THE EFFECT OF UNSATURATED CHROMOPHORES ON PYRONINE DYESTUFFS

Part II. Dyes obtained from Maleic and Succinic Acids

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The effect of unsaturation in the pyronine type of dyestuffs has been studied in the first part of the series,1 where a comparative study of the dyes obtained from aconitic and tricarballylic acids was made. In the present communication a further study is made from the same point of view of the dyes obtained by condensing various aromatic hydroxy and amino compounds with maleic acid, which are directly compared with the analogous dyes obtained from succinic acid, the saturated acid corresponding to maleic acid. A study of the eosine like compounds of the typical dyestuff of these series gave some interesting results. A few of the condensation products of both maleic2 and succinic3 acids with aromatic hydroxy compounds and of the latter acid with a few aromatic amino compounds have already been prepared but no comparative study of the dyestuffs thus obtained has so far been made. Workers in this field have obtained an eosine-like compound by brominating resorcinol-succinein but attempts4 to prepare corresponding eosine-like compound from resorcinol-malein have been unsuccessful. In the present case a bromoderivative has been obtained from resorcinol-malein. Examination of the structure of the two typical compounds of each series reveals that whereas there is only one possible position the bromine atoms can occupy in the case of resorcinol-succinein, there are two possibilities in the case of resorcinol-malein.

![Diagram](image-url)
In (1) bromine can occupy by substitution the free positions in the two benzene nuclei but in (3) it can also be added to the double bond (just as maleic anhydride forms on bromination dibromosuccinic anhydride A Pictet, Ber., 1881, 13, 1669) and the remaining two atoms could occupy two of the positions in the benzene nuclei. It is obvious that these two possibilities in the case of brominated resorcinol-malein would not have arisen if the compound had taken up as was expected six atoms of bromine. But the results of repeated estimations of bromine in the compound by the method of Paria and Schiff indicate that like resorcinol-succinein, resorcinol-malein also takes up only four atoms of bromine. Thus to ascertain as to which of the two structures (4) or (5) represent the correct formula of the tetrabromoresorcinol-malein, brominated succinic acids were employed as starting material. Both mono- and di-bromosuccinic acids condense with resorcinol, without any condensing agent. It indicates that on heating both the bromoacids lose hydrogen bromide and form maleic and acetylene-di-carboxylic acids which get condensed with aromatic hydroxy and amino compounds in presence of liberated hydrogen bromide acting as condensing agent giving the corresponding fluoresceins and rhodamines which do not contain any bromine in the molecule. In both the cases the brominated resorcinol compounds contain only four atoms of bromine in the aromatic portion of the molecule. Fumaric acid also gives condensation products identical to maleic acid because on heating it changes to maleic anhydride.

The dyestuffs of these series tenaciously hold one molecule of water which is removed only by heating for about six to seven hours in the air oven. They have the general formulae (6) and (7) similar to those in the case of aconiteins and tricarballyleins.
Malein Succineins

The absorption maxima of the dyestuffs given in the table at the end of the paper clearly show that unsaturation in the molecule considerably enhances the intensity of the colour.

**Experimental**

*Phenol-malein.*—A mixture of 3 grams of maleic acid and 5 grams of phenol was heated in an oil bath at 125–35° C. for about ten hours with a few drops of concentrated sulphuric acid. The melt which solidified on cooling was freed from excess of phenol by steam distillation and filtered. The precipitate was extracted with dilute ammonia; from the extract the dyestuff was precipitated by the cautious addition of dilute hydrochloric acid, and was further purified by boiling in alcohol with animal charcoal, filtering and precipitating by cautiously diluting the alcohol and adding a little of hydrochloric acid. The purified dyestuff which is a light-brown powder, dissolves in ethyl and methyl alcohols with brown colour and in acetone with a deep reddish brown colour and was insoluble in chloroform, benzene and petroleum ether. Addition of alkali produces bright pink colour. It blackens at 170° C. and melts at 195° C. (Found: C, 71.53%; H, 4.64%. \( C_{16}H_{12}O_4 \) requires C, 71.64%; H, 4.47%.)

