LXXV.—*The Colouring Principles of Ventilago Madraspatana.*

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Ventilago madraspatana is a large, climbing shrub, belonging to the order Rhamnaceæ, the root-bark of which furnishes a dye-stuff much valued in Southern India. It is very common in the Western Peninsula from the Konkan southwards, as well as in Ceylon and in Burma, and, according to Liotard, it is largely collected in Mysore at certain

periods of the year and exported to other districts of India. The annual production is given as 1—3 tons, its price being variously stated as $1\frac{1}{2}$ — $7\frac{1}{2}d.$ per lb.

The following are a few of its Indian vernacular names: pitti (*Hindi*); raktapita (*Bengali*); pappili-chakka, suralpattai (*Tamil*); poplichukai (*Kan.*); lokandi, kanwail (*Bomb.*).

Our attention was first attracted to it under the name of souroul-puttay, in Gouffroy's "L'art de la Teinture des Laines," 1849, p. 539, where it is mentioned as a dye-stuff yielding fast colours, namely violet, dull red, and black. The identity of this product with *Ventilago madraspatana* was established by correspondence with the authorities of the Imperial Institute, to whom we are also indebted for a supply of 10 lbs. of the root-bark with which the experimental work here recorded has been carried out.

The root-bark appears as dark, purplish-brown scales, ribbons, or filaments, the dust from which when it is ground to powder, irritates the throat in a marked manner. When treated with boiling water or alcohol, it gives a red solution, which, on the addition of caustic alkali, changes to a deep crimson.

Many writers on the economic products of India, as Bidie, Liottard, Wardle, and others, refer to this dye-stuff, but we find no record that any previous chemical examination of it has been made; at most, the actions of various chemical agents, metallic salt solutions, &c., on its aqueous decoction, are referred to, e.g., by Gouffroy (*loc. cit.*), and also by Dymock, Warden, and Hooper in the *Pharmacographia Indica*, i, 355, the last named authors hazarding the suggestion that the colouring matter is probably one of the derivatives of anthracene.

The present examination is of interest as showing that *Ventilago madraspatana* contains a colouring matter differing from all others at present known.

Summary of Results.

On treating this dye-stuff with carbon bisulphide, five crystalline substances are extracted, together with a wax and a resinous colouring matter. The separation of these from one another by fractional crystallisation and other means proved to be a matter of considerable difficulty, the details of which will be found in the experimental portion of this paper.

1. *A Substance of the Formula $C_{16}H_{12}O_5$.*—This crystallises in long, orange-red needles melting at 200° ; it sublimes at higher temperatures, partially carbonising. Its alkaline solutions have a purple tint, and the corresponding salts can be obtained in the form of violet-coloured needles sparingly soluble in alcohol. It yields a diacetyl

compound, $C_{16}H_{10}O_5(C_2H_5O)_2$, in long, yellow needles melting at $185-186^\circ$, and a mononitro-compound, $C_{16}H_{11}O_5 \cdot NO_2$, melting at $215-217^\circ$. When distilled with zinc dust, a hydrocarbon is obtained melting at 203° , evidently α -methylantracene, and its behaviour with zinc dust in alkaline solution shows it to be an α -methyl-anthraquinone-derivative. Treatment with hydriodic acid showed that it contained one methoxy-group, a pale yellow, crystalline reduction product, probably an anthranol derivative, being formed at the same time; the quantity thus obtained was insufficient for analysis. The substance $C_{16}H_{12}O_5$ is therefore a *monomethyl ether* of a *trihydroxy- α -methylanthraquinone*. It does not dye mordanted fibre; when heated with sulphuric acid to 160° it yields a substance of the formula $C_{15}H_{10}O_5$, crystallising in orange-red needles melting at 254° . Although only a small quantity of this compound has as yet been obtained, owing to lack of material, it is evidently a *trihydroxy- α -methylanthraquinone*, the reactions of which, so far as they could be studied, being almost identical with those of emodin.

The substance $C_{16}H_{12}O_5$ yields a nitro-compound, $C_{16}H_9O_5(NO_2)_4$, which in appearance and properties closely resembles tetranitro-chrysophanic acid, $C_{15}H_6O_4(NO_2)_4$; when heated with sulphuric acid, it yields a new product soluble in alkalis with a violet coloration, a property possessed by numerous nitroanthraquinone derivatives. If the substance $C_{16}H_{12}O_5$ be an emodin methyl ether, it would be expected that emodin itself, when treated in a similar way, should yield a tetranitro-compound. Experiment proved this to be the case, the product obtained, evidently a *tetranitroemodin*, closely resembling the above compound $C_{16}H_9O_5(NO_2)_4$, which should be its methyl ether. This, together with the general similarity in appearance, properties, and melting point between emodin from *Rhamnus frangula*, and the substance $C_{15}H_{10}O_5$, both also derivatives of α -methylantracene, seems to point almost conclusively to their identity. Until, however, a comparison can be made of the properties and melting points of their acetyl derivatives, this point cannot be absolutely decided, although in this paper we shall regard the substance $C_{16}H_{12}O_5$ as *emodin monomethyl ether*.*

2. *A Substance of the formula $C_{16}H_{14}O_4$ (A).*—This forms long, colourless needles, which decompose at about 260° before melting; it is soluble in alkaline solutions with a yellowish-brown coloration. It yields α -methylantracene, and what is probably a triacetyl compound, $C_{16}H_{11}O_4(C_2H_5O)_3$. On gentle oxidation with chromic acid, it is converted into the previously described emodin methyl ether, and the same reaction takes place when its alkaline solution is oxidised

* It is probable that several months will elapse before we receive a fresh supply of the *Ventilago madraspatana*, so as to enable us to confirm our opinion.

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with hydrogen peroxide. Boiling nitric acid (sp. gr. 1.5) converts it into the tetranitro-compound, $C_{16}H_3O_5(NO_2)_4$. The substance $C_{16}H_{14}O_4$ (A) appears, therefore, to be a *trihydroxy- α -methylantranole monomethyl ether*. As an alternative constitution for this substance, it might be considered as a hydranthrone derivative, thus:

Anthranole.

