LXXXIV.—*The Colouring and other Principles contained in Chay Root.* Part II.

By A. G. PERKIN and J. J. HUMMEL.

THE results of a previous investigation of this dye stuff (Trans., 1893, **63**, 1160) showed that its tinctorial properties were due to the fact that it contained both alizarin and its glucoside, ruberythric acid, and that in this and other respects it bore a somewhat close resemblance to madder. Special interest, however, lay in the fact that it contained over 1 per cent. of a mixture of yellow substances soluble in baryta water, which is a large quantity compared with the amounts of similar products known to exist in madder, mang-koudu (*Morinda umbellata*, Trans., 1894, **65**, 851), and other allied roots.

The isolation of the principal constituents of chay root was effected by four methods, namely, extraction with alcohol, alum solution, dilute sulphurous acid, and lime water. The product thus obtained consisted of cane sugar, chlororubin, ruberythric acid, alizarin, two dimethylic ethers of anthragallol, an alizarin methyl

* Nitrobenzene treated with sulphuric acid, and reduced with zinc dust (without salicylic acid) gave, in two experiments, N 11·09 and 11·33. When salicylic acid also was used, as in the full Jodlbauer method, the more concordant and accurate results above given were obtained.

† Zinc reduction only, without the use of salicylic acid, gave nitrogen only 20·06, 20·12, and 20·18.

‡ Zinc reduction only, without salicylic acid, gave nitrogen only, 16·27 and 16·27. The substitution of sugar for salicylic acid gave 17·93 and 17·93—a fact interesting in the light of some subsequent results.

§ Zinc reduction only, without salicylic acid, gave also nitrogen, 4·85.

ether, and metahydroxyanthraquinone. In addition to these, there were indications of the presence of at least two other substances, but in quantity too small to admit of their identification, and it seemed evident that this could only be accomplished by the examination of a very large quantity of raw material.

Application was therefore made to the Imperial Institute, and our thanks are due to the authorities of this Institution, who very readily supplied us with 2 cwts. of the root for further examination. The results now obtained, whilst corroborating those of the former communication, have shown the existence in this dye stuff of two new substances which have been examined and identified. The details of their isolation are given in the experimental portion of this paper.

Substance of the formula $C_{15}H_{10}O_4$.—This was obtained as long, orange-yellow needles, melting at 232° ; it sublimes partially at higher temperatures. A characteristic property of this substance, when compared with those accompanying it in chay root, is that its potassium and ammonium derivatives are readily soluble in ethylic or methylic alcohols, but insoluble in cold isobutylic alcohol. They crystallise in fine, garnet-red needles, the ammonium derivative being decomposed on exposure to air with evolution of ammonia. By its reaction with zinc dust in alkaline solution, it appeared to be an anthraquinone or allied compound. When heated with hydrochloric acid at 180° , it yielded a yellow, crystalline colouring matter of the formula $C_{14}H_8O_4$, dissolving in alkalis with a blue-green coloration, and yielding a diacetyl derivative, $C_{14}H_6O_4(C_2H_3O)_2$, which melted at 206° . This substance was found to be identical with the *hystazarin* of Liebermann and Schoeller (*Ber.*, 1888, **21**, 2501),

which is obtained, together with alizarin, by the action of phthalic anhydride on catechol in the presence of sulphuric acid. Its dimethylic ether has recently been obtained by heating 3:4-dimethoxy-orthobenzoylbenzoic acid with sulphuric acid (Lagodzinski, *Ber.*, 1895, **28**, 116). The first-mentioned authors state that, when heated, hystazarin darkens at 260° without melting. A darkening effect was certainly observed at this temperature, but this was evidently due to the action of the alkali of the glass on a trace of sublimed substance surrounding the product, for, on heating to 316° , it was still unmelted, and on inverting the tube the original product can be recovered with its yellow colour unchanged. Examination by Zeisel's method showed

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readily decomposed, and this accounts for its not being produced by the usual methods.

During this investigation, metahydroxyanthraquinone was obtained in larger amount than could be accounted for on the supposition that it had been produced during the decomposition of the ruberythric acid by the boiling lime water, a point previously discussed, and it must therefore be considered to exist as such in the root.