*Catechol-malein.*—A mixture of 3 grams of maleic acid and 6 grams of catechol was heated for twelve hours at a temperature of 120–30° C. in an oil bath with a long air condenser and about 5 c.c. of tin tetrachloride added. The melt which on cooling got solidified was boiled with water in order to remove excess of tin tetrachloride and filtered. The violet coloured residue which was the tin salt of the dyestuff was suspended in alcohol and a slow current of hydrogen sulphide was passed. Tin sulphide got precipitated and the dyestuff went down in solution. When all the tin salt was completely decomposed, tin sulphide was filtered off and the dyestuff precipitated from the filtrate by diluting with water and boiling off sulphuretted hydrogen, cooling and adding a few drops of hydrochloric acid. It was further purified by boiling with animal charcoal in alcohol and reprecipitating as before. The purified dyestuff which is a black powder dissolves in ethyl and methyl
alcohols with a chocolate-brown colour which deepens in acetone and is insoluble in chloroform, benzene and petroleum ether. Addition of alkali produces transient deep emerald green colour, m.p. 148°C. (Found: C, 67.53%; H, 4.01%. C_{16}H_{10}O_5 requires C, 68.06%; H, 3.54%).

Pyrogallol-malein.—A mixture of 4 grams of maleic acid and 9 grams of pyrogallol was heated on the oil bath with a few drops of concentrated sulphuric acid at a temperature of 150-55°C for ten hours. The melt which was solid on cooling was extracted with boiling water repeatedly. The collected extract was then acidified with a little dilute hydrochloric acid when a very fine black precipitate was obtained. It was allowed to stand overnight and filtered next day. The product thus obtained was further purified by boiling with animal charcoal in alcohol and filtering. The filtrate was diluted with water and evaporated on a water bath till all the alcohol was driven off and the dyestuff was precipitated as before. It dissolves in ethyl and methyl alcohols with a deep mahogany brown colour which deepens in acetone to chocolate-brown and is insoluble in chloroform, benzene and petroleum ether. Addition of alkali produces brownish-violet colour. It is a black powder and does not melt up to 300°C. (Found: C, 61.35%; H, 3.31%. C_{16}H_{16}O_7 requires C, 61.14%; H, 3.18%).

Ortho-cresol-malein.—A mixture of 3 grams of maleic acid and 6 grams of ortho-cresol was heated in an oil bath with a few drops of concentrated sulphuric acid at a temperature of 140-50°C for 14 hours. The melt on cooling became hard and brittle. It was boiled with water till free from ortho-cresol. The residue was filtered and extracted with dilute alkali and the dyestuff precipitated by gradually acidifying with dilute hydrochloric acid. This was further purified by boiling with alcohol and animal charcoal. The filtrate was diluted with water and alcohol evaporated on water bath, and the dyestuff precipitated from the solution as before, by the addition of a very little quantity of dilute hydrochloric acid. It dissolves in ethyl and methyl alcohols with orange-brown colour and in acetone with chocolate-brown, in chloroform with pale yellow and is insoluble in benzene and petroleum ether. Addition of alkali turns it deep crimson. It is a black powder and melts at 228°C. (Found: C, 77.15%; H, 5.19%. C_{18}H_{14}O_3 requires C, 77.69%; H, 5.03%).

Meta-cresol-malein.—A mixture of 3 grams of maleic acid and 6 grams of meta-cresol was heated with a few drops of concentrated sulphuric acid at a temperature of 125-35°C for 16 hours. The dyestuff was extracted and purified just in the same way as in the case of ortho-cresol-malein. It dissolves in ethyl and methyl alcohols with yellow brown colour in acetone
chocolate-brown, in chloroform dirty yellow and is insoluble in benzene and petroleum ether. Addition of alkali turns it brown. It is a black powder which melts at 155° C. (Found: C, 77.34%; H, 5.22%. C_{18}H_{14}O_{3} requires C, 77.69%; H, 5.03%.)

