

# SULPHUR DYES AND SULPHURISED VAT DYES

## Part II. Constitution of Cibanone Yellow R—Part I

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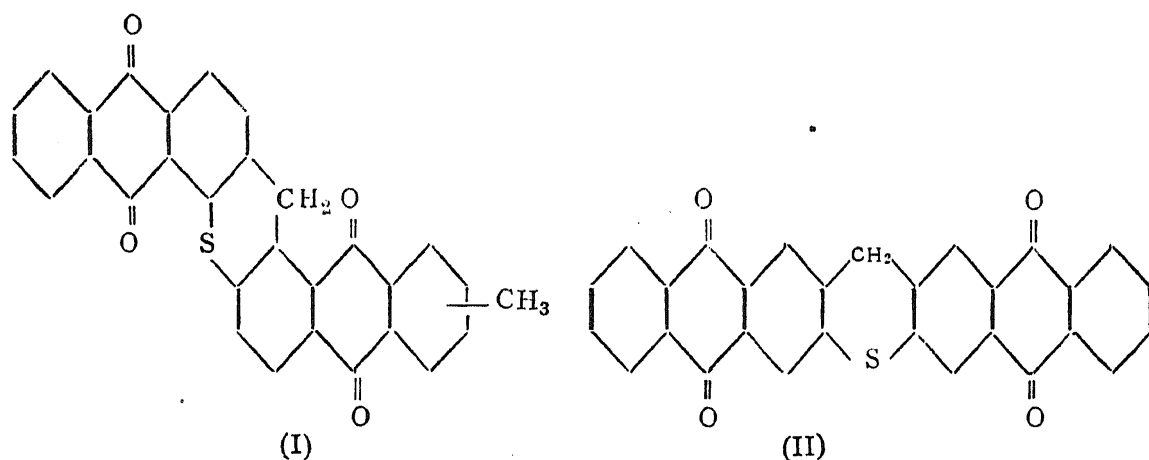
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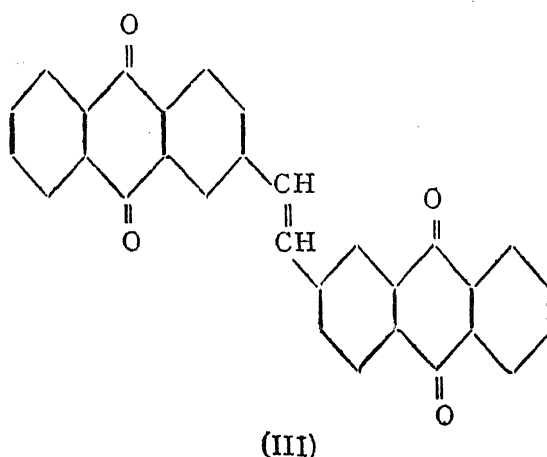
CIBANONE YELLOW R (Ciba) (Mayer and Schaarschmidt, 1908)<sup>1</sup> is a vat dye which dyes bright orange-yellow shades from a red-brown alkaline hydro-sulphite vat. The dye is prepared by the fusion of 2-chloromethylantraquinone with sulphur, followed by treatments with concentrated sulphuric acid and sodium hypochlorite. The shades are attractive and have moderate fastness to chlorine, but the dye has been withdrawn from the commercial range of Cibanone colours on account of its tendering action on cellulose when the dyed material is exposed to light. The catalytic activity in the photochemical degradation of cellulose is indeed so marked that it has been the dye of choice, together with Cibanone Orange R which is obtained by carrying out the thionation at a higher temperature, for investigators studying the accelerated oxidation of cellulose by the action of light and of oxidising agents.

The constitution of Cibanone Yellow R and Orange R has been examined by Fierz-David and Geering.<sup>2</sup> After removal of inorganic salts by means of hot water, the commercial dyes were extracted with alcohol, and from the extracts of both the dyes 2-methylantraquinone was isolated. Purified Cibanone Yellow R analysed as follows:—C, 76.1; H, 3.4; S, 8.5. M. W. by Rast's method in perylene, 495.  $C_{30}H_{16}O_4S$  requires C, 76.2; H, 3.4; S, 6.8%. M. W. 472. Chromic acid oxidation gave anthraquinone-2-carboxylic acid; but the dye was stable to hydrogen peroxide. From these results it was concluded that the dye was probably an anthraquinone-thioxanthone (diphthaloylthioxanthene) (I) or (II; with a methyl substituent). The linear compound (II) was synthesised by condensation of phthalic anhydride and thioxanthene in the presence of aluminium chloride, followed by cyclization. The product dyed much weaker shades than Cibanone Yellow R, to which the angular structure (I) was then assigned.