It is probable that those substances which are extracted by means of dilute sulphurous acid are present in the form of glucosides, though it has already been shown that these also exist to some extent in the free state. On the other hand, those which are only obtained by means of lime water, namely, metahydroxyanthraquinone and hystazarin monomethyl ether, are present in the free state only in the root.

EXPERIMENTAL PART.

The extraction of the root was effected as before by means of dilute sulphurous acid and lime water. In consequence of the difficulty of manipulating such large quantities of raw material, this portion of the work was kindly undertaken for us by Messrs. Hirst, Brooke, and Hirst, of Leeds, to whom our best thanks are due. From the "green alizarin" thus obtained, the mixed yellow substances were isolated in the laboratory in the usual manner by extraction with toluene.

Extraction of Chay Root with Lime Water.

The finely-ground, crude product thus obtained was digested as usual for several hours with boiling toluene and filtered. On standing, the filtrate deposited an orange-yellow substance, which was collected apart, a point which was not previously taken advantage of, but which has now been found to be of material advantage in separating the mixed substances. This substance was found to consist entirely of metahydroxyanthraquinone and anthragallol dimethyl ether (*B*), m. p. 225—227°, which could be readily separated, owing to the fact that the former alone yields an ammonium derivative, sparingly soluble in alcohol. In this manner, about 95 per cent. of the metahydroxyanthraquinone contained in the lime water extract can be removed from the mixture, owing to its sparing solubility in toluene. A considerable quantity was thus obtained.

The toluene mother liquors were extracted with dilute alkali, the alkaline solution neutralised with acid, and the yellow precipitate collected, washed, and dried. The product was dissolved in boiling alcohol, and, after cooling the crystalline matter which had deposited,

was washed with alcohol and dried. It consisted of two substances, which could be readily separated, owing to the fact that when their solution in hot isobutylic alcohol is treated with ammonia only one is precipitated on cooling in the form of an ammonium derivative; this was collected, washed with isobutylic alcohol, decomposed with acid, and purified by crystallisation from alcohol.

0.1325 gave 0.3452 CO_2 and 0.0468 H_2O . $\text{C} = 71.05$; $\text{H} = 3.91$.

$\text{C}_{15}\text{H}_{10}\text{O}_4$ requires $\text{C} = 70.86$; $\text{H} = 3.93$ per cent.

It appears as a glistening mass of long, orange-yellow needles, sparingly soluble in alcohol; it melts at 232° and sublimes at higher temperatures, undergoing partial decomposition. Dilute alkalis dissolve it, forming crimson coloured solutions, which, when boiled with zinc dust, become brown-orange, regaining their original tint on exposure to air. Like the ammonium derivative, the potassium compound is readily obtained in a crystalline condition by adding alcoholic potash to a solution of the substance in isobutylic alcohol. Both appear as minute, garnet-coloured needles, the former, on exposure to air, being decomposed with evolution of ammonia. The ammonium derivative is readily soluble in ordinary alcohol, a property which distinguishes the substance $\text{C}_{15}\text{H}_{10}\text{O}_4$ from anthragallol dimethyl ether (A), melting at 209° , and from alizarin methyl ether. It does not dye with mordants.

Action of Hydrochloric and Sulphuric acids.—As the substance was suspected to contain a methoxy-group, it was heated with fuming hydrochloric acid in a sealed tube at 180° for two hours. After cooling, the tube was found to contain very minute needles, considerably smaller than those of the original substance, and moreover of a decided yellow colour, which distinguished them from those of alizarin or anthragallol, for these, when produced by the decomposition of their methylic ethers in this same way, have always a red-orange tint. The substance was collected and purified by crystallisation from nitrobenzene.

0.1072 gave 0.2749 CO_2 and 0.0350 H_2O . $\text{C} = 69.93$; $\text{H} = 3.62$.

$\text{C}_{14}\text{H}_8\text{O}_4$ requires $\text{C} = 70$; $\text{H} = 3.33$ per cent.

This substance formed a pale yellow mass of minute needles which did not melt below 316° , but when strongly heated, yielded a sublimate, leaving a carbonaceous residue. Dilute alkalis dissolved it with a blue-green coloration, and these solutions when treated with lime or baryta water, yielded violet, insoluble precipitates. It dyes mordanted calico with difficulty, giving pale shades similar to but somewhat redder than those obtained with anthragallol. In order to convert it into its acetyl derivative, it was boiled with acetic anhydride for three hours. The solution obtained was treated with

a little alcohol, and the crystalline mass deposited on cooling, collected and purified by crystallisation from alcohol. On analysis the following numbers were obtained.

