

FLAVYLIUM SALTS CONTAINING PYRONE RINGS

BY L. RAMACHANDRA ROW AND T. R. SESHADRI

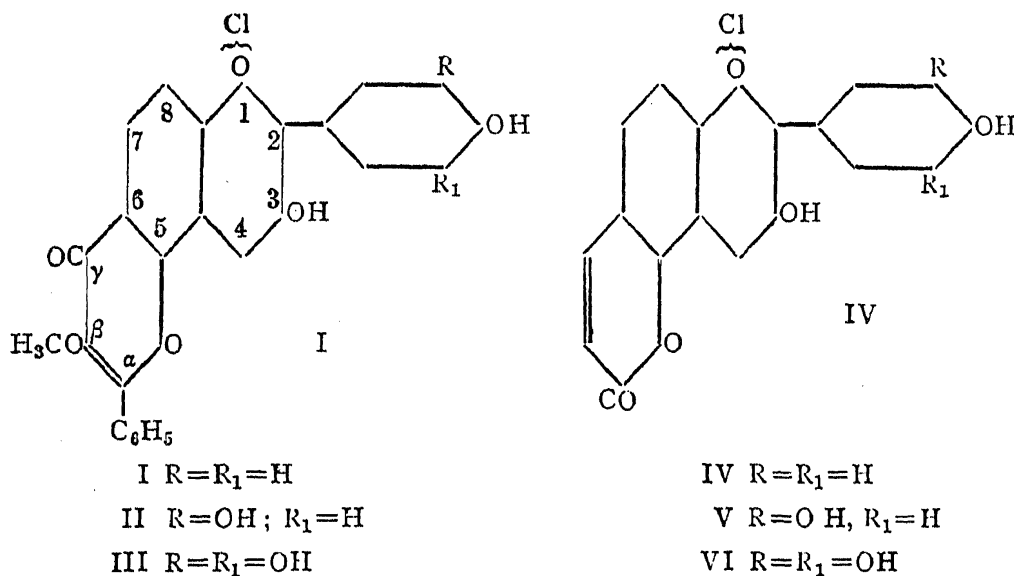
(From the Department of Chemistry, Andhra University, Waltair)

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FOR establishing the presence of *o*-hydroxy-aldehyde groups, the pyrylium salt reaction is very handy. The formation of the bright red colour is useful for quick diagnosis and the solid pyrylium salts are convenient derivatives for analysis. In the course of other work in progress in these laboratories, information was needed regarding complex flavylium salts. As convenient examples, a number of them have now been prepared from 7-hydroxy-3-methoxy-flavone-8-aldehyde¹ and umbelliferone-8-aldehyde² by condensation with typical hydroxy acetophenones and their acetyl derivatives.

Besides the synthesis of flavylium salts of anthocyanidin type, Robinson and co-workers³ made a number of synthetic flavylium compounds of simpler nature and studied them. They also made a few complex substances containing naphthalene and other condensed ring systems. Recently Russel and Speck⁴ have reported the synthesis of a number of flavylium salts starting from β -naphthol-aldehyde. The formation of pyrylium salts of the xanthylum group by the condensation of 1:4-naphthohydroquinone and some aldehydes in the presence of hydrochloric acid has been observed by Fieser.⁵ As a result of these investigations certain interesting observations regarding the influence of constitutional factors on fluorescence and colour reactions could be made and they may be useful for diagnosis of the constitution of unknown compounds.

With each of the two aldehydes, (1) 7-hydroxy-3-methoxy-flavone-8-aldehyde and (2) umbelliferone-8-aldehyde, the following three ketones have been condensed: (a) ω :*p*-dihydroxy-acetophenone,⁶ (b) ω :3:4-triacetoxy-acetophenone⁷ and (c) ω :3:4:5-tetra-acetoxy-acetophenone.⁸ The reaction takes place quite readily and the flavylium salts are obtained in good yield. The two sets of compounds can be represented conveniently by the formulæ given below. The numbering of the positions is adopted with a view to emphasise the flavylium salt structure and the substituents in the pyrone ring are marked with Greek symbols treating the flavone derivatives as γ -pyrono compounds and the coumarin derivatives as α -pyrono compounds.



The new flavylium salts exhibit no fluorescence in alcoholic or aqueous solutions. In sulphuric acid, however, the simplest members exhibit a green fluorescence, whereas the others give an almost negligible blue emission. Their solutions are comparatively feeble in colour in spite of the presence of pyrone rings. This may partly be due to the absence of hydroxyl group in the seven position. The α -pyrone derivatives give feebler colour reactions as compared with the γ -pyrone compounds. Not only are the chlorides sparingly soluble, but they are also very unstable. Recrystallisation should be effected from alcoholic hydrogen chloride. If aqueous alcoholic medium should be used for their crystallisation, the products contain very low percentage of halogen, probably due to partial conversion into the colour-bases. Even long exposure of the pure salts to atmosphere produces similar loss in halogen. Such products, however, give the same colour reactions as the original flavylium salts.

Experimental

The procedure for the preparation of the flavylium salts is given below using the simplest example and all the others are made similarly. Their properties and colour reactions are recorded in the form of Tables.

