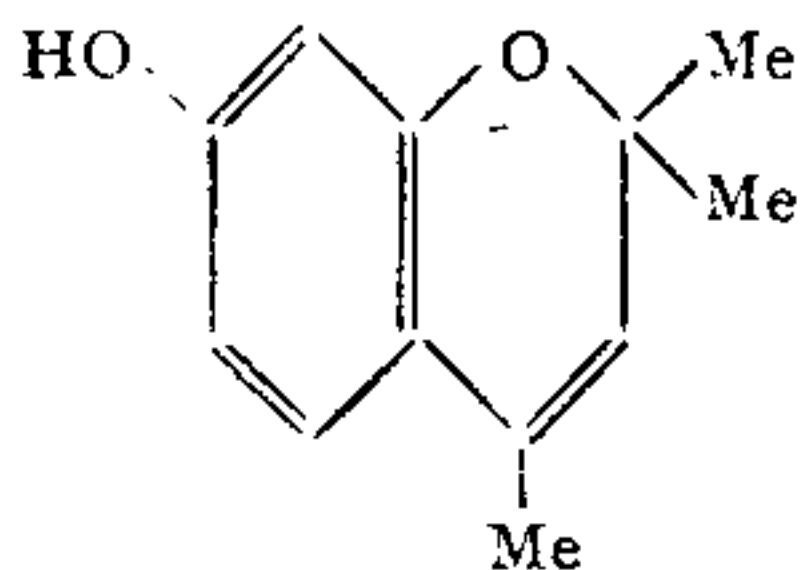
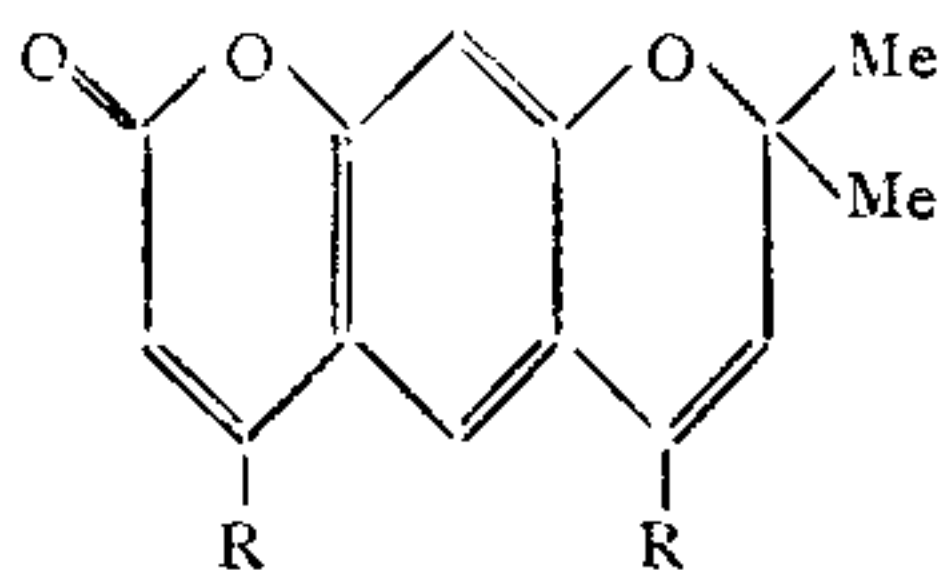


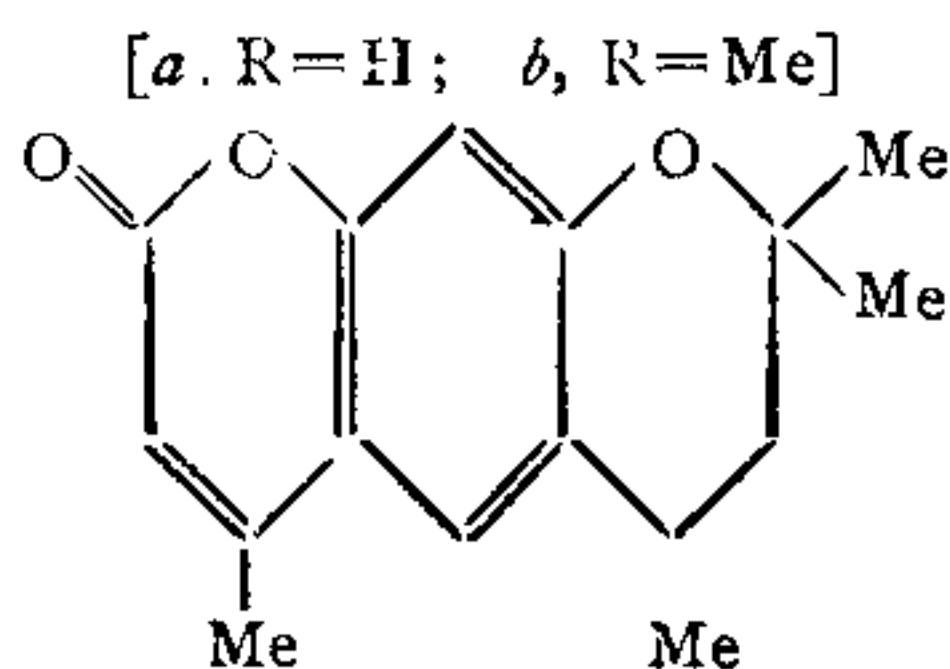
to condensation in position 8 of (I). Had it been angular structure then there would have been doublets for the aromatic protons (at C-5 and C-6) due to vicinal coupling. U.V. absorption values also closely agree with those reported for xanthyletin^{1c} (II a) ($\lambda_{\text{Max}}^{\text{M:OH}}$ 266, 348; $\log \epsilon$ 4.34, 4.15).



