

on which there is no record of any chemical work and our results are recorded here.

Shade dried leaves of *S. pallens* were extracted with hot 80% ethanol under reflux and the hot aqueous alcoholic concentrate was partitioned using petroleum ether, peroxide-free ether and ethylacetate. The petrol fraction did not yield any crystalline material. The ether concentrate on keeping in an ice-chest gave bright yellow needles (Me₂CO), m.p. 313–14° (decomp.), yield 0.01% and was identified as quercetin by R_f, λ_{max}, preparation of its penta-acetate and pentamethyl ether and direct comparison with an authentic sample of the flavonol as well as its derivatives.

The residue from the ethylacetate fraction was dissolved in the minimum of acetone and left in an ice-chest for a few days. No crystalline solid separated. A chromatographic examination of the solution showed the presence of two flavonol glycosides which were separated by preparative PC (Whatman No. 3 paper, *n*-butanol : 27% acetic acid, 1 : 1, descending, 30 ± 2°) and the two bands obtained (R_f: 0.67 and 0.79) were cut and separately eluted with methanol. The pigment from the lower band could not be crystallised out. However, the methanol eluate of the corresponding band was deep purple under UV changing to yellow with NH₃, turned yellow with alkali, was positive to Molisch's test and negative to Horjhammer-Hansel test. It had λ_{max} (nm) 257, 363 (MeOH) and showed shifts with various diagnostic reagents⁴ expected of a quercetin-3-O-glycoside. The methanol eluate underwent acid hydrolysis yielding quercetin and glucose in equal proportion. The identity of the sugar as glucose was confirmed by direct comparison and co-PC with an authentic sample of glucose. The pigment was therefore identified as quercetin-3-O-glucoside and the identity further confirmed by co-PC with an authentic sample of isoquercitrin, obtained from the seeds of *Crotalaria retusa*⁵. The second pigment corresponding to the upper band in the preparative PC was identified as quercetin-3-diglucoside (meratin) by its R_f and co-PC with an authentic sample and hydrolytic products.

The present record of the occurrence of quercetin, its 3-glucoside and 3-diglucoside from the leaves of *S. pallens* lends support to the assignment of a separate species status to *S. pallens* distinctly different from *S. colorata*, which is recorded² to contain unusual 6-oxygenated flavone derivatives and also confirms the view¹ of some botanists that *S. colorata* consists of three distinct species, *S. colorata*, *S. fulgens* and *S. pallens*.

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1,3-ADDITION OF BENZONITRILE OXIDES TO 2-CHLOROALKYLBENZIMIDAZOLES: SYNTHESIS OF 1-METHYL-4-ARYL-1H-[1,2,4] OXADIAZINO-[4,5-*a*]BENZIMIDAZOLES

We reported earlier the synthesis of 4-aryl-1H-[1,2,4]-oxadiazino[4,5-*a*]benzimidazoles through the 1,3-addition of benzonitrile oxides to 2-chloromethylbenzimidazole¹. In order to know the general applicability of this method to the synthesis of fused benzimidazole heterocycles, benzonitrile oxides are reacted with a number of 2-chloroalkylbenzimidazoles. Here we report the synthesis of the title compounds using 2-[1'-chloroethyl]benzimidazole in the 1,3-addition reaction.

The reaction of 2-[1'-chloroethyl]benzimidazole² with benzhydroxamic acid chloride³ (Ia) taken in 2 : 1 molar ratio yielded a colorless, crystalline compound, m.p. 185° (C₁₆H₁₄ClN₃O, M⁺ 299, ν_{OH}^{KBr} 3200–2400 cm⁻¹) whose structure has been formulated as 2-[1'-chloroethyl]-1-[(hydroxyimino)phenylmethyl]-1H-benzimidazole (II a).

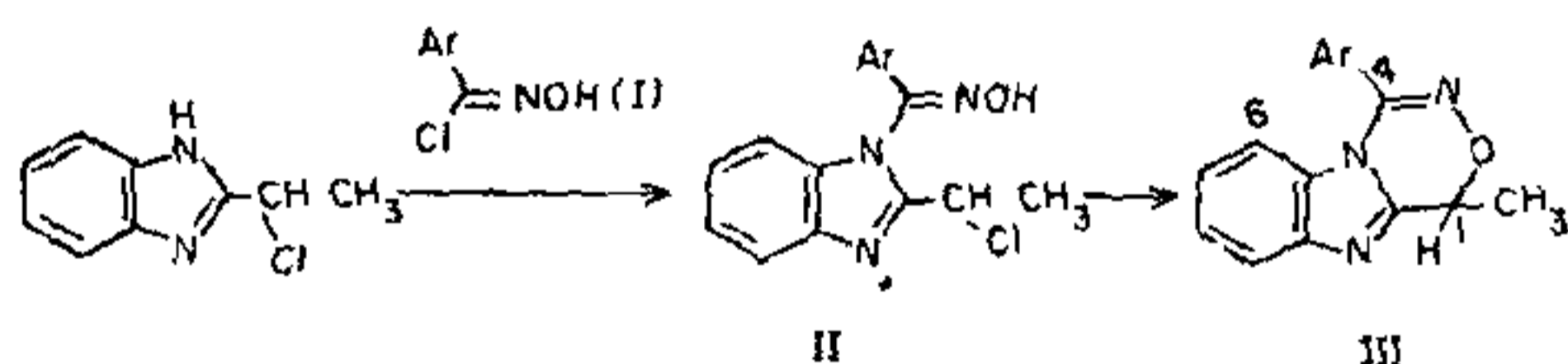
On treatment with aqueous sodium hydroxide (5%), IIa formed a colorless compound, m.p. 158°, with a molecular weight of 263 (C₁₆H₁₃N₃O from the mass spectrum), indicating that it is formed from IIa by the elimination of elements of hydrogen chloride. The IR spectrum was devoid of the oxime O–H. On the basis of the above spectral and analytical data, the compound has been assigned 1-methyl-4-phenyl-1H-[1,2,4]oxadiazino [4,5-*a*]benzimidazole structure, IIIa. The structure IIIa for the compound was further supported by its PMR spectrum (CDCl₃) which showed signals at δ 1.75 (d, 3H, J=7 Hz, C¹-CH₃), 4.92 (q, 1H, J=7 Hz, C¹-H), 6.33 (dd, 1H, J=7, 2 Hz, C⁶-H) and 7.22 (m, 8H, arom. H's).

