STUDIES IN THE CHEMISTRY OF THE LOGWOOD COLOURING MATTERS

A THESIS

submitted by

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I am indebted to the directors of the British Dyewood Co. Ltd., of Glasgow, for giving me the opportunity and the means to carry out this work; and to the late Mr.Kennedy Campbell, director of that company for his lively interest in it.

My thanks are also due to Mr.O.Newsome, of the West Indies Chemical Works Ltd., Manchester, and to the staff of that company in Spanish Town, Jamaica, for assistance with light-fastness tests; to the Yorkshire Dyeware and Chemical Co.Ltd., of Leeds for gifts of haematoxylin; and to the technical staffs of all three companies and to Mr.C.L.Bird of the Department of Colour Chemistry and Dyeing, Leeds University, for much helpful advice and discussion.

Colour Chemistry Research Laboratory,
Department of Chemical Technology,
Royal College of Science and Technology,
Glasgow. C.1.

April 1958.

PUBLICATIONS

The following papers have been published in connection with this investigation.

1) Logwood Colouring Matters - D.J.Duff, Dyer, 1950, 103, 271-273. A review of the chemistry of haematoxylin.

2) Some Reactions of Haematoxylin.- D.J.Duff, J.C.S., 1956, 3296-3298. Describes some of the reactions of haematoxylin investigated and the principal derivatives obtained during the course of this research.

3) A Study of Certain Natural Dyes. I - The Adsorption of Brazilwood and Logwood Colouring Matters by Fibres. F.M.Arshid, J.N.Desai, D.J.Duff, C.H.Giles, S.K.Jain, and I.R.MacNeal, J.S.D.C., 1954, 70, 392-401. The contributions of the present author (D.J.D.) related to the preparation of haematein from haematoxylin; and the preparation and testing for fastness to light of haematein derivatives.

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INTRODUCTION

Haematoxylin.

Haematoxylin is a colourless crystalline substance obtained from Logwood (Haematoxylon campechianum), a large tree which grows mainly in the West Indies. On oxidation, haematoxylin yields haematein, the red colouring matter on which the tinctorial properties of logwood extracts depend. Its chemistry has been extensively studied, especially by the schools of Herzig, Perkin, Robinson and Pfeiffer, and its structure established with certainty, although no synthesis has yet been published; recently, however, the synthesis of the closely related natural product brazilin has been accomplished.

History of Logwood.

The following account is condensed from the survey of the history of logwood made by Newsome (M.Sc. Thesis, Leeds, 1949, 1).

Introduced into Europe by the Spaniards shortly after the discovery of America, logwood appears to have been first used in England during the reign of Queen Elizabeth I, but its use as a dye was prohibited on the ground that it gave

fugitive colours. Possibly this was due to unsuitable methods of application, as later on logwood began to grow in importance, until by the mid-nineteenth century it was the most important of all dyes. With the growth of the synthetic dye industry its use has declined, but it is still commercially notable and is certainly by far the most widely used natural dye at the present time. It is principally applied in the dyeing of blacks on wool, silk and leather, but its application has been extended to the synthetic fibres, especially cellulose acetate rayon and nylon.

Commercial Logwood Products.

Logwood is mainly used today in the form of extracts, made by percolation of the freshly cut chipped heartwood of the tree with boiling water, followed by concentration (liquid extracts) and drying (solid extracts, "Hematine Crystals"). Such extracts contain colourless haematoxylin, with very little haematein. Partly and wholly oxidised extracts are also manufactured, the latter containing all the colouring matter in the form of haematein. Some pure haematoxylin is made commercially, but is not used in dyeing; it has applications as an acid-alkali indicator and a staining medium in microscopy. Pure haematein is not a commercial product.

Methods of Dyeing with Logwood.

While the red colouring matter haematein is capable of staining wool, the result is of little value unless a metallic mordant is used. Logwood is therefore always applied in practice with the aid of a mordant, the actual colour obtained being dependent on the metallic compound used. Newsome (op.cit , p.8) lists the following colours as being obtained with various metals:-

Chromium	blue to black
Iron	blue-grey to black
Copper	dull greenish blue
Aluminium	dull violet
Tin	bright reddish violet
Tungsten	reddish violet
Molybdenum	blue to black
Titanium	black
Zirconium	reddish blue.

By far the most important of these in wool dyeing is the chromium mordant, sufficient mordant and dye being used to give a rich deep black shade. Usually the wool is mordanted first by treatment with sodium dichromate solution, with or without additions of sulphuric acid or organic acids, washed, and dyed in a fresh bath with one of the logwood extracts.

In silk dyeing, an iron/tin mordant is frequently used, partly on account of its weighting properties. Iron and iron/copper mordants have been successfully applied to wool, and Newsome (op.cit., p.138; also Bird and Newsome, J.S.D.C., 1950, 66, 430) obtained the best fastness to light of which logwood appears to be capable with an iron/copper/tartaric acid mordant. For wool dyeing, however, the chrome mordant is still preferred, because of its simple method of application and the superior shade of black obtainable with it, although the fastness to light is only moderate.

PRELIMINARY DISCUSSION

Objects of Research.

1.) Improving fastness to light.

It was already known that logwood gave a shade of moderate fastness to light (up to grade 6 on S.D.C. scale) on chrome mordants. Superior fastness to light (Grade 7) may be obtained on an iron mordant, but the dyeing is inferior in other respects. Good chrome blacks, on the other hand, are very fast (even up to Grade 7-8), although the quality of shade is not up to the standard of logwood.

Much research has already been carried out on methods of application of logwood, including the use of a wide variety of metallic mordants, (Bird and Newsome, J.S.D.C., 1950, 66, 423) and there seemed to be little need of further investigation along these lines. The question therefore arose - can the molecule of haematein, the colouring matter of logwood, be altered in such a way that products of superior fastness to light are obtained?

2.) Improving the method of application of logwood.

Present methods of application generally involve separate mordanting and dyeing operations, usually in separate baths. This is especially the method for dyeing

logwood on a chrome mordant on wool. One-bath processes are difficult to control and give loose colour. Modifications in the molecule of haematoxylin or haematein, which would impart greater affinity for wool or otherwise assist in application would be welcome, even if there were no appreciable improvement in fastness to light.

The first object, namely improving fastness to light, was the principal one in this work, the second being borne in mind as it progressed.

Fastness to light.

The literature on photochemical reactions covers such a vast field that it was considered beyond the scope of the present investigation to review it in any detail; there is also a considerable body of information on the fastness to light of synthetic dyes, most of which is inapplicable to the present work as it refers to products having constitutions quite unrelated to that of haematein. However, certain points are of importance in connection with this investigation.

Photochemical changes take place when light is absorbed by a medium at a sufficiently high energy level to promote chemical changes. The changes may take place in the substance responsible for the absorption or in other substances associated with it. Cotton dyed with certain dyes of the

vat and other classes becomes tendered on exposure to light; the dye absorbs light energy, but it is the substrate that is destroyed. Some cyanine dyes are photographic sensitisers, i.e. they absorb energy in spectral ranges to which the emulsion itself is not sensitive, and make it available to the photosensitive silver salts. The fading of dyes and the tendering of fabrics on exposure to light are frequently associated with the production of a volatile oxidising agent, believed to be hydrogen peroxide (see, e.g. Egerton, J.S.D.C., 1949, 65, 764) and in many cases the effects can be attributed to its presence. In any event, fading may often be prevented by exclusion of oxygen, indicating that the fastness to light may be connected with stability to oxidising agents*; no general rule can be formulated, however, since fading depends not only on the amount of high level energy absorbed, but also upon purely physical factors such as crystal size of dye and even upon the degree of crystallinity of the fibre (see, e.g. Baxter et al, J.S.D.C., 1955, 71, 218; Giles, ibid., 1957 (April), 127),

Dyes of related constitution may differ greatly in their fastness to light, and some series show no consistent

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* Since the present work was completed, it has been shown (Cumming, Giles, and McEachran, J.S.D.C., 1956, 72, 373; Giles, ibid., 1957, (April), 73, 127) that fading on wool probably is associated with reduction of dye, at the expense of oxidation of part of the wool molecule.

level of fastness as between one member and another. However, triphenylmethane and xanthene dyes generally have comparatively low fastness, whether combined with a mordant or not. This is of interest here, as haematein has certain structural similarities to both classes; it is in fact a hydroxylated derivative of diphenylmethane, with fused pyran and hydrindan rings.

Dyes of poor fastness to light can sometimes be improved by minor alterations in structure. The protection of sensitive groups, e.g. by methylation or acetylation, condensation with aldehydes to give larger molecular aggregates, diazotisation and coupling, or reaction with diazonium salts may serve for this purpose. The trifluoromethyl ($-CF_3$) group has been introduced into some dyes to improve fastness to light. The improvement of fastness by treating with copper salts may be rather different in nature, as metallic complexes may be formed; this treatment is generally useful only with azo dyes. Halogen substitution frequently fenders aromatic compounds less sensitive to oxidation, but may actually increase sensitivity to light, e.g. chlorinated diazonium salts are decomposed rapidly by light, while being fairly stable to heat. Haematein resembles most closely the hydroxylated triphenylmethane dyes among the synthetic types and no general method of improving fastness to light of this type appears to be known.

Application.

Wool consists of polypeptide chains with both basic and acidic side chains. Affinity for wool might be improved by the introduction of strongly polar groups such as the sulpho-, carboxyl- or thiouronium (acidic) or amino- (basic) groups. Larger molecules produced by condensation of several haematein units would also be expected to show increased affinity. Such alterations would not be expected to affect fastness to light notably, although their behaviour in this respect cannot be predicted.

The modification of natural dyes is subject to severe limitations; the dye is obtained in its finished form, the starting products and intermediates used in its synthesis being inaccessible. Improvements in synthetic dyes are frequently carried out at an early stage in the synthesis, e.g. the introduction of the trifluoromethyl group already mentioned. On the other hand, two well-known synthetic dyes - alizarin and indigo - which were originally manufactured from natural sources, are both capable of considerable modification, e.g. sulphonation, halogenation etc. When we consider the structure of haematoxylin and haematein, however, several limitations to alteration are evident. These products are readily oxidised and dehydrated, owing to the large number of hydroxyl groups; some of the theoretically most reactive centres in the benzenoid rings are

already occupied, so that the possibilities of aromatic substitution are limited. For many of the reactions contemplated, some form of protection of the hydroxyl groups is essential, but they must be capable of regeneration at the end of the process, since they are responsible for the mordanting and dyeing properties. There is a limit to the temperatures to which haematoxylin and haematein can be subjected (both decompose at 220-240°C.), although protected derivatives appear to be more stable.

Modification of haematein must not adversely affect the shade, the tinctorial value, or the fastness to washing as these are precisely the most attractive features of logwood as a commercial product. The improvement would have to be exceptional to compensate for a loss of these characteristics. Questions of cost or technical feasibility were not considered, however; the central problem was:- Could logwood be improved, especially in fastness to light, by any means at all?

PREVIOUS WORK ON THE STRUCTURE AND MODIFICATION OF THE BRAZIL WOOD AND LOGWOOD COLOURING MATTERS

Structure of Haematoxylin.

While the present research was concerned only with Logwood and its colouring matters, reference to the literature showed that the history of the chemistry of haematoxylin, even in its early stages, was closely linked with that of brazilin, the colouring principle of Brazil Wood. It is therefore convenient to review the chemistry of these two substances together, at least up to the time that their constitutions were established with certainty.

The French chemist Chevreul first reported the preparation in crystalline form of both brazilin (Ann.Chim., 1808 i , 66, 225) and haematoxylin (Ann.Chim., 1810 ii , 82 53, 126). Formulae for brazilin were suggested by Bolley (Schweiz.polyt.Zeitsch., 1864, 9, 267), $C_{22}H_{20}O_7$, and Kopp (Ber., 1873, 6, 446), $C_{22}H_{18}O_7$. Liebermann and Burg determined it accurately as $C_{16}H_{14}O_5$ (Ber., 1876, 9, 1883).

Bolley (loc.cit.) had treated brazilin with nitric acid and obtained what he thought was picric acid; Reim, however, proved the product to be styphnic acid - trinitroresorcinol (Ber., 1871, 4, 334). Kopp (loc.cit.) obtained a good yield of resorcinol by dry distillation of brazilin, while

Liebermann and Burg obtained it by fusing brazilin with caustic potash; they also, by acetylation, proved that brazilin contained four hydroxyl groups, and drew attention to the resemblance of its known reactions to those of haematoxylin, which they suggested might well be hydroxy-brazilin.

On oxidation, brazilin loses two hydrogen atoms to form brazilein, $C_{16}H_{12}O_5$, the true colouring matter of brazil wood. Liebermann and Burg exposed an alkaline solution of brazilin to the air, and treated an alcoholic solution with iodine. Hummel and Perkin (Ber., 1882, 15, 2343) passed air through a solution of brazilin in aqueous ammonia; Buchka and Erck (Ber., 1884, 17, 685; 1885, 18, 1140) employed nitric acid; while Schall and Dralle (Ber., 1890, 23, 1433) added sodium nitrite to a solution of brazilin in glacial acetic acid.

Haematoxylin is likewise oxidised to the dyestuff haematein. Hummel and Perkin (J.C.S., 1882, 41T, 367) obtained pure crystalline haematein by exposing an ammoniacal solution of commercial logwood extract to the air, collecting the precipitated ammonia compound of haematein, and acidifying it with acetic acid. Mayer (J.C.S., 1904, Ai, 909) used sodium iodate; Geigy (in Ullmann's "Encyclopaedia der Technischen Chemie", II, 543, 556) records the use of nitrous acid.

Some years after its discovery, the study of haematoxylin was taken up by O.L.Erdmann (J.pr.Chem., 1842, 26, 193-216), who improved the method of preparation and examined its physical and chemical properties. He obtained amorphous haematein by leaving an ammoniacal solution of haematoxylin exposed to the air, then acidifying with acetic acid. For haematoxylin he proposed the formula $C_{40}H_{17}O_{15}$ (Ann., 1842, 44, 292), later altered by Gerhardt (cit. Hesse, Reim) to $C_{32}H_{14}O_{12}$, with which Hesse agreed (Ann., 1859, 109, 332). Reim (Ber., 1871, 4, 329) and E.Erdmann and Schultz (Ann., 1882, 216, 232) modified this in accordance with the modern system of atomic weights, and agreed on the expression $C_{16}H_{14}O_6$.

Reim (loc.cit.), by the action of acetyl chloride on haematoxylin, obtained an acetyl derivative which he believed to contain six acetyl groups; Erdmann and Schultz showed that it contained only five such groups, and that therefore haematoxylin must be a pentahydroxy compound. On fusing haematoxylin with caustic potash Reim succeeded in isolating pyrogallol. Richard Meyer (Ber., 1879, 12, 1392) claimed that this reaction also yielded resorcinol, but the qualitative tests which he used were inadequate, and this assertion was later disproved (Perkin and Yates, J.C.S., 1902, 81T, 235).

The reactions of both haematoxylin and brazilin were investigated by Dralle (Ber., 1884, 17, 372), who repeated

the work of some of the earlier investigators, and extended it in some ways; his findings may be summarised as follows:-

Haematoxylin, heated in a sealed tube at 110°- 115° with a tenfold quantity of concentrated HCl, yielded black oily masses in which white crystals were embedded, along with unchanged material. It was not found possible to isolate any characteristic product from the reaction; 40% hydrobromic acid gave a similar result; colourless crystals, long plates and needles, were noted but could not be isolated.

Chlorine gas passed into an aqueous solution of haematoxylin reacted, but again the products could not be isolated. However, when the chlorine was added in the form of chlorine water, in known molecular proportions, better results were obtained. Various chlorine-substituted products appeared to be formed, which separated as an amorphous brick-red precipitate on adding salt, and formed a lustrous mass on drying, but were not crystallised. A definite product appeared to result from the action of 2 mols. chlorine on 1 mol. haematoxylin. Apparently oxidation and substitution took place simultaneously, giving a monochlorohaematein as the end-product, but this was not claimed to be homogeneous.

Bromine (4 mols.) dissolved in glacial acetic acid, added to a hot solution of haematoxylin (1 mol.) in glacial

acetic acid yielded a red crystalline product, the bromine content of which agreed with that calculated for dibromo-haematoxylin.

Concentrated or fuming sulphuric acid reacted with haematoxylin, and Dralle considered the product to be a sulphonic acid, although O.L.Erdmann and Hesse had reported that no sulphonic acid was formed.

Pyrolysis with zinc dust yielded resorcinol, as found previously by Reim. Hydriodic acid and red phosphorus at 130° gave no results. Nitrous acid gave only a small quantity of dark-coloured precipitate.

Addition of benzene diazonium chloride (1mol.) to haematoxylin (1 mol.) in aqueous caustic potash (2 mols.) produced a yellow-brown precipitate containing nitrogen, which did not crystallise. It dissolved in alkali with a colour similar to that of haematoxylin, but was reprecipitated by acid.

Dralle attempted the alkylation of haematoxylin and brazilin with methyl or ethyl iodides and caustic potash in methanol, but was unable to isolate pure products from the reactions.

Less success attended the efforts to form derivatives of brazilin, no crystalline halogen derivatives being isolated. Benzene diazonium chloride yielded a substance

containing 2.1% nitrogen (one azo group would require 7%) and unchanged brazilin.

Some experiments were carried out with the acetyl derivatives. Permanganate oxidised acetylhaematoxylin to carbon dioxide and oxalic acid. Nitric acid did not give a nitro-compound but oxidised the substance, and chlorine did not give a recognisable product. The acetyl compound (1 mol.) with bromine (2 mols.) in acetic acid, in a sealed tube for 3-4 hours at 100-110° gave red crystals, which on isolation analysed for a tetrabromo-pentaacetyl haematoxylin. The yield was small (15-20%) and when 4 mols. bromine were used no crystals were obtained. Acetylbrazilin did not yield a recognisable product.

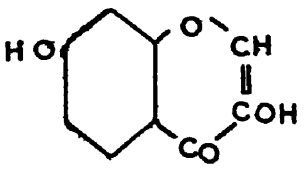
Monobromacetylhaematoxylin was prepared by Buchka (Ber., 1884, 17, 683), and hydrolysed to bromohaematoxylin, which was not isolated although its colour reactions with alkalis were noted. Similarly, monobromacetylbrazilin was prepared. Buchka and Erck (Ber., 1885, 18, 1138) continued the investigation of bromine derivatives of brazilin, and further described a triacetylbrazilin, m.pt. 105-6°, in addition to the tetraacetylbrazilin, m.pt. 149-151° already prepared by Liebermann and Burg.

