Variation of $\log(f_r/T)$ with $1/T$ is shown in Fig. 1 for pure ethyl salicylate. The observed
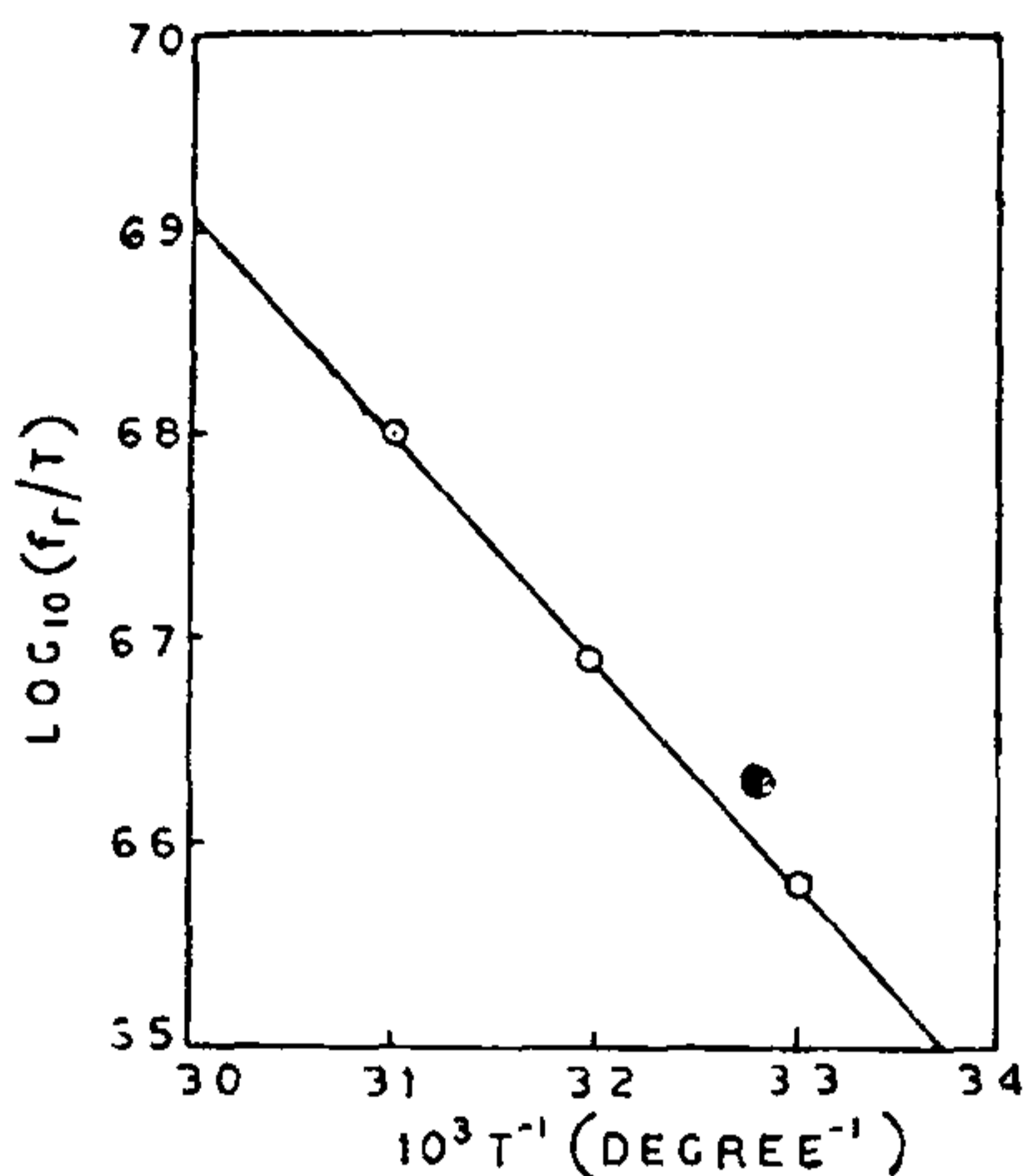

FIG. 1. Plot of $\text{Log}_{10}\,(f_r/T)$ vs. T^{-1} for ethyl salicylate.

linear variation with negative slope is consistent with the theory proposed by Davies and Lamb[5] for rotational isomerism. Estimated value of activation energy of the rate determining mechanism is 5 K.cals/mole.

