PYRONINE DYESTUFFS DERIVED FROM SUCCINIC ACID

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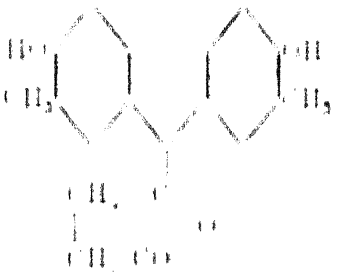
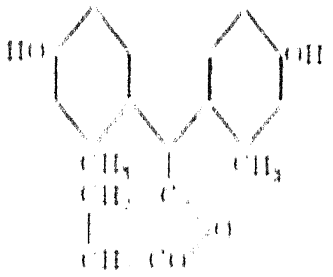
Resorcinolsuccinein or what is commonly known as succinyl-fluorescein has been known in an impure condition ever since Baeyer[1] prepared ordinary fluorescein or resorcinol-phthalein by the action of phthalic anhydride on resorcinol. In 1923 Biggs and Pope[2] obtained resorcinol-succinein in a pure condition and in the following year Dutt and Thorpe[3] were successful in getting it in a finely crystalline form. The same authors also prepared succinyl-rhodamine or *m*-dimethylamidophenol-succinein hydrochloride in glistening needles, having properties almost identical with ordinary rhodamine or *m*-dimethylamidophenol-phthalein hydrochloride. Two years later on, that is in 1926, Dutt[4] prepared phenol-succinein for the first time as colourless prisms melting at 252° C., and dissolving in dilute sodium hydroxide with intense crimson colour, just like ordinary phenol-phthalein. A large number of analogous derivatives of succinic acid were prepared by the same author by condensation of the anhydride with aromatic phenols and amino compounds, and the results although incorporated in the thesis for the degree of Doctorate of Science of the London University, were not subsequently published in consideration of the fact, that, as the most important compounds of the series had already been published, the analogous compounds were not of sufficient importance to deserve publication by themselves. But in view of a recent paper by Dass and Tewari[5] describing many of these analogous succineins and containing results which are not only highly surprising but are beyond all normal expectations, that the present author has thought it necessary and desirable to publish his own experimental results carried out in this connection in the London University nearly 16 years ago and also corroborated by recent experiments carried out in India. The results have been tabulated at the end of the experimental portion of the paper, and for the sake of comparison have been grouped against the corresponding results of Dass and Tewari and also against known data regarding the corresponding phthaleins.

The most remarkable feature about the work of Dass and Tewari mentioned above with regard to the succineins is that they have described the

greater majority of them as a series of *black powders*, whereas the present author could only isolate them as colourless crystalline substances, just like the corresponding phthaleins. *O* cresol-succinein and *m* cresol-succinein have been given the molecular formula of $C_{18}H_{16}O_4$ by Dass and Tewari which is definitely wrong, since undoubtedly they possess the following molecular structures :

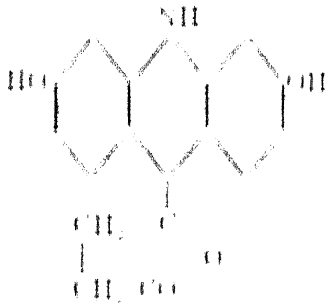


o Cresol-succinein



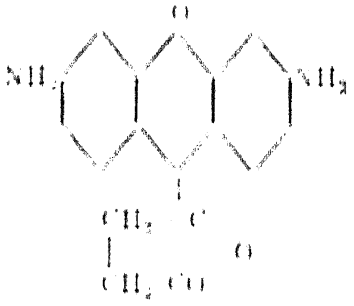
m Cresol-succinein

and therefore the molecular formula $C_{18}H_{16}O_4$. Similar is the case with the compound, *m* amidophenol succinein, which they have described as a violet powder soluble in caustic soda and insoluble in acids. The formula that Dass and Tewari have given to the substance, that is $C_{16}H_{11}O_2N_3$, is apparently wrong, as it is undoubtedly phenolic in character and therefore possesses the molecular structure given below :



m-Amidophenol succinein

which corresponds to the formula $C_{16}H_{11}O_4N$. Had the authors determined the nitrogen content of their compound, they would have easily found out their mistake. The structural formula assumed by Dass and Tewari for their substance, that is :



is incompatible with the properties of the compound described by themselves since with the above formula, it is not possible even by a stretch of imagination

to visualise how the substance could dissolve in caustic soda and get precipitated by acids. On the contrary one would easily think that with such a formula which is that of a true rhodamine, this substance would, like a rhodamine, get easily dissolved in acids and precipitated by alkalies. Apparently the authors are not aware of the fact that *m*-amidophenol condenses with diabasic acid anhydrides in a different way to that of *m*-dimethyl amidophenol, and the two condensation products have different properties. This has already been clearly shown by Dutt[6] as early as 1923.

