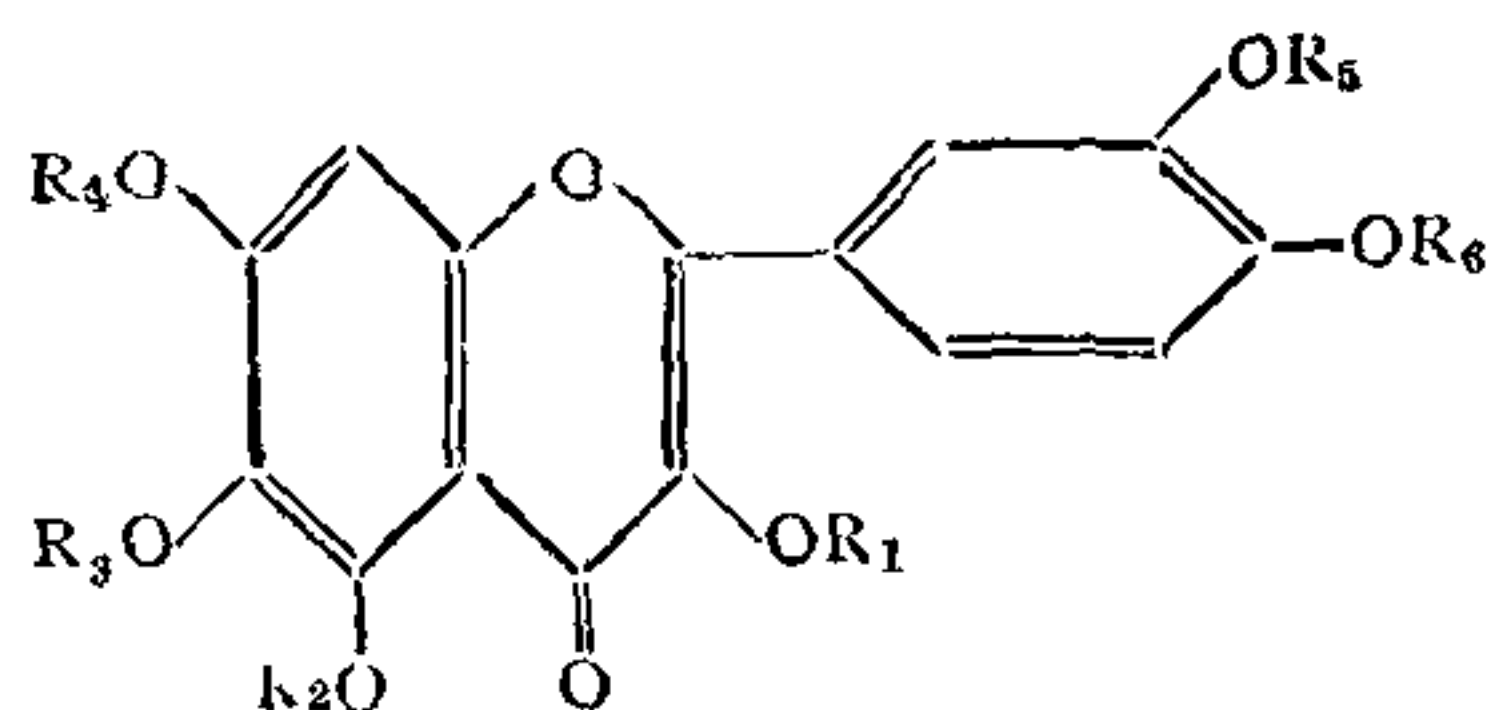


The second part consisted of the methylenation of 3,6,7,3',4'-pentahydroxy-5-methoxyflavone(II) using methylene iodide and potassium carbonate in acetone and N : N-dimethylformamide mixture to yield a product that was characterised as 3-hydroxy-5-methoxy-6,7,3',4'-dimethylenedioxyflavone(III) based on the following considerations. The methylenation product (a) analysed for  $C_{18}H_{12}O_8$ , (b) gave positive Labat test<sup>5,6</sup>, showing the presence of methylenedioxy substituent, (c) did not respond to Asahina Inubuse test<sup>7,8</sup> showing the presence of free hydroxyl at  $C_8$ , (d) on alkali degradation gave piperonylic acid thereby fixing a methylenedioxy group at  $C_3$  and  $C_4$ , (e) did not respond to Gibbs test<sup>9,10</sup> showing the absence of a free hydroxyl having an unsubstituted para position and (f) on methylation under mild conditions yielded 3,5-dimethoxy-6,7,3',4'-dimethylenedioxyflavone(IV) identical with the authentic sample of meliternatin in all respects. Since the methylenation product III was different from the demethylation product of meliternatin reported by Briggs *et al.*<sup>2</sup> the constitution of the latter could be indirectly confirmed as 3-methoxy-5-hydroxy-6,7,3',4'-dimethylenedioxyflavone(V) and not as 3-hydroxy-5-methoxy 6,7,3',4'-dimethylenedioxyflavone(III).