3:4'-Dihydroxy-5:6- γ -(α -phenyl- β -methoxy)-pyronoflavylium chloride (I).—7-Hydroxy-3-methoxy-flavone-8-aldehyde (0.4 g.) and ω : 4-dihydroxy-acetophenone (0.2 g.) were dissolved in ethyl acetate (about 100 c.c.) and the solution was saturated with dry hydrogen chloride at 0° C. After the saturation, the current of gas was continued for about 2–3 hours and the flask with the contents was then left in the frigidaire overnight. The bright red crystalline solid was then collected and washed with ether (yield 83%). It was crystallised by dissolving in a small quantity of 5% methyl alcoholic hydrogen chloride and saturating it with dry hydrogen chloride gas in the cold. It

was obtained as bright red shining crystals which appeared as elongated rectangular plates under the microscope and melted at 227–29°.

In the case of the other ketones an anhydrous mixture of ethyl acetate and ethyl alcohol in equal proportions was employed as the solvent. During the course of the condensation, deacetylation took place giving rise to flavylum salts with hydroxyl groups.⁸

TABLE I

No.	Name of the Compound	Yield %	Appearance	Melting point	Analysis	
					Found	Calculated
<i>Flavylum salts obtained from 7-hydroxy-3-methoxy-flavone-8-aldehyde.</i>						
I	3:4'-Dihydroxy-5:6-γ (α-phenyl-β-methoxy) pyrono-flavylum chloride $C_{25}H_{17}O_8Cl, 2H_2O$	83	Red shining rectangular plates	227–29°	C, 61.7 H, 4.4 Cl, 7.6	C, 61.9 H, 4.3 Cl, 7.3%
II	3:3':4'-Trihydroxy-5:6-γ (α-phenyl-β-methoxy) pyrono-flavylum chloride $C_{25}H_{17}O_7Cl, 2H_2O$	60	Bright red micro-crystalline powder	240–42° (decomp.)	Cl, 6.5	Cl, 7.0%
III	3:3':4':5'-Tetrahydroxy-5:6-γ (α-phenyl-β-methoxy)-pyrono-flavylum chloride $C_{25}H_{17}O_8Cl, 4H_2O$	58	Dark red micro-crystalline powder	does not melt below 320°	Cl, 6.8	Cl, 6.4%
<i>Flavylum salts obtained from Umbelliferone-8-aldehyde</i>						
IV	3:4'-Dihydroxy-5:6-α-pyrono-flavylum chloride $C_{18}H_{11}O_5Cl, \frac{1}{2}H_2O$	65	Deep brown micro-crystalline powder	255–57° (decomp.)	C, 61.1 H, 3.8	C, 61.4 H, 3.4%
V	3:3':4'-Trihydroxy-5:6-α-pyrono-flavylum chloride $C_{18}H_{11}O_6Cl, H_2O$	65	Dark violet micro-crystalline powder	225–27° (decomp.)	Cl, 8.9	Cl, 9.4%
VI	3:3':4':5'-Tetrahydroxy-5:6-α-pyrono-flavylum chloride $C_{18}H_{11}O_7Cl, 3H_2O$	91	Dark violet micro-crystalline powder	does not melt below 320°	Cl, 6.9	Cl, 6.6%

Colour reactions.—Solutions of the substances in 1% alcoholic hydrochloric acid were employed for all tests except 8 and 9 and the particular reagents were added. For the ferric chloride reaction an alcoholic solution without the acid was employed and for the study of fluorescence in concentrated sulphuric acid, the solids were directly used. All the compounds were

TABLE II

No.	Reagents	I	II	III	IV	B	VI
1	Colour of solution in 1% alcoholic HCl	Orange	Deep red	Deep red; violet tinge in thin layers	Orange yellow	Purple	Deep red
2	1% aqueous HCl	Very rapidly becomes colourless	Colour fades rapidly and becomes colourless	Turns pink and fades to very pale pink	Rapidly fades to colourless	Colour fades slowly to pale purple	Colour fades very slowly to pale red
3	20% HCl	Colour deepens; immediately precipitate forms	Colour deepens with a precipitate	Colour deepens and precipitate forms	Colour deepens; only slight precipitation	Colour not deepened	Colour not deepened
4	Sodium Acetate	Very pale yellow	Pale yellow	Turns pale yellow and then green	Immediately colourless	Pale blue	Light brown
5	Sodium Carbonate	First red, then quickly golden yellow	Yellowish brown	Brownish yellow changing to deep yellow	First pink and then yellow	Pale green	Brown
6	Sodium Hydroxide	Deep yellow	At first brown, rapidly fades to very weak yellow	Orange	Pale yellow to yellowish brown	Brownish yellow	Brown
7	Oxidation Test	Stable	Not very stable	Unstable	Stable	Not very stable	Unstable
8	Ferric Chloride	Not given	Olive green	Blue	Not given	Olive green	Blue
9	Conc. H ₂ SO ₄	Yellow solution with green fluorescence	Red solution with no fluorescence	Red solution with a violet tinge with very feeble blue fluorescence	Yellow solution with green fluorescence	Red solution with negligible blue fluorescence	Pale violet solution with dull blue fluorescence

extractable by amyl alcohol and by the Cyanidin Reagent from aqueous solutions.

Summary

Flavylium salts containing γ - and α -pyrone rings have been prepared by condensing 7-hydroxy-3-methoxy-flavone-8-aldehyde and umbelliferone-8-aldehyde with hydroxy-aceto-phenones or their acetyl derivatives. They are found to have very feeble tinctorial properties and their fluorescence in concentrated sulphuric acid is not marked. The salts readily lose halogen and undergo conversion into colour bases.

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