Hydranthrone.

but the analysis of its acetyl derivative shows it to be a trihydroxy-rather than a dihydroxy-derivative.

3. *A Substance of the Formula $C_{16}H_{14}O_4$ (B).*—This crystallises in pale yellow needles melting at 173° . With acetic anhydride, it yields what is probably a triacetyl compound melting at $227-229^\circ$, the alcoholic solution of which has a strong blue fluorescence. It dissolves in alkalis forming yellowish-brown solutions which on long exposure to air become red, and on treatment with acid yield a precipitate of emodin methyl ether. Oxidation with chromic acid gives a similar result, whilst with nitric acid the tetranitro-derivative, $C_{16}H_3O_5(NO_2)_4$, is formed, identical with that obtained from the emodin methyl ether by similar means. The substance $C_{16}H_{14}O_4$ should therefore represent the second *trihydroxy- α -methylantranole monomethyl ether* capable of yielding the emodin methyl ether by oxidation.

The only compound of the anthracene group previously isolated from natural sources, and which can be considered as nearly related to the substances $C_{16}H_{14}O_4$ (A and B), is the chrysarobin obtained from Goa powder, and examined by Liebermann and Seidler (*Annalen*, **212**, 29). This, when oxidised in alkaline solution, yields chrysophanic acid, dihydroxymethylanthraquinone, the constitution assigned to it being $O[CH < \begin{smallmatrix} C_6H_3(OH) \\ C_6H_2(CH_3)(OH) \end{smallmatrix} > CH \cdot OH]_2$.

If the trihydroxy- α -methylantraquinone methyl ether here described is an emodin methyl ether, these results are of considerable interest, for, as is well known, emodin is considered to be a hydroxychrysophanic acid. It is remarkable that the reduction products of these two similarly constituted compounds should be the only ones of the anthraquinone group known to exist in a natural condition. That the substances $C_{16}H_{14}O_4$ (A and B), however, have not the complicated

constitution assigned to chrysarobin is evident, for if formulæ explaining their reactions be constructed on similar lines, they should contain 3 per cent. less carbon than is shown by the analytical results.

The effect of the presence and absence of the quinone group on the colour of these substances is here well illustrated, for whilst $C_{16}H_{14}O_4$ (A) is colourless and $C_{16}H_{14}O_4$ (B) nearly so, the emodin methyl ether has a marked orange-red tint.

4. *A substance of the Formula $C_{16}H_8O_8$.*—This is an orange-red, crystalline powder, which, when heated, begins to darken at 260° , and melts and carbonises at 275 – 280° . It is distinguished from the preceding substances by its sparing solubility in most solvents. Solutions of the alkalis dissolve it with an orange-red coloration, and it yields an acetyl derivative, $C_{16}H_7O_8(C_2H_3O)$, which crystallises in yellow needles melting and decomposing at 216 – 220° . When heated with zinc dust, it yields a hydrocarbon, which is probably α -methyl-anthracene. Treated with hydriodic acid, it loses one methoxy-group, and at the same time a pale yellow, crystalline reduction product is formed, probably a hydranthrone derivative. Sulphuric acid at 160° converts it into what is probably a new colouring matter, evidently by elimination of methyl from the methoxy-group, and from this result it also appears that the hydroxy- and methoxy-groups are in the ortho position relatively to one another. The action of alkaline reducing agents is very interesting, for they change the orange-red solutions to yellow, but on exposure to air they become, first orange-red, and finally blue-violet, when they contain the alkali salt of a new colouring matter; this, although still most probably a methoxy-derivative, must, from its reactions, be distinct from the colouring matter produced by sulphuric acid at 160° . From its deep orange-red colour and other reactions, it appears to be an α -methyl-anthraquinone derivative, and if it has the formula $C_{16}H_8O_8$, and not a multiple of the same, it may be represented as $CH_3 \cdot C_{14}HO_4(O_2)''(OH) \cdot OCH_3$. The production also of a colouring matter from it by means of reducing agents, and subsequent oxidation, points to the presence of more than one quinone group in it. It might therefore belong to a class of compounds suggested by the following formula,

As no more than 1 gram of pure substance has been obtained from

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10 lbs. of the root-bark, it will be extremely difficult to thoroughly investigate the nature of this most interesting substance.

5. *A substance of the Formula $C_{17}H_{12}O_5$.*—This is a chocolate-coloured, crystalline powder. When treated with dilute alkali, it dissolves with a yellow coloration, but on exposure to air the solution deposits a blue, amorphous precipitate, and it therefore appears to contain in its molecule a reduced quinone group. The study of this substance will be continued when sufficient material is to hand.

6. *The Wax, $(C_9H_{16}O)_n$,* consists of nearly colourless, minute needles melting at 72° .

7. *The Colouring Matter* is a reddish-brown, brittle resin of the formula $C_{15}H_{14}O_6$, and, up to the present, has resisted all attempts to obtain it in a crystalline condition. It softens at about 100° , and melts at 100 — 110° . Dilute alkalis dissolve it with a purple-violet coloration, and the corresponding salts are obtained as violet, amorphous precipitates on adding common salt to these solutions. When distilled with zinc dust, it yields α -methylantracene, and when treated with zinc dust in alkaline solution, behaves as a derivative of methyl-anthraquinone. Nitric acid converts it into oxalic acid. On mordanted calico, it dyes shades which remind one somewhat of those given by brazilein, although the reds are much more purple in hue, and faster to boiling soap solution. From its nature and properties, it appears possible that it is allied to alkannin, $C_{15}H_{14}O_4$, the colouring matter of the roots of the *Anchusa tinctoria*, investigated, among others, by Liebermann and Romer (*Ber.*, 20, 2428). Alkannin is also of a resinous nature, is a derivative of α -methylantracene, and appears to contain two hydroxyl groups. It is possible, therefore, that the colouring matter of the *Ventilago madraspatana*, for which we propose the name *Ventilagin*, is represented by alkannin containing two additional hydroxyl groups. The investigation of this colouring matter will be continued when a further supply of raw material has been obtained.

EXPERIMENTAL PART.