0.1154 gave 0.2827 CO₂ and 0.0412 H₂O. C = 66.81; H = 3.96.

C₁₄H₆O₄(C₂H₃O)₂ requires C = 66.66; H = 3.70.

It was, therefore, a diacetyl derivative. Thus obtained it forms almost colourless needles, melting at 206°, insoluble in cold dilute alkalis.

The formula and reactions of this substance indicated that it was a hydroxyanthraquinone, and, since it was a dyestuff, that the two hydroxyls it contained were in the ortho-position relatively to one another. It was evidently neither alizarin nor quinizarin, but its properties agreed somewhat closely with those given for *hystazarin*,

Liebermann and Schoeller (*loc. cit.*). Since, however, there appeared to be some slight points of difference between this substance and the one described by these authors, a specimen of *hystazarin* was prepared from catechol and phthalic anhydride by the method given by them. As a result it was found to be identical with the substance C₁₄H₈O₄ in every respect; this fact is of interest, as *hystazarin* or its compounds have not hitherto been known to exist in plants. In order to determine the methoxy-group evidently present in the substance C₁₅H₁₀O₄, it was examined by Zeisel's method.

0.1310 gave 0.1130 AgI. Found CH₃ = 5.50 per cent.

C₁₄H₇O₃(OCH₃) requires CH₃ = 5.90 per cent.

The substance C₁₅H₁₀O₄ is therefore *hystazarin monomethyl ether*.

The ammoniacal isobutylic acid mother liquors from which the ammonium salt of *hystazarin methyl ether* had been deposited, were poured into water, neutralised with acid, and the alcohol boiled off. A lemon-yellow mass was thus obtained, which, after crystallisation from alcohol, was found to consist entirely of the anthragallol dimethyl ether (*B*), melting at 225—227°.

The alcoholic mother liquors (p. 820) obtained during the isolation of the two preceding substances were treated with water, and the small quantity of yellow precipitate thus obtained was collected, washed, and dried. A sample heated with sulphuric acid to 180° yielded no colouring matter, and it was therefore free from the substances described above. By crystallisation from cumene, a yellow

glistening mass of fine needles was obtained, which melted at about 270° , but not sharply, and even when further purified the product was not satisfactory in this respect. Analysis gave $C = 74.16$; $H = 3.6$ per cent., and since by fusion with alkali, a violet-coloured derivative was obtained, it appeared to be most probably meta-hydroxyanthraquinone contaminated with a trace of some other substance. What this foreign substance is, it was impossible to say. To determine the point, more of the substance would be required, and to obtain this it would be necessary to work with enormous quantities of raw material. On this account the labour involved would be too great to warrant its investigation.

Extraction by means of Aqueous Sulphurous Acid.

As previously shown, the mixed yellow substances obtained by extraction with sulphurous acid consisted of two anthragallol dimethyl ethers (*A* and *B*), melting at 209° and $225-227^{\circ}$ respectively—alizarin α -monomethyl ether, and the so-called resinous substance. The latter could be isolated by the method previously given, but having gained a better knowledge of the characteristic reactions of each constituent, a much more rapid method was now adopted for their separation.

The yellow mass was dissolved in boiling isobutylic alcohol, the hot solution carefully neutralised with ammonia, and the blood-red liquid thus obtained was allowed to stand some hours. The ammonium derivative which crystallised out, contained the whole of the anthragallol dimethyl ether (*A*, m. p. 209°), and the alizarin monomethyl ether, and this was collected, washed with a little of the alcohol, and strongly pressed; it was then treated with acid and the regenerated ethers separated by taking advantage of the well-marked difference of their solubilities in alcohol.

The ammoniacal filtrate, after neutralising with acid, was poured into water and the isobutylic acid boiled off; the yellow liquid, containing a somewhat resinous precipitate in suspension, was then rendered alkaline with ammonia, diluted with half its volume of methylated spirit, and treated with excess of baryta water. On cooling, the barium derivative of the so-called resinous substance separated, and was collected and washed with dilute alcohol. By neutralising the filtrate with acid, a crystalline, yellow precipitate was formed which consisted of almost chemically pure anthragallol dimethyl ether (*B*, m. p. $225-227^{\circ}$).

