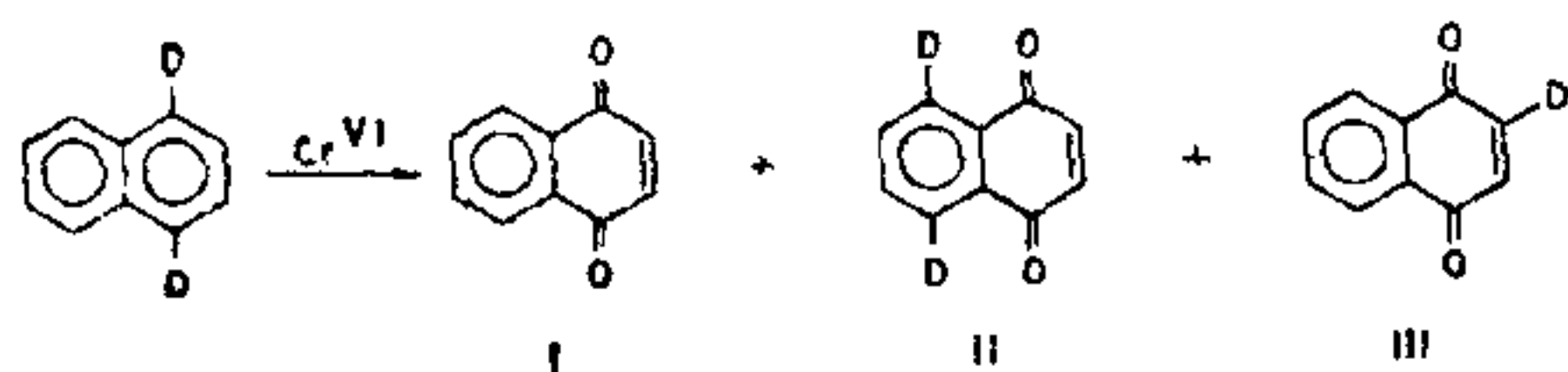


Naphthaquinone, obtained from naphthalene 1, 4-D₂ on oxidation, showed the intensity of the peaks in NMR for $\alpha:\beta$: quinonoid hydrogens = 2 : 4 : 3 (instead of 2:4:4 expected for equimolar mixture of I and II in Scheme I). Clearly, the hydrogen of the quinonoid moiety was partly substituted with deuterium. This view was confirmed by mass spectrum which showed the M⁺ peaks corresponding to I, II and III (Scheme I) at 158, 159 and 160.

SCHEME I



Also, the fragmentation patterns fully supported this assignment (*m/e*, 130, 131 and 132 (M⁺-CO), 102, 103, 104 (M-2CO), 104 and 106 (130 and 132-C₂H₂ and 131-C₂HD) and 76 & 78 (benzynes and benzyne-D₂). The formation of naphthaquinone-D provides the crucial evidence for the intermediacy of a naphthalene 1, 2-epoxide, or an 1, 2-epoxide like transition state. The migration of deuterium from 1 to 2 position is caused apparently by the 'NIH shift', well recognised as a diagnostic feature of arene-oxide involvement. These findings place the chromic acid oxidation on a similar basis mechanistically to chromyl chloride oxidations⁶.

Table III presents the kinetic behaviour in the presence of Mn^{II} (which is usually employed to trap Cr^{IV} and Cr^V). Instead of the expected decrease in rate, surprisingly the reaction was found to be catalysed by Mn^{II} ions. Further, the order with respect to Cr^{VI} changed from two to one on increasing Mn^{II} concentration. Difference spectra indicated as max 500 nm, which could be assigned to Mn^{III} species⁷.

