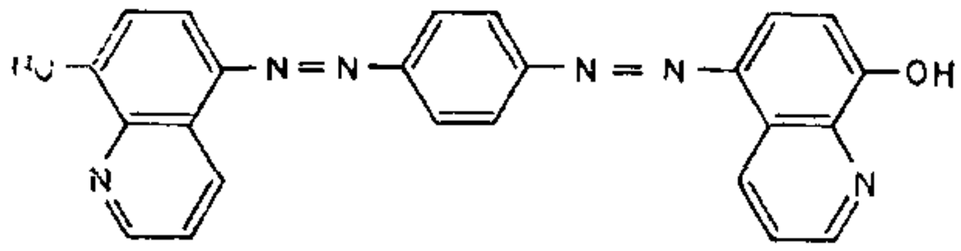
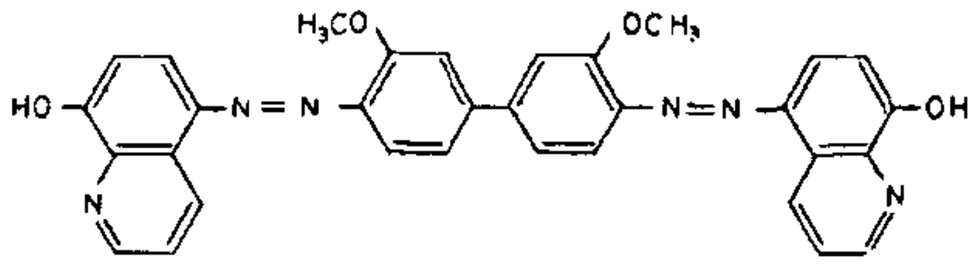
In 5, 5′-(*o*-dianisidinedisazo)-8-hydroxyquinoline, bands are observed at 3105, 1572 and 1370 cm^{-1}, corresponding to the above three assignments, as well as at 1220, 1020 , 430 cm^{-1} due to OCH_3.

On the basis of structure proposed by Boyd[1] for the disazo dye derived from 8-hydroxyquinoline and benzidine, the structures of the dyes reported here are



I. 5, 5′-(*p*-phenylenediaminedisazo)-8-hydroxyquinoline.



II. 5, 5′-(*o*-dianisidinedisazo)-8-hydroxyquinoline.

The coupling occurs on position five, *i.e.*, *p*- to the OH group of 8-hydroxyquinoline and not at position seven *i.e.*, *o*- to the OH group[5]. This is evident because though the *o*- and *p*- positions are sites of high electron density, *p*- is favoured[6,7] because of the following factors : (i) Steric effect due to large entering group[8] (tetrazonium electrophile), prevents coupling at position seven. (ii) Polarisability effect (+ E) created by the electrophile selectively activates *p*-position[9]. (iii) Inductive effect in the phenoxide ion (– I) through its direct effect create an electrostatic potential difference between *o*- and *p*- positions making *p*- more rich in electron density[10]. The above two effects result in the establishment of considerable electron density difference, and the tetrazonium cation which is very sensitive to small electron density differences[11] due to its lower stability[12], concentrates at the *p*-position. (iv) Furthermore mesomeric effect in the phenoxide ion can give both *o*- and *p*- quinonoid transition state for *o*- and *p*-substitution respectively but since *p*-quinonoid form is much more stable[13] it tends to couple at terminal (*p*-) carbon atom in the conjugated series of double bonds.

Work on the metal complexes of these dyes is in progress and will be reported in subsequent communications.

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Chemical Laboratories,
University of Allahabad,
Allahabad, *June* 27, 1977.

V. Banerjie.
Arun K. Dey*.

* For correspondence.

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NEW METHODS FOR THE SYNTHESIS OF BENZOXAZOLIN-2-ONES

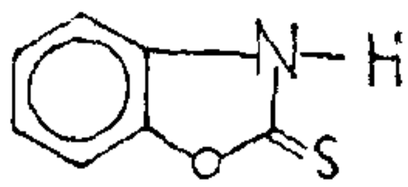
Two new synthetic methods have been developed to give good yields of benzoxazolin-2-ones (I).

Benzoxazolin-2-ones (I) are biologically versatile compounds[1–5]. The reaction of phosgene[6] with *o*-aminophenols or their fusion with urea[7] are the general methods for obtaining them ; while these methods give good yields of unsubstituted benzoxazolin-2-one, the yields are generally lower in the case of substituted derivatives. In addition, the use of phosgene is hazardous. We wish to report two new methods for the synthesis of I.

