Colouring Matters of the Aphididae. Part XIII. The Structure of the Erythroaphins.*

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Consideration of all available evidence leads to the conclusion that two structural formulæ, differing from each other in the location of an angular methyl group, are possible for erythroaphin. These structures contain two dioxan rings fused to a tetrahydrocoronene nucleus and additional support for them is provided by infra-red spectroscopic evidence. The stereochemical difference between erythroaphin-*fb* and erythroaphin-*sl* remains to be discussed.

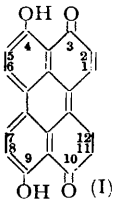
The colouring matters of the *Aphididae* which we have described as aphins present structural problems of peculiar complexity. The glucosidic water-soluble protoaphin present in the haemolymph of the living insect is converted rapidly by enzyme action after the death of the insect into a yellow fat-soluble xanthoaphin, and thence through an orange chrysoaphin into the end-product, a relatively stable deep red erythroaphin (Part I, *Nature*, 1948, **162**, 759). Examination of some thirty species of coloured aphids has revealed the existence of at least two series of aphins (Parts IV and V; *J.*, 1950, 3304; 1951, 2633) which have been distinguished by the use of a suffix indicative of the commonest species from which they have been isolated; thus there are the aphins-*fb*, first isolated from *Aphis fabae* parasitic on broad beans (Part II, *J.*, 1950, 477), and the aphins-*sl* from the willow aphid *Tuberolachnus salignus* (Part III, *J.*, 1950, 485). Only the aphins-*fb* and -*sl* have as yet been examined by us in any detail, mainly for reasons of accessibility, and apart from determination of the glucosidic character of the protoaphins, attention has been largely concentrated on the erythroaphins. It seemed clear that only by elucidating the structure of the erythroaphins would the way be opened to an understanding of the remarkable series of changes leading to their formation from protoaphin—a series which, as far as we are aware, has no analogy in the field of natural colouring matters.

Much of the evidence necessary to establish the structure of the erythroaphins has already been published in earlier papers of this series. It is the purpose of the present communication to interpret this evidence and to amplify it in certain respects so that structural formulæ may be advanced for the erythroaphins. As has already been reported, the erythroaphins-*fb* and -*sl* are isomeric compounds $C_{30}H_{22}O_8$ having identical ultra-violet and visible absorption spectra but differing in infra-red absorption, solubility, and crystalline habit, and in optical rotation. Their extraordinary similarity in chemical behaviour, coupled with the fact that they both yield identical diamino- and dihydroxy-derivatives converted by the action of zinc and acetic acid into erythroaphin-*fb* (Part XII, preceding paper), makes it certain that the difference between the two pigments is stereochemical. This fortunate circumstance enables us first to consider evidence derived from studies on either pigment and to deduce from it a general structure for erythroaphin; the stereochemical difference between them and the mechanism of their interconversion form the subject of the following communication.

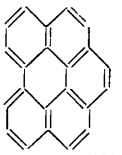
There can be no reasonable doubt that the erythroaphins are derivatives of 4 : 9-dihydroxyperylene-3 : 10-quinone (I). Evidence leading to this conclusion comes (1) from infra-red spectroscopic studies (Part V, *loc. cit.*), (2) from the production of perylene derivatives on zinc-dust fusion (Part VIII, *J.*, 1954, 107) and of mellitic acid on oxidation (Parts II and III, *locc. cit.*), (3) from analogies in chemical behaviour between the erythroaphins, perylene-3 : 10-quinone (Part IX, *J.*, 1954, 1280) and particularly 4 : 9-dihydroxyperylene-3 : 10-quinone (Part X, *J.*, 1954, 1285), and (4) from the observed close similarity between the absorption spectra of the tetra-acetyldihydroerythroaphins and perylene

* Part XII, preceding paper.

(Part VIII, *loc. cit.*) on the one hand and the erythroaphins and 4 : 9-dihydroxyperylene-3 : 10-quinone on the other (Part X, *loc. cit.*). Equally it is clear that the sole chromophoric system in the molecule is that of 4 : 9-dihydroxyperylene-3 : 10-quinone (I).