There are several considerations which render the constitution (I) very improbable. There is a considerable difference in the sulphur content between the theoretical and experimental values. Diaryl sulphides are



generally oxidised to sulphones and do not undergo fission by treatment with chromic acid in glacial acetic acid.<sup>3</sup> If, however, oxidation accompanied by desulphurisation does take place, (I) should give a mixture of anthraquinone-1-carboxylic acid and the 2-isomer, while only the latter acid has been isolated. The elementary analysis of the synthetic compound prepared by Fierz-David and Geering was also not in agreement with the theoretical value for (II), and the differentiation made by them between the angular (I) and the linear structure (II) on the basis of colour in concentrated sulphuric acid (I gives a blue and II a dark green colour) does not appear to be significant. Purified Cibane Yellow R actually gives a characteristic purple and not a blue solution in sulphuric acid, and 2:2'-dianthraquinonyl-ethylene (III) (Anthraflavone), which can be regarded as a linear *trans* compound, also gives a similar colouration.



The chemistry of Cibane Yellow R and Orange R has now been reinvestigated, and it has been found that the purified Yellow R, assumed as homogeneous by Fierz-David and Geering, is a mixture of several substances. When a solution of the purified Yellow R in acetylene tetrachloride was chromatographed on alumina, three small bands developed on the column and were strongly adsorbed. The major part of the dye, which was unadsorbed, was recovered by concentration of the percolate and gave curved

orange needles, m.p. 368–70°, which we consider to be the essential tinctorial constituent of Cibanone Yellow R from the dyeing and other properties. The dye, m.p. 368–70°, was further recrystallized from acetylene tetrachloride, and subsequently from trichlorobenzene, but the m.p. and the elementary analysis remained unaltered. Concentration of the mother liquor after separation of the pure dye, m.p. 368–70°, gave a second crystalline component, m.p. 385–405°. The second component on further recrystallization from acetylene tetrachloride gave lemon yellow needles, m.p. 418–20°, which was not depressed by admixture with Anthraflavone (III) prepared according to Ullmann and Klingenberg.<sup>4</sup> One of the minor constituents of commercial Cibanone Yellow R is therefore Anthraflavone. A search was then made for further components. The commercial dye was purified by extraction with hot water, alcohol and nitrobenzene. The nitrobenzene extract was steam distilled and gave the more soluble components of the commercial dye which were distinguished from the pure dye and Anthraflavone by the olive-yellow solution the first gave in sulphuric acid as against the purple solution given by the pure dye and Anthraflavone. The more soluble components (m.p. 200–50°) contained sulphur, but they did not dye cotton, and we have not so far succeeded in further fractionating the mixture.

Elementary analysis of the pure dye (referred to hereafter as pure Cibanone Yellow R), m.p. 368–70°, corresponds to the empirical formula  $C_{45}H_{26}O_7S$  indicating three methylanthraquinone residues to one atom of sulphur. In order to determine if the dye is a derivative of 2-methylanthraquinone obtained by sulphurisation through the alkyl group or if it possesses a structure such as (I), in which two anthraquinone residues are linked through a methylene group, desulphurisation of the pure dye by means of Raney nickel was undertaken. If the dye had the structure (I), removal of sulphur should lead to a dianthraquinonylmethane derivative, while if the dye was derived from 2-methylanthraquinone by sulphurisation through the alkyl group it should lead to a derivative of 2-methylanthraquinone, which could then be compared with the reduction product obtained from 2-methylanthraquinone.

Desulphurisation of the dye in boiling morpholine by means of Raney nickel gave a mixture of products from which a pale yellow crystalline sulphur-free compound (M. W. 250), m.p. 170°, was isolated after exhaustive purification; it was different from 2-methylanthraquinone as shown by the lower m.p. on admixture with the latter. Reduction of the dye in aqueous sodium hydroxide with Raney nickel gave a sulphur-free semi-solid product which was very difficult to purify. When a chloroform solution of this