250 grams of the coarsely-powdered root-bark was treated in the cold with 2 litres of carbon bisulphide for 48 hours, with occasional shaking, and, after removal of the extract, the residual root was twice treated in a similar manner, and the carbon bisulphide was distilled off from the deep brown liquid until there remained 200 c.c. of extract, which was then mixed with 50 c.c. of alcohol. The crystals which separated on cooling (Cryst. prod. A) were collected, and then washed with about 100 c.c. of alcohol; the washings, on being added to the mother liquor, caused a further crystalline precipitate after some

hours (Cryst. prod. B). It was evident that some separation of the constituents of the product had been effected in this way, for whereas the crystals first deposited were reddish-brown, the second crop was pale yellow. The filtrate, after standing for some days, frequently deposited a third fraction, which was usually added to the second. A quantitative estimation in this way gave 2·834 grams of crystalline product from 250 grams of root-bark or 1·13 per cent., and, as subsequent investigation showed, this represents approximately the amount present in the root. As stated in the introduction, this crude product consisted principally of four substances, the separation of which was most readily effected by the methods described in the following pages.

Substance of the Formula $C_{16}H_8O_8$.

The finely-powdered, "crystalline product, A," was extracted two or three times with small quantities of boiling benzene or carbon bisulphide, which left a small amount of a sparingly soluble residue; this was dissolved in a large quantity of boiling benzene, treated with animal charcoal, and filtered. On cooling, a finely divided, crystalline precipitate separated, and was further purified by a second treatment in a similar manner.

- I. 0·1062 gave 0·2277 CO_2 and 0·0295 H_2O . C = 58·45; H = 3·08.
 II. 0·1138 „ 0·2440 CO_2 and 0·0310 H_2O . C = 58·47; H = 3·02.
 III. 0·0825 „ 0·1775 CO_2 and 0·0235 H_2O . C = 58·66; H = 3·16.
 $C_{16}H_8O_8$ requires C = 58·5; H = 2·4 per cent.

The amount of this substance present in the dye-stuff is exceedingly small, not more than 1 gram of it having been hitherto obtained in the pure condition. It forms an orange-red, glistening powder, consisting of microscopic prisms, and when heated it begins to darken at 260°, and melts and carbonises at 275—280°. If heated rapidly between watch glasses, it yields a small quantity of a sublimate, which melts in a similar manner. It is almost insoluble in boiling alcohol, and but sparingly soluble in benzene, carbon bisulphide, and cumene, crystallising from the latter in orange-yellow needles. It was at first thought that dissolving it at the high boiling point of this liquid had effected decomposition, but this was negatived by the results of analysis III. Dilute alkalis, if cold, dissolve it very sparingly, more readily, however, if boiling, with formation of crimson-red solutions, from which the corresponding salts are thrown out as brownish-violet precipitates on adding excess of alkali. In baryta water it is insoluble. On boiling the alkaline solutions with zinc dust, pale orange-coloured liquids are obtained, which, on exposure to air, first become red, and then blue-violet; if acid is now added, claret-coloured flocks of a new colouring matter are precipitated

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On fusing the substance $C_{16}H_8O_8$ with potash, a blue-violet melt is obtained, from which, on neutralisation, a similar, though probably not identical, colouring matter is obtained. Distillation with zinc dust yielded a hydrocarbon crystallising in greenish leaflets; the quantity was too small for purification, but on oxidation it yielded, first, a quinone, crystallising from dilute acetic acid in colourless needles, and, finally, an acid soluble in dilute ammonia. This substance is believed to be α -methylantracene, not only on account of its behaviour, but also because this hydrocarbon appears to be the basis of the other principal substances described in this paper. It is but little attacked by nitric acid (sp. gr. 1.42) in the cold, but on heating it gives a beautiful, violet-red solution, which gradually passes to brown, and then to yellow. By this reaction, the compound, $C_{16}H_8O_8$, can be readily distinguished from all other substances found in the root-bark.

Action of Hydriodic Acid.—0.101 gram, heated with hydriodic acid in Zeisel's apparatus, gave 0.081 gram of $AgI = 4.57$ per cent. methyl groups.

$C_{16}H_8O_7 \cdot OCH_3$ requires 5.15 per cent. methyl groups.

The substance $C_{16}H_8O_8$ therefore contains one methoxy-group.

The residual hydriodic acid contained a nearly colourless, crystalline product in suspension, which was collected, washed, dried, and recrystallised from toluene. It dissolved in alkalis, forming brownish-yellow solutions which gradually oxidised on exposure to air, becoming of a dull, reddish-violet tint; it appeared therefore to be a hydranthrone or allied compound.

Cold sulphuric acid dissolves the substance $C_{16}H_8O_8$, forming a purple liquid resembling aqueous sodium anthrapurpurate. On heating to 160° this solution becomes deep blue-violet, and on adding water a new substance, evidently a colouring matter, is precipitated; this forms, with alkalis, an almost insoluble, purple-red compound. The above reaction is no doubt caused by the decomposition of the methoxy-group, and this result is interesting, showing, as it does, that the methoxy-group is in the ortho-position relatively to a hydroxyl group. This colouring matter (*b*) must not be confounded with (*a*) that produced by the reduction and oxidation of the substance $C_{16}H_8O_8$, as it differs from it in its sparing solubility in alkaline solutions. It is most probable that the colouring matter (*c*), produced by the action of fused alkali, is distinct, and forms a third, which should consist of (*a*) from which the methoxy-group has been removed.

Action of Acetic Anhydride.—When digested with acetic anhydride, the substance, $C_{16}H_8O_8$, dissolved only after prolonged boiling, and the solution thus formed was digested for four hours longer.

On cooling, a yellow, crystalline powder separated, which was washed with methylic alcohol and recrystallised from acetic acid.

0.1158 gave 0.2447 CO_2 and 0.0345 H_2O . $\text{C} = 57.8$; $\text{H} = 3.31$.

$\text{C}_{16}\text{H}_7\text{O}_8(\text{C}_2\text{H}_3\text{O})$ requires $\text{C} = 58.37$; $\text{H} = 2.70$ per cent.