(I)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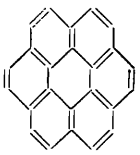

(III)

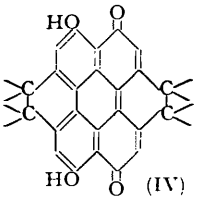
Zinc dust fusion of erythroaphin-*sl* (Part VIII, *loc. cit.*) yielded, not only perylene derivatives, but also derivatives of 1 : 12-benzoperylene (II) and of coronene (III). From this it may be concluded with some certainty that in erythroaphin the perylene system must bear carbon substituents on *at least* two of the central positions in the molecule, *i.e.*, at least one at position 1 or 12 and the other at position 6 or 7. Further, the fact that the erythroaphins yield a diamino-dibromoerythroaphin in which the substituents are attached to the chromophoric system (Part VII, *J.*, 1952, 4928; Part XII, *loc. cit.*) indicates that positions 2, 5, 8, and 11 in the perylene nucleus of erythroaphin are unsubstituted. Steric considerations would preclude entry of a bromine atom or an amino-group into either of the vacant central positions if one out of each of the pairs 1—12 and 6—7 were already occupied.

4 : 9-Dihydroxyperylene-3 : 10-quinone has a formula $C_{20}H_{10}O_4$ whereas erythroaphin has a formula $C_{30}H_{22}O_8$. It is clear from the evidence of hydrogenation that the erythroaphin molecule contains no unsaturation apart from that represented in the dihydroxyperylenequinone nucleus. Moreover, apart from the two hydroxyl and two quinonoid carbonyl groups it contains neither hydroxyl nor carbonyl groups, as shown by infra-red spectroscopic evidence and the failure of all attempts to make derivatives. The conclusion that the 4 " missing " oxygen atoms in erythroaphin must be present in ether linkages seems inescapable. At the same time the generally negative outcome of Zeisel determinations indicates that the 4 oxygen atoms are not present in methoxy-groups. Small non-stoicheiometric amounts of silver iodide which are formed in Zeisel determinations carried out under extreme conditions do not invalidate this statement; their origin will be discussed later.

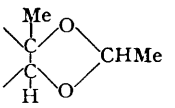
If we now make the minimum deduction from the results of zinc dust fusion of erythroaphin-*sl*, *viz.*, that the dihydroxyperylenequinone system bears additional substituents only in positions 1 (or 12) and 6 (or 7), we are left with the problem of accommodating in these two substituents the residue $C_{10}H_{14}O_4$ which, being saturated and containing only ethereal oxygens, must contain 4 rings. Now the erythroaphins show no peroxidic properties so that the absence of C·O·O·C groupings may be reasonably inferred; nor, as above indicated, do they contain methoxy-groups. Application of the Kuhn–Roth procedure for the estimation of *C*-methyl to the erythroaphins (Parts II and III, *locc. cit.*) consistently yields some 3·8 mols. of acetic acid. Excluding, then, C·O·O·C and methoxy-groupings, and allowing for 4 *C*-Me groups (or their equivalent), it can be seen that the task of accommodating the saturated residue $C_{10}H_{14}O_4$ on the basis of a two-point, or even three-point, attachment is well-nigh impossible, and it must be concluded that the perylene nucleus in the erythroaphins is substituted in all four positions 1, 6, 7, and 12. Further, if we are to accommodate four rings, each at least five-membered, in the " missing " part of the molecule, it is necessary to assume that two of these rings are formed by joining $C_{(1)}$ to $C_{(12)}$ and $C_{(6)}$ to $C_{(7)}$ in each case by two atoms, and in all probability by two carbon atoms. The possibility that one of the junctions might be effected by one carbon and one oxygen atom leads to the postulation of highly unsymmetrical or otherwise unsatisfactory structures; it seems to us preferable to consider, first, more or less symmetrical structures for the pigments and therefore to expand the erythroaphin partial structure to (IV).

Taking into account the above facts and inferences it becomes apparent that if the erythroaphins are symmetrical only structures (V) and (VI) could occur on each side of the

perylene system between positions 1 and 12, and 6 and 7. Other arrangements (*e.g.*, seven-membered ring systems and others without an angular methyl group) are excluded either by inability to explain the results of *C*-methyl determinations, the production of alkylcoronene derivatives on zinc dust fusion, or the failure of the erythroaphins to dehydrogenate extremely readily yielding true coronenes. It is known that dioxan yields



(IV)



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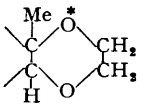


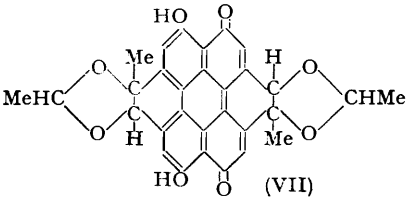
(VI)

acetaldehyde when heated with zinc chloride or with sulphuric acid (Favorsky, *J. Russian Phys. Chem. Soc.*, 1906, **38**, 741; *Chem. Zentr.*, 1907, I, 15), and similar treatment of a dioxolan structure such as that in (V) should also yield acetaldehyde. The suggestion that structures (V) or (VI) occur in erythroaphin is supported by the fact that the pigments do yield acetaldehyde when heated with zinc chloride. It is important to note that no volatile carbonyl compound other than acetaldehyde is produced in this reaction; this we take as strong evidence for the presence of $-O\cdot CH_2\cdot CH_2\cdot O-$ or $-O\cdot CHMe\cdot O-$ groupings.