From Tables II and III it is apparant that the relaxation frequency f_r of ethyl salicylate is not significantly altered by the foreign environment of either m-xylene or nitrobenzene. Polar and non-polar solvents have no influence on the relaxation, except for providing a dilution effect on relaxation strength. It can therefore be concluded that the mechanism of relaxation in ethyl salicylate is of an intramolecular origin.

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SYNTHESIS OF 3″-METHYL-FURO-(5″, 4″:7, 8)-FLAVONES

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FUROFLAVONE, karanjin and furocoumarins, psoralene, angelecin and xanthotoxin are reported to possess fish-toxic and photodynamic properties[1-3]. Several methyl substituted furocoumarins and furoflavones are also reported to possess similar physiological properties[4-6]. 3′, 4, 8-Trimethylpsoralene, available in large quantities by synthesis, is the most effective photodynamic agent[7]. 3″-Methyl-furo-(5″, 4″ : 7, 8)-flavones, considered to be analogous of karanjin, do not seem to have been synthesized earlier. In this communication we report their synthesis, spectral characteristics and fish-toxicity.

7-Hydroxy-(I a)[8], 7-hydroxy-3-methyl-(I b)[9], 7-hydroxy-3-methyl-3′, 4′-dimethoxyl(Ic)[9] and 7-hydroxy-3-phenyl(I d)[10]-flavone were condensed with chloroacetone by heating in acetone-potassium carbonate medium to give the corresponding 7-acetonoloxyflavones (II a–d). Their melting points, ir and uv data are given in Table I and the nmr data are given in Table II. The cyclodehydration of acetonoloxybenzenes with polyphosphoric acid, leading to the formation of 3-methylbenzofurans,

was reported earlier[11]. The 7-acetonoloxyflavones (II a–d) were heated in polyphosphoric acid for 2 hours at 110–120°. In each case a pale yellow semi-solid was obtained. The semi-solids were subjected to chromatography, resulting in the isolation of (1) cyclized product ~30%, (2) unconverted starting compound ~50%, and (3) the corresponding 7-hydroxyflavones ~20% in each case. The melting points, ir and uv data of the cyclized products III a–d are given in Table I and their nmr data are given in Table II. The data suggest that the cyclized products possess 3-methyl-furo-(5″, 4″ : 7, 8)-flavone structure (III a–d). In the ir spectra of furoflavones the frequency appearing around 1630 cm^{-1} is due to the flavone carbonyl group. The carbonyl frequency found around 1725 cm^{-1} in 7-acetonoloxyflavones (II a–d) due to acetonoloxy carbonyl disappears in the furoflavones. In their nmr spectra, a doublet appears in the region 2·45–2·65 δ (J = 1 Hz) assignable to the C3″-methyl group and the splitting is due to the adjacent C2″ proton. An AB doublet appears in the region 8·20–8·24 δ (J = 9–10 Hz), characteristic

TABLE I

Mp, ir, uv and fish-toxicity data of 7-acetonoloxyflavones and the corresponding 3″-methyl-furo-(5″, 4″: 7, 8)-flavones*

Compound	mp °C	ir (CHCl₃) cm⁻¹		uv MeOH max. nm (Log ε)	Fish-toxicity at 20 ppm turning time Mts. Sec.
		Acetonol- oxy carbonyl	Flavone carbo- nyl		
II a**	179	1730	1630	222 (4·04), 252 (4·04) and 306 (4·17)	10–00
II b**	132	1725	1625	236 (4·25) and 300 (4·26)	4–30
II c**	95	1730	1620	224 (4·31) and 308 (4·31)	12–00
II d**	170	1725	1630	232 (4·38), 258 (4·23) and 306 (4·25)	35–00
III a**	130	..	1635	224 (4·30), 256 (4·32), 264 (4·33) and 300 (4·10)	Not toxic within 45 miutes
III b†	190	..	1630	222 (4·28), 254 (4·38) and 310 (3·99)	do.
III c†	184	..	1630	222 (4·36), 244 (4·45), 248 (4·45) and 316 (4·23)	do.
III d†	215	..	1630	224 (4·56), 250 (4·57), 258 (4·57) and 308 (4·15)	do.

