methylanthraquinone), oroxylin-A (5,7-dihydroxy-6-methoxyflavone) and 5,5″-di-O-methylcupressuflavone (5,5″-di-O-methyl-8,8″-biapigeninyl).

3-Methylalizarin[2] was partially methoxymethylated using methoxymethyl chloride in acetone medium in the presence of anhydrous potassium carbonate. The 2-O-methoxymethyl-3-methylalizarin, which crystallized from ethanol as yellow needles (m.p. 108–10°), was then methylated using excess of dimethyl sulphate and dry potassium carbonate to yield 1-O-methyl-2-O-methoxymethyl-3-methylalizarin (yellow needles from ethanol, m.p. 123–25°). Final demethoxymethylation of this by warming with acetic acid containing a few drops of 2N sulphuric acid afforded digitolutein which crystallized from ethanol as yellow needles, m.p. 220–22° (lit.[3] m.p. 222°). U.V.: λ_{max}^{EtOH} (log ϵ) 240 (4·31), 281 (4·34) and 385 (3·39) nm. I.R.: ν_{max}^{KBr} 1655 and 1590 cm^{-1}.

For the synthesis of oroxylin-A, baicalein[4] was selectively methoxymethylated in the 7-position using methoxymethyl chloride and dry sodium bicarbonate in acetone medium. The 7-O-methoxymethylbaicalein (m.p. 160–62°; from ethanol) was partially methylated using dimethyl sulphate to get 6-O-methyl-7-O-methoxymethylbaicalein (m.p. 142–44°; from ethanol). Final demethoxymethylation, carried out in the above way, yielded oroxylin-A (m.p. 221–23°; from ethanol; lit.[5,6] m.p. 220–21°). Paper chromatography in several solvent systems as well as ultraviolet spectral comparison with an authentic specimen confirmed its identity.

The synthesis of 5, 5″-di-O-methylcupressuflavone was done on similar lines, by first partially methoxymethylating cupressuflavone[7] to get its 7,4′,7″,4‴-tetramethoxymethyl ether (m.p. 150–52°; from ethanol). Further methylation of this partial ether using dimethyl sulphate under forcing conditions yielded 7,7″,4′,4‴-tetra-O-methoxymethyl-5,5″-di-O-methylcupressuflavone (m.p. 69–70°) which on demethoxymethylation using acetic acid-sulphuric acid mixture gave 5,5″-di-O-methylcupressuflavone (m.p. 230° d.; from ethanol). Its acetate, prepared by the pyridine-acetic anhydride method, crystallized from ethanol as colourless needles, m.p. 202–05°.

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1. Eswaran, V., Gandhidasan, R., Neelakantan, S. and Raman, P. V., *Indian J. Chem.* (in press).
2. Burnett, A. R. and Thomson, R. H., *Phytochemistry*, 1968, **7**, 1421.
3. Thomson, R. H., *Naturally Occurring Quinones*, Academic Press, New York, 1971, p. 377.
4. Harborne, J. B., *Comparative Biochemistry of the Flavonoids*, Academic Press, London, 1967, p. 44.
5. Varady, J., *Tetrahedron Lett.*, 1965, p. 4281.
6. Sarin, P. S. and Seshadri, T. R., *J. Sci. Industr. Res.*, 1960, **19B**, 117.
7. Murti, V. V. S., Raman, P. V. and Seshadri, T. R., *Tetrahedron Lett.*, 1964, p. 2995.