TABLE III
Effect of Mn^{II}

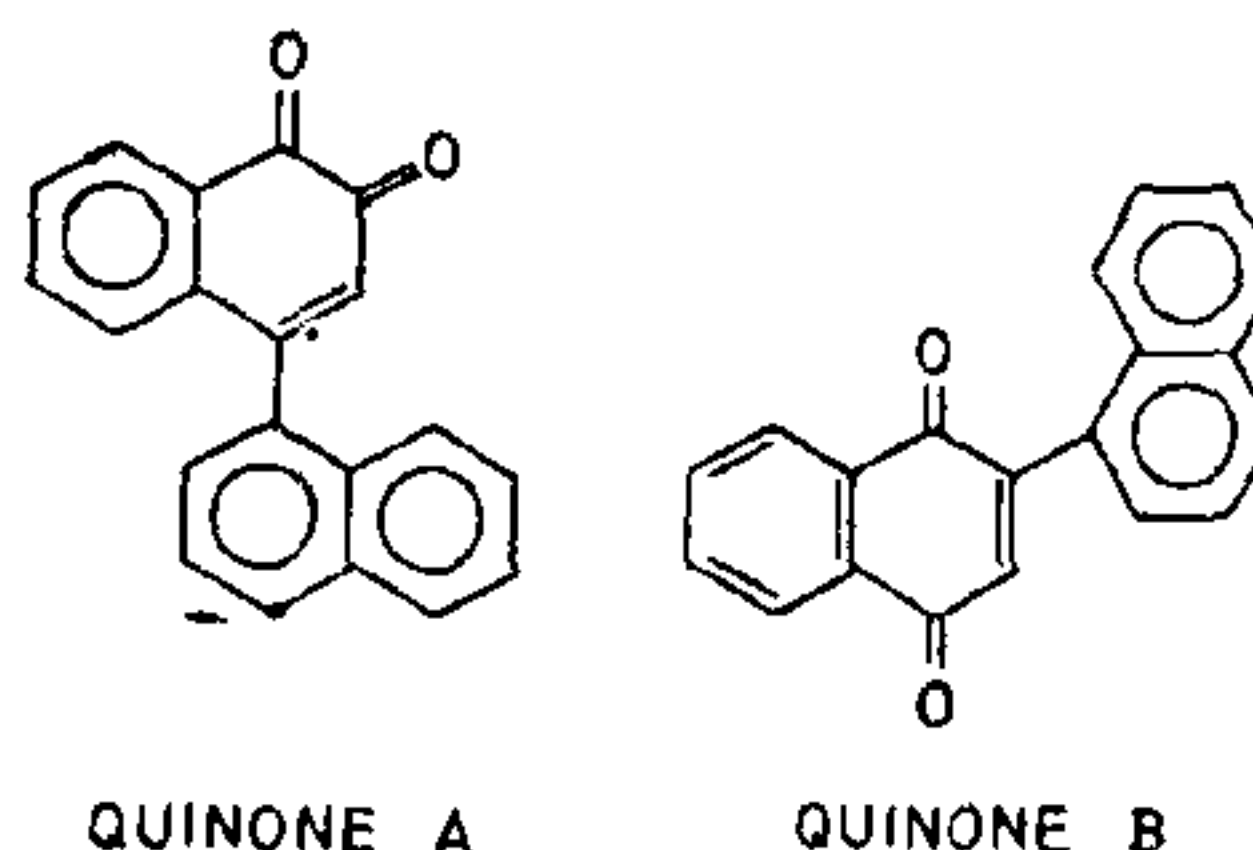
Mn ^{II}	$k'_2 M^{-1} S^{-1}$	$k'_1 S^{-1}$	$k'_3 M^{-1} S^{-1}$
0.000	0.3745		9.3632
0.002	0.9257		23.1430
0.010	2.0200		50.5040
0.050		8.688×10^{-3}	72.4000
0.200		8.808×10^{-3}	73.4000

Naphthalene = 0.04 M, CrO₃ = 0.003 M, H⁺ = 0.1 M, μ = 0.3, HOAc = 95%, and T = 30° C.

The reaction order with respect to Mn^{II} was found to be 0.2, indicative of a radical process. Product

analysis showed that, along with naphthaquinone, two new quinones were produced. Their structures were found to be A and B (Scheme II) on the basis of IR, NMR, mass, UV spectra and confirmed also by synthesis. The formation of these quinones in presence of Mn^{II} could again mean radical processes, the intermediate radicals being trapped by the excess naphthalene present in the medium.

SCHEME II



QUINONE A

QUINONE B

We are planning to discuss these results in a more detailed paper.

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SYNTHESIS OF ISOXAZOLO (7, 6-d)- COUMARINS AND ISOXAZOLO (7, 8-d)- COUMARINS

ISOXAZOLO (7, 8-d) flavones are known to possess antibacterial activity¹. Some furano (6, 7-d)-1, 2-benzisoxazoles and isoxazolo (6, 7-d)-1, 2-benzisoxazoles also exhibit antifungal activity². In view of this, the synthesis of a few isoxazolo (7, 6-d) coumarins (I) and isoxazolo (7, 8-d) coumarins (II) was carried out for the first time.

The starting materials, 7-hydroxy-6-aryl-4-methylcoumarins were obtained by known method³, while 7-hydroxy-8-acetylcoumarins were prepared by the Fries migration of 7-acetoxycoumarins⁴. The corresponding oximes on acetylation yielded the oxime acetates which on cyclization by the pyridine method reported by us earlier⁵ gave the corresponding isoxazolo (7,6-d) coumarins (I) and isoxazolo (7,8-d)-coumarins (II). The physical data of these compounds is reported in Table I.

ppm; but none of the compounds was found to possess any significant activity. The screening was done by dry weight method.