I



II



III

Catalytic hydrogenation of II b over Raney Nickel at 45 lb. pressure gave 4,6-dimethyl-6,7-dihydroxanthyletin (III) in nearly quantitative yield (crystallised from ethanol as colourless needles, m.p. 155-56°; Found C, 74.4, H, 6.9; $\text{C}_{16}\text{H}_{18}\text{O}_3$ requires C, 74.4, H, 6.9%. U.V. absorption $\lambda_{\text{Max}}^{\text{M:OH}}$ 230, 328 ($\log \epsilon$ 4.73, 4.92). Condensation of 7-hydroxy-2,2-dimethylchroman⁶ with ethyl acetoacetate in presence of H_2SO_4 (80%) also gave (III) in very good yield as adjudged by m.p. and mixed m.p. of the two samples.

The authors offer their thanks to Dr. T. R. Govindachari, Director, CIBA Research Centre, for NMR spectrum.

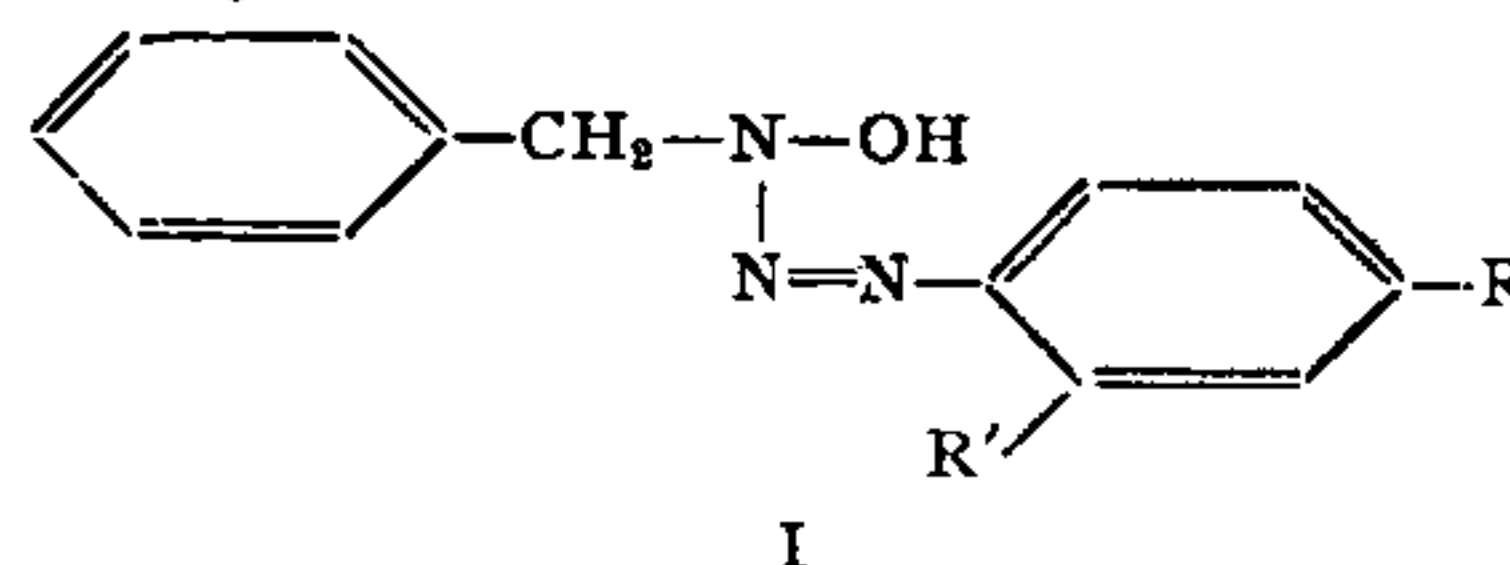
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STUDIES IN HYDROXYTRIAZENES

THE successful use of 3-hydroxy-1,3-diphenyl triazene and its substituted derivatives in the gravimetric and colorimetric determination¹ of Cu, Pd, Ni, Ti, etc., suggests that the synthesis and examination of some analogous compounds may be profitable. Another observation² that 3-hydroxy-1-phenyl-3-benzyltriazenes imparts an indigo colour to ferric chloride solution and gives a brownish buff precipitate with Cu(II) led the present authors to synthesise other analogous compounds and study their properties and reactions towards metal ions. In this communication, ten hydroxytriazenes (represented by the general formula I)



prepared by condensing benzyl hydroxylamine with various diazonium compounds prepared from aniline or substituted anilines have been reported, most of them for the first time.