The yield of acetaldehyde obtained in the initial experiments with zinc chloride was low, as measured by the weight of dimedone derivative or of 2 : 4-dinitrophenylhydrazone isolated, but this was perhaps to be expected since much of the aldehyde liberated in presence of zinc chloride at high temperature would be expected to undergo a variety of transformations. It was nevertheless important to discover how much acetaldehyde could be obtained from the erythroaphins under milder conditions and we therefore turned our attention to the effect of sulphuric acid on the pigments. The erythroaphins are of course virtually insoluble in dilute sulphuric acid but dissolve readily enough in acid of 60% or higher concentration. Such solutions, even in concentrated sulphuric acid, do not appear to undergo any rapid change at room temperature but, on heating, acetaldehyde is evolved. The most favourable conditions for acetaldehyde production appear to be refluxing with 62% sulphuric acid, reaction appearing to be virtually complete in 12 hours. In a series of experiments it was established that under these conditions the amount of acetaldehyde obtained (as its 2 : 4-dinitrophenylhydrazone) from erythroaphin-*fb* was *ca.* 1·65 mols. and from erythroaphin-*sl* *ca.* 0·75 mol. From these results and those of model experiments on dioxan and benzodioxan, which similarly yield acetaldehyde under the same conditions, it may be concluded that erythroaphin-*fb* contains two separate groupings each capable of yielding 1 mol. of acetaldehyde. This, in turn, makes it highly probable that the molecule is symmetrical at least to the extent that there are two groups $C_5H_8O_2$ attached one to each side of the perylene system through the two central positions, and that these groups are of either type (V) or type (VI) [or conceivably one of type (V) and one of (VI)]. Even if it is assumed that the groupings yielding acetaldehyde are the source of 2 mols. of acetic acid in the Kuhn–Roth estimations, two additional *C*-Me groups must be present. These can only be located in angular positions as shown in (V) and (VI), and structures based on the assumption of two angular methyl groups on the alicyclic ring junction on one side of the perylene system and two hydrogen atoms on the other can be ruled out in view of the marked tendency of 13 : 14-dihydro-1 : 12-benzoperylene derivatives to lose two hydrogen atoms and become fully aromatic (cf. Clar, *Ber.*, 1932, **65**, 846).

As has already been mentioned, the erythroaphins-*fb* and -*sl* are undoubtedly stereoisomers and the fact that erythroaphin-*sl* yields only half as much acetaldehyde as the *fb*-isomer with sulphuric acid must have a stereochemical explanation. The production of 1 mol. of acetaldehyde from structure (VI) would presumably be due to an elimination reaction with subsequent formation of a vinyl ether which would then split yielding acetaldehyde. If the ring junction in (VI) were *cis*, then clearly the oxygen atom marked with an asterisk would be in the *trans*-position relative to the angular hydrogen atom and

elimination should occur readily; with a *trans*-junction it would be in the *cis*-position and an elimination reaction would probably not occur. Similar arguments apply to structure (V), for, although it might be argued that acetaldehyde could be formed by hydrolysis, we do not consider that the reaction is one of simple hydrolysis of the erythroaphins; it is difficult to understand the remarkable difference in the yields of acetaldehyde obtained from the two isomeric pigments if the process is simply one of hydrolysis. If an initial elimination reaction is assumed, then stereochemical factors would in theory affect (V) in the same way as (VI). It therefore appears that four structures can be considered for the erythroaphins, *viz.*, (VII), (VIII), (IX), and (X), and that the difference between erythroaphin-*fb* and erythroaphin-*sl* is that in the former both the alicyclic rings are fused in the *cis*-position while in the latter one junction is *cis* and the other *trans*.



