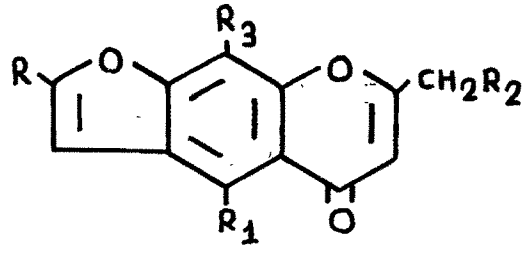
CHAPTER II

STUDIES IN THE SYNTHESIS OF CHROMONE DERIVATIVES

THEORETICAL

SYNTHESIS OF FUROCHROMONES

Furochromones or Furobenzopyrones[1,2] occur mainly in the fruits and seeds of Ammi Visnaga L., are of the linear type and are limited in number. Khellin(I), Khellinol(II), Ammiol(III), Visnagin(IV), Khellinin(V), Khellol(VI) and Visamminol(VII) are important furochromones isolated from the natural products. Some of them and other linear as well as angular type of furochromones have been studied synthetically by many grops of workers[3-13].



(I) $R = R_2 = H$, $R_1 = R_3 = OCH_3$

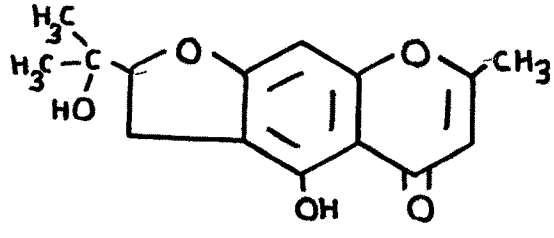
(II) $R = R_2 = H$, $R_1 = OH$, $R_3 = OCH_3$

(III) $R = H$, $R_2 = OH$, $R_1 = R_3 = OCH_3$

(IV) $R = R_2 = R_3 = H$, $R_1 = OCH_3$

(V) $R = R_3 = H$, $R_1 = OCH_3$, $R_2 = OC_6H_{11}O_5$

(VI) $R = R_3 = H$, $R_1 = OCH_3$, $R_2 = OH$



(VII)

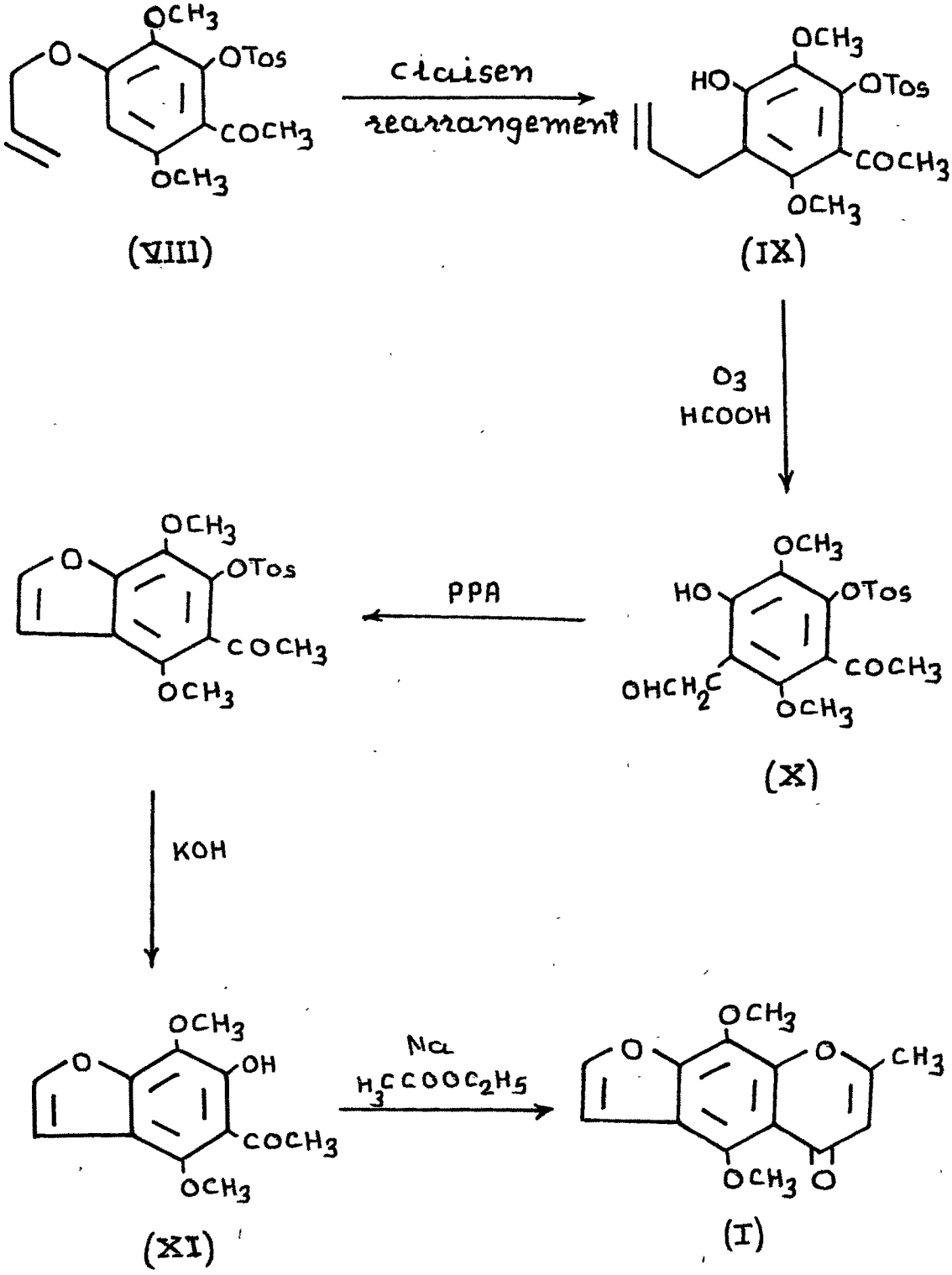
Physiological activity :

Khellin(I) has pronounced physiological activity. It has selective antispasmodic effect upon ureter[14,15], gall bladder[16] and bile duct[17]. A bronchodilating action of(I) has been reported[18,19]. It is used as potent coronary vasodilator[20-22] and in whooping cough.

Khellol glucoside, Khellinin(V) exerts a stimmulating action on the heart and increases the coronary flow. It is not converted into Khellin in the digestive tract or in the body tissue[23]. Schönberg and Sina[24] studied antispasmodic activity of a number of furochromones with the relation to their chemical constitutions.

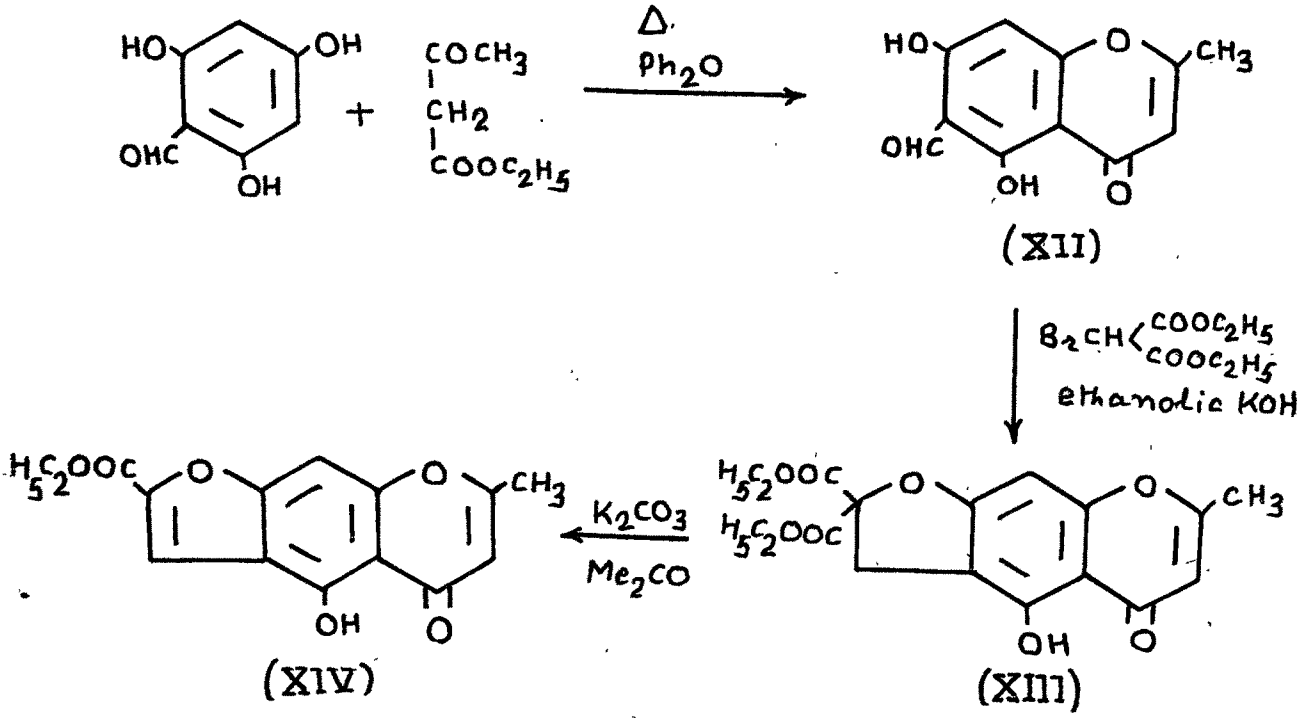
Synthesis :

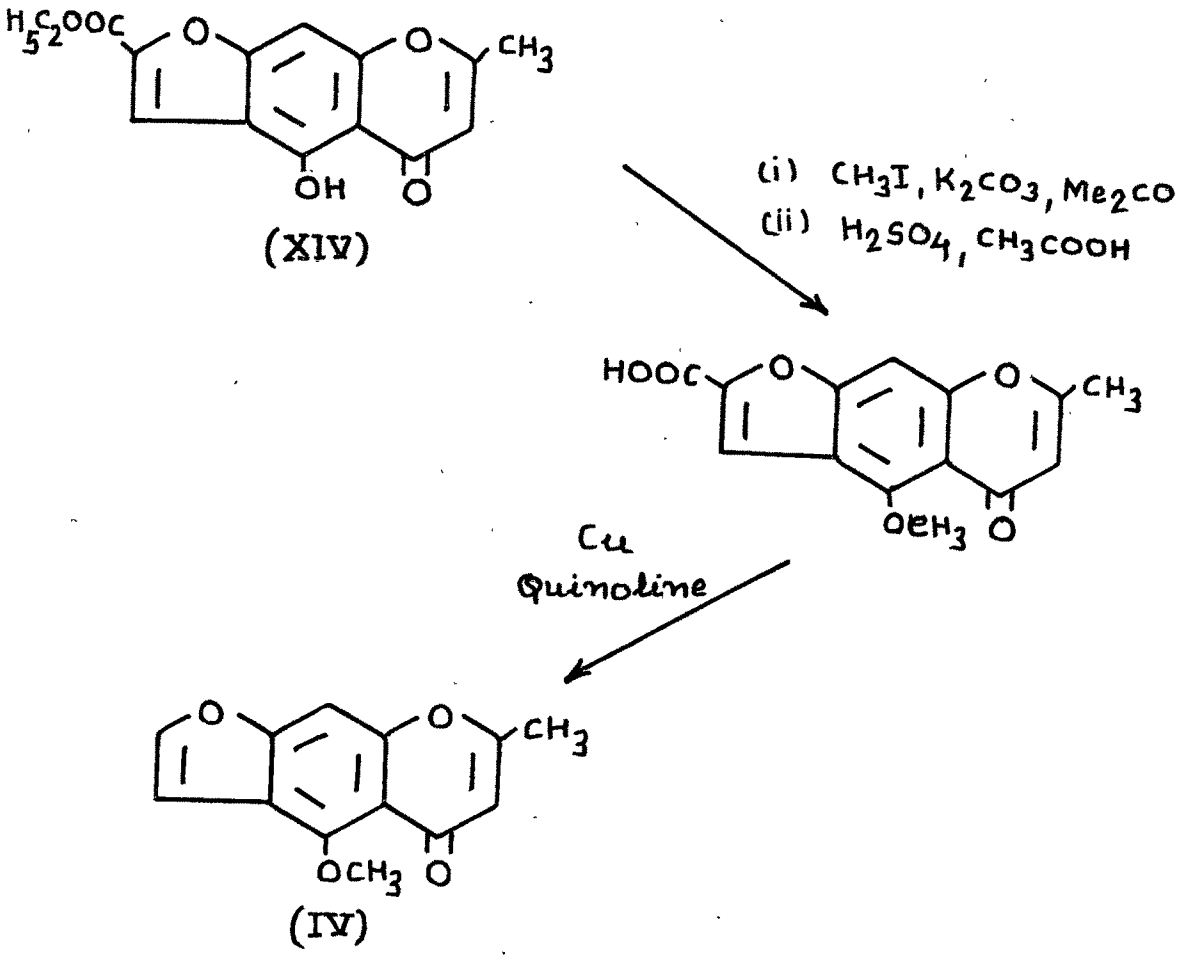
The synthesis of Khellin or 4,9-dimethoxy-7-methyl-5H-furo(3,2-g)benzopyran-7-one(I) has been achieved by many workers. Seshadri and coworkers[3] gave an important method for the synthesis of (I) from 4-allyloxy-3,6-dimethoxy-2-tosyloxyacetophenone(VIII), which on Claisen rearrangement gave 5-allyl derivative(IX). Ozonolysis followed by catalytic hydrogenation of IX gave the corresponding 5-acetaldehydo derivative(X), which on cyclization with polyphosphoric acid (PPA), followed by hydrolysis yielded important intermediate Khellinone(XI). Claisen condensation of XI with ethyl acetate in presence of sodium gave Khellin (I).


OCH3
OTos
COCH3
OCH3
Claisen
rearrangement
HO
(VIII)
(IX)
O3
HCOOH
PPA
OHCH2C
(X)
KOH
OH
Na
H3CCOOC2H5
CH3
(XI)
(I)

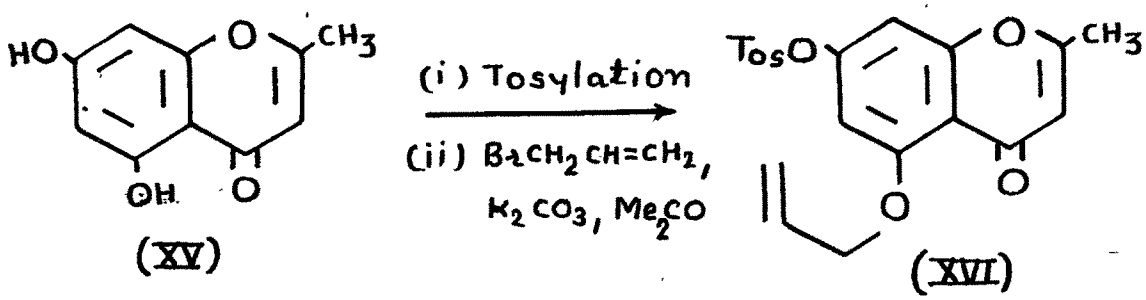
Khellinol (II) is a demethylkhellin, obtained by the selective demylation of Khellin[25]. Ammiol(III), a hydroxykhellin has been synthesised from Khellin by Mustafa and his colleauges[26]

Badawi and Fayez synthesised[4] Visnagin or 4-methoxy-7-methyl-5H-furo(3,2-g)benzopyran-5-one(IV), starting with 2-methyl-5,7-dihydroxy-6-formylchromone(XII), which was prepared from 2,4,6-trihydroxybenzaldehyde on thermal condensation with ethyl acetoacetate in diphenyl ether according to Desai, Trivedi and Sethna[27]. The condensation of XII with diethyl bromomalonate in ethanolic alkali gave XIII, which on hydrolysis with potassium carbonate in acetone afforded mainly XIV. Methylation followed by hydrolysis and decarboxylation of XIV gave Visnagin(IV).



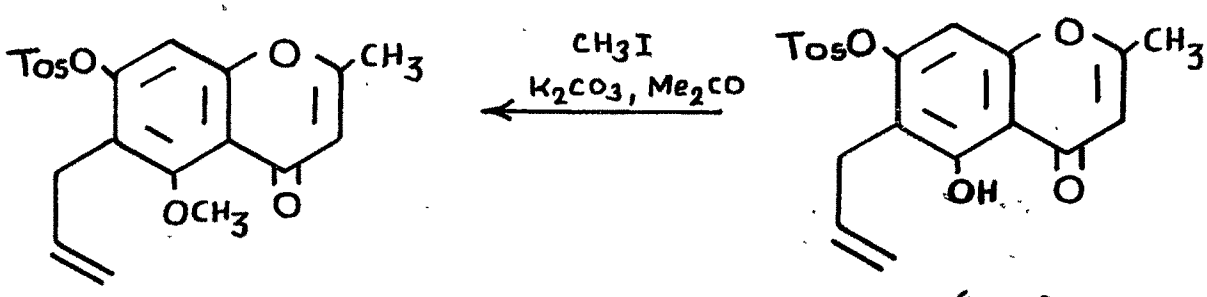


Seshadri et al[5]. had also synthesized Visnagin(IV) from 5,7-dihydroxy-2-methylchromone(XV). They had introduced an allyl group into the 6-position(XVII) by Claisen rearrangement of 5-allyl ether(XVI). The initial protection of the 7-hydroxy group was affacted by tosylation, which was then removed just before ozonolysis. Methylation followed by detosylation, ozonolysis and cyclization of XVII gave Visnagin(IV) in good yield.



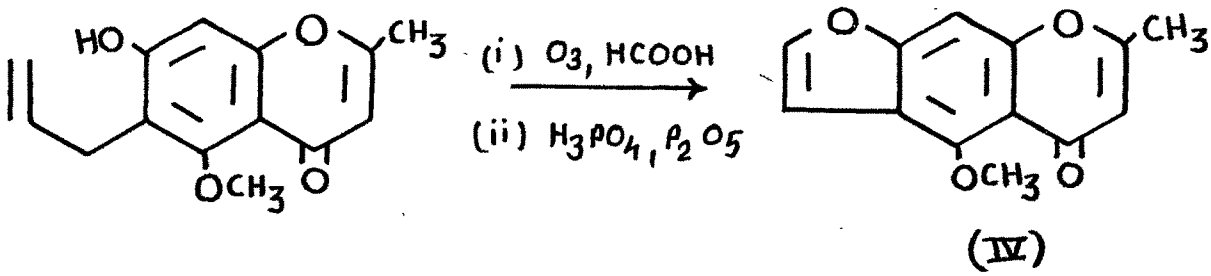
(XV) (XVI)

C.R.
190-95°
Red. Press.



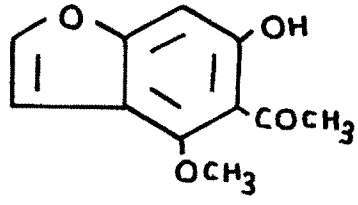
(XVII)

Ethanol
10% aq. NaOH



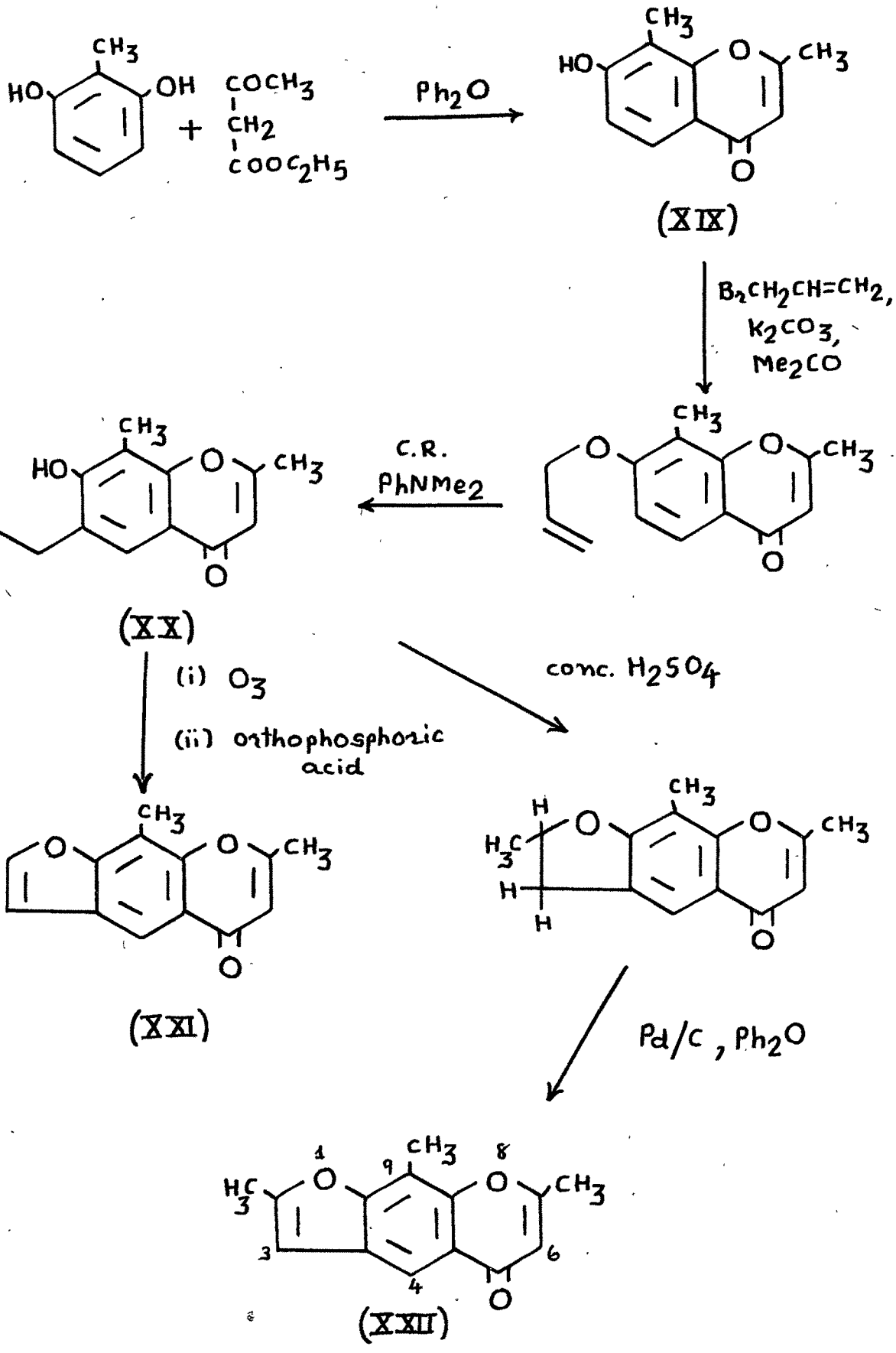
(IV)

Khellinin(V), is glucoside of hydroxyvisnagin, which on alkali hydrolysis gave Visnaginone(XVIII), but on treatment with acid gave Khellol(VI), which has been synthesised[6] and also obtained from Visnagin by Mustafa et al[26]. Visamminol(VII), a dihydroxyvisnagin derivative has been synthetically studied by Schmid[7].

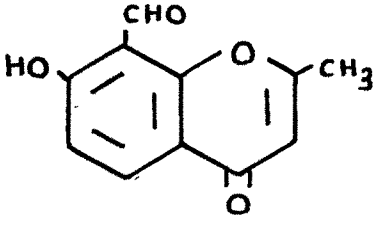


(XVIII)

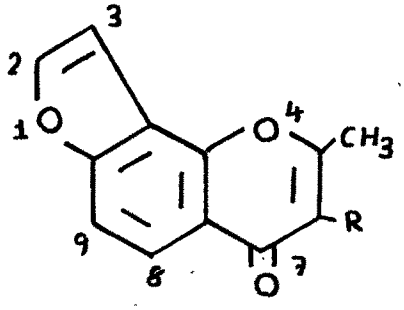
Pardanani and Trivedi[8] have recently synthesised linear type of furochromones from 2,8-dimethyl-7-hydroxychromone(XIX), which was obtained by thermal condensation of 2-methylresorcinol with ethyl acetoacetate in diphenyl ether[27]. XIX, on allylation and Claisen rearrangement gave 2,8-dimethyl-6-allyl-7-hydroxychromone(XX). This on ozonolysis, followed by cyclization with orthophosphoric acid gave 2,9-dimethyl-5H-furo(3,2-g)benzopyran-5-one(XXI). While XX, on cyclization with conc.sulphuric acid followed by dehydrogenation afforded 2,7,9-trimethyl-5H-furo(3,2-g)-benzopyran-5-one(XXII).


Ph2O
(XIX)
Br CH2CH=CH2, K2CO3, Me2CO
C.R. PhNMe2
(XX)
(i) O3
(ii) orthophosphoric acid
conc. H2SO4
(XXI)
Pd/C , Ph2O
(XXII)

The synthesis of substituted 7H-furo(2,3-h) benzopyran-7-one was achieved by many workers. Rao et al[9]. constructed a furan ring on a suitably substituted chromones viz., 8-formyl-7-hydroxy-2-methylchromone(XXIII), which on condensation with ethyl bromoacetate followed by hydrolysis and cyclization with acetic anhydride and sodium acetate gave 5-methyl-7H-furo(2,3-h)benzopyran-7-one(XXIV). They have also synthesised 6-acetyl-5-methyl-7H-furo(2,3-h) benzopyran-7-one(XXV) starting from 3-formyl-2,4-dihydroxy-acetophenone.

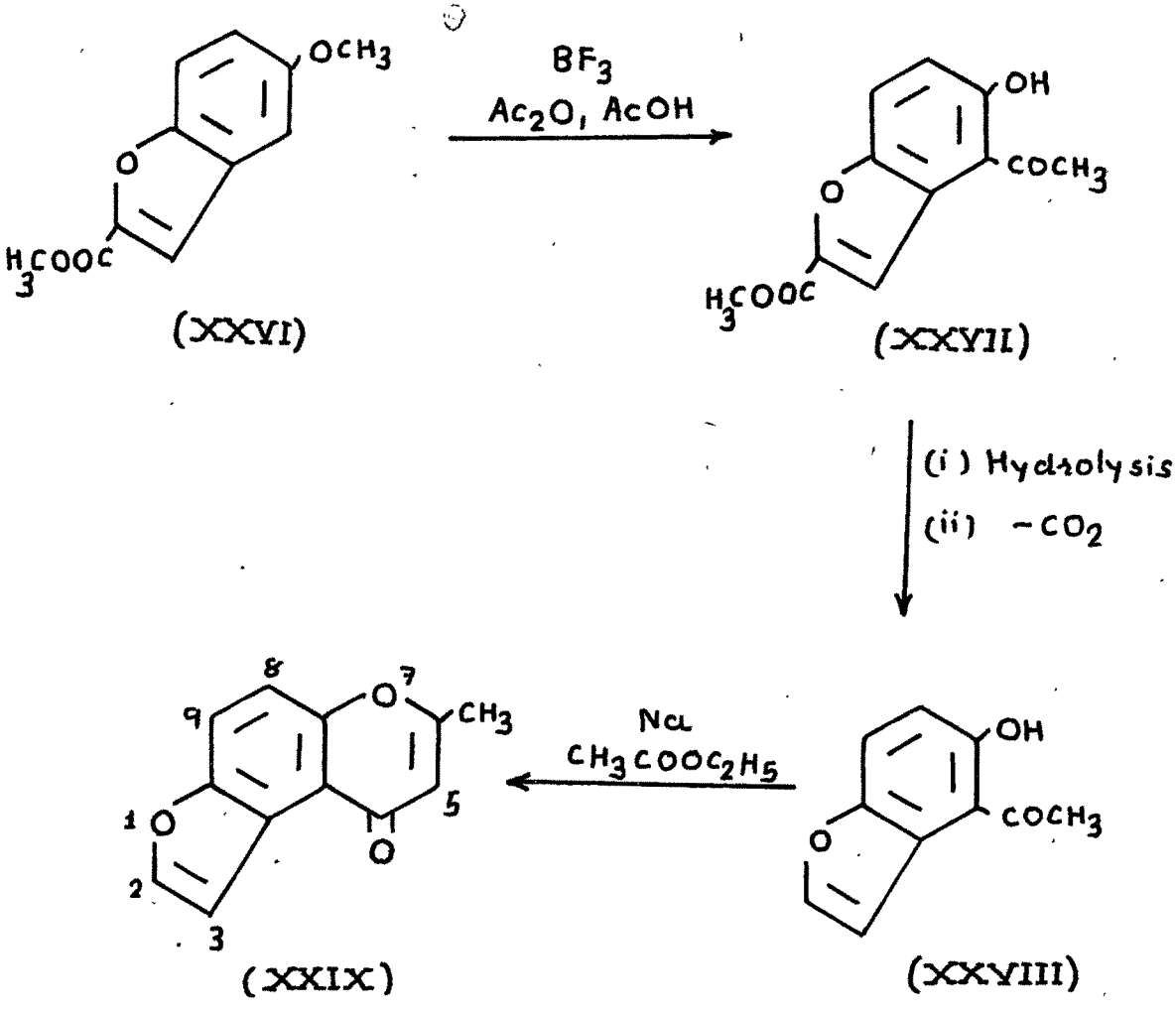


(XXIII)



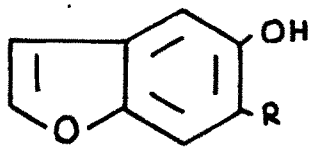
(XXIV) R = H
(XXV) R = $COCH_3$

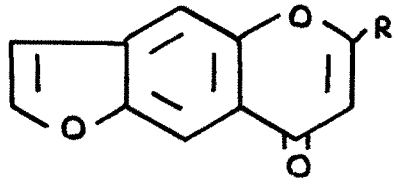
The other route for the synthesis of furochromones involves the building up of the γ-pyrone ring on benzofurans. Ramchandran and coworkers[10] acetylated 2-carbmethoxy-5-methoxybenzofuran(XXVI) with acetic acid-acetic anhydride in presence of boron trifluoride to obtain 2-carbmethoxy-4-acetyl-5-hydroxybenzofuran(XXVII), which on hydrolysis followed by decarboxylation gave 4-acetyl-5-hydroxybenzofuran(XXVIII). Claisen condensation of XXVIII with ethyl acetate directly gave 6-methyl-4H-furo(3,2-f)benzopyran-4-one(XXIX).



Ramage and Stead[11] synthesised 5-hydroxy-6-acetylbenzofuran(XXXa) from 1,4-dimethoxybenzene by carrying out the reaction with chloroacetyl chloride followed by cyclization, hydrogenation with Raney nickel, acetylation and dehydrogenation. XXXa, on Claisen condensation with ethyl acetate in presence of sodium underwent simultaneous cyclization and afforded 6-methyl-8H-furo(2,3-g)benzopyran-8-one(XXXIa). The use of ethyl oxalate instead of ethyl

acetate in Claisen condensation of XXXa gave the diketo aester(XXXb), which on cyclization and decarboxylation yielded a unsubstituted product, 8H-furo(2,3-g)benzopyran-8-one(XXXIb).