Further brominated derivatives of brazilin were prepared by Schall and Dralle (Ber., 1888, 21, 3009; 1889, 22, 1547; 1890, 23, 1428). These authors contributed notably to the

investigation of the constitution of brazilin when they succeeded in methylating it with methyl iodide and sodium in alcohol (Ber., 1887, 20, 3365). They believed at the time that they had obtained the tetramethyl ether, corresponding to the known tetraacetyl ester, but later Herzig (Monatsh., 1893, 14, 56) reported that on analysis he found only three methoxyl groups; he proved the presence of a fourth hydroxyl by acetylation of the trimethyl ether to acetyltrimethylbrazilin. Schall (Ber., 1894, 27, 528) confirmed these observations, and also succeeded in preparing the tetramethyl ether from the trimethyl compound. Herzig (Monatsh., 1894, 15, 143) extended his investigations to haematoxylin, and prepared the tetra- and pentamethyl ethers, and acetyltetramethylhaematoxylin. Thus in brazilin four of the five oxygen atoms were shown to be hydroxylic, one of the hydroxyl groups being different from the other three; in haematoxylin five out of six were hydroxylic, with again one hydroxyl different.

Schall and Dralle at the same time studied the oxidation of brazilin in alkaline solution with air. Brazilein, which was at first formed was gradually destroyed, and from the residue two products were isolated. The first was identified as ß-resorcyclic acid, $C_6H_3(COOH)(OH)_2$ 1:2:4 ; the second, a compound of formula $C_9H_6O_4$, was the subject of further study by them and by Herzig (Monatsh.,1891, 12, 187);

afterwards Schall (Ber., 1894, 27, 528) suggested that it might be a phenyl γ-pyrone derivative and this was proved



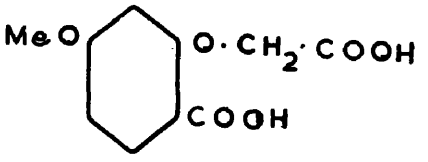
correct by Feuerstein and Kostanecki (Ber., 1899, 32, 1025).

The study of brazilin and haematoxylin was taken up about this time by W.H.Perkin and his school, and the principal contributions to the chemistry of these compounds during the next decade came from him and from Kostanecki and Herzig - studies which finally led to the presently accepted formulae. The first important step was reported by Herzig (Monatsh., 1895, 16, 907), who oxidised acetyltetramethyl-haematoxylin and acetyltrimethylbrazilin with chromic acid. The reaction in each case appeared to involve the removal of four atoms of hydrogen, and the conversion of the alcoholic hydroxyl to a phenolic hydroxyl group. Another significant discovery by Herzig was that brazilin on fusion with caustic potash gave not only resorcinol, as previously known, but also protocatechuic acid, from which catechol could be obtained (Monatsh., 1898, 19, 738).

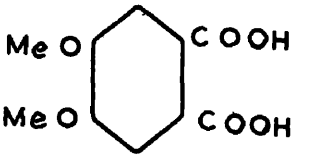
Oxidation with chromic acid was applied by Gilbody and Perkin to trimethylbrazilin and tetramethylhaematoxylin

(Proc.C.S., 1899, 15, 27-29), when products were obtained which were called respectively trimethylbrazilone and tetramethylhaematoxylone. These could be dehydrated by heating, and acetylation of the dehydro-bodies yielded acetyl derivatives which were considered to be identical with the products obtained by Herzig on treating acetyltrimethylbrazilin and acetyltetramethylhaematoxylin respectively with chromic acid.

Perkin, however, also directed his attention to the oxidation of the methylated derivatives with permanganate. In the hands of Perkin and other eminent chemists this technique had proved its worth as a degradative method of studying the constitution of various natural products, especially alkaloids and colouring matters. The oxidation proceeds further than with chromic acid, there is seldom any significant constitutional change (e.g. ring closure), and recognisable fragments may be isolated with comparative ease. Trimethylbrazilin was oxidised with aqueous permanganate to yield in addition to formic, acetic and oxalic acids, four other acids (J.C.S., 1901, 79T, 1396). Two of these were quickly shown to be 2-carboxy-5-methoxyphenoxyacetic acid (I) and m-hemipinic acid (II) respectively.

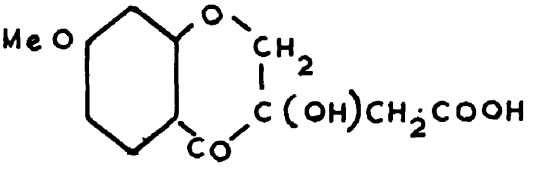


I



II

The other two acids were called brazilic acid ($C_{12}H_{12}O_6$) and brazilinic acid ($C_{19}H_{18}O_9$). For brazilic acid Perkin deduced the structure III (J.C.S., 1902, 81T, 221) in



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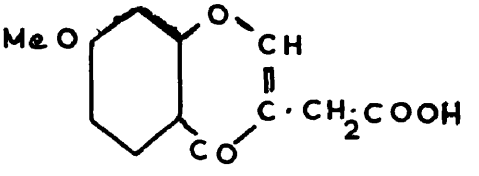
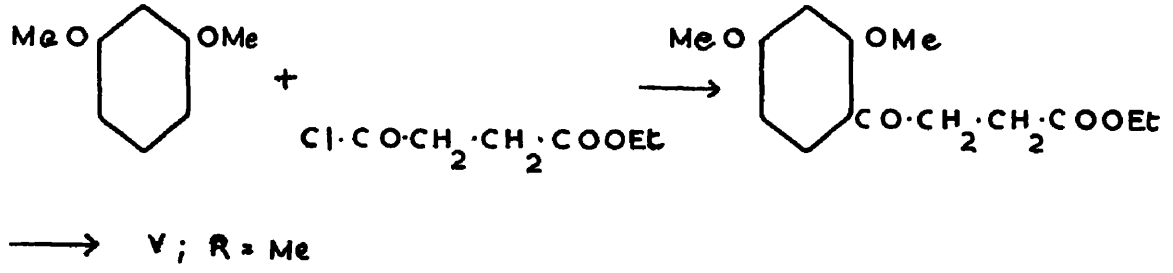


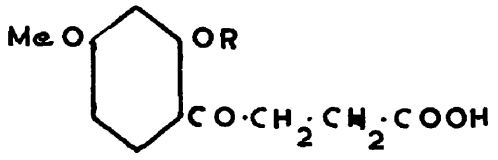
IV

conformity with its dehydration to anhydrobrazilic acid (IV)

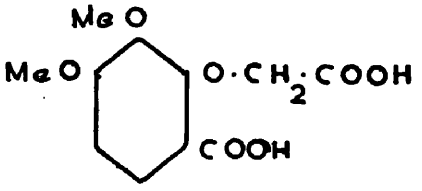
which on hydrolysis gave 6-hydroxy-4-methoxybenzoylpropionic acid (V; R=H). The methyl ether of this acid (V; R=Me), was prepared synthetically by Perkin by condensing dimethyl-resorcinol with the chloride of the monoester of succinic acid in presence of aluminium chloride:-



⟶ V; R = Me



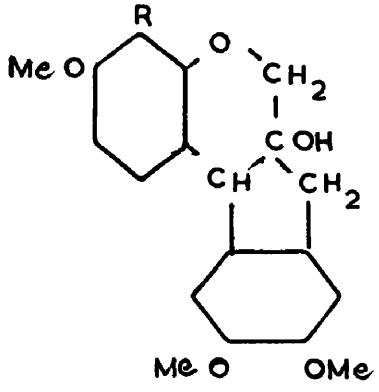
V



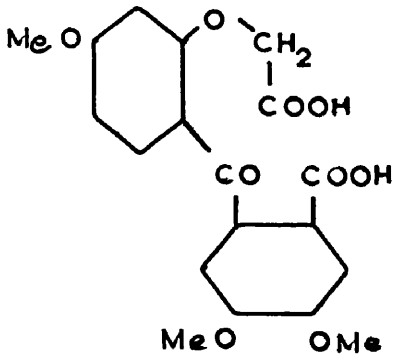
VI

With permanganate, tetramethylhaematoxylin yielded 2-carboxy-5:6-dimethoxyphenoxyacetic acid (VI) and m-hemipinic acid; a more complex product, designated haematoxylinic acid, analogous to brazilinic acid was also

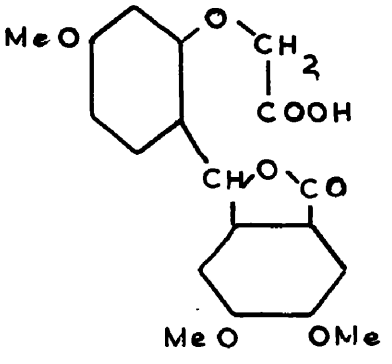
isolated (Perkin and Yates, J.C.S., 1902, 81T, 235). Both of these products were shown to be keto-acids, and on reduction with sodium amalgam yielded dihydro-compounds (reduction of -CO- to -CHOH-) which readily lactonised in presence of acid. Perkin and Robinson (J.C.S., 1908, 93T 489), considering possible structures for brazilin and haematoxylin based on the known degradation products, postulated formula VII (R=H) for trimethylbrazilin, whence brazilinic acid would be VIII, and the lactone of its dihydro derivative IX. The correctness of VIII and IX was confirmed by synthesis.



VII



VIII



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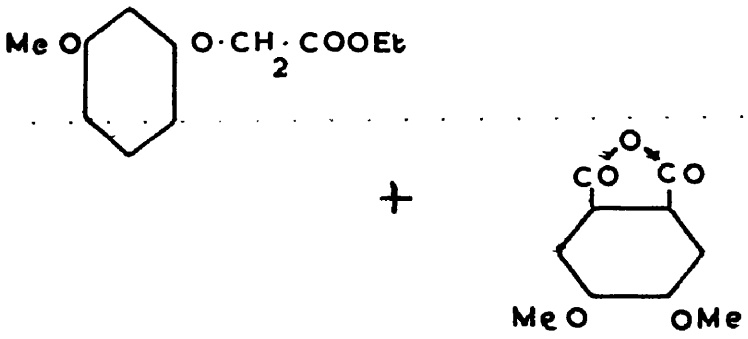
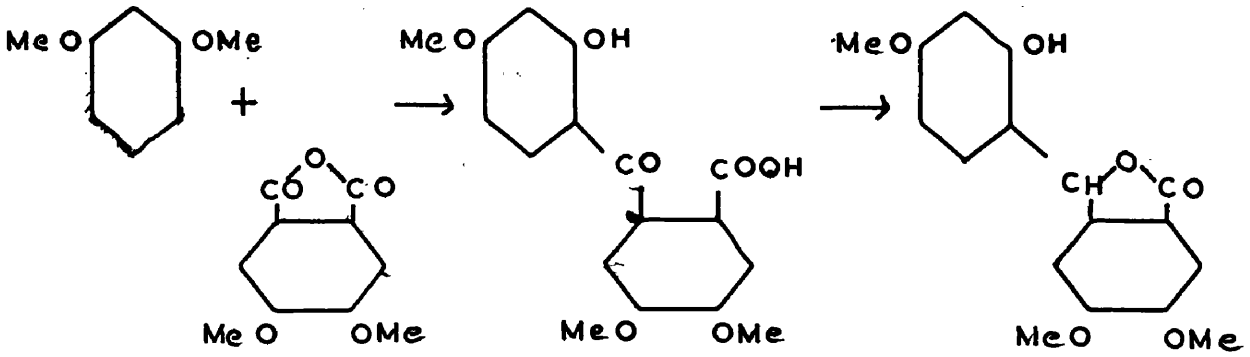


⟶ VIII

Resorcinol monomethyl ether condensed with ethyl chloroacetate gave the ester of 3-methoxyphenoxyacetic acid, which reacted with m-hemipinic anhydride in carbon disulphide in presence of $AlCl_3$ to give brazilinic acid.

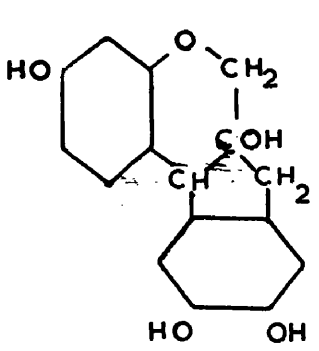
Resorcinol dimethyl ether and m-hemipinic anhydride in presence of $AlCl_3$ condensed to 2-hydroxy-4:4′:5′-trimethoxybenzophenone-2′-carboxylic acid, which was reduced with sodium amalgam and converted to the corresponding lactone; this with chloracetic acid in presence of alkali yielded the lactone of dihydrobrazilinic acid.



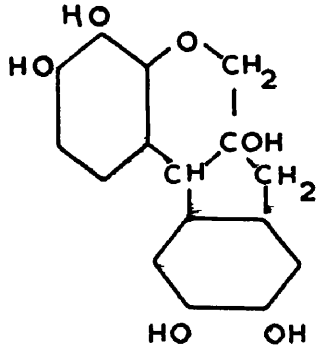
⟶ IX

The lactone of dihydrohaematoxylinic acid was similarly prepared from pyrogallol trimethyl ether, so that tetramethyl haematoxylin must be VII (R=OMe). The formulae for brazilin (X) and haematoxylin (XI) follow*.

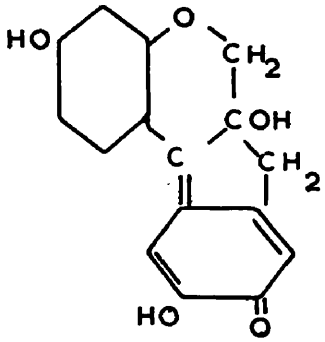
Subsequently, Engels, Perkin and Robinson (J.C.S., 1908, 93T, 1115) elucidated not only the structure of brazilein (XII) and haematein (XIII), but also the derivatives obtained by the action of mineral acid on them first described by Hummel and A.G.Perkin (J.C.S., 1882, 41T, 367), and known as isobrazilein and isohaematein salts.



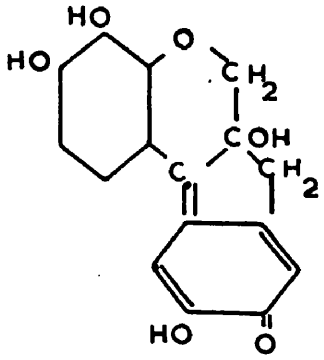
X



XI



XII

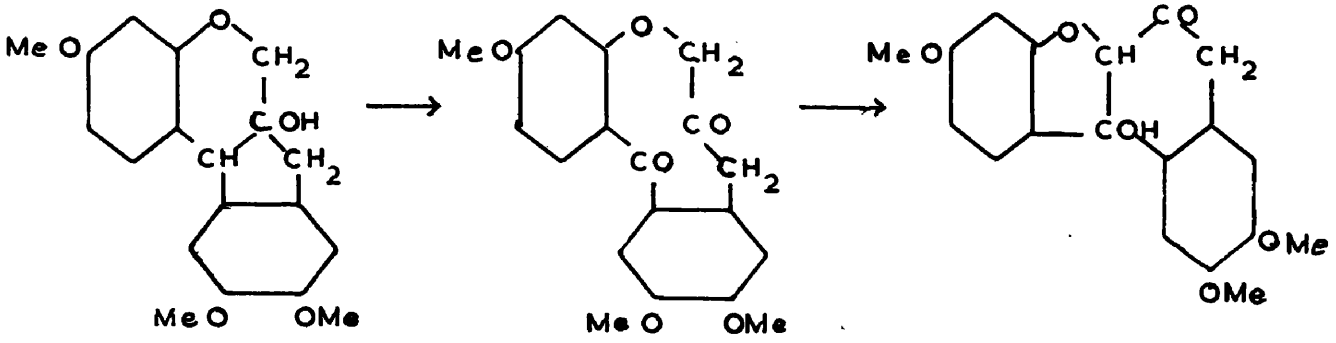


XIII

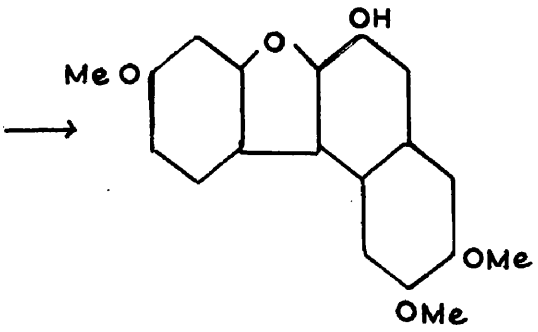
In the light of their investigations on brazilin and haematoxylin, Perkin and Robinson (J.C.S., 1909, 95T, 381) now proposed formulae for the products of oxidation of their methyl derivatives with chromic acid, which had engaged their

* Structure VII (R=H) for trimethylbrazilin was suggested by Werner and Pfeiffer (Chem.Zeit., 1904, 3, 421).

attention so much, as well as that of Herzig and Kostanecki, at an earlier period. They believed that, in the brazilin series, the following reactions took place:-



XIV XV XVI



XVII

Thus trimethylbrazilin (XIV) with chromic acid yielded trimethylbrazilone, formulated as the diketone XV. In presence of dehydrating agents (alkali, acetic anhydride) a kind of internal aldol condensation apparently took place, followed by elimination of water and aromatisation of the new six-membered ring XV ⟶ XVI ⟶ XVII. If acetic

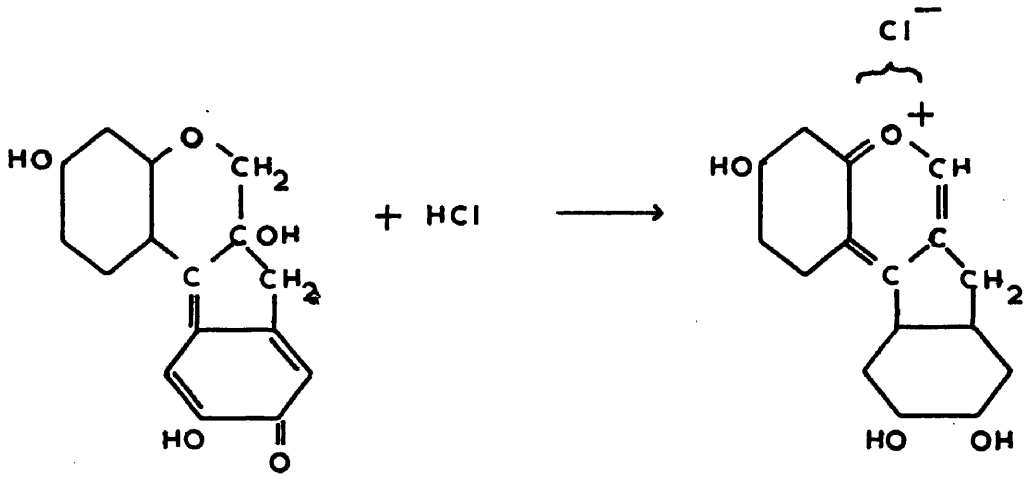
anhydride was used the product was acetylanhydrotrimethylbrazilone (the acetyl derivative of XVII), which on hydrolysis with alkali yielded α-anhydrotrimethylbrazilone (XVII). Trimethylbrazilone might have either structure XV or XVI, as it formed an oxime and reacted with phenylhydrazine to form a condensation product, probably a pyrazoline derivative (but did not form a phenylhydrazone). Recently evidence in favour of XV as the structure of trimethylbrazilone has been contributed by a study of the infra-red spectrum, which indicates the presence of carbonyl groups (Richards and Tomlinson, Nature, 1948, 162, 693).

