# CCCXLV.—*The Effect of Unsaturated Chromophores on Pyronine Dyestuffs. Part I.*

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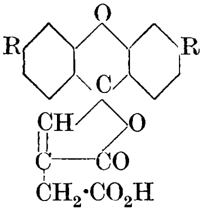
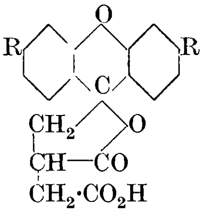
Saturated compounds behave as frictionless media for the passage of light waves in the visible and ultra-violet region of the spectrum, as is evident from the fact that such compounds show no absorption in these two regions. The entrance of unsaturation introduces friction into the molecule, causing it to absorb light waves in these two regions, and, in general, the converse holds. Any increase of unsaturation in the dye molecule enhances the colour of the compound. Examples of this type are found in dyes derived from succinic (Dutt and Thorpe, J., 1924, **125**, 2524) and maleic acids (Lunge and Burckhardt, *Ber.*, 1884, **17**, 1598, 1600; Burckhardt, *Ber.*, 1885, **18**, 2864, 2878). In order to elucidate this point, dyes have been prepared by condensing various aromatic hydroxy- and amino-compounds with aconitic acid, and these are directly compared with the analogous dyes obtained from tricarballylic acid, the saturated acid corresponding to aconitic acid. The resulting dyes will have the general formulæ (I) and (II). The free carboxyl group has very little effect on the colour of the dyestuffs (Tewari and Dutt, *J. Indian Chem. Soc.*, 1928, **5**, 60).

(I.)



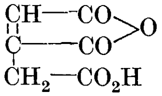
Aconiteins.

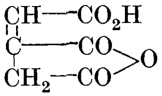
(II.)



Tricarballyleins.

Aconitic anhydride could, theoretically, have either of the structures (III) and (IV), but the former is the more stable of the two because the interposition of a double bond between the two carbon atoms brings their two carboxyl groups so near each other that the anhydride formation between them takes place with greatest ease

(III.)



(IV.)

(Beesley, Ingold, and Thorpe, J., 1915, **107**, 1080; Ingold and Thorpe, 1919, **115**, 320; Kon, 1921, **119**, 810; Dhar and Dutt, *J. Indian Chem. Soc.*, 1927, **4**, 253).

The absorption maxima of the dyestuffs given in Table I clearly show that unsaturation in the molecule considerably enhances the intensity of the colour.

## EXPERIMENTAL.

*Phenol-*, *resorcinol-*, *phloroglucinol-*, and m-*diethylaminophenol-aconiteins* and *-tricarballyleins* were prepared and purified in the same way as the corresponding cinchomeroneins (Tewari, J., 1929, 1642) and iminazophthaleins (Tewari and Dutt, *J. Indian Chem. Soc.*, 1927, **4**, 202). The isolation and purification of catechol-aconitein and -tricarballylein were effected as for catecholitaconein (Dhar and Dutt, *ibid.*, p. 248). These compounds, being insoluble in water, were extracted from the insoluble tin sulphide by means of alcohol.

The preparation and purification of the *m*-dimethylaminophenol compounds were the same as for the corresponding diethyl compounds (see above).

The condensation of *m*-phenylenediamine with these acids was done in an oil-bath at 150—160°, dry hydrogen chloride being used as a condensing agent. The dyestuff was extracted with glacial acetic acid, largely diluted with water, and precipitated from this acid solution by the addition of ammonia. It was recrystallised from acetic acid.

TABLE I.

*Absorption maxima*, $\mu\mu$.

| Phenol, etc. | Aconiteins. | Tricarballyleins. |
|---|---|---|
| Phenol- | 5530 | 5480 |
| Resorcinol- | 4930 | 4870 |
| Phloroglucinol- | 4940 | 4880 |
| *m*-Diethylaminophenol- | 5560 | 5500 |
| *m*-Dimethylaminophenol- | 5550 | 5480 |
| Catechol- | 4960 | 4920 |
| *m*-Phenylenediamine- | 4910 | 4840 |
| Pyrogallol- | 4950 | 4910 |
| *o*-Cresol- | 5540 | 5500 |
| *m*-Cresol- | 5530 | 5470 |
| Tetrabromoresorcinol- | 5490 | 5400 |
| Tetraiodoresorcinol- | 5600 | 5540 |

