# 382. *The Pigments of "Dragon's Blood" Resin. Part I. Dracorubin.*

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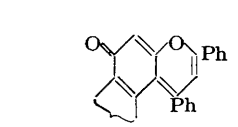
From preliminary experiments on dracorubin, isolated from commercial specimens of "dragon's blood" resin, it is concluded that the compound is an anhydro-2 : 4-diphenylbenzpyranol, $C_{32}H_{24}O_5$, of type (I) derived from the 7-hydroxy-2 : 4-diphenylbenzpyranol, dracorubanol (III; R = H). Contrary to Brockmann and Haase it seems likely that dracorubin contains a methoxyl group but not an active carbonyl group; the oximation product is considered to have a structure of the type (VI). Formed by methylation of dracorubin, *O*-methyldracorubanol (III; R = Me) gave rise to salts with acids and on degradation furnished a product (V; R = Me) identical with the monomethyl ether of draconol (V; R = H) which is obtained by the oxidation of dracorubin with hydrogen peroxide. Dracorubin is represented by the partial formula (I).

From "dragon's blood" resin of Indian origin Brockmann and Haase (*Ber.*, 1936, **69**, 1950) isolated the main colouring matter which they named dracorubin and suggested that the compound had the empirical formula $C_{19}H_{14}O_3$. By a somewhat different procedure Hesse (*Annalen*, 1936, **524**, 14) obtained two pigments from the blood-red resin of fruit-bearing parts of the palm *Dracaena Draco Blume* and named the chief compound dracocarmine for which he proposed the formula $C_{31}H_{26}O_5$. For the minor pigment $C_{28}H_{24}O_7$ Hesse proposed the name dracorubin. Subsequently Brockmann and Haase (*Ber.*, 1937, **70**, 1733) re-examined their dracorubin which they found to be lævorotatory; they regarded it as very similar to, if not identical with, Hesse's dracocarmine and, as a result of analyses of the hydrochloride, perchlorate, and picrate, proposed a revised empirical formula $C_{32}H_{24}O_5$. In addition to describing two hydrogenation products Brockmann and Haase showed that on fusion with potassium hydroxide dracorubin gave rise to acetophenone. In a more recent communication which became available to us after the completion of the present work, these authors in collaboration with Freiensehner (*Ber.*, 1944, **77**, 279) have described further degradation experiments on dracorubin, the chief of which is the oxidation of the compound with hydrogen peroxide to give a phenol, draconol $C_{24}H_{20}O_6$, and an acid $C_{16}H_{14}O_5$, for which they tentatively suggest formulæ containing the residue (V; R = H). They consider that dracorubin may be a derivative of anhydro-7-hydroxy-2 : 4-diphenylbenzpyranol substituted in the 5-position by the residue $C_{11}H_{11}O_3$.

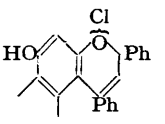
In the course of our preliminary studies * on the colouring matters of "dragon's blood" resin, dracorubin was isolated from a number of samples of commercial resin by a procedure similar to that employed by Brockmann and Haase (*loc. cit.*) and subsequently by their method. The compound was also obtained according to the method employed by Hesse (*loc. cit.*) for the isolation of his dracocarmine. From a comparison of the properties of dracorubin with those of dracocarmine described by Hesse (*loc. cit.*) and of their respective derivatives we consider that dracocarmine and dracorubin are in all probability the same compound (cf. Brockmann and Haase, *loc. cit.*). Further, it has been confirmed that dracorubin is an anhydropyranol base, $C_{32}H_{24}O_5$, of the quinonoid type (I), derived from the carbinol base of type (III; R = H) for which we propose the name dracorubanol. The quinonoid base forms salts by the addition of acids, *e.g.*, with hydrochloric acid it gives the hydrochloride of type (II), *viz.*, dracorubylium chloride. On treatment with sodium acetate this chloride (II) regenerates the parent base (I)

* Our experimental studies on the complex mixture of pigments present in "dragon's blood" resin were undertaken in conjunction with studies on rottlerin and were initiated in 1936 independently of the work of the German authors. The degradation experiments described in the present paper were completed before 1940 and detailed descriptions of them were included in theses presented by my co-workers for higher degrees in the University of Liverpool, *viz.*, Thesis for Degree of Master of Science by Mrs. Dorothy A. Collins (née Jones) in 1939 and Theses for the Degree of Doctor of Philosophy by Dr. K. Isarasena in 1940 and by Dr. F. Haworth in 1946. A. R.