Tetramethylhaematoxylin in a similar manner yielded tetramethylhaematoxylone, which on dehydration gave α-anhydrotetramethylhaematoxylone.

The most interesting feature of these anhydro-derivatives is their relationship to β-naphthol, which in fact they both resemble in a remarkable way. Thus they may be oxidised with ferric chloride to dinaphthol derivatives, nitrated to give mononitro compounds, and coupled with diazonium salts to form azo dyes.

The action of acids on haematein and brazilein has been mentioned, and reference made to the suggestions of Engels, Perkin and Robinson (J.C.S., 1908, 93T, 1115) regarding the constitution of the isobrazilein and isohaematein salts obtained. According to them the reaction involves loss of

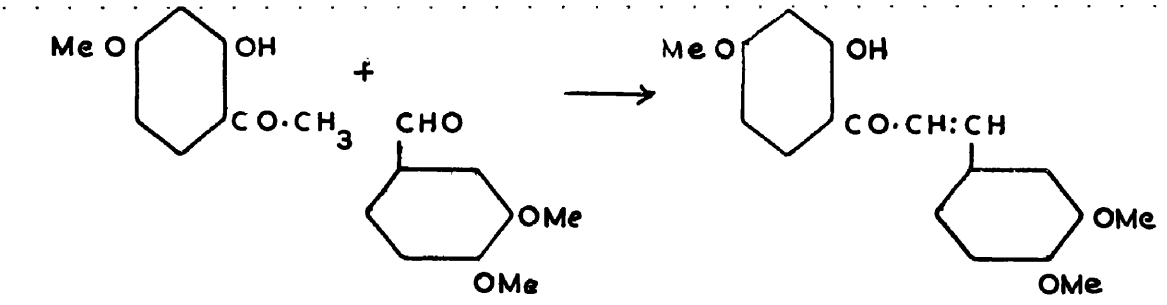
the elements of water with formation of a double bond in the pyran ring, while the hydrogen ion adds on to the quinonoid oxygen atom, forming a complex cation (i.e. a benzopyrilium salt is formed), viz.:-



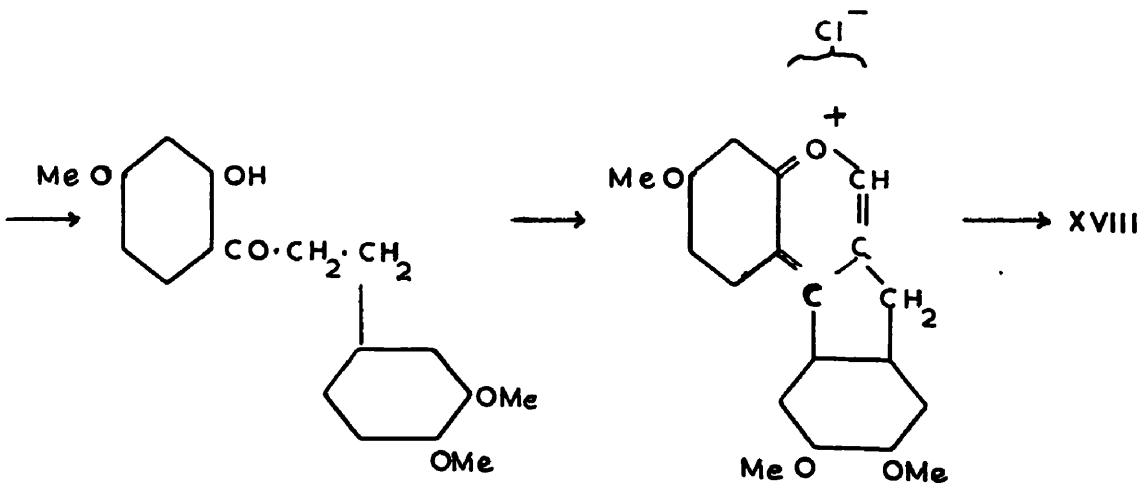
XII = Brazilein XVIII

Following the successful study of haematoxylin and brazilin by degradative methods, attention was now directed to confirming the formulae proposed by unambiguous syntheses. The first success was reported by Crabtree and Robinson (J.C.S., 1918T, 113, 859) in the preparation of isobrazilein chloride. Paeanol (XIX) and veratraldehyde (XX) condensed to butein trimethyl ether (XXI), the dihydro derivative (XXII) of which on boiling with absolute formic acid in presence of zinc chloride yielded the hydrochloride of isobrazilein trimethyl ether (XXIII). Demethylation (HCl at 150°) gave isobrazilein chloride, which was found to be

identical with the natural product.



XIX XX XXI

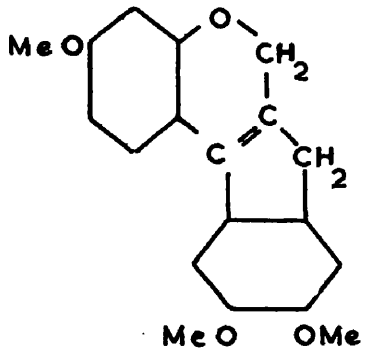


XXII XXIII

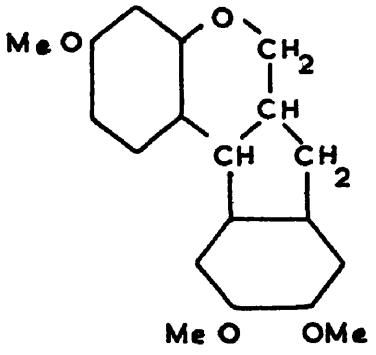
<u>iso</u>Haematein chloride was obtained when the synthesis was carried out with gallacetophenone dimethyl ether in place of paeanol (Crabtree and Robinson, <u>J.C.S.</u>, 1922, <u>121</u>T, 1033).

The study of brazilin and haematoxylin was also taken up by Pfeiffer at Bonn about this time, and both Perkin and Pfeiffer, with their colleagues continued to develop the

subject. Thus methods for the synthesis of deoxytrimethylbrazilone (or anhydrotrimethylbrazilin)XXIV, its reduction to the dihydro derivative XXV, and oxidation of this to trimethylbrazilone were described by both authors. (Perkin, Råy, and Robinson, J.C.S., 1927T, 2094; 1928T, 1504; Pfeiffer and Oberlin, Ber., 1927, 60, 2142; Pfeiffer, Angern, Haack and Willems, Ber., 1928, 61, 839).



XXIV



XXV

It might be thought that the elements of mineral acids such as HBr could be added on to the double bond of XXIV, giving a brazilin derivative from which brazilin could be prepared by hydrolysis. Attempts to carry out this reaction failed, however, derivatives of isobrazilein being obtained instead. In presence of acid XXIV became the base of pyrilium salts; for example, passing dry HCl through a solution of XXIV in chloroform, excluding air, yielded the trimethyl ether of isobrazilein hydrochloride (Perkin, J.C.S., 1928T, 1504).

The reduction of trimethylbrazilone was the subject of extensive researches by both schools, a wide variety of reducing agents being tried, and the reduction products exhaustively examined. At no time was trimethylbrazilin itself obtained, even in minor quantities, although closely related isomers could be prepared and characterised. Similar results were obtained in the haematoxylin series*, and Pfeiffer lists the following products, which appear to have been more thoroughly characterised than in the brazilin series. (Pfeiffer, Döring, Kobs and Werner, J.prakt.Chem., 1938, 150, 199).

Tetramethylhaematoxylonol, XXVI; m.p.188°.

Tetramethylhydroxyhaematoxylin, XXVII; m.p. 194°.

Tetramethylisohaematoxylin, XXVIII; α-, m.p.196°;
ß-, m.p.163°.

Tetramethylallohaematoxylin, XXIX; α-, m.p.166°;
ß-, m.p.150°.

Tetramethyldesoxyhaematoxylin, XXX; m.p.147-148.5°.

A pinacone, XXXI; m.p.287°(dec.)

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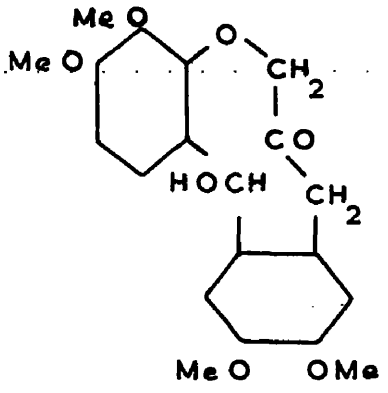
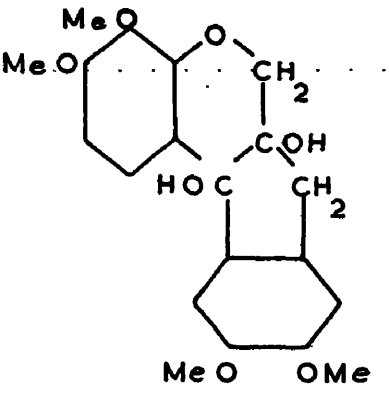
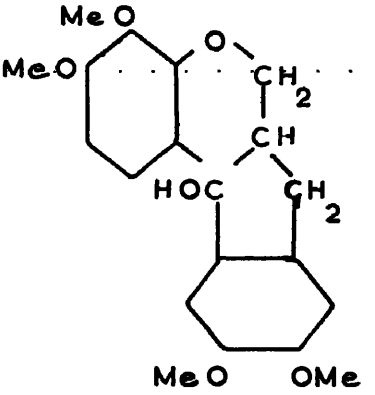
* by reduction of tetramethylhaematoxylone



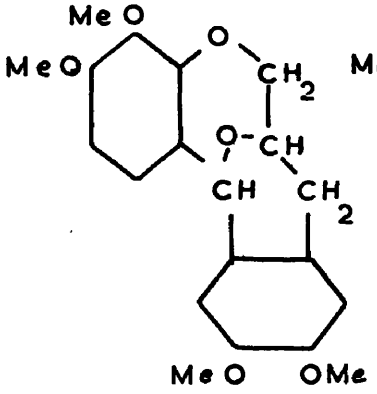
XXVI



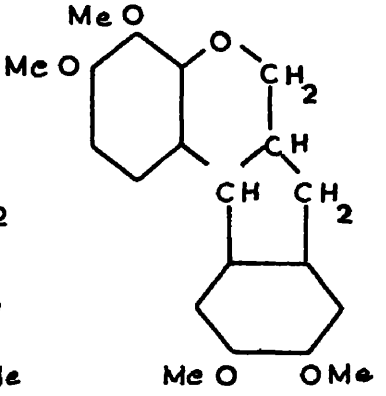
XXVII



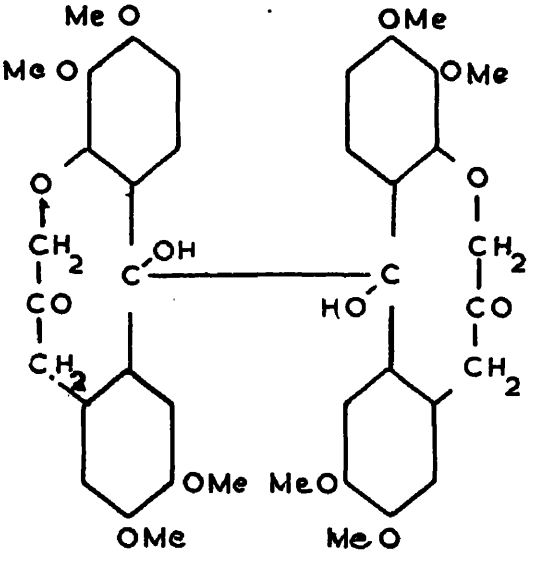
XXVIII



XXIX



XXX



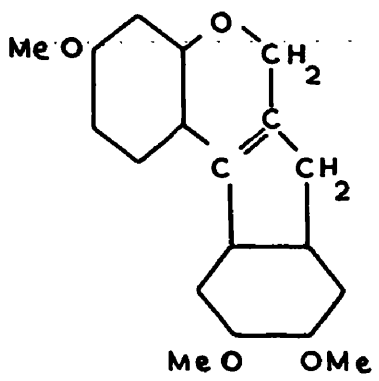
XXXI

Pfeiffer and Christelheit (J.pr.Chem., 1942, 160, 315) showed that reduction of tetramethylhaematoxylone with sodium amalgam and acetic acid yielded products XXVI, XXVIII, and XXIX, separated by chromatography in benzene on activated alumina; the relative position which should be occupied by tetramethylhaematoxylin on the alumina column was ascertained, and this compound shown to be absent in the mixture obtained by the reduction process.

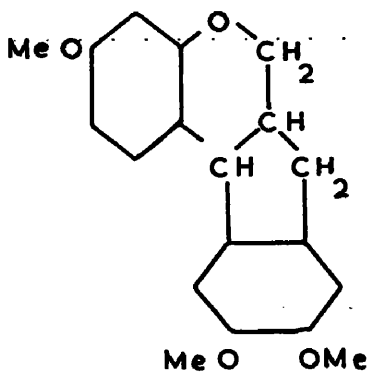
Brief details have been published of a synthesis of brazilin by Robinson and Morsingh (Congress Handbook, XIVth International Congress of pure and applied Chemistry, Zurich 1955, p.260).

Anhydrotrimethylbrazilin (XXXII) had already been synthesised. On reduction it yielded O-trimethylbrazilane-A (XXXIII), which was demethylated and the resulting trihydric phenol acetylated to O-triacetylbrazilane (XXXIV); this was oxidised to O-triacetylbrazilone (XXXV).

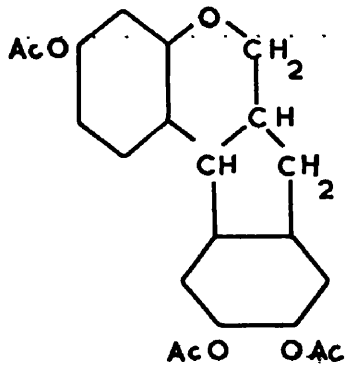
On reduction with zinc dust in alcoholic acetic acid triacetylbrazilone gave, among other products, a pinacol (XXXVI), which on hydrolysis with alkali and acidification yielded d,l-brazilein (XII), reduced by borohydride to d,l-brazilin (X). This was resolved via the o-tetra-l-menthyloxyacetyl derivative into two isomerides, the more fusible of which on hydrolysis yielded d-brazilin (i.e. natural brazilin).



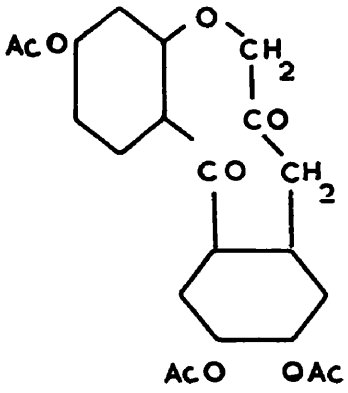
XXXII



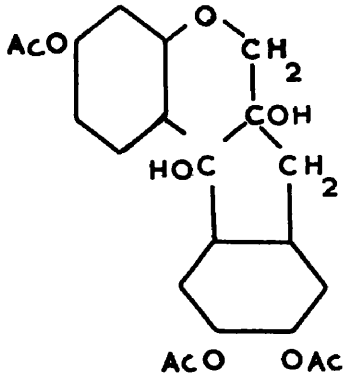
XXXIII



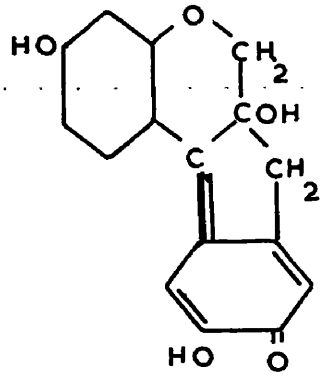
XXXIV



XXXV



XXXVI



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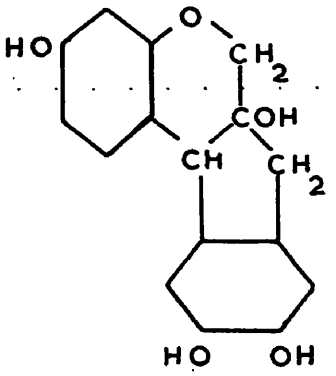


X

No synthesis of haematoxylin or haematein has appeared so far, but it seems probable that they could be produced by an analogous method from anhydrotrimethyl-haematoxylin.

Recent Investigations on Brazilin and Haematoxylin.

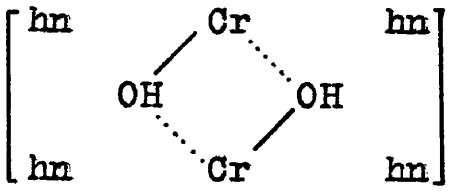
The absorption of brazilwood and logwood colouring matters by fibres has been studied by Arshid et al. (J.S.D.C., 1954, 70, 392). Brazilein and haematein, being weak acids, are absorbed by wool and nylon appreciably only from acid solutions, probably by hydrogen bonding between the fibre and undissociated haematein or brazilein molecules, as well as

by acid-base combination with the charged amino groups in the fibre. Absorption becomes very low from solutions less acid than pH about 7.

