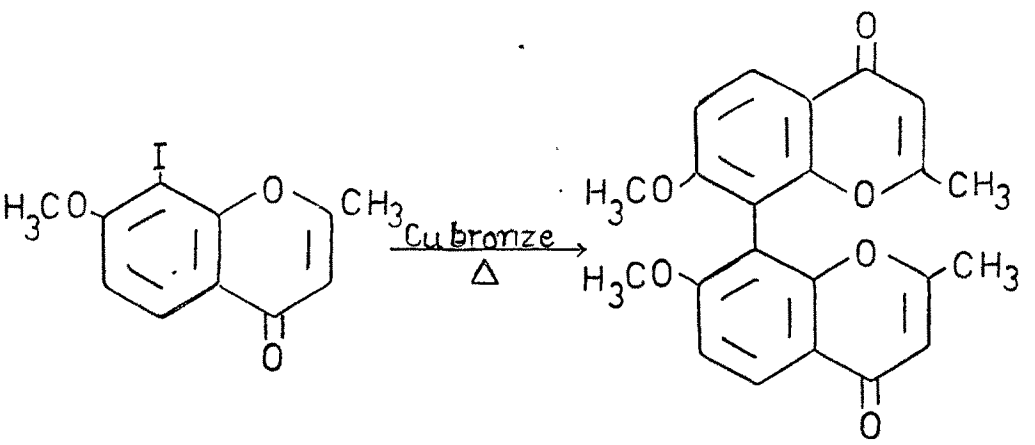
Chapter II

SYNTHESIS OF 2,3'-BICHROMONES

Bichromones are formed when two chromones nuclei are linked together directly. Compounds of these types are impotant because some of them occur naturally.[1-7] Bichromones have been synthesized by Ullmann reaction of iodochromone in the presence of copper bronze or copper powder. Shah[8] heated 8-Iodo-7-methoxy-2-methyl chromone (1) for about 10 minutes with copper bronze and obtained a low yield of 7,7'-dimethoxy-2,2'-dimethyl-8,8'-bichromone (2). A similar reaction with 6-Iodo-7-methoxy-2-methyl chromone (3) gave 7,7'-dimethoxy-2,2'-dimethyl-6,6'-bichromone (4) and both the products were demethylated with $AlCl_3$. A higher yield of similar bichromones was achieved by heating the iodochromone with copper powder in diphenyl ether[9] or dimethyl formamide.[10]

Shah and Sethna[11] carried out the iodination of 5-Hydroxy-2-methyl chromone (5) with equimolar proportion of iodine and iodic acid and obtained a product to which they assigned 5-hydroxy-8-iodo-2-methylchromone structure (6) on the basis of following reactions. On nitration it gave a compound (8) identical with the iodination product of 5-hydroxy-2-methyl-6-nitrochromone (7). Methyl ether of (6) on alkaline hydrolysis, gave an iodoketone (9) different from that obtained by iodination of 2-hydroxy-6-methoxy acetophenone (10), but the derived ethers (11) were identical. The iodoketone therefore obtained on hydrolysis therefore has structure (9) and that obtained by direct iodination has structure (10).

Shah et al.[8]



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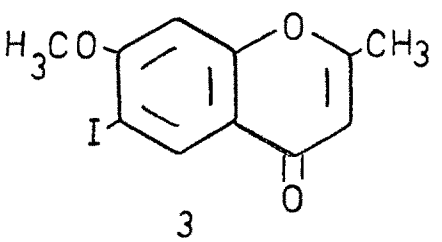
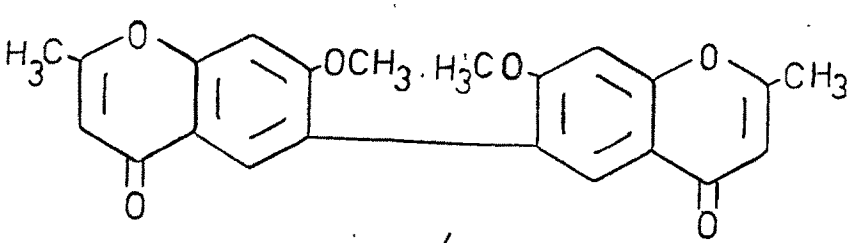


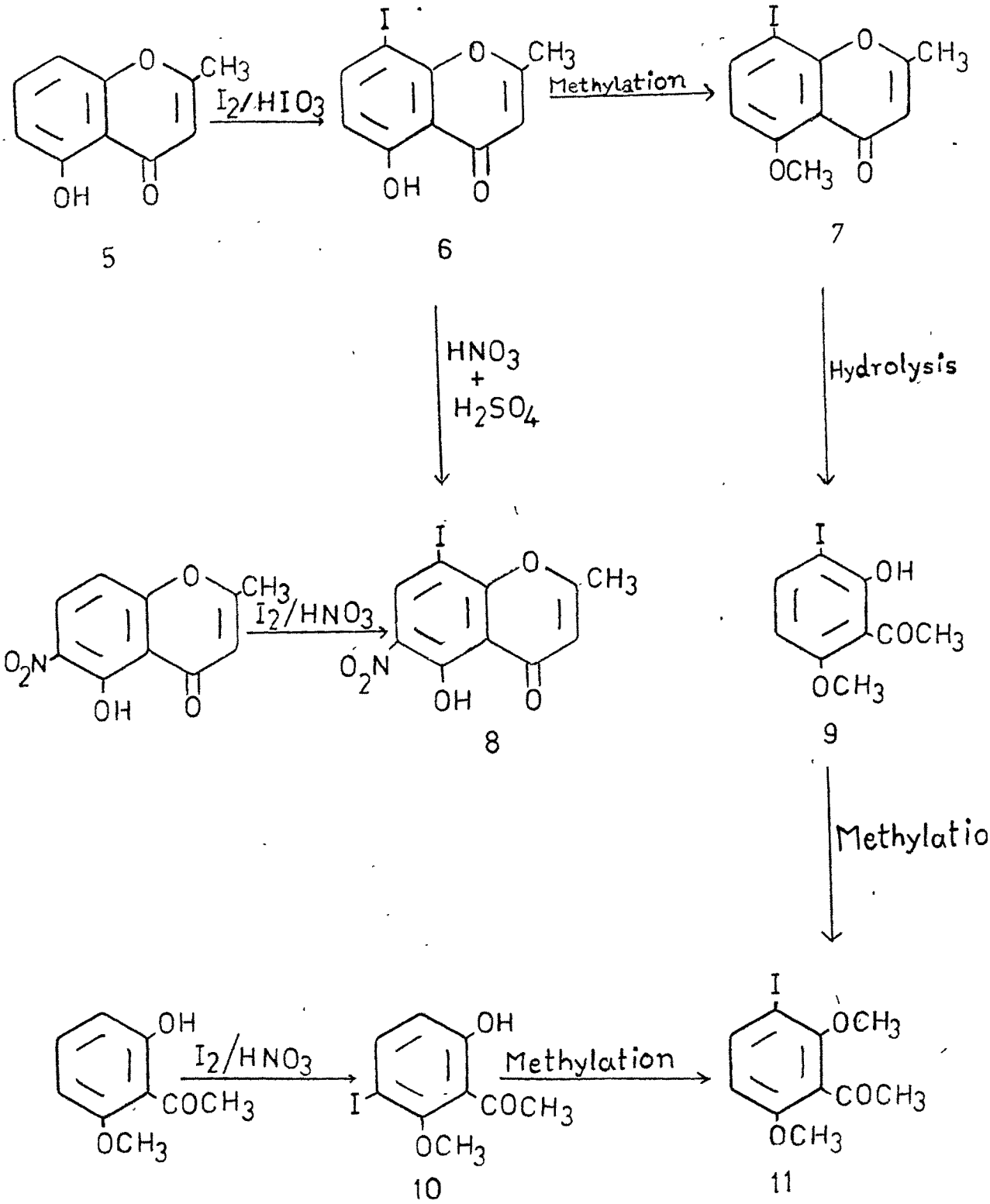
3

△
Cu bronze



4

Shah and Sethna[11]