β-Naphthol-malein.—A mixture of 3 grams of maleic acid and 7 grams of β-naphthol was heated in an oil bath at a temperature of 150–55° C. with fused zinc chloride for 10 hours. The brittle melt thus obtained was ground and repeatedly extracted with water in order to get rid of the zinc chloride. The residue was then dissolved in glacial acetic acid, filtered and the dyestuff precipitated from the filtrate by adding water. It was further purified by dissolving in glacial acetic acid and precipitating as before. It dissolves in ethyl alcohol with orange, in methyl with yellow-orange, in acetone with brownish red, in chloroform deep orange and in benzene pale yellow colour, and is insoluble in petroleum ether. It is a dirty brown powder and has got a green fluorescence in solution which gets considerably increased by the addition of alkali and the colour of the solution also becomes bright yellow. On heating it softens at 133° C. and melts at 140° C. (Found: C, 82.71%; H, 4.24%. C_{24}H_{16}O_{4} requires C, 82.28%; H, 4.00%.)

Meta-amido-phenol-malein.—A mixture of 3 grams of maleic acid and 6 grams of meta-amido-phenol was heated at a temperature of 160-70° C. with a few drops of concentrated sulphuric acid for 6 hours. The melt was then boiled with water and filtered. The residue was then dissolved in dilute alkali, filtered and precipitated by the addition of dilute hydrochloric acid. It was further purified by boiling with alcohol and animal charcoal, filtered and precipitated by diluting and adding a trace of acid. In ethyl and methyl alcohols it dissolves with a dark yellow colour, in acetone yellowish brown and is insoluble in chloroform, benzene and petroleum ether. It is a light brown powder and gives green fluorescence in alcoholic solution. It changes colour at 212° C. and melts at 225° C. (Found: C, 68.14%; H, 4.6%. C_{16}H_{12}O_{3}N requires C, 68.57%; H, 4.28%.)

ResorcinolS and naphthol maleins.—They were prepared according to the methods already given in literature.

Catechol-succinein.—This was prepared and purified in the same way as the corresponding catechol-malein with the difference that the temperature of the bath was kept at 150-60° C. and the mixture was heated for 12 hours. It is a black powder and dissolves in ethyl and methyl alcohols with dirty greenish yellow, in acetone yellow-brown colour and is insoluble in chloroform, benzene and petroleum ether. Addition of alkali gives dull green colour. It does not melt till 290° C. (Found: C, 68.01%; H, 4.54%. C_{16}H_{12}O_{5} requires C, 67.60%; H, 4.22%.)
Pyogallol-succinein.—This was prepared and purified in the same way as the corresponding pyrogallol-malein with the only difference that the mixture was heated for 14 hours. It is a grey black powder dissolves in ethyl and methyl alcohols with deep mahogany brown and in acetone with a deep chocolate-brown colour and is insoluble in chloroform, benzene and petroleum ether. Addition of alkali turns the solution violet. It shows no signs of melting till 290°C. (Found: C, 60·27%; H, 2·35%. \( \text{C}_{16} \text{H}_{12} \text{O}_{2} \) requires C, 60·75%; H, 3·79%).

Ortho-cresol-succinein.—This was prepared and purified in the same way as the corresponding ortho-cresol-malein with the difference that the temperature of the oil bath was kept at 150–60°C for 16 hours. It dissolves in ethyl and methyl alcohols with a chocolate brown colour which deepens in acetone. In chloroform it gives a pale yellow colour and is insoluble in benzene and petroleum ether. Addition of alkali gives reddish violet colour. It is a chocolate brown powder which blackens at 195°C and melts at 230°C. (Found: C, 77·16%; H, 5·47%. \( \text{C}_{18} \text{H}_{16} \text{O}_{3} \) requires C, 77·14%; H, 5·71%).