Haematoxylin is absorbed by cellulose acetate, nylon and protein fibres, its affinity being due apparently to hydrogen bond formation. It also has appreciable substantivity for cellulose, on which the absorption appears to differ from that for the other fibres, and to be due to weaker forces, probably Van der Waals attraction.

Logwood colouring matters are invariably applied in practice with the aid of a mordant, usually chrome for wool, and iron with tin for silk. The structures of the metallic lakes of brazilein and haematein were investigated by Arshid et al. (J.S.D.C., 1954, 70, 402). They describe two types of chromium lake formed by haematein, viz. (1) a purple lake containing one atom of chromium per molecule of haematein; this is formed in low-boiling organic solvents such as ethanol, and - transiently - in aqueous solution or during the dyeing of chrome-mordanted wool: (2) a deep blue lake containing one atom of chromium per two molecules of haematein; this is the stable form produced on boiling aqueous solutions of haematein with chromium salts (or haematoxylin with chromates), and on chrome-mordanted wool when brought to the boil during dyeing with haematein. It

is suggested that olation takes place, giving a structure of the type



$8\ H_2O$ (hn = haematein anion).

RESULTS AND DISCUSSION

Effect of Purity of Haematein.

Commercially available logwood products are

1) the concentrated (unoxidised) aqueous extract;
2) unoxidised "crystals" (the dry form of the aqueous extract);
3) partially or completely oxidised "crystals", formed by oxidation and drying of the aqueous extract.

The product known as "Hematine Crystals ZA" is a completely oxidised solid extract of logwood, and contains approximately 30% of haematein, along with other substances extracted from the wood, e.g. tannins and carbohydrates.

To test the effect of purity of haematein on light fastness, wool patterns mordanted with 3% potassium bichromate and 6% tartaric acid were dyed with (1) 3% haematein and (2) 10% Hematine Crystals ZA, these giving practically the same depth of shade on each pattern. The fastness to light of these patterns was practically identical.

It was considered possible that partial oxidation of haematein might occur in the dyebath. A series of patterns was dyed in conical flasks, using various proportions of haematein; before adding the colour the water used was

boiled, with carbon dioxide passing, to expel oxygen, then cooled while the stream of carbon dioxide was maintained. The colour and mordanted pattern were added, and dyeing completed in the normal way, except that carbon dioxide was passed through until the end of the process. With 3% haematein the pattern obtained was similar to that obtained by the normal process using the same proportion of colour, and had the same light-fastness. The light-fastness was found to vary with the amount of dye used, higher proportions of colour giving better fastness, but this was to be expected.

Impurities normally present in logwood extracts, or generated during the dyeing process, do not appear to affect the fastness to light. The fading of patterns dyed with logwood is therefore due to the fading of haematein itself. A similar conclusion was reached by Newsome (M.Sc. Thesis, Leeds, 1949, 126).

Effect of Mordant.

The extensive researches of Newsome (op.cit.; also Bird and Newsome, J.S.D.C., 1950, 66, 423) on the application of logwood using various metallic mordants were mentioned in the Introduction. The chrome mordant is preferred to all others for dyeing wool with logwood, although the fastness to light is only moderate (6 on S.D.C. scale). Better fastness

to light (6-7) was obtained on a molybdenum mordant, and the best of all with iron/copper/tartaric acid (7).

On wool mordanted with 3% potassium bichromate and 6% tartaric acid, a rich blue-black shade was obtained with 3% pure haematein; 10% haematein gave a dead black, indicating that too much colour had been used, but naturally fading on exposure to sunlight took place more slowly on the more heavily dyed pattern. When, however, haematein alone was used to dye clean wool containing no mordant, weak reddish colours were produced. Even 10% of haematein gave a reddish pattern, the fastness to light of which was extremely low, corresponding approximately to the most fugitive of the standard light-fastness patterns (fastness = 1). It can not therefore be assumed that the metallic mordants promote or catalyse the fading process in any way, since haematein itself is so readily degraded on exposure to sunlight. Rather it is probable that if a light-fast derivative of haematein could be found, its metal derivatives would also be fast to light.

Since a metallic mordant was necessary for the development of the full shade of haematein, and the most suitable mordant for wool appeared to be the chrome/tartaric acid mordant, all haematein derivatives described in the following pages were tested on wool mordanted in this way.

Mechanism of Fading.

Practically all published work on the mechanism of fading of dyes relates to synthetic dyes, and few of these resemble haematein in structure. The actual reactions which take place on exposure to light depend on the dye structure and the substrate. With some anthraquinone vat dyes on cotton the dye remains but the fibre is degraded; in this instance it has been shown by Ashton, Clibbens and Probert (J.S.D.C., 1949, 65, 650) that during exposure to light a volatile oxidising agent is produced, probably hydrogen peroxide, and this attacks the fibre. It is natural to assume that when the dye is more sensitive than the fibre to oxidising agents, the dye will be destroyed and the fibre remain.

There appear to be other possible fading mechanisms. Blaisdell (J.S.D.C., 1949, 65, 618) observed that azobenzene and 4-amino-4'-nitroazobenzene underwent reduction on irradiation in isopropyl alcohol and isooctane, the solvent being oxidised. Cumming, Giles and McEachran (J.S.D.C., 1956, 72, 373) found that on protein fibres acid and basic dyes may be photochemically reduced. The effect appears to be associated with the histidine side-chains of the fibre; wool, containing 0.7% histidine, would thus account for up to 2% of an average commercial dye. It was suggested that once

this reaction is completed, the remaining dye might fade by oxidation. Metal-complex and mordant dyes were not included in the investigation.

The reactions which take place in any particular instance probably depend on the relative reactivities of the various possible reactants, e.g. dye, dye assistants, substrate, oxygen, water vapour etc. Absorption of light, ensured by the presence of a dye, supplies the requisite energy. Some dyes are relatively resistant to oxidising agents, e.g. the chrome blacks, whose colour is only fully developed when they are after-chromed with bichromate. Haematein, on the other hand, is easily oxidised to brown amorphous products of no tinctorial value, and eventually to colourless end-products, e.g. malonic acid. Great care has to be taken during the technical manufacture of logwood products to prevent over-oxidation and consequent loss of colour value. Haematein is not affected by mild reducing agents, such as hydrogen sulphide or hydroxylamine; it forms a colourless addition product with sulphurous acid and is reduced by hydrogen in presence of palladium black, these reactions being reversible. Haematoxylin is very resistant to reducing agents, being unchanged on boiling with phosphorus and iodine in glacial acetic acid.

Newsome (M.Sc. Thesis, Leeds, 1949, 126; see also Bird

and Newsome, J.S.D.C., 1950, 66, 423) considered the fading of logwood to be due to oxidation; the presence of oxygen was required, since patterns exposed to light behind glass faded much more quickly if kept some distance from the glass than if pressed closely against it, thus restricting access of air.

The necessity for the presence of oxygen has been further demonstrated as follows: a number of small wool patterns dyed with 2% logwood crystals "C" on the reduced chrome mordant were mounted in boiling tubes, half of each pattern being shielded from light; the whole pattern in each tube was mounted above the level of added liquid. The tubes were filled according to Table I and carefully sealed with greased rubber stoppers. The patterns were exposed to sunlight until No.1 had markedly faded (except tube No.6, which was kept in the dark). Results are in Table I.

TABLE I

Tube No.	Contents	Effect of Sunlight
1	Air only	Faded
2	Oxygen-free air; 5 c.c.pyrogallol/KOH	Unaffected
3	Air; 5 c.c. KOH solution	As No.1
4	Air; 2 g. powdered P_2O_5	As No.1
5	Air; 1 c.c. 100 vol. H_2O_2	Very rapidly faded
6	Air; 1 c.c. 100 vol. H_2O_2	Rapidly faded

Effect of Ultraviolet Radiation on Haematein.

Ultraviolet radiation decolourised haematein in solution. Pure haematein (0.0125 g.) was dissolved in ethanol (1 litre). A 500 c.c. quartz flask was filled with this solution, which was exposed to the full radiation of a quartz mercury vapour lamp (Thermal Syndicate, Ltd.) at a distance of 12 inches. A sample was withdrawn after one hour, when the colour had faded from deep red to pale amber, and again after 4 hours, when the solution had become completely colourless.

The absorption spectra of haematoxylin, haematein and the irradiated solutions were obtained with the aid of the Hilger Spectrograph, and are shown in Fig.1. The spectra of the

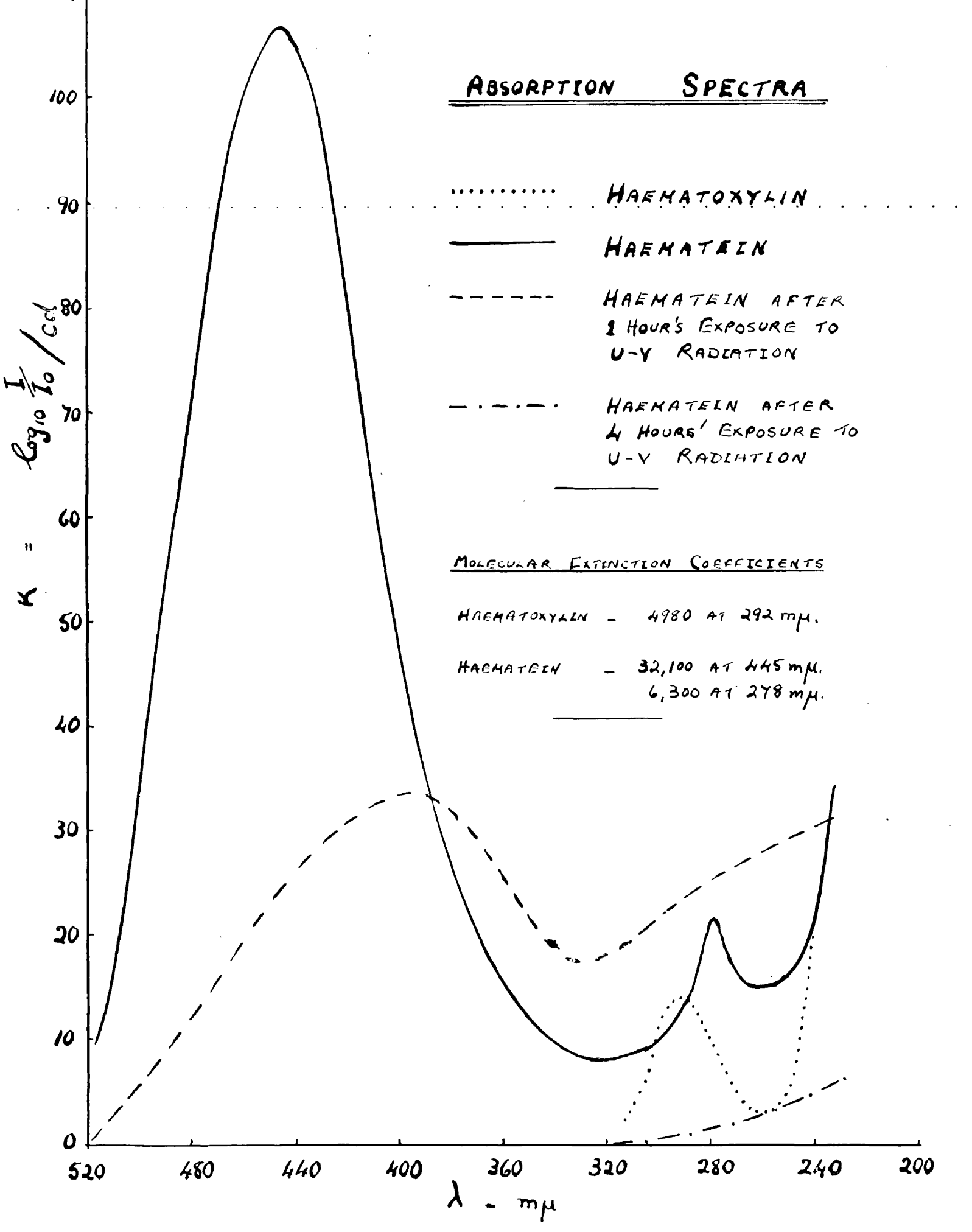

ABSORPTION SPECTRA
HAEMATOXYLIN
HAEMATEIN
HAEMATEIN AFTER 1 HOUR'S EXPOSURE TO U-V RADIATION
HAEMATEIN AFTER 4 HOURS' EXPOSURE TO U-V RADIATION
MOLECULAR EXTINCTION COEFFICIENTS
HAEMATOXYLIN - 4980 AT 292 mμ.
HAEMATEIN - 32,100 AT 445 mμ.
6,300 AT 278 mμ.
K = log10 I/Io /cd
λ - mμ
100
90
80
70
60
50
40
30
20
10
0
520
480
440
400
360
320
280
240
200

FIG. 1

irradiated haematein samples show the reduction of the characteristic peak of the haematein curve, and its transfer from the visible to the ultraviolet region, but do not show any characteristic features. There was no evidence of any characteristic intermediate in the degradation of haematein under these conditions.

Attempts to Form Haematein Derivatives of Improved Stability to Oxidising Agents.

Methyl Derivatives.

Haematein contains three phenolic hydroxyl groups, and its susceptibility to oxidation is no doubt in part due to its phenolic nature. It was appreciated that some of the phenolic centres are involved in the combination with chromium to form the blue lake required in practical dyeing, but it had not been shown that all the phenolic groups are necessary. It was therefore thought worth while to attempt partial methylation of haematoxylin and haematein, to find if any of the products were still capable of combining with chromium while having the free phenolic hydroxyl groups protected by methylation.

Beginning with haematoxylin, it was soon found that partially methylated products could be obtained, but they could not be separated from eath other and identified. Moreover, in some experiments it was possible to isolate both unchanged haematoxylin and the known compound tetramethyl-haematoxylin in which all four phenolic centres are methylated. It is therefore likely that the crude partially methylated material contained all the possible intermediates in varying proportion, depending on the experimental conditions. Some crude amorphous partially methylated haematoxylin was isolated

and oxidised with alkaline peroxide to a reddish dye, capable of dyeing clean wool a reddish shade. On chrome-mordanted wool, the shade was a little deeper, but still red, not blue. Attempts at resolution of the mixture of methyl derivatives did not succeed. Chromatographic methods were hampered by the insolubility of the material in the less polar solvents. Ethyl acetate gave some separation into coloured bands, but these on separation from the silica column could not be crystallised. Most of the methylation experiments were carried out with dimethyl sulphate and alkali, but diazomethane in ether solution added to haematoxylin dissolved in methanol gave similar results.

Haematein is not so readily methylated as haematoxylin, and in presence of alkali tends to add on the elements of water. Thus partial methylation with dimethyl sulphate and alkali yielded some colourless material which appeared to be tetramethyldihydrohaemateinol, along with oily products. Ethereal diazomethane added to a solution of haematein in pyridine also gave an amorphous mixture, which dyed chrome-mordanted wool a reddish shade, not unlike that obtainable with brazilein.

Evidently partial methylation did not give products of the required type, as they failed to yield blue lakes with the chrome mordant. Also, the fastness to light of the reddish shades obtainable was inferior to that of haematein.

Reaction with Diazonium Salts.

It was expected that owing to their phenolic nature haematoxylin and haematein might form azo dyes by coupling with diazonium salts. Azo dyes thus derived should be of interest not only in themselves but as intermediates for the synthesis of new derivatives, e.g. amino-compounds.

The reaction of haematoxylin with benzenediazonium chloride was studied by Dralle (Ber., 1884, 17, 372), who obtained a yellow-brown precipitate containing nitrogen, which he was unable to crystallise. Brazilin yielded an amorphous compound (N = 2.1%), whereas the presence of one azo group per mol. of brazilin requires N = 7%; some unchanged brazilin was recovered, and again the reaction product could not be purified.

Addition of benzenediazonium chloride solution to an ice-cold solution of haematoxylin in dilute alcohol, buffered with sodium acetate, caused immediate frothing, due to evolution of nitrogen, and a brown amorphous precipitate appeared. Other diazonium salts gave similar results. With p-nitrobenzenediazonium chloride the odour of nitrobenzene appeared during the reaction. The reddish-brown amorphous products contained no more than traces of nitrogen, while that obtained from p-chlorobenzenediazonium chloride contained only a trace of chlorine. The only exception was

p-sulphobenzenediazonium chloride, which evolved nitrogen, but did not give a precipitate at all (the product may have remained in a dispersed form).

Reaction of haematoxylin with benzenediazonium chloride in a closed apparatus showed that the evolution of nitrogen in the reaction is quantitative. The amorphous brown substance on treatment with ether followed by alcohol yielded a crystalline residue of haematein. Thus the diazonium salt merely acted as an oxidising agent, itself being reduced. Haematein in pyridine solution was also readily oxidised by diazo solutions, giving amorphous brown products, and evolving nitrogen.

The reaction appears to be common to hydroxylated derivatives of di- or triphenylmethane, e.g. the dyes Eriochrome Azurol B (Colour Index No.720) and Eriochrome Cyanine R (Colour Index No.722) both react in alkaline solution with benzenediazonium chloride, evolving nitrogen, but much more slowly than haematoxylin or haematein. Tetramethyl- and pentaacetylhaematoxylin also caused decomposition of diazonium salts, but were recovered unchanged from the reaction mixture. Thus, there does not seem to be any possibility of forming azo dyes from haematoxylin.

Halogen Derivatives.

The stability of benzene derivatives to oxidising agents can frequently be improved by introducing electronegative substituents, such as halogens, or the groups $-NO_2$, -COOH, $-SO_3H$. Halogen may be introduced into haematoxylin with comparative ease, and is the least likely to cause any change of shade or dyeing behaviour.

Haematoxylin itself is so readily oxidised that it is not practical to treat it directly with chlorine or bromine. A crystalline "dibromohaematoxylin" prepared by Dralle (Ber., 1884, 17, 372) by the action of bromine on haematoxylin in hot acetic acid was almost certainly a bromo-derivative of iso-haematein. Buchka (Ber., 1884, 17, 683) prepared monobromacetylhaematoxylin by the action of bromine on penta-acetylhaematoxylin in cold acetic acid. There is no authentic record of true halogen derivatives of haematoxylin or haematein in the literature.

