

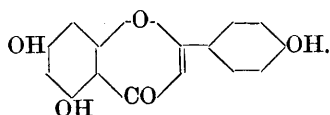
LXIX.—*Azobenzene Derivatives of some Natural Yellow Colouring Matters: Apigenin, Chrysin, Morin, Euxanthone, and Gentisin.*

By ARTHUR GEORGE PERKIN, F.R.S.E.

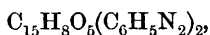
IN previous investigations, the azobenzene compounds of maclurin (Trans., 1897, 71, 186), cotoin, and phloretin (Trans., 1897, 71, 1149) have been studied, and it now appeared desirable to examine analogous derivatives of the allied flavone and xanthone groups. Of the former class, chrysin, apigenin, and morin were selected, with the object of accumulating further evidence as to their relationship, and, of the latter, euxanthone and gentisin were interesting for comparison, for it seemed probable that the position of the methoxy-group in gentisin could be thus determined.

Apigenin.

A recent examination of this substance, the colouring matter of parsley (Trans., 1897, 71, 805), *Apium petroselinum*, revealed a striking similarity between its properties and those of chrysin; its behaviour with fused alkali specially indicated this resemblance, as it yielded phloroglucinol and parahydroxyacetophenone, and a study of its derivatives also pointed to the fact that it was an hydroxychrysin or trihydroxyflavone,



With diazobenzene, it formed disazobenzeneapigenin,



although at the time the properties of this compound were not fully examined. During its purification, for which acetic acid was partly

employed, a bye-product was isolated which had the characteristics of an acetyl derivative, and a notice of this substance was communicated to the Society (Proc., 1897, p. 54). Owing, however, to a lack of material necessary to establish its identity, it was not described in the full paper (*loc. cit.*), but reserved for further examination.

Crude disazobenzeneapigenin was extracted with alcohol to remove a resinous impurity, and subsequently with a boiling mixture of nitrobenzene and acetic acid until an orange-yellow mass of the almost pure disazo-derivative remained. The nitrobenzene extracts on cooling yielded no deposit, but when diluted with hot alcohol a crystalline product separated, which was collected and washed with alcohol.

0.1274 gave 0.3105 CO₂ and 0.0493 H₂O. C = 66.47; H = 4.29.

0.1266 „ 0.3095 CO₂ „ 0.0463 H₂O. C = 66.66; H = 4.06.

C₁₅H₇O₅(C₂H₃O)(C₆H₅N₂)₂ requires C = 66.92; H = 3.84 per cent.

It formed a glistening mass of orange-red leaflets melting at 259—260° somewhat more soluble in nitrobenzene than the disazobenzene derivative itself, and insoluble in dilute alkali. As disazobenzeneapigenin is very sparingly soluble in alkaline solutions, owing apparently to the formation of an insoluble salt with the alkali, further proof was necessary to determine if this was in reality an acetyl compound. This appeared to be the case, for by decomposition with sulphuric acid, a process in which a purification does not occur, crystals of disazobenzeneapigenin melting at 290—292° were obtained; other preparations of this product gave a like result, but a slight variation in the melting point of each was observed; the yield, however, was very small and the process troublesome, and as it was likely that the acetyl compound contained traces of the unaltered substance, it was considered more advisable to study its preparation by the ordinary methods. The apigenin employed in these experiments was prepared from the glucoside apiin, by the method previously described (*loc. cit.*), the apiin being purchased from Merck of Darmstadt. A sample of the disazobenzene derivative, C₁₅H₃O₅(C₆H₅N₂)₂, on analysis, gave 11.38 per cent. of nitrogen, theory requiring 11.71 per cent.

In order to acetylate this product, 1 gram was boiled with 20 c.c. of acetic anhydride for 3 hours, but at the expiration of this time no action appeared to have taken place, although the crystals had a more glistening appearance; subsequent experiment showed, however, that a partial acetylation had occurred. Experiments were now carried out employing a very large excess of acetic anhydride, 150 c.c., the disazobenzene compound, 1 gram, being added to this in small portions at a time. A clear solution was gradually formed, but this on longer boiling commenced to deposit crystals, which, after 8 hours digestion, were collected, washed with acetic acid, and finally with alcohol. 0.733 gram was

thus obtained. In appearance and general properties, this product so closely resembled the original disazobenzene compound that at first it appeared doubtful whether reaction had taken place. Analysis, however, showed this to be incorrect.