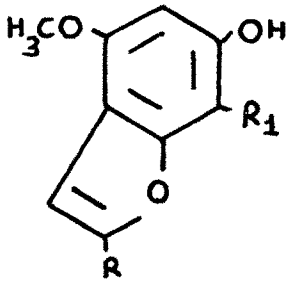
(XXXa) R = $COCH_3$

(XXXb) R = $COCH_2COCOOC_2H_5$

(XXXIa) R = CH_3

(XXXIb) R = H

Clarke, Glaser and Robertson[12] prepared furochromones by the application of Hoesch reaction with acetonitrile or Friedel-Craft reaction with acetyl chloride on 2-carbethoxy-4-methoxy-6-hydroxybenzofuran(XXXII), where carbethoxy group served to protect the reaction in 2-position, gave 7-acetyl derivative(XXXIII), which on hydrolysis and subsequent decarboxylation afforded 4-methoxy-6-hydroxy-7-acetylbenzofuran(XXXIV). Claisen condensation of XXXIV with ethyl acetate gave the diketone(XXXV), which was cyclized to 4-methoxy-7-methyl-9H-furo(2,3-f)benzopyran-9-one(XXXVI)

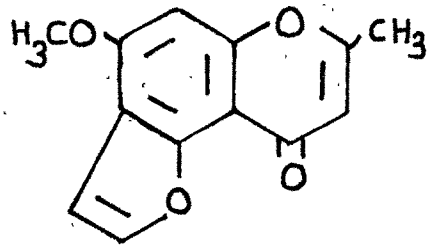


(XXXII) R = $COOC_2H_5$, R_1 = H

(XXXIII) R = $COOC_2H_5$, R_1 = $COCH_3$

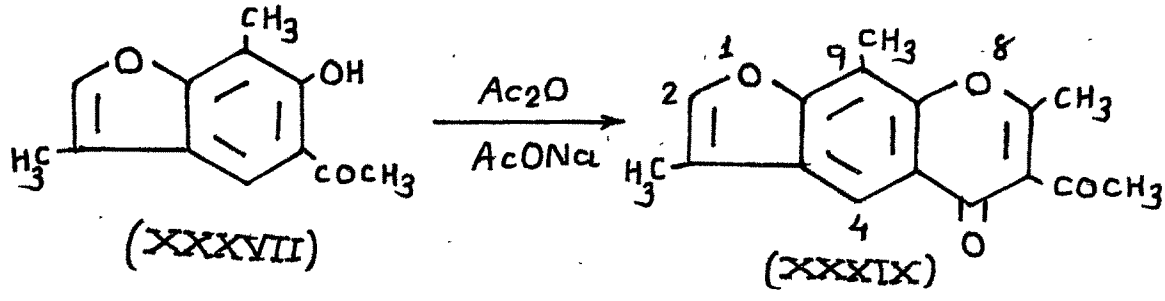
(XXXIV) R = H, R_1 = $COCH_3$

(XXXV) R = H, R_1 = $COCH_2COCH_3$

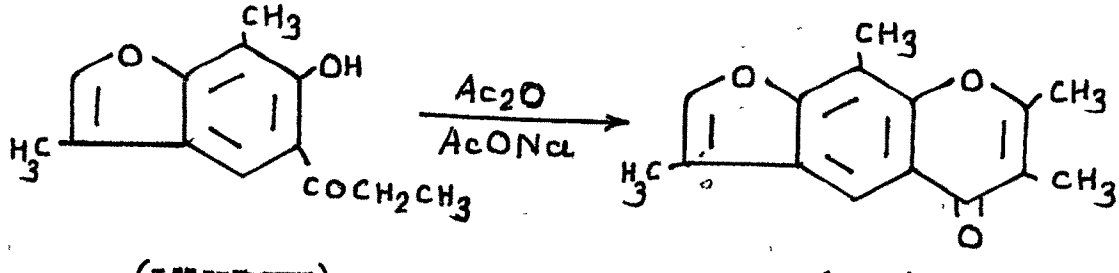


(XXXVI)

The synthesis of 6-acetyl-3,7,9-trimethyl-5H-furo(3,2-g)benzopyran-5-one(XXXIX) and 3,6,7,9-tetramethyl-5H-furo(3,2-g)benzopyran-5-one(XL), was reported by Shaikh and Trivedi[13]. They carried out Kostanecki-Robinson acetylation on 3,7-dimethyl-6-hydroxy-5-acetylbenzofuran (XXXVII) and 3,7-dimethyl-6-hydroxy-5-propionylbenzofuran (XXXVIII), to obtain XXXIX and XL respectively.



(XXXVII) (XXXIX)



(XXXVIII) (XL)

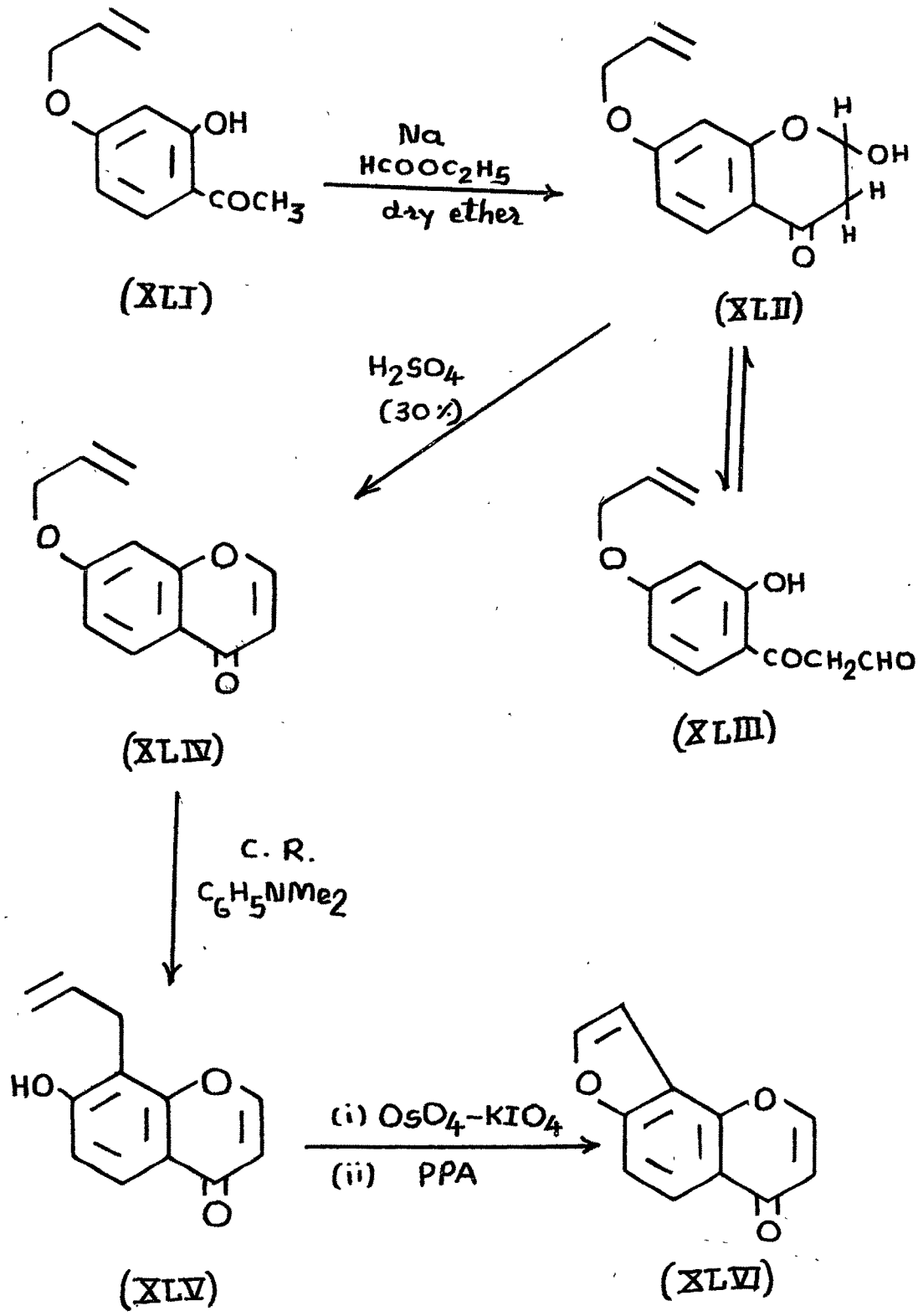
Present work :

From the above review, it is revealed that earlier workers had synthesised furochromones carrying one or two substituents in γ-pyrone ring. So it was thought of interest to synthesise different chromones with unsubstituted γ-pyrone ring and to build up furan ring as to get the corresponding furochromones. The following furochromones are synthesised in the present work :

1. 7H-Furo(2,3-h)benzopyran-7-one (XLVI)
2. 2-Methyl-7H-furo(2,3-h)benzopyran-7-one (XLVIII)
3. 9-Methyl-5H-furo(3,2-g)benzopyran-5-one (LIII)
4. 2,9-Dimethyl-5H-furo(3,2-g)benzopyran-5-one (LVIII)
5. 4H-Furo(3,2-f)benzopyran-4-one (LXIII)
6. 2-Methyl-4H-furo(3,2-f)benzopyran-4-one (LXV)
7. 9-Methyl-4H-furo(3,2-f)benzopyran-4-one (LXXIII)
8. 2,9-Dimethyl-4H-furo(3,2-f)benzopyran-4-one (LXXV)

Synthesis of 7H-furo(2,3-h)benzopyran-7-one (XLVI) :

2-Hydroxy-4-allyloxyacetophenone(XLI), prepared according to the method given by Baker and Lothian[28], was condensed with freshly distilled ethyl formate in presence of pulverised sodium in dry ether to yield 7-allyloxy-2-hydroxychromanone(XLII) and not 3-(4-allyloxy-2-hydroxyphenyl)-3-oxo-3H-propanal(XLIII). The NMR spectrum of the compound showed the absence of aldehydic proton around δ 9.0 and also the signals for methylene protons are not at δ 3.75 but



(XLI) (XLII) (XLIII) (XLIV) (XLV) (XLVI)

they are quite upfield at δ2.75. Moreover no shift was observed, when UV spectra was recorded in dilute sodium hydroxide solution. Its structure was confirmed by its spectral data :

The IR spectrum in nujol (Fig. 1) showed the bands at 1650 cm^{-1} (γ-pyronyl >C=O group) and a broad band at 3227 cm^{-1} (-OH group). The NMR spectrum in DMSO-d_6 (Fig. 2) showed the following signals : δ 2.62-2.90, multiplet, 2H, methylene protons at 3-position ; 4.65, doublet, J=7Hz, 2H, two methylene protons of allyloxy group, at the carbon which involved in ether linkage, -O-$\underline{CH_2}$-CH=CH_2 ; 5.20-5.50, multiplet, 2H, two methylene protons of allyloxy group at the end carbon atom, -O-CH_2-CH=$\underline{CH_2}$; 5.75, quartet, 1H, methine proton at 2-position ; 5.80-6.20, multiplet, 1H, methine proton at the middle carbon of allyloxy group -O-CH_2-$\underline{CH}$=CH_2 ; 6.57, doublet, J=1.5Hz, 1H, aromatic proton at 8-position ; 6.64, double doublet, J=10Hz, 1.5Hz, 1H at 6-position ; 7.55, broad doublet, J=7Hz, 1H, -OH group at 2-position ; 7.65, doublet, J=10Hz, 1H at 5-position.

Dehydration of XLII by sulphuric acid (30 %) afforded 7-allyloxychromone(XLIV), which on Claisen rearrangement in dimethylaniline gave 7-hydroxy-8-allyl-chromone(XLV). This on treatment with osmium tetroxide-potassium periodate in ethyl acetate-water gave the 8-acetaldehydo product from the organic layer by evaporation of the solvent, was cyclized to 7H-furo(2,3-h)benzopyran-7-one(XLVI), using polyphosphoric acid (PPA). The structure of

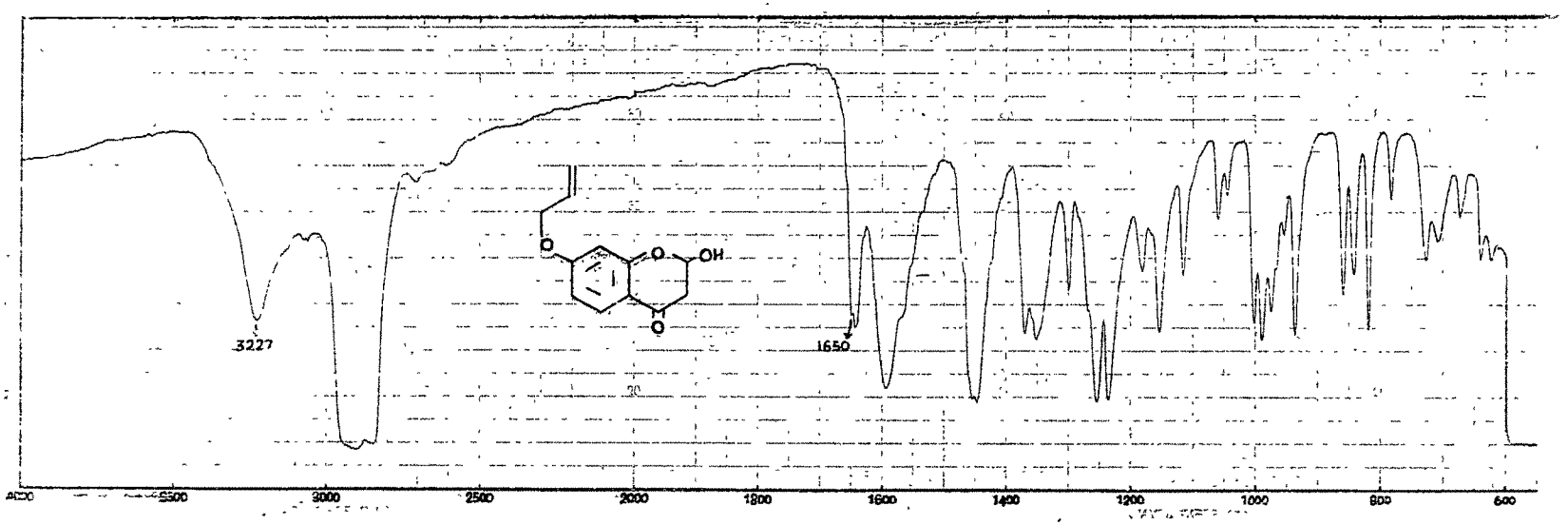


Fig. 1 : IR spectrum of 7-Allyloxy-2-hydroxychromanone(XLII) in nujol.

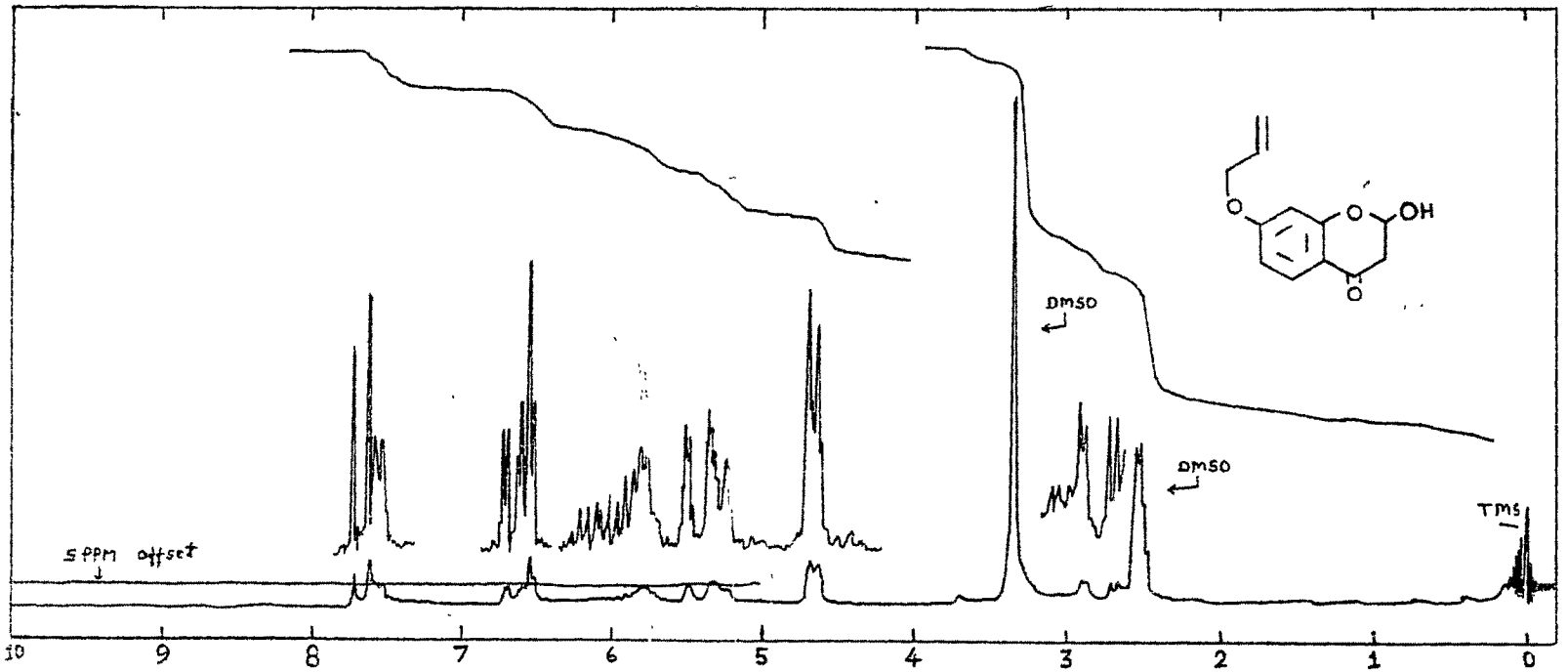


Fig. 2 : NMR spectrum of 7-Allyloxy-2-hydroxychromanone (XLII) in DMSO-d_6 (90 MHz).

XLVI, was confirmed on the bais of its NMR spectrum in $CDCl_3$ (Fig. 3) : δ6.38, doublet, J=6Hz, 1H at 6-position ; 7.08, doublet, J=1.8Hz, 1H at 3-position ; 7.52, doublet, J=10Hz, 1H at 9-position ; 7.72, doublet, J=1.8Hz, 1H, at 2-position ; 7.90, doublet, J=6Hz, 1H at 5-position ; 8.13, doublet, J=10Hz, 1H at 8-position.

The spectral data of XLVI also confirmed that the Claisen rearrangement of 7-allyloxychromone(XLIV) took place at 8-position and not at 6-position, in the latter case the spectrum of cyclized product would have shown two singlets for the aromatic protons instead of doublet doublets of ortho protons with J=10Hz, each for one aromatic proton.

Synthesis of 2-methyl-7H-furo(2,3-h)benzopyran-7-one(XLVIII) :

7-Hydroxy-8-allylchromone(XLV) on trituration with sulphuric acid (85 %) according to Shaikh and Trivedi[29] afforded 2-methyl-2,3-dihydro-7H-furo(2,3-h)benzopyran-7-one(XLVII). The structure of which was confirmed by the NMR spectrum in $CDCl_3$ (Fig. 4) : δ1.55, doublet, J=6Hz, 3H, CH_3 group at 2-position ; 2.60-3.30, two symmetrical quartets, 2H, methylene protons at 3-position ; 4.96-5.36, multiplet, 1H at 2-position ; 6.28, doublet, J=6Hz, 1H at 6-position ; 6.78, doublet, J=9Hz, 1H at 9-position ; 7.72, doublet, J=6Hz, 1H at 5-position ; 8.04, doublet, J=9Hz, 1H at 8-position.

Dehydrogenation of XLVII with palladised charcoal (10 %) in diphenyl ether gave 2-methyl-7H-furo(2,3-h)benzopyran-

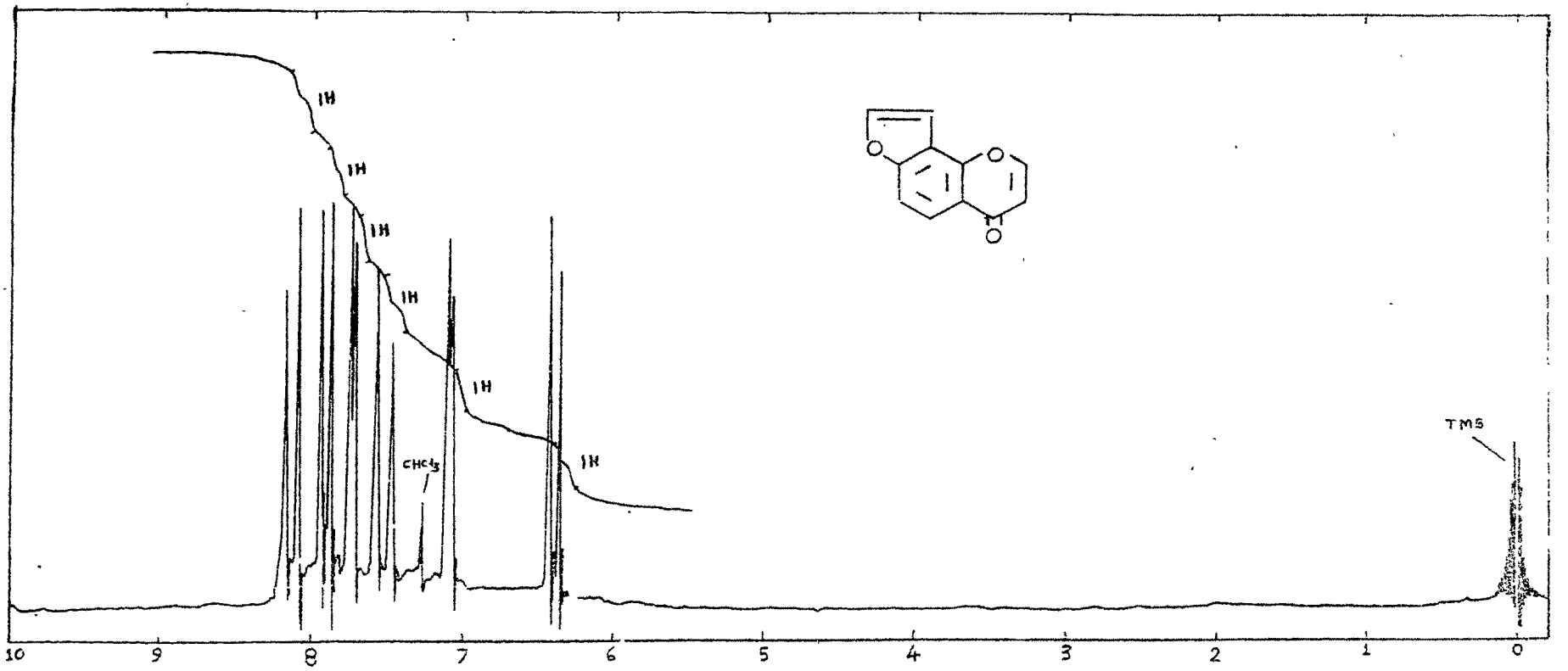
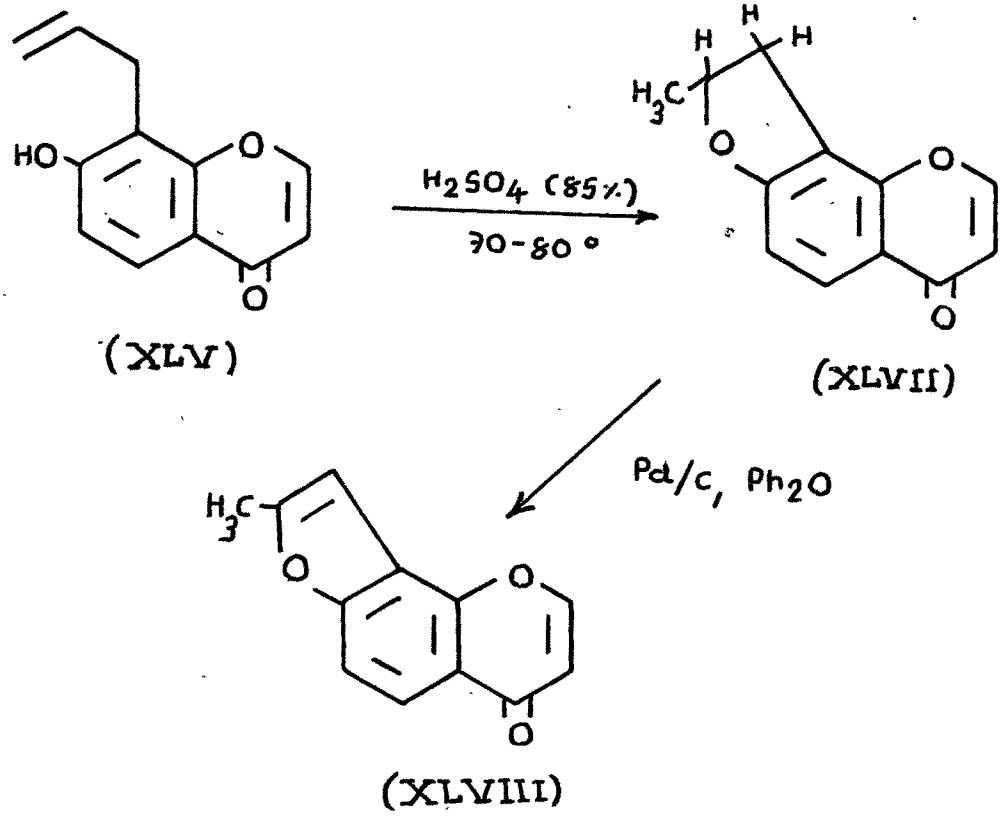


Fig. 3 : NMR spectrum of 7H-furo(2,3-h)benzopyran-7-one (XLVI) in $CDCl_3$ (90 MHz).

7-one(XLVIII). Its NMR spectrum in $CDCl_3$ (Fig. 5) showed the following signals, which confirmed the above structure : δ 2.52, singlet, 3H, CH_3 group at 2-position ; 6.42, doublet, J=6.5Hz, 1H at 6-position ; 6.77, singlet, 1H at 3-position ; 7.45, doublet, J=10Hz, 1H at 9-position ; 7.92, doublet, J=6.5Hz, 1H at 5-position ; 8.06, doublet, J=10Hz, 1H, at 8-position.



(XLV) (XLVII) (XLVIII)

Synthesis of 9-Methyl-5H-furo(3,2-g)benzopyran-5-one(LIII) :

2,4-Dihydroxy-3-methylacetophenone, on allylation with allyl bromide in presence of anhydrous potassium carbonate in dry acetone, gave 2-hydroxy-3-methyl-4-allyloxy-acetophenone(XLIX)[30]. This on Claisen condensation with

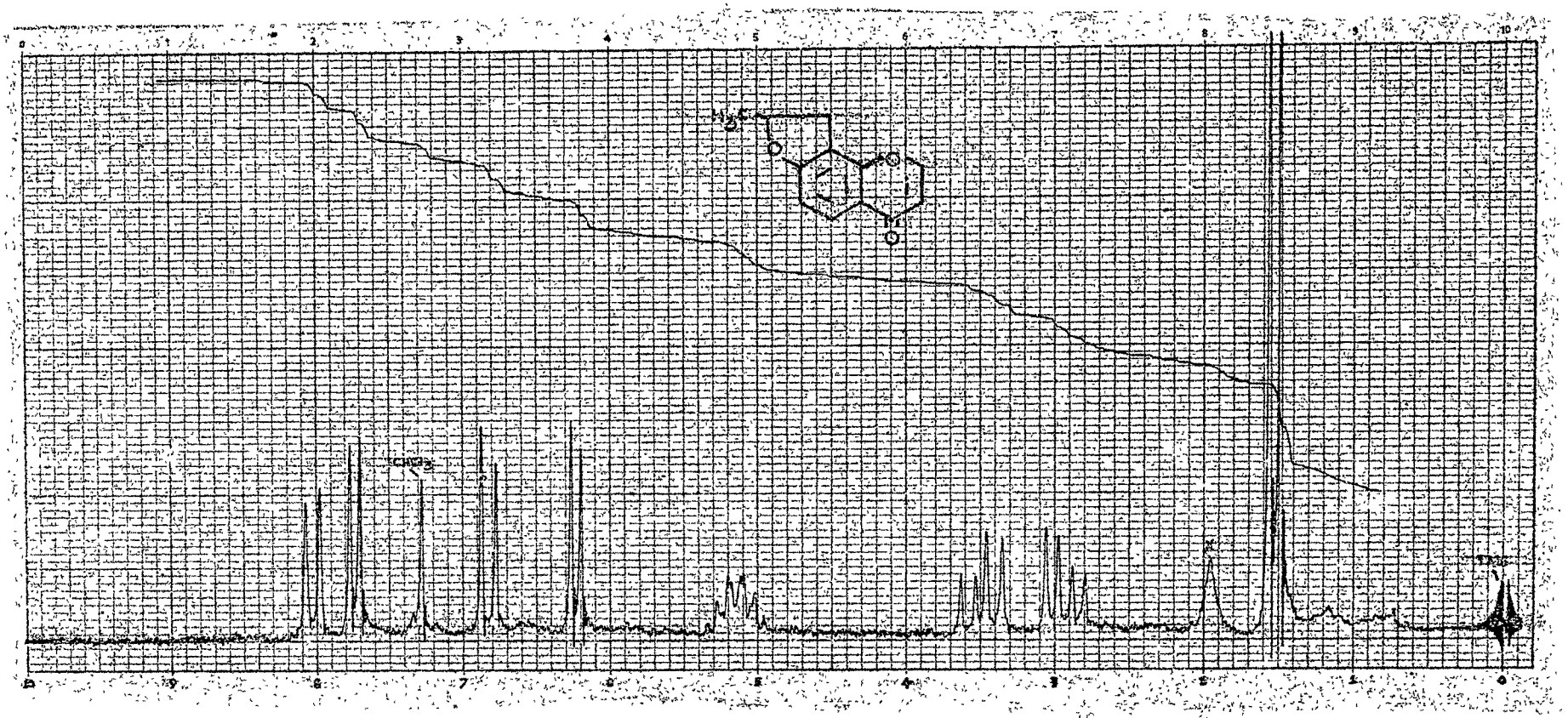


Fig. 4 : NMR spectrum of 2-Methyl-2,3-dihydro-7H-furo(2,3-h)benzopyran-7-one (XLVII) in $CDCl_3$ (90 MHz).

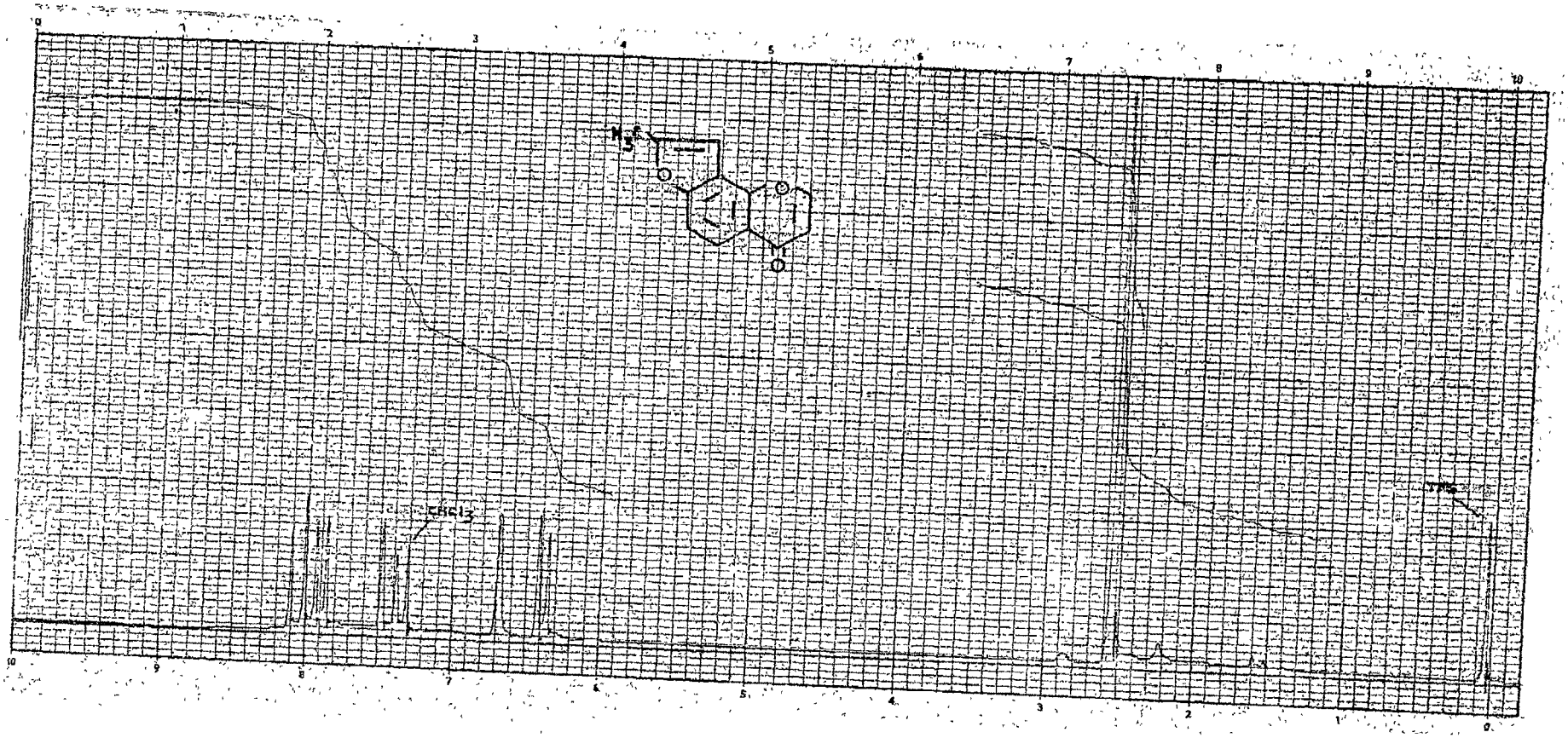
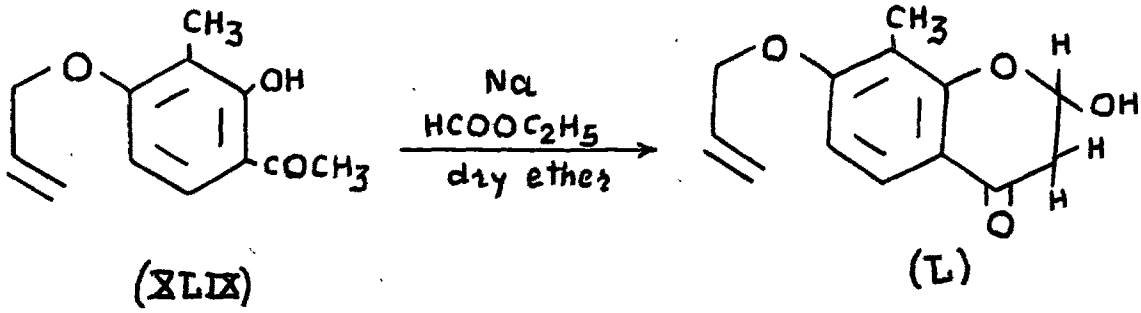


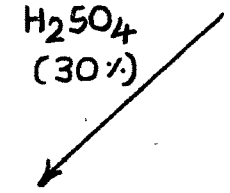
Fig. 5 : NMR spectrum of 2-Methyl-7H-furo(2,3-h)benzopyran-7-one(XLVIII) in $CDCl_3$ (90 MHz).