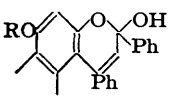
without the formation of the intermediate dracorubanol (III; R = H) (cf. Irvine and Robinson, *J.*, 1927, 2086). In accordance with the established conversion of anhydro-benzpyranols into the methyl ethers of the hydroxybenzpyranols (cf., *e.g.*, Pratt and Robinson, *J.*, 1923, 739, and Robinson and Armit, *J.*, 1925, 1604) methylation of dracorubin with an excess of methyl sulphate and alkali gave rise to optically active (lævorotatory) *O*-methyldracorubanol of type (III; R = Me) from which there were prepared by means of the appropriate acids *O*-methyldracorubylium chloride (IV; R = Cl), picrate (IV; R = $C_6H_2O_7N_3$), perchlorate (IV; R = $ClO_4$), and ferrichloride (IV; R = $FeCl_4$). In the conversion of optically active dracorubin into *O*-methyldracorubanol a second asymmetric centre is produced at the 2-position and consequently the carbinol base (III; R = Me) (but not the salts) would be expected to exist in two forms capable of being separated by crystallisation, but this has not yet been attempted. The base (III; R = Me) was also prepared by the standard method of Armit and Robinson (*loc. cit.*) for the methylation of anhydro-7-hydroxybenzpyranol, and the methosulphate (IV; R = $MeSO_4$) obtained in red prisms which gave *O*-methyldracorubanol on treatment with aqueous sodium acetate or alkalis. This procedure, however, tended to yield a product contaminated with unchanged dracorubin and was less suitable than the alkali method for the preparation of *O*-methyldracorubanol in quantity.



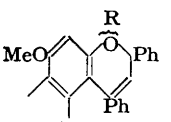

$C_{10}H_9$,(OMe),2(-O-) (I.)



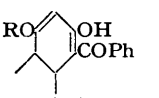

(II.)



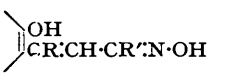

(III.)




(IV.)




(V.)




(VI.)

Like Brockmann and Haase (*loc. cit.*) we have found that the application of the standard tests for a methylenedioxy-group to dracorubin gives inconclusive results and we are unable to decide at present whether dracorubin contains this group. Contrary to the views of the German authors, however, we have obtained evidence that dracorubin contains an alkoxyl group, in all probability methoxyl. Although in determinations by the standard micro-Zeisel method dracorubin gave only traces of a volatile iodide, the use of the conditions employed for the estimation of alkylimide groups gave results in agreement with the presence of one methoxyl group (the results obtained by Dr. Ing. A. Schoeller, late of Berlin, and by Mr. R. Rothwell of this laboratory were consistent). In agreement with this view it was found that *O*-methyldracorubanol and *O*-methyldracorubylium ferrichloride gave results indicating the presence of two methoxyl groups. Though it is conceivable that under the conditions employed the alkyl halide might arise by a deep-seated change in the dracorubin molecule, in the absence of concrete evidence for this we regard the compound as containing a methoxyl group. Further, Brockmann and Haase (*loc. cit.*) envisage the possibility of dracorubin containing a keto-group; but although they form colourless products on oximation by the pyridine method we believe that dracorubin and *O*-methyldracorubanol do not contain an active carbonyl group and consider that the oximation products, which give anomalous analytical results (cf. Brockmann and Haase, *loc. cit.*), may be derivatives of the oximes, of type (VI; R = R' = Ph), of the corresponding styryl ketones obtained by the opening of the oxonium ring. This view is supported by the observation that when flavylium salts are warmed with pyridine–hydroxylamine hydrochloride colourless oximation products are formed which are usually amorphous or resinous. In a favourable case it was found that 8 : 4'-dimethoxyflavylium chloride gave rise to the crystalline oxime, of type (VI; R = H; R' = $C_6H_4$·OMe), of 2-hydroxy-*p*-methoxyphenyl 3-methoxystyryl ketone, which on being heated with alcoholic hydrochloric acid regenerated the parent flavylium chloride. Crystalline oximation products were also obtained from anhydro-7-hydroxy-2 : 4-diphenylbenzpyranol and from 7-methoxy-2 : 4-diphenylbenzpyranol or its salts, but these derivatives did not give analytical results in agreement with the values required for the oximes of the corresponding styryl ketones. Like the oximation product from dracorubin the derivative obtained from anhydro-7-hydroxy-2 : 4-diphenylbenzpyranol readily dissolved in dilute aqueous sodium hydroxide.

Of the five oxygen atoms in dracorubin two are present in the anhydrobenzpyranol residue and one probably in a methoxyl group, leaving two unaccounted for. From the properties of dracorubin and of *O*-methyldracorubanol we consider that the two remaining oxygen atoms are present in ether systems.