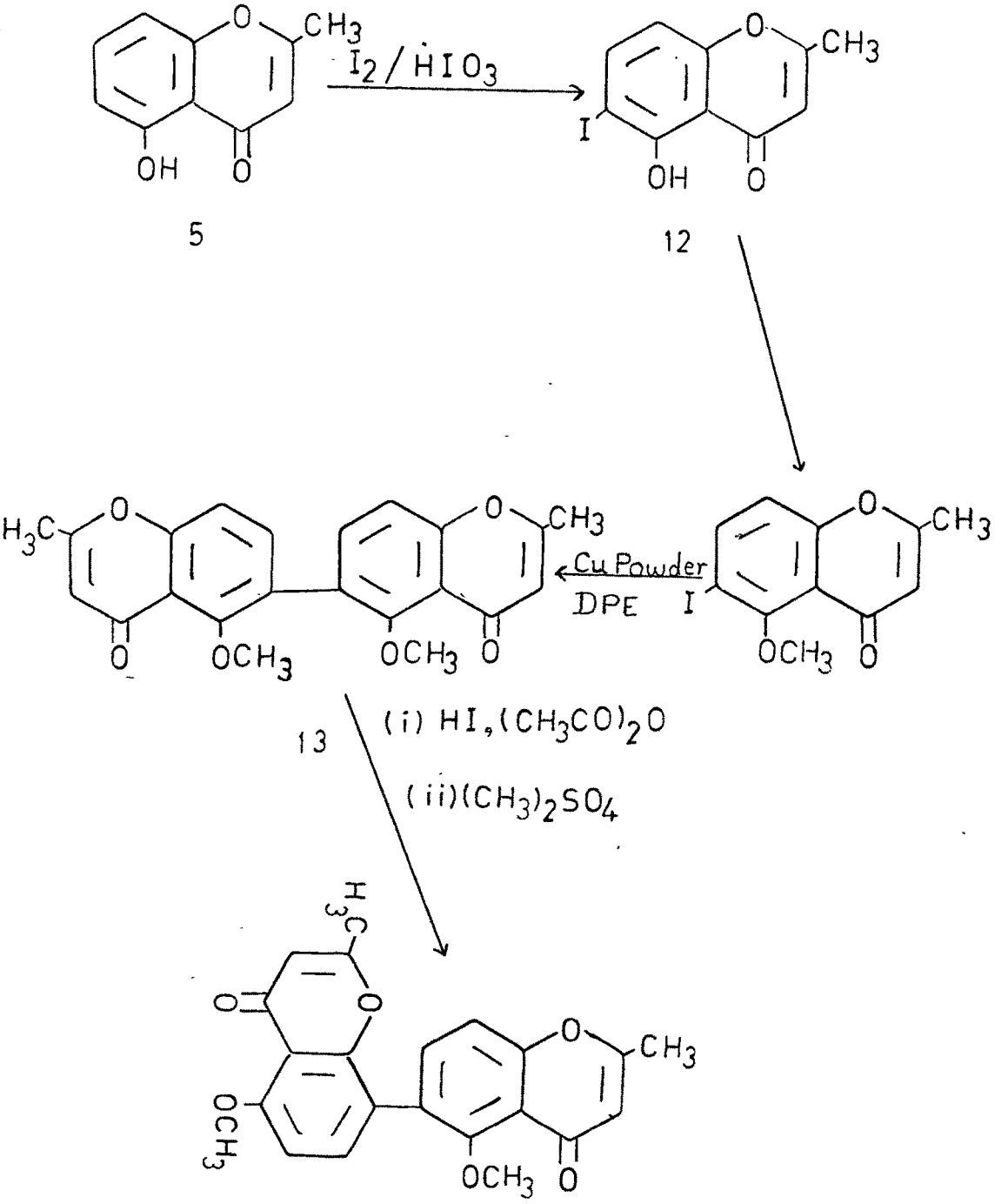


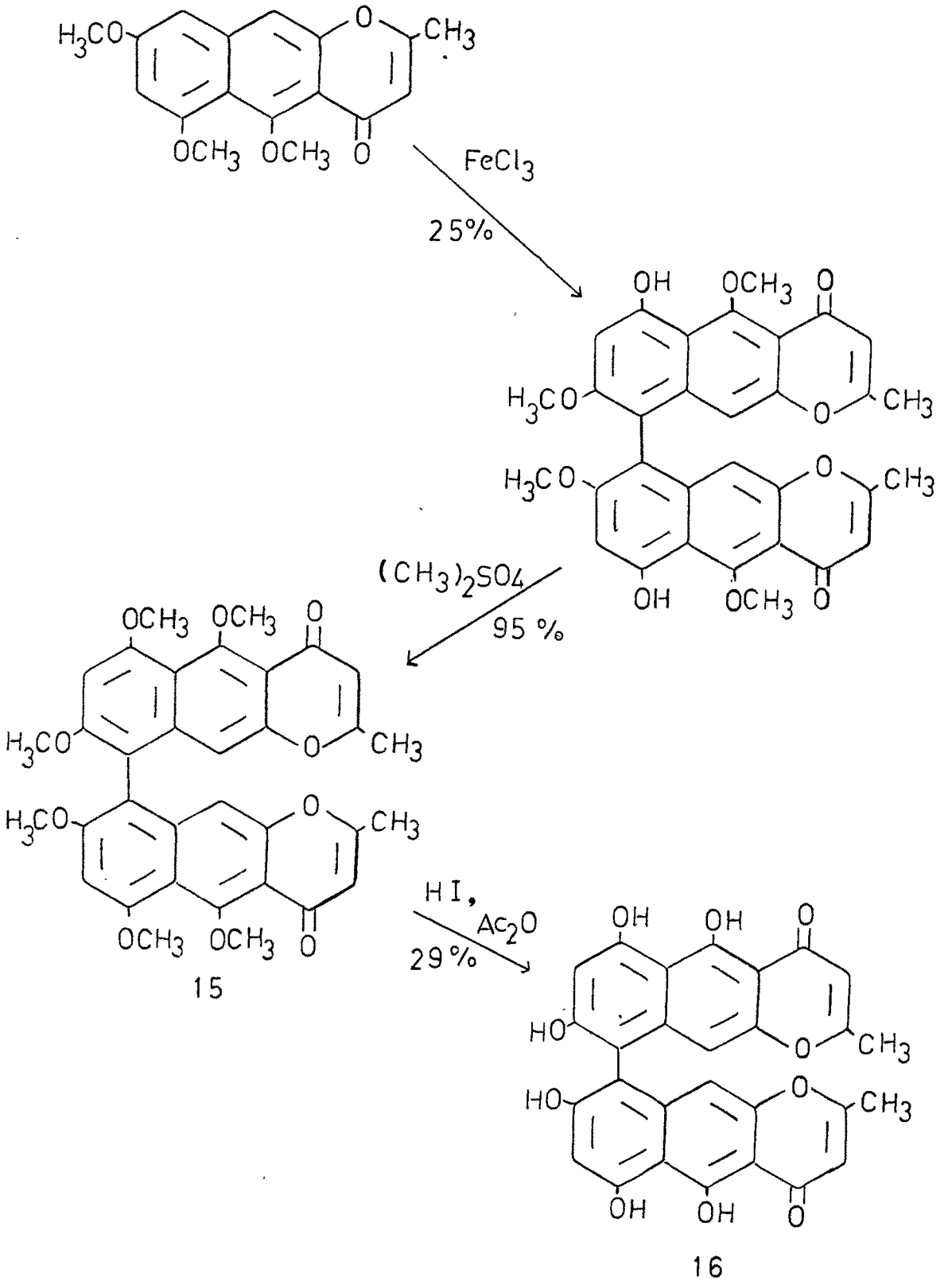
On the basis of Shah and Sethna's work, Franck and Baumann[9] synthesized bichromones from 5-methoxy--iodo-2-methylchromone by Ullmann synthesis and assigned 5,5'-dimethoxy-2,2'-dimethyl -8,8'-bichromones but later on Whalley [12] and co-workes proved that the iodination product 5-hydroxy-2-methylchromone gave 5-hydroxy-6-iodo-2-methyl chromone (12) and therefore the bichromones synthesized by FrancK and Baumann was not 8,8'-bichromone but it was 5,5'-dimethoxy-2,2'-dimethyl-6,6'-bichromones (13) which on treatment with hydroiodic acid and acetic anhydride followed by methylation gave 5,5'-dimethoxy-2,2'-dimethyl-6,8'-bichromone (14) as Wessely-Moser rearrangement took place during the course of reaction. They also revised the structures of iodoketones obtained by Shah and Sethna.

Oxidative coupling of a reactive naphtho [2,3-b] pyran-4-one has been used to synthesize Ustilaginoidin (16) a red pigment isolated from a parasite fungus that grown on rice.[1,13,1] The structure of bichromone (16) was demonstrated by spectroscopy,[15] and it must be assumed that a Wessly-Moser rearrangement did not occur when the tetramethyl ether (15) was treated with hydroiodic acid.

Schonberg and Sina[16] condensed o-hydroxyacetophenone with ethyl formate in the presence of sodium and claimed to have obtained ω-formyl derivatives (17). It's structure assignments was carried out by it's strong ferric reaction and it's conversion to chromone by alcoholic H_2SO_4.

Franck and Baumann[9]





15

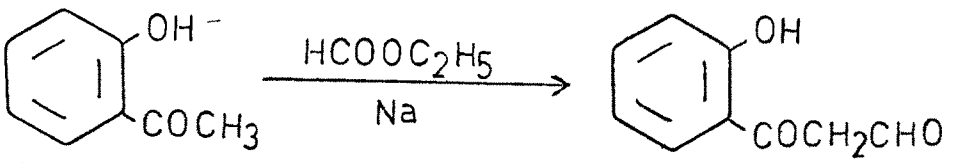
16

Narsimhachari et al[17] carried out the condensation of phloroacetophenone dimethyl ether[18] with ethyl formate in the presence of sodium and obtained product which on the basis of colour reaction and change in melting point on recrystallization was considered to be a tautomeric mixture of ω-formyl derivative (19) and the cyclic product 2,3-dihydro-2-hydroxy-5,7-dimethylchromene (20). Ahluwalia and Prakash[18] made a detailed study about the Claisen condensation products of 2-hydroxy-4,6-dimethoxyacetophenone[18] and 2-hydroxy-4-methoxy-6-methylacetophenone (21) with ethyl formate and confirmed the cyclic 2-hydroxy chromanone structure (20) and (22) respectively. On the basis of different reactions viz., acetylation with acetic anhydride, pyridine and methylation with dimethyl sulphate or methyl iodide.

Present work

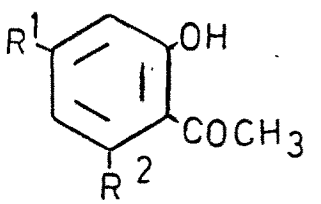
o-hydroxyacetophenone was condensed with ethylformate and sodium gave 2-hydroxychromanone (m.p. 105°C) the structure of which was confirmed by PMR spectrum and elemental analysis. The PMR spectrum ($CDCl_3$) of simple 2-hydroxychromanone shows peaks at δ 2.85, 2.15, m, 2H at C-3 ; 5.92, t, J=5Hz, 1H at C-2 ; 6.9 - 7.5, m, 3H, at C-6, C-7 and C-8 ; 7.8 dd, J=8Hz, 2Hz, 1H at C-5 ; 4.3, bs, 1H (-OH) at C-2, and there was complete absence of aldehydic protons around δ 9.0. This compound was unexpectedly unstable around its melting point, it underwent a rapid transformation to a yellow compound m.p.

Schomberg and Sina[16]

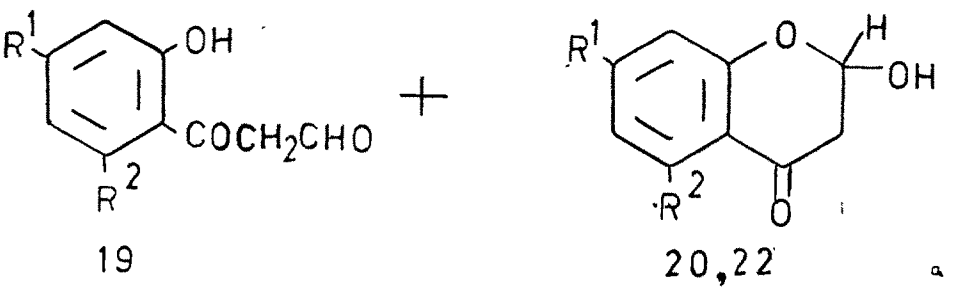


17

Nasimhachari et al.[17]