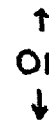
ethyl formate in presence of pulverized sodium in dry ether gave 2-hydroxy-7-allyloxy-8-methylchromanone(L). Its structural assignment was consistant with its spectral data :

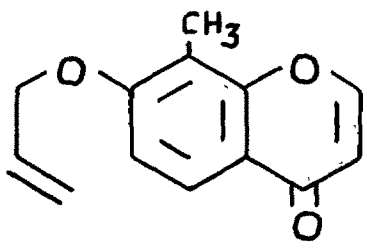
The IR spectrum in nujol (Fig. 6) showed the bands at 1650 cm^{-1} (γ-pyronyl >C=O group) and a broad band at 3170 cm^{-1} (-OH group). The NMR spectrum in $CDCl_3$ (Fig. 7) showed the following signals : δ 2.11, singlet, 3H, $-CH_3$ group at 8-position ; 2.80-3.10, multiplet, J=16Hz, 5Hz, 2Hz, 2H, methylene protons at 3-position ; 4.65, doublet, J=6Hz, 2H, methylene protons a of $-O-\underline{CH_2}-CH=CH_2$ group ; 5.31-5.51, multiplet, 2H, methylene protons of $-O-CH_2-CH=\underline{CH_2}$ group ; 5.92, triplet, J=5Hz, 2Hz, 1H at 2-position ; 6.05-6.19, multiplet, 1H, methine proton of $-O-CH_2-\underline{CH}=CH_2$ group ; 6.60, doublet, J=9Hz, 1H at 6-position ; 7.80, doublet, J=9Hz, 1H at 5-position. In fig. 8 , the NMR spectrum of (L) is subjected to double irradiation to confirm the signals for the protons of allyloxy group and that of chromanone ring system. By irradiating the doublet at δ 4.65, the multiplet at δ 6.12 collapsed into simple double doublets. This suggested the presence of other neighbouring protons and therefore the multiplet at δ 6.12 is assigned for the methine proton of $-O-CH_2-\underline{CH}=CH_2$ group. In a second irradiation experiment, the multiplet at δ 2.90 was irradiated, this affaceted the triplet at δ 5.92, by collapsing the latter into a singlet. This confirmed that the triplet at δ 5.92 cannot be due to aldehydic proton as it appeared in the upfield,



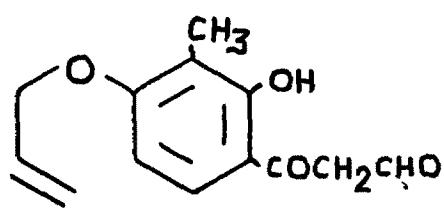
(XLIX) (L)

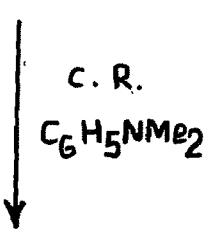


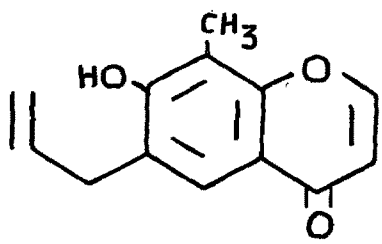




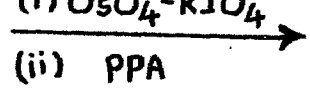
(LI)

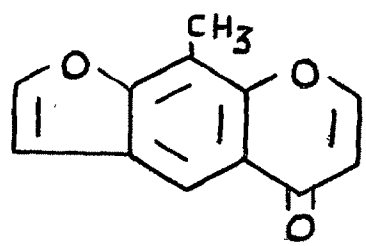






(LII)





(LIII)

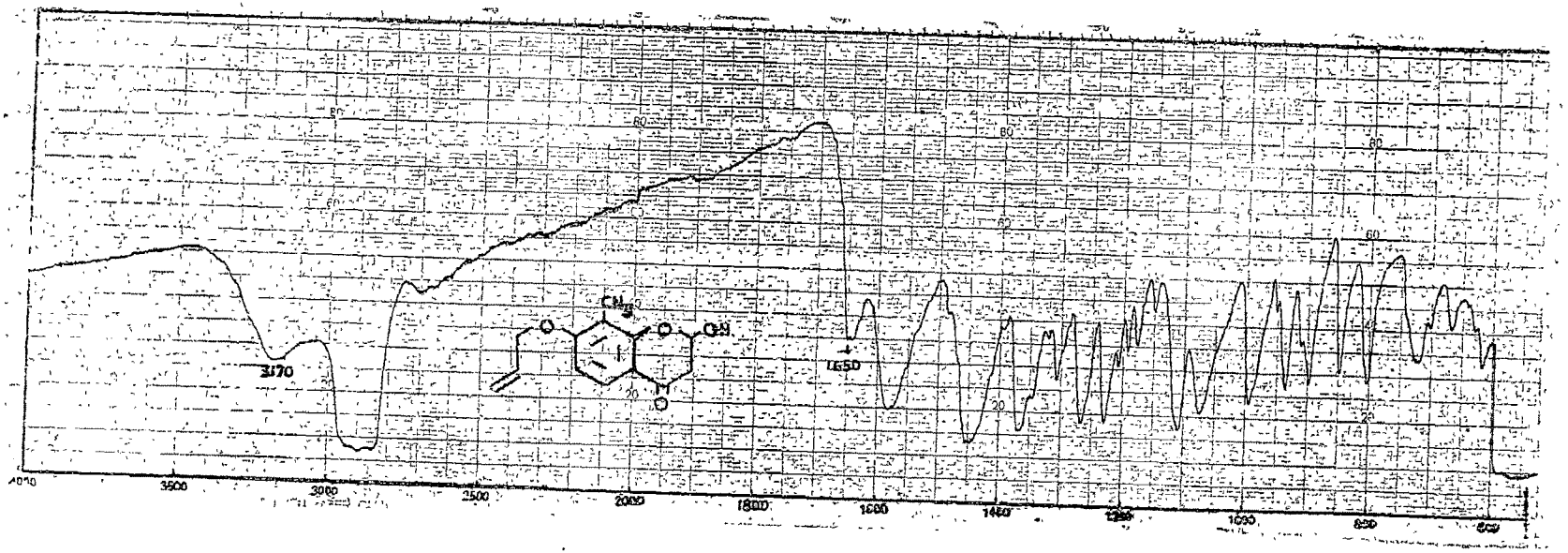


Fig. 6 : IR spectrum of 2-Hydroxy-7-allyloxy-8-methylchromanone (L) in nujol.

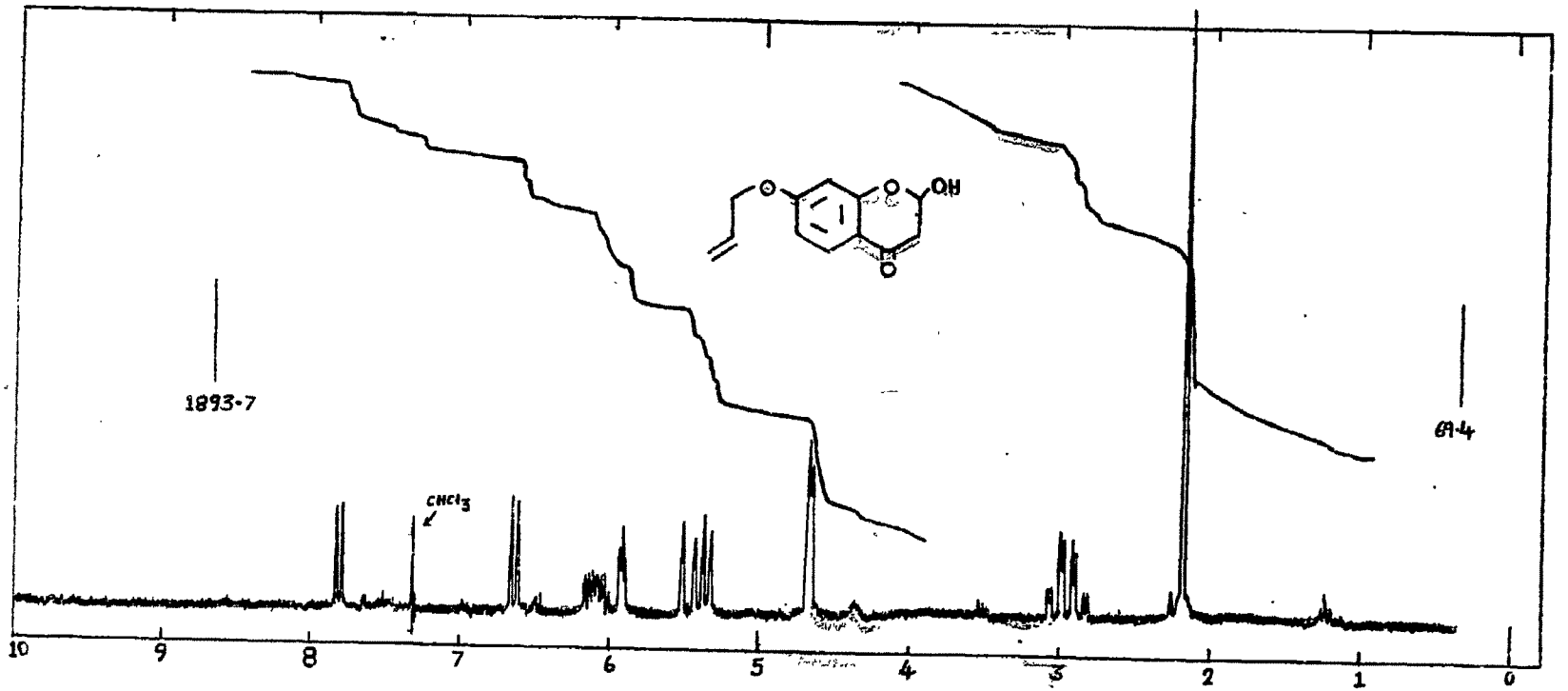


Fig. 7 : NMR spectrum of 2-Hydroxy-7-allyloxy-8-methylchromanone (L) in $CDCl_3$ (220 MHz) at 50° temperature.

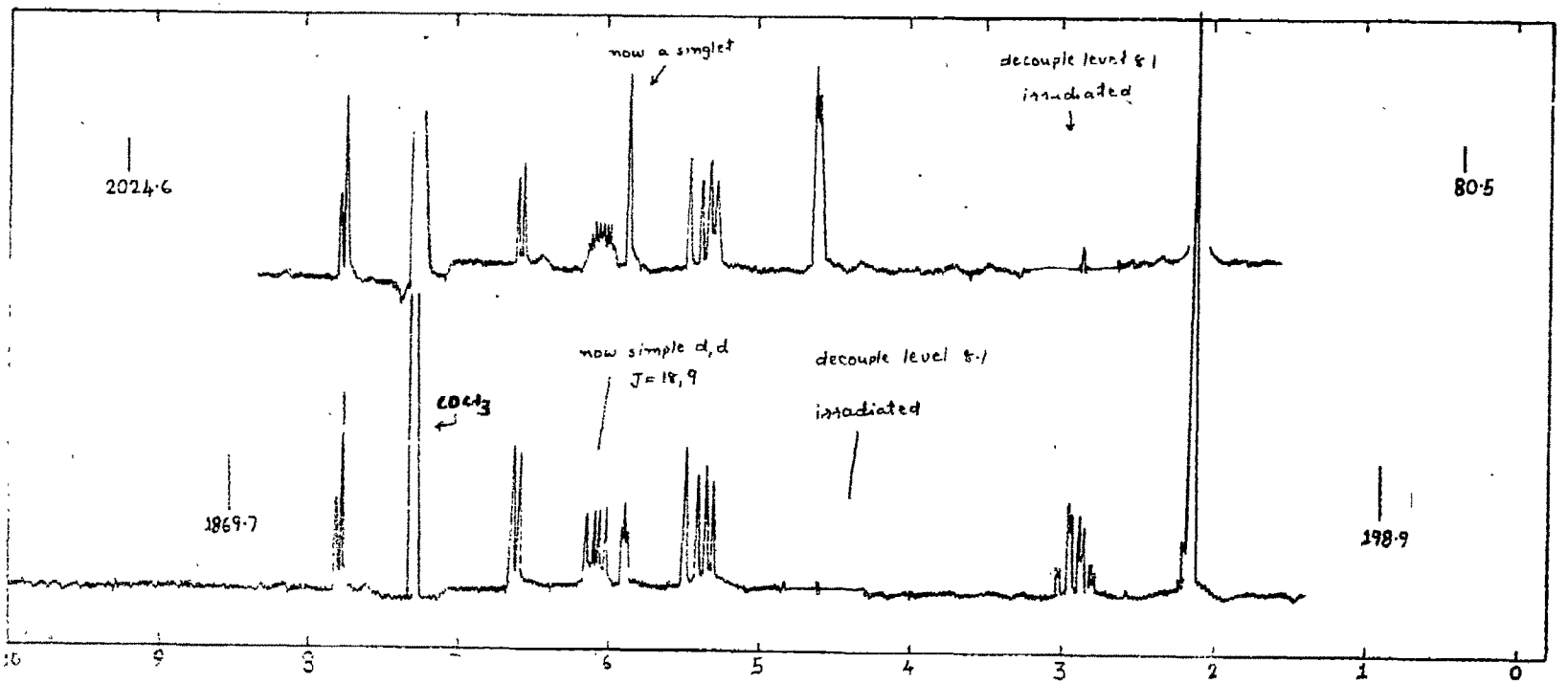


Fig. 8 : NMR spectrum (double irradiation) of 2-Hydroxy-7-allyloxy-8-methylchromanone (L) in $CDCl_3$ (220 MHz) at 50° temperature.

but due to the methine proton, situated in the cyclic chromanone ring system at 2-position.

The compound (L) on treament with sulphuric acid (30 %) yielded a dehydrated product 7-allyloxy-8-methyl-chromone(LI), which was subjected to Claisen rearrangement in dimethylaniline to yield 6-allyl-7-hydroxy-8-methylchromone (LII). Oxidation of LII with osmium tetroxide-potassium periodate in ethyl acetate-water followed by cyclization of intermediate 6-acetaldehydo product with PPA afforded 9-methyl-5H-furo(3,2-g)benzopyran-5-one(LIII). Its structure was confirmed on the basis of its NMR spectrum in $CDCl_3$ (Fig. 9): δ2.62, 3H, singlet, $-CH_3$ group at 9-position ; 6.32, doublet, J=6Hz, 1H at 6-position ; 6.88, doublet, J=1.8Hz, 1H at 3-position ; 7.71, doublet, J=1.8Hz, 1H at 2-position ; 7.95, doublet, J=6Hz, 1H at 7-position ; 8.30, singlet, 1H at 4-position.

Synthesis of 2,9-dimethyl-5H-furo(3,2-g)benzopyran-5-one(LVIII):

For the synthesis of title furochromone, 6-allyl-7-hydroxy-8-methylchromone(LII), on treatment with sulphuric acid (85 %) for 12 minutes, underwent cyclization to furan ring with simultaneous ring opening of γ-pyrone ring followed by its conversion to 2,3-dihydro-2,7-dimethyl-5-acetyl-6-hydroxybenzofuran(LIV). This is an unusual case of γ-pyrone ring opening with sulphuric acid (85 %). The structure of LIV was confirmed by its NMR spectrum in $CDCl_3$ (Fig. 10) :

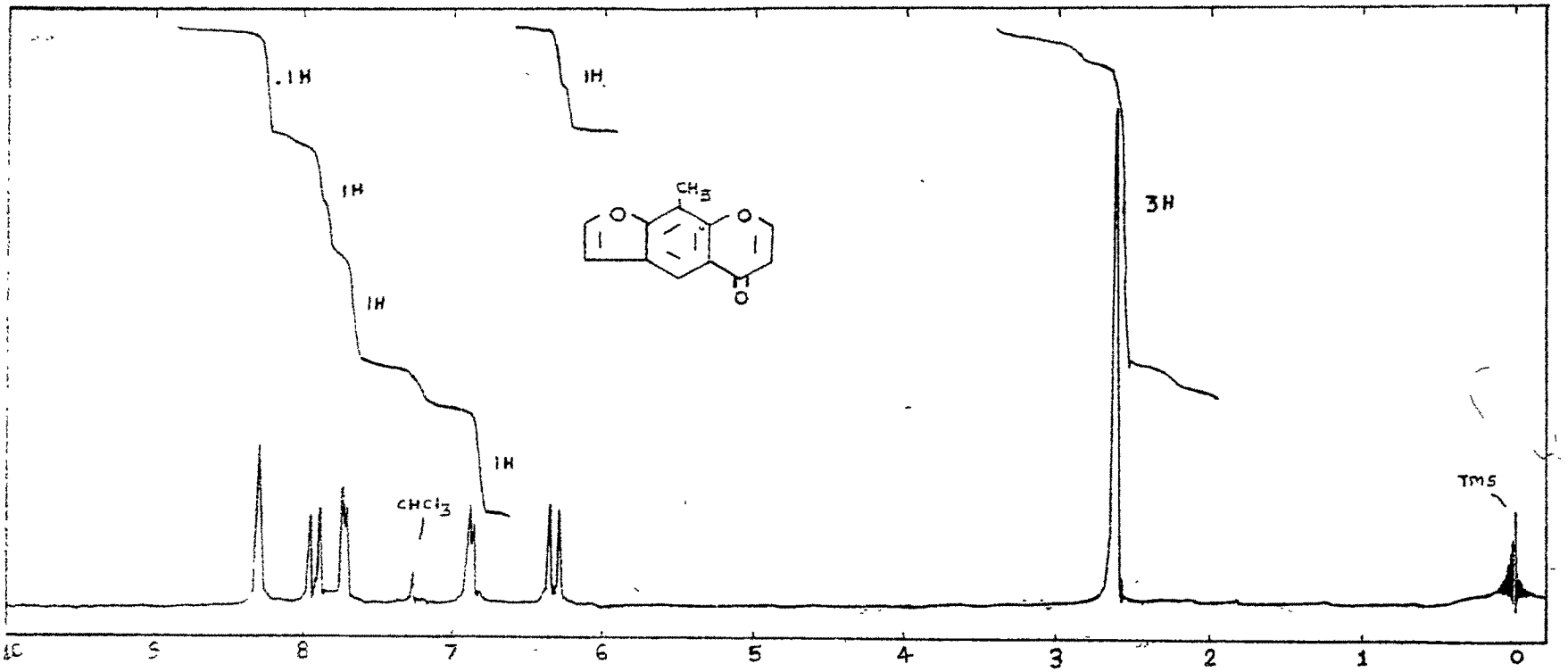
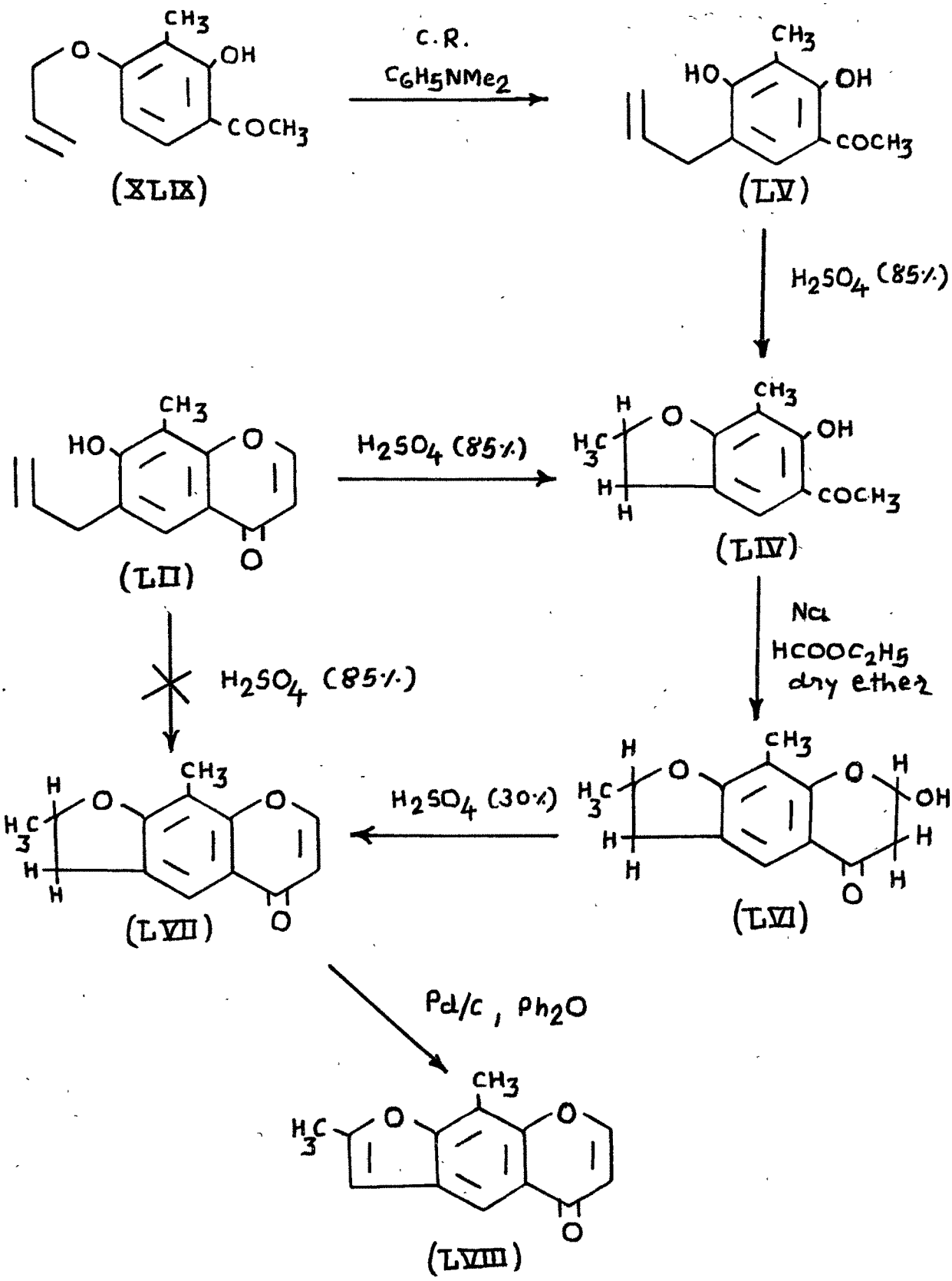


Fig. 9 : NMR spectrum of 9-Methyl-5H-furo(3,2-g)benzopyran -5-one (LIII) in $CDCl_3$ (90 MHz).

δ 1.44, doublet, J=7Hz, 3H, $-CH_3$ group at 2-position ; 2.02, singlet, 3H, $-COCH_3$ group at 5-position ; 2.45, singlet, 3H, $-CH_3$ group at 7-position ; 3.52-3.77, two symmetrical quartets, 2H, methylene proton of furan ring at 3-position ; 4.85, multiplet, 1H, methine proton, at 2-position ; 7.21, singlet, 1H, aromatic proton at 4-position.

The synthesis of above benzofuran(LIV) was also achieved by first carrying out Claisen rearrangement of 2-hydroxy-3-methyl-4-allyloxyacetophenone(XLIX) in dimethyl-aniline to give 2,4-dihydroxy-3-methyl-5-allylacetophenone(LV), which was cyclized to LIV using sulphuric acid (85 %). The product obtained by this method was identical with LIV in all respects viz., m.p., mixed m.p. 103° and IR spectrum.

The Claisen condensation of LIV with ethyl formate in presence of pulverized sodium in dry ether gave 2,9-dimethyl-7-hydroxy-2,3,6,7-tetrahydro-5H-furo(3,2-g)benzopyran-5-one (LVI), which was dehydrated to 2,3-dihydro-2,9-dimethyl-5H-furo(3,2-g)benzopyran-5-one(LVII), using sulphuric acid (30 %). The structure of LVII was cinfirmed by its NMR spectrum in $CDCl_3$ (Fig. 11) : δ 1.49, doublet, J=7Hz, 1.4Hz, 3H, $-CH_3$ group at 2-position ; 2.24, singlet, 3H, $-CH_3$ group at 9-position ; 2.68-3.51, two symmetrical quartets, 2H, methylene protons at 3-position ; 5.03, multiplet, 1H, methine proton at 2-position ; 6.18, doublet, J=7Hz, 1H, at 6-position ; 7.70, doublet, overlapped with a singlet, J=7Hz, 1H at 7-position ; 7.76, singlet, 1H, aromatic proton at


CH3
O
OH
COCH3
(XLIX)
C.R.
C6H5NMe2
HO
(LV)
H2SO4 (85%)
(LII)
(LIV)
NaH
HCOOC2H5
dry ether
H2SO4 (30%)
(LVI)
(LVII)
Pd/C , Ph2O
(LVIII)

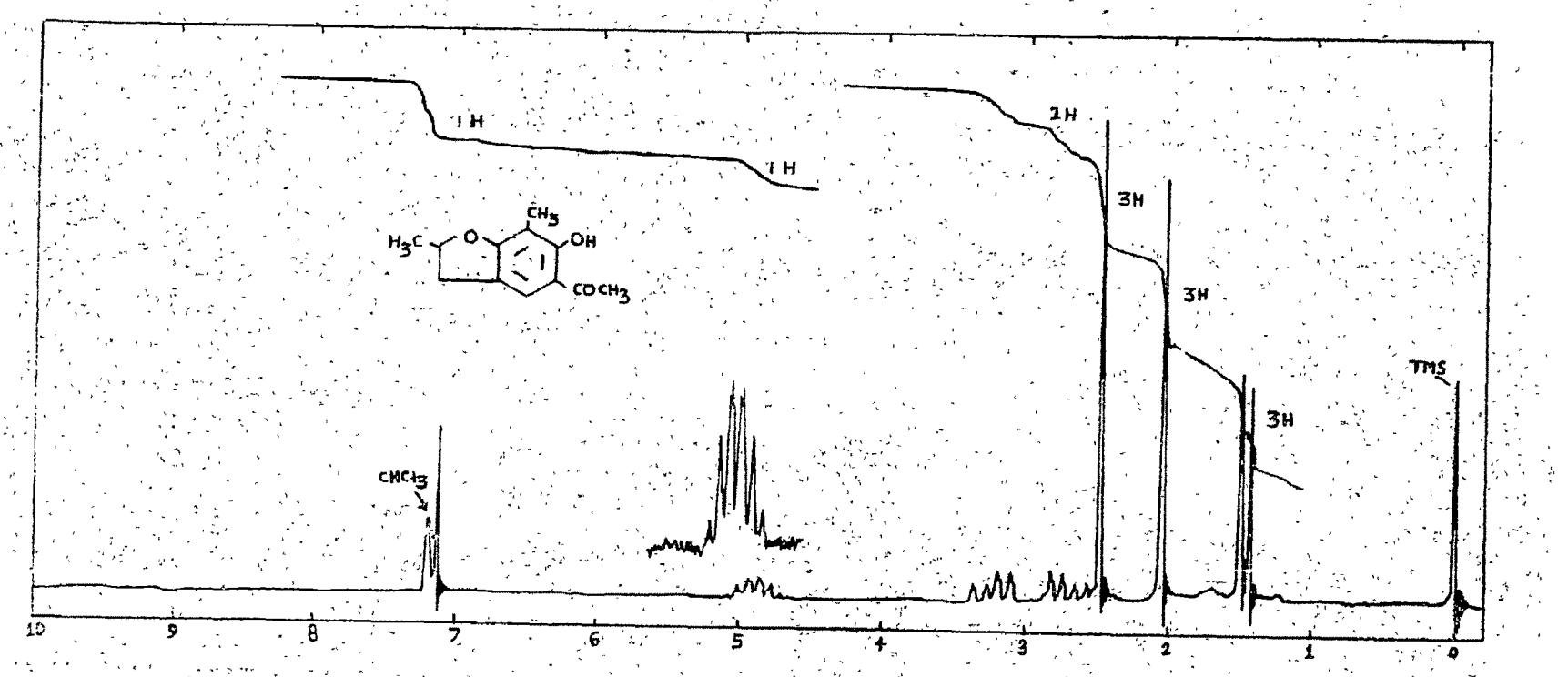


Fig. 10 : NMR spectrum of 2,3-Dihydro-2,7-dimethyl-5-acetyl-6-hydroxybenzofuran (LIV) in $CDCl_3$ (90 MHz).

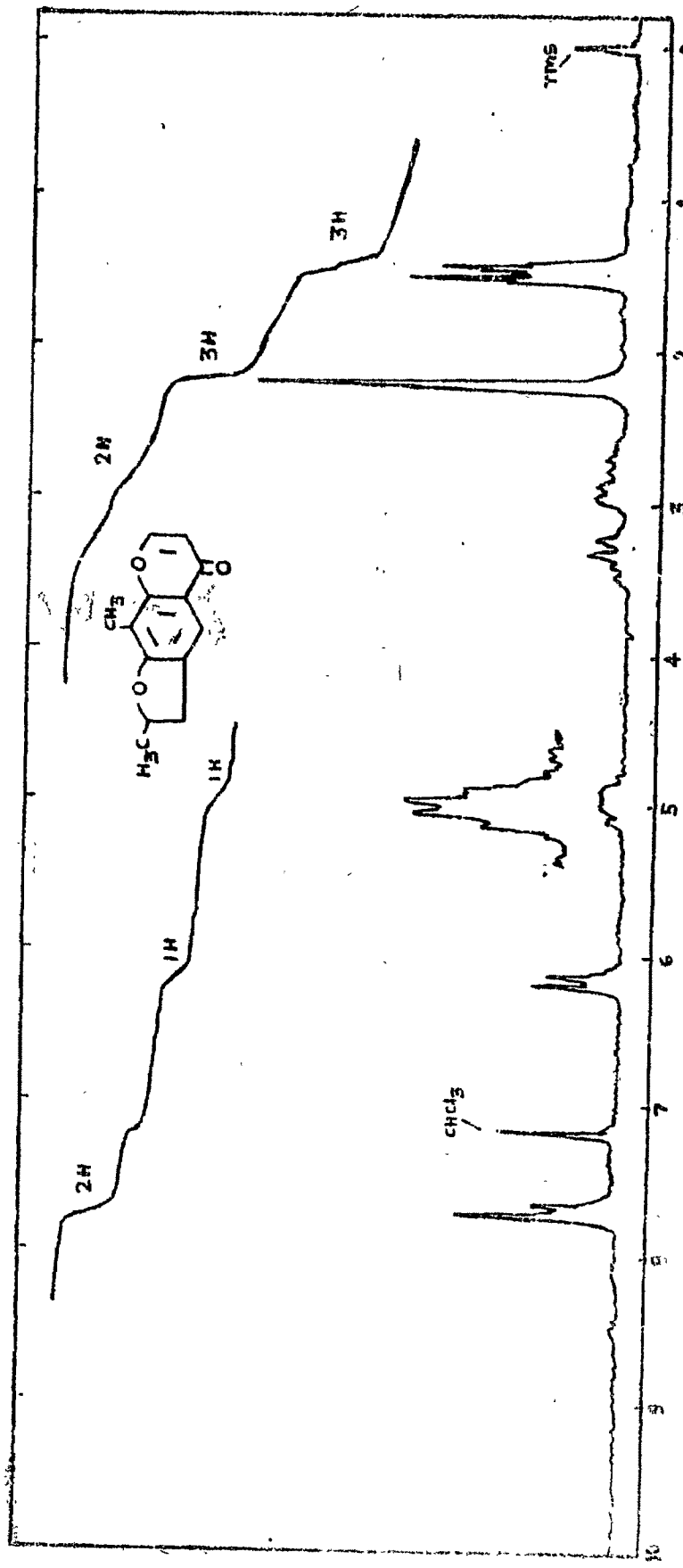


Fig. 11 : NMR spectrum of 2,3-Dihydro-2,9-dimethyl-5H-furo(3,2-g)-benzopyran-5-one (LVII) in $CDCl_3$ (90 MHz).