0.1104 gave 10.5 c.c. nitrogen at 18° and 748 mm. $N = 10.80$.

$C_{15}H_7O_5(C_2H_3O)(C_6H_5N_2)_2$ requires $N = 10.77$ per cent.

To corroborate this result, the substance, suspended in boiling acetic acid, was decomposed by sulphuric acid, and to the clear solution boiling water was cautiously added, the crystals of the free disazo-compound which separated being collected and weighed.

0.4020 gave 0.3680 $C_{15}H_8O_5(C_6H_5N_2)_2$. Found 91.54.

0.6053 „ 0.5540 „ „ „ 91.52.

The theory for the loss of one acetyl group requires 91.92 per cent.

Acetyldisazobenzeneapigenin forms a glistening mass of orange-red needles insoluble in alkaline solutions, and is in appearance practically indistinguishable from the free disazo-compound, which is itself almost insoluble in these reagents. In their behaviour also with the usual solvents, no characteristic differences could be observed, although the acetyl compound is somewhat more readily dissolved by hot nitrobenzene. When rapidly heated, acetyldisazobenzeneapigenin melts at 277—280°, and if slowly heated at 266—268°, signs of decomposition appearing at about 260°; on the other hand, disazobenzeneapigenin, when heated in a similar manner, melts at 290—292° and 270—272° respectively. So close a similarity between a substance and its acetyl derivative is unusual, and it thus appeared advisable to determine whether disazobenzeneapigenin is decomposed or suffers loss by treatment with a solution of sulphuric acid in boiling acetic acid. This was evidently not the case, for 0.7410 in this way gave 0.7382, or 99.60 per cent. of unaltered substance.

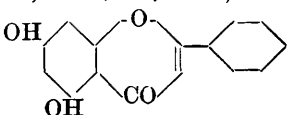
Finally, disazobenzeneapigenin was heated with acetic anhydride in a sealed tube at 160—170° for 4 hours, to determine if a more highly acetylated product could be obtained. The crystals which separated on cooling were collected and recrystallised from a mixture of nitrobenzene and alcohol.

It was identical in melting point and general properties with the monacetyl derivative above described, and it is thus apparent that disazobenzeneapigenin contains but one free hydroxyl group. Consequently, apigenin itself would appear to contain three such, the diazobenzene groups in each case neutralising one of these, and this has been proved by the following examination of chrysin.

Chrysin.

Evidence was still required to prove with certainty the exact positions of the diazobenzenes in the apigenin compound, for this appears to contain, not only a phloroglucinol, but a phenol nucleus.

Chrysin, the colouring matter of poplar buds, has been shown by Kostanecki (*Ber.*, 1893, 26, 2901) to be a dihydroxyflavone of this

constitution,  and should this yield a

disazo-derivative the constitution of the apigenin compound would be at once evident.

Some chrysin was therefore prepared from poplar buds according to Piccard's method (*Ber.*, 1873, 6, 884), and a solution of this in dilute alkali treated with an excess of diazobenzene sulphate; the orange-red, gelatinous precipitate thus produced was collected, washed, dried, and repeatedly extracted with boiling alcohol, to remove a resinous product present in considerable quantity. The orange-coloured residue was dissolved in the least possible quantity of hot nitrobenzene, the solution mixed with half its bulk of alcohol, and the crystals which separated collected and washed with alcohol.

0.1175 gave 0.3022 CO₂ and 0.0430 H₂O. C = 70.14; H = 4.06.

0.1138 „ 12 c.c. nitrogen at 22° and 752 mm. N = 11.81.

C₁₅H₈O₄(C₆H₅N₂)₂ requires C = 70.13; H = 3.89; N = 12.12 per cent.

Disazobenzenechrysin forms an orange-coloured, glistening mass of fine needles melting with decomposition at 251—252° when slowly heated. It is very sparingly soluble in boiling alcohol, somewhat more readily in acetic acid and nitrobenzene, and insoluble in alkaline solutions. Sulphuric acid dissolves it, giving a liquid of a scarlet colour. This substance, when boiled with acetic anhydride for 6 hours, remained unchanged, the crystals which separated on cooling giving the following results on analysis.