The degradation of dracorubin with hot alkalis under a variety of conditions gave only benzoic acid and acetophenone in addition to intractable products, whereas oxidation in acetone with aqueous potassium permanganate yielded benzoic acid along with gummy material. In quantitative experiments it was found that the estimation of the phenyl residues from the combined amounts of acetophenone (isolated as the 2 : 4-dinitrophenylhydrazone) and benzoic acid formed with boiling 20% alcoholic potassium hydroxide indicated the presence of more than one phenyl residue in dracorubin, a result in agreement with the Kuhn–Roth estimation given by Brockmann and Haase (*loc. cit.*). Chiefly owing to the insolubility of dracorubin in suitable solvents it was not possible to effect a stepwise oxidative degradation of the base, but with alkaline hydrogen peroxide in methanol we obtained a compound, m. p. 256° (decomp.), which gives a ferric reaction and appears to be identical with the phenol, draconol, described by Brockmann and Haase (*loc. cit.*). On methylation with diazomethane this compound readily gave a monomethyl ether $C_{23}H_{16}O_4(OMe)_2$ (V; R = Me) identical with the phenolic product formed in small yield along with acetophenone by the hydrolytic fission of *O*-methyldracorubanol with alkalis. The same ether was obtained in somewhat better yield when *O*-methyldracorubanol was oxidised in acetone with aqueous potassium permanganate, and the presence of the free phenolic hydroxyl group in it was confirmed by the formation of an acetate and a *p*-nitrobenzoate. Although we have failed to prepare a diagnostic carbonyl derivative, *O*-methyldraconol like draconol gives a ferric reaction in alcohol and therefore appears to contain a carbonyl group in the *ortho*-position to the phenolic hydroxyl group. On hydrogenation with a palladium–charcoal catalyst *O*-methyldraconol gave rise to *O*-methyldihydrodraconol which forms a diacetate and gives an amorphous product with pyridine–*p*-nitrobenzoyl chloride and we consider that in the hydrogenation the >CO group is reduced to >CH(OH). Oxidation of *O*-methyldraconol with potassium permanganate or chromic anhydride gave resinous material along with benzoic acid. Estimated by the Kuhn–Roth method, the amount of benzoic acid obtained from *O*-methyldraconol clearly indicated the presence of one phenyl residue.

In order to clarify the behaviour of dracorubin on methylation by the alkali–methyl sulphate method the application of this reaction to several anhydro-pyranol bases of known structure was studied. In addition to the known bases from 7-hydroxy- and 7-hydroxy-4-phenylflavylium chloride the red crystalline anhydro-pyranols were prepared from 7-hydroxy-6-methyl-, 7-hydroxy-8-methyl-, and 7-hydroxy-5 : 6-dimethyl-flavylium chloride. With the exception of anhydro-7-hydroxy-2 : 4-diphenylbenzpyranol which gave rise to 7-methoxy-2 : 4-diphenylbenzpyranol, the remaining bases furnished only intactable gummy products under the conditions employed in the preparation of *O*-methyldracorubanol, a result which is in keeping with the partial formula (I) for dracorubin.

## Experimental.

*Dracorubin.*—(*a*) The methods originally devised for the isolation of dracorubin were similar to those employed by Brockmann and Haase (*loc. cit.*) and the following modified procedure was ultimately adopted for the preparation of the compound in quantity. The powdered resin (300 g.) was extracted with boiling benzene (2 l.) for 4 hours and the filtered extract was mixed with a solution of picric acid (15 g.) in benzene (130 ml.) and heated under reflux for 6 hours, until the gelatinous brown precipitate, which had separated initially, became granular. Next day the solid (20—25 g.) was collected, washed with benzene (200 ml.), air-dried (with slight darkening), and triturated with a little methanol or alcohol to remove resinous material, leaving the impure picrate as a bright orange powder which did not darken on exposure to air. Decomposition of this product (50 g.) in 95% alcohol (1 l.) with 25% aqueous sodium hydroxide (200 ml.) at room temperature and then at 40° for 1 hour gave crude dracorubin which was collected, well washed with boiling water, and dried; yield, 8 g. of a semi-crystalline, deep scarlet powder. This material was extracted with chloroform, leaving a small amount of a brown residue, the chloroform extract poured on a column of aluminium oxide and, after the lower bluish-purple zone had been washed through the column with much chloroform, the main red zone containing dracorubin was eluted with methanol–chloroform (1 : 9). Concentration of the red solution in a vacuum gave crystalline dracorubin which was purified by repeated chromatography on aluminium oxide to remove trades of accompanying pigments: yield, 150 g. of pure dracorubin from 15 kg. of resin. Crystallised from benzene and then benzene–methanol (1 : 9), dracorubin was obtained in dark red plates, m. p. 315°, having a greenish-golden reflex (Found, in a specimen dried in a high vacuum at 90° : C, 78·6; H, 4·9; OMe, 6·2. Calc. for $C_{31}H_{21}O_4 \cdot OMe$, C, 78·7; H, 5·0; OMe, 6·2%). Purified from chloroform, the compound formed dark red prisms, m. p. 315°, containing solvent of crystallisation which was not completely removed when a specimen was dried in a high vacuum at 90° (Found, in a dried sample: Cl, 1·5%). The m. p. of dracorubin varies somewhat with the rate of heating. On

being slowly heated it melts at 299° but placed in a bath at 250—300° and rapidly heated the compound has been found to melt invariably at 315°.