Experimental

O-*Cresol-succinein.*—This was prepared by heating *o*-cresol with succinic anhydride in presence of stannic chloride in the same way as phenol-succinein (Dutt[4]). Two products were simultaneously formed, one being *o*-cresol-succinein (major fraction) and the other *o*-cresol-succinein-anhydride, and they were separated from each other by the action of caustic soda in which the former only is soluble.

O-Cresol succinein crystallises from alcohol in colourless prisms melting at 264° C. and dissolving in alkalies with an intense crimson colour. (Found : C = 72·3; H = 6·3. $C_{18}H_{18}O_4$ requires C = 72·5; H = 6·0%.)

O-Cresol-succinein-anhydride crystallises from glacial acetic acid in colourless glistening needles melting at 178–79° C. and is insoluble in alkalies or ammonia. It has properties very similar to *o*-phenol-phthalein-anhydride or fluoran first prepared by Baeyer[7] in 1892. (Found : C = 76·8; H = 5·9. $C_{18}H_{16}O_3$ requires C = 77·1; H = 5·7%.)

M-*Cresol-succinein.*—This was prepared from succinic anhydride and *m*-cresol in the same way as *o*-cresol-succinein. It crystallises from dilute alcohol in colourless glistening prisms melting at 146° C. and dissolves in dilute alkalies and ammonia with a bright pink colour. (Found: C = 72·2; H = 6·2. $C_{18}H_{18}O_4$ requires C = 72·5; H = 6·0%.)

α-Naphthol-succinein.—This was prepared by heating a mixture of succinic anhydride (10 g.), α-naphthol (14 g.) and chlorosulphonic acid (5 g.) at 100–110° C. for 4 hours in a stream of carbon dioxide. The melt was then poured into a litre of boiling water and the insoluble grey precipitate filtered off and repeatedly crystallised from alcohol with the addition of animal charcoal ultimately as colourless needles melting at 245° C. It dissolves in dilute alkalies and ammonia with an intense blue colour. (Found : C = 81·6; H = 4·8. $C_{24}H_{18}O_4$ requires C = 81·8; H = 4·5%.)

Quinol-succinein.—This was prepared by heating a mixture of succinic anhydride (10 g.), quinol (22 g.) and concentrated sulphuric acid (1 c.c.) at

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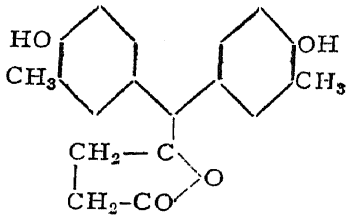
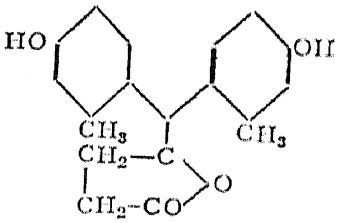


o-Cresol-succinein



m-Cresol-succinein

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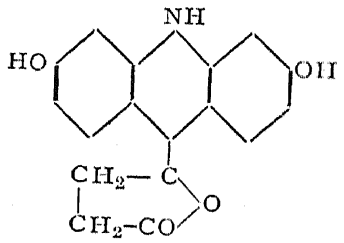

m-Amidophenol-succinein

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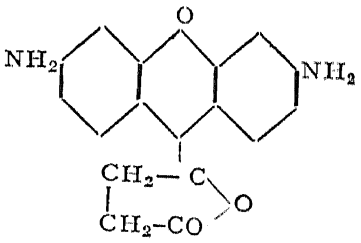

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TABLE I

General Properties of the Succineins

(D = prepared by Dutt. DT = prepared by Dass and Tewari
S = succinein)