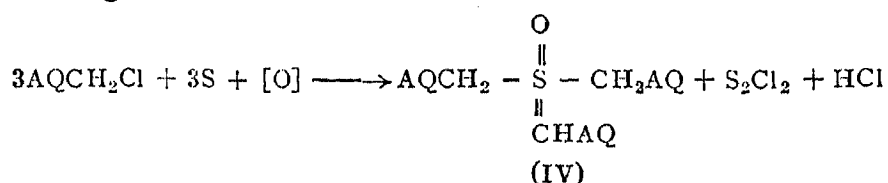
product was chromatographed through a column of alumina four fractions were isolated. The major fraction gave a product which after repeated crystallization gave pale yellow needles, m.p. 225–27° (M.W. 250) which analysed for  $C_{15}H_{16}O_3$ . The last fraction in the chromatographic separation gave a colourless crystalline substance which was similar to the crystalline reduction product obtained from 2-methylantraquinone by treatment with Raney nickel under similar conditions.<sup>5</sup> When Anthraflavone was treated with Raney nickel in aqueous alkali, most of it was recovered unchanged, indicating the stability of the carbon-carbon linkage between the two anthraquinone molecules in Anthraflavone. It has likewise been observed by Diesbach and Quinza<sup>6</sup> that Anthraflavone was unaffected by catalytic reduction or by treatment with copper powder and hydrochloric acid, but was reduced to the corresponding dianthraquinonylthane by reduction with aluminium powder and hydrochloric or sulphuric acid. The M.W. of the major part of the reduction products from pure Cibane Yellow R isolated in either of the reductive desulphurizations, the close similarity of the reduction products from the dye and 2-methylantraquinone and the resistance of the ethylene linkage in Anthraflavone to fission by similar treatment with Raney nickel, indicate the absence of a dianthraquinonylmethane residue as in the constitution (I) proposed by Fierz-David and Geering. On the other hand, these observations offer strong support to a structure such as (IV) in which sulphurisation through the alkyl group in 2-methylantraquinone is visualized.

Reductive degradation of pure Cibane Yellow R by zinc dust, fused zinc chloride and sodium chloride,<sup>7</sup> at 430–40°, led to 2-methylantracene, which was identified by direct comparison with an authentic specimen prepared from 2-methyl anthraquinone by a similar reduction. In addition to 2-methylantracene a very small quantity of another sulphur-free degradation product was also isolated, which has not as yet been characterized. Treatment of Anthraflavone (III) under similar conditions also gave 2-methylantracene and another degradation product which has not been identified. While the cleavage of the carbon-carbon linkage in Anthraflavone is understandable in view of its ethylenic character and the drastic pyrolytic treatment involved, it is doubtful whether the methylene bridge between the anthraquinone groups in dianthraquinonylmethane ( $AQ - CH_2 - AQ$ ;  $AQ = 2\text{-anthraquinonyl}$ ), which forms the essential feature in the constitution (I) proposed by Fierz-David and Geering, will break down even under such drastic treatment. The degradation of pure Cibane Yellow R to 2-methylantracene, therefore, gives further support to the conclusion that the dye is formed by the sulphurization of 2-methylantraquinone through the methyl group. A study of the Clar degradation<sup>7</sup>

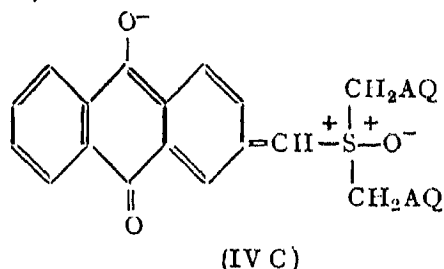
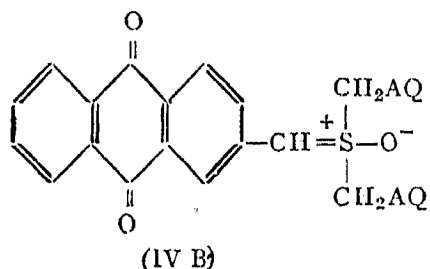
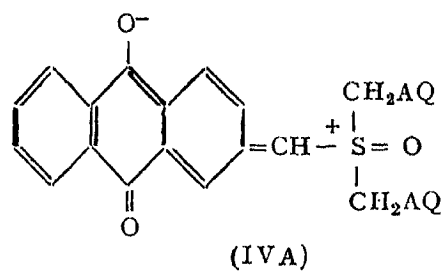
of dianthraquinonylmethanes and their derivatives, however, will be undertaken for comparison with the behaviour of pure Cibane Yellow R and Anthraflavone.