4-position.

The dihydrofurochromone(LVII), on dehydrogenation with palladized charcoal in diphenyl ether gave 2,9-dimethyl-5H-furo(3,2-g)benzopyran-5-one(LVIII). The NMR spectrum of which (Fig. 12) showed the following signals : δ 2.45, singlet, 3H, $-CH_3$ group at 2-position ; 2.55, singlet, 3H, $-CH_3$ group at 9-position ; 6.23, doublet, J=6.5Hz, 1H at 6-position ; 6.37, singlet, 1H at 3-position ; 7.78, doublet, J=6.5Hz, 1H at 7-position ; 8.11, singlet, 1H at 4-position.

Synthesis of 4H-furo(3,2-f)benzopyran-4-one(LXIII) :

2-Hydroxy-5-allyloxyacetophenone(LIX), prepared according to Baker and Lothian[28] from 2,5-dihydroxyacetophenone, on Claisen condensation with freshly distilled ethyl formate in presence of pulverized sodium in dry ether gave 2-hydroxy-6-allyloxychromanone(LX). Its UV spectrum in methanol showed no shift in its characteristic bands on addition of dilute sodium hydroxide solution. This result is agreeable with its cycliclic structure. The structure of LX was also confirmed by its NMR spectrum in DMSO-d_6 (Fig. 13) : δ 2.70-3.10, multiplet, 2H, methylene group at 3-position ; 4.60, doublet, J=6Hz, 2H, methylene protons of $-O-\underline{CH_2}-CH=CH_2$ group ; 5.10-5.40, multiplet, 2H, methylene protons of $-O-CH_2-CH=\underline{CH_2}$ group ; 5.85, quartet, 1H at 2-position ; 5.90-6.20, multiplet, 1H, methine proton of $-O-CH_2-\underline{CH}=CH_2$ group ; 6.95, doublet, J=10Hz, 1H at 7-position ; 7.20, overlapping of a doublet and a singlet, 2H at 5- and 8-position ; 7.45, broad doublet,

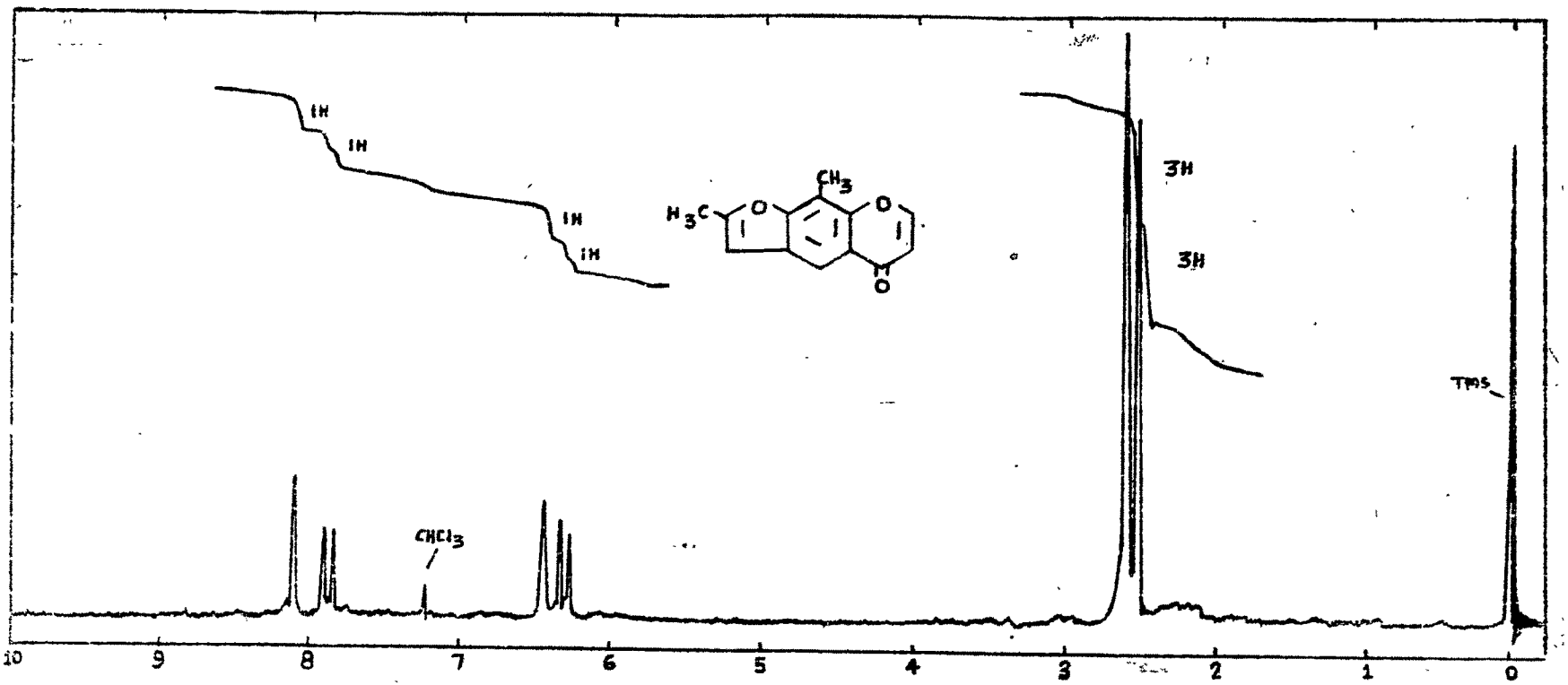


Fig. 12 : NMR spectrum of 2,9-Dimethyl-5H-furo(3,2-g)benzo pyran-5-one (LVIII) in $CDCl_3$ (90 MHz).

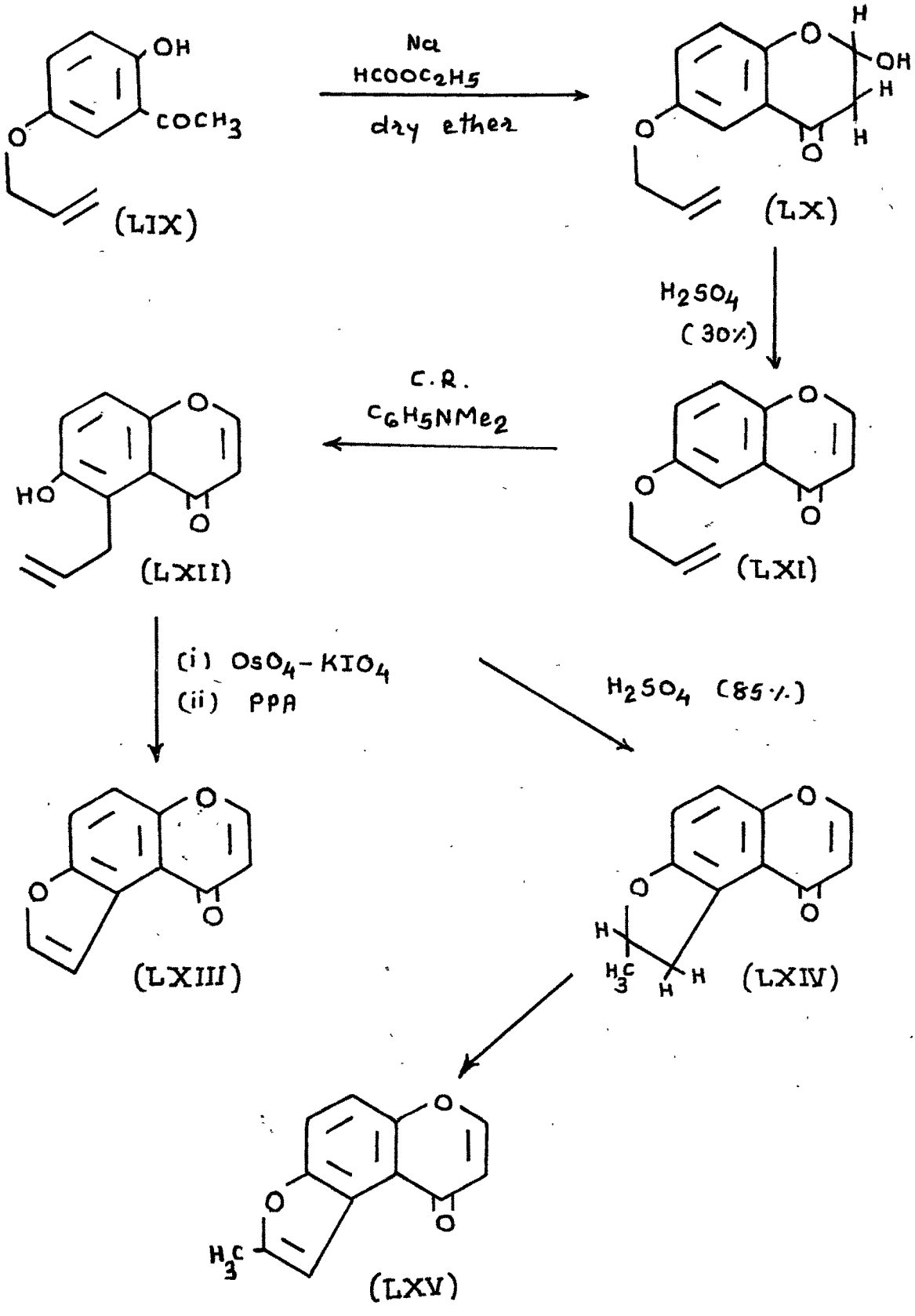
J=6Hz, 1H, -OH group at 2-position.

The product LX was dehydrated to corresponding 6-allyloxychromone(LXI) using sulphuric acid (30 %). Claisen rearrangement of LXI in dimethylaniline gave 5-allyl-6-hydroxychromone(LXII), which on treatment with osmium tetroxide-potassium periodate in ethyl acetate-water followed by cyclization of 5-acetaldehydo product with PPA afforded 4H-furo(3,2-f)benzopyran-4-one(LXIII). Its NMR spectrum in $CDCl_3$ (Fig. 14) showed the following signals : δ 6.38, doublet, J=6Hz, 1H at 5-position ; 7.35, doublet, J=10Hz, 1H, at 9-position ; 7.70-7.90, multiplet, 4H at 2-, 3-, 6- and 8-position.

Synthesis of 2-methyl-4H-furo(3,2-f)benzopyran-4-one(LXV) :

5-Allyl-6-hydroxychromone(LXII) on trituration with sulphuric acid (85 %) gave 2-methyl-2,3-dihydro-4H-furo-(3,2-f)benzopyran-4-one(LXIV). The structure of which was confirmed by its NMR spectrum in $CDCl_3$ (Fig. 15) : δ 1.46, doublet, J=7Hz, 3H, $-CH_3$ group at 2-position ; 3.12-3.98, two symmetrical quartets, 2H, two methylene protons at 3-position ; 4.86-5.11, multiplet, 1H, methine proton at 2-position ; 6.11, doublet, J=7Hz, 1H at 5-position ; 6.91 and 7.12, two doublets, J=10Hz, each 1H, aromatic protons at 9- and 8-position respectively ; 7.61, doublet, J=7Hz, 1H at 6-position.

These spectral data also showed that the Claisen rearrangement of 6-allyloxychromone(LXI) took place at


OH
COCH3
O
(LIX)
Na
HCOOC2H5
dry ether
H
O
OH
H
O
H
O
(LX)
H2SO4
(30%)
C.R.
C6H5NMe2
HO
O
O
(LXII)
O
O
(LXI)
(i) OsO4-KIO4
(ii) PPA
H2SO4 (85%)
O
O
(LXIII)
O
O
H
H3C
H
(LXIV)
O
O
H3C
(LXV)

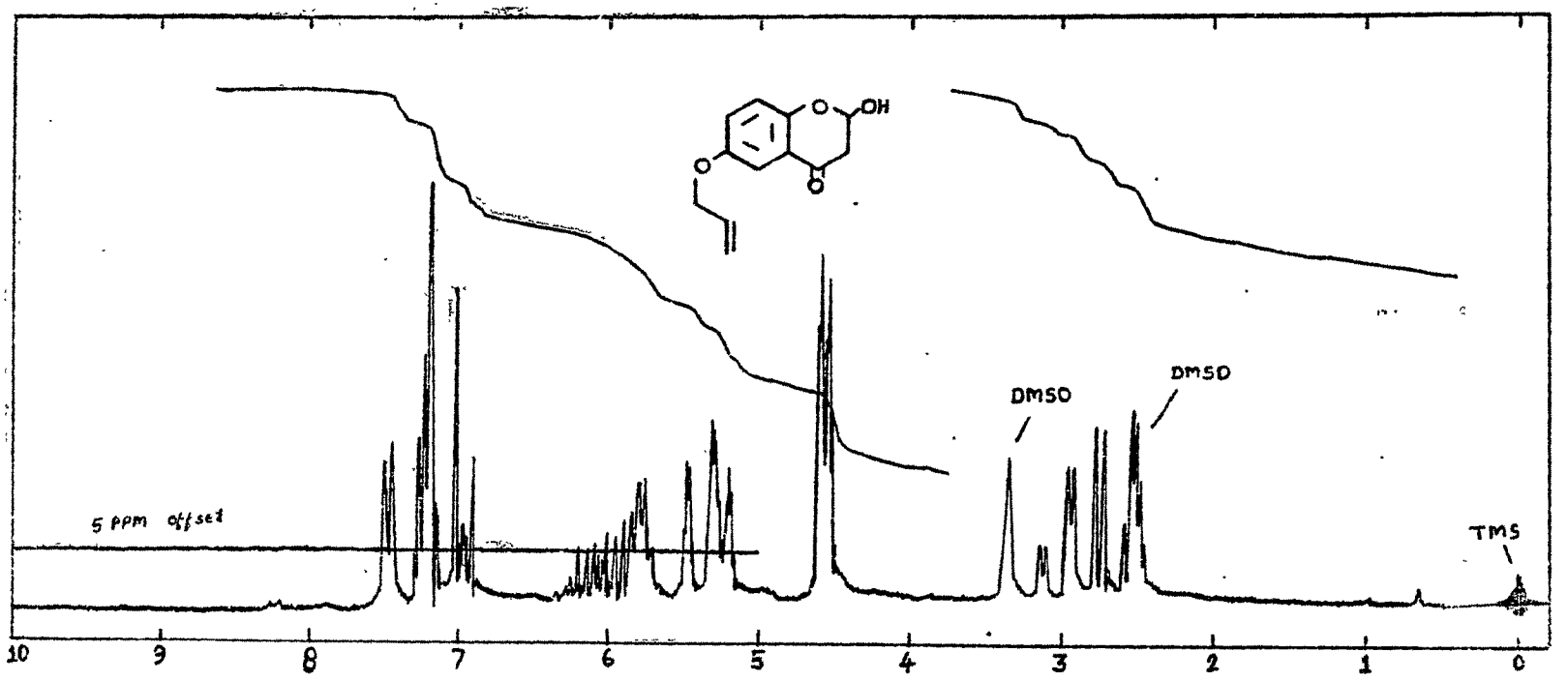


Fig. 13 : NMR spectrum of 2-Hydroxy-6-allyloxychromanone (LX) in DMSO-d_6 (90 MHz).

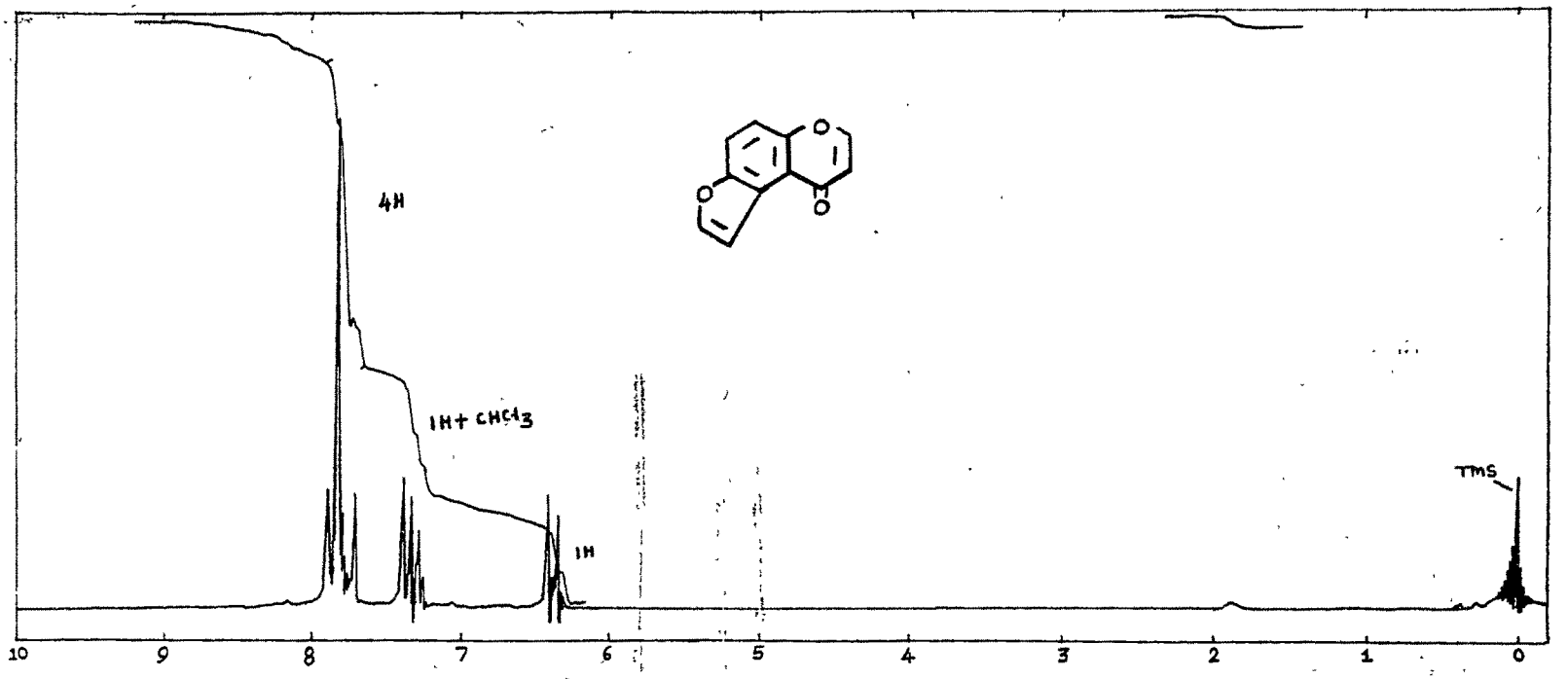


Fig 14 : NMR spectrum of 4H-Furo(3,2-f)benzopyran-4-one (LXIII) in $CDCl_3$ (90 MHz).

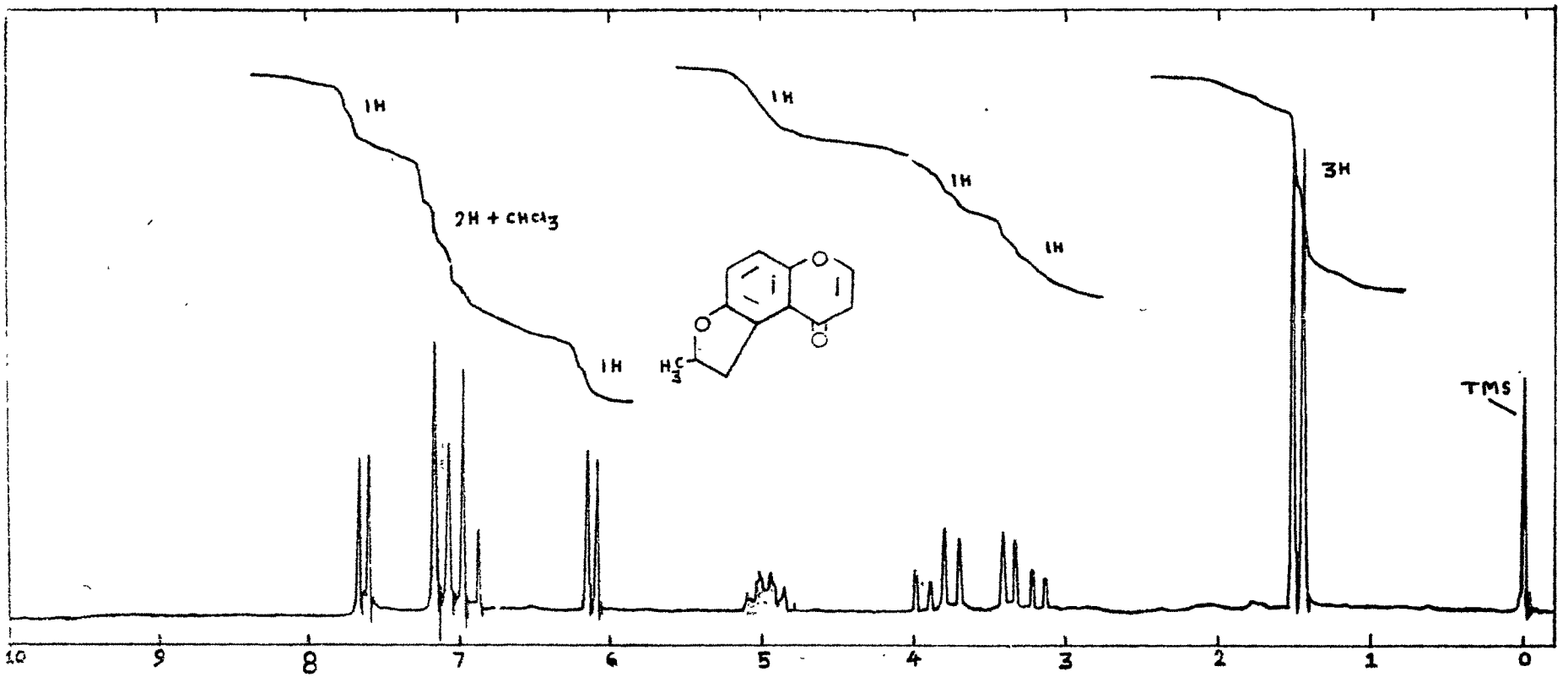


Fig. 15 : NMR spectrum of 2-Methyl-2,3-dihydro-4H-furo(3,2-f)-benzopyran-4-one (LXIV) in $CDCl_3$ (90 MHz).

5-position and not at 7-position. In the latter case, the spectrum of cyclized product would have shown two singlets in the aromatic region instead of two doublets for the two adjecent aromatic protons.

Dehydrogenation of LXIV with palladized charcoal (10 %) in diphenyl ether gave 2-methyl-4H-furo(3,2-f)-benzopyran-4-one(LXV). Its structure was confirmed on the basis of its NMR spectrum in $CDCl_3$ (Fig. 16) : δ2.53, singlet, 3H, $-CH_3$ group at 2-position ; 6.33, doublet, J=7Hz, 1H at 5-position ; 7.22, doublet, J=9Hz, 1H at 9-position ; 7.42, singlet, 1H at 3-position ; 7.65, doublet, J=9Hz, 1H at 8-position ; 7.85, doublet, J=7Hz, 1H at 6-position.

Synthesis of 9-methyl-4H-furo(3,2-f)benzopyran-4-one(LXXIII) :

2,5-Dihydroxytoluene(LXVI), on acetylation with acetic anhydride and pyridine gave 2,5-diacetoxytoluene (LXVII), which was subjected to Fries migration with anhydrous aluminium chloride, resulted into 2,5-dihydroxy-4-methyl-acetophenone(LXVIII). The acetophenone LXVIII on allylation with allyl bromide in presence of anhydrous potassium carbonate in dry acetone furnished 2-hydroxy-4-methyl-5-allyloxyacetophenone(LXIX). This was condensed with ethyl formate in presence of pulverized sodium in dry ether to give 2-hydroxy-6-allyloxy-7-methylchromanone(LXX). Its structure was confirmed on the basis of its NMR spectrum in DMSO-d_6 (Fig. 17) : δ2.23, singlet, 3H, $-CH_3$ group at

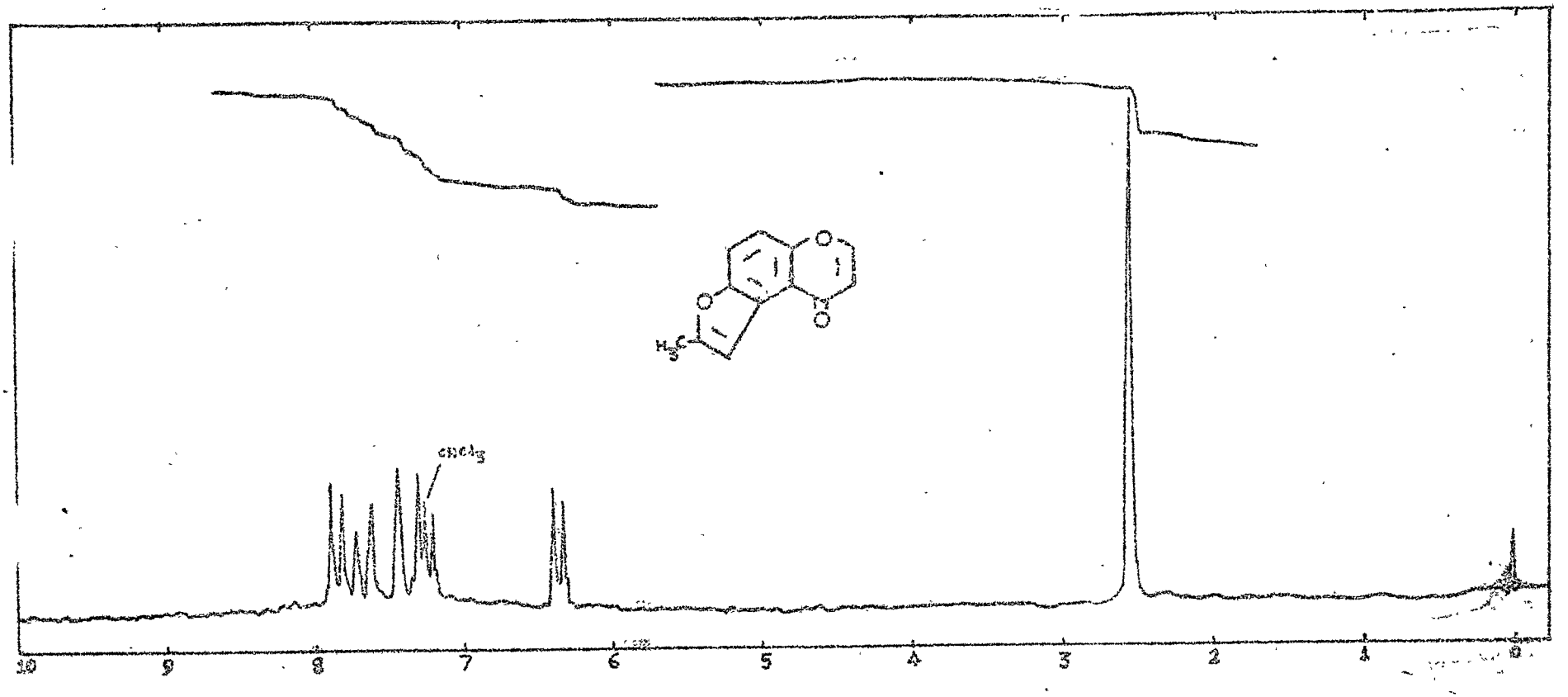
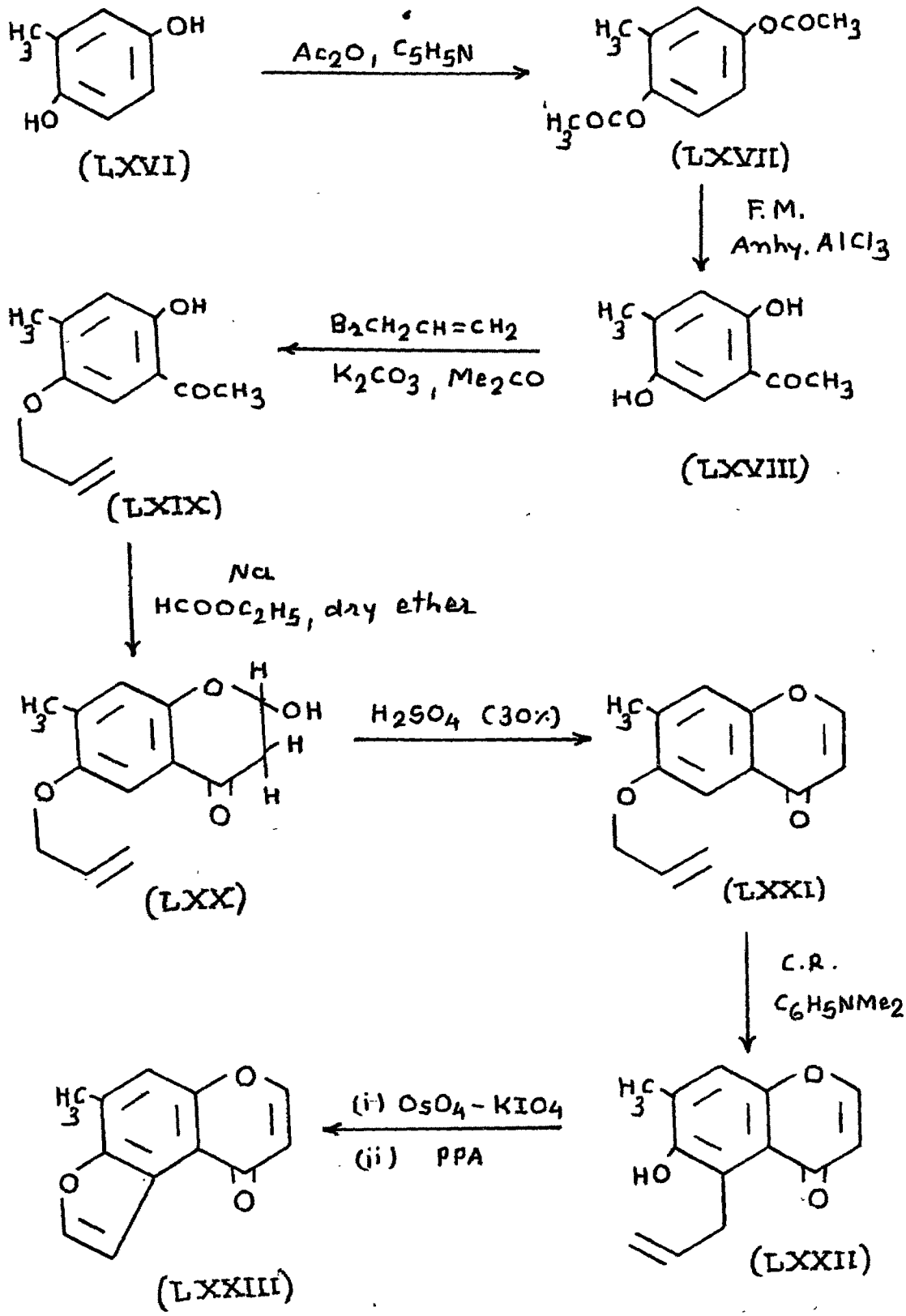


Fig. 16 : NMR spectrum of 2-Methyl-4H-furo(3,2-f)benzopyran-4-one (LXV) in $CDCl_3$ (90 MHz).

