—213° (filtrate A), were digested with boiling 10% alcoholic potash until the solution had become bluish-green. After removal of potassium toluene-*p*-sulphonate, the solution was partly evaporated and the *anthragallol* 1-*methyl ether* which separated was recrystallised from methyl alcohol. The deep yellow, rhombic plates (0·5 g.) contained methyl alcohol of crystallisation and melted at 248—250° (Found: loss at 100°, 9·3. $C_{15}H_{10}O_5,CH_4O$ requires CH_4O, 10·6%. Found: C, 66·6; H, 3·7. $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7%). The ether sublimes with some decomposition, and in alcohol gives green and red precipitates respectively with barium hydroxide and lead acetate solutions. The *diacetyl* compound, obtained in the usual manner, crystallises in pale greenish-yellow needles, m. p. 165—166°.

Monotoluene-p-*sulphonylanthragallol* 1-*Methyl Ether*.—The ditoluene-*p*-sulphonyl compound in acetone was boiled with excess of 1% methyl-alcoholic potash, the red liquid acidified while hot, the potassium chloride removed, and the product, which now separated, recrystallised from much acetone. The yellow plates obtained melted at 289—291° (Found: C, 62·3; H, 3·7. $C_{22}H_{16}O_7S$ requires C, 62·2; H, 3·8%).

Methylation. This compound (1 g.) in acetone (10 c.c.) was treated with diazomethane (from nitrosomethylurethane, 4 c.c.). The pale yellow crystals deposited over-night (0·6 g.), m. p. 175—177°, evidently consisting of 2-toluene-*p*-sulphonylanthragallol 1 : 3-dimethyl ether, were treated in boiling acetone solution with 1% methyl-alcoholic potash; the violet leaflets obtained (0·3 g.) were dissolved in water and the solution was acidified, giving anthragallol 1 : 3-dimethyl ether as yellow needles, m. p. 212—213°.

The methylation mother-liquor, treated in a similar manner, gave, on acidification and recrystallisation of the product, plates (0·15 g.) of anthragallol 1 : 2-dimethyl ether, m. p. 230—232°.

2-*Ethylcarbonato*-1-*acetylalizarin*.—When 2-ethylcarbonatoalizarin is acetylated with acetic anhydride and pyridine in the usual manner, diacetylalizarin, m. p. 188—189°, is obtained, a replacement of the ethylcarbonato by the acetyl group occurring. If, however, 2-ethylcarbonatoalizarin (0·2 g.) in hot pyridine (0·6 c.c.) is cooled, and acetic anhydride (0·4 c.c.) added, crystals of the acetyl compound quickly separate which, after recrystallisation from acetone–alcohol, form pale greenish-yellow needles, m. p. 177—179°.

When 1 : 2-diethylcarbonatoalizarin (0·5 g.) is gently treated with chromic acid (0·5 g.) in boiling acetic acid solution during 1 hour, appreciable destruction of the ethylcarbonato-group does not occur, for, when cold, crystals (0·3 g.) of the original compound, m. p. 146—148°, separate, and a further amount can be isolated from the filtrate.

2-*Ethylcarbonato*-1-*hydroxyanthrone*.—To 2-ethylcarbonatoalizarin (2 g.) in glacial acetic acid (20 c.c.), stannous chloride (4 g.) in hydrochloric acid (10 c.c.) was added, the mixture boiled for 12 minutes (not longer), and the solution poured into an excess of hydrochloric acid. The viscid deposit, after being washed with hydrochloric acid and then with water, was dissolved in a little alcohol, and the solution concentrated to 40 c.c. The crystalline aggregates which separated (yield, 50%), after repeated crystallisation from alcohol, formed pale yellow plates or leaflets, m. p. 130—133° after sintering at 120° (Found: C, 68·4; H, 4·7. $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7%). The *compound* dissolved in dilute alcoholic potash with a yellow colour, and in sulphuric acid with an orange colour which on keeping became purple. Acetylation in cold pyridine solution with acetic anhydride gave 2-*ethylcarbonato*-1 : 9-*diacetylanthranol*, which, precipitated from the mixture by addition of methyl alcohol, crystallised from alcohol in heavy flat needles, m. p. 177—180° (Found: C, 65·7; H, 4·6. $C_{21}H_{18}O_7$ requires C, 65·9; H, 4·7%). The alcoholic solution exhibited a deep blue fluorescence.