The hydrolysis of pure Cibane Yellow R has not led to any definite conclusions as regards its constitution. The dye was stable to boiling alkaline hydrosulphite. The solution in carbitol gave a characteristic red-brown colour change on treatment with sodium hydroxide. It was stable to concentrated sulphuric acid at room temperature, to aqueous sodium hypochlorite (28 g. of available chlorine per litre) at 100° for one hour, and to boiling with copper bronze in nitrobenzene for 5 hours.

Taking into consideration the method of preparation of Cibane Yellow R from 2-chloromethylantraquinone, as well as its properties, it is suggested that the dye has the constitution (IV) and is probably formed by the following overall reaction.



The intense colour of the dye and its stability are associated with resonance among structures such as (IV), (IV A), (IV B) and (IV C). The constitution (IV) is in agreement with the following facts: (1) Elementary analysis of

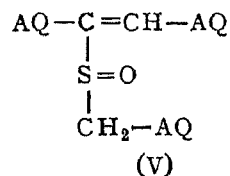


pure Cibane Yellow R; (2) Oxidation of the dye to anthraquinone-2-carboxylic acid; and (3) Reductive desulphurization of the dye to derivatives of 2-methylantraquinone and to 2-methylantracene.

Considering the difficulties in the preparation of pure 2-chloromethylantraquinone due to simultaneous production of 2-dichloromethylantra-

quinone, it is conceivable that the starting material employed for the thionation may be either the dichloro derivative, which is more readily accessible, or the crude chlorination product, containing mono- and dichloro methylanthraquinones, instead of pure 2-chloromethylanthraquinone. When the dichloromethyl derivative was fused with sulphur at 280°, a brownish yellow dye, m.p. > 500°, was however obtained. Thionation of pure 2-chloromethylanthraquinone under similar conditions on the other hand, gave a mixture of two dyes, one of which was identical with pure Cibalone Yellow R; the other dyed orange-yellow shades and did not melt up to 500°.

In addition to the constitution (IV), alternative structures such as (V), derived from Anthraflavone (III) are also being considered for pure Cibalone Yellow R, in view of the following:—(1) the facile conversion of 2-methyl- and 2-dichloromethylanthraquinone to (III); (2) the conversion of *bis*-



2-anthraquinonylmethyl sulphide (AQCH<sub>2</sub>SCH<sub>2</sub>AQ) to (III); (3) the occurrence of (III) in the commercial dye; and (4) the possibility of an addition reaction between (III) and 2-mercaptomethylanthraquinone. However, since Anthraflavone is stable to catalytic reduction while the dye is degraded to derivatives of 2-methylanthraquinone under these conditions, the constitution (IV) appears on the present evidence to be the most probable.

Experiments to synthesise the compound (IV) and other analogous model structures starting from the relevant sulphides such as *bis*-2-anthraquinonylmethyl sulphide (AQCH<sub>2</sub>SCH<sub>2</sub>AQ) and halogeno derivatives such as 2-chloromethylanthraquinone through the sulphonium chlorides [e.g., (AQCH<sub>2</sub>)<sub>2</sub>SCI] have been undertaken. It is interesting to record that a small quantity of Cibalone Yellow R has been isolated from the product obtained by Fierz-David from commercial Cibalone Orange R and regarded by him as a homogeneous dye.

#### EXPERIMENTAL

##### *Purification of Cibalone Yellow R*

(i) Commercial Cibalone Yellow R (8 g.) was purified by the exhaustive extraction method of Fierz-David; yield 1.85 g. A solution of the purified dye (0.25 g.), m.p. 358–60°, in acetylene tetrachloride (700 c.c.) was chromatographed through alumina when three small brown-coloured bands

developed. The unadsorbed dye was recovered from the acetylene tetrachloride percolate, and after concentration and cooling gave short, curved, orange needles, m.p. 368–70°. After recrystallization from the same solvent, the m.p. remained unaltered. (Found: C, 76.1; H, 3.6; S, 4.4.  $C_{45}H_{26}O_7S$  requires C, 76.1; H, 3.7; S, 4.5%.) It was also observed that the elementary analysis of the dye crystallized twice from acetylene tetrachloride did not change after further recrystallization of the dye from trichlorobenzene.