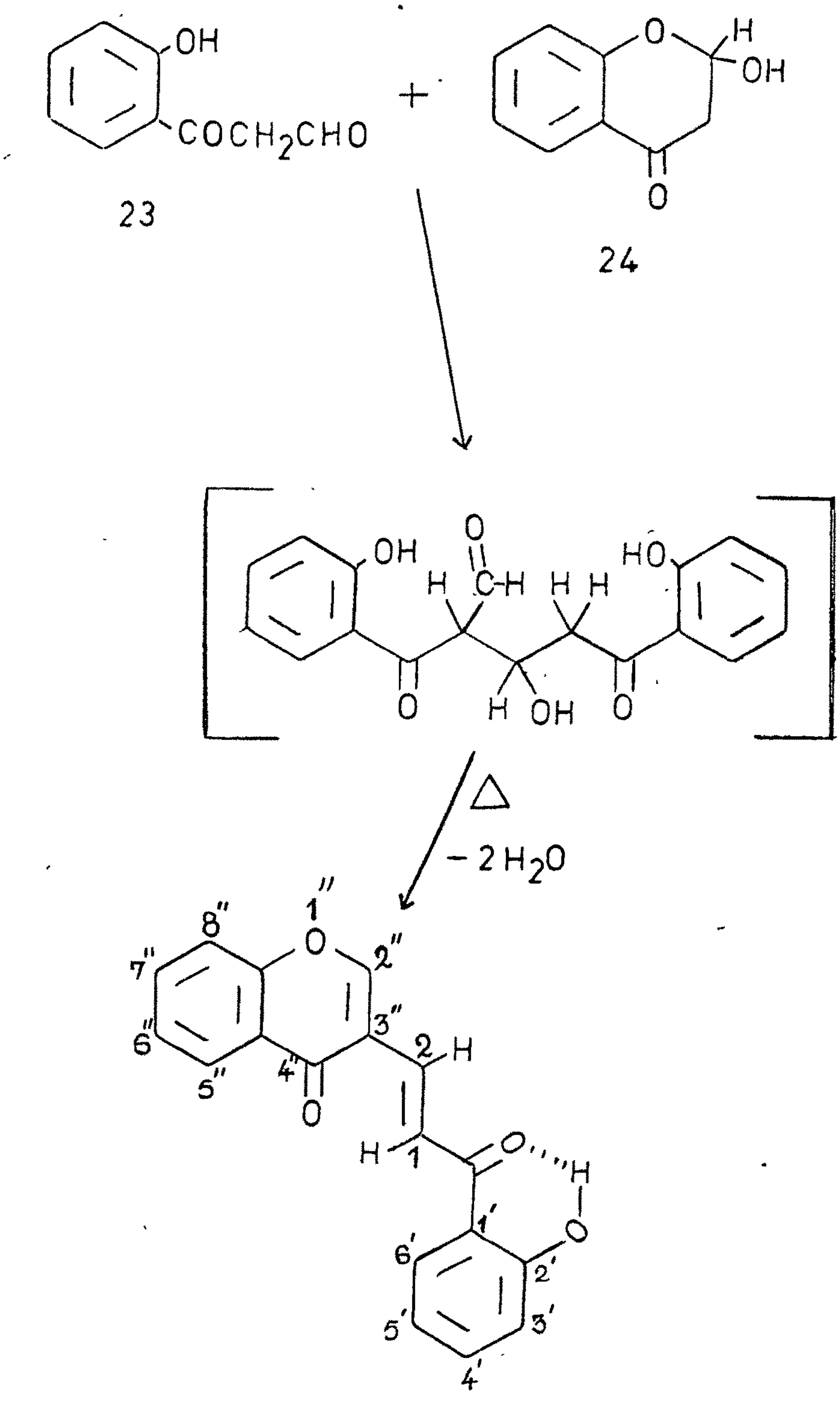
18, 21



19 20, 22

18, 19, 20 $R^1 = R^2 = OCH_3$

21, 22 $R^1 = OCH_3$ $R^2 = CH_3$



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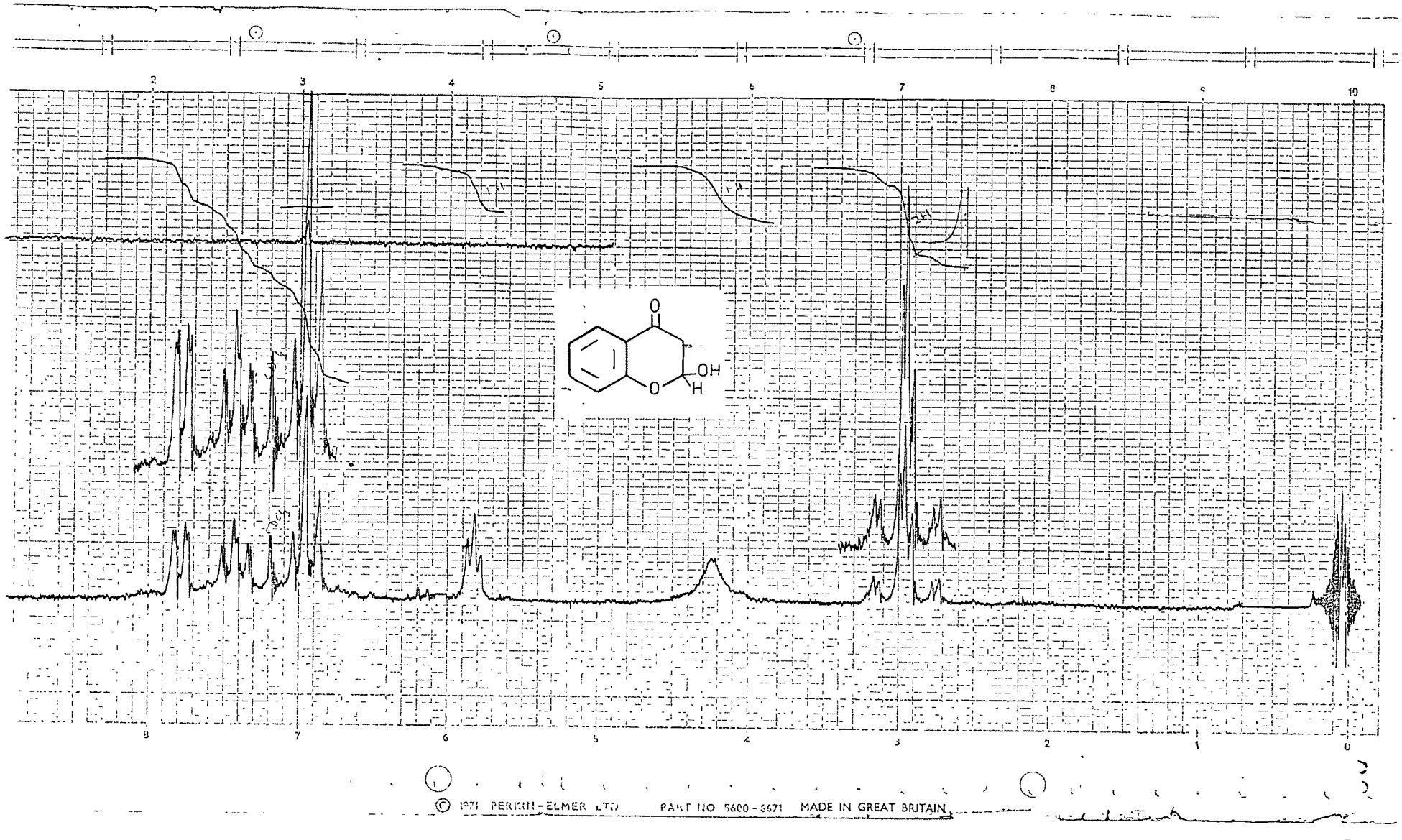
2
3
4
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6
7
8
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10
1H
1H
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O
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8
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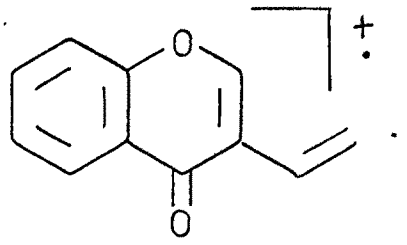
178-179°. This thermal reaction appear to be a bimolecular condensation between -formylacetophenone (23) and 2-hydroxychromanones (24) followed by elimination of two molecules of water to give 1-(2-hydroxybenzoyl)-2-(4-oxo-4H-1-benzopyran-3-yl) ethylene (25).

This is a novel observation of thermal dimerization taking place at the melting point of the substance. The change in m.p. observed by earlier workers may be due to this type of thermal dimerization. The structure of (25) was confirmed from the spectral data. PMR ($CDCl_3$) showed signals at δ 12.7, 1H, s, (bonded OH) ; 8.75, d, J=16Hz, H-1 ; 7.45, d, J=16Hz, H-2 trans-alkene ; 8.2, dd, J=9,2Hz, H-5" ; 8.14, s, 1H, H-2" 7.95, dd, J=9,2Hz, 1H, H-6' ; 6.85-6.94, m, 2H, H-5' and H-3' ; 7.4-7.7, m, 4H, aromatic. Mass spectrum of (25) showed peaks at m/e 292 (M^+) 171 (26) and 121 (27).

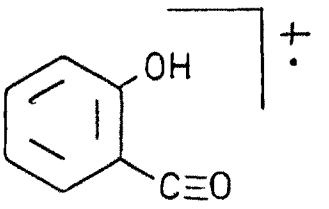
Synthesis of (28), similar to that of (25) was carried out earlier by the reaction of chromone derivatives with sodium ethoxide in ether for 2 hrs [19-21] and also with pyridine.[22]

Nohara[23] synthesized 4-oxo-4H-1-benzopyran-3-carboxaldehyde by the application of Vilsmeier-Haack reaction to various o-hydroxyacetophenone derivatives, in this reaction small amount of by-product (25) was also obtained, it's structure was confirmed by nmr spectra and also by converting (25) in to 4-oxo-chroman derivatives (29) by heating with 85% H_3PO_4. (25) when refluxed with selenium dioxide in iso amyl alcohol