(*b*) A specimen of dracorubin was isolated according to the method employed by Hesse (*loc. cit.*) for dracocarmine and, on repeated purification by chromatography with aluminium oxide followed by recrystallisation from benzene, had m. p. 315° (rapid heating) and was identical in every way with a specimen isolated by method (*a*) (Found, in a specimen dried in a high vacuum at 90°: C, 78·4; H, 5·0%).

Dracorubin (1 g.) was heated with hydroxylamine hydrochloride (1 g.) in pyridine (60 ml.) on the steam-bath for 6 hours and the resulting almost colourless solution poured on ice (200 g.). Next day the solid was collected and repeatedly crystallised from moist acetone, giving a *compound* in colourless needles which charred at 220° after becoming pink at 190° and was readily soluble in dilute aqueous sodium hydroxide (Found, in material dried in a high vacuum at 100°: C, 73·4; H, 5·4; N, 3·0. $C_{32}H_{27}O_6N$ requires C, 73·7; H, 5·2; N, 2·7%. $C_{32}H_{25}O_5N$ requires C, 76·3; H, 5·0; N, 2·8%). This product, which had a negative ferric reaction, separated from chloroform or aqueous alcohol in colourless rectangular plates and on being boiled with 2N-hydrochloric acid gave rise to dracorubylium chloride which, on treatment with aqueous sodium hydroxide, regenerated dracorubin.

*Dracorubylium Salts.*—(*a*) When a solution of the dracorubin (0·1 g.) in ethyl acetate (80 ml.) was saturated with hydrogen chloride an almost theoretical yield of dracorubylium chloride separated in reddish-orange needles. Recrystallised from a mixture of 10% hydrochloric acid and methanol or alcohol, the chloride formed slender orange-red needles, readily soluble in acetic acid, moderately soluble in carbon tetrachloride, benzene, or ethyl acetate (Found: C, 73·2; H, 4·9; Cl, 6·7. Calc. for $C_{32}H_{25}O_5Cl$: C, 73·2; H, 4·8; Cl, 6·8%). The chloride slowly decomposes in moist air with loss of some hydrogen chloride and readily regenerates dracorubin on treatment with aqueous sodium acetate or with much water.

(*b*) A warm saturated solution of dracorubin in ethyl acetate (40 ml.) was mixed with an excess of 30% perchloric acid and the resulting precipitate collected, washed with ethyl acetate, and crystallised from acetic acid, giving dracorubylium perchlorate in clusters of orange needles, m. p. 291° (decomp.) after sintering at 259°, identical with a specimen prepared from the chloride (Found: C, 65·4; H, 4·3; Cl, 6·1. Calc. for $C_{32}H_{25}O_9Cl$: C, 65·3; H, 4·4; Cl, 6·0%). This salt is much more stable than the chloride but on treatment with aqueous-alcoholic sodium acetate it regenerates dracorubin.

(*c*) The addition of picric acid (0·2 g.) in benzene (5 ml.) to a saturated solution of dracorubin (0·25 g.) in warm methanol–benzene (1 : 9) gave dracorubylium picrate which separated from methanol or acetic acid in slender yellow needles, decomposing at 260° (Found: C, 63·5; H, 3·9; N, 5·9. Calc. for $C_{38}H_{27}O_{12}N_3$: C, 63·6; H, 3·8; N, 5·9%).

(*d*) A solution of dracorubylium chloride (0·5 g.) in the minimum amount of acetic acid at 30° was treated with an excess of a concentrated solution of ferric chloride in concentrated hydrochloric acid, and the buff-coloured precipitate collected, washed with a little acetic acid, and dried in the air. Crystallised from acetic acid containing a little formic acid, the solid gave a substance which does not appear to be a normal ferrichloride (Found, in a specimen dried in a high vacuum at 80°: C, 56·8; H, 4·6. Calc. for $C_{32}H_{25}O_5Cl_4Fe$: C, 55·9; H, 3·7%). This product is sparingly soluble in chloroform or ethyl acetate and somewhat more soluble in methanol or alcohol.

