CCXV.—*Dyes derived from Cinchomeronic Acid.*

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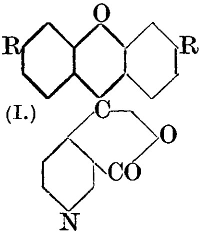
THE dyes obtained by the condensation of quinoline-2 : 3 : 4-tricarboxylic acid with aromatic amino- and hydroxy-compounds (Tewari and Dutt, *J. Indian Chem. Soc.*, 1928, **5**, 59) have deeper colours than the corresponding dyes derived from naphthalic acid (Terrisse, *Annalen*, 1885, **227**, 133). It was therefore of interest to prepare dyes from pyridinedicarboxylic acids and compare them in regard to intensity of colour with the corresponding dyes derived from phthalic acid.

Quinolinic acid has already been condensed with aromatic hydroxy- and amino-compounds by Ghosh (J., 1919, **115**, 1102). The condensation of cinchomeronic acid with phenol, resorcinol, phloroglucinol, *m*-diethylaminophenol, and *m*-phenylenediamine has now been carried out. The resulting dyes, which have the general formula (I), resemble the corresponding dyes from quinolinic acid (Ghosh, *loc. cit.*) in general properties and there is very little difference in the intensity of colour of the two series, as the following table of absorption maxima shows (the figures indicate wave-lengths):

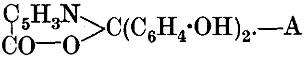


(I.)

Compound derived from	quinolinic acid,	cinchomeronic acid,
and phenol	5560	5520
,, resorcinol	4950	4950
,, phloroglucinol	4990	4980
,, *m*-diethylaminophenol	5540	5540
,, *m*-phenylenediamine	4990	4980

These results indicate that the closer juxtaposition of the two chromophores in the dyes derived from quinolinic acid produces greater intensity of colour (compare Dutt, J., 1926, 1171).

EXPERIMENTAL.

Phenolcinchomeronein,  $\begin{matrix}C_5H_3N \\ CO{-}O\end{matrix}\!>C(C_6H_4{\cdot}OH)_2$.—A mixture of 2 g. of cinchomeronic acid, 6 g. of phenol, and 10 g. of stannic chloride was heated at 100—110° for 14 hours, until the melt was dark and brittle. It was then finely powdered, the excess of phenol distilled in steam, and the residue washed with water, extracted with dilute aqueous ammonia, precipitated with dilute hydrochloric acid, and dissolved in alcohol; on addition of water the *dye* separated in small, brick-red crystals, which did not melt at 275°. The dye gave a pale yellow solution in alcohol and a bright pink solution in alkalis (Found : C, 71·1; H, 4·8. $C_{19}H_{13}O_4N$ requires C, 71·5; H, 4·1%).

Resorcinolcinchomeronein (in the general formula, R = OH).—A mixture of 2 g. of cinchomeronic acid and 4 g. of resorcinol was heated with a few drops of concentrated sulphuric acid at 160—180° for about 4 hours. The melt, solid and brittle when cold, was extracted with aqueous sodium hydroxide, and the filtered solution acidified with dilute hydrochloric acid. The precipitate obtained, after repeated crystallisation from its solution in alcohol, the orange-red colour and green fluorescence of which are greatly intensified on addition of a little alkali, gave orange-red crystals, m. p. 200°. The *dye* is slightly soluble in water, the solution having an orange colour and a green fluorescence (Found : C, 68·2; H, 3·6. $C_{19}H_{11}O_5N$ requires C, 68·5; H, 3·3%).

Phloroglucinolcinchomeronein, prepared and purified in a similar manner, crystallised from alcohol in deep brown crystals, m. p. 270° (Found : C, 62·2; H, 3·0. $C_{19}H_{11}O_7N$ requires C, 62·4; H, 3·0%).

m-*Diethylaminophenolcinchomeronein* (R = NEt_2).—This was similarly prepared from a mixture of 1 g. of the acid and 3 g. of *m*-diethylaminophenol (heating, 6 hours). An extract of the melt in hydrochloric acid was treated with a dilute solution of sodium carbonate. The *dye* obtained crystallised from alcohol in small pink crystals, m. p. 127°. The pink colour and the brown fluorescence of the solution in alcohol are considerably intensified on addition of hydrochloric acid (Found : N, 9·1. $C_{27}H_{29}O_3N_3$ requires N, 9·4%).

m-*Phenylenediaminecinchomeronein.*—A mixture of 1 g. of cinchomeronic acid and 3 g. of *m*-phenylenediamine hydrochloride was quickly heated in a test-tube until the melt became dark red, and brittle on cooling. An extract of the melt in absolute alcohol was diluted with water, and the alcohol evaporated. The *dye* was dissolved in acetic acid and reprecipitated by dilute sodium carbonate solution, being obtained in fine brown crystals, m. p. 275°. The substance dissolves in alcohol, the solution having a yellow colour and a deep green fluorescence. Its solutions in acids are red and have a green fluorescence (Found : N, 16·7. $C_{19}H_{14}O_2N_4$ requires N, 17·0%).

In conclusion, I beg to thank Dr. S. B. Dutt for his kind guidance and interest in this work.

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