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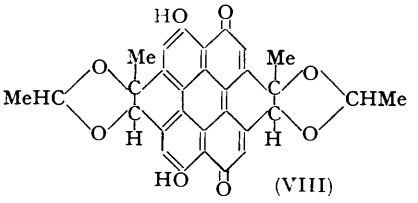

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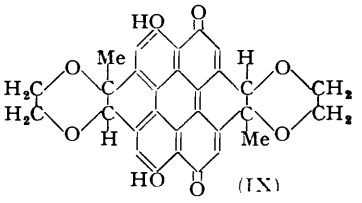

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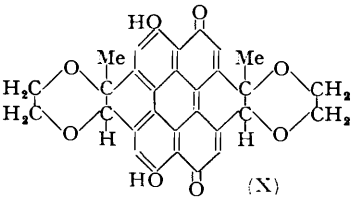

(X)

It is of interest that the production of acetic acid on pyrolysis of erythroaphin finds an explanation on any of these formulæ by invocation of a reaction analogous to that brought about by zinc chloride, and that the formation of small non-stoicheiometric amounts of silver iodide in Zeisel determinations carried out under very drastic conditions is also understandable. Another small point in agreement with these structures is that careful chromatographic study of the products of nitric acid oxidation of the erythroaphins failed to reveal the presence of any polybasic acids other than mellitic or oxalic acids, although succinic acid is completely stable to nitric acid under the reaction conditions employed.

The contrast between the production of twice as much acetaldehyde from erythroaphin-*fb* as from erythroaphin-*sl*, and the exactly similar yields (*ca.* 3·8 mols.) of acetic acid from both pigments in the Kuhn–Roth estimations calls for some comment. To explain this it is necessary to assume, on any formula, that the initial reaction under the Kuhn–Roth conditions (chromic acid in sulphuric acid) is oxidative attack by the chromic acid on the carbon atoms bearing methyl groups rather than an elimination reaction due to the acid; such an initial oxidation would, of course, remove stereochemical effects. As for as we are aware, no example of the production of acetic acid from $-O\cdot CH_2\cdot CH_2\cdot O-$ groupings in Kuhn–Roth estimations has been recorded in the literature, but it appears to us a reasonable assumption on the results of acid fission and pyrolysis of the erythroaphins. True, neither dioxan nor benzodioxan yields acetic acid under the conditions of the Kuhn–Roth estimation, but this does not necessarily invalidate our assumption since, in our view, the presence of an alkyl or other group in an angular position of a fused dioxan ring system would probably be essential for reaction to take the desired course.

We have as yet been unable to obtain decisive evidence of a positive nature for any one of these four formulæ, but various considerations lead us to believe that the choice can be narrowed down to two. Structures (VII) and (VIII) involve the presence in erythroaphin-*sl* of a dioxolan ring fused in the *trans*-position to a six-membered ring. Instances of *trans*-fused dioxolan rings are very rare (cf. *e.g.*, Angyal and Macdonald, *J.*, 1952, 686; Christian, Gogek, and Purvis, *Canad. J. Chem.*, 1951, **29**, 911); so much so, indeed, that

formation or non-formation of cyclic acetals is commonly regarded as satisfactory evidence of *cis*- or *trans*-orientation of hydroxyl groups in a cyclic 1 : 2-diol (*e.g.*, Angyal and Macdonald, *loc. cit.*). There is no doubt that structures (VII) and (VIII) would be under great strain if they contained a *trans*-junction and it is well-nigh impossible to build models of such structures using scale atomic models. Moreover, as will be shown in a later paper it is possible to convert a derivative of erythroaphin-*fb* into the corresponding one of erythroaphin-*sl* by irradiation in solution, and this *cis* → *trans* conversion is most improbable on the dioxolan formulæ (VII) and (VIII). For these reasons we feel that structures (VII) and (VIII) must be regarded as unlikely.

Structures (IX) and (X) present no such difficulty since there is no great difference between the stability of *cis*- and *trans*-fused dioxan systems and *fb*–*sl* interconversions are readily admissible. Taking into account all the facts and arguments so far presented, we feel justified in putting forward the view that the erythroaphin molecule is represented by structure (IX) or (X). The evidence so far presented does not permit of a decision between them. Such a decision can only be reached from a consideration of the stereochemical difference between erythroaphin-*fb* and erythroaphin-*sl* and the factors governing their interconversion.