7-position ; 2.67-2.93, multiplet, 2H, methylene protons at 3-position ; 4.54, doublet, J=6Hz, 2H, methylene protons of $-O-\underline{CH_2}-CH=CH_2$; 5.17-5.55, multiplet, 2H, methylene protons of $-O-CH_2-CH=\underline{CH_2}$; 5.75, quartet, 1H, methine proton at 2-position ; 5.85-6.25, multiplet, 1H, methine proton of $-O-CH_2-\underline{CH}=CH_2$; 6.88, singlet, 1H, aromatic proton at 8-position ; 7.14, singlet, 1H, aromatic proton at 5-position ; 7.45, broad doublet, J=6Hz, 1H, -OH group at 2-position.

This spectrum showed two singlets in the aromatic region, suggests that the Fries migration of 2,5-diacetoxy-toluene(LXVII) has given only one monoacetyl product(LXVIII), and acetylation took place at para to the methyl group.

2-Hydroxy-6-allyloxy-7-methylchromanone(LXX), was dehydrated with sulphuric acid (30 %) to obtain 6-allyloxy-7-methylchromone(LXXI), which was subjected to Claisen rearrangement in dimethylaniline to obtain 5-allyl-6-hydroxy-7-methylchromone(LXXII), which on treatment with osmium tetroxide-potassium periodate in ethyl acetate-water, followed by cyclization of intermediate 5-acetaldehydo product with PPA furnished 9-methyl-4H-furo(3,2-f)benzopyran-4-one(LXXIII). Its structure was confirmed on the basis of its NMR spectrum in $CDCl_3$ (Fig. 18) : δ2.62, singlet, 3H, $-CH_3$ group at 9-position ; 6.35, doublet, J=6Hz, 1H, at 5-position ; 7.18, doublet, J=1.8Hz (coupling is not clearly observed in the figure), 1H at 3-position ; 7.78-7.89, multiplet, 3H at 2-, 6- and 8-position.


(LXVI)
Ac2O, C5H5N
(LXVII)
F.M.
Anhy. AlCl3
(LXVIII)
B2CH2CH=CH2
K2CO3, Me2CO
(LXIX)
Na
HCOOC2H5, dry ether
(LXX)
H2SO4 (30%)
(LXXI)
C.R.
C6H5NMe2
(LXXII)
(i) OsO4 - KIO4
(ii) PPA
(LXXIII)

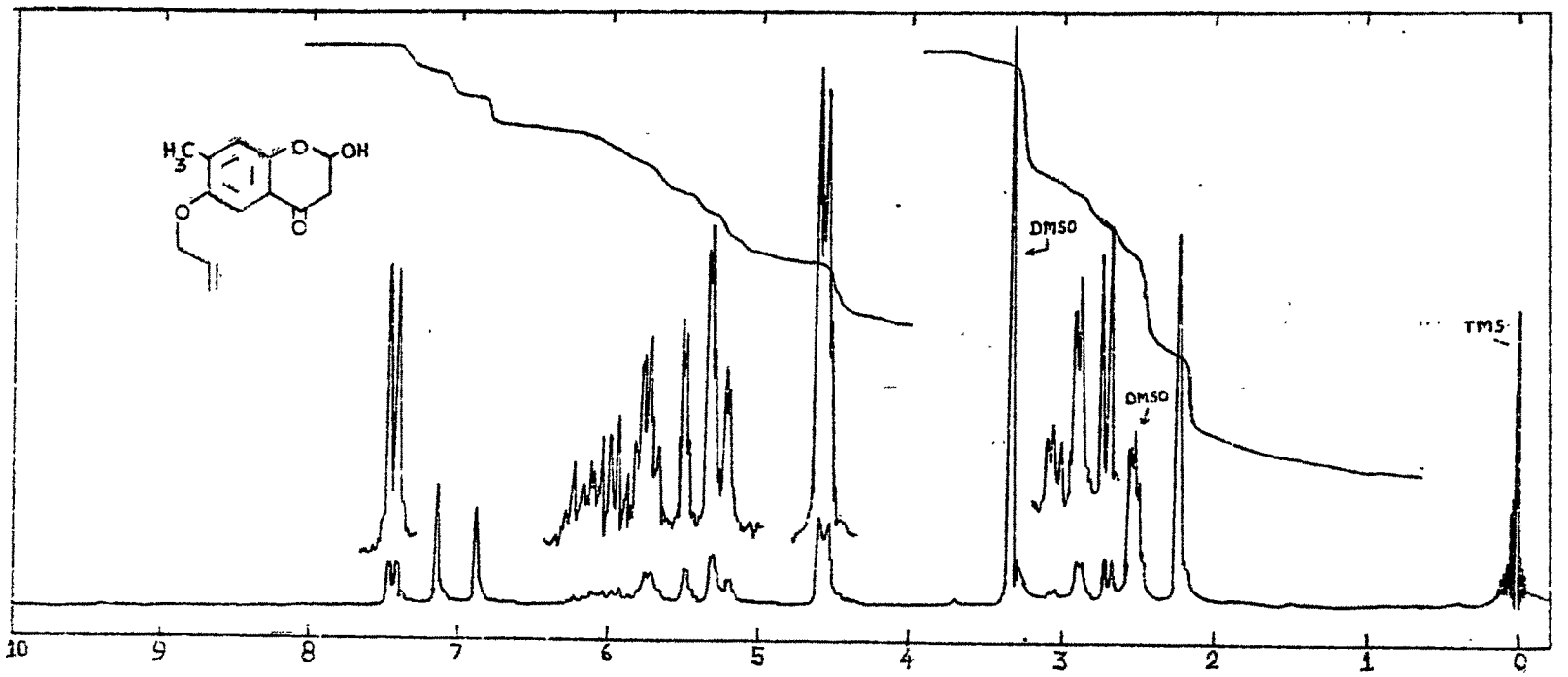


Fig. 17 : NMR spectrum of 2-Hydroxy-6-allyloxy-7-methyl-chromanone (LXX) in DMSO-d_6 (90 MHz).

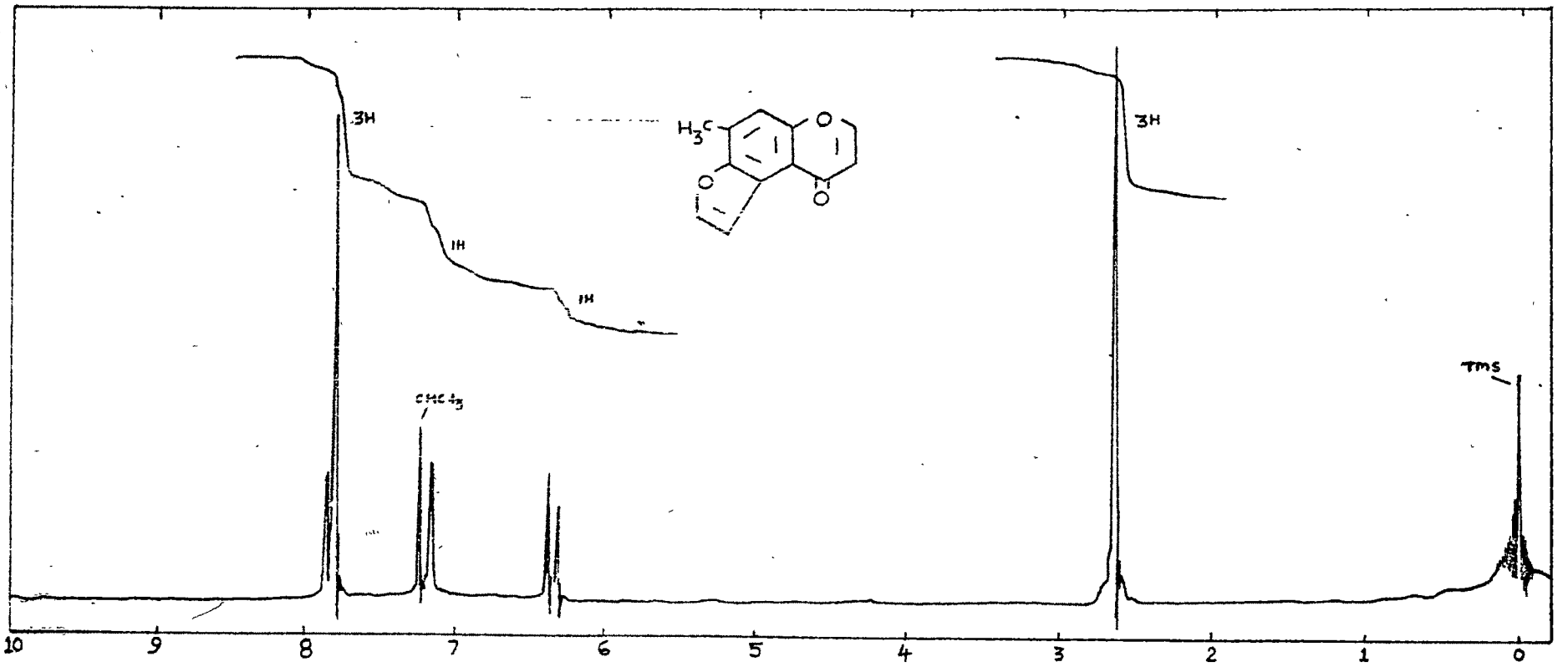
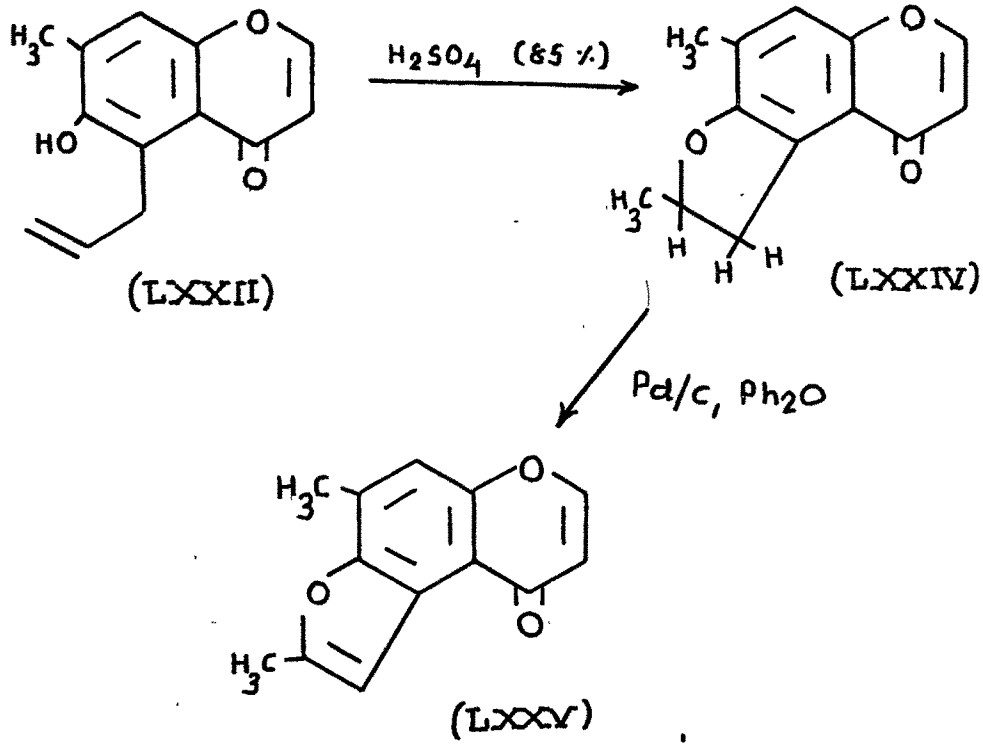


Fig. 18 : NMR spectrum of 9-Methyl-4H-furo(3,2-f)benzopyran-4-one (LXXIII) in $CDCl_3$ (90 MHz).

Synthesis of 2,9-dimethyl-4H-furo(3,2-f)benzopyran-4-one(LXXV):

5-Allyl-6-hydroxy-7-methylchromone(LXXII), was cyclized to 2,3-dihydro-2,9-dimethyl-4H-furo(3,2-f)benzopyran-4-one(LXXIV) by dissolving it in sulphuric acid (85 %). The compound LXXIV was dehydrogened to 2,9-dimethyl-4H-furo-(3,2-f)benzopyran-4-one(LXXV) by palladized charcoal (10 %) in diphenyl ether. The structure of which was consistant with its NMR spectrum in $CDCl_3$ (Fig. 19) ; δ 2.51, singlet, 3H, $-CH_3$ group at 2-position ; 2.57, singlet, 3H, $-CH_3$ group at 9-position ; 6.29, doublet, J=6Hz, 1H at 5-position ; 7.01, singlet, 1H at 3-position ; 7.37, singlet, 1H at 8-position ; 7.76, doublet, J=6Hz, 1H at 6-position.



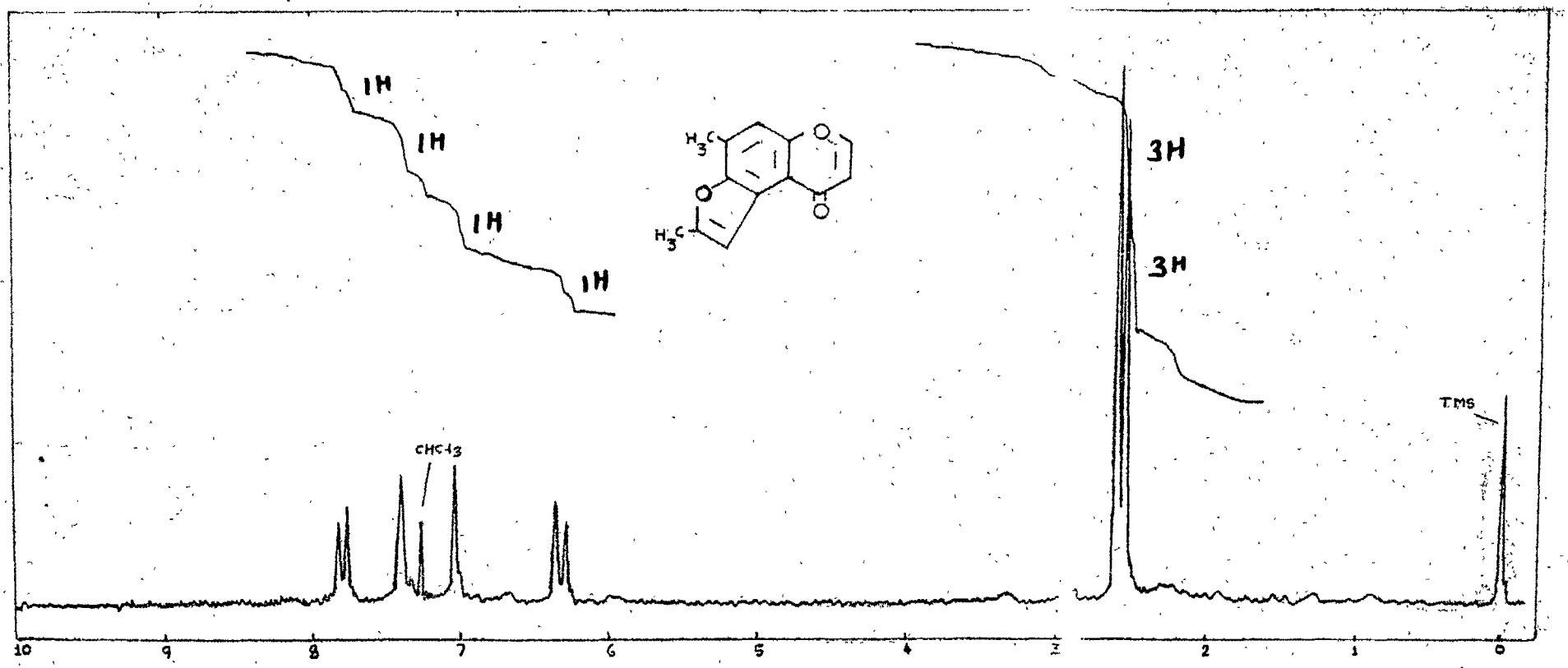
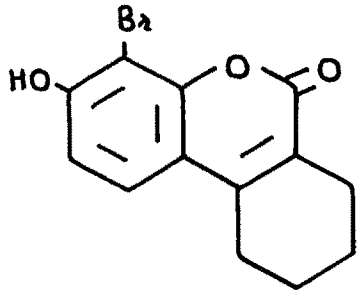


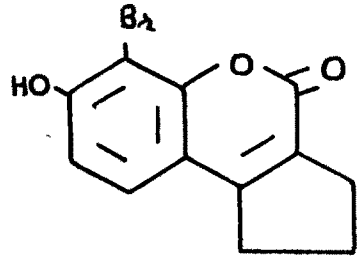
Fig. 19 : NMR spectrum of 2,9-Dimethyl-4H-furo(3,2-f)benzopyran-4-one (LXXV) in $CDCl_3$ (90 MHz).

SYNTHESIS OF CYCLOHEXA- AND CYCLOPENTAFUROCHROMONES

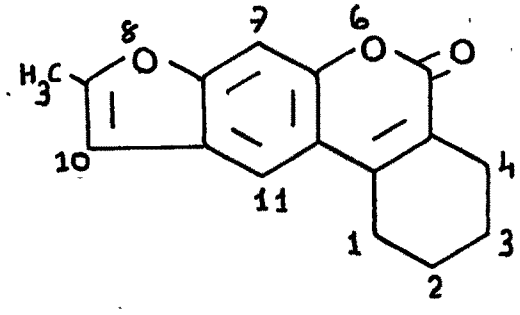
A new variety of compounds have been prepared by Shah and Trivedi[31] with a fused five or six membered ring system. The Pechmann condensation of 2-bromoresorcinol with ethyl cyclohexanone-2-carboxylate and with ethyl cyclopentanone-2-carboxylate in presence of conc. sulphuric acid gave coumarin derivatives LXXVI and LXXVII respectively. These derivatives LXXVI and LXXVII, on allylation followed by Claisen rearrangement, acetylation, bromination and cyclization afforded furocoumarins viz., 9-methyl-1,2,3,4-tetrahydro-5H-benzofuro[6,5-c][2]benzopyran-5-one(LXXVIII) and 8-methyl-1,2,3-trihydro-4H-cyclopenta[c]furo[3,2-g][1]-benzopyran-4-one(LXXIX).



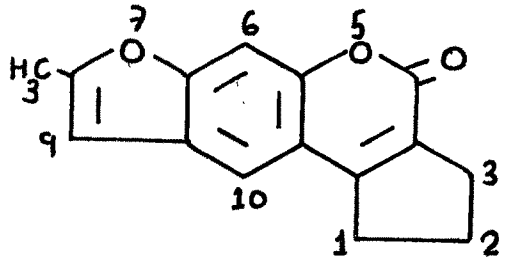
(LXXVI)



(LXXVII)

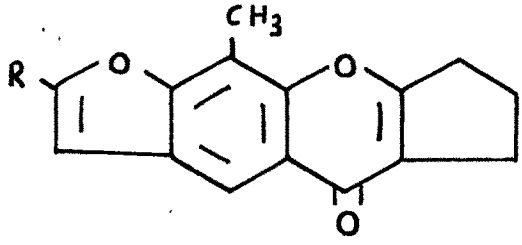


(LXXVIII)



(LXXIX)

Similarly the synthesis of 9-methyl-1,2,3-trihydro-4H-cyclopenta[b]furo[3,2-g]benzopyran-4-one(LXXXa) and 7,9-dimethyl-1,2,3-trihydro-4H-cyclopenta[b]furo[3,2-g]-benzopyran-4-one(LXXXb) was reported by the same group of authors[32], starting from 2-methylresorcinol and ethyl cyclopentanone-2-carboxylate.



(LXXXa) R = H

(LXXXb) R = CH_3

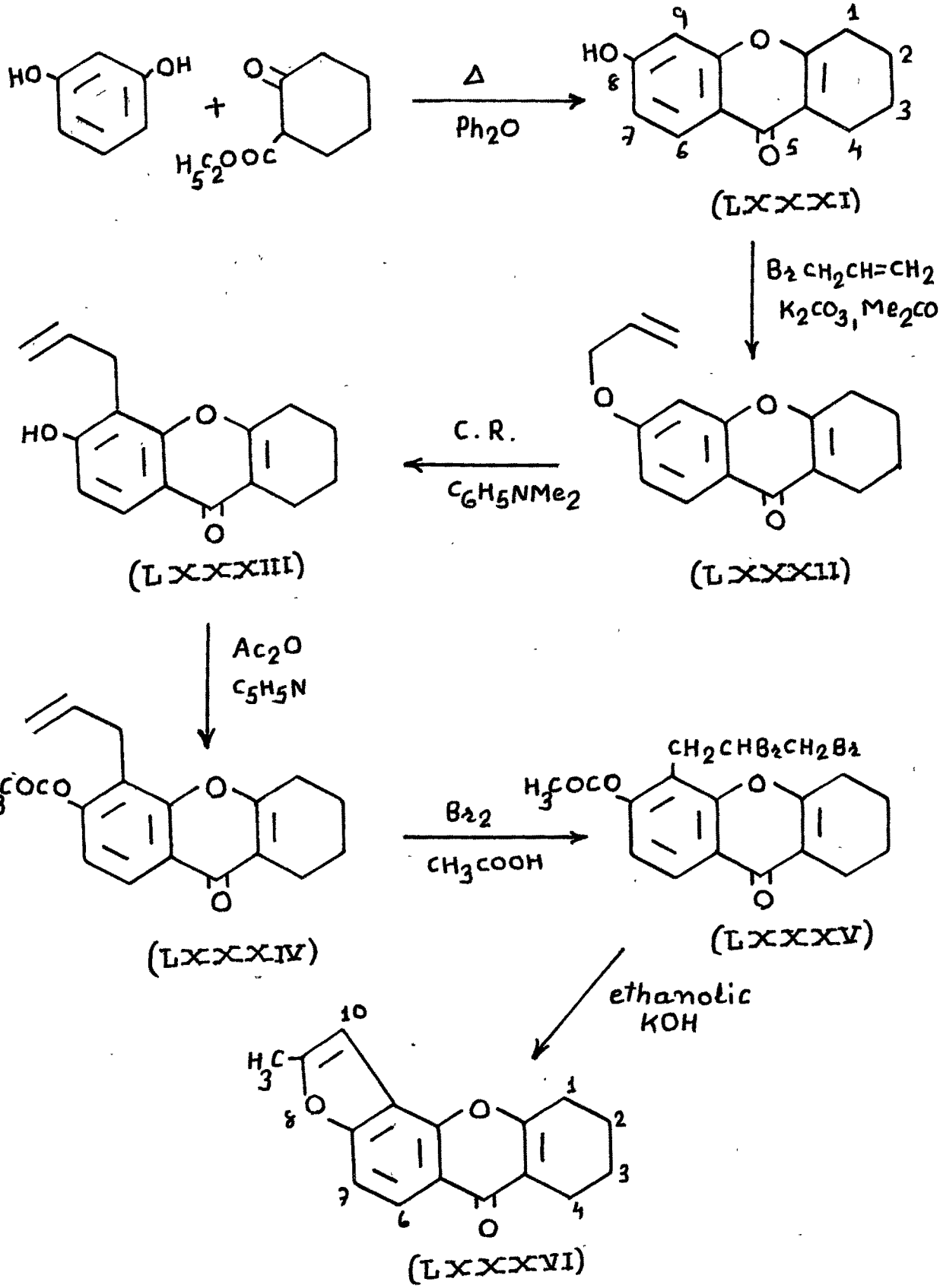
Present work :

It was therefore thought of interest to synthesise such furo compounds with a fused five or six membered ring system. The following furo compounds are synthesised in the present work.

1. 9-Methyl-1,2,3,4-tetrahydro-5H-benzofuro[4,5-b][2]-benzopyran-5-one(LXXXVI)
2. 6-[2'-Methyl-4'-hydroxybenzofuran-5'-yl]-6-oxo-6H-hexanoic acid(XCII)

Synthesis of 9-methyl-1,2,3,4-tetrahydro-5H-benzofuro[4,5-b][2]-benzopyran-5-one(LXXXVI) :

Resorcinol on thermal condensation with ethyl cyclohexanone-2-carboxylate in diphenyl ether, according to Desai, Trivedi and Sethna[27] gave 8-hydroxy-1,2,3,4-tetrahydro-


HO
OH
O
H_5C_2OOC
Δ
Ph_2O
HO
O
1
2
3
4
5
6
7
8
9
(LXXXI)
$Br_2CH_2CH=CH_2$
K_2CO_3, Me_2CO
O
O
O
(LXXXII)
C.R.
$C_6H_5NMe_2$
HO
O
O
(LXXXIII)
Ac_2O
C_5H_5N
H_3COCO
O
O
(LXXXIV)
Br_2
CH_3COOH
$CH_2CHBrCH_2Br$
H_3COCO
O
O
(LXXXV)
ethanolic
KOH
10
H_3C
O
O
1
2
3
4
6
7
8
O
(LXXXVI)

5H-dibenzo[b,e]pyran-5-one(LXXXI). This on allylation with allyl bromide in presence of anhydrous potassium carbonate in dry acetone followed by Claisen rearrangement in dimethyl-aniline afforded 9-allyl-8-hydroxy-1,2,3,4-tetrahydro-5H-dibenzo[b,e]pyran-5-one(LXXXIII), which was acetylated by acetic anhydride and pyridine to give 9-allyl-1,2,3,4-tetra-hydro-5-oxo-5H-dibenzo[b,e]pyran-8-yl acetate(LXXXIV). Bromination of LXXXIV with bromine in glacial acetic acid yielded 9-(2',3'-dibromopropyl)-1,2,3,4-tetrahydro-5-oxo-5H-dibenzo[b,e]pyran-8-yl acetate(LXXXV). The cyclization and dehydrobromination of LXXXV was carried out in presence of ethanolic potassium hydroxide to synthesise 9-methyl-1,2,3,4-tetrahydro-5H-benzofuro[4,5-b][2]benzopyran-5-one(LXXXVI). Its structure was confirmed by its NMR spectrum in $CDCl_3$ (Fig. 20) : δ 1.82, broad multiplet, 4H, two methylene groups at 2- and 3-position ; 2.50, singlet, 3H, overlapped with a broad multiplet, $-CH_3$ group at 9-position ; 2.64, broad multiplet, 4H, two methylene groups at 1- and 4-position ; 6.65, singlet, 1H at 10-position ; 7.35, doublet, J=10Hz, 1H at 7-position ; 8.02, doublet, J=10Hz, 1H at 6-position.

Synthesis of 6-[2'-methyl-4'-hydroxybenzofuran-5'-yl]-6-oxo-6H-hexanoic acid(XCII) :

Condensation of resorcinol with ethyl cyclopentanone-2-carboxylate in diphenyl ether gave 7-hydroxy-1,2,3-trihydro-4H-cyclopenta[b]benzopyran-4-one(LXXXVII), which on allylation with allyl bromide followed by Claisen rearrangement in

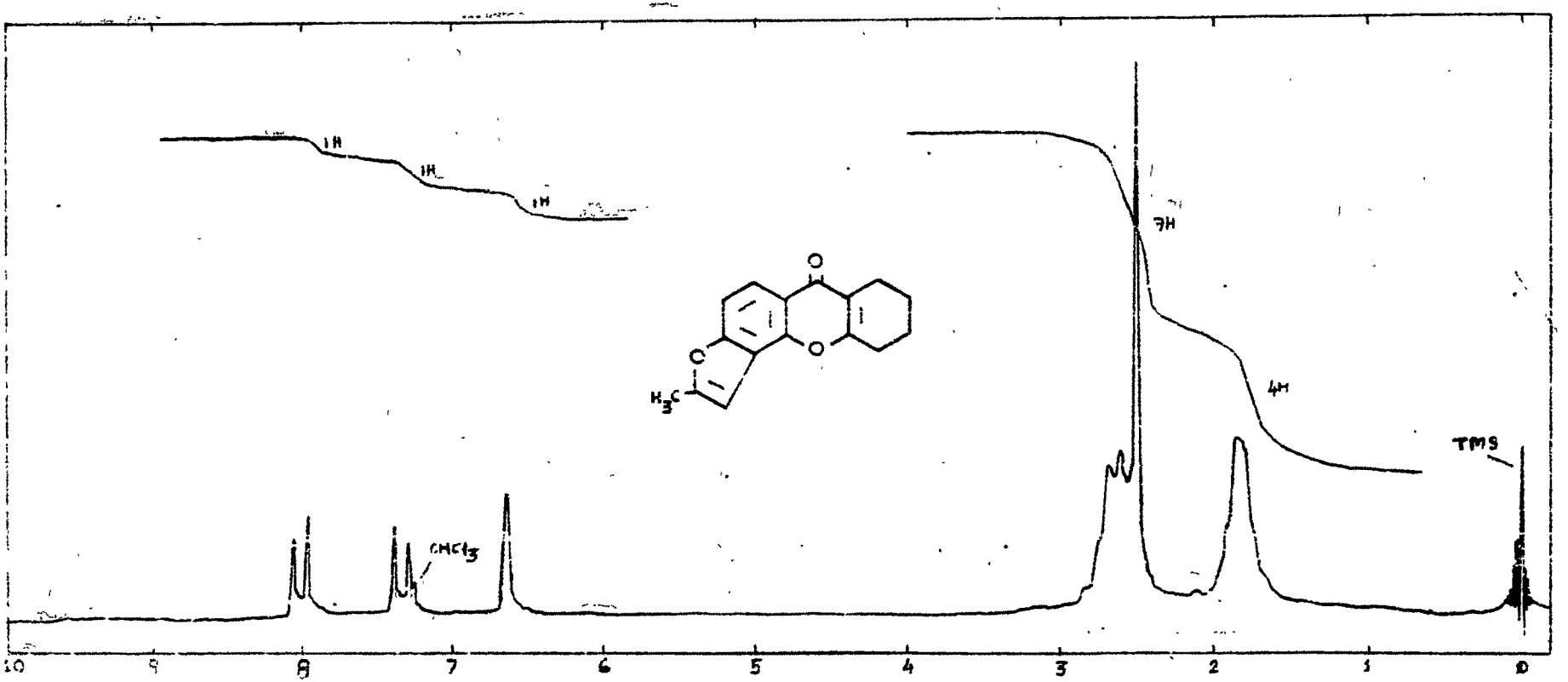
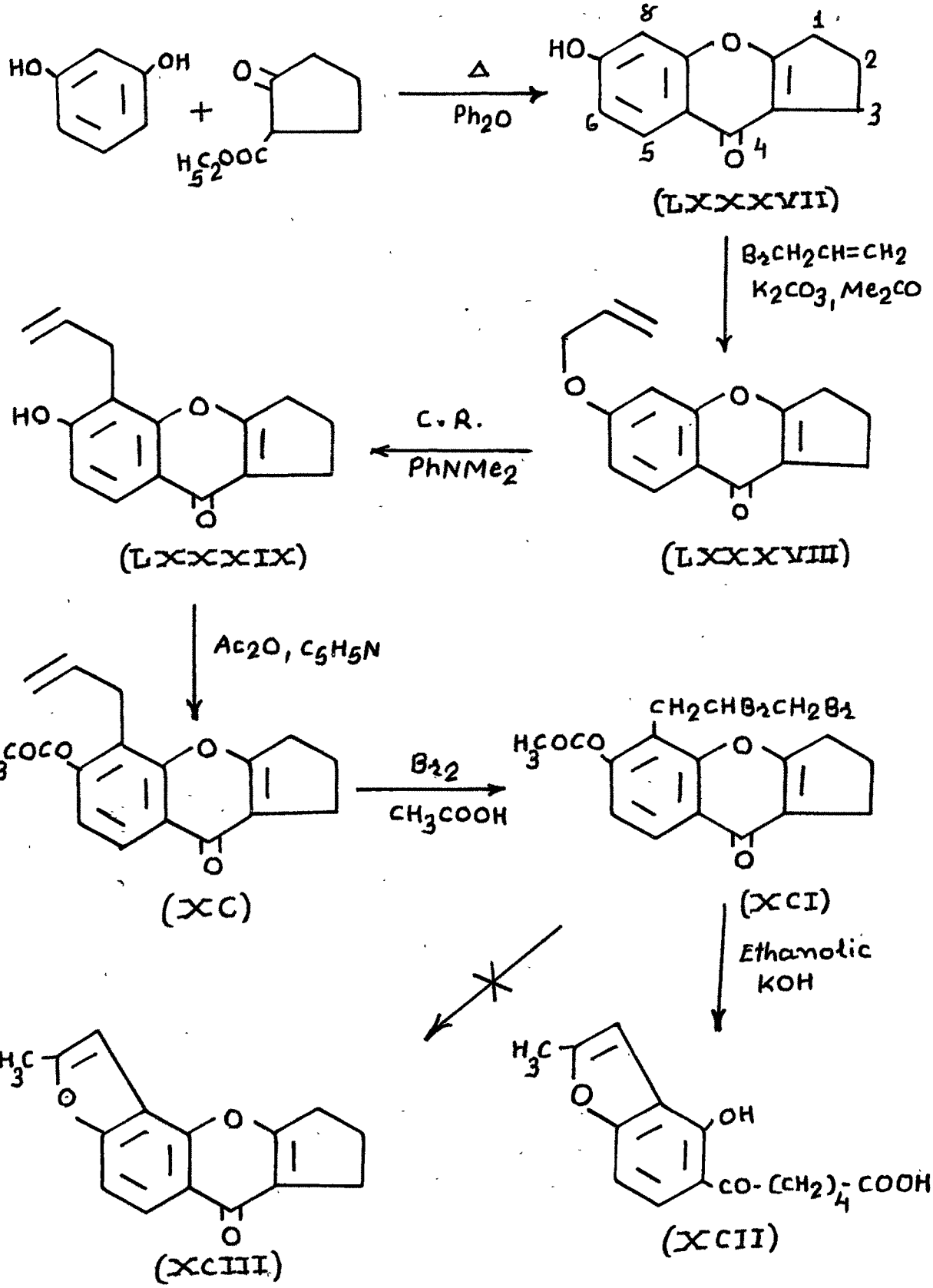


Fig. 20 : : NMR spectrum of 9-Methyl-1,2,3,4-tetrahydro-5H-benzofuro[4,5-b][2]benzopyran-5-one (LXXXVI) in $CDCl_3$ (90 MHz).

dimethylaniline gave 8-allyl-7-hydroxy-1,2,3-trihydro-4H-cyclopenta[b]benzopyran-4-one(LXXXIX). This was acetylated to 8-allyl-1,2,3-trihydro-4-oxo-4H-cyclopenta[b]benzopyran-7-yl acetate(XC) by acetic anhydride and pyridine. The acetate derivative XC, on bromination with bromine in glacial acetic acid yielded 8-(2',3'-dibromopropyl)-1,2,3-trihydro-4-oxo-4H-cyclopenta[b]benzopyran-7-yl acetate(XCI), which when treated with ethanolic potassium hydroxide underwent cyclization to furan ring with simultaneous ring opening of γ-pyrone and cyclopentane to give an acidic product 6-[2'-methyl-4'-hydroxybenzofuran-5'-yl]-6-oxo-6H-hexanoic acid (XCII). Thus the product obtained is totaly different from the expected one 8-methyl-1,2,3-trihydro-4H-cyclopenta-[b]furo[2,3-h]benzopyran-4-one(XCIII). The acidic product XCII is soluble in sodium bicarbonate solution and repricipitated on addition of mineral acid and gave red colouration with ethanolic ferric chloride. The structure of XCII was confirmed by its NMR spectrum in CF_3COOH (Fig. 21): δ 1.95, broad multiplet, 4H, two methylene groups at 3- and 4-position ; 2.47, singlet, 3H, overlapped with the second broad multiplet, $-CH_3$ group at 2'-position ; 2.65, broad multiplet, 2H, one methylene group at 2-position ; 3.18, broad multiplet, 2H, one methylene group at 5-position ; 6.07, singlet, 1H, at 3'-position ; 7.10, doublet, J=10Hz, 1H at 7'-position ; 7.78, doublet, J=10Hz, 1H at 6'-position.