* Satisfactory elemental analyses were obtained for all the compounds.
** Solvent of crystallization: Benzene-Petroleum ether (60–80°).
† Solvent of crystallization: Benzene.

TABLE II

Nmr spectral data of 7-acetonoloxy-, and 3″-methyl-furo-(5″, 4″: 7, 8)-flavones
Solvent (CDCl₃) 60 MHz, δ values, (J in Hz)

Compound	C3″ (d)	−O−CH₂− (s)	−CO−CH₃ (s)	C3 substituent (H or CH₃ or Ph)	C5	C2″, C2 phenyl, C6 and C8 (m)	Methoxyls (s)
II a	..	4·70	2·18	6·85 s (H)	8·25 (J = 9)	7·00–7·50 (7H)	..
II b	..	4·70	2·10	2·30 s (CH₃)	8·25 (J = 10)	6·75–7·70 (7H)	..
II c	..	4·62	2·12	2·28 s (CH₃)	8·15 (J = 9)	6·70–7·40 (5H)	3·9 (6H)
II d	..	4·72	2·30	6·90–7·40* m (C₆H₅)	8·30 (J = 10)	6·90–7·40* (12H)	..
III a	2·65 (J = 1)	..	..	6·90 s (H)	8·20 (J = 9)	7·30–7·75 (7H)	..
III b	2·45 (J = 1)	..	..	2·24 s (CH₃)	8·24 (J = 9·5)	7·30–7·90 (7H)	..
III c	2·55 (J = 1)	..	..	2·35 s (CH₃)	8·23 (J = 9)	7·00–7·63 (5H)	4·05 (6H)
III d	2·52 (J = 1)	..	..	7·18–7·60* m (C₆H₅)	8·20 (J = 10)	7·18–7·60* (12H)	..

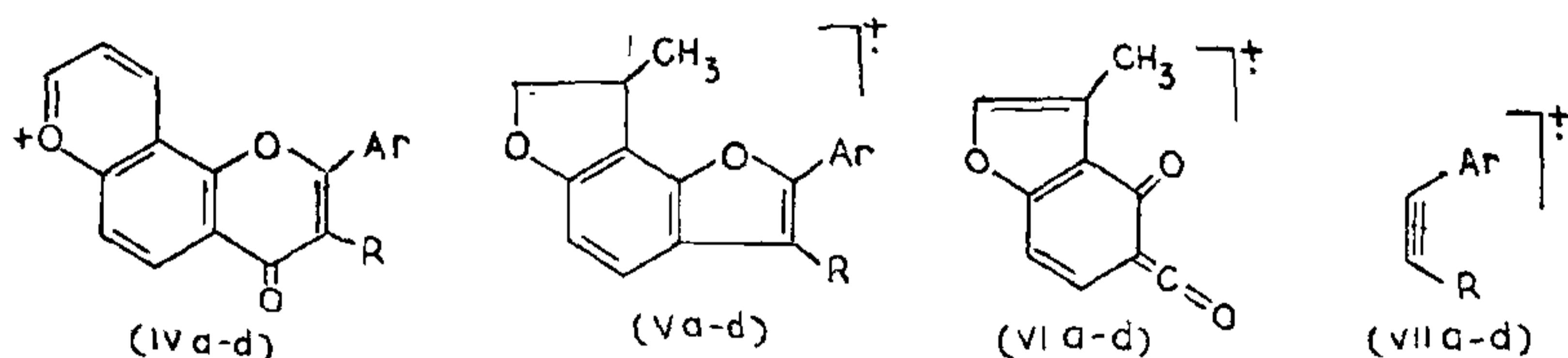* C3 Phenyl protons merged with other aromatic protons.