Meta-cresol-succinein.—This was prepared and purified in the same way as the corresponding meta-cresol-malein. The temperature of the oil bath was kept at 145–50°C. It dissolves in ethyl and methyl alcohols and acetone with brownish orange colour, in chloroform with a deep orange and in benzene orange-brown colour and is insoluble in petroleum ether. It is a light brown powder which melts at 112°C. (Found: C, 77·18%; H, 6·06%. \( \text{C}_{18} \text{H}_{16} \text{O}_{3} \) requires C, 77·14%; H, 5·71%).

\( \alpha \)-Naphthol-succinein.—A mixture of 4 grams of succinic acid and 6 grams of \( \alpha \)-naphthol was heated with a few drops of concentrated sulphuric acid in an oil bath at a temperature of 140–50°C for 12 hours. The melt was then boiled with water and filtered. The residue was dissolved in alkali and precipitated by the addition of dilute hydrochloric acid. The product obtained was further purified by boiling with animal charcoal and alcohol and filtered. The alcoholic solution was diluted with water and heated over a water bath till a good deal of alcohol got evaporated. More water was added to the cold solution and dyestuff was precipitated by adding a trace of hydrochloric acid. It is a black powder which dissolves in ethyl alcohol with pink orange colour and green fluorescence, in methyl alcohol with pale pink colour with same fluorescence. In acetone it gives deep crimson, in chloroform chocolate-brown and in benzene brown colour, and is insoluble in petroleum ether. It melts at 185°C. (Found: C, 82·61%; H, 5·02%. \( \text{C}_{24} \text{H}_{18} \text{O}_{4} \) requires C, 81·81%; H, 4·54%).
Meta-amido-phenol-succinein.—This was prepared and purified in the same way as the corresponding maleic acid compound. It is a violet powder and dissolves in ethyl and methyl alcohols with a violet red and in acetone with a deep violet red colour and is insoluble in chloroform, benzene and petroleum ether. Addition of acetic acid produces deep reddish violet colour. If alkali is added to the alcoholic solution it gives a green fluorescence. It changes colour at 120° C. and melts at 198° C. (Found: C, 67·28%; H, 4·94%. C_{12}H_{14}O_{2}N_{2} requires, C, 67·28%; H, 5·01%).

Resorcinol-succinein.—This was prepared according to the method already given in literature.

Meta-phenylene-diamine malein and succinein.—These compounds were prepared and purified in the same way as the corresponding cinchomeronein. These were not obtained in sufficient quantity, so they have been studied only qualitatively. They dissolve in ethyl and methyl alcohols with yellow colour and green fluorescence, in acetone orange colour and same fluorescence, and are insoluble in chloroform, benzene and petroleum ether. Addition of acetic acid produces bright yellow colour and the fluorescence is also increased. Malein is dark brown powder which does not melt till 285° C., succinein is clay coloured powder which changes colour at 192° C. and melts at 210° C.

Condensation of resorcinol with mono- and di-bromo-succinic acids.—This was carried out in the same way as in the case of resorcinol-succinein at a temperature of 180–85° C. without any condensing agent. The purification of the dyestuffs was also done in the same way. The product obtained from monobromo-succinic acid was found similar to resorcinol-malein. Dibromo-succinic acid gave substance containing acetylenic linkage which gives a deep green fluorescence in solution which gets intensified by the addition of alkali. It dissolves in ethyl alcohol with crimson colour and in methyl alcohol with deep magenta, in acetone deep crimson, in chloroform orange-red and in benzene orange-brown colour. It is insoluble in petroleum ether. Addition of alkali produces violet crimson colour. It is light mahogany brown powder which darkens at 250° C. and then decomposes. It was not analysed. Its bromoderivative (eosine-like compound) was obtained which is described later on.