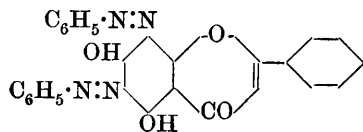
0.1042 gave 11.2 c.c. nitrogen at 21° and 752 mm. N = 12.10.

C₁₅H₈O₄(C₆H₅N₂)₂ requires N = 12.12 per cent.

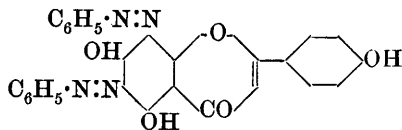
To be certain of this, however, the small quantity remaining, 0.2726 gram was digested with an acetic acid solution of sulphuric acid. The crystals which separated on dilution weighed 0.2703 gram, a yield of 99.15 per cent.

Disazobenzenechrysin, as was to be expected, cannot therefore be acetylated, and contains no free hydroxyl groups, consequently the

constitutions of disazobenzenechrysin and disazobenzeneapigenin may be thus represented.



Disazobenzenechrysin.

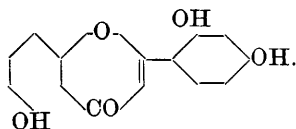


Disazobenzeneapigenin.

Dyeing Properties.—The properties of these two substances in this respect are very similar, although of little interest. Upon wool mordanted with chromium and on the unmordanted material, they gave respectively (*a*) red orange and orange, and (*b*) pale red-orange and pale orange shades. As was to be expected from the insoluble pigment-like nature of these products, a considerable portion of the colour of these patterns could be removed by mere friction.

Morin.

This substance, the principal colouring matter of old fustic (*Morus tinctoria*), has been shown in a recent communication (Trans., 1896, 69, 792) to possess properties closely in harmony with the following constitution.



On account of its analogy to the foregoing substances, a study of its behaviour towards diazobenzene was interesting; and some of the substance, prepared and purified by the methods previously described, was therefore dissolved in dilute alkali, and the solution treated with diazobenzene sulphate in excess of that necessary for the formation of a trisazo-derivative. A deep maroon-coloured product separated, which was collected, washed, dried, and extracted with boiling alcohol, to remove an easily soluble, somewhat resinous product, which is present in considerable quantity. To a solution of the residue in boiling nitrobenzene, alcohol was cautiously added, and the amorphous precipitate which separated on cooling was collected, washed with alcohol, and again dissolved in a very small quantity of nitrobenzene; on adding acetic acid, a crystalline powder separated, which was collected and washed with acetic acid.

0.1128 gave 11 c.c. nitrogen at 15° and 754 mm. $N = 11.32$.

$C_{15}N_8O_7(C_6H_5N_2)_2$ requires $N = 10.98$ per cent.

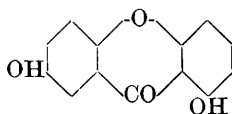
Disazobenzene morin is a red-brown powder, appearing under the microscope as warty nodules interspersed with rosettes of very minute needles. It is almost insoluble in hot alcohol or acetic acid, moderately soluble in nitrobenzene; sulphuric acid dissolves it with an orange-brown coloration. Cold dilute alkalis do not attack it, but on boiling it dissolves somewhat slowly, forming a brownish-red solution.

The yield of pure product obtained by the above method was exceedingly small, the main bulk consisting of the soluble resinous substance above referred to, and on this account its acetylation could not be properly studied without the employment of very large quantities of pure morin. It was ascertained, however, that, by digestion with acetic anhydride, an orange-coloured acetyl compound could be obtained. Morin, therefore, behaves similarly to apigenin in yielding a disazo-derivative, a point of interest, in that both substances containing, as they do, respectively phloroglucinol and resorcinol, and phloroglucinol and phenol nuclei, might be expected to form trisazo-compounds. The readily soluble, so-called resinous, products which are formed in each case when diazobenzene sulphate is added to an alkaline solution of these colouring matters could hardly contain trisazo-derivatives, for these are, as a rule, characterised by their sparing solubility. It is probable that, with this class of compound, these cannot exist, or that their production is at once followed by decomposition.