- I,  $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = H$   
 II,  $R_1 = R_3 = R_4 = R_5 = R_6 = H$ ;  $R_2 = CH_3$   
 III,  $R_1 = H$ ;  $R_2 = CH_3$ ;  $R_3R_4 = R_5R_6 = -CH_2-$   
 IV,  $R_1 = R_2 = CH_3$ ;  $R_3R_4 = R_5R_6 = -CH_2-$   
 V,  $R_1 = CH_3$ ;  $R_2 = H$ ;  $R_3R_4 = R_5R_6 = -CH_2-$   
 VI,  $R_1 = R_2 = H$ ;  $R_3R_4 = R_5R_6 = -CH_2-$   
 VII,  $R_1 = R_4 = H$ ;  $R_2R_3 = R_5R_6 = -CH_2-$

#### EXPERIMENTAL

##### 3-Hydroxy-5-methoxy-6,7,3',4'-dimethylenedioxyflavone(III)

A mixture of 3,6,7,3',4'-pentahydroxy-5-methoxyflavone<sup>1</sup>(II) (0.17 g), methylene iodide (0.4 ml), anhydrous potassium carbonate (1 g) in N : N-dimethylformamide-acetone mixture (75 ml; 1 : 9) was refluxed for 40 hr. The inorganic salts were filtered, washed with acetone and the solvent was removed under reduced pressure. The residue thus obtained was treated with water and left overnight. 3-Hydroxy-5-methoxy-6,7,3',4'-dimethylenedioxyflavone(III) thus obtained, crystallised from ethyl acetate-petroleum ether as light yellow micro-needles (0.09 g), m.p. 270-271° (Found: C, 60.95; H, 3.75.  $C_{18}H_{12}O_8$

requires C, 60.68; H, 3.40%). It gave positive Labat test<sup>5,6</sup> did not respond either to Asahina-Inubuse test<sup>7,8</sup> or to Gibbs test<sup>9,10</sup>.

##### 3,5-Dimethoxy-6,7,3',4'-dimethylenedioxyflavone(IV)

A solution of III (50 mg) in dry acetone (20 ml) was treated with dimethyl sulphate (0.04 ml) and anhydrous potassium carbonate (0.2 g) and the resulting reaction mixture was heated under reflux for 12 hr. The inorganic salts were filtered, washed with acetone and the solvent was removed under reduced pressure. The residue, thus obtained, was treated with ice-cold water and 3,5-dimethoxy-6,7,3',4'-dimethylenedioxyflavone(IV) thus obtained crystallised from ethyl acetate-petroleum ether as colourless needles (35 mg), m.p. 198° (Found: C, 61.2; H, 3.60.  $C_{19}H_{14}O_8$  requires C, 61.62; H, 3.81%) NMR ( $\delta$   $CDCl_3$ , TMS as internal standard); 3.95 (3H, s, 1x-OCH<sub>3</sub>), 3.98 (3H, s, 1x-OCH<sub>3</sub>), 5.95 (2H, s, -O-CH<sub>2</sub>-O-), 5.98 (2H, s, -O-CH<sub>2</sub>-O-), 6.88 (1H, s, C<sub>8</sub>-H), 7.31 (1H, d, J = 9Hz, C<sub>6</sub>'-H), 7.62 (2H, m, C<sub>2</sub>'-H and C<sub>2</sub>-H).

The authors wish to thank Council of Scientific and Industrial Research, New Delhi and University Grants Commission, New Delhi, for financial assistance.

July 21, 1981.