m/z -171

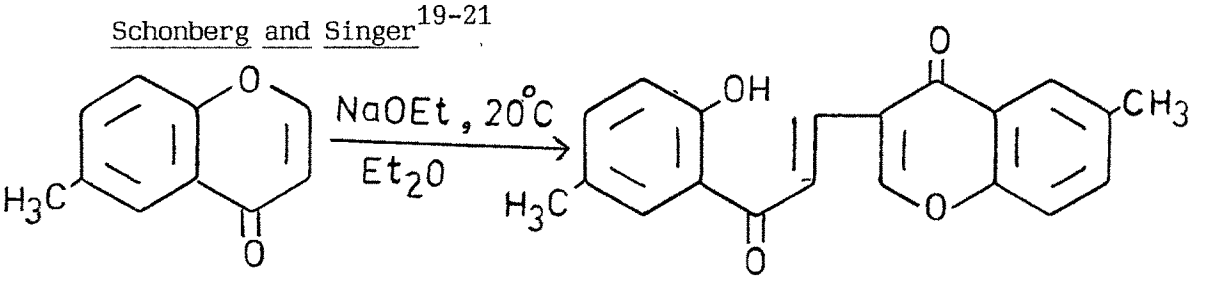
26



m/z -121

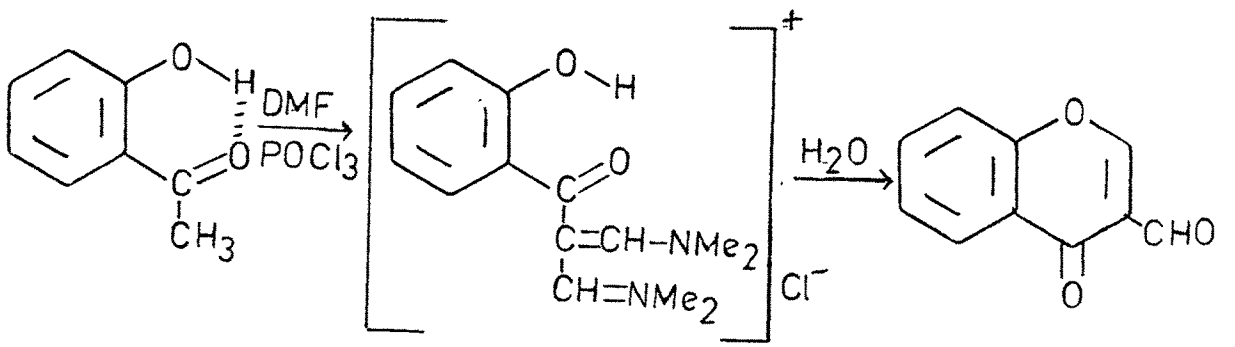
27

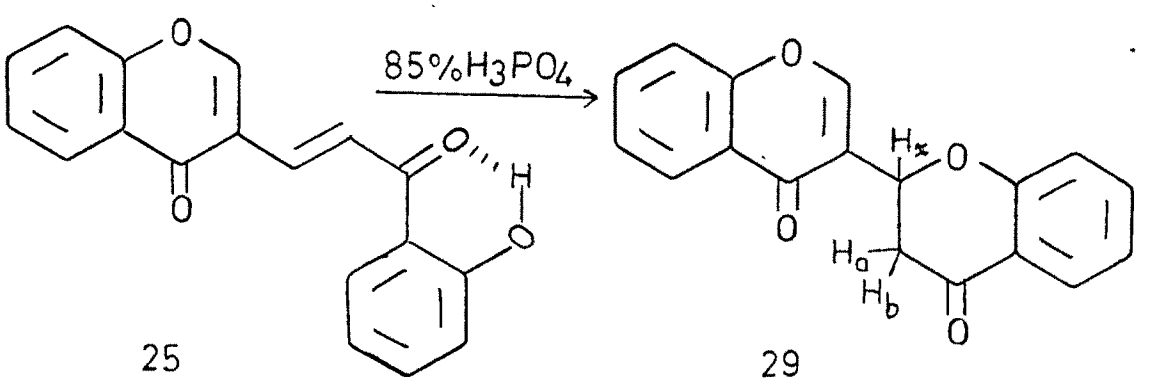
Schonberg and Singer[19-21]



28

Nohara[23]





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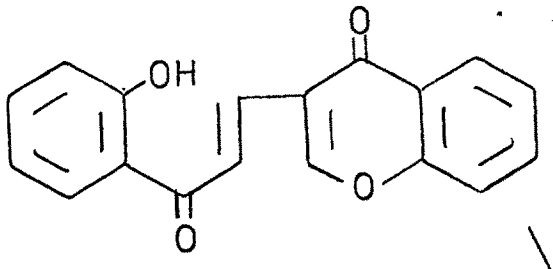
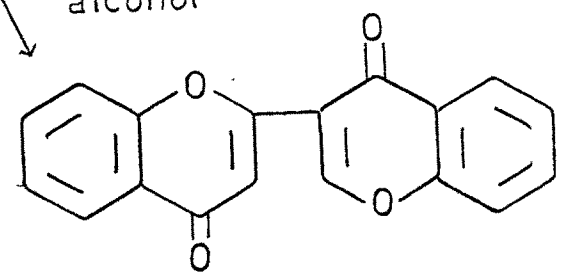
29



25

SeO_2, 48 h

Isoamyl alcohol



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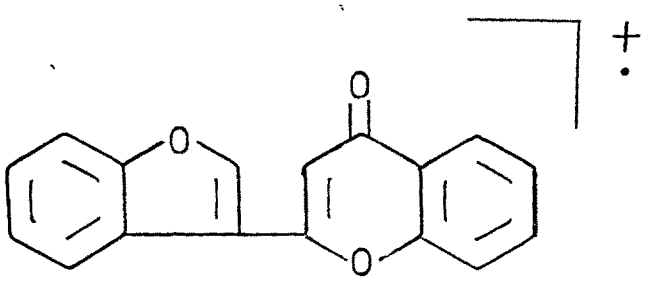
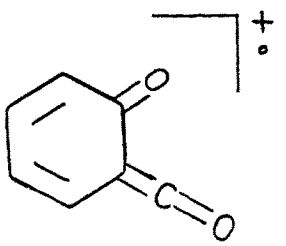
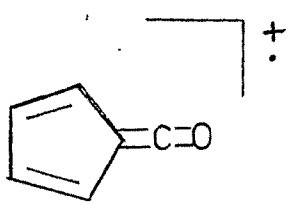


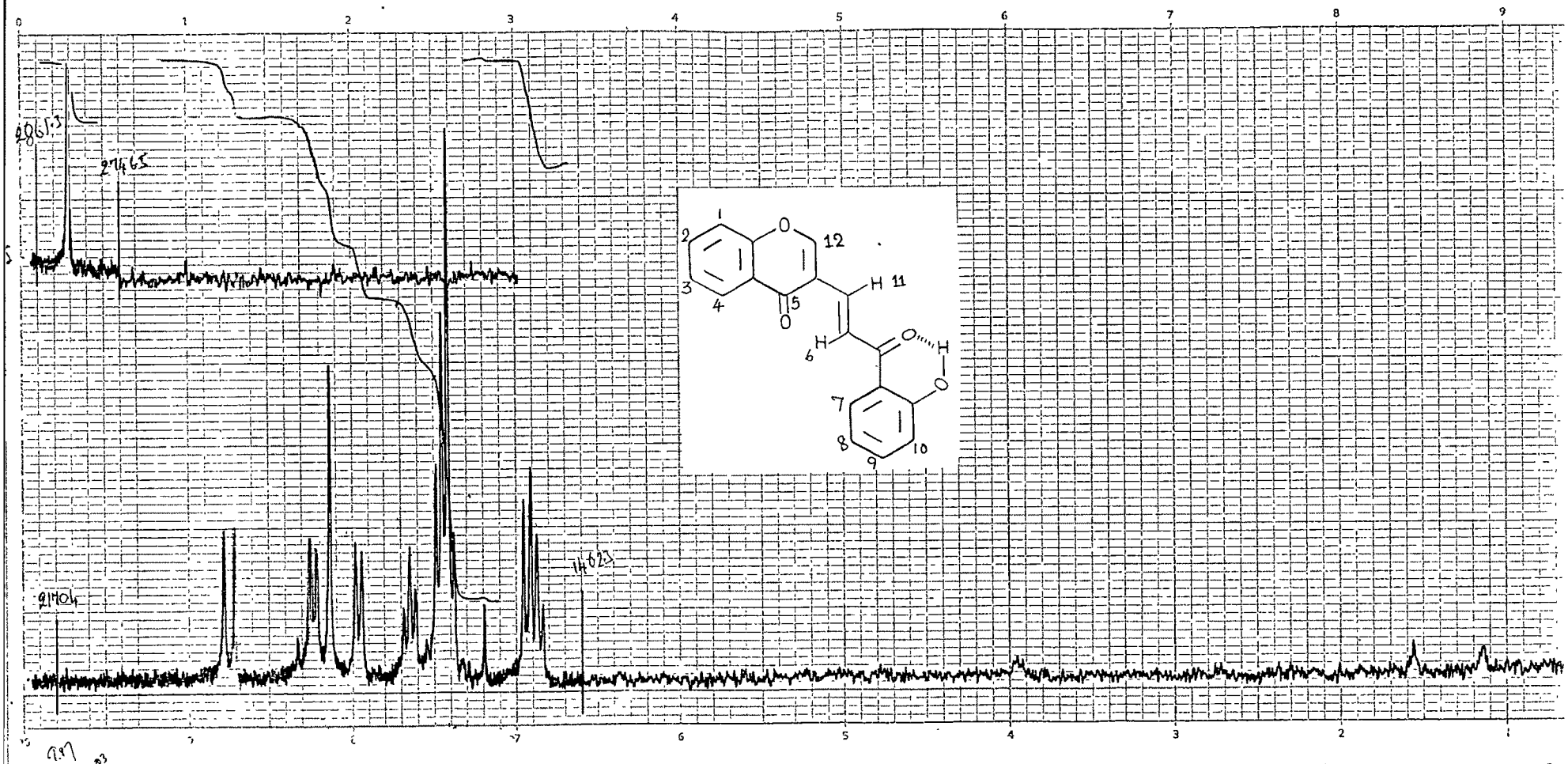
m/z - 262



m/z-120



m/z - 92



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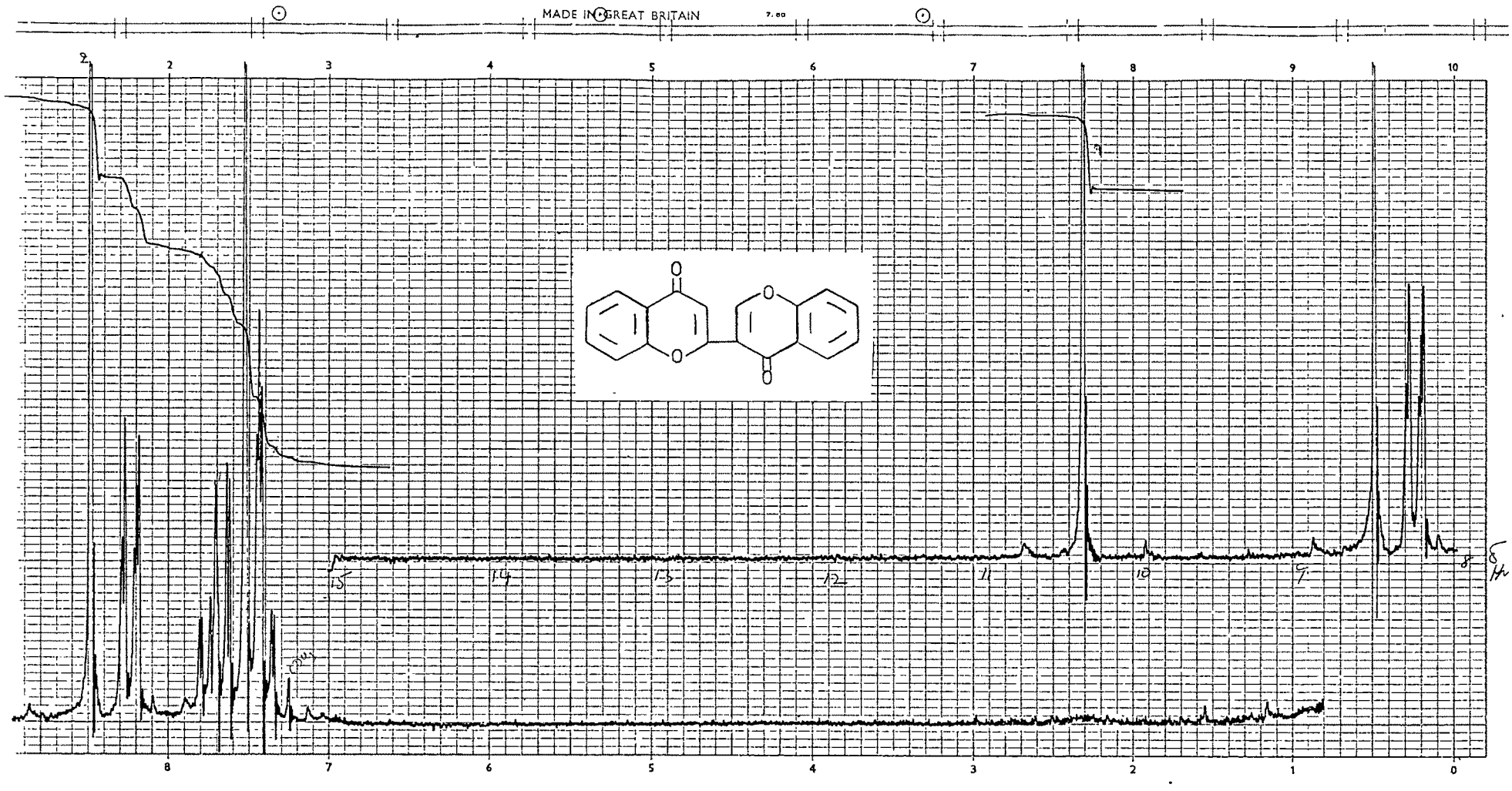