Euxanthone.

Euxanthone is derived from the Indian dyestuff "purrée" or piuri (*jaune indien*), a deposit obtained from the urine of cows and consisting of the magnesium salt of euxanthic acid; by treatment with hydrochloric acid, this is decomposed into euxanthone and glycuronic acid, $C_{19}H_{18}O_{11} = C_{13}H_8O_4 + C_6H_{10}O_7$.

Kostanecki and Nessler (*Ber.*, 1891, 24, 3980) have synthesised this substance by distilling resorcinol with quinolcarboxylic acid, and assign to it the following constitution as probable.



To a slightly alkaline solution of euxanthone, a solution containing diazobenzene sulphate (2 mols.) was added and the deep red precipitate was collected and washed. After extraction with boiling alcohol, the residue was suspended in boiling acetic acid, and nitrobenzene added drop by drop until a clear solution was obtained; on cooling, crystals separated which were collected and washed with alcohol.

0.1084 gave 12.6 c.c. nitrogen at 19° and 744 mm. $N = 13.07$.

$C_{13}H_6O_4(C_6H_5N_2)_2$ requires $N = 12.85$ per cent.

Disazobenzene-euxanthone forms a glistening, brick-red mass of fine needles melting at 249—250° with decomposition, readily soluble in boiling nitrobenzene. It is insoluble in cold dilute alkali, and even on boiling is but little attacked, so that at first sight it seemed as if this substance contained no free hydroxyl groups. To determine whether this was the case, its behaviour with acetic anhydride was studied. It was very slowly attacked by this reagent, but eventually dissolved; after boiling the solution for 3 hours, and allowing it to cool, the addition of alcohol caused a separation of crystals, which were collected, and recrystallised first from acetic acid and finally from toluene.

0.1064 gave 10.2 c.c. nitrogen at 17° and 756 mm. $N = 11.06$.

$C_{13}H_4O_4(C_2H_3O)_2(C_6H_5N_2)_2$ requires $N = 10.77$ per cent.

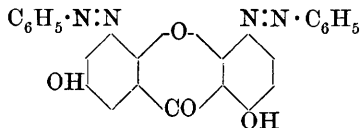
Acetyl disazobenzene-euxanthone was obtained as a pale ochre-coloured mass of glistening needles melting at 197—199°, sparingly soluble in acetic acid, more readily in toluene. It is not attacked by cold alkaline solutions, and when boiled with them becomes red, a trace only dissolving. To determine with certainty the number of acetyl groups, it was decomposed with sulphuric acid in the manner previously described.

0.4307 gave 0.3643 $C_{13}H_6O_4(C_6H_5N_2)_2$. Found 84.58. The theory for the loss of two acetyl groups requires 83.84 per cent.

The regenerated disazobenzene-euxanthone was analysed.

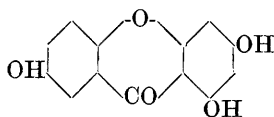
0.1228 gave 14.4 c.c. nitrogen at 20° and 749 mm. $N = 13.21$. Theory requires $H = 12.85$ per cent.

Disazobenzene-euxanthone, like euxanthone itself, contains, therefore, two free hydroxyl groups, consequently the diazobenzene groups cannot be in the ortho-position relatively to these. Its most probable constitution is as follows.

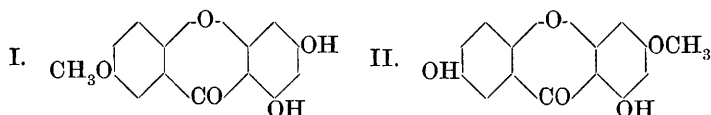


Gentisin.

This substance, the colouring matter of gentian root, has been investigated by Kostanecki (*Chem. Centr.*, 1891, i, 587), and found to be a monomethyl ether of gentisein, $C_{13}H_8O_5$. As the latter when decomposed with alkali yields phloroglucinol and quinolcarboxylic acid, they assigned to it the constitution of a trihydroxyxanthone.