Haematoxylin is readily acetylated, and the acetyl derivative brominated by the method of Buchka (loc.cit.). Hydrolysis ought to yield bromohaematoxylin, but efforts to isolate it were not successful. It was very easily oxidised in solution to crystalline bromohaematein. This behaviour was found to be typical of the halogen derivatives, those of haematoxylin being amorphous, while those of haematein

crystallised readily. Dibromohaematein and chlorohaematein were prepared by a similar procedure. It was not found possible to produce more highly brominated or chlorinated derivatives of haematein.

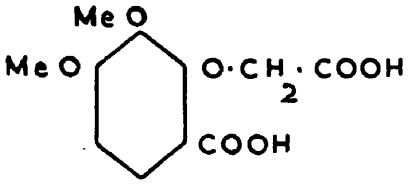
While monochloro- and monobromohaematoxylin could not be isolated, they could be methylated directly in solution with dimethyl sulphate and alkali to yield the corresponding tetramethyl derivatives.

The dyeing properties and fastness to light of the three new derivatives of haematein, viz. chloro-, mono- and dibromo-haematein, were very similar to those of the parent substance. They were much more soluble in water and organic solvents than haematein.

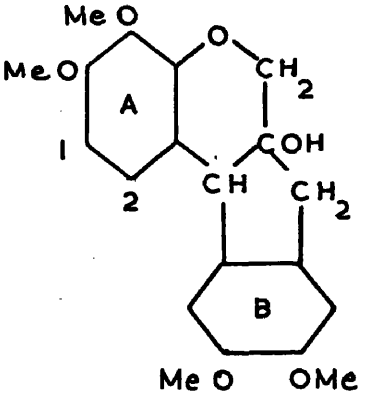
Although the expected improvement in fastness to light did not materialise, there was some evidence that the new products did have a greater resistance to oxidation than haematein itself. Desai (Ph.D. Thesis, Glasgow, 1948, p.132) reported that aqueous solutions of haematein, when heated in presence of air, graddally deepened in colour, then faded. The changes were prevented by exclusion of air. The change of colour intensity in air also took place with chloro-haematein solutions, but more slowly. Bromohaematein was even more stable.

Some efforts were made to establish the constitution of

the halogen derivatives. As already mentioned, bromotetramethylhaematoxylin could be prepared by hydrolysis and methylation of bromopentaacetylhaematoxylin and is identical with a product obtained by brominating tetramethylhaematoxylin - a more convenient method of preparation. Tetramethylhaematoxylin itself on oxidation with saturated aqueous permanganate readily yielded 2-carboxy-5:6-dimethoxyphenoxyacetic acid (VI). Unfortunately the bromotetramethylhaematoxylin proved to be much more difficult to oxidise, even in presence of acetone, used to improve the solubility, and did not yield recognisable fragments. The compound VI can be so easily isolated, however, that if it were formed it would be unlikely to escape detection. This evidence is unsatisfactory, but rather supports the conclusion that the halogen enters ring A of tetramethylhaematoxylin(XXXVII).



VI



XXXVII

Bromotetramethylhaematoxylin was described by Pfeiffer et al. (J.pr.Chem., 1938, 150, 227); by degradation with nitric acid a fragment was obtained containing a nitro-group in the position corresponding to (1) in formula XXXVII, and this was the position of the Br atom assumed by these authors. The most reactive positions in the catechol (B) nucleus are already occupied, and it seems at least probable that the second Br atom would enter at position (2) in ring A.

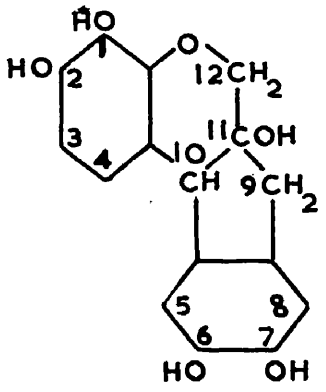
Thiocyanogen.

This pseudo-halogen forms thiocyano derivatives with some phenols. Owing to its instability, it is best generated in situ as required, e.g. by addition of bromine to sodium thiocyanate in acetic acid. This method was applied to pentaacetylhaematoxylin. The yellow solid which separated was polymeric thiocyanogen, and the pentaacetylhaematoxylin was recovered unchanged. It is apparently not sufficiently reactive to form a thiocyano derivative.

Protection of the Alcoholic Hydroxyl Group of Haematoxylin.

The effect of nuclear substituents on fastness to light being negligible, attention was directed to the saturated ring system of haematoxylin (XI) and haematein. The only functional group not directly connected to an aromatic ring is

the tertiary alcoholic group attached to C-11 and there is evidence that the bonds joining this carbon atom to its neighbours are comparatively easily ruptured by oxidising agents. Tetramethylhaematoxylin is converted by chromic acid to tetramethylhaematoxylone by rupture of the bond between carbon atoms 10 and 11, both of these atoms becoming ketonic. Pentamethylhaematoxylin is exceedingly difficult to oxidise, even with permanganate, and it was the great stability of this substance that suggested the methylation of the hydroxyl group at C-11 in haematoxylin and haematein as a means of preventing oxidation.



XI

The phenolic hydroxyl groups must be protected during the methylation by some alkali-stable group, then regenerated at the end by some means that does not disturb the methyl group. Several methods have been found useful in the past for solving problems of this type. Phenolic hydroxyl groups may be methoxymethylated with chloromethyl ether and alkali; the methoxymethyl groups can later be removed with dilute

acid. Similarly triphenylchloromethane yields ethers which are stable to alkali and readily decomposed by dilute acid. With haematoxylin, however, chloromethyl ether formed an alkali-soluble condensation product, probably identical with that formed by formaldehyde, and not the expected ether. Triphenylchloromethane could not be made to react at all, either in pyridine or in presence of alkali.

An alternative procedure involves benzylation followed by methylation, then removal of the benzyl groups by catalytic hydrogenation.

While a tetrabenzyl ether of haematoxylin was reported by Perkin, Pollard and Robinson (J.C.S. 1937, 52), no details of its preparation were given and it was described as amorphous, giving a crystalline acetyl derivative melting at 112°. It has been found possible to prepare tetrabenzylhaematoxylin in crystalline form, in good yield, by boiling haematoxylin and benzyl chloride in methanol under reflux, while slowly adding methanolic potash. Nitrogen was passed through the mixture during the process to prevent losses by oxidation. The product was finally crystallised from an acetone-alcohol mixture.

Hydrogenation of tetrabenzylhaematoxylin in ethyl acetate in presence of a palladium catalyst (Adams) gave pure haematoxylin. Platinum was not suitable, and several failures

showed that even the palladium catalyst must be freshly prepared.

The methylation of tetrabenzylhaematoxylin presented new problems. When haematoxylin is methylated some pentamethyl derivative is formed in addition to the tetramethyl compound, especially when ethyl alcohol is used as the solvent in place of methyl alcohol. However, the conversion of the tetramethyl to the pentamethyl compound is not easily effected. Published methods involve (1) reaction in benzene with sodium, followed by methyl iodide under pressure at 120° (Schall, Ber., 1894, 27, 524), and (2) heating with solid potassium hydroxide and alcohol, then with methyl iodide (Herzig, Monatsh. 1894, 15, 143). Method (1) cannot be used for benzyl ethers as sodium causes fission. Method (2) is also unsuitable, as under the conditions described even tetramethylhaematoxylin appears to be partly demethylated. A method had to be found which would leave the protecting groups intact, while giving a good yield of the required methyl derivative.

Experiments were carried out with tetramethylhaematoxylin, and a satisfactory method for its conversion to the pentamethyl compound worked out. A solution of the tetramethyl compound in benzene was refluxed with sodium methoxide powder and excess methyl iodide. When the method was adopted for the tetrabenzyl derivative, it proved suitable, provided that

a large excess of sodium methoxide was avoided.

The final step, hydrogenolysis to 11-O-monomethyl-haematoxylin, was successfully carried through, but unfortunately it was not found possible to crystallise the product. The 11-O-monomethylhaematein prepared from it was also amorphous. Methoxyl determinations gave somewhat low results, and it is possible that some tetrabenzyl- (or even pentabenzyl-) haematoxylin was present in the product submitted to hydrogenation. The benzyl derivatives are not easily purified owing to their close similarity in properties.

The amorphous red end-product of the synthesis was undoubtedly substantially haematein monomethyl ether, and proved to be very similar to haematein in dyeing properties. The fastness to light was however not improved.

Sulphone Derivatives of Haematein

Ring substituents have a marked effect on the oxidation-reduction potential of systems such as quinol/quinone; generally, saturated radicals tend to promote the oxidation reaction, while acidic substituents retard it. Halogens have some retarding action, but $-SO_3H$, $-NO_2$, and $-SO_2R$ groups are much more effective. The possibility of introducing such substituents into haematoxylin was examined.

With cold concentrated sulphuric acid, haematoxylin

formed a water-insoluble amorphous brown substance which contained sulphur, but was not a sulphonic acid. Even 50% sulphuric acid formed the same product on boiling. The saturated ring system of haematoxylin contains a hydroxyl group, and it is probable that dehydration occured with some rearrangement of the molecule: compare the known reaction of haematein with strong acids, i.e. conversion to iso-haematein salts.

Nitration of haematoxylin was impossible as oxidation took place so readily. Pentaacetylhaematoxylin was decomposed by concentrated sulphuric acid, while concentrated nitric acid in glacial acetic acid gave only oxalic acid.

It has not been found possible to carry out the Friedel-Crafts reaction with haematoxylin or its derivatives; acetyl chloride and tosyl chloride have been tried, but only the esters were formed. A possible method of introducing the sulphone substituent appeared to be by reaction of haematoxylin with benzene-sulphinic acid. This compound readily yields sulphones with phenols, e.g.

$$3\ C_6H_5.SO_2H + 1{:}4\text{-}C_6H_4(OH)_2 \longrightarrow C_6H_3(OH)_2.SO_2C_6H_5 + C_6H_5.SO.SO.C_6H_5 + 2H_2O$$

(Three mols. of the acid are heated with 1 mol. of the phenol for an hour or two on the water bath).

Benzene-sulphinic acid is prepared by reduction of benzene sulphonyl chloride with zinc dust in presence of water. It does not keep well, as it gradually forms phenyl disulphoxide and phenyl disulphone.

Haematoxylin reacted with benzene-sulphinic acid, forming two distinct products. (1) On heating for a short time, or in presence of a solvent such as acetone, an amorphous compound was obtained. This could be oxidised to a red dye, which gave a blue shade on chrome-mordanted wool. (2) On long heating (2 hours), in absence of any solvent, a reddish crystalline product was formed. It could be freed from other products by washing with acetone, but was insoluble in organic solvents. On boiling with water it formed a dark-coloured oil, but was capable of dyeing chrome-mordanted wool a reddish shade. It therefore resembled the product of reaction of haematoxylin with other acids.

Reaction of Haematoxylin with Aldehydes.

Haematoxylin condenses readily with aldehydes in presence of dilute acid, and the reaction has been investigated as a possible route to new derivatives. Formaldehyde yielded an amorphous brick-red powder, which could be oxidised to a dark red amorphous dye, of low tinctorial value compared with haematein, and of poor fastness to light.

An attempt was made to characterise the formaldehyde condensation product of haematoxylin by methylation with dimethyl sulphate and alkali, but only a brown amorphous residue could be obtained.

Benzaldehyde (1 mol.) condensed readily with haematoxylin (2 mols.) in aqueous alcohol acidified with hydrochloric acid, the product crystallising readily from alcohol. Oxidation with alkaline peroxide gave a red amorphous dye, apparently a benzal derivative of haematein. It gave a blue shade on chrome-mordanted wool, but the tinctorial value was only about one-third that of haematein. The fastness to light was similar to that of haematein at the same depth of shade.

Benzaldehyde o-sulphonic acid (sodium salt) condensed with haematoxylin in presence of hydrochloric acid to give an oil which crystallised from alcohol. The product was the sodium salt of a sulphonic acid, and the analyses for sulphur and sodium showed that two mols. haematoxylin condensed with one of aldehyde. Oxidation with alkaline peroxide yielded an amorphous red dye, giving a weak greyish-blue shade on chrome-mordanted wool, very fugitive to light.

Acetaldehyde, glyoxal and m- and p-nitrobenzaldehydes gave water-insoluble amorphous products. p-Hydroxybenzaldehyde and vanillin appeared to condense to form very soluble products, which could not be purified, but protocatechualdehyde yielded a crystalline condensation product. Chloral did not

react with haematoxylin. The products isolated were oxidised to the corresponding haematein derivatives, but in each case the tinctorial power was low, being at best about one-third that of haematein.

Formaldehyde and sodium sulphite condense with phenols to give products containing the grouping $-CH_2.SO_3Na$. Frequently a number of methylene linkages are formed at the same time, depending on the reactivity of the phenol. Condensation with haematoxylin gave a very soluble product, which did not separate on acidifying. However, after long standing, the acid solution gradually deposited lustrous red leaflets, almost insoluble even in hot water. It was realised after investigation that the product was a derivative of haematein, and appeared in fact to be the sodium salt of the methane-sulphonic acid derived from haematein. The yield was later greatly improved by oxidising the reaction mixture with alkaline peroxide, after removing free sulphur dioxide by distillation with acid.

The product dyed chrome-mordanted wool a reddish-violet shade, resembling that obtained with isohaematein salts, but the tinctorial value was comparatively low.

Reaction of Haematoxylin with Phosphorus Trichloride.

It was hoped that the alcoholic hydroxyl-group in haematoxylin could be replaced by chlorine, which in turn

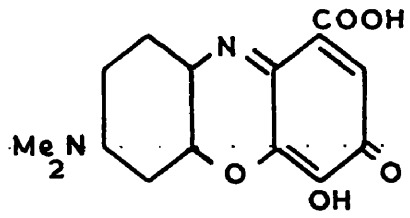
should be sufficiently reactive to be replaced by a methoxy group on boiling with methanol.

It was necessary to find a suitable solvent for the reaction of haematoxylin with phosphorus trichloride. The solubility of haematoxylin in ordinary ether is very low, but it is very soluble in dioxan, which is not affected by phosphorus trichloride. The two reactants in dioxan solution gave a brown amorphous precipitate on heating, which when filtered off and washed with cold dioxan formed a hygroscopic mass, containing no chlorine. It was very soluble in water, but not in ether. However, after warming with aqueous alkali and acidifying, an ether extraction yielded haematoxylin. The product was therefore a phosphorus ester of haematoxylin.

A large excess of phosphorus trichloride in the reaction merely caused solution of the product; the reaction was not affected by the presence of possible catalysts such as dimethylaniline or aluminium chloride. The alcoholic hydroxyl-group may be in a sterically hindered position, as its lack of reactivity is unexpected.

Reaction with Nitroso Compounds.

Nitroso compounds frequently condense with phenols to give oxazine dyes, e.g. p-nitrosodimethylaniline and gallic acid on boiling in alcohol yield gallocyanine (XXXVIII).



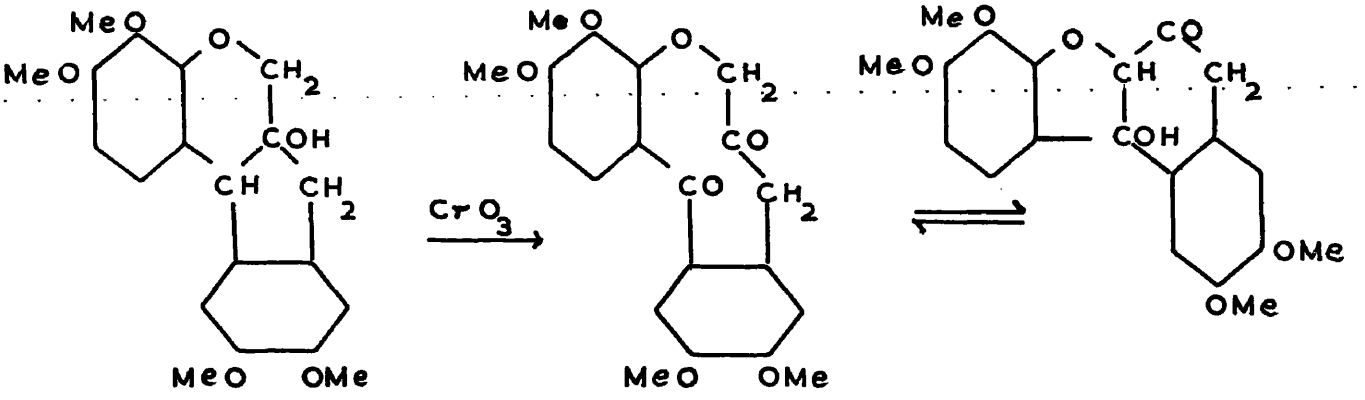
XXXVIII

Haematoxylin and p-nitrosodimethylaniline in boiling alcohol yielded mainly crystalline haematein and a small amount of dark-coloured insoluble matter. p-Nitrosophenol yielded only crystalline haematein.

The nitroso-group appeared to act in much the same way as nitrous acid. Nitrobenzene had no action on haematoxylin in boiling alcohol.