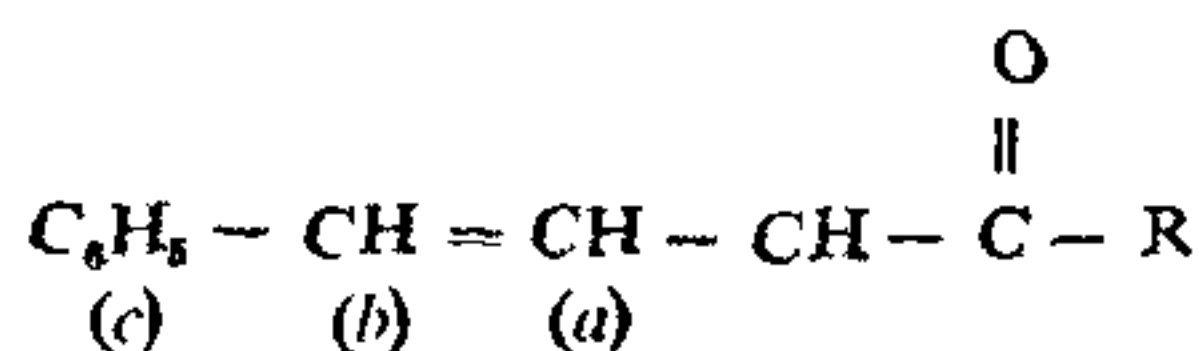
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#### A NOVEL ROUTE TO POLYHALOARYLCHALCONES

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POLYHALOARYLCHALCONES have been prepared from polyhaloarylcopper(I) compounds or the cuprates and cinnamoyl chloride in THF. Their spectral data are presented.

TABLE I  
Spectral data of chalcones



Compound	R	UV (Cyclohexane) nm (log ε)	IR (CCl <sub>4</sub> )			NMR (CCl <sub>4</sub> ) (δ, ppm)		
			ν <sub>C=O</sub>	ν <sub>C=C</sub>	ν <sub>aromatic</sub> cm <sup>-1</sup>	(c)	(b)	(a)
I. Pentafluorophenyl		300 (4.39) 306sb (4.37)	1660	1625	1603	(c) 2.58	(b) 2.78	(a) 3.23
II. Pentachlorophenyl		300 (4.43) 305 (4.37)	1661	1626	1600	(c) 2.50	(b) 2.77	(a) 2.97
III. 2,3,5,6-Tetrachloropyridyl		299 (4.47) 306sh (4.39)	1655	1630	1605	(c) 2.52	(b) 2.77	(a) 3.00

As part of our studies on the synthesis of some polyhaloaryl-compounds, we earlier reported some polyhaloarylketones<sup>1</sup>, RCOR' and diketones<sup>2</sup>, RCO(CH)<sub>n</sub>COR, where R is pentafluorophenyl, pentachlorophenyl or 2,3,5,6-tetrachloropyridyl and n = 0, 1, 2, 3, 4. In this communication, we report the preparation, through Cu(I) compounds or cuprates and cinnamoyl chloride, of three chalcones, namely, pentafluorophenyl styryl ketone(I), pentachlorophenyl styryl ketone(II) and 2,3,5,6-tetrachloropyridyl styryl ketone(III). The copper(I) compounds were formed from RLi or RMgX and Cu(I) halides in THF. For convenience, the intermediates from RLi or RMgX and Cu(I) halide are represented as simple RCu(I) compounds despite several investigations<sup>3</sup> which indicate that they may be as complex and diverse as those of phenyl<sup>4</sup> or tolylcoppers<sup>5</sup>.

All the compounds reported here gave satisfactory elemental analysis. The spectral data of the chalcones are presented in Table I.

#### Experimental

To pentafluorophenylcopper<sup>6</sup> (prepared from 0.025 mol of pentafluorophenylmagnesium chloride and 0.025 mol of cuprous iodide) in THF was added 0.025 mol of cinnamoyl chloride in THF at 0°C and stirred at the ambient temperature for ca 6h. The solvent was removed under vacuum and the residue was extracted with hot petroleum ether (60-80°C). Removal of solvent afforded a faint yellow solid (4.62 g, 62%), identified as pentafluorophenyl styryl ketone(I), m.p. 102-103°C, after crystallization from petroleum ether.

Similar experiments employing pentachlorophenylcopper<sup>6</sup> or 2,3,5,6-tetrachloropyridylcopper<sup>6</sup> and cinnamoyl chloride gave, respectively, (II) or (III),

in yields of 82% and 52% (respective m.p.s 176° and 148°).

August 31, 1981.

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#### DOUBLE INFECTION BY CITRININ-PRODUCING FUNGI ON SORGHUM

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THE mycotoxin citrinin was first isolated from *Penicillium citrinum* by Hetherington and Raistrick<sup>1</sup>. Later it has been reported in several species belonging