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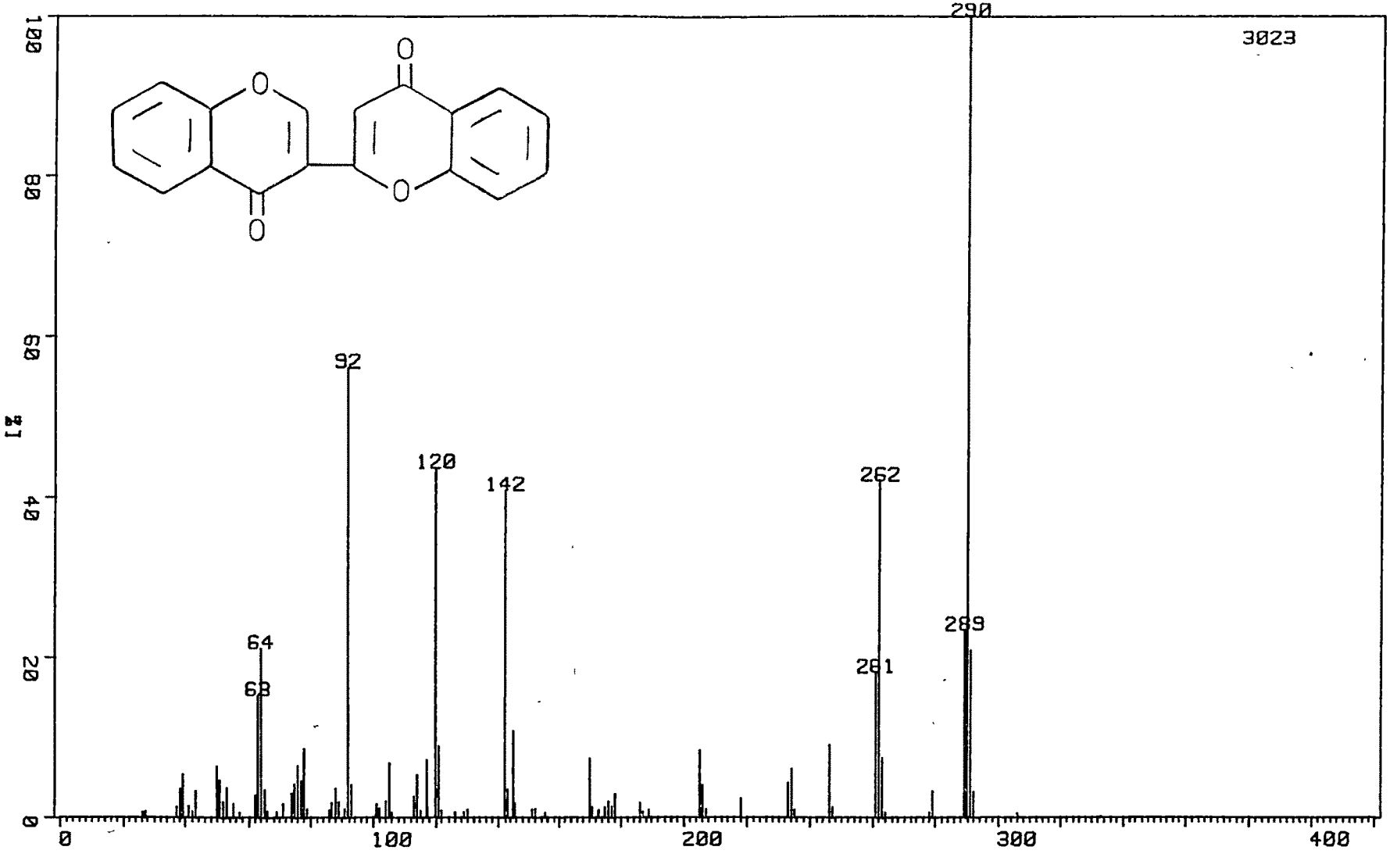
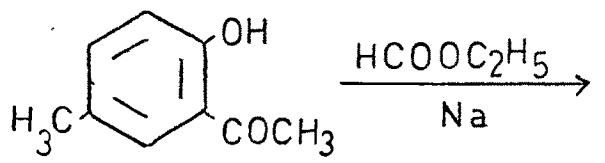


furnished (2,3'-bi-4H-1-benzopyran)-4,4'-dione (30).

The structural assignment of (30) was based on the spectral datas. PMR spectra of (30) shows signals at δ 8.5, s, 2H, H-3, H-2' ; 8.25, d, J=9Hz, H-5, H-5' ; 7.6, m, 2H, H-7, H-7' ; 7.55, d, J=9Hz, H-8, H-8' and 7.35, m, 2H, H-6, H-6'. Mass spectrum of (30) showed peaks at m/z 290 (M^+), 262, 120 and 92 for the following fragments.

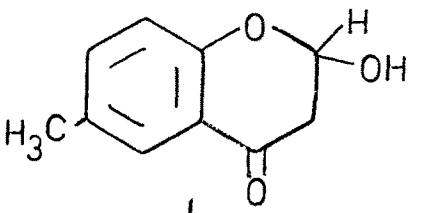
6,6'-Dimethyl-(2,3'-bi-4H-1-benzopyran)-4,4'-dione (34)

5-Methyl-2-hydroxyacetophenone (31), on Claisen condensation with ethylformate in presence of pulverised sodium in dry ether gave 2-hydroxy-6-methyl chromanone (32) which on heating slightly above it's melting point dimerized with elimination of water molecules to 1-(2-hydroxy-5-methylbenzoyl)-2-(6-methyl-4-oxo-4H-1-benzopyran-3-yl) ethylene (33). The structure of (33) was established by it's spectral data. It's PMR ($CDCl_3$) spectrum showed signals at δ 8.9, d, J=16Hz, 1H, H-1 ; 7.45, d, J=16Hz, 1H, H-2 ; 8.26, s, 1H, H-2" ; 8.16, d, J=2Hz, 1H, H-5" (m-coupled) ; 7.85, d, J=2Hz, 1H, H-6' (m-coupled) ; 7.62, d, J=9Hz, 1H,H-8" ; 7.55, m, J=9Hz,1H, H-7" ; 7.4, d, J=9Hz, 1H, H-4' ; 7.0, d, J=9Hz, 1H, H-3' ; 2.55, s, 3H, $C_{6'}$-CH_3 ; 2.4, s, 3H, $C_{5"}$-CH_3. (33) when refluxed with SeO_2 in isoamyl alcohol furnished 6,6'-dimethyl-2,3'-bi-4H-1-benzopyran-4,4'-dione (34). The structural assignment of (34) is based on elemental analysis and mass spectral datas. Mass spectra of (34) showed peaks at m/z 318(M^+), 290, 134, 106.