Anhydrohaematoxylong

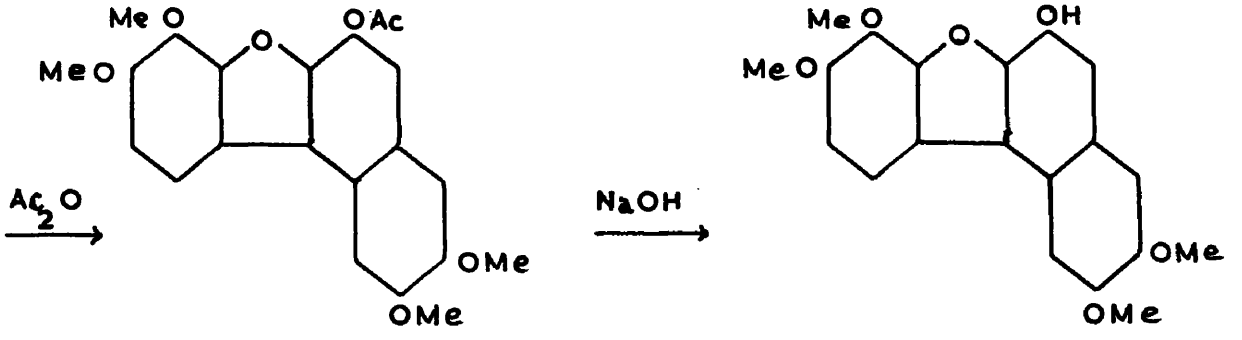
The oxidation of acetyltetramethylhaematoxylin with chromic acid was first investigated by Herzig (Monatsh., 1895, 16, 907). Later, Gilbody and Perkin (Proc.C.S., 1899, 15, 27) oxidised tetramethylhaematoxylin with chromic acid to a product which they called tetramethylhaematoxylone. Following their work on the structure of haematoxylin, Perkin and Robinson (J.C.S., 1909, 95T, 381) proposed the following scheme for the formation and reactions of tetramethyl-haematoxylone -



XXXVII
Tetramethyl-haematoxylin

XXXIX
Tetramethyl-haematoxylone

XL

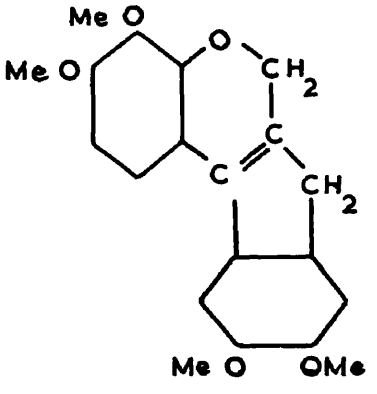


XLI
Acetylanhydrotetra-methylhaematoxylone

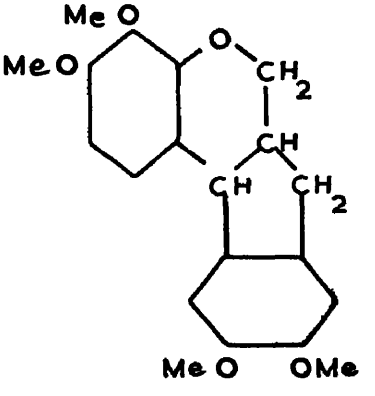
XLII
α-anhydrotetramethyl-haematoxylone

The synthesis of tetramethylhaematoxylone (XXXIX or XL) was accomplished by Pfeiffer, Angern, Haack, and Willems (Ber., 1928, 61, 839) by oxidation with chromic acid of the dihydro-

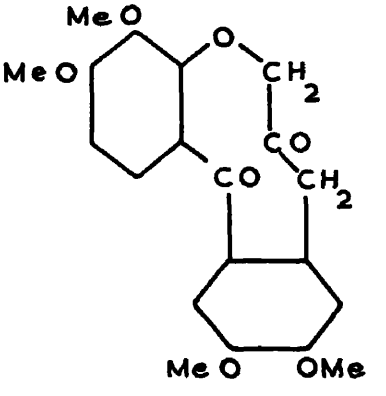
compound (XXX) of tetramethylanhydrohaematoxylin (XLIII), already synthesised by Pfeiffer, Haack and Willems (Ber., 1928, 61, 294).



XLIII



XXX

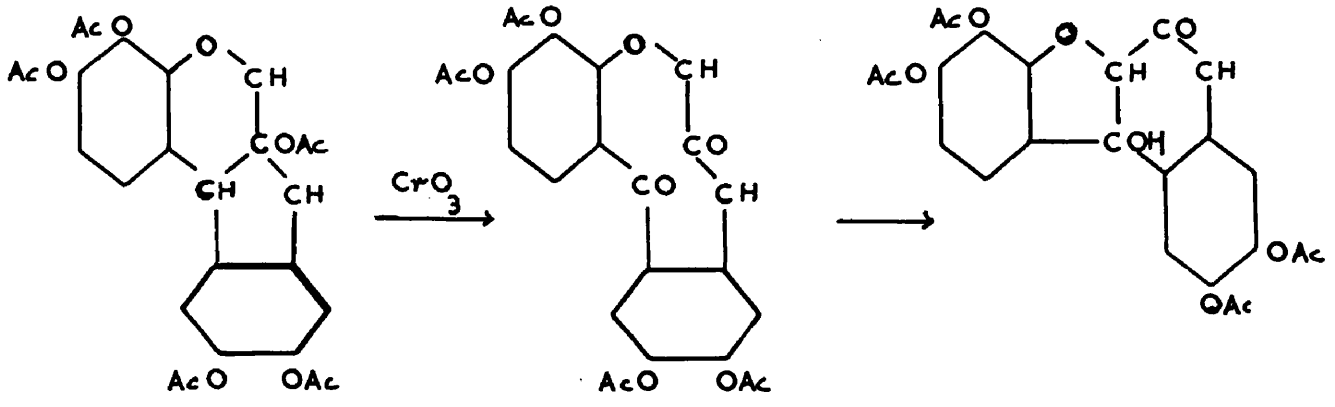


XXXIX

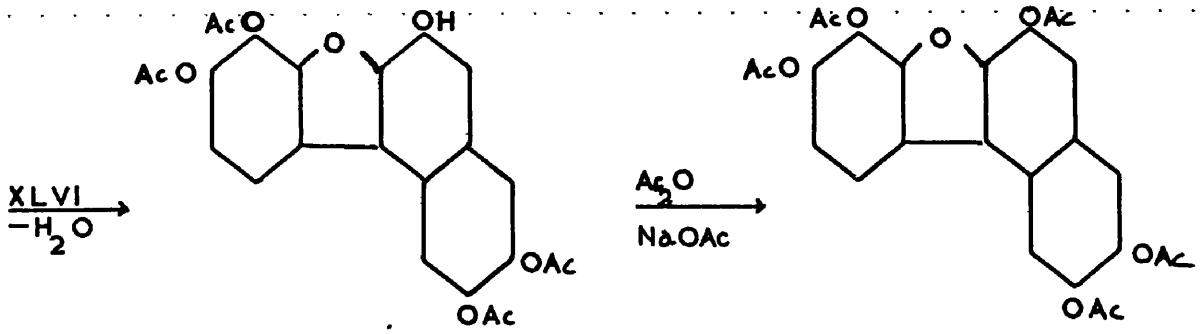
Perkin, Rây, and Robinson reported the oxidation of triacetylbrazilin with chromic acid to triacetylbrazilone (J.C.S.(T), 1928, 1504), and Perkin, Pollard and Robinson prepared tetraacetylhaematoxylone, described as colourless needles from alcohol, m.p.125-127° (J.C.S.(T), 1937, 52). The parent compounds brazilone and haematoxylone were however not described.

The oxidation of pentaacetylhaematoxylin with chromic acid in glacial acetic acid proceeded readily at a low temperature, and the product crystallised readily from alcohol in the form of lustrous leaflets. The original m.pt. of about 80°(dec)

was raised by successive recrystallisations first to about 140°(dec.) then to 160°(without dec.). Heating at 150°, or in toluene, formed the product of m.pt.160°. If the original material of m.pt.80° was heated beyond this temperature in a melting point tube it resolidified, then melted again at 140°(dec.). Treatment with acetic anhydride alone gave the product melting at 140°, but in presence of sodium acetate it gave a new substance, m.pt.258°. Heating for some time at 200° gave a product melting at about 240°, apparently the same substance as a by-product sometimes obtained during the oxidation reaction. It seems likely, by analogy with the reactions of tetramethylhaematoxylone, that the following represents the course of these transformations -



XLIV XLV XLVI

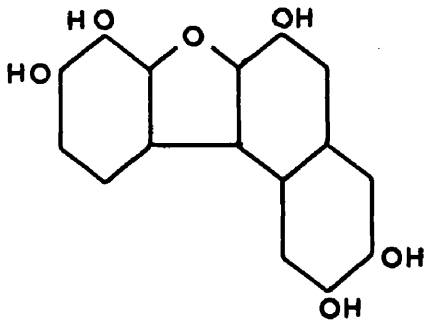


XLVII XLVIII

It seems probable that the marked changes in m.pt. on recrystallising may be due to the changes XLV ⟶ XLVI or XLVI ⟶ XLVII and that the lowest-melting substances were mixtures. It is significant that a little material of m.pt. about 240°, presumably XLVII, was obtained on recrystallising the crude reaction product of step XLIV ⟶ XLV. Attempts were made to establish whether solvent of crystallisation was present in some of the products, but no evidence could be found to support this; it was not possible to proceed from a higher melting material to one of lower m.pt. by recrystallising either from alcohol or aqueous alcohol.

All the oxidation products isolated, and their dehydrated and acetylated derivatives gave the same product on hydrolysis with aqueous alkali, hence it must be anhydrohaematoxylone

(XLIX), not haematoxylone. This again is analogous to the behaviour of tetramethylhaematoxylone.



XLIX

Hydrolysis of the acetyl compounds was readily effected by warming with aqueous alcoholic alkali. The product was isolated by acidifying and extracting with ether. It was insoluble in water, but could be obtained in the form of dark-coloured flakes on allowing a solution in aqueous alcohol to evaporate slowly. It did not crystallise from the commoner solvents, but separated from dioxan in hard greyish-yellow granules. The product had no definite melting point, beginning to darken slightly in colour at 80°, becoming almost black at 300°, but still not liquid at 360°.

Benzenediazonium chloride coupled readily with anhydro-haematoxylone in either alcohol or dioxan. There was only very slight evolution of nitrogen, and the dye was readily obtained as an amorphous red precipitate on diluting with

water. In this respect anhydrohaematoxylone was completely different from haematoxylin; it even formed an azo dye more readily than pyrocatechol itself, which gave only an amorphous oily product, with evolution of nitrogen, on reaction with benzenediazonium chloride.

Anhydrohaematoxylone was not itself a dye nor did it form one by oxidation, but on boiling with wool in presence of dichromate a green stain was obtained, rather like that from pyrocatechol. It formed a bluish-green lake with anodised aluminium, while pyrocatechol formed a light green lake. It therefore resembled both pyrocatechol and ß-naphthol in certain respects, and was far removed from haematoxylin and haematein in behaviour.

EXPERIMENTAL

Purification of Haematoxylin.

Haematoxylin gifted by the Yorkshire Dyeware and Chemical Co., Ltd., of Leeds, was used in this work. It was of good quality, being sufficiently pure for much of the preparative work. Where necessary, the following method was employed to give a very pure product:-

Haematoxylin (300 g.) was dissolved in boiling water (1500 c.c.) acidified with a few c.c. sulphurous acid. Active carbon (about 20 g.) and a similar quantity of filter aid were added, and the mixture filtered through canvas filter cloth on a Buchner filter. Haematoxylin monohydrate (about 250 g.) crystallised on cooling; m.pt.140°(dec.). Usually it had a pale yellowish-brown colour; repeated recrystallisation was necessary to produce a white product. More dilute solutions, acidified with sulphurous acid, produced colourless needles of the trihydrate, m.pt.100-120°.

Haematein.

The method of preparation given by A.G.Perkin and Everest*, which involved drawing a current of air through a solution of haematoxylin in dilute ammonia, did not give good

* ("The Natural Organic Colouring Matters", p.345)

results, yields being only about 10%.

The commercial "Hematine Red Paste" of the British Dyewood Co., Ltd., Glasgow, was found to be a useful source of haematein; it is prepared by oxidising a commercial logwood extract with air in presence of sodium nitrite. The paste was filtered, and the solid residue dissolved in the minimum quantity of hot ethanol. On cooling, a large volume of ether was added, and the amorphous precipitate allowed to settle. The ethereal liquid was decanted and evaporated, when the characteristic lustrous crystals of haematein separated. These were filtered, and washed with a little hot ethanol.

The most convenient method was found to be the oxidation of haematoxylin with alkaline peroxide. Haematoxylin (60 g.) was dissolved in water (600 c.c.) and ethanol (20 c.c.), and the solution cooled to room temperature. Sodium hydroxide, 40% aqueous solution (40 c.c.) was added before crystallisation could begin, followed by hydrogen peroxide, 15% solution (50 c.c.), keeping solution cool. After a few minutes the solution was neutralised with dilute hydrochloric acid, then acidified with 25% acetic acid. The amorphous brown precipitate of haematein was filtered off and washed with water. It was then gently heated with water (300 c.c.) when it crystallised. The lustrous crystals were filtered and washed

with a little cold methanol. Yield 42 g., m.pt.210-216°(dec).

Methylation of Haematoxylin.

(1) Tetramethylhaematoxylin.

This was prepared by the method of Perkin (J.C.S., 1902,81 1059). Haematoxylin dried at 100° (10 g.) was dissolved in hot methanol (100 c.c.), mixed while still warm with potassium hydroxide (10 g.) dissolved in methanol (100 c.c.), and dimethyl sulphate (25 g.) added all at once. As soon as the reaction subsided, a second addition of the same quantities of methanolic potassium hydroxide and dimethyl sulphate was made, the product cooled, and mixed with four volumes of water. After two days the crystals which separated were collected, washed with water, and dried at low temperature (8 g.). Recrystallisation from methanol or ethanol yielded the anhydrous form, m.pt.142°; from dilute methanol colourless needles of the hydrate separated, m.pt.65-68°.

(2) Partial Methylation.

Taking the above preparation as a basis, a series of preparations of partially methylated products was carried out, by reducing the dimethyl sulphate and alkali to the amounts required for methylation of only one or two hydroxyl groups. Taking, for example, haematoxylin (10 g.), potassium

hydroxide (2 g.) and dimethyl sulphate (5 g.), the main product was an uncrystallisable oil; it is noteworthy that a small amount of tetramethylhaematoxylin was obtained, although the proportion of methylating agent used was only 20% more than required for one hydroxyl group. When the proportion of methylating agent was reduced, unchanged haematoxylin was recovered. Higher proportions of methylating agent invariably yielded oily products, the only recognisable fragment being tetramethylhaematoxylin. One further example will suffice:-

Haematoxylin (20 g.) was dissolved in methanol (200 c.c.) and cooled. Potassium hydroxide (12 g.) in water (200 c.c.) was added, followed by dimethyl sulphate (30 g.) slowly, keeping the mixture cool. When the reaction was complete (indicated by change of colour of the solution), the methanol was removed by warming on the water bath, when an oily product separated. The aqueous layer was decanted, and the oil dried under vacuum at low temperature. It was dissolved in ethyl acetate; the solution was dried over desiccated sodium sulphate, filtered and evaporated. A reddish amorphous powder (22g.) was obtained. This was the partially methylated haematoxylin used in dyeing trials.

Methylation of haematoxylin (in methanol) was also attempted with diazomethane (from nitrosomethylurea: Organic

Syntheses, Vol.II, p.462), with similar results.

Methylation of Haematein.

(1) Haematein (10 g.) was mixed with water (50 c.c.) and ice (25 g.). Potassium hydroxide (43% solution : 47 c.c.) and dimethyl sulphate (29 c.c.) were added in alternate portions. Addition of water produced a red precipitate, which was collected, and dried on porous porcelain. It was extracted repeatedly with cold ethyl acetate. The white crystalline residue was recrystallised once from ethanol, yielding colourless prisms, m.pt.185°. This was probably the tetramethyldihydrohaemateinol described by Engels, Perkin and Robinson (J.C.S.(T), 1908, 93, 1121), obtained by them by the action of alkali on tetramethylhaematein, from which it is formed by the addition of the elements of water.

(2) Partial Methylation.

Haematein is only sparingly soluble in most solvents, but does dissolve readily in pyridine, from which it can be recovered by dilution with water or dilute acid. (In this respect it differs from haematoxylin, which forms a complex with pyridine, insoluble in water, very soluble in dilute acid, but decomposed by alkali).

Haematein (2 g.) was dissolved in pyridine (20 c.c.), and an ethereal solution of diazomethane prepared from

nitrosomethylurea (10 g.) added. Addition of water precipitated a red powder, which was collected and dried at a low temperature. This partially methylated haematein was used in dye trials.

Pentaacetylhaematoxylin.

Hot acetic anhydride (200 c.c.) was added portionwise to a mixture of dry haematoxylin (60 g.) and fused sodium acetate (20 g.). After the violent reaction subsided, the mixture was kept hot on the water bath for 2 hr. Water was added to decompose excess acetic anhydride, and the solution either poured into 2 l. cold water to precipitate the acetate, or, with further careful dilution with water, it could be obtained crystalline. It was recrystallised from alcohol; 57 g., m.pt.165-166°.

Monobromopentaacetylhaematoxylin.

This was prepared by the method of Buchka (Ber., 1884, 17, 683). To pentaacetylhaematoxylin (5 g.) in glacial acetic acid, bromine (1.1 c.c.) in glacial acetic acid was added slowly, keeping the mixture cold. After one hour, the mixture was poured into dilute sulphurous acid; the precipitate was recrystallised 3 times from alcohol; 3.4 g. colourless needles, m.pt.205-206°. Hydrolysis with aqueous

alcoholic sodium hydroxide yielded a solution of bromohaematoxylin, but efforts to crystallise this failed. The product which eventually separated was a dard red crystalline material with a green lustre when dry - apparently bromohaematein produced by aerial oxidation of the bromohaematoxylin. In absence of air, no crystals were obtained.

Bromohaematein.

Monobromopentaacetylhaematoxylin (5 g.) was warmed on the water bath with alcohol (25 c.c.) and 40% aqueous sodium hydroxide (10 c.c.) until all dissolved. To the deep blue solution an equal volume of water was added, then 10 vol. hydrogen peroxide (10 c.c.). After a few minutes the solution was acidified with hydrochloric acid; the red precipitate was collected, dried, and recrystallised from aqueous alcohol: 1.8 g. lustrous red leaflets which shrank with charring at ca. 300° but did not melt below 360°. (Found: C,48.0; H,3.6; Br,19.4; loss at 100°, 5.93; $C_{16}H_{11}O_6Br,H_2O$ requires C,48.4; H,3.3; Br,20.2; H_2O,4.53%)

Dibromopentaacetylhaematoxylin.

Pentaacetylhaematoxylin (25 g.) was dissolved in glacial acetic acid, and bromine (5.5 c.c.) added, the temperature being allowed to rise. After two hours the solution was diluted with alcohol and poured into dilute sulphurous acid.