The ligands were prepared by adding diazotised aniline or its substituted derivative in thin stream to a freshly prepared solution of benzylhydroxylamine in 70% alcohol at 0° C. under constant stirring. The pH of the reaction medium was adjusted to be near 5 by adding small portions of sodium acetate solution (10% wt./vol.) at regular intervals. The temperature was maintained at 0° C. by adding ice. All of the hydroxytriazenes got precipitated and were filtered, washed repeatedly with distilled water and dried in vacuum except in the case of the sulphonic acid derivative which was water-soluble and hence salted out of the medium with sodium chloride. The *ortho*-tolyl derivative was a liquid and hence recovered by extraction with ether.

TABLE I
Physical characteristics of hydroxytriazenes

Compound		Colour	m.p. °C.	Microanalysis data					
R	R'			Found (%)			Calculated value (%)		
				C	H	N	C	H	N
H	H	White	105°C.	69.21	5.9	17.91	68.71	5.76	18.4
Cl	H	"	112-144°C.	60.38	4.84	15.92	59.67	4.61	16.05
H	Cl	"	75°	59.60	5.2	15.82	59.67	4.61	16.05
CH ₃	H	"	106	70.49	6.5	17.27	69.09	6.26	17.42
H	CH ₃	Brown	129 (B.P.)	70.36	6.36	17.31	69.69	6.26	17.42
NO ₂	H	Yellow	174	57.92	5.0	21.01	57.35	4.44	20.58
Br	H	White	153	51.57	4.3	13.52	51.00	3.95	13.73
-COOH	H	Yellow	199	63.6	5.03	15.21	61.98	4.83	15.49
H	COOH	"	138	62.31	5.23	15.81	61.98	4.83	15.49
So ₃ Na	H	Pale violet	Stable upto 235°C.	45.37	4.31	11.90	44.94	4.062	12.10

The physical characteristics of these hydroxytriazenes are given in Table I. They are stable under atmospheric conditions and are highly soluble in alcohol, benzene, acetone, dioxane, etc., except in the case of the sulphonato derivative which is water-soluble. Their aqueous and alcoholic solutions are stable and can be preserved for several weeks.

Reactions of these ligands towards metal ions have been observed. The formation of stable coloured precipitates or complexes in solution has been indicated in several cases under certain pH conditions. The colour reactions of 3-hydroxy-1-parachlorophenyl-3-benzyl-triazene have been summarized in Table II.

TABLE II
Reactions of 3-hydroxy-1-parachloro-phenyl-3-benzyltriazene

Metal ion added	Colour of ppt / soln	pH	Remarks
Pd ²⁺	Violet ppt.	1.6-7	Stable, granular and insoluble in water
Cu ²⁺	Chocolate-brown ppt	1.7-7	do.
Co ²⁺	Brown ppt.	4.7-7	do.
Ni ²⁺	Yellow ppt.	4.7-7	do.
Fe (III)	Green soluble complex; becomes blue at higher pH	~2	Unstable to heat
Fe (II)			
Ti (IV)	Yellow colour	~2	Unstable
V (IV)	Dirty green ppt.	~2	Unstable to heat
V (V)	Green ppt.	~2	do.
Mo(VI)	Orange-yellow ppt.	~2	do.
Ce (IV)	Slightly pale yellow	~2	do.

All other hydroxytriazenes synthesised gave similar reactions with metal ions. Ag(I) and Au(III) solutions get reduced by the reagents to the metallic state. Alkaline metals, alkaline

earth metals, Zr, Th, Pt, Rh, Ru, Ir, Ge, Be, Mn, UO₂²⁺, Cr, Al, As, Sb, Bi, Zn, Cd, Hg, Pb, Sn, do not show any reaction. Similarly, anions like oxalate, tartrate, fluoride, phosphate and borate do not give any reaction with the reagent. The precipitation of some of the metal ions seems to be complete as evident from the application of known spot tests to the respective metal ions in the filtrate.

The use of some of these hydroxytriazenes as gravimetric reagents is very much indicated and is under study.

The authors wish to thank Prof. S. C. Bhattacharyya and Prof. Hira Lal for their interest in the work and Prof. A. B. Biswas for providing the facilities.

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ON THE METHYL ETHERS OF LIMONENE

REACTION of (+) or (±)-limonene with alcohols in presence of acid catalysts leads to ethers.¹⁻⁵ Royals⁵ demonstrated that (+)-limonene on heating with methanol containing conc. sulphuric acid (10% by weight) at 55-60° for 5 hr. afforded (i) 7% 1,8-dimethoxy-p-methane (I) and (ii) 40% terpinyl methyl ether. These ethers were identified exclusively through molecular refractions which compared excellently with calculated values. As regards the monoether, it was presumed to be an isomeric mixture, the major