General procedure for the preparation of:

Oximes—The acylcoumarin (0.1 mole) was treated with hydroxylamine hydrochloride (0.12 mole) and sodium acetate (1 g) in an aqueous solution and refluxed for 40 min. The solid separated on cooling was filtered, washed with water and crystallized from

TABLE I

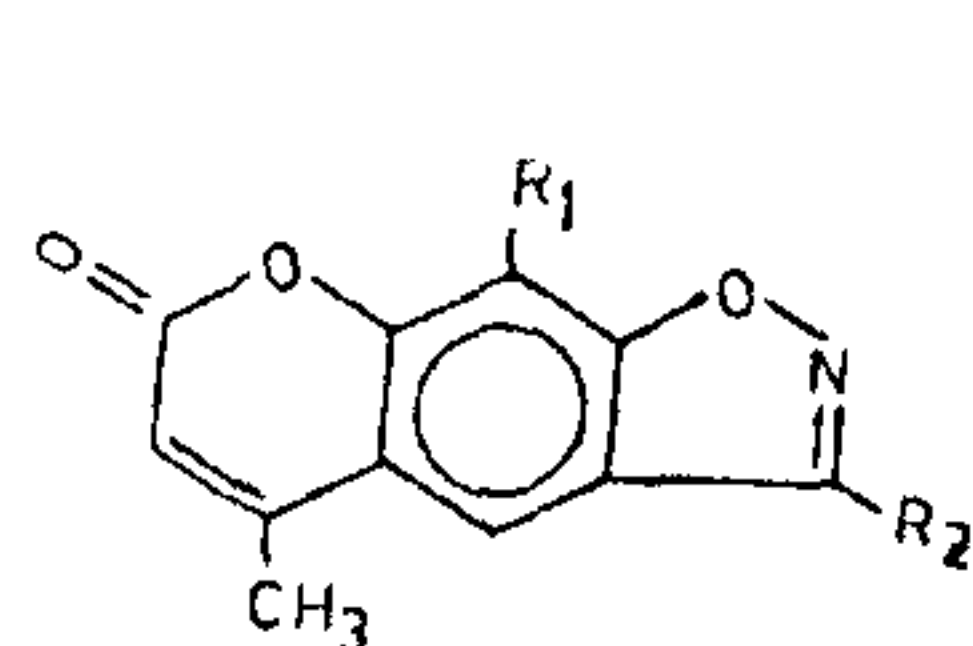
Physical data of hydroxy-acyl-coumarins and their corresponding oximes, oxime acetates and isoxazolo (7,6-d)-coumarins (I) and isoxazolo (7,8-d) coumarins (II)

7-Hydroxy-acyl-coumarins	M.P. °C	Yield %	Corresponding oximes M.P. °C	Corresponding oxime acetate M.P. °C	Corresponding isoxazolo coumarins *(I and II) M.P. °C
6-Acetyl-4-methyl-	212 ^a	22	256 ^b	188 ^a	Ia 269 ^b
6-Propionyl-4-methyl-	226 ^b	25	230 ^b	178 ^a	Ib 213 ^b
6-Acetyl-4,8-dimethyl-	193 ^b	25	254 ^b	212 ^b	Ic 256 ^b
6-Propionyl-4,8-dimethyl-	191 ^a	23	245 ^b	173 ^a	Id 210 ^b
8-Acetyl	167 ^a	56	227 ^b	161 ^a	IIa 228 ^a
8-Acetyl-6-ethyl-4-methyl-	131 ^a	83	172 ^a	125 ^a	IIb 160 ^a

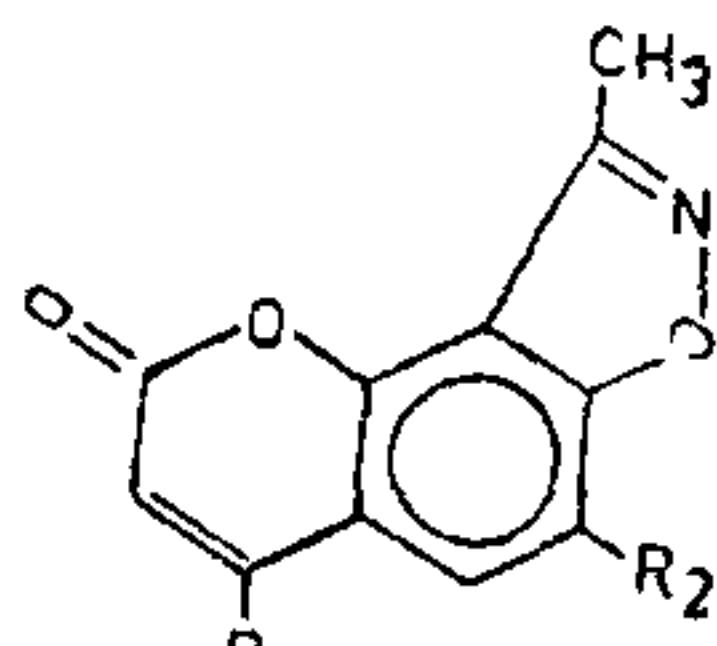
* All compounds gave satisfactory elemental analyses.

a = Crystallised from ethanol ; b = crystallised from acetic acid ; c = crystallised from 70% acetic acid.