O-*Methyldracorubanol* (III; R = Me).—To a vigorously agitated solution of dracorubin (5 g.) in a mixture of methanol (100 ml.) and methyl sulphate (200 ml.), 20% aqueous sodium hydroxide was added gradually at a rate sufficient to maintain the temperature of the mixture at about 70°. When the reaction mixture became permanently alkaline, indicated at this stage by the appearance of a red colour, a further portion of methyl sulphate (100 ml.) was added, followed by more 20% aqueous sodium hydroxide until the mixture again became alkaline. This procedure was repeated until an almost colourless insoluble product was separated. The mixture was then diluted with water (about 2 l.) and next day the pale brown, almost colourless solid was collected, washed, and dried. Sufficient N-sodium hydroxide was added to the yellow solution of this product in the minimum amount of methanol necessary to discharge the colour (due to traces of acid) and to precipitate the crude O-*methyldracorubanol* (4·5 g.) which was collected, well washed with water, dried, and crystallised from aqueous acetone and then from benzene–light petroleum (b. p. 60—80°), forming masses of colourless slender needles, m. p. 205°, after slight darkening at 180°, $[\alpha]_D^{21}$ −119·0° in chloroform (*c*, 0·4 g.) [Found, in a specimen dried in a high vacuum at 90°: C, 76·2; H, 5·5; OMe, 12·6. $C_{31}H_{22}O_4(OMe)_2$ requires C, 76·2; H, 5·4; OMe, 11·9%]. This compound, which is readily soluble in pyridine or acetone and moderately soluble in methanol or alcohol, quickly absorbs acidic vapours when exposed to the atmosphere and becomes yellow. On being heated with hydroxylamine hydrochloride and pyridine on the steam-bath for 6 hours *O*-methyldracorubanol gave a *product* which separated from aqueous pyridine in long colourless needles, m. p. 285° (decomp.) (Found: C, 74·0; H, 5·4; N, 5·2. $C_{33}H_{29}O_6N$ requires C, 74·0; H, 5·4; N, 2·6%). When the hydroxylamine hydrochloride was replaced by semicarbazide hydrochloride in this experiment a *compound* was obtained which formed small colourless prisms, m. p. 210° (decomp.), from aqueous pyridine or acetone (Found: C, 69·5; H, 5·3; N, 6·7. $C_{34}H_{31}O_6N_3$ requires C, 70·7; H, 5·4; N, 7·3%).

O-*Methyldracorubylium Chloride* (IV; R = Cl).—This salt was prepared quantitatively by the addition of an excess of 2N-hydrochloric acid to *O*-methyldracorubanol (0·5 g.) in acetic acid (50 ml.). Crystallised from dilute hydrochloric acid or dilute hydrochloric acid–acetic acid (2 : 1), the *chloride* formed long orange needles which began to decompose at 260° and finally fused at about 280° (Found: C, 73·0; H, 5·2; Cl, 6·4. $C_{33}H_{27}O_5Cl$ requires C, 73·5; H, 5·1; Cl, 6·6%). This compound is readily soluble in acetic acid, methanol, ethanol, or chloroform and, on treatment with aqueous sodium acetate or sodium hydroxide, regenerates the carbinol base.

Treatment of *O*-methyldracorubanol, dissolved in the minimum amount of acetic acid, with an excess of aqueous alcoholic picric acid gave an almost theoretical yield of the *picrate* (IV; R = $C_6H_2O_7N_3$) which is remarkably stable and crystallised from acetic acid as well as alcohol or ethyl acetate in long orange needles, m. p. 203° (decomp.) after darkening at 140° (Found: C, 64·1; H, 4·1; N, 5·8. $C_{39}H_{29}O_{12}N_3$ requires C, 64·0; H, 4·0; N, 5·7%).

The addition of a solution of ferric chloride in concentrated hydrochloric acid to *O*-methyldracorubanol or its chloride in a little acetic acid precipitated *O-methyldracorubylium ferrichloride* (IV; R = $FeCl_4$) which separated from formic or acetic acid in orange-red needles, m. p. 190° (decomp.) [Found : C, 56·6; H, 4·1; OMe, 10·5; Fe, 7·7. $C_{31}H_{31}O_3Cl_4Fe(OMe)_2$ requires C, 56·5; H, 3·9; OMe, 8·9; Fe, 8·0%].

O-*Methyldracorubylium perchlorate* (IV; R = $ClO_4$) separated from acetic acid in slender orange needles, m. p. 284—285° (decomp.) (Found : C, 65·4; H, 4·6; Cl, 6·0. $C_{33}H_{27}O_9Cl$ requires C, 65·7; H, 4·5; Cl, 5·9%).

*Draconol* (V; R = H).—A solution of dracorubin (0·25 g.) in methanol (60 ml.) was mixed with 15% hydrogen peroxide (1·5 ml.) and 2N-aqueous sodium hydroxide (25 ml.). The deep red colour of the mixture changed to yellow and, on acidification with acetic acid, a yellow solid separated. Crystallised from dilute ethanol, this compound formed yellow prisms, m. p. 256° (decomp.), soluble in methanol, chloroform, or pyridine and giving a brownish-green ferric reaction in alcohol. Owing to the tendency of this compound to retain solvent of crystallisation consistent analytical results were not obtained (cf. Brockmann and Haase, *loc. cit.*). Methylation of this phenol with diazomethane in ether–chloroform, however, gave *O*-methyldraconol which formed slender, pale yellow needles, m. p. 247°, from ethyl acetate and was identical with a specimen obtained from *O*-methyldracorubanol.