$\text{C}_{16}\text{H}_6\text{O}_8(\text{C}_2\text{H}_3\text{O})_2$ „ $\text{C} = 58.25$; $\text{H} = 2.91$ „

$\text{C}_{16}\text{H}_5\text{O}_8(\text{C}_2\text{H}_3\text{O})_3$ „ $\text{C} = 58.15$; $\text{H} = 3.08$ „

The analytical numbers, therefore, are insufficient to decide whether it is a mono-, di-, or triacetyl compound, but from a consideration of the results obtained above it is evident that the substance $\text{C}_{16}\text{H}_8\text{O}_8$ is most probably $\text{CH}_3\cdot\text{C}_{14}\text{H}_2\text{O}_7\cdot\text{OCH}_3$, and accordingly it can, at most, form no higher derivative than a diacetyl compound. On the other hand, if this substance is represented by the formula $\text{C}_{16}\text{H}_8\text{O}_8$ and not a multiple of the same, it is highly possible that a hydrogen in one of the two side rings is not displaced, in which case a monacetyl derivative alone can exist.

That this substance is a monacetyl derivative appears to us most probable, in which case the formula of the substance $\text{C}_{16}\text{H}_8\text{O}_8$ might be written $\text{CH}_3\cdot\text{C}_{14}\text{HO}_4(\text{O}_2)''(\text{OH})\cdot\text{OCH}_3$. The acetyl compound forms lemon-yellow needles melting and decomposing at $216\text{--}220^\circ$, almost insoluble in boiling alcohol, but more soluble in acetic acid. Cold solutions of the alkali hydroxides do not dissolve it, but, on boiling, orange-red solutions are gradually formed.

The benzene extracts and mother liquors from the preparation of the previously described substance (p. 929) were boiled with animal charcoal and concentrated; on cooling, a crystalline product was deposited, which, on examination under the microscope, was seen to consist of thin leaflets interspersed with a few needles. On examination, however, it was found that the mixture was by no means so simple as appeared at first sight, crystallisation from carbon bisulphide giving four fractions having the respective melting points 180.5° , $167\text{--}172^\circ$, 163° , and 172° ; similar results were obtained with benzene, although under the microscope each fraction usually appeared homogeneous. Further crystallisations from the various solvents gradually raised the melting points of these fractions, but the labour and loss of product involved rendered it necessary to adopt some better means of separation. It was clear that at least two substances were present, as the portions having the higher melting point dissolved in cold sulphuric acid with a reddish-violet coloration, whilst those of the lower melting point gave a deep brown. Ultimately, by the use of two or three solvents, and after several months' labour, three principal products were isolated, two melting respectively at 200° and 173° , and a third decomposing at about 260° , before melting.

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Substance of the Formula $C_{16}H_{12}O_5$, m. p. 200° .

The mixed product obtained from the benzene extracts and mother liquors (p. 931) was crystallised from a large quantity of carbon bisulphide, and the product which melted at 183° was recrystallised from benzene, and the product twice crystallised from boiling acetone, and finally from isobutylic alcohol. There could be no doubt that this final product consisting of slender needles was a homogeneous substance, and this was further corroborated by the analysis of three distinct preparations.

0.1198 gave 0.2958 CO_2 and 0.0454 H_2O . C = 67.34; H = 4.21.

0.1139 „ 0.2811 „ „ 0.0435 „ C = 67.29; H = 4.24.

0.1180 „ 0.2922 „ „ 0.0480 „ C = 67.53; H = 4.52.

$C_{16}H_{12}O_5$ requires C = 67.6; H = 4.22 per cent.

It crystallises in long, glistening, orange-yellow, hair like needles melting at 200° , and at higher temperatures partially carbonising and yielding a sublimate of leaflets. It is sparingly soluble in alcohol, acetone, and isobutylic alcohol, more readily in benzene and carbon bisulphide. Solutions of the alkali hydroxides dissolve it, yielding red liquids, and the corresponding salts may be obtained in violet, microscopic needles by treating hot alcoholic solutions of the substance with alkali, and cooling. It is not affected by boiling barium hydroxide solution.

When distilled with zinc dust, a small quantity of greenish leaflets were obtained, which were proved to be α -methylantracene. Treated with zinc dust in alkaline solution, the original blood-red colour changes to orange, but on exposure to air the original tint returns, and it is probable, therefore, that the substance is a derivative of α -methylanthraquinone. It dissolves in sulphuric acid with a violet-red coloration, this reaction distinguishing it from the substances $C_{16}H_{14}O_4$ A and B described later.

Action of Acetic Anhydride.—The substance $C_{16}H_{12}O_5$, when boiled with a small quantity of acetic anhydride for six hours and the solution cooled, gave a mass of needles, which were washed with alcohol and recrystallised from the same solvent.

On analysis, the following numbers were obtained.

0.1078 gave 0.257 CO_2 and 0.0435 H_2O . C = 65.01; H = 4.48.

$C_{16}H_{10}O_5(C_2H_5O)_2$ requires C = 65.21; H = 4.34 per cent.

It was, therefore, a *diacetyl* derivative.

It crystallises in long, yellow needles melting at 185 – 186° , sparingly soluble in alcohol, readily in acetic acid. In cold alkaline solutions it is insoluble, but, on boiling, it is decomposed with formation of red solutions.

Action of Hydriodic acid.—From the formula of this substance, and the fact that it yielded only a diacetyl derivative, it appeared possible that it might contain a methoxy-group. It was, therefore, submitted to the action of hydriodic acid quantitatively by Zeisel's method.

0.1848 gave 0.1676 AgI. $\text{CH}_3\text{O} = 5.78$ per cent.

$\text{C}_{15}\text{H}_9\text{O}_5\text{OCH}_3$ contains 5.28 per cent.

The substance $\text{C}_{16}\text{H}_{12}\text{O}_5$ is, therefore, a *monomethylic ether* of a trihydroxy- α -methylantraquinone.