IR spectra (nujol) of I and II showed bands around 1725, 1630, 1220 and 830 cm⁻¹ characteristic of C=O coumarins, C=C, N-O-C and isoxazole ring stretch respectively.



	R ₁	R ₂
a	H	CH ₃
b	CH ₃	CH ₃
c	H	C ₂ H ₅
d	CH ₃	C ₂ H ₅



	R ₁	R ₂
a	H	H
b	CH ₃	C ₂ H ₅

a proper solvent. The yields of these oximes were between 60–72%.

Oxime acetates.—The oxime (0.05 mole) was heated with acetic anhydride (0.075 mole) on a water-bath till dissolved and kept aside for 30 min. It was then poured over crushed ice. The solid thus obtained was filtered, washed with water and crystallized from a proper solvent. The oxime acetates were obtained in 65–72% yield.

Cyclization of oxime acetates to corresponding isoxazolo (7,6-d) coumarins (I) isoxazolo (7,8-d) coumarins (II)

The oxime acetate (1 g) was refluxed with dry pyridine (10 ml), for 3 hr. The reaction mass was then poured over crushed ice containing enough hydrochloric acid to neutralise pyridine present in it. The resulting solid was filtered, washed with water and crystallized from a proper solvent. The isoxazolo-coumarins were formed in yields ranging from 70–85%.

Physiological activity.—Some of the compounds were tested against plant pathogenic fungi, viz., *Helmenthosporium apatternae* and *Pestalotia* sp. at 50

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COMPLEXES OF PROTOCATECHUIC ACID WITH LANTHANIDES

COMPLEX formation by several dihydroxybenzoic acids with Al(III)^{1,2} and lanthanide, complexes with the ortho hydroxybenzoic acids³, orthohydroxy hapthoic acid⁴ and Protocatechualdehyde⁵ (3, 4 dihydroxy benzaldehyde) have been reported. In the present investigation, the preparation and characterisation of Y³⁺, La³⁺, Pr³⁺, Nd³⁺, Sm³⁺ and Gd³⁺ — Protocatechuates are reported.

The lanthanide complexes were prepared by the published procedure⁵. The analytical data of the complexes indicated that the ligands are attached to the lanthanide ion in the ratio of 3 : 1. Conductivity measurements indicated that all the complexes are non-electrolytes. Analytical data is represented in the Table.

The studies in the ultraviolet region were restricted to solutions in methanol and ethanol due to the

TABLE

COMPLEXES	ANALYSIS			U.V. ABSORPTION BANDS			INFRARED BANDS		
	Metal %	Carbon %	Hydrogen %	W.L. nm	Log ϵ_{\max}		C=O Str.	-OH Str.	
					Methanol	Ethanol			
Y (C ₇ H ₅ O ₄) ₃	14.00	40.05	2.90	255	2.39	3.47	1660	2900	
	(13.80)	(39.40)	(2.94)	290	3.36	3.51			3300
				355	2.38	1.91			
La (C ₇ H ₅ O ₄) ₃	16.82	38.00	1.93	255	3.72	3.80	1640	2900	
	(16.85)	(38.46)	(1.81)	285	3.77	3.73			3400
				350	2.42	2.43			
Pr (C ₇ H ₅ O ₄) ₃	23.00	42.33	2.40	260	3.65	2.30	1660	2900	
	(23.38)	(42.09)	(2.44)	290	3.65	3.65			3300
				355	2.39	2.30			
Nd (C ₇ H ₅ O ₄) ₃	22.15	37.00	2.30	255	3.77	4.08	1640	2900	
	(21.83)	(38.15)	(2.27)	290	3.90	4.08			3350
				355	2.34	2.74			
Sm (C ₇ H ₅ O ₄) ₃	22.54	38.00	2.41	260	3.71	4.04	1650	2900	
	(22.54)	(37.80)	(2.25)	290	3.90	4.01			3300
				355	2.39	2.30			
Gd (C ₇ H ₅ O ₄) ₃	20.58	37.00	2.33	250	3.84	2.53	1640	2900	
	(20.30)	(37.41)	(2.22)	290	3.84	3.92			3300
				355	2.04	4.02			

Note: Numbers given in brackets are observed values.