Attempts to produce further degradative evidence of a positive nature to confirm or disprove structure (IX) or (X) have so far met with little success. Oxidative degradation of the pigments or their derivatives using a variety of reagents has led either to the production of hydroxylated erythroaphins or to complete disruption of the molecule, and no perylenecarboxylic acids have been obtained. Again, heating the erythroaphins with hydrogen bromide in acetic acid under various conditions has failed to yield ethylene dibromide; reaction occurs at temperatures above 160° with production of a black material insoluble in organic solvents but no volatile products seem to be formed. Ethylene dibromide is readily obtained under similar conditions from dioxan and benzodioxan, but this need not necessarily be significant since these compounds are not strictly analogous to the proposed erythroaphin structure. No compounds have as yet been described containing a dioxan ring fused to a second ring and bearing an angular methyl group; the presence of such a group might well have a profound effect on the ease of fission of one of the ether linkages. Other degradations depending on the fission of ether linkages which can be applied to dioxan itself have yielded no results of value with erythroaphin. The tetra-acetyldihydroerythroaphins do indeed form metal halide complexes, *e.g.*, with ferric chloride and aluminium bromide, just as dioxan does, but the formation of such complexes, although an argument in favour of ethereal oxygen atoms, is hardly specific to the dioxan system.

A more detailed examination of the infra-red spectra of the erythroaphins-*fb* and -*sl* (cf. Part V, *loc. cit.*) shows that they contain a number of features which are in accord with the structures (IX) and (X), especially in the light of the infra-red spectrum of dioxan (Malherbe and Bernstein, *J. Amer. Chem. Soc.*, 1952, **74**, 4408; Burket and Badger, *ibid.*,

Absorption maxima (cm.$^{-1}$).

	Erythroaphin-*fb*	Erythroaphin-*sl*	Dibenzoylerythroaphin-*sl*	Dioxan
Aromatic CH	3058	3040	*	—
	1481	1481	*	—
CH_2	2985	2950	2950	2967
	1456	1453	1449	1445
CH_3	2907	2899	2907	—
	1385	1383	1379	—
C–O–C	874 (864)	852	870	877

* Excluded because of presence of benzoyl groups.

1950, **72**, 4397). The erythroaphins, as mulls in hexachlorobutadiene, show absorption maxima ascribed to the aromatic CH group, CH_2, CH_3, and ether-oxygen (C–O–C) which are listed in the annexed Table. In addition several other bands, the origin of which is uncertain, are common to the spectra of the erythroaphins and dioxan, *e.g.*, at 1295—1285, 1266—1255, 1120—1111 and 1081—1074 cm.$^{-1}$, and the existence of these bands would also be consistent with the structures (IX) or (X).

Clearly further work will be necessary to establish conclusively the structure of the erythroaphins but we believe that, on the evidence available, (IX) and (X) give the most satisfactory representation and can at least be regarded as an adequate working hypothesis. When heated with sulphuric acid erythroaphin-*fb* yields in addition to acetaldehyde an almost black solid; this product might be expected, on the basis of (IX) and (X), to be a tetrahydroxydimethylcoronenequinone. Efforts to confirm or disprove this are in progress but are handicapped by the extreme insolubility of the material in solvents other than concentrated sulphuric acid, and by the poverty of existing knowledge of the chemistry of coronene derivatives. It may be mentioned, however, that the difficulty encountered in working with the much simpler 4 : 9-dihydroxy-3 : 10-perylenequinone (Calderbank, Johnson, and Todd, *loc. cit.*) suggests that a coronene derivative of the type mentioned would be very intractable. The results of these experiments and of synthetic studies designed to produce structural analogues of the erythroaphins will be reported in due course.

Experimental

*Reaction of Erythroaphin-*sl *with Zinc Chloride.*—(i) Erythroaphin-*sl* (943 mg.) was intimately mixed with zinc chloride (20 g.) and placed in a small flask connected to a cooled (solid carbon dioxide) U-tube. The system was evacuated and the mixture heated at 300°/10^{-3} mm. for 45 min. The contents of the U-tube were washed with water into an aqueous solution of dimedone (250 c.c. of 0·3%) and kept for 2 days; then the crystalline precipitate (15 mg.) was separated, having m. p. 155° but not sharp. After recrystallisation from aqueous ethanol the product had m. p. 176°. A further quantity (28 mg.) of the product, m. p. 174°, was obtained from the original dimedone solution after it had been kept for 3 weeks. A sample of the dimedone derivative of acetaldehyde prepared in the same way had m. p. 139° (lit., 140°) but after 4 hours' heating under reflux in acetic acid the corresponding anhydride was obtained which had m. p. 175° (lit., 174°), not depressed on admixture with the specimen obtained from the degradation of erythroaphin-*sl* (Found, in a sample dried at 100° for 2 hr. at 10^{-3} mm.: C, 75·2; H, 8·2. Calc. for $C_{18}H_{24}O_3$: C, 75·0; H, 8·4%). The combined yield of acetaldehyde dimedone derivative (43 mg.) so obtained corresponds to 4% of the theoretical value for two mols. of acetaldehyde from one of erythroaphin-*sl*.

