SYNTHESIS, CHARACTERISATION AND ANTIMICROBIAL ACTIVITY OF SOME PYRAZOLONE AZO DYES

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Abstract
Synthesis of some 1-anilinomalonyl-3-phenyl-4-substituted (o-bromo-p-methyl) phenyl azo-5-pyrazolones is reported. Ethylbenzoyl acetate on condensing with diazotized aromatic amine gave ethyl-α-substituted phenyl azo benzoyl acetate, which on treatment with acid hydrazides of malonanilic acid series in glacial acetic acid gave pyrazolone azo dyes. The yields have been increased when trichloro acetic acid was used as the condensing agent. These dyes impart mostly yellow and orange colours to cotton, silk, wool and polyester fibres. The identification and characterization of all the compounds were confirmed by elemental analysis, melting point, thin layer chromatography, IR, 1H-NMR and mass spectral data. Synthesized compounds were screened for antimicrobial activities in view of good biological activities and pharmacological importance associated with pyrazolone derivatives. Hence, some of the derivatives of pyrazolone using acid hydrazides of malonanilic series have been used as bio-potentially.

Key words: Pyrazolone derivatives, azo dyes, malonanilic acid hydrazide, antimicrobial activity, biological activity.

INTRODUCTION
Azocompounds are the widely used as dyes due to their versatile application in various fields such as the dyeing of textile fibers, colouring of different materials, biological-medical studies and advanced applications in organic synthesis.1,2 Pyrazolone derivatives have often shown to possess bacteriostatic3-8 anticancerous9-16, antioxidant 11-14 and fungicidal 15,18, activities and have also been used as dyes. Rathore and Ittyerah19 have synthesised acid hydrazides of malonanilic acid series with the view to assess their antitubercular activity. Though considerable work has been done on the synthesis of pyrazolone azo dyes no study has appeared on the formation of dyes using acid hydrazides of malonanilic acid series until this investigation Jolly13 and co-workers20-22 have reported synthesis of pyrazolone azo dyes with malonanilic acid hydrazide moiety with a view to assess the dyeing and antimicrobial activities of the products. The present work is a continuation of the earlier studies.

The structure of the dyes was confirmed by IR, 1H NMR and 13C NMR spectroscopic techniques and elemental analysis. The present investigation has been designed to synthesize new bromine containing pyrazolone azo dyes and to uncover their potentialities. We undertook the synthesis of ten new pyrazolone azo dyes of the type (II) by condensing ethylbenzoyl acetate with diazotized aromatic amine affording ethyl-α-(o-bromo-p-methyl) phenyl azo benzoylacetate. Later on heating these with acid hydrazides of malonanilic acid series furnished pyrazolone azo dyes (II).

EXPERIMENTAL
Materials and methods
All the reagents and solvents used were of laboratory grade. The melting points of synthesised compounds were determined by open capillary method and were uncorrected. The purity and homogeneity of compounds were checked using TLC with iodine vapours as visualizing agent.

IR spectra of compounds were recorded using KBr pellets on Perkin Elmer 577 spectrophotometer. 1H NMR spectra and Mass spectra of the synthesized compounds were recorded at RSIC Lucknow. The compounds were also subjected to C,H,N and Br analysis at RSIC.
Solution was concentrated and cooled in ice when the dye separated. It was filtered and recrystallised from aqueous acetic acid in orange red crystals. Yield: 0.320 g (61.7 %)

M.P: 270 °C

Molecular formula: C₉H₁₀O₂N₃Br

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IR (KBr): 1580 cm⁻¹ (N=N-str. Vibr.), 810 cm⁻¹ (C-Br vibr.) and 1250 cm⁻¹ (>C=O, str. Vibr.)

RESULTS AND DISCUSSION

The data of the substituted pyrazoloneazo dyes (Melting points, percent yields, colour and results of analysis) were set out in the given table.

The identity of the new products was established by physical and chemical methods and spectral studies. The IR spectra of the pyrazoloneazo dyes showed the following sharp and strong characteristic peaks. 1585-1560 cm⁻¹ (N=N-str. Vibr.), 1610 cm⁻¹ (>C=N-pyrazolone ring vibration) and 1670 cm⁻¹ (>C=O cyclic vibr.), 810 cm⁻¹ (C-Br vibr.), 1410 cm⁻¹ (>C-H str.). Trisubstituted benzene ring (unsymmetrical) at 830 cm⁻¹, disubstituted benzene ring at 760 cm⁻¹, mono substituted benzene ring at 710 cm⁻¹, NH-(str.Vibr.) of secondary amide (-CONH) at 3100-3300 cm⁻¹. NMR (RFA): 7.35 ppm (aryl protons) 2.3 ppm (CH₃ protons) and 7.85 ppm (proton at C₄).

DYEING CHARACTERISTICS

Some of these dyes (Sl. Nos. 1, 3, 6 and 9) showed dyeing characteristics on cotton, silk, wool and polyester fibres using different mordants. These dyes produced yellow or orange shades. These shades have good fastness to light and soap.

BIOLOGICAL ACTIVITY

The activity was determined using disc diffusion method by measuring zone of inhibition in mm. The compounds (Sl. Nos. 1, 3, 6 and 9) were screened in vitro at concentration of 5µg/disc for their antibacterial activity against Staphylococcus aureus and Bacillus subtilis Gram-positive strains and Escherichia coli and Pseudomonas aeruginosa Gram-negative strains. Antifungal evaluation was carried out against Candida albicans and Aspergillus niger at concentration of 10µg/disc. These dyes exhibited moderate antibacterial and antifungal activities.

CONCLUSION

The study was to synthesize and evaluate the characteristics of some novel pyrazoloneazo dyes (type II), were synthesized by condensing ethylbenzoy acetate with diazotized aromatic amine affording ethyl-alpha-(o-bromo-p-methyl) phenylazo benzoylacetaet and heating...
these with acid hydrazides of malonilic acid series. The yields of the dyes increased when condensations are done in presence of a drop of Trichloroacetic acid. The dyes were bright in shades. Most of compounds were orange and yellow in colour and possessed high melting points.

**ACKNOWLEDGEMENT**

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**REFERENCES**

2. &nbsp; Zollinger H: Color chemistry: synthesis, properties, and application of organic dyes and pigments. Weinheim; Wiley–VCH; 2003

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Ac = Acetic Acid, TCA = Trichloroacetic acid.

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