HO
OH
O
H_5C_2OOC
+
Δ
Ph_2O
8
1
HO
O
2
6
3
5
O
4
(LXXXVII)
$Br_2CH_2CH=CH_2$
K_2CO_3, Me_2CO
HO
O
C.R.
$PhNMe_2$
O
O
(LXXXIX)
(LXXXVIII)
Ac_2O, C_5H_5N
H_3COCO
O
Br_2
CH_3COOH
$CH_2CHBrCH_2Br$
H_3COCO
O
(XC)
(XCI)
Ethanolic
KOH
H_3C
O
O
OH
$CO-(CH_2)_4-COOH$
(XCII)
(XCIII)

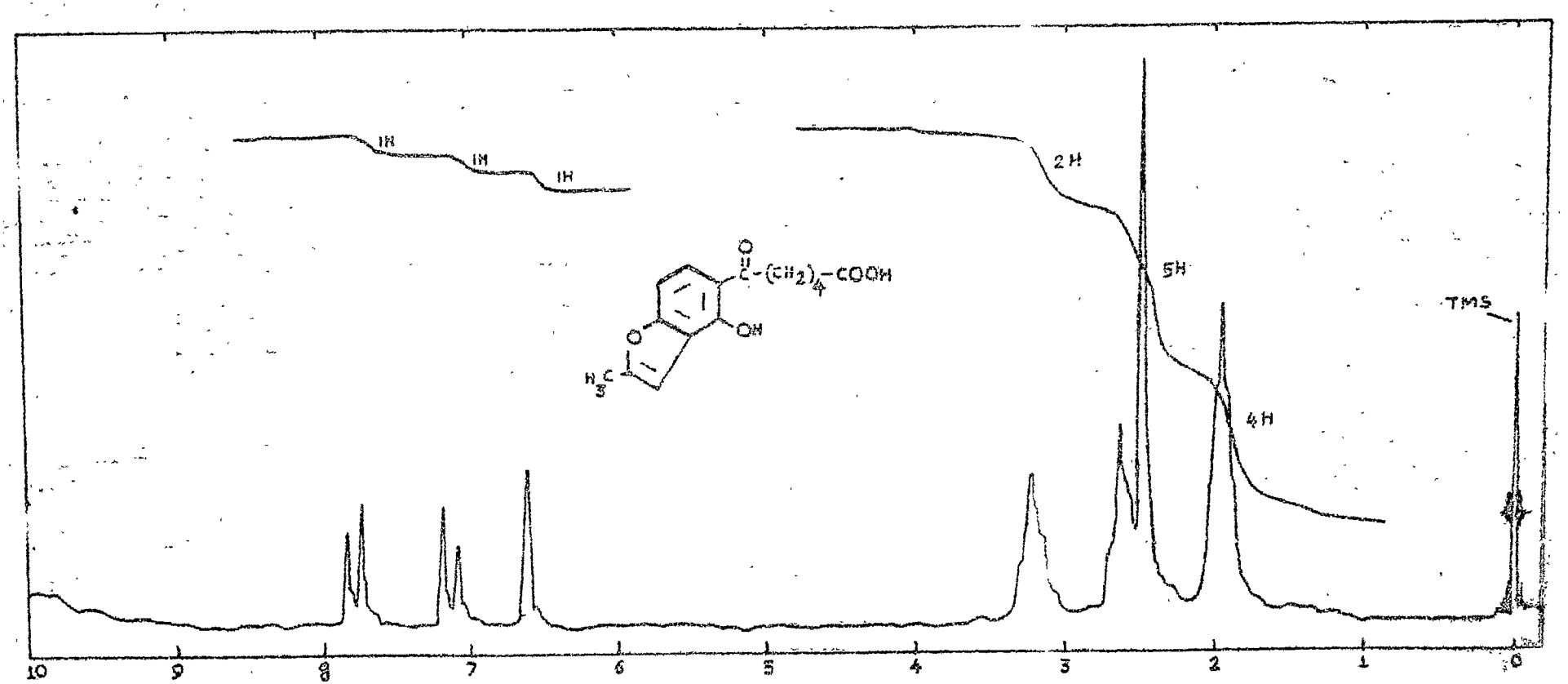
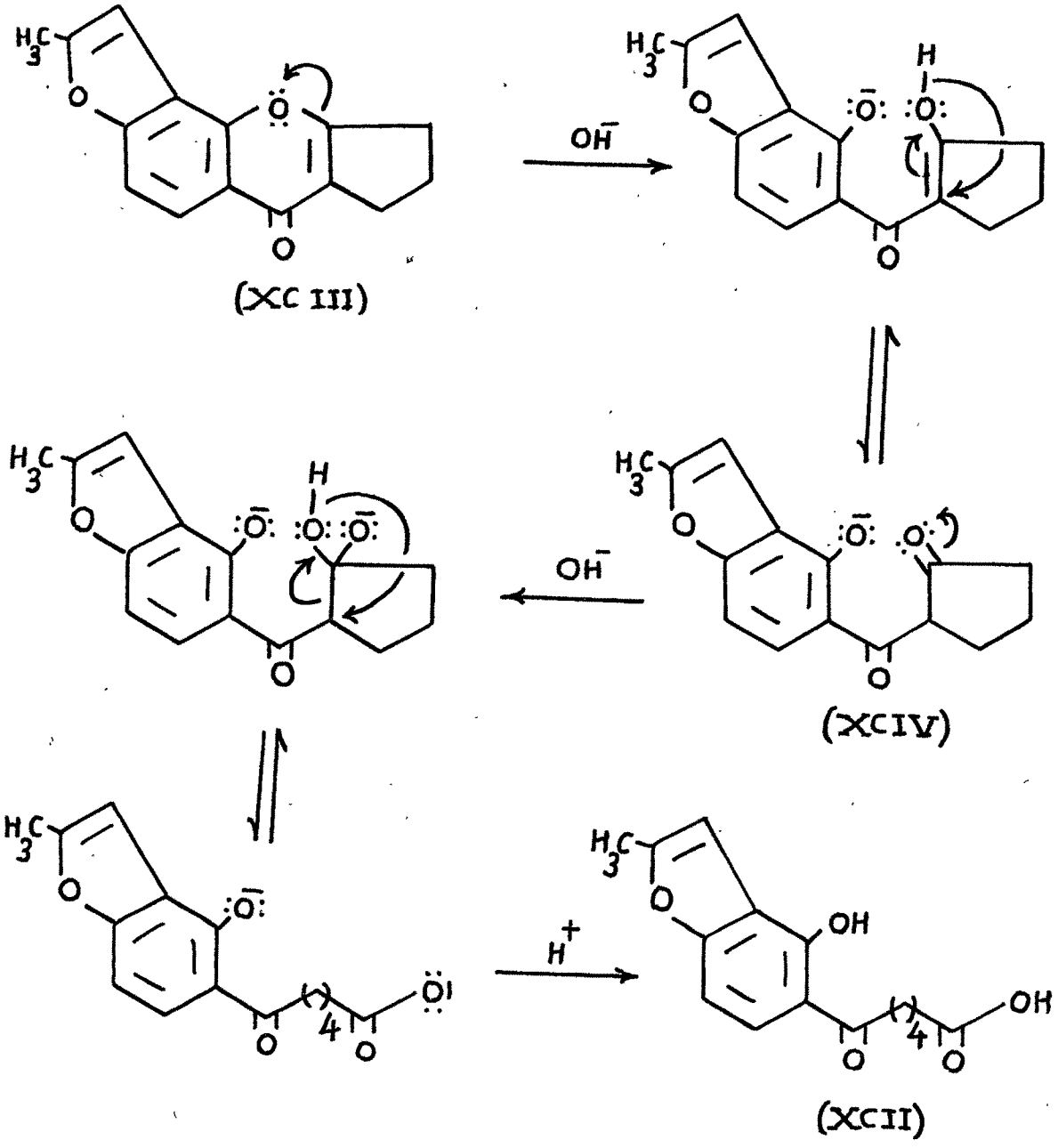


Fig. 21 : NMR spectrum of 6-[2'-Methyl-4'-hydroxybenzofuran-5'-yl]-6-oxo-6H-hexanoic acid (XCII) in CF_3COOH (90 MHz).

The mechanism of conversion of XCIII to XCII can be explained by the ring opening of the γ-pyrone to give an intermediate 1,3-diketo product XCIV, followed by its conversion to 6-oxo-6H-hexanoic acid derivative (XCII) through cyclopentanone ring opening in basic media. This is shown in the following scheme :

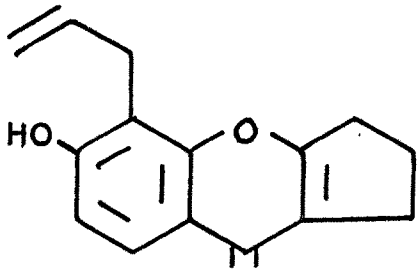


(XC III)

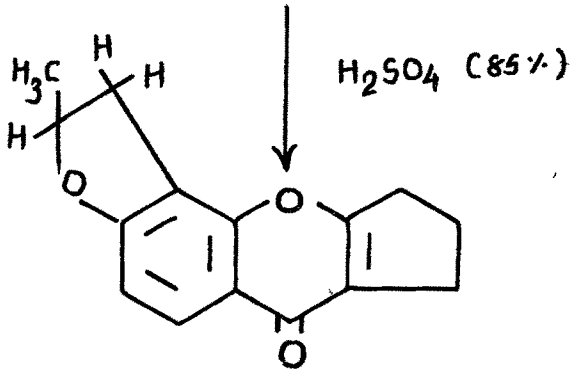
(XCIV)

(XCII)

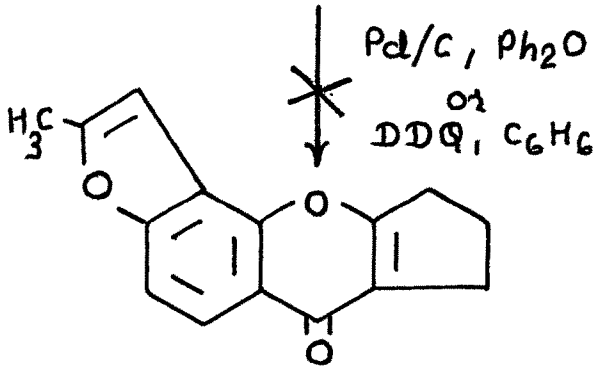
8-Allyl-7-hydroxy-1,2,3-trihydro-4H-cyclopenta[b]-benzopyran-4-one(LXXXIX), was triturated with sulphuric acid (85 %) to give 8-methyl-1,2,3,8,9-pentahydro-4H-cyclopenta[b]furo[2,3-h]benzopyran-4-one(XCV). This could not be dehydrogenated to 8-methyl-1,2,3-trihydro-4H-cyclopenta[b]furo[2,3-h]benzopyran-4-one(XCIII) by palladized charcoal (10 %) in diphenyl ether or by DDQ in dry benzene.



(LXXXIX)



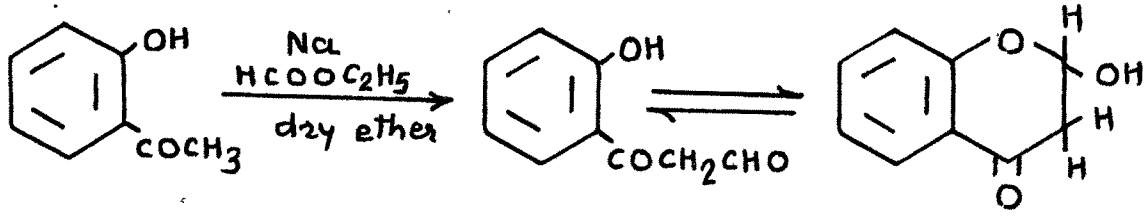
(XCV)



(XCIII)

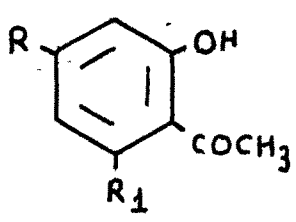
A NOVEL THERMAL DIMERIZATION REACTION OF 2-HYDROXYCHROMANONE DERIVATIVES :

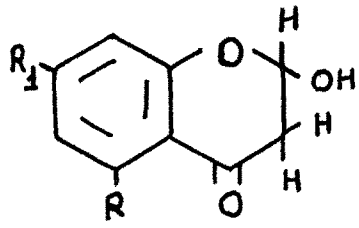
Schöneberg and Sina reported[33] the Claisen condensation of o-hydroxyacetophenone(XCVI) with ethyl formate in the presence of sodium and isolated ω-formyl-o-hydroxyacetophenone or 3-(2'-hydroxyphenyl)-3-oxo-3H-propanal (XCVII).



(XCVI) (XCVII) (XCVIII)

Leter on it was found[34] that such a derivative is a tautomeric mixture of XCVII and cyclic 2-hydroxychromanone (XCVIII), as it showed change in colour reaction and also in m.p. on recrystallization. Recently Ahluwalia and Prakash[35] made a detailed study about the Claisen condensation products of 2-hydroxy-4,6-dimethoxyacetophenone(XCIX) and 2-hydroxy-4-methoxy-6-methylacetophenone(C) with ethyl formate and confirmed the cyclic 2-hydroxychromanone structures CI and CII respectively, on the basis of different reactions viz., acetylation with acetic anhydride-pyridine and methylation with dimethyl sulphate or methyl iodide.



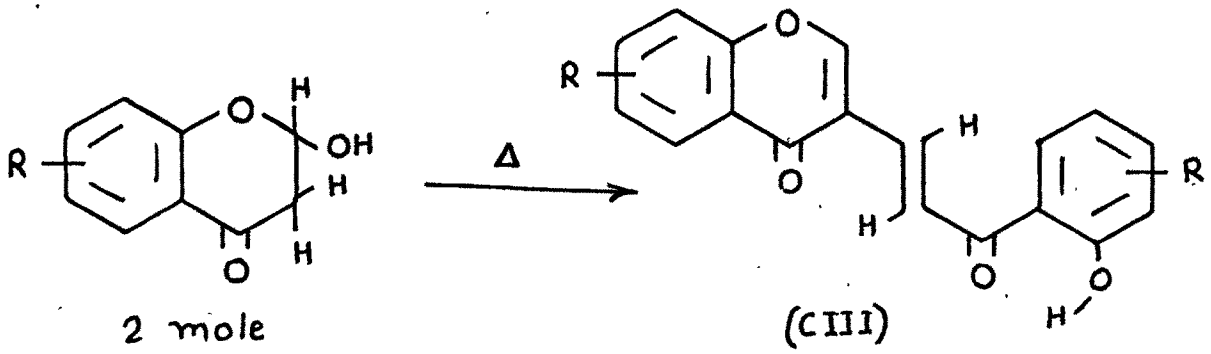


(XCIX) $R = R_1 = OCH_3$ (CI) $R = R_1 = OCH_3$

(C) $R = OCH_3$, $R_1 = CH_3$ (CII) $R = CH_3$, $R_1 = OCH_3$

Present work :

A new reaction leading to the formation of a yellow dimeric product 1-(3-chromonyl)-2-(2-hydroxybenzoyl)-ethylene(CIII) from a 2-hydroxychromanone derivative is first time reported in the present work. The formation of dimeric products (CIII, R = H, CH_3 etc.) from the corresponding chromone derivatives was reported with sodium ethoxide[36] and with pyridine[37].



2 mole (CIII)

2-Hydroxy-3-methyl-4-allyloxyacetophenone(XLIX), on Claisen condensation with ethyl formate in presence of pulverized sodium gave 2-hydroxy-7-allyloxy-8-methyl-chromanone(L). We observed a typical behaviour in the melting points of the product (L), which melts at 128-31° with evolution of water vapour, resolidifies as shinning yellow crystals above 161° and melts again above 190° . This unique behaviour of 2-hydroxychromanones led us to investigate the detailed study about these products. It was observed that such derivatives were quite unstable at their melting points and when heated 20 to 30° above their melting temperatures, they dimerized to give yellow coloured products.

Conclusion :

The 2-hydroxychromanone derivatives on acid catalyzed dehydration gave chromones, while on thermal catalyzed dehydration gave yellow dimeric 1-(3-chromonyl)-2-(2-hydroxybenzoyl)-ethylene derivatives. Both the type of reactions take place with the elimination of water molecules. The yellow dimeric products were also formed from chromones through base catalyzed reaction.

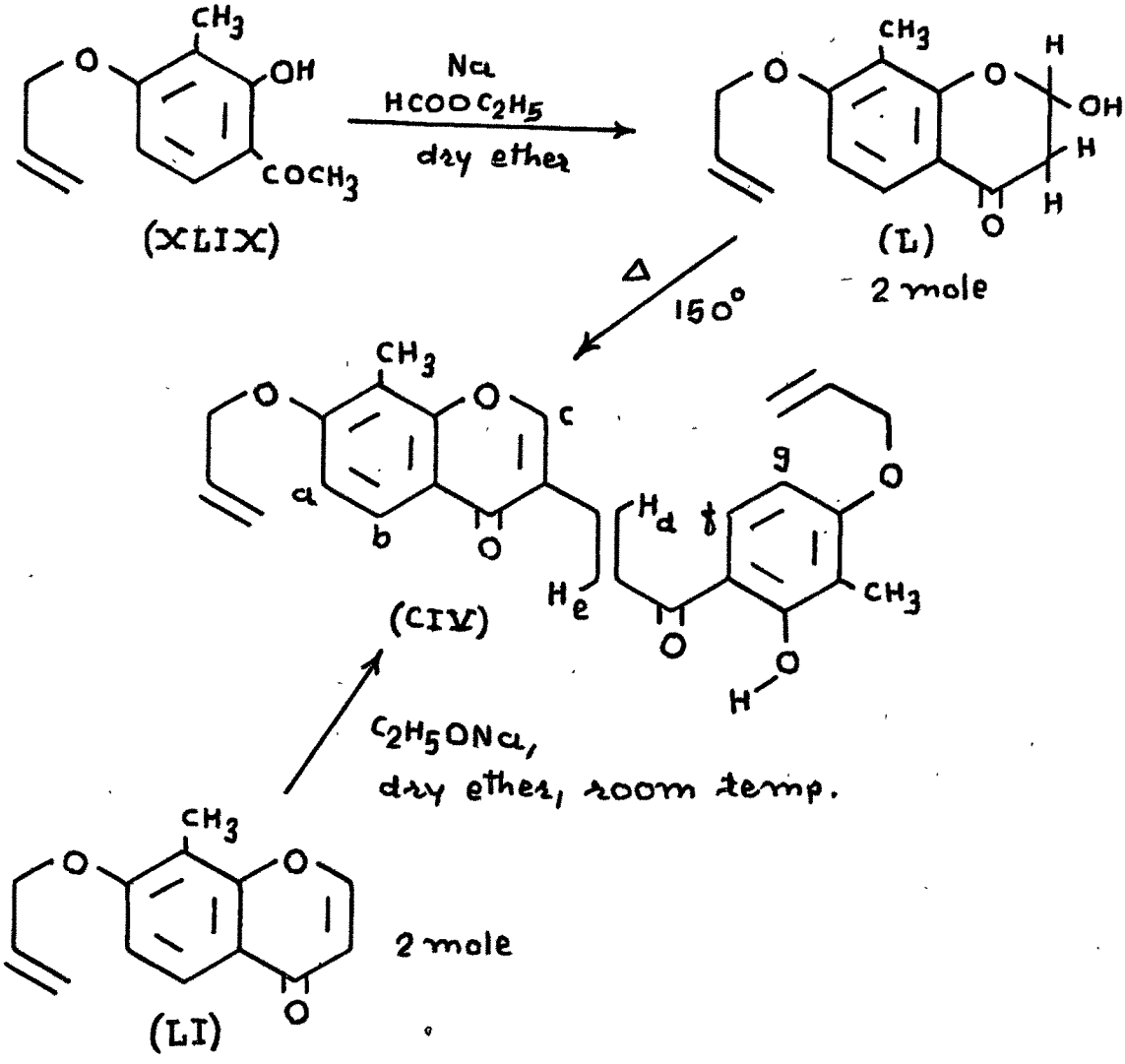
Synthesis of 1-(7-allyloxy-8-methyl-3-chromonyl)-2-(2-hydroxy-3-methyl-4-allyloxybenzoyl)-ethylene(CIV) :

2-Hydroxy-7-allyloxy-8-methylchromanone(L), on heating in an oil bath at 150° for 15 minutes, gave yellow

coloured product 1-(7-allyloxy-8-methyl-3-chromonyl)-2-(2-hydroxy-3-methyl-4-allyloxybenzoyl)-ethylene(CIV). This was also synthesized from 7-allyloxy-8-methylchromone(LI), prepared as described before, by the action sodium ethoxide[36] in dry ether. The m.p. and mixed m.p. of CIV were 216°. The structure of CIV was also confirmed on the basis of its spectral data.

Its IR spectrum in nujol (Fig. 22) showed the bands at 1630 cm^{-1} (γ-pyronyl >C=O group), 1665 cm^{-1} (carbonyl >C=O group) and a weak band at 3080 cm^{-1} (-OH group). The NMR spectrum in $CDCl_3$ (Fig. 23 and 24) showed the following signals : δ 2.12, singlet, 3H, $-CH_3$ group at 3-position of aromatic system ; 2.31, singlet, 3H, $-CH_3$ group at 8-position of chromone nucleus ; 4.65, double doublet, 4H, J=7Hz, 1.4Hz, two methylene groups of two $-O-\underline{CH_2}-CH=CH_2$ groups ; 5.35, multiplet, 4H, two methylene groups of two $-O-CH_2-CH=\underline{CH_2}$ groups ; 6.04, multiplet, 2H, two methine protons of two $-O-CH_2-\underline{CH}=CH_2$ groups ; 6.45, doublet, 1H, J=10Hz, aromatic proton $-H_g$; 7.08, doublet, J=10Hz, 1H, chromatic proton $-H_a$; 7.43, doublet, J=16Hz, 1H, trans olefinic proton $-H_e$; 7.86, doublet, J=10Hz, 1H, aromatic proton $-H_f$; 8.10, doublet, J=10Hz, 1H, chromatic proton $-H_b$; 8.14, singlet, 1H, γ-pyrone ring proton $-H_c$; 8.72, doublet, J=16Hz, 1H, trans olefinic proton $-H_d$; 12.20, singlet, 1H, -OH group. From the (Fig. 24) : Ortho-chromatic and ortho-aromatic protons, all the four protons appeared as doublets, with J=10Hz, are confirmed by spin decoupling

technique. By irradiating the doublet at δ7.08 the doublet at δ8.10 collapsed into a singlet, and the latter downfield doublet must be assigned to the peri-proton $-H_b$, then the former one at δ7.08 is fixed for $-H_a$. The remaining two doublets with J=10Hz are assigned for the two adjacent aromatic protons $-H_f$ and $-H_g$. In a second irradiation experement, the doublet at δ8.72, was irradiated, which affected the doublet at δ7.43 by collapsing the latter into a singlet, These two doublets with J=16Hz are assigned to two <u>trans</u> olefinic protons $-H_d$ and $-H_e$ respectively.



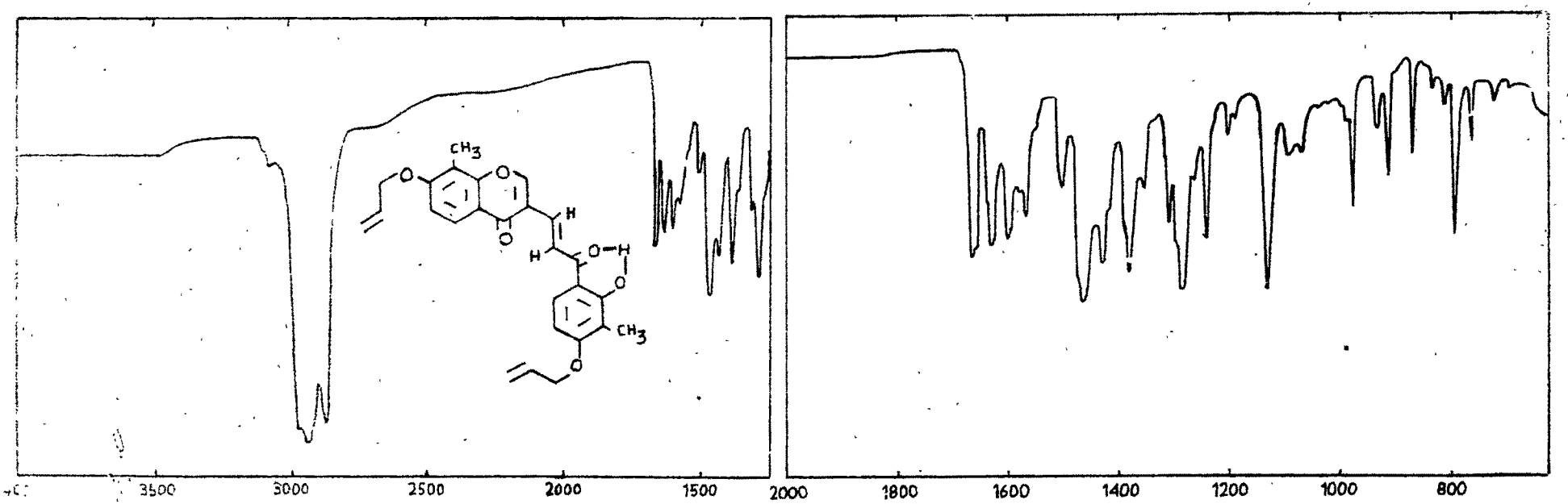


Fig. 22 : IR spectrum of 1-(7-Allyloxy-8-methyl-3-chromonyl)-2-(2-hydroxy-3-methyl-4-allyloxybenzoyl)-ethylene (CIV) in nujol.

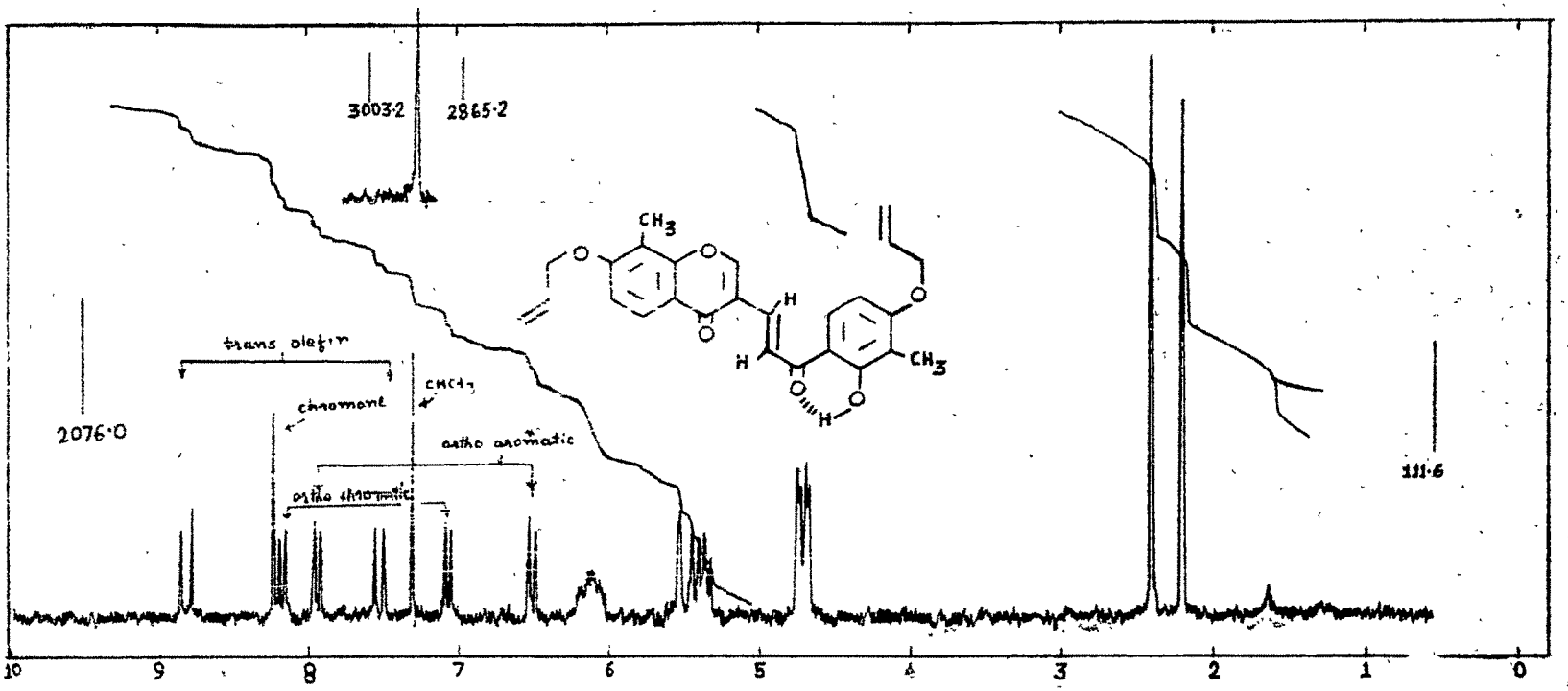


Fig. 23 : NMR spectrum of 1-(7-Allyloxy-8-methyl-3-chromonyl)-2-(2-hydroxy-3-methyl-5-allyloxybenzoyl)-ethylene (CIV) in $CDCl_3$ (220 MHz) at 50° temperature.