1 : 2-*Dihydroxyanthrone*.—A boiling solution of 2-ethylcarbonato-1-hydroxyanthrone in methyl alcohol containing a little aqueous sodium hyposulphite was treated in an atmosphere of hydrogen with alcoholic potassium hydroxide, and then acidified. The brown deposit was crystallised from carbon disulphide, and then from dilute acetic acid containing stannous chloride and hydrochloric acid. The orange-yellow leaflets obtained, m. p. 149—151°, dissolved in alkali with a bright crimson colour, and in sulphuric acid with a yellow colour which slowly became purple.

Methylation. 2-Ethylcarbonato-1-hydroxyanthrone (1 g.) in benzene (12 c.c.) was treated with diazomethane (from nitrosomethylurethane, 4 c.c.) in an atmosphere of hydrogen. After 12

hours, the solution was evaporated to dryness and the residue extracted with alcohol, reddish-brown crystals remaining undissolved. As neither from the latter, by fractional crystallisation, nor from the extract could a pure compound be isolated, the whole, dissolved in acetic acid, was oxidised with chromic acid in the usual manner. The product, isolated by addition of water, was digested with methyl-alcoholic potash to eliminate the ethylcarbonato-group, baryta solution added, the precipitate collected (A), and the filtrate acidified. Impure alizarin 1-methyl ether separated, and this, treated with ammonia, gave an extract from which, on neutralisation, needles of the pure substance separated, m. p. 175—178°. The barium precipitate (A), on acidification, gave a brown viscid product, in which the presence of alizarin 2-methyl ether could not be detected. In a second methylation experiment, employing acetone as solvent and carried out in an atmosphere of hydrogen, the liquid deposited over-night fine colourless crystals (B), melting at about 290° and sparingly soluble in solvents. On oxidising this substance with chromic acid, a product was obtained from which, after elimination of the ethylcarbonato-group in the usual manner, alizarin 1-methyl ether was obtained. There can be little doubt, therefore, that (B) consists of 2 : 2′-diethylcarbonatodianthrone 1 : 1′-dimethyl ether, though analytical figures are as yet lacking, and that its presence is due to oxidation of 2-ethylcarbonato-1-methoxyanthrone, the first product of the methylation process. The mother-liquors were evaporated, the residue was oxidised with chromic acid, the product hydrolysed with alcoholic potash, the solution treated with baryta solution, and the precipitate collected (filtrate C) and neutralised with boiling hydrochloric acid. After removal of the brown precipitate by hot filtration, the liquid deposited crystals of alizarin 2-methyl ether, m. p. 224—227° after crystallisation from acetone. On acidification, (C) deposited some quantity of alizarin 1-methyl ether, identified as the acetyl compound, m. p. 211—213°.

4 : 4′ - *Dihydroxy* - 3 : 3′ - *dimethoxydianthrone.*—3 : 4 - Dihydroxyanthranol (deoxyalizarin) (2 g.) in tetrachloroethane (80 c.c.) was treated with diazomethane (from nitrosomethylurethane, 8 c.c.) and kept over-night. After removal of ether and tetrachloroethane, the viscid residue was dried at room temperature and extracted with small amounts of boiling alcohol (filtrate D). The undissolved colourless powder crystallised from acetic acid in prisms, m. p. 290—292° (Found : C, 75·5; H, 4·9. $C_{33}H_{22}O_6$ requires C, 75·3; H, 4·6%). As the product, by oxidation with chromic acid in the usual manner, gave alizarin 2-methyl ether (m. p. 228—230°), it evidently consisted of 4 : 4′-*dihydroxy*-3 : 3′-*dimethoxydianthrone.*

If the tetrachloroethane employed in this methylation experiment was replaced by ether, the yield of dianthrone increased, whereas, when benzene was the solvent and an atmosphere of hydrogen was employed, the presence of dianthrone could not be detected.

Filtrate (D) was evaporated, the residue oxidised with chromic acid, the product dissolved in dilute alcoholic potash, and the solution treated with aqueous baryta. From the precipitate obtained, alizarin 2-methyl ether (m. p. 228—230°) was isolated. The filtrate slowly deposited a small quantity of yellow needles, m. p. 211—213°, consisting of alizarin dimethyl ether (mixed melting point).