As the residual hydriodic acid contained some crystalline matter in suspension, it was diluted with water, and the solid collected, washed, dried, and purified by crystallisation from toluene, in which it was but sparingly soluble. It appeared as a pale yellow, crystalline powder, soluble in caustic soda with a brown coloration, which on exposure to air changed to purple. The quantity of this substance obtained was insufficient for analysis, but, judging by its properties, it is most probably a trihydroxy- α -methylantranole or hydranthrone. A somewhat similar product is obtained from the substance $\text{C}_{16}\text{H}_{12}\text{O}_5$ by digestion in acetic acid solution with fuming hydrochloric acid and tin. These products will be further investigated when more material is to hand.

Action of Sulphuric acid.—In order to decompose the methoxy-group of the substance $\text{C}_{16}\text{H}_{12}\text{O}_5$, it was heated with sulphuric acid at 160° for about a quarter of an hour, by which means the violet-red solution became considerably browner. It was then diluted, first with twice its volume of acetic acid, then with alcohol, and the small amount of black precipitate so formed was filtered off. To the hot filtrate, boiling water was then carefully added, so that on cooling a brownish, crystalline product was deposited; this was purified by crystallisation from benzene with the aid of animal charcoal.

0.0581 gave 0.1421 CO_2 and 0.022 H_2O . $\text{C} = 66.7$; $\text{H} = 4.20$.

$\text{C}_{15}\text{H}_{10}\text{O}_5$ requires $\text{C} = 66.66$; $\text{H} = 3.70$ per cent.

It forms long, orange-red needles somewhat resembling alizarin in appearance, melting at 254° , and at higher temperatures yielding a sublimate of needles. The small amount of substance available for analysis might perhaps throw some doubt on the trustworthiness of this result. On consideration, however, it is evident that the action of sulphuric acid on the substance $\text{C}_{16}\text{H}_{12}\text{O}_5$ at this temperature would most probably result either in the decomposition of the methoxy-group, or in the oxidation of the methyl group of the α -methylantraquinone with formation of a carboxylic acid. That the substance obtained cannot be the product of the latter action is evident, as in that case it would only contain 60 per cent. of carbon. It dissolves in alkalis with a crimson-red coloration, which, on treatment

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with zinc dust, becomes pale yellow, and, on exposure to air, regains its original tint. Its sulphuric acid solution is orange-red, changing to pale yellow when treated with a crystal of potassium nitrate.

The melting point and general actions of this trihydroxy- α -methyl-anthraquinone appeared exceedingly similar to those described for emodin, and in order to make a comparison a sample of crude emodin was obtained from Merck, of Darmstadt. This was purified by extracting with boiling toluene, treating the latter with dilute caustic soda solution, and precipitating the red aqueous liquid with acid. The orange-coloured precipitate was crystallised two or three times from acetic acid, and finally from benzene. As stated in the introduction, in general reactions, appearance, and melting point, no difference could be detected between emodin and the trihydroxy-methylanthraquinone above described. Moreover, an examination of their behaviour with boiling nitric acid (sp. gr. 1.5) resulted in both cases in the formation of a yellow, crystalline substance, probably a tetranitro-derivative. It is believed that when more material can be obtained, a comparison of the acetyl derivatives of these two substances will further confirm this identity.

Action of Nitric acid on the substance $C_{16}H_{11}O_5$.—It is not attacked by nitric acid (sp. gr. 1.42) in the cold, but on boiling it dissolves, forming a brownish-red solution, which, if rapidly cooled, deposits a crystalline, orange powder, consisting of microscopic, prismatic needles. These were collected, washed with nitric acid, then with water, and dried.

0.1410 gave 4.9 c.c. moist nitrogen at 22° and 756 mm. $N = 3.91$.

0.1132 „ 0.243 CO_2 and 0.0383 H_2O . $C = 58.54$; $H = 3.75$.

$C_{16}H_{11}O_5(NO_2)$ requires $C = 58.36$; $H = 3.34$; $N = 4.25$ per cent.

Mononitroemodin methyl ether forms a bright yellow mass, melting at 215 — 217° , which, when heated strongly, decomposes suddenly with emission of a cloud of black vapour. If suspended in water and treated with sodium amalgam, the original scarlet colour of the solution first formed passes to blue-violet, resembling that of sodium alizarate, and on adding acid brick-red flocks are precipitated, evidently an amido-compound. It dissolves in sulphuric acid with a bright red coloration, which, on heating, becomes dirty violet; the addition of water then throws down dark brown flocks, dissolving in alkali with a beautiful violet coloration, but possessing only feeble dyeing power.

The preceding nitro-compound of the substance $C_{16}H_{12}O_5$ was added to nitric acid of sp. gr. 1.54, the solution boiled, evaporated to a small bulk and cooled, when a semi-solid, crystalline mass was obtained; this was treated with a little glacial acetic acid, collected,

and purified by crystallisation from the same liquid. An analysis gave the following result.

0.1284 gave 13.7 c.c. moist nitrogen at 23° and 753 mm. N = 11.90.

$C_{16}H_6O_5(NO_2)_4 = 12.07$ per cent. N.

$C_{15}H_6O_5(NO_2)_4 = 12.40$ „ N.

This substance is, therefore, either a *tetranitroemodin methyl ether* or a *tetranitroemodin*, a point which cannot be definitely decided until more material is obtainable. It forms a beautiful, glistening mass of long, thin, orange-yellow needles which melt and decompose at about 275°; when more strongly heated there is a slight explosion. It dissolves in solutions of the alkali hydroxides or ammonia with a red coloration, and if the crystals be exposed in an atmosphere which contains but a minute trace of ammonia, they are at once reddened. When treated with alkaline reducing agents, a beautiful, blue-violet liquid is obtained, from which a similar coloured precipitate gradually separates, whilst on neutralising the solution maroon-coloured flocks are deposited. It is insoluble in cold sulphuric acid, but, on heating, it dissolves with an orange-red coloration; the solution, when strongly heated, becomes of a brownish-violet tint, gas being evolved; on now pouring it into water, dirty brown-violet flocks are precipitated, soluble in alkalis with a violet coloration.

The action of nitric acid on emodin itself is undergoing investigation.

Substance of the Formula $C_{16}H_{14}O_4$ (A).