Subsequently Tambor and Kostanecki (*Monatsh.*, 1894, 15, 1—8) synthesised this substance by distilling phloroglucinol with quinol-carboxylic acid, and further by a partial methylation this yielded gentisin. Their experiments indicated as possible two formulæ for gentisin according to the position of the methoxyl group, of which the second here given seemed preferable.



As the true position of this group is still doubtful, it appeared to me that this could be indicated with certainty by a study of its azobenzene derivative.

Gentisin, procured from Merck of Darmstadt, was dissolved in dilute alkali, treated with excess of diazobenzene sulphate, and the bright red precipitate collected and dried. After extraction with alcohol, it was dissolved in hot acetic acid with the aid of nitrobenzene, and the crystals which separated on cooling collected and washed with alcohol. On analysis,

0.1175 gave 0.2878 CO_2 and 0.0448 H_2O . $\text{C} = 66.80$; $\text{H} = 4.23$.

0.1262 „ 13.7 c.c. nitrogen at 15° and 748 mm. $\text{N} = 12.50$.

0.1304 „ 14.1 c.c. „ 17° „ 748 mm. $\text{N} = 12.34$.

$\text{C}_{14}\text{H}_8\text{O}_5(\text{C}_6\text{H}_5\text{N}_2)_2$ requires $\text{C} = 66.95$; $\text{H} = 3.86$; $\text{N} = 12.02$ per cent.

Disazobenzenegentisin forms a glistening mass of scarlet needles melting at $251\text{--}252^\circ$ with decomposition, readily soluble in hot nitrobenzene, almost insoluble in alcohol. Hot alkaline solutions dissolve it somewhat slowly, with formation of an orange-coloured liquid.

To acetylate this product, it was dissolved in hot acetic anhydride, and the solution boiled for 3 hours. On cooling, the addition of alcohol caused the separation of crystals, which were collected and crystallised, first from acetic acid, and finally from toluene.

0.1189 gave 10.2 c.c. nitrogen at 19° and 743 mm. $\text{N} = 9.64$.

$\text{C}_{14}\text{H}_6\text{O}_6(\text{C}_2\text{H}_3\text{O})_2(\text{C}_6\text{H}_5\text{N}_2)_2$ requires $\text{N} = 10.18$ per cent.

To determine the acetyl groups with certainty, it was decomposed with sulphuric acid in the presence of acetic acid.

674 DERIVATIVES OF SOME YELLOW COLOURING MATTERS.

0·8803 gave 0·7538 $C_{14}H_8O_5(C_6H_5N_2)_2$. Found 85·62.

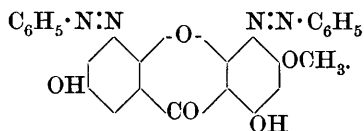
0·7141 „ 0·6067 „ „ 84·96.

Theory for the loss of two acetyl groups requires 84·73 per cent.

The regenerated disazobenzenegentisin was analysed.

0·1182 gave 12·8 c.c. nitrogen at 17° and 743 mm. N = 12·27.
Theory requires N = 12·02 per cent.

Diacetyldisazobenzenegentisin forms orange-red needles melting at 218—220°, moderately soluble in hot acetic acid, but only very sparingly in alcohol. It is not attacked by cold dilute alkali, but is decomposed by digestion at the boiling temperature. Disazobenzene-gentisin, therefore, like gentisin itself, contains two free hydroxyl groups, which cannot thus be in the ortho-position relatively to the diazobenzene groups. If formula I truly represented the constitution of gentisin, it should, like chrysin, form a disazobenzene derivative containing no free hydroxyl groups. From a substance of the constitution II, on the other hand, a diazobenzene derivative should result of a nature similar to that of euxanthone; this is the case, and II must, therefore, be the true constitution of gentisin. Disazobenzenegentisin may be thus represented.



Diazobenzene-euxanthone and diazobenzene-gentisin are devoid of tinctorial property, for when applied, in the form of finely divided pastes, to wool alone or mordanted with chromium, the patterns are hardly even stained during this process. This is interesting, for although gentisin and euxanthone are dyestuffs, and their original hydroxyls, as shown above, are intact in these compounds, their tinctorial effect has evidently been neutralised by the presence of the azobenzene group.

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