The pure dye gave a uniform chromatogram when chromatographed in the oxidised state on alumina or in the reduced condition on filter-paper by the glass plate technique.<sup>8</sup> It is to be noted, however, that a mixture of pure Cibanone Yellow R, m.p. 368–70°, and Anthraflavone, m.p. 418–20° melted at 366–368°, and hence the constancy of m.p. in the purification of Cibanone Yellow R cannot be regarded as indicative of its homogeneity. Secondly, the above artificial mixture could also not be separated by chromatography in the oxidised or in the leuco state. The constancy of the elementary analysis in the further recrystallization of the pure dye however supports the view that it is a homogeneous chemical compound. The empirical formula  $C_{45}H_{26}O_7S$  indicates three methyl anthraquinone residues to one atom of sulphur. The pure dye dyed a shade similar to the original dye and is regarded as the essential tinctorial constituent of the commercial dye.

The filtrate after the removal of pure Cibanone Yellow R was further concentrated and cooled, when the second component of the purified dye separated. This component after crystallization from acetylene tetrachloride gave lemon-yellow needles, m.p. 418–20°, alone or mixed with an authentic sample of Anthraflavone,<sup>4</sup> described later.

The mother liquor after the separation of the second component was diluted with excess of light petroleum (60–80°), when a yellow precipitate, m.p. 200–50°, separated. It could not be crystallized and had no affinity for cotton.

(ii) A quick method of isolation of pure Cibanone Yellow R was to extract commercial Cibanone Yellow R (25 g.) with water and then with carbon disulphide. The purified dye (15 g.) thus obtained was then extracted with boiling nitrobenzene (500 c.c.) when a moderately pure Cibanone Yellow R (10 g.), m.p. 368–76°, was obtained as residue. After further extraction with boiling acetylene tetrachloride to remove traces of Anthraflavone, it gave m.p. 368–72°.

*Degradation of Cibanone Yellow R*

*Raney nickel reduction of Cibanone Yellow R.*—(i) The dye (1 g.), Raney nickel (15 g.) and morpholine (50 c.c.) were heated under reflux for 12 hours with mechanical agitation and filtered. The filtrate was concentrated and then poured into hydrochloric acid, and the precipitate obtained (0.72 g.) was extracted with chloroform. The chloroform solution was chromatographed through alumina, and the chromatogram developed with the same solvent. Two brown fractions were strongly adsorbed; the percolate gave a sticky solid on removal of the solvent. It was dissolved in benzene and again passed through alumina. Two brown and a pink fraction were strongly adsorbed, and concentration of the percolate gave pale yellow needles, m.p. 170–172°, unaltered by further recrystallization from benzene-alcohol. (Found: C, 81.3; H, 7.3%. M.W. cryoscopic in camphor 250). The M.W. of the product indicates that it contains one anthraquinone residue, but the analysis could not be correlated with any definite structure. It was reducible by alkaline hydrosulphite and could be recovered back by air oxidation. When mixed with 2-methylantraquinone, m.p. 172–73°, it gave m.p. 130–35°.

(ii) Cibanone Yellow R (3 g.), sodium hydroxide (3 g.), Raney nickel (30 g.) and water (200 c.c.) were boiled under reflux for 8 hours. The reaction mixture was then acidified and filtered. The nickel residue was extracted in a soxhlet with chloroform when a sticky yellow solid (2.13 g.) was obtained. It was redissolved in chloroform and then chromatographed through alumina, using benzene for developing and eluting the chromatogram. A major yellow band and two smaller bands developed. The major fraction after concentration and dilution with alcohol gave a yellow solid (0.6 g.), m.p. 140–210°. The product from the final fraction, giving a red solution in chloroform-benzene, was crystallized from benzene-light petroleum (40–60°) and gave colourless needles, m.p. 225–30°.

The major reduction product was dissolved in chloroform and rechromatographed as above. The pale yellow product, isolated from the major fraction, m.p. 195–205°, after two recrystallizations from alcohol-benzene, gave pale yellow needles, m.p. 225–27°. (Found: C, 74.6; H, 6.5. M.W. cryoscopic in camphor 250).

The second reduction product (m.p. 225–30°) when crystallized from benzene and light petroleum (60–80°) gave short needles, softening and shrinking above 232°, m.p. 235–40°; when admixed with the reduction product (which softens and shrinks above 237°, m.p. 242–46°) from 2-methylantraquinone prepared under similar conditions of reduction, it



softened and shrank above 235° and melted at 240–46°, indicating the probable identity of the two reduction products.

(iii) Cibanone Yellow R (0.2 g.), Raney nickel (0.2 g.) and morpholine (100 c.c.) were shaken with hydrogen in a Parr hydrogenator at 40 lbs. per sq. inch at room temperature for 5 hours. The dye was unaffected under these conditions.