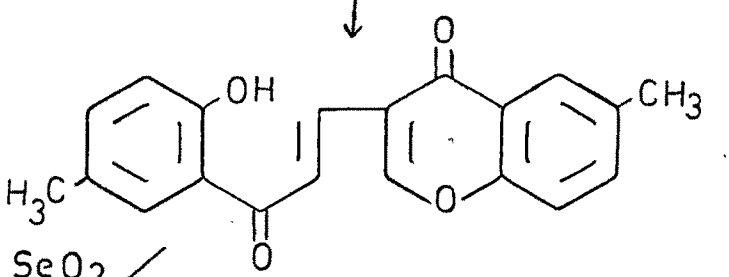
31

$HCOOC_2H_5$
Na



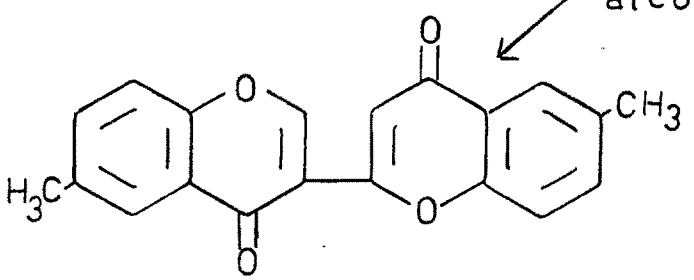
32

140°C Δ

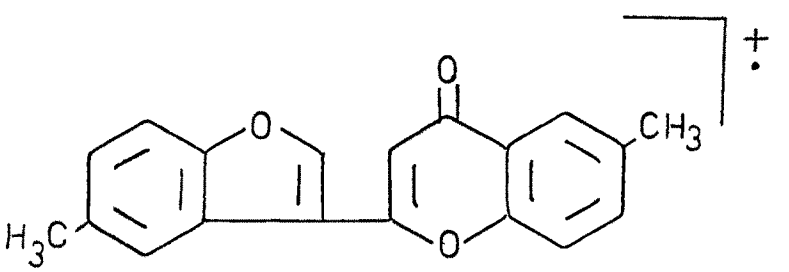


33

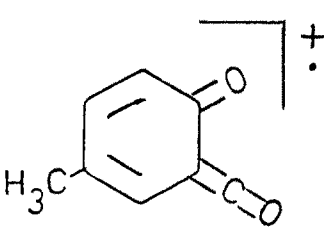
SeO_2
48 h
Isoamyl alcohol



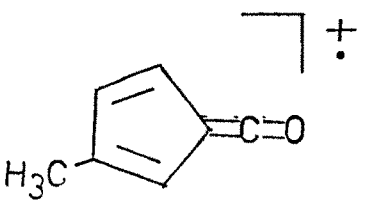
34



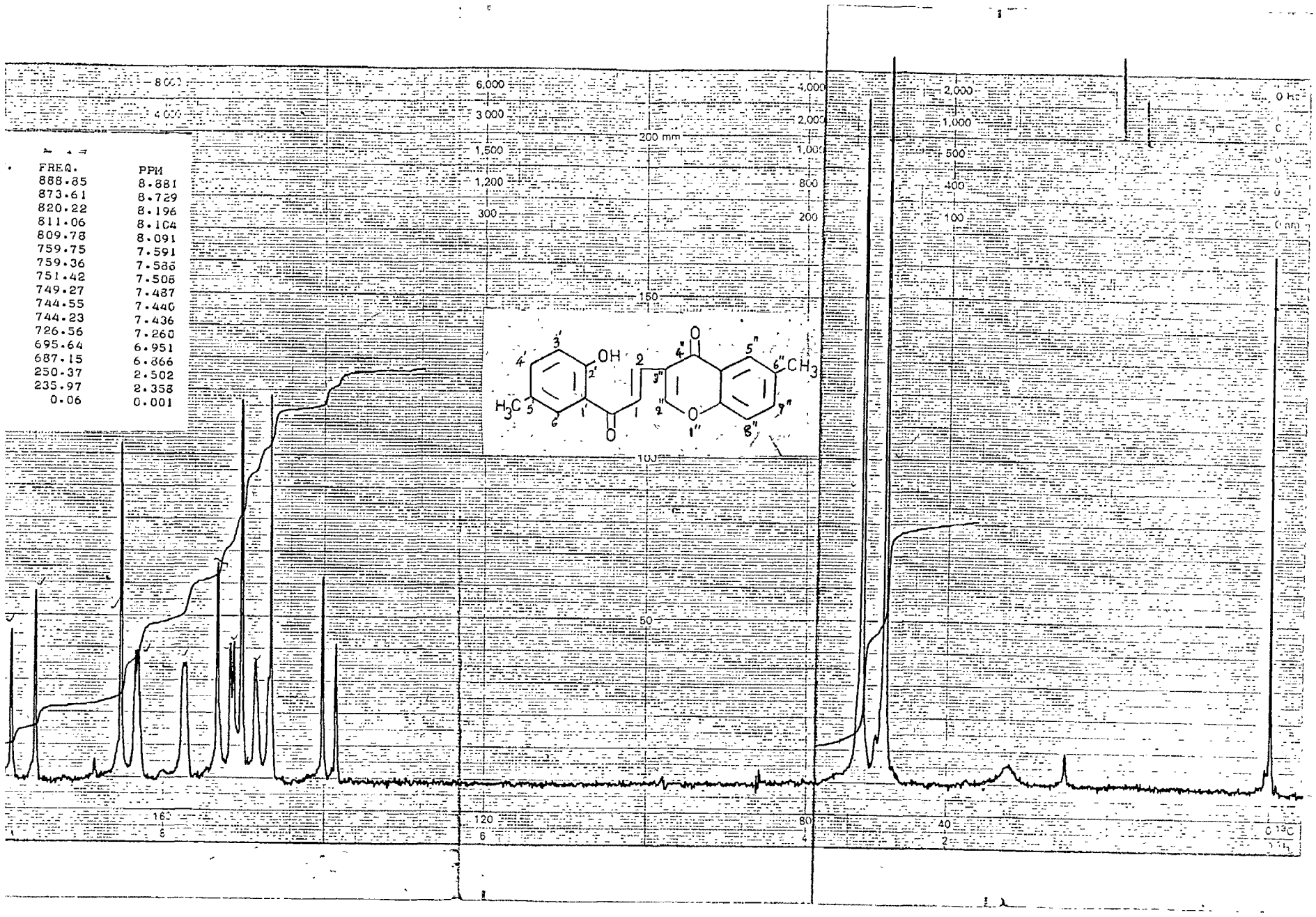
m/z - 290



m/z - 134



m/z - 106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749.27 7.487
744.55 7.440
744.23 7.436
726.56 7.260
695.64 6.951
687.15 6.866
250.37 2.502
235.97 2.358
0.06 0.001
OH
H_3C
CH_3
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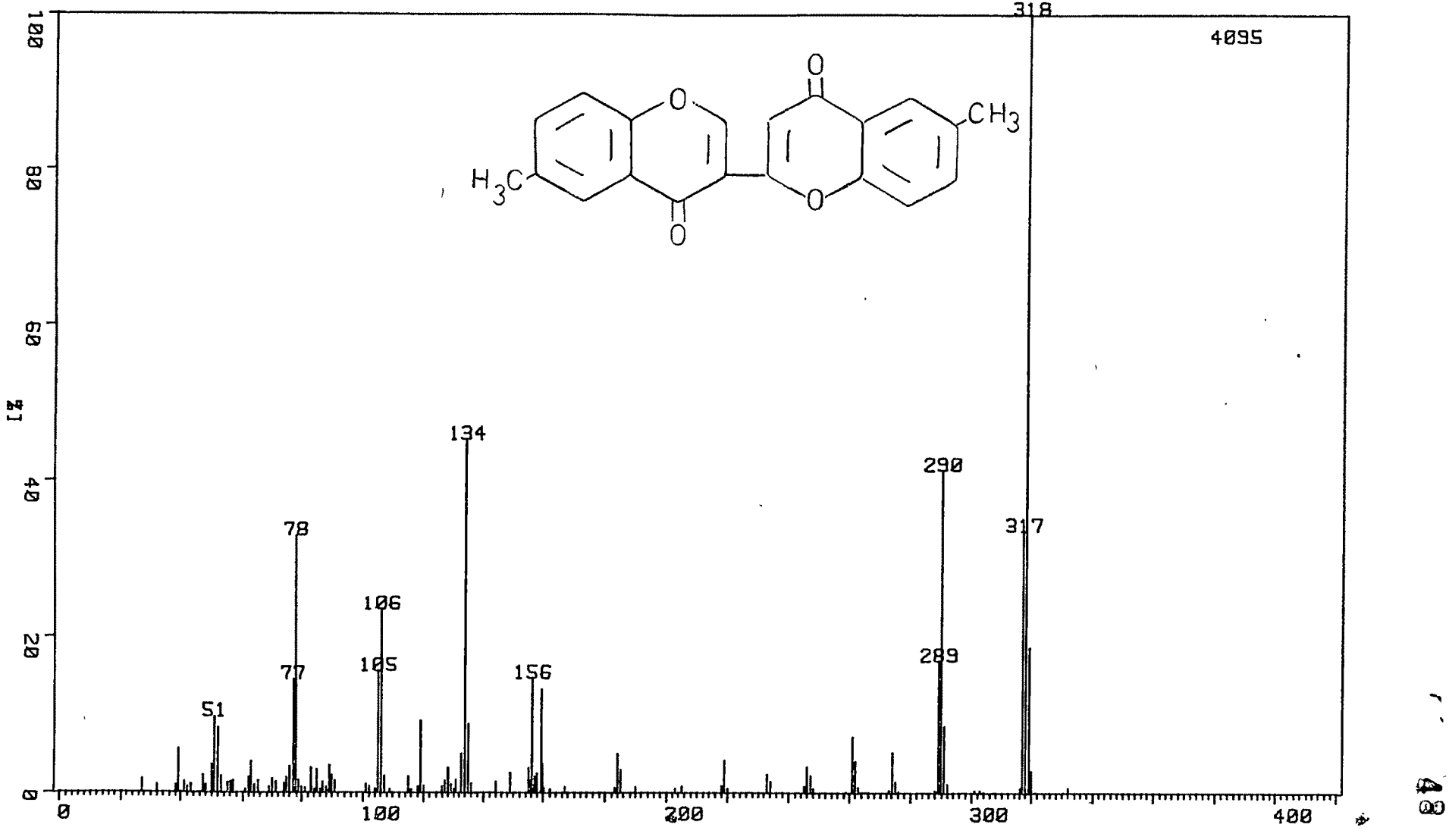
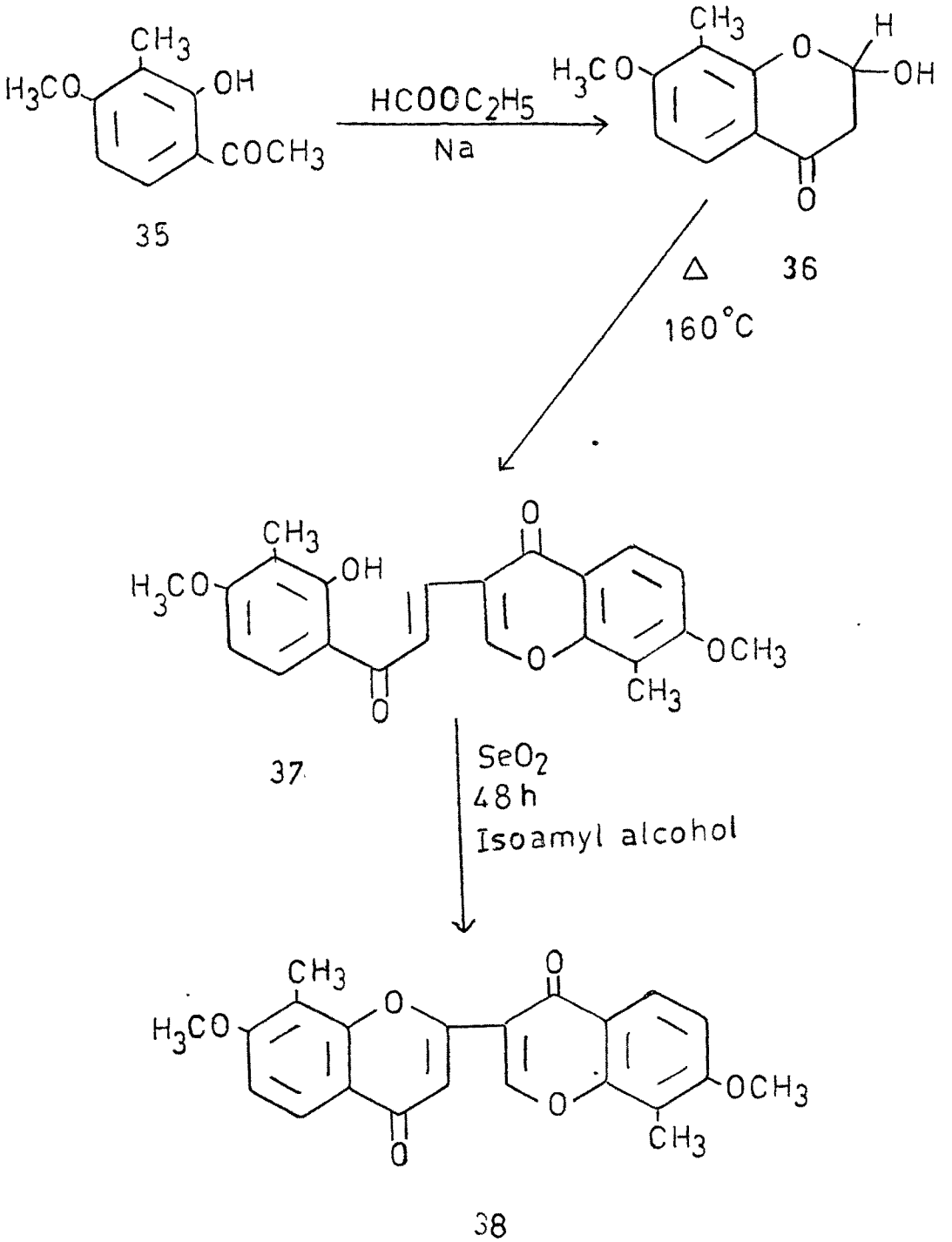


7,7'-Dimethoxy-8,8'-dimethyl-(2,3'-bi-4H-1-benzopyran)-4,4' dione (38)

3-Metyl-4-methoxy-2-hydroxyacetophenone (35) on Claisen condensation with ethylformate in presence of pulverized sodium in dry ether gave 7-methoxy-8-methyl-2-hydroxychromanone (36) which on heating slightly above it's melting point converted to 1-(2-hydroxy-4-methoxy-3-methylbenzoyl)-2-(7-methoxy-8-methyl-4-oxo-4H-1-benzopyran-3-yl) ethylene (37) which was on refluxing with SeO_2 in isoamyl alcohol furnished 7,7'-dimethoxy-8,8'-dimethyl-(2,3'-bi-4H-1-benzopyran)-4,4'-dione (38). The structural assignments of (38) is based on the elemental analysis and mass spectral datas. PMR spectra of (38) could not be recorded due to insolubility in common pmr solvents. Mass spectra of (37) shows peaks at m/z 378, 363, 335, 215.