The acetone mother liquors from the purification of the substance $C_{16}H_{12}O_5$ (p. 932) were evaporated to a small bulk and cooled, when an almost colourless crystalline product separated; this was collected and extracted two or three times with cold, and finally with a little boiling benzene, and the sparingly soluble residue purified by two or three crystallisations from much toluene with the aid of animal charcoal.

0.1143 gave 0.2962 CO_2 and 0.0512 H_2O . C = 70.69; H = 4.98.

$C_{16}H_{14}O_4$ requires C = 71.11; H = 5.18 per cent.

It forms a mass of beautiful, colourless glistening needles, and decomposes at about 260° before melting. It is almost insoluble in benzene and alcohol, more soluble in acetone and acetic acid, crystallising readily from the latter. It dissolves in sulphuric acid with an orange-red coloration, which, on heating, becomes green; on adding water, a greenish-black precipitate is produced, which is partially soluble in alkalis with a purple, red-violet coloration. When distilled with zinc dust, a sublimate of greenish-yellow leaflets is obtained,

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consisting of methylantracene, identical with that obtained in a similar manner from the emodin methyl ether. The substance (A) is insoluble in cold alkaline solutions, but, on warming, gradually dissolves, forming a brownish-yellow solution; on continued boiling, this darkens, and if it be now treated with acid a brownish-green precipitate is deposited.

Action of Acetic Anhydride.—The substance $C_{16}H_{14}O_4$ was heated with acetic anhydride until completely dissolved, about two hours usually being required to effect this; it was then boiled for four hours longer. The resulting red solution, which had a strong green fluorescence, was mixed with a little methylic alcohol, and the greenish semi-crystalline mass which was precipitated, was collected, washed with methylic alcohol, and purified by redissolving it in acetic anhydride and precipitating with methylic alcohol.

0.1177 gave 0.2842 CO_2 and 0.0524 H_2O . $C = 65.85$; $H = 4.95$.

$C_{16}H_{11}O_4(C_2H_5O)_3$ requires $C = 66.66$. C and 5.05 H .

Thus obtained it forms a pale yellowish-green powder which, when heated, darkens at $200-210^\circ$, and decomposes before melting. It is almost insoluble in alcohol, moderately soluble in benzene or acetic acid, and may be obtained from the latter in an indistinct crystalline form. Its solution in benzene is red, with a strong, greenish fluorescence. It is insoluble in cold alkali, but on continued boiling it is decomposed with formation of a brownish-red solution.

Oxidation of the substance $C_{16}H_{14}O_4$ (A).—In studying this action, it was dissolved in excess of boiling glacial acetic acid, and a few drops of a dilute solution of chromic acid in the same solvent added; the solution, when mixed with an equal volume of water and allowed to cool, deposited glistening orange-red needles, which were collected and analysed with the following result.

0.1293 gave 0.3193 CO_2 and 0.05 H_2O . $C = 67.35$; $H = 4.29$.

$C_{16}H_{12}O_5$ requires $C = 67.6$; $H = 4.22$ per cent.

The product melted at 200° , and was identical with the emodin methyl ether previously described. As stated in the introduction, this substance appears to be a *trihydroxy- α -methylantracene mono-methyl ether*.

Action of Nitric acid on $C_{16}H_{14}O_4$ (A).—It is not attacked by cold nitric acid (sp. gr. 1.42), but on heating a violent action takes place; on now adding water to the deep brown solution, orange-yellow flocks are deposited. Cold nitric acid (sp. gr. 1.5) gives a similar result, but on boiling, followed by evaporation and the addition of a trace of acetic acid, a crystalline product is obtained; this, after purification, was found to be identical with the tetranitroemodin or tetranitroemodin methyl ether previously described (p. 935).

Substance of the Formula $C_{16}H_{14}O_4$ (B), m. p. 173.

The extraction of this fourth substance from the residual crystalline products was at first a matter of considerable difficulty, for though these usually melted at temperatures varying between 163° and 176° , they still contained about 30 per cent. or more of the two previously described substances melting at 200° and above 260° respectively. This difficulty was further increased by the fact that this fourth substance can be obtained in two very distinct crystalline forms. The crystallising media found most useful for the separation were benzene, and sometimes acetic acid, and by their use a definite product was obtained melting at 173° .

0.1021 gave 0.2653 CO_2 and 0.0470 H_2O . C = 70.86; H = 5.11.

0.1197 „ 0.3108 „ „ 0.0540 „ C = 70.82; H = 5.01.

$C_{16}H_{14}O_4$ requires C = 71.11; H = 5.18 per cent.

It crystallises in pale yellow or almost colourless needles, melting at 173° , and at higher temperatures gives a sublimate and at the same time carbonises strongly. Frequently it crystallises from benzene in long needles of a more orange tint, which appear to contain benzene of crystallisation, since they become opaque and devoid of lustre on drying. One form was frequently obtained from the other during recrystallisation from benzene, though it was not possible to find any definite means by which this change could with certainty be brought about. Both forms melt at 173° , have identical properties, and on analysis give similar numbers. The substance $C_{16}H_{14}O_4$ (B) is sparingly soluble in alcohol, more readily in acetone, acetic acid, or benzene. When distilled with zinc dust, it yields methylanthracene, identical with that obtained from the previous products. It dissolves in cold sulphuric acid with an orange-brown coloration, which, on heating, becomes green, and deposits greenish flocks on adding water (compare substance $C_{16}H_{14}O_4$ A, p. 935).

Action of Acetic Anhydride.—It was boiled for six hours with acetic anhydride, and the hot solution was then mixed with a little alcohol. On cooling, a crystalline powder separated, which under the microscope was seen to consist of minute prisms of a light yellow colour. It melts at $227-229^\circ$, and is moderately soluble in acetic acid, from which it can be crystallised. Its solution in alcohol has a strong blue fluorescence.

Though chemically distinct from one another, the resemblance between the substance $C_{16}H_{14}O_4$ B and chrysarobin, obtained from Goa powder, is remarkable. They melt respectively at 173° and $171-178^\circ$, their acetyl derivatives each at $227-229^\circ$, and the solutions of the latter in alcohol both have a strong blue fluorescence.