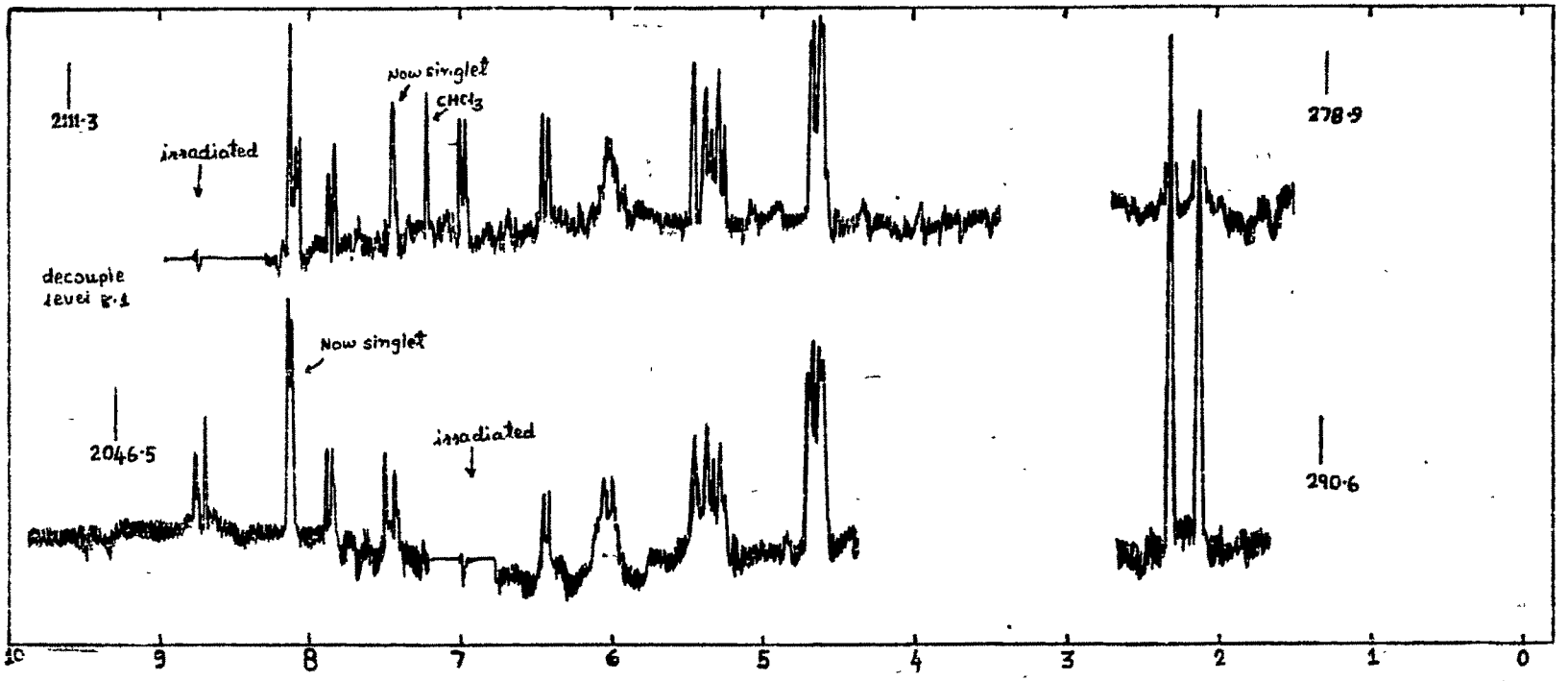
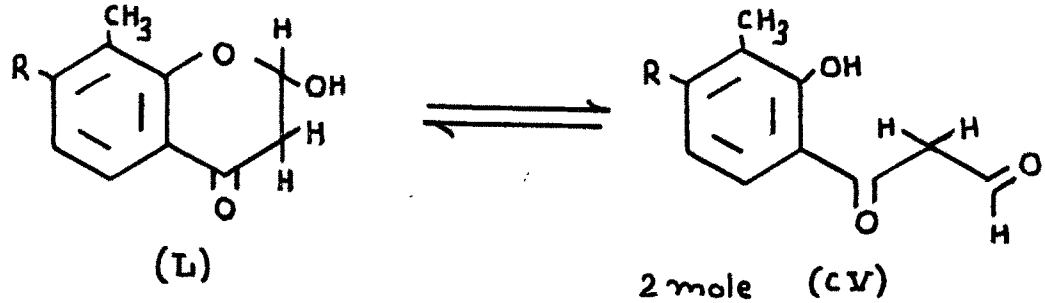


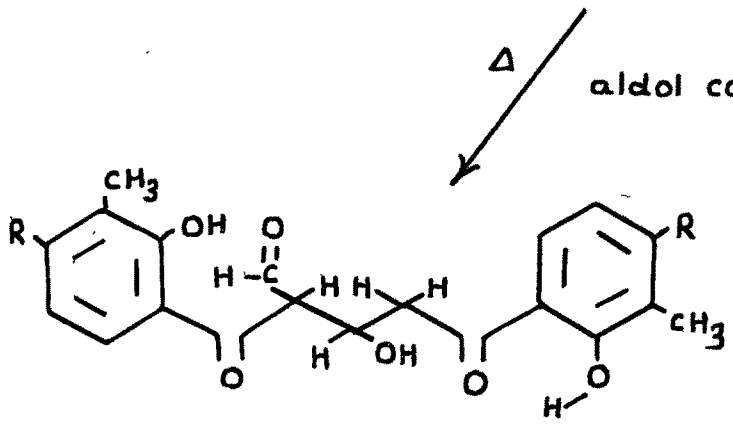
Fig. 24 : NMR spectrum of (double irradiation) of 1-(7-Allyloxy-8-methyl-3-chromonyl)-2-(2-hydroxy-3-methyl-4-allyloxy-benzoyl)-ethylene (CIV) in $CDCl_3$ (220 MHz) at 50° temp.

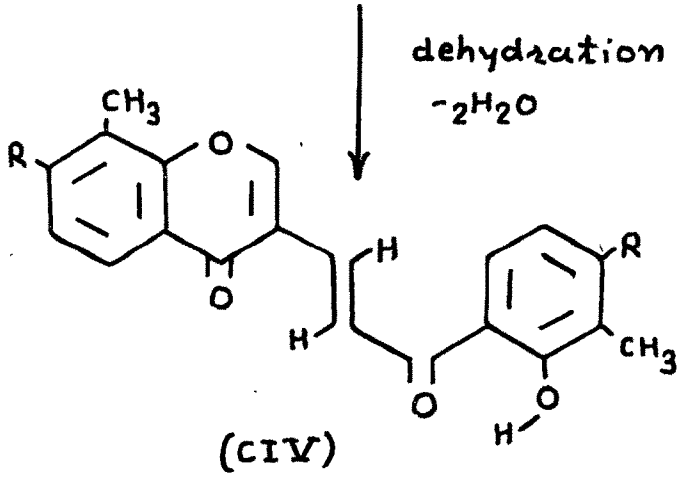
The thermal catalyzed dehydration of 2-hydroxy-chromanone derivatives (e.g.L) to dimeric products (CIV) can be explained by ring opening to aldehyde CV, followed by aldol condensation of two aldehyde molecules and recyclization to dimeric product CIV, with the elimination of two water molecules.



(L)

2 mole (CV)





(CIV)

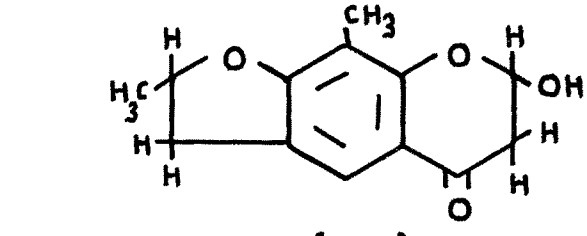
R = -O-CH2-CH=CH2

Synthesis of 1-[2,3-dihydro-2,9-dimethyl-5-oxo-5H-furo-(3,2-g)benzopyran-6-yl]-2-[2,3-dihydro-2,7-dimethyl-6-hydroxy-5-benzofuranoyl]-ethylene(CVI) :

2,9-Dimethyl-7-hydroxy-2,3,6,7-tetrahydro-5H-furo-(3,2-g)benzopyran-5-one(LVI), which was prepared starting from 2-hydroxy-3-methyl-4-allyloxyacetophenone (XLIX), according to the scheme described before, was heated in an oil bath at 155° temperature for 12 minutes to give a yellow coloured product 1-[2,3-dihydro-2,9-dimethyl-5-oxo-5H-furo-(3,2-g)benzopyran-6-yl]-2-[2,3-dihydro-2,7-dimethyl-6-hydroxy-5-benzofuranoyl]-ethylene(CVI). It was also synthesised from 2,3-dihydro-2,9-dimethyl-5H-furo(3,2-g)benzopyran-5-one(LVII), by the action of sodium ethoxide[36] in dry ether.

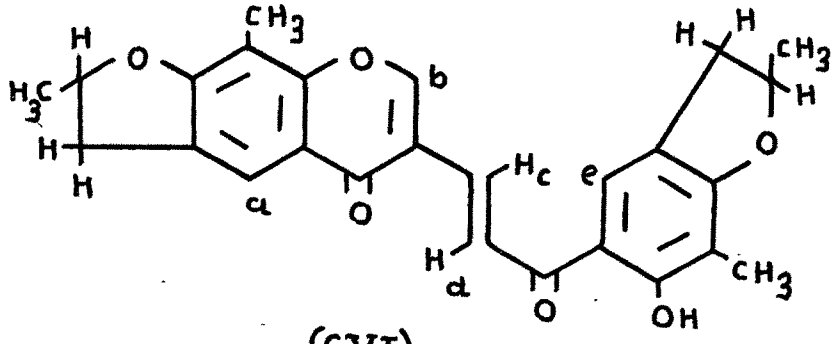
The structure of CVI was also confirmed by its NMR spectrum in $CDCl_3$ (Fig. 25) ; δ1.52, overlapping of two doublets, J=7Hz, 6H, two $-CH_3$ groups at 2-position of two furan rings ; 2.14, singlet, 3H, $-CH_3$ group at 7-position of benzofuran ; 2.30, singlet, 3H, $-CH_3$ group at 9-position of furobenzopyrone nucleus ; 3.20, multiplet, 4H, two methylene groups at 3-position of two furan rings ; 5.09, multiplet, 2H, two methine protons at 2-position of two furan rings ; 7.50, doublet, J=16Hz, 1H, trans olefinic proton $-H_d$; 7.70, singlet, 1H, aromatic proton $-H_e$; 7.95, singlet, 1H, chromatic proton $-H_a$; 8.20, singlet, 1H, γ-pyrone ring proton $-H_b$; 8.80, doublet, J=16Hz, 1H, trans olefinc proton $-H_c$; 14.05, singlet, 1H, -OH group.

The irradiation of multiplet at δ5.09, affected the multiplet of methylene groups at δ3.20, by collapsing the latter into two symmetrical quartets. This is the example of geminal coupling of the protons at the same carbon atom.



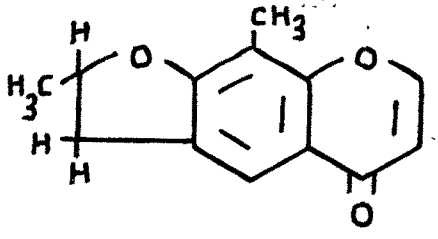
(LVI) 2 mole

Δ 155° $-2H_2O$



(CVI)

C_2H_5ONa, dry ether, room temp.



2 mole

(LVII)

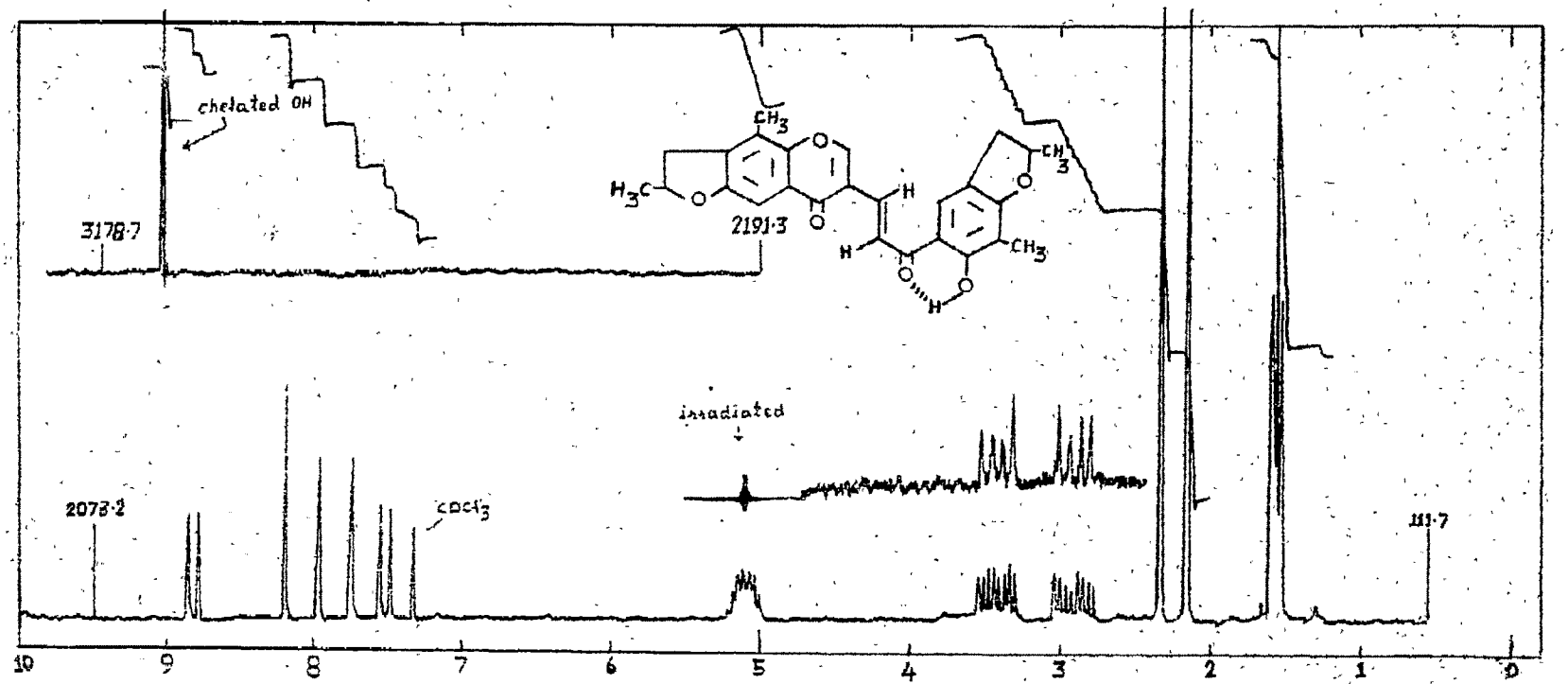
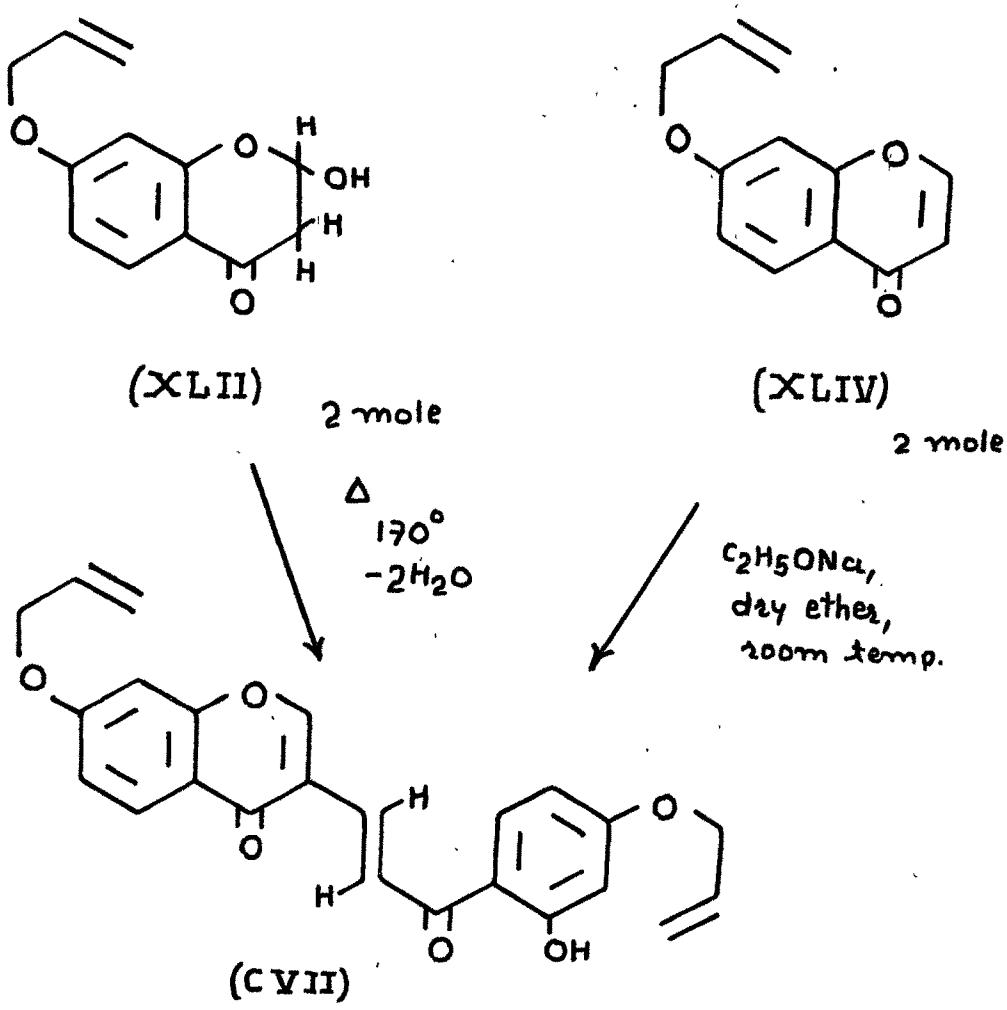


Fig. 25 : NMR spectrum (with double irradiation) of 1-[2,3-Dihydro-2,9-dimethyl-5-oxo-5H-furo(3,2-g)benzopyran-6-yl]-2-[2,3-dihydro-2,7-dimethyl-6-hydroxy-5-benzofuranoyl]-ethylene (CVI) in $CDCl_3$ (220 MHz) at 50° temperature.

Synthesis of 1-(7-allyloxy-3-chromonyl)-2-(2-hydroxy-4-allyloxybenzoyl)-ethylene(CVII) :

The title yellow coloured compound was prepared from 2-hydroxy-7-allyloxychromanone(XLII) on heating at 170° for 15 minutes. The structure of CVII was confirmed by its synthesis from 7-allyloxychromone(XLIV) by the action of sodium ethoxide[36] in dry ether. Both the compounds were found identical in respect to m.ps. and mixed m.p. 198°, co-TLC R_f 0.64 in chloroform and co-IR in nujol showed bands at 1630 cm^{-1} (γ-pyronyl >C=O group), 1652 cm^{-1} (carbonyl >C=O group) and a weak band at 3080 cm^{-1} (-OH group).



EXPERIMENTAL

NMR spectra were recorded on Perkin-Elmer 90 MHz and 220 MHz spectrometer using TMS as an internal standard. IR spectra were taken on Perkin-Elmer 457 grating and on Backmann IR-20 spectrophotometer. UV spectra were recorded on Beckmann DU-2 spectrophotometer.

Synthesis of 7H-furo(2,3-h)benzopyran-7-one(XLVI):

7-Allyloxy-2-hydroxychromanone(XLII):

The solution of 2-hydroxy-4-allyloxyacetophenone[28] (3.84 g) in ethyl formate (22 ml) was allowed to react slowly with pulverized sodium (2.3 g) kept in dry ether (8 ml) at 20° for 1 hr. More ethyl formate (10 ml) was added slowly and the reaction mixture was refluxed in a water bath at 55° for 15 minutes. It was then left overnight. Ethanol and water were successively added with care and the resulting alkaline solution was extracted twice with ether. The aqueous alkaline layer was acidified with cold dilute acetic acid. A crystalline yellow solid separated slowly was filtered and washed with water. It crystallined from benzene and aqueous ethanol as small needles, m.p. 154° (decom.), yield 2.5 g. It gave a pale brownish violet colour with alcoholic ferric chloride and on standing fastess of the colour increased.

Analysis : Found : C, 65.90 ; H, 5.71 %

$C_{12}H_{12}O_4$ reqires : C, 65.45 ; H, 5.45 %.

UV λ_{max}(methanol): 272 nm (log e 4.51), 311 nm (log e 4.21); (methanol + dil.Sodium hydroxide): 272 nm (log e 4.50), 311 nm (log e 4.29).

7-Allyloxychromone(XLIV):

7-Allyloxy-2-hydroxychromanone (2 g) was taken in sulphuric acid (30 %; 60 ml) in a flask and heated on a water bath for 2 hr. On cooling, the white crystalline product separated was filtered and washed with water and sodium bicarbonate solution. It crystallised as colourless shining reactangular rods, m.p. 84°, yield 1.6 g.

Analysis : Found : C,71.48 ; H, 5.09 %

$C_{12}H_{10}O_3$ requires : C,71.28 ; H, 4.95 %.

Fig. 26 : NMR($CDCl_3$): δ 4.62 (d, J=6Hz, 2H, -O-$\underline{CH_2}$-CH=CH_2), 5.40 (m, 2H, -O-CH_2-CH=$\underline{CH_2}$), 5.89-6.18 (m, 1H, -O-CH_2-$\underline{CH}$=CH_2), 6.25 (d, J=7Hz, 1H, C_3-H), C. 6.85(s, 1H, C_8-H), C. 6.95(d, J=9Hz, 1H, C_6-H), 7.78(d, J=7Hz, 1H, C_2-H), 8.10(d, J=9Hz, 1H, C_5-H).

7-Hydroxy-8-allylchromone(XLV):

7-Allyloxychromone (1.5 g) was refluxed with dimethylaniline (12 ml) for 8 hr. After cooling the reaction mixture was poured into ice containing hydrochloric acid (20 ml). The separated product was treated with sodium hydroxide solution, filtered and acidified with dilute hydrochloric acid. The product chromatographed on silica gel, using a mixture of benzene-chloroform (7 : 3) as eluent. It

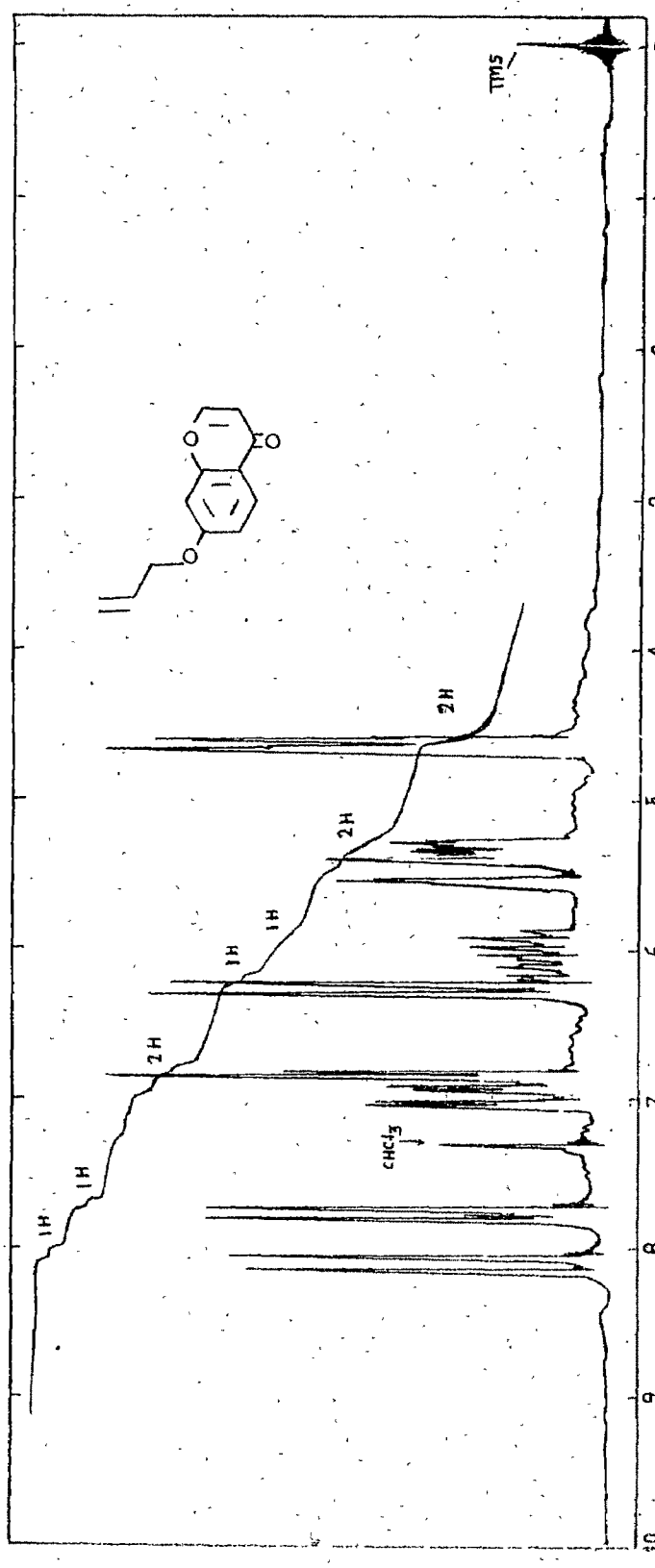


Fig. 26 : NMR spectrum of 7-Allyloxychromone (XLIV) in $CDCl_3$ (90 MHz).

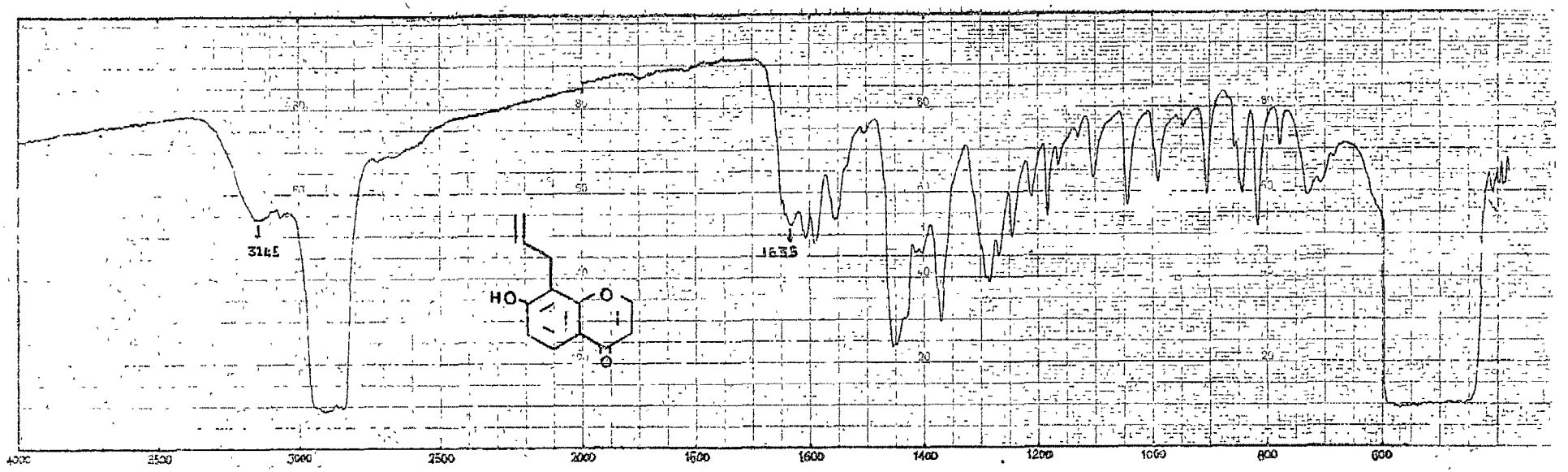


Fig. 27 : IR spectrum of 7-Hydroxy-8-allylchromone (XLV) in nujol.

crystallised as colourless small needles from aqueous ethanol m.p. 184°, yield 1.2 g.

Analysis : Found : C, 71.63 ; H, 5.45 %

$C_{12}H_{10}O_3$ requires : C, 71.28 ; H, 4.95 %.

Fig. 27 : IR ν_{max} (nujol) : 1635 cm^{-1} (γ-pyronyl)C=O group), and a broad band at 3145 cm^{-1} (aromatic -OH group).

7H-furo(2,3-h)benzopyran-7-one(XLVI):

7-Hydroxy-8-allylchromone (0.6 g) in ethyl acetate (120 ml) and osmium tetroxide (60 mg) in water (50 ml) were vigorously stirred for 15 minutes. Potassium periodate (1.7 g) was added in small quantities to the dark solution over a period of 2 hr. The reaction mixture was stirred 2 hr. more. The ethyl acetate layer was separated,washed with water, dried with sodium sulphate and distilled. The residue, the intermediate 8-acetaldehydo product,was taken in PPA (15 ml) and heated in an oil bath for 1.5 hr. at 115°. It was then poured over ice. The separated solid was extracted with chloroform, washed successively with very dilute sodium hydroxide solution and water, dried with sodium sulphate and the solvent distilled off. The crude product was dissolved in chloroform (2 ml) and percolated through a column of silica gel. and eluted with a mixture of benzene-chloroform (9:1), yielded XLVI (180 mg) which crystallised from benzene-petroleum ether as a colourless prisms, m.p. 186°.

Analysis : Found : C, 70.49 ; H, 3.32 %

$C_{11}H_6O_3$ requires : C, 70.98 ; H, 3.23 %.

Synthesis of 2-methyl-7H-furo(2,3-h)benzopyran-7-one(XLVIII):

2-Methyl-2,3-dihydro-7H-furo(2,3-h)benzopyran-7-one(XLVII):

7-Hydroxy-8-allylchromone (1 g) was triturated with sulphuric acid (85 % ; 8 ml) in a water bath for 15 minutes. The contents were poured into crushed ice, the separated product was filtered and washed with dilute sodium hydroxide solution. It crystallised from benzene-petroleum ether as pale yellow coloured prisms, m.p. 136°, yield 0.7 g.

Analysis : Found : C, 71.12 ; H, 5.24 %

$C_{12}H_{10}O_3$ requires : C, 71.28 ; H, 4.95 %.

2-Methyl-7H-furo(2,3-h)benzopyran-7-one(XLVIII):

2-Methyl-2,3-dihydro-7H-furo(2,3-h)benzopyran-7-one (0.4 g) was refluxed in diphenyl ether (7 ml) with palladized charcoal (10 % ; 0.6 g) for 9 hr. The reaction mixture was filtered hot and filterate was steam distilled to remove diphenyl ether. The remaining residue was extracted with ethyl acetate, the solvent was distilled off and the residue was chromatographed over silica gel and eluted with petroleum ether-benzene mixture (3:2). Removal of solvent on water bath gave the product, which crystallised from aqueous ethanol as colourless needles, m.p. 152°, yield 0.25 g.

Analysis : Found : C, 71.74 ; H, 4.33 %

$C_{12}H_8O_3$ requires : C, 72.00 ; H, 4.00 %.

UV λ_{max} (methanol): 240 nm (log e 4.69), 250 nm (log e 4.64), 306 nm (log e 4.09).

Synthesis of 9-methyl-5H-furo(3,2-g)benzopyran-5-one(LIII):

2-Hydroxy-7-allyloxy-8-methylchromanone(L) :

Pulverized sodium (1.72 g) was kept in dry ether (5 ml) in a flask fitted with water condenser and maintained with stirring at 20° for 1.5 hr. During this the solutin of 2-hydroxy-3-methyl-4-allyloxyacetophenone[30] (3.0 g) in ethyl formate (12 ml) was added drop by drop as to react with sodium. When the reaction subsided more ethyl formate (8 ml) was added and left for two days. The reaction mixture was worked out as before. The product crystallised from aqueous ethanol as colourless seeds, m.p. 131° (decom.), yield 1.8 g.

Analysis : Found : C, 66.58 ; H, 5.78 %

$C_{13}H_{14}O_4$ requires : C, 66.67 ; H, 5.98 %.

UV λ_{max}(methanol) : 281 nm (log e 4.55); (methanol + dil. sodium hydroxide) : 276 nm (log e 4.33).