Eosine-like compounds.—The bromo compounds of resorcinol-malein and succinein and of the products obtained from mono- and di-bromo-succinic acids with resorcinol, were prepared in the same way as eosine from fluorescein. Bromosuccinyl fluorescein is already known. Bromoresorcinol-malein is a dark red powder which dissolves in ethyl and methyl alcohols.
with crimson colour, in acetone with maroon, in chloroform deep orange, in benzene brown and is insoluble in petroleum ether. Addition of alkali produces deep violet crimson colour. It changes colour with decomposition at 185°C. (Found: Br, 52.98%. \( C_{18}H_{6}O_5Br_4 \) requires Br, 53.51%). Bromo compound from resorcinol-acetylenedicarboxylein is a greyish terracotta powder which contracts at 183°C and melts into globules at 220°C. It dissolves in ethyl alcohol with crimson colour, in methyl alcohol with a deep magenta, in acetone deep crimson, in chloroform orange red, in benzene orange-brown and is insoluble in petroleum ether. Addition of alkali produces violet crimson colour. (Found: Br, 53.03%; \( C_{18}H_{4}O_5Br_4 \) requires Br, 53.03%). Resorcinol-malein prepared from monobromosuccinic acid and resorcinol was also brominated, the eosine-like compound was similar to that obtained from resorcinol-malein. (Found: Br, 52.84%; \( C_{18}H_{4}O_5Br_4 \) requires Br, 53.51%).

### Table

**Absorption Maxima Å (Extinction coefficient 0.9)**

<table>
<thead>
<tr>
<th>Phenols, etc.</th>
<th>Maleins</th>
<th>Succineins</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In alcohol alone</td>
<td>With alkali</td>
</tr>
<tr>
<td>Phenol</td>
<td>5000</td>
<td>5500</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>5750</td>
<td>6640</td>
</tr>
<tr>
<td>Catechol</td>
<td>5950</td>
<td>6100</td>
</tr>
<tr>
<td>Pyrogallol</td>
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<td>7000</td>
</tr>
<tr>
<td>Ortho-cresol</td>
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<td>6300</td>
</tr>
<tr>
<td>Meta-cresol</td>
<td>4450</td>
<td>4600</td>
</tr>
<tr>
<td>( \alpha )-Naphthol</td>
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<td>5775</td>
</tr>
<tr>
<td>( \beta )-Naphthol</td>
<td>4750</td>
<td>5250</td>
</tr>
<tr>
<td>Meta-amidophenol</td>
<td>4200</td>
<td>No change with acid</td>
</tr>
<tr>
<td>Meta-phenylenediamine</td>
<td>4900</td>
<td>5090 with acid</td>
</tr>
<tr>
<td>Tetra-bromo-resorcinol</td>
<td>6100</td>
<td>6750</td>
</tr>
<tr>
<td>Resorcinol-malein from monobromosuccinic acid and resorcinol</td>
<td>same as resorcinol</td>
<td>malein</td>
</tr>
<tr>
<td>Resorcinol-acetylenein from dibromosuccinic acid and resorcinol (1)</td>
<td>6450</td>
<td>6950</td>
</tr>
<tr>
<td>Eosine like compound from (1)</td>
<td>6800</td>
<td>No change</td>
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</table>
We thank Prof. Dr. B. K. Singh for going through the manuscript of the paper.

Summary

(1) Maleic and succinic acids have been condensed with aromatic hydroxy and amino compounds and the properties of the resulting dyestuffs examined. Their study reveals that as expected the dyestuffs obtained from maleic acid were more coloured than the corresponding ones obtained from succinic acid, the only exception being meta-amido-phenol compounds, due obviously to the presence of unsaturation in the chromophore.

(2) The eosine-like bromo compound of resorcinol-malein was also obtained, attempts to prepare which have hitherto been unsuccessful.

(3) Interesting results have been arrived at by the study of bromo-resorcinol-malein in which bromine does not attach itself at the double bond as was originally expected. This has definitely been shown by using brominated succinic acids as starting material and examining the products obtained as well as their bromo derivatives.

REFERENCES

2. Lunge and Burckhardt \textit{Ber.}, 1884, 17, 1598.
4 & 5. Burckhardt \textit{Ber.}, 1885, 18, 2864.