*Degradation of* O-*Methyldracorubanol.*—(*a*) A solution of the compound (0·5 g.) in alcohol (100 ml.) containing potassium hydroxide (5 g. in water 5 ml.) was evaporated and the residue heated to 240° (metal-bath) for 10 minutes. After having been washed with a little ether the cooled melt was dissolved in water at 0°, and the solution was acidified with concentrated hydrochloric acid (added drop-wise with cooling) and repeatedly extracted with ether. From the combined ethereal extracts a little benzoic acid was isolated by means of aqueous sodium hydrogen carbonate. Subsequent evaporation of the dried extracts then left a small amount of O-*methyldraconol* which separated from warm acetone, ethyl acetate, or acetic acid in pale yellow slender needles, m. p. 247°, sparingly soluble in the usual organic solvents in the cold except pyridine, insoluble in dilute aqueous sodium hydroxide, and having a brownish-green ferric reaction in alcohol [Found : C, 71·8; H, 5·4; OMe, 14·1; *M*, 382. $C_{23}H_{16}O_4(OMe)_2$ requires C, 71·8; H, 5·3; OMe, 14·8%; *M*, 418. Calc. for $C_{19}H_{12}O_3(OMe)_2$ : C, 72·0; H, 5·2; OMe, 17·7%; *M*, 352]. With alcoholic sodium hydroxide this ether forms a sparingly soluble yellow sodium salt.

Evaporation of the ethereal washings of the potassium hydroxide melt left a small amount of acetophenone which was identified by conversion into the 2 : 4-dinitrophenylhydrazone, m. p. 237° after purification.

(*b*) 3% Aqueous potassium permanganate (100 ml.) was added drop-wise to a solution of *O*-methyldracorubanol (1 g.) in boiling acetone (200 ml.) during 1½ hours. Next day the mixture was cleared with the minimum amount of sulphur dioxide and diluted with water (100 ml.), the acetone was allowed to evaporate spontaneously, and the pale yellow solid collected. A further small amount of the same product mixed with benzoic acid was obtained after extraction of the filtrate with ether in a continuous extractor for 30 hours. Crystallisation of the combined solids from acetone gave *O*-methyldraconol (0·1 g.), m. p. and mixed m. p. 247°, identical with a specimen obtained by method (*a*). With methanolic sodium methoxide this compound furnished a canary-yellow precipitate of the sodium derivative from which the phenol was readily regenerated on treatment with acid. Acetylation of this phenol (1 g.) with pyridine (5 ml.) and acetic anhydride (10 ml.) on the steam-bath for 6 hours gave a product which was difficult to purify. Repeated crystallisation of the material alternately from ethyl acetate, acetone, and methanol–chloroform ultimately furnished the *acetate* in colourless rhombic plates (0·4 g.), m. p. 243° (Found, in a specimen dried in a high vacuum at 60° : C, 70·0; H, 5·3. $C_{27}H_{24}O_7$ requires C, 70·4; H, 5·0%. $C_{23}H_{20}O_6$ requires C, 70·4; H, 5·1%). A mixture of the yellow sodium salt of *O*-methyldraconol (0·1 g.), *p*-nitrobenzoyl chloride (0·1 g.), and toluene (50 ml.) was agitated for 10 minutes and then heated on the steam-bath for ½ hour. The solid which separated from the cooled mixture was washed with water, dried, and crystallised from pyridine, giving the p-*nitrobenzoate* in rosettes of small, almost colourless needles, m. p. 307° (decomp.) (Found, in a dried specimen : C, 67·7; H, 4·5; N, 2·7. $C_{32}H_{25}O_9N$ requires C, 67·7; H, 4·4; N, 2·5%).

Oxidation of *O*-methyldraconol (0·5 g.) in boiling acetone (450 ml.) with saturated aqueous potassium permanganate (150 ml., added dropwise) gave rise to benzoic acid (about 0·02 g.) along with unchanged phenol (0·87 g.) and a small amount of yellow amorphous product. Oxidation of the phenol (0·6 g.) with 5N-chromic acid (40 ml.) and concentrated sulphuric acid on the steam-bath for 1 hour yielded benzoic acid which was isolated with ether and purified by crystallisation from light petroleum (yield, 0·15 g. of benzoic acid; theory for 1 phenyl residue in *O*-methyldraconol is 0·21 g.).

*Hydrogenation of* O-*Methyldraconol.*—A solution of the compound (1 g.) in acetic acid (150 ml.) at 100° was agitated with hydrogen and a palladium–charcoal catalyst (from 5 g. of charcoal and 0·2 g. of palladium chloride) for 1 hour, filtered (wash charcoal with acetic acid), and evaporated in a vacuum. Crystallised from ethyl acetate and then acetone or toluene, the residue gave the *dihydro*-derivative in pale yellow rhombic plates (0·6 g.), m. p. 221°, soluble in alcohol or chloroform and having a bottle-green ferric reaction in alcohol [Found : C, 71·5; H, 5·8; OMe, 14·1. $C_{23}H_{18}O_4(OMe)_2$ requires C, 71·4; H, 5·7; OMe, 14·7%]. Acetylation of this compound by the pyridine method on the steam-bath for 6 hours gave rise to the *diacetate* which was repeatedly recrystallised from dilute acetone, alcohol, and then ethyl acetate, forming colourless diamond-shaped prisms, m. p. 218° [Found : C, 69·3; H, 5·5. $C_{29}H_{28}O_8$ (diacetate) requires C, 69·1; H, 5·6%. Calc. for $C_{27}H_{26}O_7$ (mono-acetate) : C, 70·1; H, 5·6%].