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Oxidation of the Substance $C_{16}H_{14}O_4$ (B).—This was readily carried out by adding chromic acid to an acetic acid solution of the substance in a manner similar to that described under the head of " $C_{16}H_{14}O_4$ (A)" (p. 936). The glistening mass of orange-yellow needles thus obtained melted at 200° , and was identical with the emodin methyl ether previously described.

0.1080 gave 0.266 CO_2 and 0.043 H_2O . C = 67.16; H = 4.4.

$C_{16}H_{12}O_5$ requires C = 67.6; H = 4.22 per cent.

The substance $C_{16}H_{14}O_4$ (B) is almost insoluble in cold, dilute alkalis, but, on warming, it dissolves, forming an orange-brown solution; this, on exposure to the air, slowly acquires a blood-red colour, and on now adding an acid to it, a brown precipitate is thrown down, which, after washing and drying, was extracted with much light petroleum. On concentrating and cooling the petroleum solution, yellow needles were obtained, melting at 200° , and identical with emodin methyl ether.

Action of Nitric acid.—Nitric acid (sp. gr. 1.5) attacked it violently, and, on boiling and concentrating, a crystalline mass was obtained, which after purification gave yellow needles, identical with the tetra-nitroemodin or tetranitroemodin methyl ether obtained from emodin methyl ether in a similar way.

A comparison of the behaviour of the substances $C_{16}H_{14}O_4$ (A) and (B) shows that their properties are very similar, the only difference of note appearing to be the slightly readier oxidation of the latter in alkaline solution. The substance $C_{16}H_{14}O_4$ (B) appears to be the second trihydroxy- α -methylantranolemonomethyl ether.

The second main crystalline product, B, referred to on p. 929, affords perhaps the most ready material for the preparation of the substance $C_{16}H_{14}O_4$ (B), consisting, as it does, chiefly of a mixture of this with the substance (A), only a trace of emodin methyl ether being present. Its isolation is effected in the manner previously described.

In the various fractions and mother liquors obtained during the purification and isolation of the four previously described crystalline compounds, no other substance has been detected; should anything of the kind be present, it can only exist in the root-bark in minute quantity. Further search will be instituted when larger quantities of material have accumulated.

Substance of the Formula $C_{17}H_{12}O_5$.

The main carbon bisulphide filtrate, which contained some quantity of alcohol (pp. 928—929), was evaporated to about one-third of its bulk; on cooling, it became almost semi-solid, owing to the deposition of

a somewhat gelatinous product. This was collected, and, after being repeatedly washed with small quantities of methylated spirit, the dark brownish residue, consisting of an amorphous substance mixed with a wax, was freed from the latter by repeated extractions with large quantities of methylated spirit, the treatment being continued as long as the filtrates deposited waxy matter on evaporation and cooling. The insoluble residue was then purified by crystallisation from benzene, and analysed, with the following result.

0.104 gave 0.262 CO_2 and 0.0448 H_2O . $\text{C} = 68.7$; $\text{H} = 4.78$.

$\text{C}_{17}\text{H}_{12}\text{O}_5$ requires $\text{C} = 68.92$; $\text{H} = 4.05$ per cent.

As thus obtained, it appears as a chocolate-coloured, friable mass, having an indistinct, crystalline appearance when examined under the microscope. Its most interesting reaction is that which takes place on boiling it with alkali solutions, for it dissolves, forming an orange-brown solution, which on exposure to air deposits a blue precipitate, probably the alkali salt of a new compound; from this behaviour, it appears to be an anthranole or allied compound. The above preparation most probably represents a pure specimen of this substance; as, however, only a small quantity has been obtained in this condition up to the present time, it is desirable to obtain more before extending the study of its reactions.

The Wax of the Formula $\text{C}_9\text{H}_{16}\text{O}_n$, m. p. 72° .

The hot, alcoholic extracts obtained during the purification of the substance mentioned in the preceding paragraph were evaporated to a small bulk, and the wax which separated on cooling was collected, rinsed with alcohol, pressed, dissolved in a large quantity of boiling alcohol, animal charcoal being added, and filtered. While still warm, a considerable quantity of a nearly colourless product separated, and this was filtered off before the whole had cooled down. The filtrate contained a small quantity of a crystalline product, which adhered to the wax with much tenacity, and from which it could only be freed by warm filtration. The wax was further purified by crystallisation from alcohol with use of animal charcoal.

0.1078 gave 0.303 CO_2 and 0.111 H_2O . $\text{C} = 76.66$; $\text{H} = 11.44$.

$(\text{C}_9\text{H}_{16}\text{O})_n$ requires $\text{C} = 77.14$; $\text{H} = 11.42$ per cent.

It forms a light, friable mass, having a faint flesh-coloured tint, and under the microscope is seen to consist of minute tangled needles. It melts at 72° , and at higher temperatures gives off a vapour having the acrid smell of heated wax.

Purification of the Crude Colouring Matter.

The main alcoholic filtrate, on standing, frequently deposited a

3 x 2

small quantity of the two substances previously described; the dark red filtrate from these, when evaporated, left a thick, treacly mass of the colouring matter still contaminated with wax and other impurities; this was dissolved in a large quantity of boiling benzene, and treated with an excess of animal charcoal; the filtrate was then agitated with a boiling solution of dilute caustic soda, and the blue-violet alkaline solution containing all the colouring matter was separated from the benzene; this was a matter of some difficulty, as the latter now held in suspension a semi-solid substance in some quantity, very often necessitating the previous removal of the latter by filtration of the whole mixture through calico. This semi-solid substance was crystallised from alcohol, and proved to be a wax-like substance, containing, no doubt, a certain quantity of the wax previously described. It will, however, be more thoroughly investigated when larger quantities can be obtained.

The orange-coloured benzene solution, from which the colouring matter had been extracted by treatment with alkali, was evaporated to dryness; the viscid residue after a time deposited crystals, which were thrown on to calico, washed with a little alcohol, and finally purified by crystallisation from the same solvent with the aid of animal charcoal.

0.11 gave 0.2722 CO_2 and 0.044 H_2O . $\text{C} = 67.48$; $\text{H} = 4.4$.