6,6',7,7'-Tetramethyl-(2,3'-bi-4H-1-benzopyran)-4,4'dione (42)

3,4-Dimethylphenol on acetylation and Fries migration gave 4,5-dimethyl-2-hydroxyacetophenone (39) which on Claisen condensation with ethylformate and sodium metal gave 6,7-dimethyl 2-hydroxychromanone (40) which on heating slightly above it's melting point converted to 1-(2-hydroxy-4,5-dimethylbenzoyl)-2-(6,7-dimethyl-4-oxo-4H-1-benzopyran-3-yl) ethylene (41) which when refluxed with SeO in isoamyl alcohol for 45 hrs furnished 6,6',7,7'-tetramethyl-2,3'-bi-4H-1-benzopyran-4,4'-dione (42). All the intermediates of (42) gave the satisfactory elemental analysis.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OH
COCH3
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CH3
H
H3CO
O
OH
O
35
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160°C
36
CH3
OH
H3CO
O
O
OCH3
CH3
O
37
SeO2
48 h
Isoamyl alcohol
CH3
O
H3CO
O
O
OCH3
CH3
O
38

RTP160 17 R.T.PADASANI. RTP.25. 05-DEC-84
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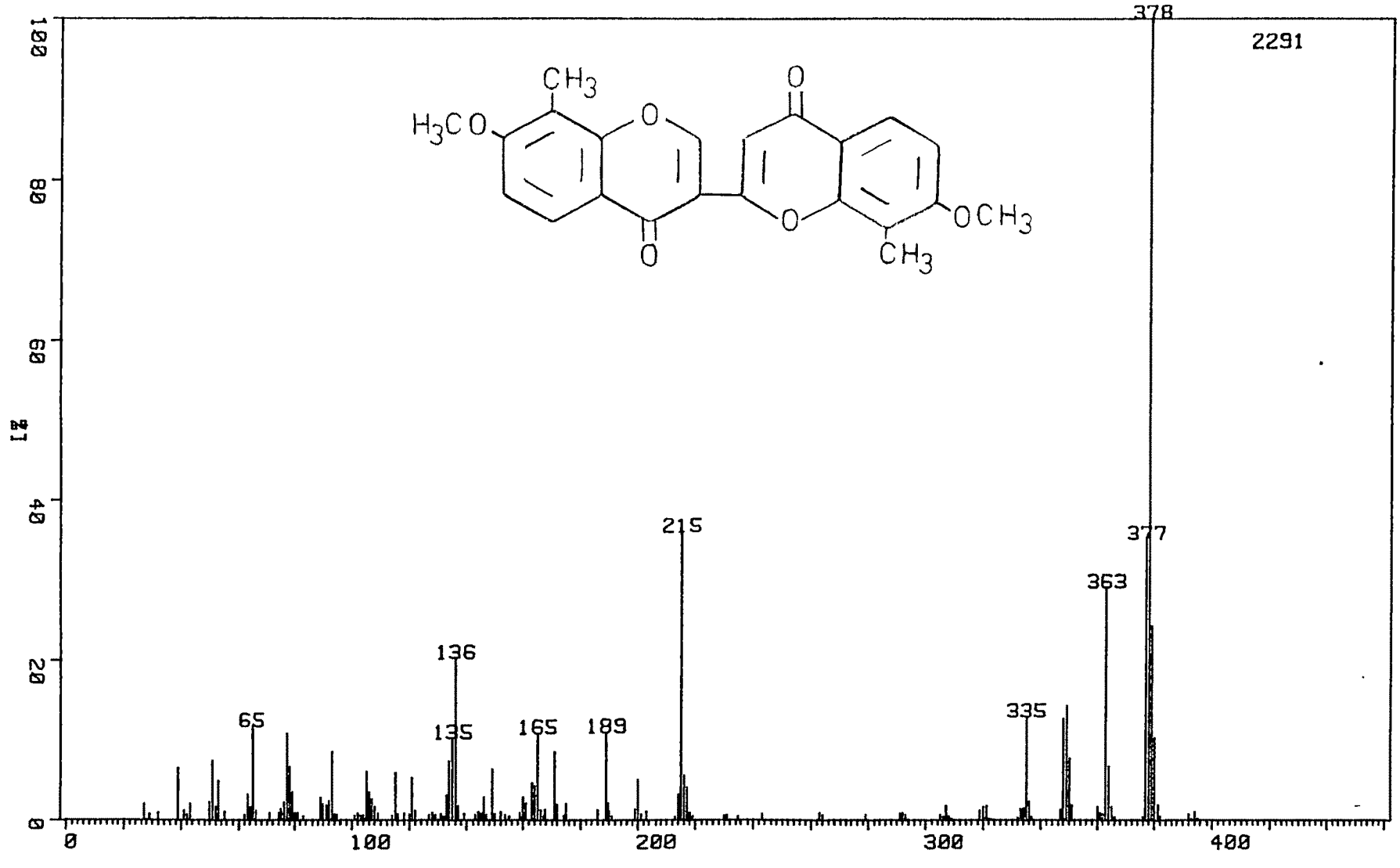
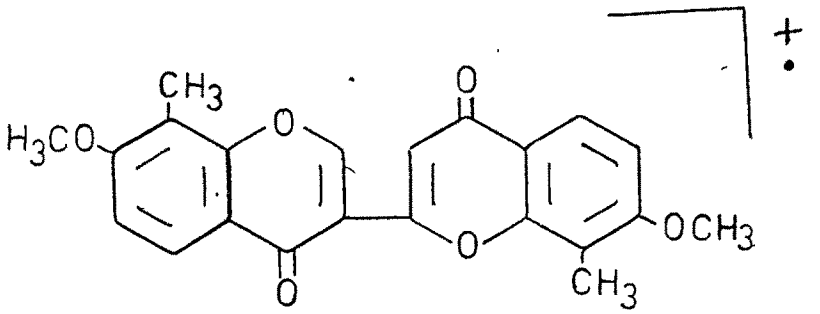
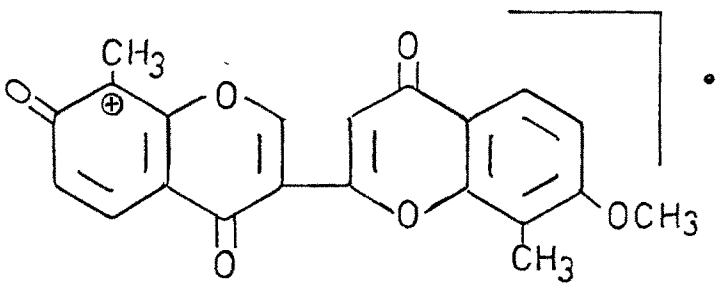
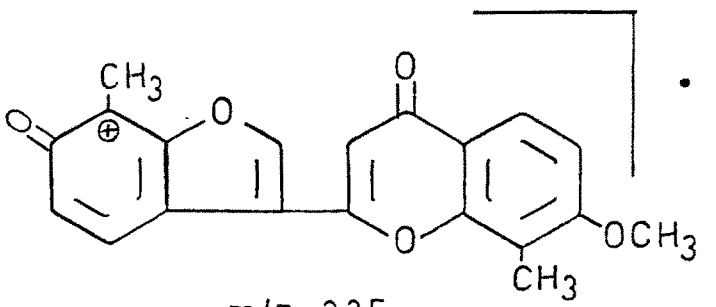