## TABLE II.

| | | | | | Analysis, %. | | | |
|---|---|---|---|---|---|---|---|---|
| Aconitein. | Appearance. | M. p. | Colour in alcohol, and effect of addition of alkali (or acid *). | Fluorescence. | Found. | | Required. | |
| | | | | | C. | H. | C. | H. |
| Phenol- | Colourless needles | 250° (decomp.) | Light pink; deepened | — | 66·8 | 4·1 | 66·4 | 4·3 |
| Resorcinol- | Orange-yellow powder | 190° (decomp.) | Orange-yellow; increased | Green | 63·0 | 3·5 | 63·5 | 3·5 |
| Catechol- | Dark needles | 150° | Red; transient green | — | 63·3 | 3·9 | 63·5 | 3·5 |
| Phloroglucinol- | Brown powder | Blackens at 195° | Red; deepened | — | 58·5 | 3·4 | 58·1 | 3·2 |
| *m*-Diethylaminophenol- | Violet-red powder | 112° | Bright pink; intensified * | Brown | (N, 6·6) | | (N, 6·2) | |
| *m*-Dimethylaminophenol- | Red powder | 118° (decomp.) | Rose-red; intensified * | — | (N, 7·2) | | (N, 7·1) | |
| *m*-Phenylenediamine- | Dull red powder | 248° | Deep yellow; intensified * | Green in acetic acid | (N, 15·8) | | (N, 15·8) | |
| *o*-Cresol- | Dark brown powder | 195° (decomp.) | Nearly colourless; pink * | — | 71·6 | 4·8 | 71·4 | 4·8 |
| *m*-Cresol- | Orange-red powder | 126° (decomp.) | Orange-yellow; pink * | — | 71·0 | 4·7 | 71·4 | 4·8 |
| Pyrogallol- | Black shining powder | >300° | Red. | — | 57·4 | 3·8 | 58·1 | 3·5 |
| Tetrabromoresorcinol- | Brick-red crystalline powder | Decomp. above 170° | Red; intensified | — | (Br, 48·9) | | (Br, 48·8) | |
| Tetraiodoresorcinol- | Dark red powder | Decomp. above 187° | Dark red; intensified | — | (I, 60·3) | | (I, 60·2) | |
| Tricarballylein. | | | | | | | | |
| Phenol- | Dark brown powder | 220° (decomp.) | Light orange; red | — | 65·3 | 4·8 | 65·7 | 4·9 |
| Resorcinol- | Bright yellow powder | 207° (decomp.) | Yellow; intensified | Bright green | 63·6 | 4·4 | 63·2 | 4·1 |
| Catechol- | Dark black powder | 180° (decomp.) | Red; transient green | — | 63·2 | 4·3 | 63·2 | 4·1 |
| Phloroglucinol- | Bright brown powder | 119° | Bright red | — | 57·9 | 3·6 | 57·8 | 3·8 |
| *m*-Diethylaminophenol- | Scarlet powder | 140° (decomp.; shrinks at 130°) | Deep rose-pink * | Brown | (N, 6·0) | | (N, 6·2) | |
| *m*-Dimethylaminophenol- | Scarlet powder | 138° | Deep pink * | Brown | (N, 7·5) | | (N, 7·1) | |
| *m*-Phenylenediamine- | Brown powder | 198—200° (decomp.; blackens at 190°) | Faint yellow; deepens * | — | (N, 15·7) | | (N, 15·6) | |
| *o*-Cresol- | Dark brown powder | 168° (decomp.) | Dirty red; brilliant red in acetic acid; on dilution turns yellow | — | 68·1 | 5·7 | 67·4 | 5·6 |
| *m*-Cresol- | Black powder | 220° (decomp.) | Deep red | — | 67·6 | 5·4 | 67·4 | 5·6 |
| Pyrogallol- | Scarlet powder | 236° (decomp.; darkens at 195°) | Rose-red; dirty red | — | 57·6 | 3·8 | 57·6 | 3·8 |
| Tetrabromoresorcinol- | Dull red powder | 187° (decomp.; darkens at 177°) | Pink; deep red | — | (Br, 48·4) | | (Br, 48·9) | |
| Tetraiodoresorcinol- | Scarlet powder | 215° (decomp.) | Pink; deep red | Faint green | (I, 60·0) | | (I, 60·0) | |

* Denotes effect of addition of acid.

Pyrogallol compounds were prepared and purified in the same way as in the case of the corresponding compound of itaconic acid (Dhar and Dutt, *loc. cit.*).

o-*Cresol-aconitein and -tricarballylein.*—A mixture of 2 g. of the required acid and 2·5 g. of *o*-cresol was heated at 120—130° with a few drops of concentrated sulphuric acid for about 10 hours, till the melt became quite hard and brittle on cooling. The dyestuff was extracted by means of dilute caustic soda solution, reprecipitated as a thick red mass by gradual addition of hydrochloric acid, and crystallised from alcohol. The corresponding *m*-cresol compounds were similarly prepared and purified.

The bromine and iodine compounds of resorcinol-aconitein and -tricarballylein were prepared in the same way as eosin and erythrosin from fluorescein.

The properties and analyses of these *compounds* are given in Table II.

In conclusion we wish to thank Dr. S. Dutt for his interest in this work.

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[*Received, July* 1*st*, 1931.]