$\text{C}_{16}\text{H}_{12}\text{O}_5$ requires $\text{C} = 67.6$; $\text{H} = 4.22$ per cent.

This substance crystallises in orange-coloured needles melting at 200° , and is evidently identical with the emodin methyl ether previously described. Its appearance at this point is singular, as, owing to its somewhat sparing solubility, one would naturally expect it to be separated at a much earlier stage. It is highly probable, therefore, that as alkali was used for the extraction of the colouring matter from the benzene solution, it is here present merely as a decomposition product, either of a small quantity of the compound $\text{C}_{16}\text{H}_{14}\text{O}_4$ (B), or of some other substance which has not yet been isolated. In further support of this suggestion, it is worthy of note that not one of the other crystalline products here described could be detected in this benzene solution.

The Colouring Matter. Ventilagin.

The red-violet alkaline solution mentioned above, when neutralised with acid, deposited a maroon-coloured resinous precipitate, which became semi-liquid when the mixture was warmed. It was dissolved on agitating with benzene, and again removed from the latter by means of dilute alkali; this treatment being continued with fresh quantities of benzene, until the final benzene solution, after extraction with alkali,

was only faintly yellow. The alkaline solution was then saturated with common salt, and the amorphous precipitate of the alkali salt of the colouring matter was washed with a strong solution of common salt containing a trace of alkali, until a nearly colourless filtrate was obtained. By this means, a small quantity of substance, soluble in alkali, with an orange-red coloration, was removed. The alkali salt was then suspended in water, neutralised with acid, and the free colouring matter dissolved in ether, and freed from a small quantity of dark-coloured impurity by filtration. The resinous residue left on evaporating the ethereal solution to dryness, was now extracted with a little warm methylic alcohol; by this means a further quantity of the sparingly soluble impurity remaining undissolved was removed, and the alcoholic extract was then poured into a large bulk of dilute potassium carbonate solution. On adding common salt to the alkaline liquid, the potassium salt could be readily precipitated in two fractions, the first of which carried down with it the last traces of the less soluble substances, the second and largest representing a very pure product. The latter was suspended in water, decomposed with acid, the colouring matter dissolved in ether, the solution evaporated, and the residue dried at 110° until the weight was constant. Analyses of different preparations gave the following numbers.

- I. 0.1182 gave 0.2675 CO_2 and 0.0535 H_2O . C = 61.72; H = 5.02.
 II. 0.1181 „ 0.2700 CO_2 and 0.0565 H_2O . C = 62.34; H = 5.31.
 $\text{C}_{15}\text{H}_{14}\text{O}_6$ requires C = 62.06; H = 4.83 per cent.

As thus obtained, ventilagin is a reddish-brown, brittle, resinous mass, possessing a slight metallic lustre; it softens at about 100° , and becomes liquid at 110° . Although the numerous attempts made to obtain it in a crystalline condition have been unsuccessful, notwithstanding the modes of purification adopted have been very varied, it is highly probable that the preparations described above consist of the substance in a pure condition. It is very readily soluble in alcohol, ether, and benzene, very strong solutions of which deposit it, on cooling, as a gelatinous mass, and it is only sparingly soluble in light petroleum and in water. When strongly heated, it is carbonised with evolution of a vapour having a phenolic odour, which is best collected by passing it through ether or alcohol; on evaporating these solutions, a pale brown-coloured oil is obtained, which does not solidify on standing; it is soluble in alkali, but gives no characteristic reaction with ferric chloride either in aqueous or in alcoholic solution. On distillation with zinc dust, ventilagin yields a small quantity of greenish leaflets consisting of α -methylantracene. Ventilagin dissolves in cold sulphuric acid, forming a magenta-coloured solution, which, on heating to 150° , evolves sulphurous acid; a carbonaceous

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from *Achusa tinctoria*, and we propose for it the name *ventilagin*; further experiments will be carried out with the object of determining its constitution, and an investigation of alkannin from the *Achusa tinctoria* will be carried out at the same time. The details of the separation of the various substances here described being somewhat difficult of explanation, the accompanying scheme (preceding page) has been drawn out in which are embodied the main methods used for this purpose.

Dyeing Properties.

Experiments in dyeing with the root-bark of *Ventilago madraspatana* have been previously made by Gonfreville (*L'Art de la Teinture des Laines*, 1849, p. 542) and by T. Wardle (*Report on the Dyes and Tans of India*, 1887, pp. 3, 21). Our experiments were made on ordinary stripe mordanted calico printed with aluminium and iron mordants, also on wool and silk with chromium and tin mordants in addition.

Its application presents no difficulty, although, owing to the slight solubility of the colouring matter in water, dyeing does not begin till the temperature reaches 70—80°. No additions to the dye-bath are necessary, except in the case of wool and silk, with which it is advantageous to use a small percentage of calcium acetate to correct the acidity of the mordanted fibre.

On cotton, it gives, with aluminium mordant, a purplish-red, much bluer in shade and duller than that given by Lima-wood; with iron mordant, it gives grey to black according to the concentration of the mordant, the grey being a more neutral tint than the purplish-grey given by Lima-wood; with a mixture of aluminium and iron mordants, the colour is purplish-chocolate.

On oil-prepared calico with aluminium, chromium, and iron mordants, one obtains rich claret-red, purplish-brown, and purplish-black colours respectively.

Colours similar to the foregoing are obtained on wool and silk, and with tin mordant a red, very similar to that given by alizarin with aluminium mordant.

Generally speaking, the *Ventilago* colours are somewhat similar to those obtainable from Camwood or from Lima-wood; like the latter, they are fugitive to light, but are decidedly faster to soap; they do not, however, equal in this respect the alizarin colours. Although the chemical part of this paper seems to indicate that the colouring matters of *Ventilago madraspatana* and of *Achusa tinctoria* (alkannin) are possibly related to each other, the colours they yield in dyeing are very different, the latter giving, with aluminium mordant, a bluish-grey, the former, as already stated, a purplish-red. We have been unable, indeed, to find any other colouring matter possessing exactly

the same dyeing properties, and, therefore, taking the latter in conjunction with the results of the chemical examination, we have come to the conclusion that this dye-stuff contains a new colouring matter.

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