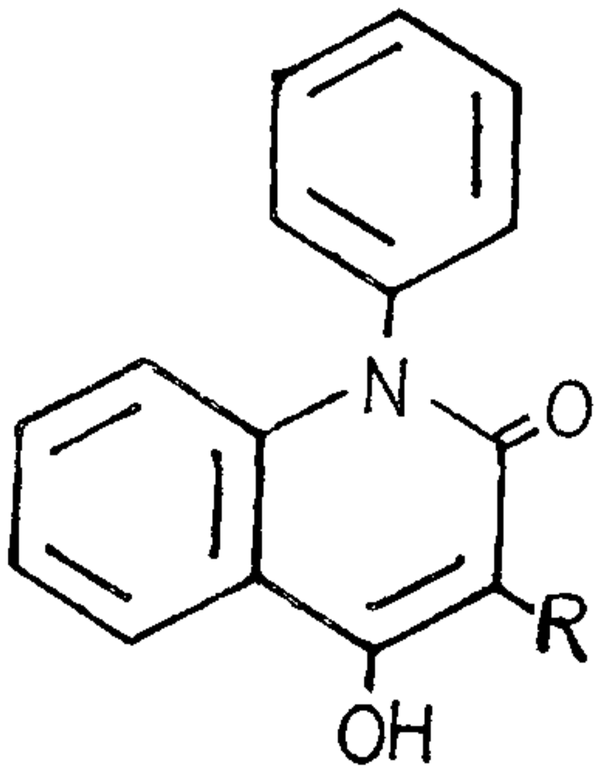
SYNTHESIS OF SOME DERIVATIVES OF 4-HYDROXY-1-PHENYL-2H(1) QUINOLONE

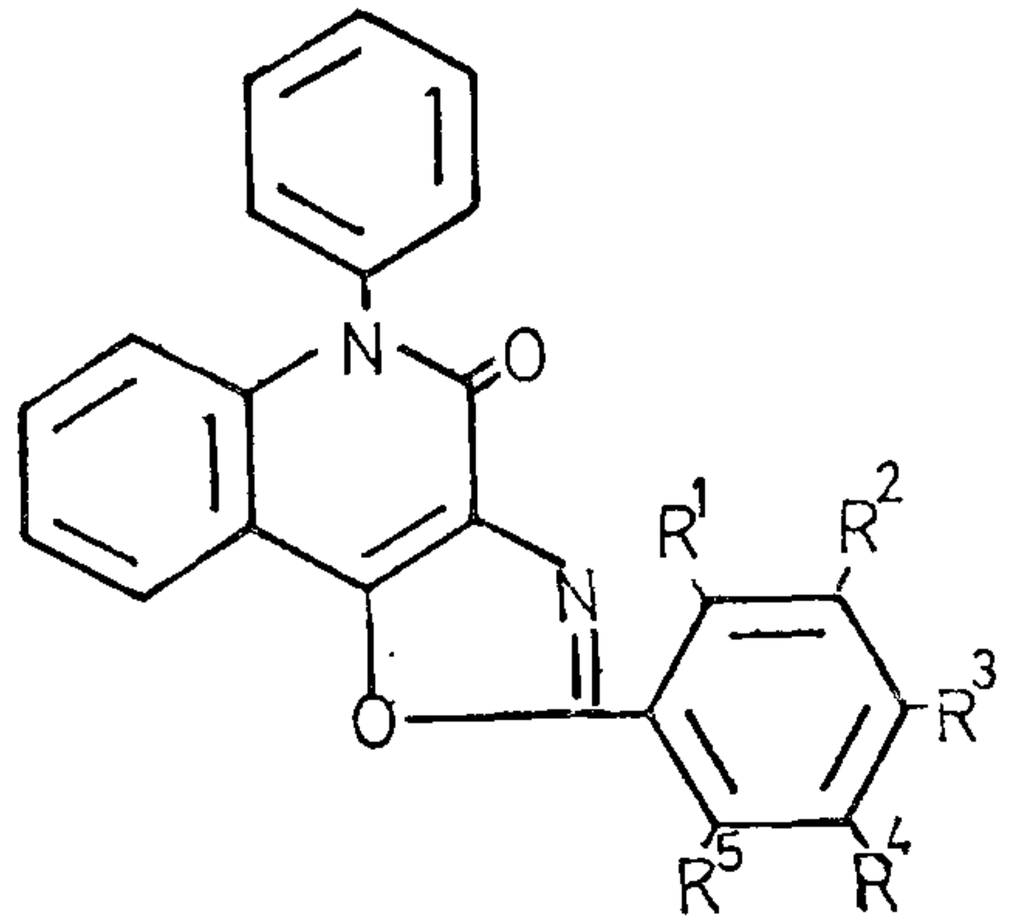
IN recent years, a number of 1-methyl and 1-phenyl-2-quinolone derivatives have been synthesised since many of them have been reported[1–3] to possess anti-allergic, antihistaminic and fungicidal properties. In view of this observation, it was thought of interest to synthesise 3-amino-4-hydroxy-1-phenyl-2H(1)-quinolone(III) (which would be more suitable for testing) and some heterocyclic compounds derived from the same. This work was prompted by the fact that the antibiotics nybomycin and deoxynybomycin possess an oxazolo (4,5-*c*) quinoline-2-one structure[4].

The parent compound, 4-hydroxy-1-phenyl-2H(1) quinolone(I) was prepared according to the method of Kim *et al.*[5]. The 3-phenyl azo derivative(II) prepared by coupling I (5 g) with phenyl-diazonium chloride [prepared from aniline (3·4 g) dissolved in conc. HCl (12 ml) and water (30 ml) diazotised with sodium nitrite (2·1 g) in water (9·6 ml)] was crystallised from alcohol as fine orange needles, m.p. 240–41°.

The quinolone III was obtained from II by the catalytic reduction in methanol solution at 26 psi in presence of palladium charcoal (10%) catalyst and crystallised from benzene-petroleum ether as fine light brown needles, m.p. 266–68°. It showed IR(KBr) bands at 3320 ($-NH_2$) 1640, 1620 ($>C=O$), 1550, 1500 (aromatic)cm^{-1} and formed the N-acetyl derivative, crystallised from benzene, m.p. 259–61°.