TABLE I
2-[1'-Chloroethyl]-1-[(hydroximino) arylmethyl]-1H-benzimidazoles(II) and 1-methyl-4-aryl-1H-[1,2,4]-oxadiazino [4,5-a] benzimidazoles(III)

II ⁱ	M.P. ⁱⁱ (° C)	Yield (%)	Molecular ⁱⁱⁱ formula	III ⁱ	M.P. ⁱⁱ (° C)	Yield (%)	Molecular ⁱⁱⁱ formula	PMR (CDCl ₃), δ ^{iv}			
								C ¹ -CH ₃ ^v	C ² -H ^{vi}	C ⁶ -H ^{vii}	Other aromatic H's
a	185	45	C ₁₆ H ₁₄ ClN ₃ O	a	158	95	C ₁₆ H ₁₃ N ₃ O	1.75	4.92	6.33	7.22 (m, 8H)
b	193	39	C ₁₇ H ₁₆ ClN ₃ O	b	179	97	C ₁₇ H ₁₅ N ₃ O	1.90	5.15	6.50	7.40 (m, 7H)
c	175	42	C ₁₆ H ₁₃ Cl ₂ N ₃ O	c	130	98	C ₁₆ H ₁₂ ClN ₃ O	1.87(m)	5.31 (m)	6.07	7.35 (m, 7H)
d	180	42	C ₁₆ H ₁₃ Cl ₂ N ₃ O	d	195	98	C ₁₆ H ₁₂ ClN ₃ O	1.87	5.12	6.48	7.37 (m, 7H)
e	135	41	C ₁₆ H ₁₃ ClN ₄ O ₃	e	221	98	C ₁₆ H ₁₂ N ₄ O ₃	1.82	5.12	6.38	7.65 (m, 7H)

i = Recrystallised from methanol; *ii* = Melting points are uncorrected; *iii* = Gave satisfactory analytical values for carbon, hydrogen and nitrogen; *iv* = PMR spectra were recorded on a Varian A-60D instrument using tetramethylsilane as internal standard; *v* = doublet, J=7 Hz; *vi* = quartet, J=7 Hz; *vii* = double doublet, J=7, 2 Hz.

2-[1'-Chloroethyl] benzimidazole was similarly reacted with four more benzhydroxamic acid chlorides (IIb-e) and in all the cases the corresponding oximes (IIb-e) were isolated in moderate yields. They were subsequently cyclised with aqueous sodium hydroxide (5%) to the corresponding oxadiazinobenzimidazoles (III b-e) in almost quantitative yields (Table I).



a, Ar = C₆H₅; b, Ar = C₆H₄.CH₃ - *p*;
c, Ar = C₆H₄.Cl - *o*; d, Ar = C₆H₄.Cl - *p*;
e, Ar = C₆H₄.NO₂ - *p*.

A methyl group in the 2-[1']-position seems to facilitate the cyclisation step since the yields of III in the present investigation are higher compared to their analogs obtained from 2-chloromethyl-1-[(hydroximino) arylmethyl]-1H-benzimidazoles¹.

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ISOLATION AND CHARACTERISATION OF DIFFERENT CONSTITUENTS OF EUPHORBIA HIRTA LINN.

Euphorbia hirta Linn. (N.O. Euphorbiaceae) is used in worms, bowel complaints, cough, dysentery, colic, bronchial infection, asthma, warts¹ and possesses hypoglycaemic and anticancer activity on different laboratory animals². Earlier workers have isolated myricyl alcohol, friedelan, β-sitosterol, β-amyrin, hentriacontane, ellagic acid³, leucocyanidol, quercitol, comphol, quercetrin and quercetol derivative containing rhamnose and chlorophenolic acid⁴. Blanc *et al.*⁵ have also reported the presence of alkaloids, carbohydrates, aminoacids and flavonoids in the plant. The anticancer activity of *E. hirta* has led us to the present detailed chemical examination of the plant.

Air dried powdered aerial parts of the plant (2 kg) was extracted with petroleum ether (60-80°) in cold. Light yellow green extract (5 l) was concentrated under reduced pressure to get a resinous mass (40 gm). This semi-solid mass was separated into two fractions as ethanol soluble (Fraction I, 22 gm) and ethanol insoluble (Fraction II, 18 gm).

Fraction I gave six spots of different colours at Rf 0.08, 0.19, 0.31, 0.47, 0.74 and 0.86 (Benzene-*n*-heptane-ethanol, 50 : 50 : 20), which were separated by silica column. All the six fractions corresponding to thin layer chromatogram were identified as 24-methylene cycloartenol [C₃₁H₅₂O, m.p. 122, [α]_D²⁵ + 122, Rf 0.19, *n*-heptane-benzene ethanol, 50 : 50 : 20,