[With J. H. Richards] *Oximation of* 8 : 4′-*Dimethoxyflavylium Chloride.*—The chloride was prepared by the condensation of *p*-methoxyacetophenone (2 g.) and *o*-vanillin (2 g.) with hydrogen chloride–ethyl acetate and formed stellate clusters of orange-brown needles from 4% hydrochloric acid (cf. Robinson *et al.*, *J.*, 1924, 207).

A solution of this chloride (2 g.) and hydroxylamine hydrochloride (1 g.) in pyridine (15 ml.) was warmed on the steam-bath for 6 hours and next day the pale yellow mixture was poured on crushed ice. Crystallisation of the colourless precipitate from alcohol gave the *oxime* of 2-hydroxy-3-methoxystyryl

4-methoxyphenyl ketone in colourless slender needles, m. p. 148° (decomp.) (Found: C, 68·2; H, 5·9; N, 4·9. $C_{17}H_{17}O_4N$ requires C, 68·2; H, 5·7; N, 4·7%). This compound (0·2 g.) was heated on the steam-bath with a mixture of concentrated hydrochloric acid (10 ml.) and alcohol (10 ml.) for 45 minutes and the dark red solution treated with an excess of ferric chloride in concentrated hydrochloric acid. Crystallised from acetic acid, the resulting solid gave the 8 : 4′-dimethoxyflavylium ferrichloride in brown needles with an orange sheen, m. p. 178°, identical with an authentic specimen which we have invariably found to have m. p. 178° (Found: C, 44·1; H, 3·2; Fe, 11·9. Calc. for $C_{17}H_{15}O_3Cl_4Fe$: C, 43·9; H, 3·2; Fe, 12·0%) (compare Robinson *et al.*, *loc. cit.*, who give m. p. 180°).

*7-Methoxy-6-methylflavylium Chloride.*—The interaction of 5-methylresorcylaldehyde (7 g.) and acetophenone (8 ml.) in ethyl acetate (200 ml.) saturated with hydrogen chloride furnished 7-hydroxy-6-methylflavylium chloride. Crystallised from 10% and then 5% hydrochloric acid, this salt was obtained as a *hydrate* in brownish-yellow needles (8 g.), m. p. 162° (decomp.), with a greenish-yellow reflex which was partly dehydrated on being dried at room temperature (Found, in a specimen dried in a vacuum over potassium hydroxide: C, 69·3; H, 5·0. $C_{16}H_{13}O_2Cl,0{\cdot}25H_2O$ requires C, 69·3; H, 4·9%).

Methylation of 2 : 4-dihydroxy-5-methylbenzaldehyde (10 g.) with methyl iodide (12 g.) and potassium carbonate (15 g.) in boiling acetone (200 ml.) during 80 minutes gave rise to *2-hydroxy-4-methoxy-5-methylbenzaldehyde* which formed needles (9 g.), m. p. 72°, from dilute methanol, having a violet ferric reaction [Found: C, 65·2; H, 6·3; OMe, 18·8. $C_8H_7O_2(OMe)$ requires C, 65·1; H, 6·0; OMe, 18·7%]. The condensation of this aldehyde (2·5 g.) with acetophenone (2·5 ml.) in ethyl acetate with hydrogen chloride furnished *7-methoxy-6-methylflavylium chloride* which formed orange-yellow needles (3·5 g.), m. p. 174° (decomp.), from 2N-hydrochloric acid (Found: C, 71·4; H, 5·4. $C_{17}H_{15}O_2Cl$ requires C, 71·2; H, 5·2%). The *perchlorate* separated from acetic acid in deep orange-yellow needles (Found: C, 58·0; H, 4·3. $C_{17}H_{15}O_6Cl$ requires C, 58·2; H, 4·3%).

*7-Hydroxy-8-methylflavylium chloride* was prepared from 2 : 4-dihydroxy-3-methylbenzaldehyde and acetophenone by means of ethyl acetate–hydrogen chloride and crystallised from 10% hydrochloric acid, forming red needles decomposing at 127° (Found: C, 70·7; H, 4·9. $C_{16}H_{13}O_2Cl$ requires C, 70·5; H, 4·8%). The perchlorate separated from acetic acid in purple needles, m. p. 187° (decomp.). Prepared in the usual way, the anhydro-base crystallised from *n*-amyl alcohol in scarlet needles, m. p. 149° (decomp.), readily soluble in methanol, alcohol, benzene, or chloroform.