#### *Raney nickel reduction of Anthraflavone*

Anthraflavone was prepared according to Ullmann<sup>4</sup> by heating  $\omega$ -dibromomethylantraquinone with copper bronze in nitrobenzene. The product obtained after crystallization from nitrobenzene and subsequently from tetralin melted at 418–20°. Ullmann has stated that Anthraflavone does not melt up to 430°. (Found: C, 82.0; H, 4.0.  $C_{30}H_{16}O_4$  requires C, 81.8; H, 3.6%.) This product was used in all the subsequent reactions and for mixed melting points.

Anthraflavone was submitted to the Raney nickel reduction treatment as in (ii) above. Most of the Anthraflavone was however recovered unchanged after the treatment.

*Clar reduction<sup>7</sup> of Cibanone Yellow R.*—The pure dye (0.5 g.), fused zinc chloride (2.5 g.), sodium chloride (0.5 g.) and zinc dust (2.0 g.) were powdered together and gradually heated to 430–40° and kept at this temperature for ten minutes. A cream coloured solid (0.1 g.) sublimed above 320°. The product was resublimed at 220–30°/0.1 m.m. when lustrous colourless flakes were obtained. On crystallization from benzene-alcohol it melted at 204–06°, alone or mixed with an authentic specimen of 2-methylantracene (0.25 g.), m.p. 205–07°, obtained from 2-methylantraquinone (0.5 g.) by a similar method.

The residue left after sublimation of the above product was boiled with dilute hydrochloric acid and filtered. The resulting product was sublimed at 450–60°/0.1 m.m., when a dull brick red solid (80 mg.), m.p. 240–60°, was obtained, which has not yet been characterised.

*Clar Reduction of Anthraflavone.*—Anthraflavone (0.5 g.) was reduced as above. The sublimed product (0.25 g.) on fractional sublimation at 210–20°/0.1 mm. gave a product which was identified as 2-methylantracene by direct comparison with an authentic specimen. The residue after removal of 2-methylantracene was further heated at 420–30°/0.1 mm., when a pale yellow substance sublimed. It was extracted with excess of hot benzene-chloroform (1:1) when a cream coloured residue was obtained which decomposes above 300°.

*Chlorination of Cibanone Yellow R and Anthraflavone.*—Cibanone Yellow R as well as Anthraflavone gave anthraquinone-2-carboxylic acid in poor yields on passing chlorine into their solution in boiling nitrobenzene for 5 hours. Other byproducts formed in the reaction could not, however, be identified.

*Thionation of 2-chloromethylantraquinone.*—2-Chloromethylantraquinone (1 g.), prepared according to Conant and Fieser,<sup>9</sup> and sulphur (1 g.) were heated under stirring for 3 hours at 290°. The product was powdered and extracted with carbon disulphide. The residue (0.75 g.) was boiled with acetylene tetrachloride (100 c.c.) and filtered while hot. The insoluble product (0.3 g.) did not melt up to 500° and dissolved in sulphuric acid with a purple colour. It was unaffected by treatment with sulphuric acid and sodium hypochlorite. The reaction product which crystallized from the acetylene tetrachloride solution melted at 364–72°, alone or mixed with pure Cibanone Yellow R and dyed the same shade as pure Cibanone Yellow R. The mother liquor after separation of the above crystalline product on dilution with light petroleum (60–80°) melted at 150–60° (decomp.).

#### SUMMARY

The invalidity of the constitution (I), proposed by Fierz-David and Geering, for Cibanone Yellow R, a dye which is noted for its catalytic activity in the photochemical degradation of cellulose, is discussed. The purified dye, assumed to be homogeneous by Fierz-David, has been shown to be a mixture of several substances by chromatographic adsorption on alumina. The major tinctorial constituent crystallized from acetylene tetrachloride in curved needles, m.p. 368–70°. Anthraflavone was among the other products isolated.

Elementary analysis of pure Cibanone Yellow R is in agreement with the empirical formula  $C_{45}H_{26}O_7S$ , corresponding to three methylantraquinone residues for one atom of sulphur. Reductive desulphurisation of the pure dye by treatment with Raney nickel and pyrolysis with zinc dust indicate that 2-methylantraquinone residues are linked together through the methyl groups by means of sulphur, as against the methylene bridge between anthraquinone groups in the constitution (I) proposed by Fierz-David. The structure (IV) is suggested for pure Cibanone Yellow R.

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