Name of the compound	Appearance	M.P. (° C.)	Colour in alcohol	Colour in alkali
Phenol—S (D)	Colourless prisms	252	Colourless	Crimson
Do. (DT)	..	..	..	..
O-cresol—S (D)	Colourless prisms	264	Colourless	Crimson
Do. (DT)	Chocolate-brown powder	195 blacken, 230 melt	Chocolate-brown	Reddish-violet
M-cresol—S (D)	Colourless prisms	146	Colourless	Crimson
Do. (DT)	Light brown powder	112	Brownish-orange	Brownish-orange
α-Naphthol—S (D)	Colourless prisms	245	Colourless	Deep blue
Do. (DT)	Black powder	185	Pink-orange	Pink-orange
Resorcinol—S (D)	Brown needles	234	Yellow	Orange-yellow
Do. (DT)	..	..	..	..
Catechol—S (D)	Colourless prisms	286	Colourless	Transcient green
Do. (DT)	Black powder	Above 290	Dirty greenish-yellow	Dull green
Quinol—S (D)	Colourless prisms	258	Colourless	Transcient violet
Do. (DT)	..	..	..	..
Pyrogallol—S (D)	Colourless prisms	276	Colourless	Blue
Do. (DT)	Grey-black powder	Above 290	Deep mahogany-brown	Violet
Phloroglucinol—S (D)	Orange-yellow prisms	Above 290	Orange-yellow	Orange-red
Do. (DT)	..	..	..	..
M-amidophenol—S (D)	Light brown prism	224	Brownish-yellow	Brownish-yellow
Do. (DT)	Violet powder	198	Violet-red	Violet-red
M-dimethylamido-phenol-S (HCl) (D)	Brown needles	225–30	Bluish-red	Insoluble
Do. (DT)	..	..	..	..
M-phenylene-diamine—S (D)	Yellow plates	242	Yellow	Insoluble
Do. (DT)	Clay-coloured powder	210	..	..

TABLE II

Colour and Absorption Maxima of the Succineins

(D = prepared by Dutt. DT = prepared by Dass and Tewari.
S = Succinein. P = Phthalein)

Name of the compound	Colour in alcohol	Absorption maxima in ditto (Å)	Colour in alkali	Absorption maxima in ditto (Å)
Phenol—S (D)	Colourless	..	Crimson	5450
Do. —S (DT)	..	..	..	5450
Do. —P	Colourless	..	Crimson	5550
O-cresol—S (D)	do.	..	do.	5460
Do. —S (DT)	Chocolate-brown	4800	Reddish-violet	6250
Do. —P	Colourless	..	Crimson	5565
M-cresol—S (D)	do.	..	do.	5450
Do. —S (DT)	Brownish-orange	4000	Brownish-orange	4000
Do. —P	Colourless	..	Crimson	5555
α-naphthol—S (D)	do.	..	Deep blue	6080
Do. —S (DT)	Pink-orange	4400	Pink-orange	4850
Do. —P	Colourless	..	Deep-blue	6100
Resorcinol—S (D)	Yellow	4709	Orange	4936
Do. —S (DT)	..	5000	..	5200
Do. —P	Yellow	4800	Orange	4940
Catechol—S (D)	Colourless	..	Green	6500
Do. —S (DT)	Dirty greenish-yellow	4300	Dull green	4600
Do. —P	Colourless	..	Green	6650
Quinol—S (D)	do.	..	Violet	5810
Do. —S (DT)	..	..	..	..
Do. —P	Colourless	..	Violet	5900
Pyrogallol—S (D)	do.	..	Blue	5950
Do. —S (DT)	Deep mahogany	5970	Violet	6750
Do. —P	Colourless	..	Blue	5980

TABLE II—*Contd.*

Name of the compound	Colour in alcohol	Absorption maxima in ditto (Å)	Colour in alkali	Absorption maxima in ditto (Å)
Phloroglucinol—S (D)	Orange-yellow	4800	Orange	4920
Do. —S (DT)	..	..	..	..
Do. —P	Orange-yellow	4850	Orange	4980
M-amidophenol—S (D)	Brownish-yellow	4750	Brownish-yellow (acid)	4800 (acid)
Do. —S (DT)	Violet-red	5900	Violet-red („)	5950 („)
Do. —P	Brown	4850	Brown („)	4910 („)
M-dimethylamido-phenol—S (HCl) (D)	Bluish-red	5465	Bluish-red („)	5465 („)
Do. —S (DT)	..	..	..	..
Do. —P (HCl)	Deep pink	5550	Deep pink („)	5550 („)
M-phenylene-diamine—S (D)	Yellow	4550	Orange-red („)	5000 („)
Do. —S (DT)	..	4450	..	4750 („)

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