(ii) Erythroaphin-*fb* (1 g.) was mixed with zinc chloride (30 g.) and heated at 280°/10^{-3} mm. for 45 min. in a similar apparatus. The distillate was mixed with an ethanolic solution of 2 : 4-dinitrophenylhydrazine (10 c.c. of 0·1% solution containing 1% hydrochloric acid), warmed, and kept overnight; acetaldehyde 2 : 4-dinitrophenylhydrazone (24 mg., 0·015 mol.) was obtained as pale orange needles. This was separated but no more could be obtained from the filtrate. The acetaldehyde derivative was dissolved in benzene and chromatographed on a column of alumina (11 × 2·5 cm.), with benzene–ether (20 : 1) for the elution. Apart from a small brown band of impurity which remained at the top of the column, the product formed a single brownish-yellow zone; the eluate on evaporation and addition of ethanol gave the product (12 mg.) as light orange-yellow crystals, m. p. 158—160° (Found: C, 43·5; H, 3·5. Calc. for $C_8H_8O_4N_4$: C, 42·9; H, 3·6%). A sample mixed with authentic acetaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 162—163°, had m. p. 161—162°, and in benzene formed one band on a column of alumina.

Reaction of the Erythroaphins with Sulphuric Acid.—Finely powdered erythroaphin-*sl* (50 mg.) was mixed with 62% sulphuric acid (15 c.c.) in a small flask fitted with condenser and gas inlet and outlet tubes. A slow stream of nitrogen was passed through the solution, and the exit gases from the top of the condenser were passed through four gas-absorption bottles in series, each containing cooled (<10°) 2 : 4-dinitrophenylhydrazine solution. The reaction mixture was heated at 120° for 12 hr., no further precipitate of acetaldehyde 2 : 4-dinitrophenylhydrazone being obtained thereafter. The precipitate was collected, washed and dried over phosphoric oxide at reduced pressure to constant weight (17 mg., 0·77 mol.). After crystallisation from ethanol the product was obtained as orange-yellow needles, identical with that obtained in the previous experiment.

A similar experiment with erythroaphin-*fb* (50 mg.) gave acetaldehyde 2 : 4-dinitrophenylhydrazone (36 mg., 1·65 mol.).

Metal Halide Complexes of Erythroaphin Derivatives.—(i) *Ferric chloride.* The addition of ferric chloride to tetra-acetyldihydroerythroaphin-*fb*, both in acetic anhydride solution, gave a purple-red solution, the visible spectrum of which resembled that of the original tetra-acetyl

compound except for a general displacement towards the red. Warming the solution led to a dark purple precipitate which was separated and dried. It had a green metallic appearance but was non-crystalline and insoluble in all the common solvents, including nitrobenzene. The complex in water decomposed to the original components and in concentrated sulphuric acid it gave a spectrum identical with that of erythroaphin (Part III, *loc. cit.*). No complex was obtained from 3 : 10-diacetoxyperylene and ferric chloride in acetic anhydride, even after 1½ hours' heating under reflux.

(ii) *Aluminium bromide.* Tetra-acetyldihydroerythroaphin-*fb* (166 mg.) was dissolved in dry benzene and a solution of anhydrous aluminium bromide (1·67 g.) in benzene (25 c.c.) was added. The precipitated orange-coloured complex was separated (centrifuge) quickly, suspended in fresh benzene (50 c.c.), and heated under reflux for 3 hr. The solution was poured into water (200 c.c.), and the mixture extracted repeatedly with benzene (6 × 200 c.c.). The combined benzene extracts were washed and dried and then chromatographed on silica (4 × 3 cm.), benzene–ether (100 : 8) being used to elute the product (40 mg.) which was crystallised first from benzene–ethanol and finally from chloroform–ethanol, to yield tetra-acetyldihydroerythroaphin-*fb* (18 mg.) (Found : C, 67·2; H, 4·7. Calc. for $C_{38}H_{32}O_{12}$: C, 67·1; H, 4·7%). The infra-red spectrum was identical with that of the authentic material. In another experiment the aluminium bromide complex was heated in benzene for 9 hr. but again the only product isolated was the original tetra-acetyl compound.

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