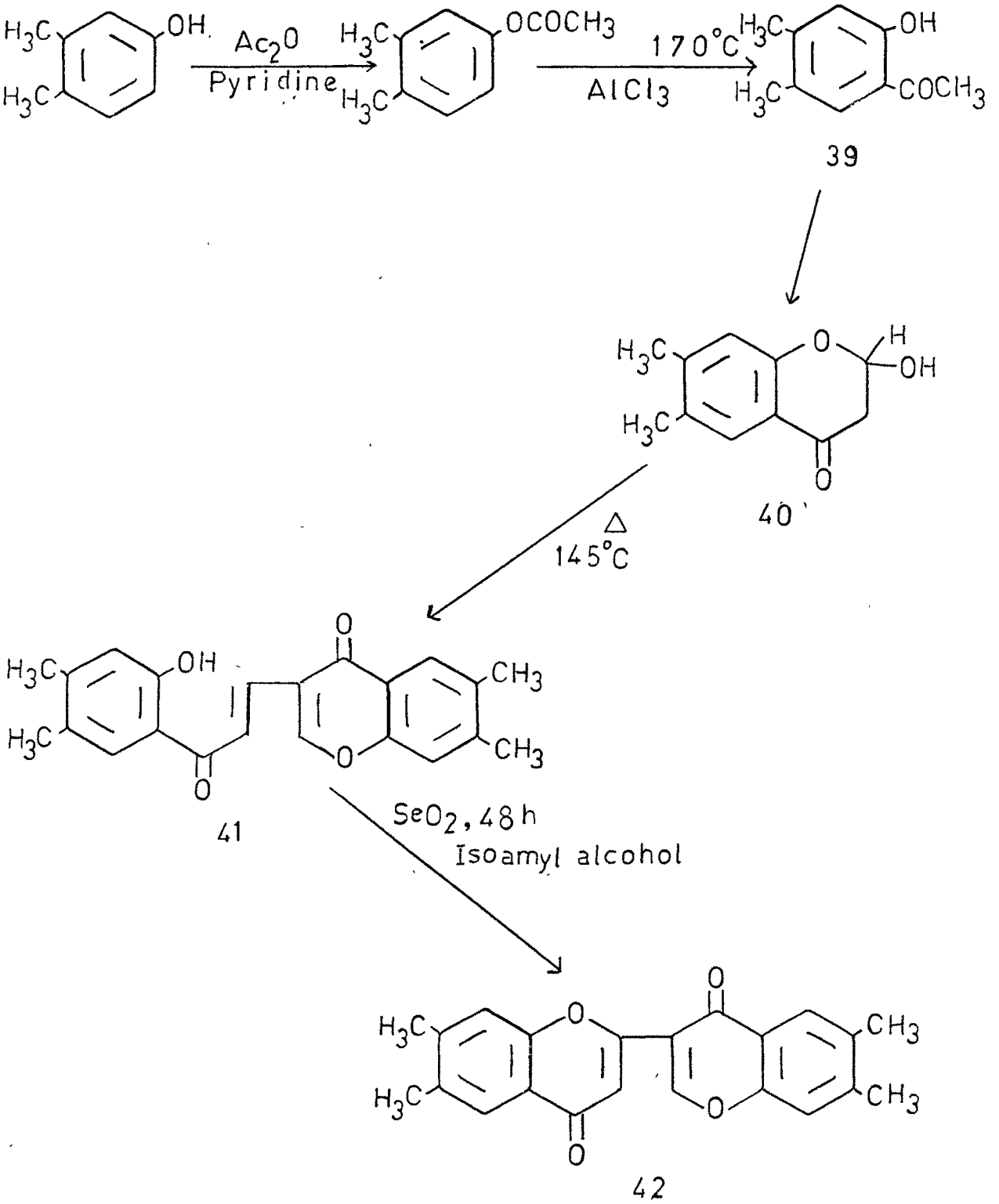
m/z - 378



m/z - 363



m/z - 335


Ac2O
Pyridine
OCOCH3
170°C
AlCl3
OH
COCH3
39
40
145°C
41
SeO2, 48 h
Isoamyl alcohol
42

EXPERIMENTAL

EXPERIMENTAL

M.ps. are uncorrected. NMR spectra were recorded on Perkin-Elmer 90MHz and 220 MHz spectrometer using TMS as an internal standard. Mass spectra were recorded on Kratrs MS 30 instrument fitted with a DS 55 data system.

2-Hydroxychromanones (24)

To o-hydroxyacetophenone (0.05 mole, 6.8 g) in warm ethylformate (30 ml) in a flask fitted with reflux condensor, was added pulverized sodium (3.0 g) suspended in dry ether, and the vigorous reaction was regulated by external cooling with ice-salt mixture. After the reaction subsided, ethylformate (6.0 ml) was added followed by sodium (1.0 g) and the reaction mixture refluxed for 10 min and left overnight. Ice and water were then added carefully and the resulting solution was extracted twice with ether. The aqueous layer was acidified with dil. acetic acid. An oil separated out which solidified quickly into a crystalline solid. It was filtered, dried and crystalklized from a 1:1 mixture of benzene and pet. ether (40°-60°) to give (24) as colourless crystals, m.p. 105°, yield 6.1 g (75%).

Analysis : Calculated ; C, 65.85% ; H, 4.87%
Obtained : C, 65.53% ; H, 4.62%

1-(2-hydroxybenzoyl)-2-(4-oxo-4H-1-benzopyran-3yl) ethylene (25)

2-Hydroxychromanone (24) (0.01 mole, 1.65 g) was taken in

dry test tube and immersed in an oil bath having temperature 110°. The substance first melted and then resolidified at the same temperature. It was crystallized from benzene to give (25) as yellow coloured needles, m.p. 178-79°, yield 0.75 g (51%).

Analysis	:	Calculated	: C, 73.97%	; H, 4.11%
		Observed	: C, 74.28%	; H, 4.367%

2,3'-Bi-4H-1-benzopyran-4,4'-diones (26)

To a solution of (25) (0.002 mol, 0.58 g) in a minimum quantity of isoamyl alcohol was added, freshly sublimed selenium dioxide (0.5 g), and the reaction mixture refluxed at 165-170° in an oil-bath for 48 hr, filtered hot and isoamyl alcohol removed by steam distillation to give a solid which on crystallization from benzene gave (26), m.p. 238°C, yield 0.11g (20%)

Analysis	:	Calculated	: C, 74.48%	; H, 3.45%
		Observed	: C, 74.1%	; H, 3.701%

6-Methyl-2-hydroxychromanone (32)

To 5-methyl-2-hydroxyacetophenone (0.05 mol, 7.5 g) in warm ethylformate (30 ml) in a flask fitted with a reflux condensor, was added pulverized sodium (3.0 g) suspended in dry ether, and the vigorous reaction regulated by external cooling with ice-salt mixture. After the reaction subsided,

ethylformate (6.0 ml) was added followed by sodium (1.0 g) and the reaction mixture refluxed for 10 min. and left overnight Ice and water then added carefully andthe resulting solution was extracted twice with ether. The aq. layer was acidified with dil. acetic acid. An oil separated out which solidified quickly into a crystalline solid. It was filtered, dried and crystallized from a 1:1 mixture of benzene and pet. ether (40°-60°) to gave (32) as white crystals, m.p. 132°C, yield 6.6 g (74%).

Analysis : Calculated : C, 68.4% ; H, 5.62%
Obtained : C, 67.7% ; H, 5.7%

1-(2-hydroxy-5-methylbenzoyl)-2-(6-methyl-4-oxo-4H-1-benzopyran-3-yl) ethylene (33)

6-Methyl-2-hydroxychromanone (32) (0.01 mole, 1.8 g) was taken in dry test tube and immersed in an oilbath having temperature 140°. The substance first melted and then resolidified at the same temperature with the evolution of water molecule which condensed at the upper part of test tube, then it was crystallzed from benzene to give (33) as yellow coloured needles, m.p. 196°C, yield 0.8 g (50%).

Analysis : Calculated : C, 75.0% ; H, 5.0%
Obtained : C, 74.55%; H, 4.88%

6,6'-Dimethyl-(2,3'-bi-4H-1-benzopyran)-4,4'-dione (34)

To a solution of (33) (0.002 mole, 0.64 g) in a minimum

quantity of isoamyl alcohol was added, freshly sublimed selenium dioxide (0.5 g), and the reaction mixture refluxed at 165-170° in an oilbath for 48 hr. filtered hot and isoamyl alcohol removed by steam distillation to give a solid which on crystallization from ethyl alcohol gave (34), m.p. 258°C, yield 0.100 g.

Analysis : Calculated : C, 75.47% ; H, 4.4%
Obtained : C, 75.10% ; H, 4.86%

7-Methoxy-8-methyl-2-hydroxychromanone (36)

To 4-methoxy-3-methyl-2-hydroxyacetophenone (35) (0.05 mole, 9.0 g) in warm ethylformate (35 ml) in a flask fitted with a reflux condensor was added pulverized sodium (3.0 g) suspended in dry ether, and the vigorous reaction regulated by external cooling with ice. After the reaction subsided, ethylformate (6.0 ml) was added followed by sodium (1.0 g) and the reaction mixture for 10 min. and left overnight. Ice and water were then added carefully and the resulting solution was extracted twice with ether. The aq.layer was acidified with dil. acetic acid. An oil separated out which solidified quickly into a crystalline solid. It was filtered, dried and crystallized from a 2:1 mixture of benzene and pet. ether (40°-60°) to gave (36) as white crystals, m.p. 155°C, yield 7.7 g (74%).

Analysis : Calculated : C, 63.46% ; H, 5.77%
Obtained : C, 63.10% ; H, 5.65%

1-(2-hydroxy-4-methoxy-3-methylbenzoyl)-2-(7-methoxy-8-methyl-4-oxo-4H-1-benzopyran-3-yl) ethylene (37)

7-Methoxy-8-methyl-2-hydroxychromanone (36) (0.01 mole, 2.0 g) was taken in dry test tube and immersed in an oilbath having temperature 160°C. The substance first melted and then resolidified at the same temperature then it was crystallized from benzene to gave (37) as light yellow colour needles, m.p. 252°C, yield 1.0 g (53%).

Analysis : Calculated : C, 69.47% ; H, 5.26%
Obtained : C, 69.88% ; H, 5.54%

7,7'-Dimethoxy-8,8'-dimethyl-(2,3'-bi-4H-1-benzopyran)-4,4'-dione (38)

To a solution of (37) (0.002 mol, 0.76 g) in a minimum quantity of isoamyl alcohol, and freshly sublimed selenium dioxide (0.5 g) was added and the reaction mixture refluxed at 165-170° in an oil bath for 48 hr, filtered hot and isoamyl alcohol removed by steam distillation to give a solid which on crystallization from N,N-dimethylformamide gave (38), m.p. 318°C, yield 0.160 g (22%).

Analysis : Calculated : C, 69.84% ; H, 4.76%
Obtained : C, 69.74% ; H, 4.75%

6,7-Dimethyl-2-hydroxychromanone (40)

To 3,4'-Dimethyl-2-hydroxy acetophenone (39) (0.05 mol,

5.2 g) in warm ethylformate (30 ml) in a flask fitted with a reflux condensor, was added pulverized sodium (3.0 g) in dry ether and the vigorous reaction regulated by external cooling with ice. After the reaction subsided, ethylformate (6.0 ml) was added followed by sodium (1.0 g) and the reaction mixture refluxed for 10 min. and left overnight. Ice and water were then carefully added andthe resulting solution was extracted twice with ether. The aq. layer was acidified withdil. acetic acid. An oil separated out which solidified quickly into a crystalline solid. It was dried and crystallized from a 2:1 mixture of benzene and pet. ether (40°-60°) to gave (40) as white needles, m.p. 138°C, yield 7.0 g (73%).

Analysis : Calculated : C, 68.75% ; H, 6.25%
Obtained : C, 69.13% ; H, 6.08%

1-(2-Hydroxy-4,5-dimethylbenzoyl)-2-(6,7-dimethyl-4-oxo-4H-1-benzopyran-3-yl) ethylene (41)

6,7-Dimethyl-2-hydroxychromanone (40) (0.01 mol, 1.9 g) was taken in dry test tube and immersed in oilbath having temperature 145°C. The substance first melted and then resolidified at the same temperature then it was crystallised from benzene to gave (41) as yellow coloured needles, m.p. 233°C, yield 0.88 g (51%).

Analysis : Calculated : C, 75.86% ; H, 5.75%
Obtained : C, 76.17% ; H, 5.83%

6,6'-7,7'-Tetramethyl-(2,3'-bi-4H-1-benzopyran)-4,4'-dione (42)

To a solution of (41) (0.002 mol, 0.7 g) in a minimum quantity of isoamyl alcohol freshly sublimed SeO_2 (0.5 g) was added and the reaction mixture refluxed at 165-170°C for 48 hr. in an oilbath, filtered hot and isoamyl alcohol removed by steam distillation to gave asolid which on crystallization from dimethylformamide gave (42), m.p. 276°C, yield 0.14 g (20%).

Analysis	:	Calculated	:	C, 76.30% ; H, 5.20%
		Obtained	:	C, 75.91% ; H, 5.56%

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