The barium precipitate suspended in water was neutralised with acid and the product collected, washed, and dried. It was then purified by dissolving it in alcohol, and adding a solution of lead

acetate, washing the precipitate with alcohol, and decomposing it with acetic acid. On crystallising it from hot alcohol, the product contained a trace of gelatinous substance, but this was removed by extraction with small quantities of hot methylic alcohol, and the residue was then crystallised from alcohol with the aid of animal charcoal. On analysis it gave the following numbers.

0.1210 gave 0.3003 CO_2 and 0.0443 H_2O . $\text{C} = 67.68$; $\text{H} = 4.06$.

$\text{C}_{16}\text{H}_{12}\text{O}_5$ requires $\text{C} = 67.60$; $\text{H} = 4.22$ per cent.

Thus obtained it consisted of a felted mass of minute orange-yellow needles, melting at $212\text{--}213^\circ$, and yielding at higher temperatures a sublimate of leaflets. It is readily soluble in alcohol and in acetic acid, sparingly in chloroform; it usually separates from the latter in nodules. Solutions of the alkalis and ammonia dissolve it with a blood-red coloration, but owing to their great solubility, these derivatives were not obtained in a crystalline condition. The barium and lead compounds, as shown above, were useful in the process of purification; the former is obtained as an amorphous red-violet powder, soluble in water, but insoluble in dilute alcohol; the latter as a scarlet precipitate insoluble in cold alcohol and readily decomposed by acetic acid. The red alkaline solutions, when boiled with zinc dust, give the usual reaction of an anthraquinone or allied compound, for they become orange, but regain their original colour on exposure to air.

The acetyl derivative of the substance $\text{C}_{16}\text{H}_{12}\text{O}_5$ was prepared by boiling it with acetic anhydride for three hours, and then adding a little alcohol. On cooling, a crystalline mass was obtained, which, after purification, appeared as orange-coloured leaflets, insoluble in cold alkalis, and melting at 160° . Owing to the small quantity obtained, it could not be analysed, but other results given below show it to be a *monacetyl* derivative. Since there was reason to suspect that the substance $\text{C}_{16}\text{H}_{12}\text{O}_5$ contained a methoxy-group, it was suspended in a little acetic acid and heated in a sealed tube at 180° for one hour with hydrochloric acid. There was thus obtained a glistening mass of red needles, which were collected, washed, dried, and purified by crystallisation from nitrobenzene with the aid of animal charcoal. On analysis, the following numbers were obtained.

0.0518 gave 0.1245 CO_2 and 0.0170 H_2O . $\text{C} = 65.54$; $\text{H} = 3.64$.

$\text{C}_{14}\text{H}_4\text{O}_5$ requires $\text{C} = 65.62$; $\text{H} = 3.13$ per cent.

It dissolved in solutions of the alkali hydrates with a green coloration, and had the reactions of anthragallol; its identity with the latter was proved by the melting point of its acetyl derivative, $181\text{--}182^\circ$. To determine the methoxy-groups contained in the substance, it was examined by Zeisel's method.

0.1071 gave 0.1652 AgI. $\text{CH}_3 = 9.85$ per cent.

$\text{C}_{14}\text{H}_6\text{O}_5(\text{OCH}_3)_2$ requires $\text{CH}_3 = 10.56$ per cent.

This shows, therefore, that it is a *dimethyl ether of anthragallol*. It

Lime Water Extract of Chay Root.

Sulphurous acid Extract.

is interesting to find that the three possible substances of this composition exist in chay root. Apart from their melting points and those of their acetyl derivatives, their characteristic distinctions are, that whereas (A) and (C) form barium derivatives insoluble in dilute alcohol and lead salts, insoluble in cold alcohol, (A) alone yields an ammonium derivative, insoluble in cold isobutylic alcohol. The analogous salts of (B), on the other hand, are readily soluble in these liquids.

The methods employed for the separation of the yellow substances in chay root, soluble in baryta water, being somewhat intricate, the tables on p. 825 are appended with a view to explain the course pursued more clearly.

*Clothworkers' Research Laboratory,
Dyeing Department,
Yorkshire College.*