The precipitated mass was dried and crystallised from alcohol to yield 7 g. of cream-coloured sandy crystals. These were only sparingly soluble in alcohol, but more soluble in acetone. The acetone solution was mixed with alcohol and water, and left to evaporate at room temperature, when the dibromo derivative separated as a mass of soft, colourless needles, m.pt.232-234°. (Found: Br,25.5; $C_{26}H_{22}O_{11}Br_2$ requires Br,23.9%).

Dibromohaematein.

Like the monobromo derivative, dibromohaematoxylin failed to crystallise, but could be oxidised to dibromohaematein which crystallised readily. Dibromopentaacetylhaematoxylin (7 g.) in alcohol (25 c.c.) and 40% caustic soda (10 c.c.) was warmed on the water bath, cooled, and 10 vol. hydrogen peroxide (10 c.c.) added. Acidification with dilute hydrochloric acid yielded a red precipitate, which dissolved readily in acetone. On addition of water and standing, red leaflets separated (2.3 g.) charring at ca. 250°, but not melting below 360° . (Found: C,41.0; H,2.9; Br,33.0; loss at 100 , 4.2; $C_{16}H_{10}O_6Br_2 \cdot H_2O$ requires C,40.4; H, 2.5; Br,33.6; H_2O, 3.8%).

Chloropentaacetylhaematoxylin.

Chlorine was passed in a slow stream through pentaacetyl-

haematoxylin (10 g.) dissolved in glacial acetic acid, with cooling and shaking. The chloro-derivative separated as a crystalline magma. It was diluted with alcohol containing a little sulphur dioxide, and filtered, washed with more alcohol, and finally with ether. 8.5 g., colourless needles m.pt.194°. (Found: Cl,6.55; $C_{26}H_{23}O_{11}Cl$ requires Cl,6.50%). The product (5 g.) was hydrolysed and oxidised by the procedure for the monobromo-derivative, yielding chlorohaematein (2.2 g.); lustrous red leaflets from aqueous acetone which shrank at ca. 300° but did not melt below 360°. (Found: C,55.2; H,3.9; Cl,9.6; loss at 100°, 6.75. $C_{16}H_{11}O_6Cl.H_2O$ requires C,54.5; H,3.7; Cl,10.1; H_2O,5.10%. Chlorohaematoxylin could be isolated only as a dark brown oil, which resisted attempts to crystallise it.

Bromotetramethylhaematoxylin.

(a) From tetramethylhaematoxylin. Tetramethylhaematoxylin (60g.) prepared by the method of Perkin (J.C.S., 1902, 81 1059), was dissolved in acetic acid and bromine (9 c.c.) in acetic acid added in portions. On standing a crystalline mass separated, which was recrystallised from alcohol (38 g.). Colourless needles, m.pt.187-188°. The product was prepared by Pfeiffer et al. (J.prakt.Chem., 1938, 150, 227).

(b) From bromopentaacetylhaematoxylin. Monobromopentaacetylhaematoxylin (5 g.) was dissolved in alcohol, and

potassium hydroxide (10 g.) in alcohol, and dimethyl sulphate (25 g.) added alternately in portions. When cold, a little water was added and the mixture warmed again slightly. On pouring into excess water a brown precipitate was thrown down; this was dried, and extracted with cold alcohol. The crystalline residue was recrystallised from alcohol. Short colourless needles, m.pt.186-188°. Mixed m.pt. with product from (a) (186-188°).

Chlorotetramethylhaematoxylin.

(a) Tetramethylhaematoxylin (10 g.) in glacial acetic acid was kept cool while a slow stream of chlorine was passed in over 1 hr. The mixture was poured into dilute sulphurous acid, and the precipitated material crystallised from alcohol. Long, silky needles, m.pt.149-150°. (Found: C,61.5; H, 5.6; Cl,9.1; $C_{20}H_{21}O_6Cl$ requires C,61.2; H,5.9; Cl,9.0%). The mother liquor on evaporation yielded long, silky needles, m.pt.124-127°, but this product appeared to be impure.

(b) Chloropentaacetylhaematoxylin (10 g.) was mixed with warm alcohol and 40% w/w aqueous potassium hydroxide (20 c.c.) and dimethyl sulphate (15 c.c.) were added alternately in portions. When the reaction subsided, the mixture was poured into water containing sulphur dioxide. The precipitate was collected and extracted with cold alcohol,

the residue being crystallised from alcohol. Colourless needles, m.pt.166-168°. (Found: C,61.5; H,5.7; Cl,8.7%). The product was apparently isomeric but not identical with the product from (a).

Tetrabenzylhaematoxylin.

Perking, Pollard and Robinson (J.C.S., 1937, 52) reported the preparation of this product without details; they described it as amorphous, but giving a crystalline acetyl derivative, m.pt.112°. The following method gave good results. Haematoxylin (30 g.) and benzyl chloride (50 c.c.) in methanol (250 c.c.) were brought to boiling point under reflux, while nitrogen was passed through the solution to agitate it and maintain an inert atmosphere over it. Sodium hydroxide (16 g.) dissolved in methanol (250 c.c.) was dropped in slowly (about 3 hr.). Refluxing was continued for 1 hour more, then the solvent was distilled off. The oily residue was dissolved in ether, and the solution washed with dilute alkali, water and dilute sulphurous acid in turn. The ethereal layer was separated, distilled to remove ether, then steam distilled to remove benzyl chloride. The residual oil solidified on cooling and grinding with cold water. It was dried and crystallised from acetone. White, woolly needles (29 g.) m.pt.120°, rising to 130-140° on repeated re-crystallisation. (Found: C,80.0; H, 5.95. $C_{44}H_{38}O_6$ requires

C,79.8; H, 5.7%).

Methyltetrabenzylhaematoxylin.

Tetrabenzylhaematoxylin (29 g.), powdered sodium methoxide (4.5 g.), and methyl iodide (12 c.c.) were refluxed in dry benzene (300 c.c.) for 3 hours. The solution was filtered, benzene distilled off, and the residue crystallised from acetone. White silky needles (25.5 g.) softening about 60° , m.pt.120°(dec.). (Found: C,80.0; H, 5.95. $C_{45}H_{40}O_6$ requires C,79.9; H, 5.9).

Pentamethylhaematoxylin was prepared from tetramethylhaematoxylin by the same procedure. m.pt.145-146°.

Hydrogenation of Benzyl Derivatives.

Tetrabenzylhaematoxylin (1 g.) in ethyl acetate (50 c.c.) with Adams' palladium oxide catalyst (0.1 g.) absorbed 150 c.c. hydrogen during 6 hr. (theory requires 140 c.c.). The solution was filtered and evaporated under partial vacuum; the residue was dissolved in hot water containing a little sulphur dioxide, filtered, and left to crystallise. Pure haematoxylin (0.1 g.) gradually separated.

Methyltetrabenzylhaematoxylin (2 g.) and palladium oxide (0.2 g.) in ethyl acetate (50 c.c.) absorbed 300 c.c. hydrogen in 4 hr. The mixture was filtered, the solvent removed under

partial vaccum, and the oily residue dissolved in water. The aqueous solution was filtered and evaporated to dryness. The residue was dissolved in methanol. Potassium hydroxide (2 g.) in water (5 c.c.) was added, then dimethyl sulphate (3 g.); these additions were repeated, and when the reaction subsided, water was added and the methanol partly distilled off under reduced pressure. The crystalline matter which separated was extracted with ether, which was evaporated and the residue crystallised from methanol. Colourless leaflets m.pt.145-146°; in admixture with pure pentamethylhaematoxylin the melting point was unchanged. As methylation of haematoxylin under the conditions described produces mainly tetramethylhaematoxylin, the formation of pentamethylhaematoxylin only from the above product of hydrogenolysis proves that this product is 11-O-methylhaematoxylin.

11-O-Methylhaematoxylin.

Methyltetrabenzylhaematoxylin (4 g.) and palladium oxide (0.2 g.) in ethyl acetate (100 c.c.) absorbed 500 c.c. hydrogen in 4 hr. at ordinary temperature. The solution was filtered and evaporated. The residue was dissolved in a little methanol, and water (20 c.c.) added. After filtration to clarify, the solution was concentrated. It failed to crystallise. Evaporation to dryness yielded a reddish amorphous powder (1.4 g.). m.pt.75-82° (Found: OMe, 7.75.

$C_{17}H_{16}O_6$ requires OMe 9.5%).

11-O-Methylhaematein.

11-O-Methylhaematoxylin (1 g.) was dissolved in water (10 c.c.) containing sodium hydroxide (0.5 g.) 10 vol. hydrogen peroxide (4 c.c.) was added, then after a few minutes the solution was acidified with acetic acid. An oily precipitate separated. This was extracted with ether, the solution washed with water, and the ether evaporated, but it still remained oily (this procedure usually succeeds with haematein itself even in presence of much impurity). The residue was taken up in a little alcohol and water added. Partial evaporation under vacuum yielded a dark red precipitate, which formed an amorphous red powder on drying under vacuum. The substance did not melt below 360°. (Found: C,64.0; H,5.4; OMe, 7.6. $C_{17}H_{14}O_6$ requires C, 64.9; H, 4.5; OMe, 9.6%).

Reaction of Haematoxylin with Benzenediazonium Chloride.

Aniline (4.65 g.) was diazotised according to the method described in Organic Syntheses, Collective Volume I, p.49. The diazo solution was neutralised with sodium hydroxide, and added to a solution of haematoxylin (15 g.) in ethanol (30c.c.) + water (50 c.c.), cooled to 0°C. Sufficient sodium acetate

was added to prevent the mixture becoming acid to Congo Red. There was rapid evolution of gas (nitrogen) and a brown amorphous precipitate was formed. On isolation this was found to contain only traces of nitrogen; it was in fact crude haematein, which crystallised in the characteristic form on treatment with cold, then hot alcohol.

Haematein and iso-haematein sulphate also reacted with benzenediazonium chloride, evolving nitrogen and yielding amorphous nitrogen-free products, but attempts to purify these did not succeed.

Reaction of Haematoxylin with Nitroso-compounds.

p-Nitrosodimethylaniline. Haematoxylin (2 g.) and p-nitrosodimethylaniline (1 g.) were dissolved in ethanol (25 c.c.) and the solution boiled under reflux. Impure haematein gradually separated. Extraction of the separated material with hot methanol removed haematein, leaving an amorphous insoluble black powder (0.1 g.). This contained nitrogen, but had no dyeing properties.

p-Nitrosophenol. Haematoxylin (3 g.) and p-nitroso-phenol (0.6 g.) were refluxed in ethanol (25 c.c.). Pure haematein separated; there was no insoluble by-product.

Reaction of Haematoxylin with Phosphorus Trichloride.

Haematoxylin (1 g.) and phosphorus trichloride (0.5 c.c.) were separately dissolved in dry dioxan and the solutions mixed. On warming a brown solid separated. This was filtered off and washed with cold dioxan. It formed an amorphous, very hygroscopic mass, very soluble in water and free from chlorine - apparently a phosphorous acid ester of haematoxylin, as on boiling with dilute alkali and reacidifying it yielded haematoxylin.

Variation of the proportions of reactants and reaction conditions, including the addition of dimethyl-aniline or aluminium chloride, failed to yield a chlorine-containing product.

Condensation of Haematoxylin with Aldehydes.

(a) Formaldehyde. Haematoxylin (10 g.) was dissolved in boiling water (100 c.c.) then 40% formaldehyde solution (5 c.c.) and dilute hydrochloric acid (1:1; 5 c.c.) added. In a short time a pink oily precipitate settled, which solidified on cooling. After grinding with water, filtering and drying, this formed a bright red amorphous powder; attempts to crystallise it were not successful. The product was dissolved in water (25 c.c.) containing 40% sodium hydroxide solution (5 c.c.), and 100 vol. (i.e.30%) hydrogen

peroxide (3 c.c.) added. After a few mins., dilute hydrochloric acid was added until the solution was acid to Congo Red. The flocculent precipitate of haematein derivative was collected and dried. It formed a dark red powder, insoluble in water, readily soluble in alcohol, but it could not be crystallised. Further work with varying proportions of formaldehyde yielded only the same product; methylation of the condensation product with dimethyl sulphate and potassium hydroxide in alcohol also yielded amorphous substances.

(b) Benzaldehyde. Haematoxylin (6 g.), alcohol (25 c.c.) water (25 c.c.), hydrochloric acid (2 c.c.) and benzaldehyde (1 c.c.) were mixed and boiled under reflux for 1 hour. On cooling benzalhaematoxylin separated; recrystallisation from alcohol yielded colourless prisms (3 g.). Oxidation of this with alkaline peroxide yielded dark red amorphous benzalhaematein. The m.pt. of benzalhaematoxylin was rather indefinite; it turned red at about 240°, becoming black and apparently melting with decomposition at 270° . The analysis suggested that it was the pentahydrate, although it was unchanged at 100°. (Found: C, 59.5; H, 5.5. $C_{39}H_{32}O_{12}5H_2O$ requires C,59.9; H, 5.4%).

(c) Benzaldehyde o-sulphonic acid. The commercial substance is a mixture of the sodium salt of benzaldehyde o-sulphonic acid with sodium chloride. The pure sodium salt of the

sulphonic acid was obtained by extraction of the commercial substance with hot alcohol, filtration, and evaporation of the alcohol. Haematoxylin (3 g.), benzaldehyde o-sulphonic acid (pure Na salt) (1 g.), concentrated hydrochloric acid (2 c.c.), and water (20 c.c.) were refluxed for 1 hour. On cooling an oil separated which slowly solidified. It was dried under vacuum, then crystallised from alcohol. Red-tinted leaflets (0.9 g.). Analysis agreed with its formulation as a compound from 2 mols. haematoxylin and 1 mol. of the aldehyde. (Found: S,3.94; Na,2.70. $C_{39}H_{27}O_{15}SNa$ requires S,4.05; Na,2.91%). The haematein derivative prepared from it by oxidation with alkaline peroxide was an amorphous red powder.

(d) Both m- and p-nitrobenzaldehyde gave reddish-coloured amorphous condensation products with haematoxylin; on oxidation they yielded dark red amorphous haematein derivatives.

(e) Chloral did not condense with haematoxylin.

(f) Protocotechualdehyde and haematoxylin gave a very water-soluble condensation product; it crystallised from alcohol-acetone-water on slow evaporation. Its oxidation product was amorphous.

(g) p-Hydroxybenzaldehyde and Vanillin yielded very soluble

condensation products which were not obtained pure.

Reaction of Haematoxylin with Formaldehyde-bisulphite.

Haematoxylin on boiling under reflux with a large excess of formaldehyde and either sodium sulphite or bisulphite in water apparently reacted, but the product was not the methoxymethyl ether, as might have been expected. Apparently condensation took place with formation of a sodium methanesulphonate of haematoxylin. This product proved to be extremely soluble in water, and was not isolated. However, on acidifying and leaving the reaction mixture to stand for several weeks, red lustrous platelets separated. These were only very sparingly soluble even in hot water, suggesting that they were a haematein derivative produced by spontaneous oxidation of the sodium salt of haematoxylinmethane sulphonic acid. Confirmation was obtained by condensing haematoxylin (5 g.) with sodium sulphite crystals (60 g.) and 40% aqueous formaldehyde (16 c.c.) in water (100 c.c.), boiling under reflux for 5 hours. Excess sulphur dioxide was removed by distilling with the gradual addition of concentrated hydrochloric acid (50 c.c.), until crystals (sodium chloride) began to separate. The solution was cooled and made alkaline with 40% aqueous sodium hydroxide (25 c.c.), 10 volume hydrogen peroxide (19 c.c.) was added, and after a few minutes hydrochloric acid, until the liquid was just acid to Congo Red.

After heating to boiling point, red lustrous plates (2.3 g.) separated on cooling. These were filtered off, washed with water and dried. (Found: Na,4.52,4.58; $C_{16}H_{11}O_6.CH_2SO_3Na$ requires Na,5.5%).

Reaction of Haematoxylin with Benzenesulphinic Acid.

1. Haematoxylin (1 g.) and benzenesulphinic acid (1.2 g.) were powdered and mixed thoroughly together, then heated on the water bath for 1½ hours. The product partly dissolved in acetone, leaving a red crystalline residue, insoluble in water and organic solvents, but soluble in dilute sodium hydroxide with red colour. The product turned into a black oil on heating in water; and on heating a sample in a melting point tube it turned black at about 210° without definite melting point.

2. Haematoxylin (2 g.) and benzenesulphinic acid (2.2g.) were ground together and heated for a few minutes on the water bath. The substance was then almost entirely soluble in acetone. On pouring the acetone solution into water a brown precipitate appeared, which was readily dissolved by extraction from the water with ether. Dilute sodium hydroxide removed the haematoxylin derivative; the ether on evaporation yielded a colourless oil, probably phenyldisulph-oxide $C_6H_5.SO.SO.C_6H_5$. The haematoxylin derivative was

obtained as a brown oil on acidifying the alkaline solution. Better results were obtained by dissolving the mixture of haematoxylin and benzenesulphinic acid in acetone, evaporation, and heating the residue for a few minutes on the water bath. The final acidification caused the haematoxylin derivative to separate as a pale brown amorphous precipitate, which could be filtered off and dried (2.3 g.). This derivative (1 g.) was oxidised to the corresponding haematein derivative with alkali and 10 vol. hydrogen peroxide (2.5 c.c.). It formed a red amorphous powder.

Acetylhaematoxylone.

Pentaacetylhaematoxylin (10 g.) was dissolved in glacial acetic acid (50 c.c.) and a solution of chromic acid (3 g.) in water (3 c.c.) added, keeping the temperature below 20°. After standing overnight at room temperature, the mixture was diluted with alcohol and water until crystallisation of the product began. Recrystallisation from alcohol yielded 3.1 g. m.pt. about 110°(dec.). (Found: C,58.9; H,4.2. Calc. for $C_{24}H_{20}O_{11}$: C,59.5; H,4.1%).

The melting points of successive preparations varied considerably, from about 80 to 116 ; the product was apparently a mixture, the proportions of the constituents varying with the precise reaction conditions. Fractional crystallisation gave a main product (1) of m.pt. about 146° (dec.), a

second product of m.pt.160-165°, both soluble in alcohol; and a third, sparingly soluble in alcohol, recrystallised from glacial acetic acid to m.pt. about 228°. None of the products could be obtained with sharp melting point, even on repeated recrystallisation.