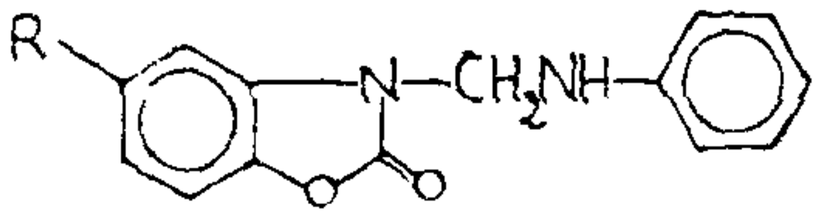
In the first procedure (A) *o*-aminophenol (0·1 mole) and urea (0·11 mole) were refluxed with excess of dry pyridine for about 14 hrs. Working up the reaction mixture furnished I (R = H) as a crystalline solid, m.p. 136–138°[6,7] in 80% yield. The method was successfully applied for the preparation of substituted I (R = CO_2H, CO_2Me) with excellent results.

The second method (B) involved the **desulfurisation of benzoxazolin-2-thione[8] (III) in DMSO. The latter (0·01 mole) in DMSO containing 5 drops of conc. H_2SO_4 was kept at room temperature for 2 weeks.**

I



III



II

Benzoxazolin-2-one (I, R = CO_2Me) was prepared similarly by methods A and B. In another method 5-carboxy-benzoxazolin-2-one (1·79 gm, 0 01 mole), dry methanol (15 ml) and thionyl chloride (1·5 ml) were refluxed for 12 hrs. The solvent was removed and the residue neutralised with 5% sodium bicarbonate. The product was recrystallised (water), m.p. 197° (Lit.[9], m.p. 196·5), yield 1·46 gm (76%). The product obtained was identical with that obtained by methods A and B (m.p., m.m.p., I.R. and T.L.C.) ; I.R. (KBr) : ν_{max} = 3210(NH), 1780 (C=O, ring), 1690 cm^{-1} (C=O, ester). Calcd. for $C_9H_7NO_4$, N = 7·25, Found N = 7·51%.

5-Carbomethoxy-3-phenylaminomethylbenzoxazolin-2-one (II, R = CO_2Me)

Aniline (0·93 gm) and formalin (1 ml) were added to a boiling ethanolic suspension of I (1·93 gm, R= CO_2Me) with shaking. The reaction mixture was stirred for 10 min. and the product was recrystallised from ethanol, m.p. 188–189° yield 2·0 gm (70%); I.R. (KBr): ν_{max}=3400 (NH), 1760 (C=O, ring) 1700 cm^{-1} (C=O, ester) ; N.M.R. ($CDCl_3$) : σ = 3·90 (Me). 4·74 (CH_2), 5·30 (NH), 6·70–7·90(Ar–H). Calcd, for $C_{16}H_{14}N_2O_4$, N = 9·39. Found N = 9·39%.

II (R = CO_2Me) prepared from I (R = CO_2Me) obtained by all the three methods was found identical (m.p., m.m.p., I.R. and T.L.C.).

5-Carboxybenzoxazolin-2-one (I, R = CO_2H)

Method A : 3-Amino-4-hydroxybenzoic acid (15·3 gm, 0·1 mole) and urea (6·60 gm, 0·11 mole) were refluxed in 30 ml of dry pyridine for 14 hrs. The product thus obtained was recrystallised from ethanol, m.p. > 297° ; (Lit.[10], m.p. 336–338°), yield 14·6 gm (82%).

Method B : 3-Amino-4-hydroxybenzoic acid (15·3 gm) and urea (8·0 gm) were fused at 150° and kept at this temperature for 4 hrs. Working up the reaction mixture gave the expected product, m.p. > 297 °, yield 10·7 gm (60%).

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Department of Chemistry,
Lucknow University,
Lucknow 226 007,
August 29, 1977.

RAJENDRA S. VARMA,
ANUP KAPOOR.

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THERAPEUTIC EVALUATION OF ANTIMYCOTIC DRUGS IN REPEAT BREEDING BOVINES DUE TO MYCOTIC INFECTIONS

THE role of mesophilic and thermophilic fungi in causing repeat breeding, metritis, abortion in females and seminal vesiculitis and orchitis in males has recently been recognised by Zeverva and Repko[1], Saxena and Pathak[2] and Ainswoith and Austwick[3].

In the present investigation an attempt has been made to evaluate a broad spectrum antifungal drug that could be effective against fungi found in repeat breeders.

Fungi were isolated to the extent of 83% from mucopurulent discharges of 92 repeat breeders on Sabouraud's dextrose agar (Saxena[4] and Lachenicht and Potel[5]). They included *Aspergillus* 21% (*Aspergillus fumigatus, A. niger, A. terrus, A. cheveleri, A. flavus*), *Candida albicans* and other *Candida* species 6%, *Cladosporium* 10%, *Penicillium* 6%, *Alternaria* 3%, *Mucor* 9%, *Rhizopus* 6%, *Geotrichum* 2%, *Cryptococcus* 1%, *Curvularia* 8%. Other typed fungi were 11% (*Phialaphora, Sporotrichum, Scopulriopsis, Botrytis, Allescheria* and *Fusidium*) closely matching the