of C5 proton of flavones[1,2], indicating that there is a proton at C6 position. The C2″ and C6 protons merge with the other aromatic protons of side phenyl nuclei. From this it can be inferred that the mode of cyclization is 7 : 8 positions of flavone skeleton rather than 6 : 7 positions. This is in agreement with the earlier observation that electrophilic substitution reactions in 7-hydroxyflavones occur exclusively at position-8[13]. In the mass spectra, the molecular ion peak is quite abundant in all the furoflavones III a–d. The base peak is due to M–1 ion (IV a–d) formed as a result of the facile loss of a hydrogen from the C3″-methyl group followed by a rearrangement to give a stable ring expanded chromenyl ion[14]. A less intense M–CO ion (V a–d) and intense ions due to retro-Diels-Alder fission (VI a–d and VII a–d) are also noticed[15].

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(I a–d)
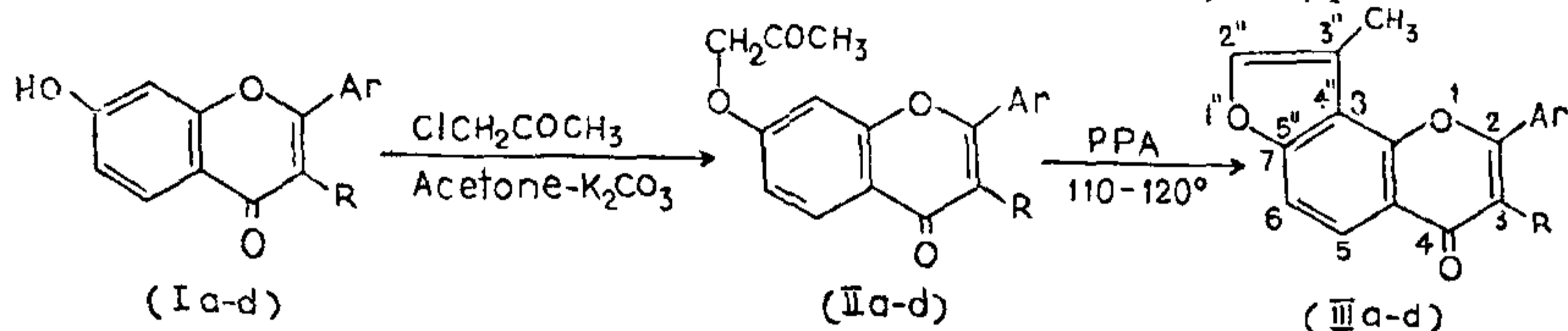
(a) R = H, Ar = Ph
(b) R = CH₃, Ar = Ph
(c) R = CH₃, Ar = C₆H₃(OCH₃)₂
(d) R, Ar = Ph

(II a–d)

(III a–d)

M⁺(IIIa) 276(60%)
(IIIb) 290(64%)
(IIIc) 352(72%) ·
(IIId) 350(34%)

(IV a–d)

(a) m/e 275(100%)
(b) "   289(100%)
(c) "   351(100%)
(d) "   349(57%)

(V a–d)

(a) m/e 248(5%)
(b) "   262(4%)
(c) "   324(4%)
(d) "   322(11%)

(VI a–d)

(a) m/e 174(27%)
(b) "   (24%)
(c) "   (28%)
(d) "   (100%)

(VII a–d)

(a) m/e 102(15%)
(b) "   116(17%)
(c) "   178(47%)
(d) ₄ 176(100%)

7-Acetonoloxyflavones II a–d at 20 ppm are fairly toxic to fish species *Barbus ticto* (Table I) when tested adopting the procedure of Krishnaswamy and Seshadri[2]. At the same concentration the furoflavones III a–d did not show any toxicity within 45 minutes. Screening of these compounds for photodynamic activity is in progress.

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