The substance (1) of m.pt.146°, on heating at 150° yielded a product, crystallising in colourless needles from alcohol, m.pt.159-162°. Substance 1 dissolved on heating in toluene, and separated as amorphous granules from the hot solvent. These on recrystallisation from alcohol also separated as colourless needles, m.pt.159-162°. Heating substance (1) at 220° produced a colourless substance, recrystallising from alcohol to m.pt.230-240°.

Substance (1) on heating with acetic anhydride alone gave a product melting at 140°; apparently the acetic anhydride merely behaved as a solvent, although possibly dehydration may have taken place. Heating with acetic anhydride and sodium acetate yielded a new derivative, m.pt. 258°, believed to be pentaacetylanhydrohaematoxylone. (Found: C,61.3; H,4.0. $C_{26}H_{20}O_{11}$ requires C,61.3; H,3.9%).

Anhydrohaematoxylone. Pentaacetylanhydrohaematoxylone (3.5 g.) was mixed with water (10 c.c.) and alcohol (10 c.c.), and 40% w/v sodium hydroxide (10 c.c.) added. The mixture rapidly became warm and the acetyl product dissolved; after

warming on the water bath for a short time the solution was cooled and acidified with hydrochloric acid, when a gelatinous precipitate separated; this was extracted with ether, which on evaporation left a resinous substance, insoluble in water, but soluble in alcohol; the alcoholic solution, on addition of water and spontaneous evaporation deposited dark flakes (1.7 g.). These were very soluble in most hydrophilic organic solvents, but the solution in dioxan gradually deposited hard sandy yellowish-grey crystals, which on heating slowly darkened in colour from about 80° to 300°, when they became almost black, but did not melt below 360°. (Found: C,65.1; H,3.4. $C_{16}H_{10}O_6$ requires C,64.5; H,3.4%). The product yielded a red azo dye with benzenediazonium chloride, both in aqueous alcohol and aqueous dioxan, and there was no evolution of nitrogen in this reaction. The substance was, therefore, quite unlike haematoxylin, and there seems no reason to doubt that it was the expected substance anhydrohaematoxylone.

The same substance was obtained on alkaline hydrolysis of the original product of oxidation (m.pt.ca.110°) of pentaacetylhaematoxylin with chromic acid.

Haematein Lakes.

The production of haematein lakes "in substance" (i.e.

as distinct from their formation on the fibre) was investigated by Desai (Ph.D. Thesis, Glasgow, 1948, 209), who found that haematein reacted with chromic chloride in alcohol solution to yield a purple-coloured lake. The low solubility of haematein makes purification of the lakes difficult. It is readily soluble only in pyridine, in which chromic salts are insoluble.

A haematein-chromium lake may be prepared by the reaction of haematoxylin with chromates; presumably oxidation to haematein takes place, followed by lake formation between this and the newly generated chromium salts. Sufficient chromate must be used to oxidise the haematoxylin, this being an excess over that required for lake formation, e.g. using potassium dichromate -

$$\underset{294}{K_2Cr_2O_7} \longrightarrow K_2O + Cr_2O_3 + O_3 = 3\ \underset{960}{C_{16}H_{14}O_6 \cdot H_2O}$$

i.e. two atoms of chromium are present for every three molecules of haematoxylin, whereas the lake formed, on analysis, appears to have one atom of chromium combined with two molecules of haematein. It is blue in colour, sparingly soluble in water when freshly prepared, but very insoluble once dried. Even the freshly prepared lake shows no substantivity for wool.

Reaction of Haematoxylin with Dichromate.

Haematoxylin (10 g.) was dissolved in water (500 c.c.). Potassium dichromate (3 g.) was separately dissolved in water (100 c.c.). These solutions were cooled, the dichromate solution slowly added to the haematoxylin, and the mixture heated to boiling point. Ammonia (10 c.c., S.G.0.88) was added, followed by active carbon and kieselguhr, and the solution filtered. The lake was precipitated by addition of 20% acetic acid (40 c.c.). After filtration it was washed well with water, dried and ground to powder. Yield - 5 g.

Chromium was estimated in the lake, after drying it for several hours at 100°C., by incineration and weighing the residual chromic oxide. (Found: Cr,9.27,9.30%. $(C_{16}H_{12}O_6)_2Cr$ requires Cr,8.4%; $(C_{16}H_{12}O_6)_3Cr_2$ requires Cr,10.9%).

Reaction of Haematein with Chromium Acetate.

The preparation of haematein-chromium lakes from haematein and chromium acetate depends on the following - (a) Freshly prepared (amorphous) haematein is moderately soluble in water. (b) Chromium hydroxide is not precipitated by alkali from chromium acetate solution unless it has previously been boiled with mineral acid. Haematein was prepared in alkaline solution by oxidation of haematoxylin

with alkaline peroxide. The solution was buffered by addition of ammonium sulphate, and chromium acetate solution added. The solution was heated to boiling and acidified with acetic acid to precipitate the lake.

(1) Haematoxylin (1 g.) dissolved in water (50 c.c.), sodium hydroxide (1.5 c.c. of 40% solution) and hydrogen peroxide (3.5 c.c. of 10 vol.) were mixed, then ammonium sulphate (1 g.) and chromium acetate(0.25 g.)dissolved in water (10 c.c.). The lake precipitated on heating and acidifying was brownish in colour and yielded traces of haematein on extraction with methanol.

(2) Haematoxylin (1 g.) oxidised as above and chromium acetate (1 g.) yielded 1.35 g. of black lake.

(3) Haematoxylin (1 g.) and chromium acetate (5 g.) by the same procedure yielded 3 g. of purplish-coloured lake, much lighter in colour than No.2. The yield is not accounted for by the quantities of haematein and chromium alone, and this lake must contain co-ordinated acetate ion.

It seems probable that the composition of the chromium lakes will vary, depending on the precise conditions of preparation. A certain minimum proportion of chromium is required, probably one atom of chromium to two molecules of haematein.

Test Patterns - Wool

These were prepared by cutting flannel pieces to weigh 5 g. each. Before mordanting or dyeing these were thoroughly scoured with warm water containing a little "Teepol", and washed with clean warm water until free from detergent.

Mordanting Procedure.

The standard chrome mordanted test pieces were prepared as follows:-

Potassium dichromate (3 g.) was dissolved in 100 c.c. hot water and added to 2 litres cold water in a stainless steel container. Twenty washed pieces of prepared wool (= 100 g. original wool flannel) were added and thoroughly stirred. A solution of tartaric acid (6 g.) in warm water (100 c.c.) was added, and the solution again stirred. It was heated to boiling point in approximately half an hour on a gas ring, then boiled gently for one hour. Stirring was continued throughout, with especial care during the first half hour when heating to the boil. The volume was kept approximately constant by addition of hot water. The mordanted pieces were washed with cold water, and stored under water in a stoppered glass bottle.

Dyeing Procedure.

Mordanted wool patterns, original weight 5 g. each, were dyed in stainless steel beakers heated directly over a gas ring in the Longclose apparatus. The weighed quantity of dyestuff was added to 350 c.c. cold water in a stainless beaker, and stirred to dissolve as far as possible before introducing one piece of mordanted wool. The dyebath temperature was raised to boiling point with constant stirring, and boiling continued for one hour, stirring frequently. The dyed pieces were cooled under the cold water tap, and rinsed several times in cold water to remove loose dye before drying and ironing.

Fastness to Light.

Newsome (Dyer, 1951, 105, 94) states that logwood blacks cannot be satisfactorily tested for fastness to light by exposure in the Fadeometer, such exposure giving considerably higher fastness figures than sunlight exposures. For this reason, all patterns to be tested for fastness to light were sent to Jamaica, by arrangement with the West Indies Chemical Works, Ltd., of Manchester and Spanish Town, each series being accompanied by a set of the standard patterns for light-fastness tests adopted by the Society of Dyers and Colourists. Exposure was normally carried on for 500 hours, one-third of

each pattern being covered from the beginning, and two-thirds after 250 hours. Where marked fading on a normal logwood-dyed pattern, e.g. wool dyed with 10% logwood crystals "ZA" on reduced chrome mordant, did not occur in 500 hours, due to unfavourable weather conditions, a further period of exposure was given, sufficient to produce definite fading on this pattern. Fastness to light was then assessed on the return of the patterns here, by comparison with the accompanying standards.

CONCLUSIONS

(1) Haematoxylin is readily oxidised to the dyestuff haematein, which in turn is itself rather easily oxidised, the products being valueless as colouring matters. Diazonium salts oxidise haematoxylin to haematein, and cause degradation of haematein; it is therefore not possible to convert these substances to azo dyes in this way. Similarly, nitroso-compounds oxidise haematoxylin to haematein, but do not form azines. The sensitivity to oxidising agents makes it impracticable to form halogen-derivatives directly, but these can be prepared by reaction of halogen with acetylated haematoxylin, followed by hydrolysis. Halogen-substituted derivatives of haematein have dyeing and light-fastness properties similar to those of haematein itself.

(2) Partial methylation of the phenolic hydroxyl groups of haematoxylin produces uncharacterised amorphous substances, probably mixtures, which appear to yield analogous haematein derivatives; similar products are obtained on partial methylation of haematein. None of these substances gives satisfactory dyeings, the power of combining with a mordant being seriously impaired. On the other hand, when the alcoholic hydroxyl group alone is methylated (by an indirect method), the dyeing properties are not affected, but there is no change in light-fastness.

(3) Enlargement of the molecule by condensation with formaldehyde and other aldehydes invariably reduces the tinctorial power, usually to no more than one-third of that of haematein itself; there is little effect on light-fastness when compared at similar depths of shade. Condensation with benzenesulphinic acid apparently yields haematoxylin phenyl sulphone, the oxidation product of which is similar in tinctorial and light-fastness properties to the aldehyde condensation products.

(4) Haematoxylin can be converted via its acetyl derivative to the oxidation product anhydrohaematoxylone, which is a derivative of catechol and ß-naphthol, capable of coupling with diazonium salts to form azo-dyes, but is not itself a dye.

Abbreviations for Titles of Journals

Ann.	Annalen der Chemie.
Ann.Chim.	Annales de Chimie et de Physique.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Chem.Zeit.	Chemische Zeitung.
Dyer.	The Dyer, Textile Printer, Bleacher and Finisher.
J.C.S.	Journal of the Chemical Society.
J.pr.Chem.	Journal für praktische Chemie.
J.S.D.C.	Journal of the Society of Dyers and Colourists.
Monatsh.	Monatshefte für Chemie.
Proc.C.S.	Proceedings of the Chemical Society.
Schweitz.polyt.Zeitsch.	Schweizerische polytechnische Zeitschrift.

Work of Reference

Ullman	Ullman's "Enzyclopaedia der technischen Chemie", Edn.II.

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A P P E N D I X

List of Patterns and Light-fastness Assessments

All patterns except those in Section III were mordanted before dyeing with 3% potassium dichromate and 6% tartaric acid; in Section III no mordant was used.

Numbers in Column 1 refer to the pattern card at the end of this thesis.

Numbers in Column 2 refer to the text.

Light-fastness assessments in Column 5 are according to the scale of the Society of Dyers and Colourists.

Section I

Haematein and "Hematine Crystals ZA"

No	Page	Dye		Colour	Light-fastness
1	37	1%	Haematein	Blue	4
2	37	2%	"	Blue-black	4
3	37	3%	"	Black	5
4	39	10%	"	Dead black	7-8
5	37	10%	"ZA"	Black	5

Section II

Haematein and "ZA" ; CO_2 through dyebath

No	Page	Dye		Colour	Light-fastness
6	37	1%	Haematein	Blue	4
7	37	2%	"	Blue-black	4-5
8	37	3%	"	Black	5
9	37	4%	"	Black	5-6
10	37	5%	"	Deep black	5-6
11	37	6%	"	Deep black	6
12	37	10%	"	Dead black	8
13	37	10%	"ZA"	Black	5
14	37	20%	"	Dead black	5-6
15	37	40%	"	Dead black	7

Section III

Haematein and partially methylated haematein without mordant

No	Page	Dye		Colour	Light-fastness
16	39	10%	Haematein	Red-brown	1
17	46	10%	Haematein methylated with diazomethane	Fawn	1
18	46	20%	Haematoxylin, methylated with Me_2SO_4 and KOH, and oxidised in dyebath with H_2O_2	Fawn-brown	1

Section IV

Partially methylated haematein

No	Page	Dye		Colour	Light-fastness
19	46	10%	Haematein, methylated with diazomethane	Red-violet	1
20	56	1%	11-O-Methylhaematein	Blue	3
21	56	3%	"	Black	5

Section V

Halogen derivatives

No	Page	Dye		Colour	Light-fastness
22	50	1%	Bromohaematein	Blue	4
23	50	2%	"	Blue-black	4-5
24	50	3%	"	Black	5
25	50	1%	Dibromohaematein	Blue	2-3
26	50	2%	"	Blue-black	4
27	50	3%	"	Blue-black	5
28	50	1%	Chlorohaematein	Blue	3
29	50	2%	"	Blue-black	4
30	50	3%	"	Black	5
31	49	1%	Dralle's "Dibromohaematein"	Violet	2
32	49	3%	" "	Violet-black	5-6
33	24	1%	iso-Haematein Chloride	Reddish-violet	4-5
34	24	2%	" "	Violet-black	5

Section VI

Aldehyde condensation products

No	Page	Dye		Colour	Light-fastness
35	58	3%	Methylene Haematein	Weak blue	2
36	58	10%	" "	Black	5-6
37	59	10%	Benzalhaematein	Black	5-6
38	59	10%	m-Nitrobenzalhaematein	Black	5-6
39	59	10%	p-Nitrobenzalhaematein	Black	5-6
40	59	10%	Sodium Benzalhaematein Sulphonate	Grey-violet	3
41	60	10%	Sodium Haematein-methane sulphonate	Black	6

Section VII

Miscellaneous haematein derivatives

No	Page	Dye		Colour	Light-fastness
42	57	3%	Haematoxylin/H_2SO_4 product	Reddish-pink	1
43	57	3%	No. 42 oxidised	Pale blue	1
44	58	1%	Soluble "Haematein Phenyl Sulphone"	Pale blue	2
45	58	10%	Soluble "Haematein Phenyl Sulphone"	Black	5-6
46	58	1%	Insoluble "Haematein Phenyl Sulphone"	Violet	3
47	68	1%	Benzeneazo-anhydro-haematoxylone	Dull red	2

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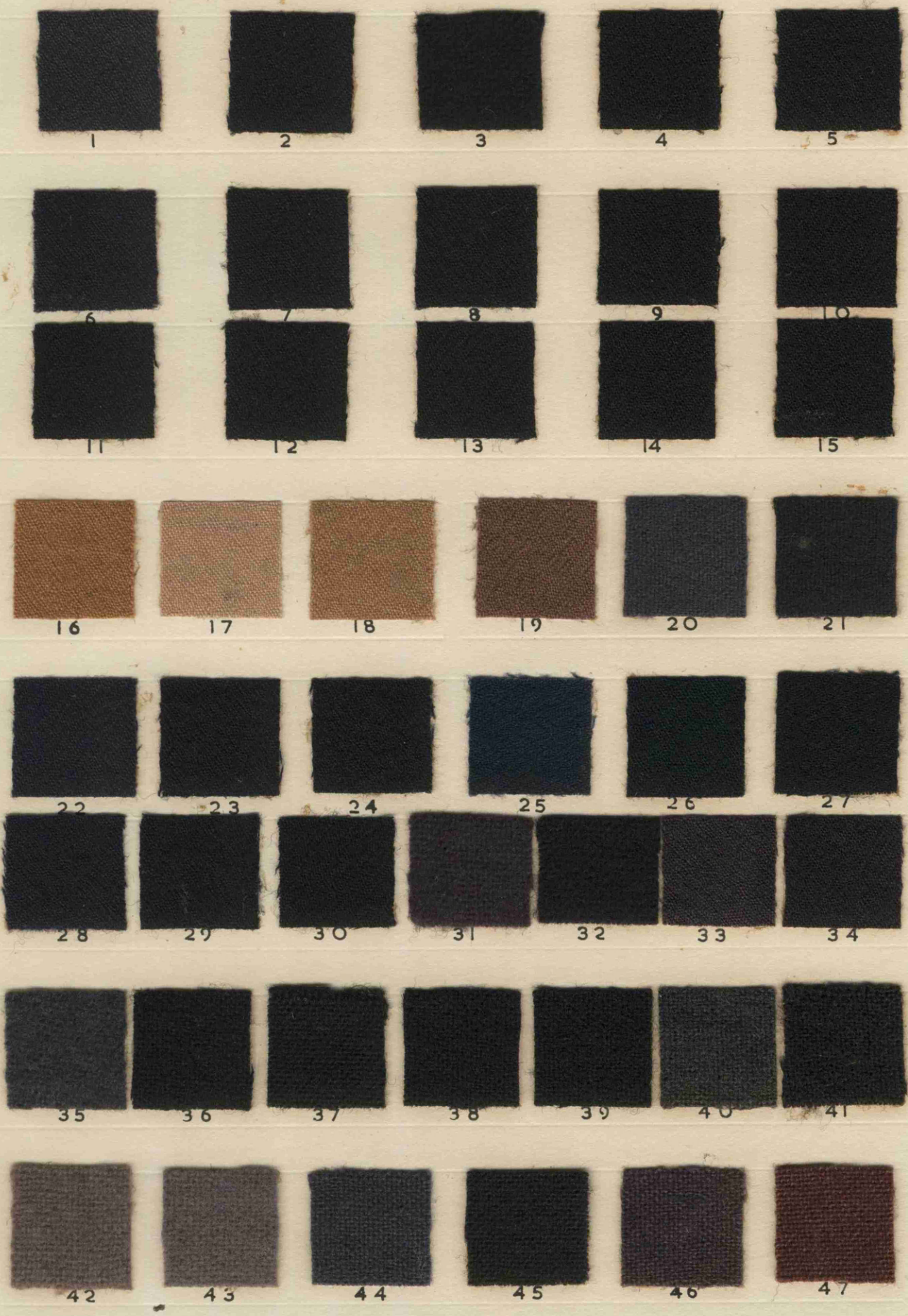
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