*7-Hydroxy-5 : 6-dimethylflavylium Perchlorate.*—7-Hydroxy-5 : 6-dimethylflavylium chloride was prepared from 4 : 6-dihydroxy-2 : 3-dimethylbenzaldehyde (Robertson and Whalley, *J.*, 1949, 3038) and acetophenone and crystallised from 10% hydrochloric acid, forming small yellow needles, m. p. 204—206° (decomp.). The *perchlorate* separated from acetic acid in reddish-brown needles (Found: C, 57·5; H, 4·6. $C_{17}H_{15}O_6Cl$ requires C, 58·2; H, 4·3%).

Treatment of an aqueous-methanolic solution of the chloride with aqueous sodium acetate gave the anhydro-base which was crystallised from *n*-amyl alcohol and then from chloroform–benzene, forming deep-red needles, m. p. 166° (decomp.), readily soluble in alcohol, chloroform, or pyridine.

*Oximation and Methylation of Anhydro-7-hydroxy-2 : 4-diphenylbenzpyranol.*—Formed from 7-hydroxy-4-phenylflavylium chloride (Bülow and Sickerer, *Ber.*, 1901, **34**, 2368), *7-hydroxy-4-phenylflavylium perchlorate* separated from acetic acid in small orange prisms, m. p. 260—262° (decomp.), having a lilac reflex (Found: C, 63·2; H, 3·8. $C_{21}H_{15}O_6Cl$ requires C, 63·3; H, 3·8%).

When a mixture of this anhydro-pyranol (Bülow and Sickerer, *loc. cit.*) (1 g.) was heated on the steam-bath with hydroxylamine hydrochloride (1·5 g.), and pyridine (15 ml.), the solution quickly became colourless and after 4 hours a test-sample on acidification and subsequent treatment with sodium acetate did not give unchanged quinonoid base. The mixture was then diluted with water and acidified with acetic acid, and the resulting viscous product was triturated with dilute acetic acid until it solidified. Crystallised from alcohol, this material gave a *substance* in clusters of colourless tiny prisms, m. p. 176° (decomp.) after sintering at 78°, which was readily soluble in dilute aqueous sodium hydroxide (Found, in material dried in a high vacuum at 60°: C, 75·4; H, 5·2; N, 7·8. $C_{21}H_{17}O_3N$ requires C, 76·1; H, 5·2; N, 4·2%).

On methylation with methyl sulphate and aqueous sodium hydroxide by the procedure employed for dracorubin anhydro-7-hydroxy-2 : 4-diphenylbenzypyranol gave an almost theoretical yield of a resinous product which was purified by conversion into 7-methoxy-4-phenylflavylium chloride. This compound separated from dilute alcohol in long orange-yellow needles which on treatment with aqueous sodium acetate furnished a gum which solidified on trituration with water and then aqueous acetone, and on crystallisation from 50% acetone gave rise to 7-methoxy-2 : 4-diphenylbenzpyranol in colourless elongated small prisms, m. p. 117° (Found, in a specimen dried in a high vacuum at 60°: C, 60·0; H, 5·5%) (cf. Robinson and Turner, *J.*, 1918, 874, who gave m. p. 55—57° for the amorphous compound). Crystallisation of the pyranol from dilute alcohol gave a mixed product in tiny colourless plates which partly melted at 85°. On one occasion the crude methylation product was repeatedly crystallised from methanol, giving the methyl ether of 7-methoxy-2 : 4-diphenylbenzpyranol in colourless elongated prisms, m. p. 116°, which became yellow on exposure to the laboratory atmosphere [Found: C, 79·8; H, 5·7; OMe, 16·7. Calc. for $C_{21}H_{14}O(OMe)_2$: C, 80·2; H, 5·8; OMe, 18·0%] (cf. Bülow and Sickerer, *loc. cit.*, who give m. p. 104° and Brockmann and Junge, *Ber.*, 1944, **77**, *B*, 44, who give m. p. 114°). Prepared from the pyranol, 7-methoxy-2-phenylflavylium ferrichloride formed elongated orange prisms, m. p. 191° (Armit and Robinson, *loc. cit.*), and the perchlorate formed orange-yellow needles, m. p. 238° (Kehrmann and Reider, *Helv. Chim. Acta*, 1926, **9**, 491).

Oximation of the 7-methoxy-2 : 4-diphenylbenzpyranol or of 7-methoxy-4-phenylflavylium chloride with pyridine-hydroxylamine hydrochloride on the steam-bath for 4 hours gave a *substance* which, on trituration with water followed by crystallisation from alcohol, formed tiny colourless plates, m. p. 164° (Found, in a specimen dried in a high vacuum at 80°: C, 76·7; H, 5·5; N, 7·3. $C_{22}H_{19}O_3N$ requires C, 76·5; H, 5·2; N, 4·1%).

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