TABLE I

Physical and spectral characteristics of 3-hydroxychromones prepared from chromone-3-carboxaldehydes by Bayer-Villiger oxidation using m-CPBA in CH_2Cl_2

Sl. No.	Compound	M.P. in 0° C*	Lit. M.P. in 0° C	Time of reflux in hours	Percentage of yield*	I.R. ν^{KBr}_{max} (cm^{-1})	U.V. λ^{MeOH}_{max} Log (ϵ) (nm)
1.	3-Hydroxychromone	180–81	181[5]	16	90	— νOH/—νC=O 3280, 1640	233(4·24), 283(3·25), 320(3·63)
2.	6-Methyl-3-hydroxychromone	174–75	175[7]	24	85	3270, 1640	237(4·33), 284(3·57), 330(3·86)
3.	8-Methyl-3-hydroxychromone	164–65	166[4]	24	87	3280, 1630	237(3·93), 283(3·18), 327(3·42)
4.	6-Chloro-3-hydroxychromone	214–15	..	18	85	3280, 1640	235(4·0), 283(3·32), 327(3·58)
5.	6-Nitro-3-hydroxychromone	200–201	..	24	80	3275, 1640	237(4·14), 285(3·48), 329(3·75)
6.	2-Hydroxy-1H-naphtho-(2,1–*b*)pyran-1-one	130–132	131–32†	24	80	3270, 1640	240(4·20), 287(3·68), 335(3·90)

* All the compounds were crystallised from methonol.

† Prepared for the first time by amylnitrite and hydrochloric acid method.

none[6] (1 g) to amylnitrite (3 ml) and hydrochloric acid (10 ml) dropwise, simultaneously, at 0° and the mixture refluxed for 2 hours. The resulting solution was poured into ice-water (200 ml). The separated yellow solid was filtered and crystalised from methanol to yield II*f* (0·30 g), mp 131–32° C.

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A SYNTHESIS OF 5,5″-DI-*O*-METHYLCUPRESSUFLAVONE AND A NEW SYNTHESIS OF DIGITOLUTEIN AND OROXYLIN-A

IN a recent communication[1] we have indicated the utility of methoxymethylation in the synthesis of partial methyl ethers of certain polyphenolic compounds. The general procedure adopted was to methoxymethylate the polyphenol first partially so that all the free unchelated phenolic hydroxyl groups present in it get protected, then methylate the chelated hydroxyl group using dimethyl sulphate and finally demethoxymethylate to get the partial methyl ether. Now we wish to record an extension of the above work and report the synthesis of the naturally occurring compounds, digitolutein (1-methoxy-2-hydroxy-3-

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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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.