Acylation of 5 : 6-*Dihydroxy*-1-*benzylidenecoumaran*-2-*one*.—Of the two methods given in the literature for the preparation of this substance (Friedländer and Rudt, *loc. cit.*), which involve respectively the condensation of chlorogallacetophenone and 5:6-dihydroxycoumaranone with benzaldehyde, the latter proved the more efficient, an almost theoretical yield of the colouring matter being obtained.

Attempts to prepare a monoacetyl derivative of the coumaranone were unsuccessful, the diacetyl compound, m. p. 202—203°, being produced in every case.

To 5 : 6-dihydroxy-1-benzylidenecoumaran-2-one (1 g.), suspended in a solution of toluene-*p*-sulphonyl chloride (0·76 g.) in chloroform (6 c.c.), pyridine (0·76 g.) was slowly added with good cooling. After 15 minutes, the addition of alcohol caused the separation of crystals (0·7 g.) of the *ditoluene*-p-*sulphonyl* compound, m. p. 178—180° after recrystallisation from acetic acid (Found : S, 11·6. $C_{29}H_{22}O_8S_2$ requires S, 11·4%).

The mother-liquor was agitated with dilute acid to remove pyridine and concentrated, causing the separation of crystals, which, by recrystallisation from acetic acid, were obtained as yellow prisms, m. p. 217—219°. From this compound (A), an acetyl compound, m. p. 177—180°, was prepared.

In a second experiment, solutions of toluene-*p*-sulphonyl chloride (0·75 g.) and of pyridine (0·8 c.c.) in chloroform were alternately added, with good stirring, to 5 : 6-dihydroxy-1-benzylidenecoumaran-2-one (1 g.) in ice-cold chloroform (6 c.c.). Dilution with alcohol then caused the separation of (A), which was recrystallised from acetic acid (Found : C, 64·9; H, 3·7; S, 7·4. $C_{22}H_{16}O_6S$ requires C, 64·7; H, 3·9; S, 7·8%). From the alcohol–chloroform mother-liquor, by keeping, a second compound could usually be obtained (B). This was more sparingly soluble than (A) in acetic acid and separated therefrom as small, greenish-yellow needles, m. p. 237—240° (Found : C, 64·6; H, 3·9; S, 7·2%). Acetylation

of this *monotoluene*-p-*sulphonyl* compound (B) gave greenish-yellow needles, m. p. 145—146°.

When the ditoluene-*p*-sulphonyl derivative is treated in the cold with alcoholic potassium hydroxide (2 mols.), the solution acidified, and the product extracted with alcohol, a greenish-yellow residue is obtained, m. p. 238—240°, which has all the properties of the toluene-*p*-sulphonyl compound (B): the alcoholic extract contains dihydroxybenzylidenecoumaranone.

5 : 6-*Diethylcarbonato*-1-*benzylidenecoumaran*-2-*one*. To the 5 : 6-dihydroxy-compound (0·5 g.) in chloroform (5 c.c.) and ethyl chloroformate (1 c.c.), pyridine (2·5 c.c.) was added. After removal of pyridine by agitation with acid, the liquid was diluted with alcohol; the *product*, after recrystallisation from the same solvent, formed pale yellow needles, m. p. 104—107° (Found: C, 63·5; H, 4·8. $C_{21}H_{18}O_8$ requires C, 63·3; H, 4·5%).

A *monoethylcarbonato*-derivative was obtained by adding pyridine (2 c.c.) to the dihydroxy-compound (1 g.) in chloroform (6 c.c.) and ethyl chloroformate (0·4 c.c.). The product, isolated by the addition of alcohol, was obtained by recrystallisation as brilliant, large, yellow prisms, m. p. 177—180°. It was apparently the sole product of the reaction (Found: C, 66·0; H, 4·3. $C_{18}H_{14}O_6$ requires C, 66·2; H, 4·3%).

When this substance was acetylated either with acetic anhydride and pyridine, or by Fischer's method in the cold, 5 : 6-diacetoxy-1-benzylidenecoumaran-2-one, m. p. 200—202°, was obtained.

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