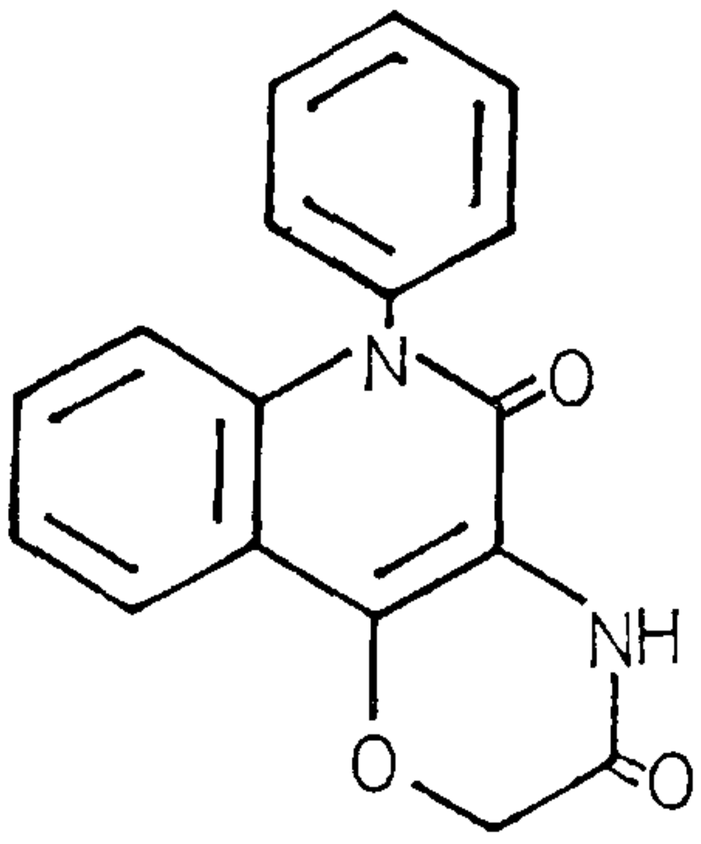
The aminoquinolone III was utilised for the synthesis of 5-phenyl-oxazolo-(4,5-*c*)-quinolin-4(5H)-ones IV–VII by a simple and convenient method[6]. The latter consists in heating III (0·002 mol) and an aromatic acid (0·002 mol) in the presence of polyphosphoric acid at 150–160° for 2 hr and then at 190–200° for 3 hr.





I : R = H
II : R = −N=N-Ph
III : R = NH_2
VIII : R = $NHCOCH_2Cl$

IV : $R_1=R_2=R_4=R_5=H$; $R_3=CH_3$; mp : 258–60°
V : $R_1=R_3=R_4=R_5=H$; $R_2=CH_3$; mp : 249–51°
VI : $R_1=R_2=R_4=R_5=H$; $R_3=Cl$; mp : 312–14°
VII : $R_1=R_3=R_4=R_5=H$; $R_2=Cl$; mp : 252–53°



IX

The oxazolo-quinolones were obtained in 25–35% yields and crystallised from ethyl acetate as bright shining needles. A typical oxazolo-quinolone IV showed bands at 1680 (>C=O), 1500, 1480 (heteroaromatic system) cm^{-1} in its IR (KBr) spectrum.

The aminoquinolone III was also used for the synthesis of another heterocyclic system, namely the oxazino-quinolone system which has not so far been reported in literature. For this purpose, 3-(N-chloroacetyl)-4-hydroxy-1-phenyl-2H (1) quinolone (VIII) was prepared by adding chloroacetyl chloride (1 ml) to a suspension of III (0·5 g) in pyirdine at 0–5° and keeping the reaction mixture at room temperature overnight. Subsequent decomposition with ice water gave VIII crystallised from CCl_4/petroleum ether as pale yellow needles, m.p. 175–78°. Refluxing VIII in alcohol in the presence of anhydrous potassium acetate for 4 thr afforded the oxazino-quinolone (IX). It crystallised from benzene-hexane as fine brown flakes, m.p. 242–44° and showed bands at 2940 (–NH), 1630–1600 (> C = O of lactone and lactam), 1500, 1480 (heteroaromatic system) cm^{-1} in its IR (KBr) spectrum.

All melting points are uncorrected. All compounds gave satisfactory elemental analysis.

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1. Fuckle, D. R., Cantello, B. C. C. and Smith, H., *Ger. Offen.* 2424076, *Chem. Abstr.*, 1975, 82, 139976 j.
2. Hardtmann, G. E., *Ger. Offen.* 2631317, *Chem. Abstr.*, 1977, 86, 189742h.
3. Sharp, J. C., U.S. Patent 3836657, *Chem. Abstr.*, 1975, 82, 81689z.
4. Forbis, R. M. and Rinehart, K. L., *J. Am. Chem. Soc.*, 1973, 95, 5003.
5. Kim, D. H., Fieber, R. A., Santilli, A. A. and Ecll, S. C., *J. Heterocyclic Chem.*, 1974, 11, 703.
6. Merchant, J. R., and Shirali, S. S., *Bull. Chem. Soc., Japan*, 1977, 50, 10.