7-Allyloxy-8-methylchromone(LI) :

2-Hydroxy-7-allyloxy-8-methylchromanone (1.8 g) was dehydrated by using dilute sulphuric acid (30 % ; 50 ml), in water bath for 90 minutes. It crystallised as colourless shining needles, m.p. 79°, yield 1.2 g.

Analysis : Found : C, 72.28 ; H, 5.41 %

$C_{13}H_{12}O_3$ requires : C, 72.21 ; H, 5.55 %.

6-Allyl-7-hydroxy-8-methylchromone(LII) :

7-Allyloxy-8-methylchromone (1.4 g) was refluxed with dimethylaniline (12 ml) for 6 hr. The reaction mixture was worked up as usual. The separated product was crystallised from benzene as colourless plates, m.p. 141°, yield 1.2 g.

Analysis : Found : C, 72.41 ; H, 5.64 %

$C_{13}H_{12}O_3$ requires : C, 72.21 ; H, 5.55 %.

IR ν_{max} (nujol) : 1640 cm^{-1} (γ-pyronyl >C=O group), 3280 cm^{-1} (aromatic -OH group).

9-Methyl-5H-furo(3,2-g)benzopyran-5-one(LIII):

6-Allyl-7-hydroxy-8-methylchromone (0.6 g) in ethyl acetate (150 ml) and osmium tetroxide (50 mg) in water (50 ml) were vigorously stirred for 15 minutes. Potassium periodate (1.5 g) was added in small quantities (as in case of XLVI). The intermediate 6-acetaldehydo product was treated with PPA (12 ml) for 2 hr. at 130°. The reaction mixture was worked up, gave the product which crystallised from ethanol as colourless needles, m.p. 186-7°, yield 150 mg.

Analysis : Found : C, 72.19 ; H, 4.21 %

$C_{12}H_8O_3$ requires : C, 72.00 ; H, 4.00 %.

UV λ_{max}(methanol): 239 nm (log e 4.94) ; 322 nm (log e 4.16).

Synthesis of 2,9-dimethyl-5H-furo(3,2-g)benzopyran-5-one (LVIII):

2,4-Dihydroxy-3-methyl-5-allylacetophenone(LV):

2-Hydroxy-3-methyl-4-allyloxyacetophenone[30] (3.5 g) was refluxed with dimethylaniline (18 ml) for 5 hr. The separated product was filtered and washed with light petroleum ether. It crystallized as shining colourless plates from ethanol, m.p. 139°, yield 3.0 g.

Analysis : Found : C, 70.13 ; H, 7.02 %

$C_{12}H_{14}O_3$ requires : C, ~~70.58~~ 69.90 ; H, ~~6.68~~ 6.79 % .

IR ν_{max}(nujol): 1636 cm^{-1} (γ-pyronyl >C=O group), and a broad band at 3330 cm^{-1} (aromatic -OH group).

2,3-Dihydro-2,7-dimethyl-5-acetyl-6-hydroxybenzofuran(LIV):

2,4-Dihydroxy-3-methyl-5-allylacetophenone (2.5 g) was dissolved in sulphuric acid (85 % ; 20 ml) and the solution was warmed on water bath for 15 minutes. The reaction mixture was poured into ice cold water and extracted with ether. It was washed with dil. sodium hydroxide solution and water. The product obtained from etherial layer, was crystallized from a mixture of benzene-petroleum ether as colourless needles, m.p. 104°, yield 2.2 g.

Analysis : Found : C, 70.15 ; H, 6.67 %

$C_{12}H_{14}O_3$ requires : C, 69.90 ; H, 6.79 % .

IR ν_{max}(nujol) : 1645 cm^{-1} ($-COCH_3$ group), 1620, 1403, 1337, 1182, 1107, 874, 860, 769.

2,9-Dimethyl-7-hydroxy-2,3,6,7-tetrahydro-5H-furo(3,2-g)benzopyran-5-one(LVI):

2,3-Dihydro-2,7-dimethyl-5-acetyl-6-hydroxybenzofuran (2.0 g) was dissolved in ethyl formate (18 ml) and the solution was added slowly to react with pulverized sodium (1.5 g) kept in dry ether (4 ml) at 10° for 1.5 hr. More ethyl formate (8 ml) was added as usual and left overnight. The reaction mixture was worked up as before. The product crystallised from ethanol, m.p. 138° (decom.), yield 1.2 g.

Analysis : Found : C, 67.07 ; H, 5.68 %

$C_{13}H_{14}O_4$ requires : C, 66.67 ; H, 5.98 % .

IR ν_{max}(nujol) : 1672 cm^{-1} (>C=O group), and a broad band at 3335 cm^{-1} (-OH group).

2,3-Dihydro-2,9-dimethyl-5H-furo(3,2-g)benzopyran-5-one-(LVII):

6-Allyl-7-hydroxy-8-methylchromone(LII) (0.8 g) was treated with sulphuric acid (85 % ; 6 ml) in a water bath for 10 minutes at 85° . The reaction mixture was poured into ice and the separated product was extracted with ether, washed with very dilute sodium hydroxide solution and then with water. Evaporation of ether, gave 2,3-dihydro-2,7-dimethyl-5-acetyl-6-hydroxybenzofuran, which crystallised from a mixture of benzene-petroleum ether as colourless needles, m.p. 104°, yield 0.4 g. It was identical (m.p. mixed m.p. and IR) with LIV.

Analysis : Found : C, 69.82 ; H, 6.85 %

$C_{12}H_{14}O_3$ requires : C, 69.90 ; H, 6.79 % .

IR ν_{max}(nujol) : 1643 cm^{-1} ($-COCH_3$ group) and 1617, 1405, 1335, 1181, 1107, 875, 860, 768.

2,9-Dimethyl-7-hydroxy-2,3,6,7-tetrahydro-5H-furo (3,2-g)benzopyran-5-one)LVI) (0.9 g) was treated with dilute sulphuric acid (30 % ; 25 ml) for 2 hr.in a water bath at 85°. The reaction mixture was poured into cold water and the separated product was extracted with ether, washed with very dilute sodium hydroxide solution and then with water. Removal of solvent ether gave 2,3-dihydro-2,9-dimethyl-5H-furo(3,2-g) benzopyran-5-one(LVII), which crystallised from aqueous ethanol as plates, m.p. 121°, yield 0.6 g.

Analysis : Found : C, 72.13 ; H, 5.54 %

$C_{13}H_{12}O_3$ requires : C, 72.21 ; H, 5.55 % .

2,9-Dimethyl-5H-furo(3,2-g)benzopyran-5-one(LVIII) :

A mixture of 2,3-dihydro-2,9-dimethyl-5H-furo(3,2-g) benzopyran-5-one (0.4 g), palladised charcoal (10 % ; 0.6 g) and diphenyl ether (6 ml) was refluxed for 10 hr. Reaction mixture was worked up as before. The product crystallised from a mixture of benzene-petroleum ether as rectangular plates, m.p. 188-9°, yield 0.18 g.

Analysis : Found : C, 73.38 ; H, 4.75 %

$C_{13}H_{10}O_3$ requires : C, 72.89 ; H, 4.67 % .

UV λ_{max} (methanol) : 244 nm (log e 4.95), 328 nm (log e 4.19).

Synthesis of 4H-furo(3,2-f)benzopyran-4-one (LXIII) :

2-Hydroxy-6-allyloxychromanone(LX):

Pulverized sodium (1.15 g) was kept in dry ether (5 ml) in a flask fitted with water condenser and maintained at 20° for 1.5 hr. During this period the solution of 2-hydroxy 5-allyloxyacetophenone[128] (1.92 g) in ethyl formatie (16 ml) was added to it drop by drop. When the reaction subsided, more ethyl formate (8 ml) was added, and the reaction mixture was refluxed at 65° for 10 minutes. It was then left at room temperature for two days. Alcohol and water were successively added with care and the resulting alkaline solution was extracted twice with ether. The aqueous alkaline layer was acidified with cold dilute acetic acid . A crystalline brown solid separated was filtered and washed with water. It crystallised from benzene as colourless small prisms, m.p. 114°, yield 1.2 g. It developed red-brown colour with alcoholic ferric chloride very slowly and colour became more fast on standing.

Analysis : Found : C, 65.43 ; H, 5.41 %

$C_{12}H_{12}O_4$ requires : C, 65.45 ; H, 5.45 % .

IR ν_{max}(nujol) : 1665 cm^{-1} ( )C=O group), and a broad band at 3235 cm^{-1} (-OH group). UV λ_{max} (methanol) : 339 nm (log e 3.95), ; (methanol + dil. sodium hydroxide): 338 nm (log e 4.28).

6-Allyloxychromone(LXI) :

2-Hydroxy-6-allyloxychromanone (2 g) was treated with sulphuric acid (30 % ; 60 ml) in a flask and heated on a water bath for 2 hr. After cooling, the pasty product separated was washed with water and sodium bicarbonate solution and purified by passing it over a column of active basic alumina using petroleum ether (b.p. 60-80°) as eluent. It crystallised as pale yellow needles from petroleum ether, m.p. 64°, yield 1.3 g.

Analysis : Found : C, 71.78 ; H, 5.11 %

$C_{12}H_{10}O_3$ requires : C, 71.28 ; H, 4.95 % .

5-Allyl-6-hydroxychromone(LXII) :

6-Allyloxychromone (1 g) was refluxed with dimethyl-aniline (6 ml) for 80 minutes, after cooling the reaction mixture was poured into ice containing hydrochloric acid (20 ml). The separated product was treated with sodium hydroxide solution, filtered and acidified with dil.hydrochloric acid. The product chromatographed over silica gel and eluted with a mixture of benzene-chloroform (4:1). It crystallised as colourless shining needles from benzene, m.p. 186°, yield 0.8 g.

Analysis : Found : C, 71.15 ; H, 4.71 %

$C_{12}H_{10}O_3$ requires : C, 71.28 ; H, 4.95 % .

IR ν_{max}(nujol) : 1635 cm^{-1} (γ-pyronyl >C=O group), and a broad band at 3160 cm^{-1} (aromatic -OH group).

4H-furo(3,2-f)benzopyran-4-one(LXIII) :

5-Allyl-6-hydroxychromone (0.6 g) in ethyl acetate (80 ml) and osmium tetroxide (60 mg) in water (30 ml) were vigorously stirred for 15 minutes, Potassium periodate (1.5 g) was added in small quantities to the dark solution over a period of 2 hr. The reaction mixture was stirred 1 hr. more. The ethyl acetate layer was separated, washed with water, dried with sodium sulphate and distilled. The residue, 5-acetaldehydo product was taken in PPA (12 ml) and heated in an oil bath for 1.5 hr. at 115°. The reaction mixture was poured over ice. The separated product was extracted with ethyl acetate, washed successively with very dil. sodium hydroxide solution and with water, dried with sodium sulphate and the solvent distilled off. The crude product dissolved in benzene (1.5 ml) and percolated through a column of silica gel. Elution with petroleum ether-benzene mixture (2:3) yielded LXIII (0.14 g) which crystallised from a mixture of benzene-petroleum ether as colourless needles, m.p. 188°.

Analysis : Found : C, 70.49 ; H, 3.32 %

$C_{11}H_6O_3$ requires : C, 70.98 ; H, 3.23 % .

UV λ_{max}(methanol) : 262 nm (log e 4.22), 291 nm (log e 4.26), 318 nm (log e 4.27).

Synthesis of 2-methyl-4H-furo(3,2-f)benzopyran-4-one (LXV) :

2-Methyl-2,3-dihydro-4H-furo(3,2-f)benzopyran-4-one (LXIV) :

5-Allyl-6-hydroxychromone (0.6 g) was triturated

with sulphuric acid (85 % ; 6 ml) in a water bath for 12 minutes, the content was poured into crushed ice, the separated product was filtered and washed with dil. sodium-hydroxide solution. It crystallised from petroleum ether as cream coloured needles, m.p. 123-4°, yield 0.4 g.

Analysis : Found : C, 71.76 ; H, 5.40 %

$C_{12}H_{10}O_3$ requires : C, 71.28 ; H, 4.95 % .

2-Methyl-4H-furo(3,2-f)benzopyran-4-one (LXV) :

A Mixture of 2-methyl-2,3-dihydro-4H-furo (3,2-f)-benzopyran-4-one (0.3 g), palladised charcoal (10 % ; 0.5 g) and diphenyl ether (5 ml) was refluxed for 8 hr. The reaction mixture was filtered hot and filterate was steam distilled to remove diphenyl ether. The remaining residue was extracted with ethyl acetate. The solvent was distilled off, the residue was chromatograph over silica gel and eluted with a mixture of petroleum ether-benzene (7:3) gave the product, which crystallised from ethanol as colourless small needles, m.p. 134°, yield 0.16 g.

Analysis : Found : C, 71.97 ; H, 4.50 %

$C_{12}H_8O_3$ requires : C, 72.00 ; H, 4.00 % .

UV λ_{max}(methanol) : 227 nm (log e 4.64), 265 nm (log e 4.28), 294 nm (log e 4.28), 328 nm (log e 4.31).

Synthesis of 9-methyl-4H-furo (3,2-f)benzopyran-4-one(LXXIII):

2,5-Dihydroxy-4-methylacetophenone (LXVIII) :

2,5-Diacetoxytoluene m.p. 49-50° (4.16 g) prepared

from 2,5-dihydroxytoluene by the action of acetic anhydride in presence of pyridine, was throughly mixed with anhydrous aluminium chloride (8.0)g) and the mixture slowly heated in an oil bath at 100° for 1 hr. and then at 120° for 1.5 hr. The reaction mixture poured over crushed ice containing conc.hydrochloric acid (20 ml). The separated product was filtered, washed with water and dissolved in sodium hydroxide solution (6 %), filtered and the filterate on acidification with hydrochloric acid gave 2,5-dihydroxy-4-methylacetophenone (1.5 g). It crystallised from aqueous ethanol, m.p. 148-9°. It developed green colour with alcoholic ferric chloride.

Analysis : Found : C, 65.50 ; H, 5.74 %

$C_9H_{10}O_3$ requires : C, 65.06 ; H, 6.02 % .

IR ν_{max}(nujol) : 1640 cm^{-1}($-COCH_3$ group), and broad band at 3305 cm^{-1}(aromatic -OH group).

2-Hydroxy-4-methyl-5-allyloxyacetophenone(LXIX) :

A mixture of 2,5-dihydroxy-4-methylacetophenone (3.3 g), anhydrous potassium carbonate (10 g) and allyl bromide (1.8 ml) in dry acetone (80 ml) was refluxed on a water bath for 8 hr. After the evaporation of acetone the remaining solution was acidified by dil.hydrochloric acid and extracted with ether. The ethereal layer was shaken with sodium hydroxide solution (12 %) and the separated sodium salt was filtered. It was then acidified and extracted with ether. On evaporation of ether, a greenish yellow liquid was obtained which was used for further reaction.

2-Hydroxy-6-allyloxy-7-methylchromanone (LXX) :

The solution of 2-hydroxy-4-methyl-5-allyloxy-acetophenone (3.0 g) in ethyl formate (16 ml) was allowed to react slowly with pulverized sodium (1.7 g) kept in dry ether (5 ml) at 15° for 1 hr. More ethyl formate (9 ml) was added as usual, and the reaction mixture was refluxed in a water bath at 55° for 15 minutes and left overnight at room temperature. The reaction mixture was worked up as before. The product crystallised from aqueous ethanol as colourless needles, m.p. 142° (decom.) yield 1.7 g. It did not develop any colour with alcoholic ferric chloride even on keeping for long time.

Analysis : Found : C, 67.08 ; H, 5.98 %

$C_{13}H_{14}O_4$ requires : C, 66.67 ; H, 5.98 % .

IR ν_{max}(nujol): 1659 cm^{-1} (>C=O group), and a broad band at 3280 cm^{-1} (-OH group). UV λ_{max}(methanol) : 228 nm (log e 4.80), 324 nm (log e 4.22); (methanol + dil.sodium hydroxide): 227 nm (log e 4.37), 324 nm (log e 4.20).

6-Allyloxy-7-methylchromone (LXXI) :

2-Hydroxy-6-allyloxy-7-methylchromanone (1.8 g) was dehydrated with sulphuric acid (30 % ; 50 ml) in a water bath for 90 minutes and the reaction mixture was worked up as before. The product crystallised as colourless shining needles, m.p. 80-82°, yield 1.1 g.

Analysis : Found : C, 72.11 ; H, 5.62 %

$C_{13}H_{12}O_3$ requires : C, 72.21 ; H, 5.55 % .

Fig. 28 : NMR ($CDCl_3$): δ 2.33 (s, 3H, C_7-CH_3), 4.58(d, J=6Hz, 2H, -O-$\underline{CH_2}$-CH=CH_2), 5.17-5.49(m, 2H, -O-CH_2-CH=$\underline{CH_2}$), 5.81-6.14 (m, 1H, -O-CH_2-$\underline{CH}$=CH_2), 6.20 (d, J=6Hz, 1H, C_3-H), 7.14 (s, 1H, C_8-H), 7.38 (s, 1H, C_5-H), 7.67 (d, J=6Hz, 1H, C_2-H).

5-Allyl-6-hydroxy-7-methylchromone (LXXII) :

6-Allyloxy-7-methylchromone (1.5 g) was refluxed with dimethylaniline (12 ml) for 3 hr. The reaction mixture was worked up as before. The product crystallised from benzene as colourless plates, m.p. 171°, yield 1.1 g.

Analysis : Found : C, 72.41 ; H, 5.76 %

$C_{13}H_{12}O_3$ requires : C, 72.21 ; H, 5.55 % .

IR ν_{max} (nujol) : 1641 cm^{-1} (γ-pyronyl >C=O group), and a broad band at 3140 cm^{-1} (aromatic -OH group).

9-Methyl-4H-furo(3,2-f)benzopyran-4-one (LXXIII) :

5-Allyl-6-hydroxy-7-methylchromone (0.7 g) in ethyl acetate (120 ml) and osmium tetroxide (50 mg) in water (40 ml) were vigorously stirred for 20 minutes. Potassium periodate (1.5 g) was added in small quantities as in case of LXIII. The intermediate 5-acetaldehydo product was treated with PPA (15 ml) for 3 hr. at 125°. The reaction mixture was worked up as before. The product crystallised from ethanol as fine needles, m.p. 140°, yield 0.16 g.

Analysis : Found : C, 71.86 ; H, 4.09 %

$C_{12}H_8O_3$ requires : C, 72.00 ; H, 4.00 % .

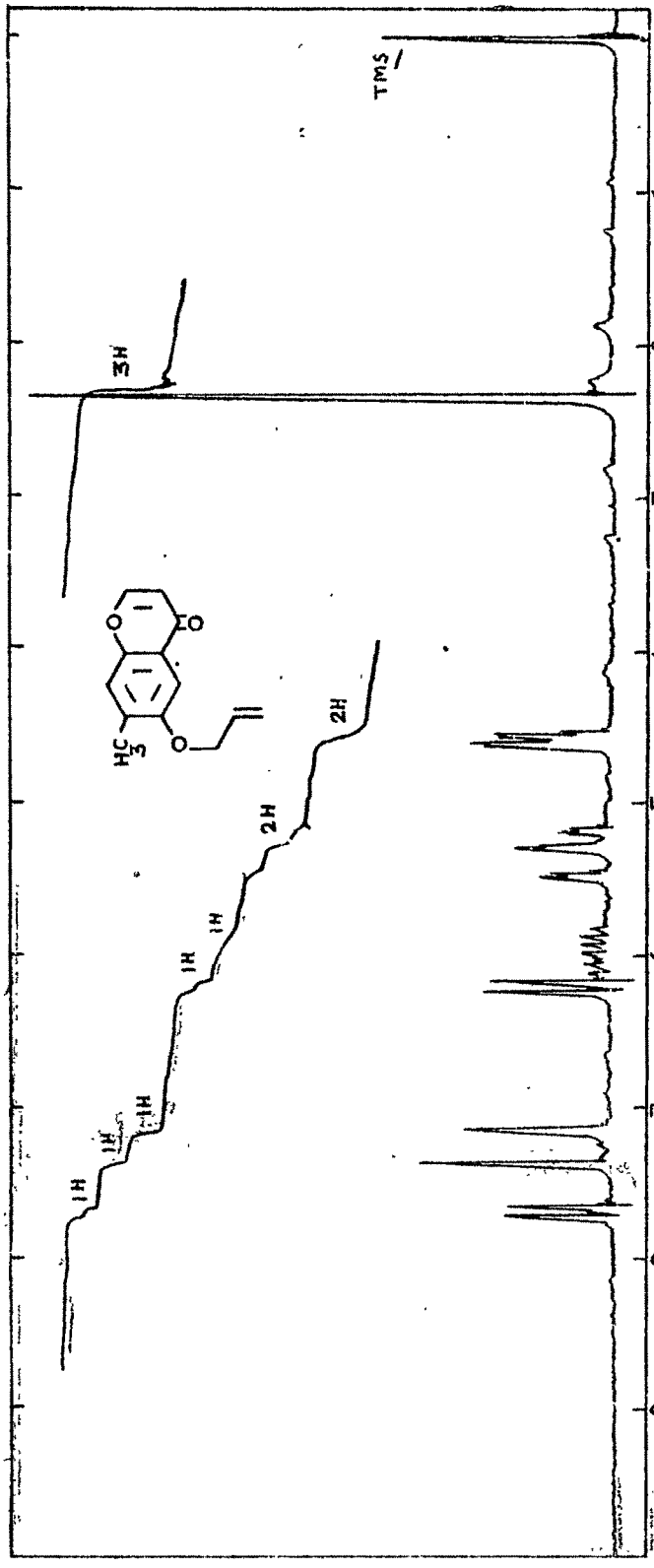


Fig. 28 : NMR spectrum of 6-Allyloxy-7-methylchromone (LXXI) in $CDCl_3$ (90 MHz).

Synthesis of 2,9-dimethyl-4H-furo(3,2-f)benzopyran-4-one (LXXV) :

2,3-Dihydro-2,9-dimethyl-4H-furo(3,2-f)benzopyran-4-one(LXXIV):

5-Allyl-6-hydroxy-7-methylchromone (1 g) was dissolved in sulphuric acid (85 % ; 20 ml) and the solution was heated in a water bath at 80° for 15 minutes. The reaction mixture was poured into ice cold water and worked up as before. The product crystallised from benzene-petroleum ether mixture as cream coloured prisms, m.p. 135°, yield 0.6 g.

Analysis : Found : C, 72.07 ; H, 5.60 %

$C_{13}H_{12}O_3$ requires : C, 72.21 ; H, 5.55 % .

2,9-Dimethyl-4H-furo(3,2-f)benzopyran-4-one(LXXV) :

2,3-Dihydro-2,9-dimethyl-4H-furo(3,2-f)benzopyran-4-one (0.4 g) was refluxed in diphenyl ether (8 ml) with palladised charcoal (10 % ; 0.7 g) for 8 hr. The reaction mixture was worked up as described before. The dried residue was purified by column chromatography over silica gel using petroleum ether-benzene mixture (2:3) as eluent. The product crystallised from ethanol as small needles, m.p. 147°, yield 0.2 g.

Analysis : Found : C, 72.93 ; H, 4.64 %

$C_{13}H_{10}O_3$ requires : C, 72.89 ; H, 4.67 % .

$UV\lambda_{max}$ (methanol) : 228 nm (log e 4.72), 264 nm (log e 4.33), 296 nm (log e 4.37), 325 nm (log e 4.30).

SYNTHESIS OF CYCLOHEXA- AND CYCLOPENTAFUROCHROMONES :

Synthesis of 9-methyl-1,2,3,4-tetrahydro-5H-benzofuro[4,5-b][2]-benzopyran-5-one(LXXXVI) :

8-Hydroxy-1,2,3,4-tetrahydro-5H-dibenzo[b,e]pyran-5-one(LXXXI):

A mixture of resorcinol (3 g) and ethyl cyclohexanone-2-carboxylate (4 ml) was refluxed with diphenyl ether (10 ml) for 3 hr. with a short condenser to facilitate the removal of alcohol formed. After cooling the separated product was filtered and washed several time with petroleum ether. It crystallised from ethanol, m.p. 278°, yield 2.0 g.

Analysis : Found : C, 72.38 ; H, 5.79 %

$C_{13}H_{12}O_3$ requires : C, 72.21 ; H, 5.55 % .

8-Allyloxy-1,2,3,4-tetrahydro-5H-dibenzo[b,e]pyran-5-one (LXXXII) :

A mixture of LXXXI (2 g), allyl bromide (1 g) and anhydrous potassium carbonate (8 g) was refluxed in dry acetone (200 ml) in a water bath for 10 hr. The reaction mixture was worked up as described before. The product crystallised from petroleum ether, m.p. 88°, yield 1.5 g.

Analysis : Found : C, 74.98 ; H, 6.24 %

$C_{16}H_{16}O_3$ requires : C, 75.00 ; H, 6.25 % .

8-Hydroxy-9-allyl-1,2,3,4-tetrahydro-5H-dibenzo[b,e]pyran-5-one (LXXXIII) :

8-Allyloxy-1,2,3,4-tetrahydro-5H-dibenzo[b,e]pyran-

-5-one (2 g) was refluxed with dimethylaniline for 8 hr. The reaction mixture was worked up as before. The product crystallised from ethanol, m.p. 236°, yield 1.5 g.

Analysis : Found : C, 74.54 ; H, 6.47 %

$C_{16}H_{16}O_3$ requires : C, 75.00 ; H, 6.25 % .

9-Allyl-1,2,3,4-tetrahydro-5-oxo-5H-dibenzo[b,e]pyran-8-yl acetate (LXXXIV) :

A mixture of LXXXIII (1.5 g) and acetic anhydride (6 ml) containing a few drops of pyridine was heated in a water bath for 6 hr. The reaction mixture was poured into crushed ice containing hydrochloric acid (2 ml). The separated product was filtered and washed with dilute sodium hydroxide solution. It crystallised from ethanol, m.p. 126°, yield 1.2 g.

Analysis : Found : C, 72.19 ; H, 5.87 %

$C_{18}H_{18}O_4$ requires : C, 72.49 ; H, 6.04 % .

9-(2',3'-Dibromopropyl)-1,2,3,4-tetrahydro-5-oxo-5H-dibenzo-[b,e]pyran-8-yl acetate (LXXXV) :

A solution of bromine (0.32 g) in glacial acetic acid (6 ml) was added drop wise to a well stirred solution of LXXXIV (0.6 g) in glacial acetic acid (8 ml) during a period of 1 hr. at room temperature. After being stirred further for 1 hr., the solution was diluted with ice cold water and allowed to stand. The product which separated out was filtered, dissolved in ethanol and decolourised by activated charcoal. It crystallised as colourless needles from

~~Analysis~~
ethanol, m.p. 171-2°(sintering from 166° and decomposed to a dark black melt at 175°), yield 0.7 g.

Analysis : Found : C,47.30 ; H,4.34 ; Br,35.41 %

$C_{18}H_{18}Br_2O_4$ requires : C,47.17 ; H,3.93 ; Br,34.93 % .

9-Methyl-1,2,3,4-tetrahydro-5H-benzofuro[4,5-b][2]benzopyran-5-one (LXXXVI) :

A solution of 9-(2',3'-dibromopropyl)-1,2,3,4-tetrahydro-5-oxo-5H-dibenzo[b,e]pyran-8-yl acetate (0.45 g) in ethanolic potassium hydroxide (0.3 g) in 20 ml absolute ethanol was heated under reflux~~ed~~ for 2 hr.,water (60 ml) was added and the solution was immediately acidified with dilute hydrochloric acid. The separated product was extracted with ethyl acetate and washed with aqueous ammonia (6 %) and then with water. The product crystallised from benzene as shining colourless needles, m.p. 169-70°, yield 0.15 g.

Analysis : Found : : C, 75.86 ; H, 5.40 %

$C_{16}H_{14}O_3$ requires : C, 75.60 ; H, 5.56 % .

Synthesis of 6-[2'-methyl-4'-hydroxybenzofuran-5'-yl -6-oxo-6H-hexanoic acid (XCII) :

7-Hydroxy-1,2,3,-trihydro-4H-cyclopenta[b]benzopyran-4-one (LXXXVII) :

A mixture of resorcinol (3 g) and ethyl cyclopentanone-2-carboxylate (4.5 g) was refluxed with diphenyl ether (6 ml) for 3 hr. with a short condenser to facilitate the

removal of alcohol formed. After cooling the product separated out was filtered and washed with petroleum ether. It crystallised from ethanol, m.p. 288°, yield 2 g.

Analysis : Found : C, 71.52 ; H, 5.35 %

$C_{12}H_{10}O_3$ requires : C, 71.29 ; H, 4.95 % .

7-Allyloxy-1,2,3-trihydro-4H-cyclopenta[b]benzopyran-4-one (LXXXVIII) :

A mixture of 7-hydroxy-1,2,3-trihydro-4H-cyclopenta[b]benzopyran-4-one (2 g), allyl bromide (1.2 g) and anhydrous potassium carbonate (6 g) was refluxed in dry acetone (200 ml) in a water bath for 10 hr. The reaction mixture was poured into water. The separated product was extracted with ether and washed with dilute sodium hydroxide solution to remove unreacted compound. It crystallised from a mixture of benzene-petroleum ether, m.p. 112°, yield 1.5 g.

Analysis : Found : C, 74.33 ; H, 5.76 %

$C_{15}H_{14}O_3$ requires : C, 74.39 ; H, 5.78 % .

8-Allyl-7-hydroxy-1,2,3-trihydro-4H-cyclopenta[b]benzopyran-4-one (LXXXIX) :

7-Allyloxy-1,2,3-trihydro-4H-cyclopenta[b]benzopyran-4-one (2 g) was refluxed with dimethylaniline (6 ml) for 8 hr. The separated crystalline product was filtered, washed with a mixture of light petroleum and benzene. The product crystallised from ethanol, m.p. 267°, yield 1.5 g.

Analysis : Found : C, 73.92 ; H, 5.84 %

$C_{15}H_{14}O_3$ requires : C, 74.39 ; H, 5.78 % .

IR ν_{max} (nujol) : 1640 cm^{-1} (γ-pyronyl >C=O group), and a broad band at 3085 cm^{-1}(aromatic -OH group).

8-Allyl-1,2,3-trihydro-4-oxo-4H-cyclopenta[b]benzopyran-7-yl acetate (XC) :

This was prepared by heating 8-allyl-7-hydroxy-1,2,3-trihydro-4H-cyclopenta[b]benzopyran-4-one (1.2 g) with acetic anhydride (8 ml) and a few drops of pyridine, in water bath and it was obtained as needles from ethanol, m.p. 158°, yield 1 g.

Analysis : Found : C, 71.80 ; H, 5.73 %

$C_{17}H_{16}O_4$ requires7 : C, 71.83 ; H, 5.63 % .

8-(2',3'-Dibromopropyl)-1,2,3-trihydro-4-oxo-4H-cyclopenta[b]-benzopyran-7-yl acetate (XCI) :

A solution of bromine (0.32 g) in glacial acetic acid (7 ml) was allowed to react with a solution of XC (0.57 g) in glacial acetic acid (10 ml). The reaction mixture was worked up as described before. The solid product ~~which~~ was separated and crystallized as small needles from alcohol, m.p. 162°(decom.), yield 0.4 g.

Analysis : Found : C,46.22 ; H, 3.73 ; Br, 35.85 %

$C_{17}H_{16}Br_2O_4$ requires : C,45.94 ; H, 3.60 ; Br, 36.03 % .

6-[2'-Methyl-4'-hydroxybenzofuran-5'-yl]-6-oxo-6H-hexanoic acid (XCII) :

8-(2',3'-Dibromopropyl)-1,2,3-trihydro-4-oxo-4H-

cyclopenta[b]benzopyran-7-yl acetate (0.45 g), when refluxed in absolute alcohol (0.25 ml) for 4 hr. gave XCII and not 8-methyl-1,2,3-trihydro-4H-cyclopenta[b]furo [2,3-h]benzo-pyran-4-one by working up the reaction mixture as described before. The product crystallized from ethanol as colourless prisms, m.p. 149-50°, yield 0.2 g. It was soluble in sodium bicarbonate solution and repricipitated on addition of acid and developed red colouration with ethanolic ferric chloride.

Analysis : Found : C, 64.90 ; H, 6.08 %

$C_{15}H_{16}O_5$ requires : C, 65.21 ; H, 5.79 % .

IR ν_{max} (nujol) : 835 cm^{-1} (furan ring breathing), 1650 cm^{-1} (>C=O group), 1730 cm^{-1} (-COOH group), and a broad band at 3400 cm^{-1} (- OH group).

8-Methyl-1,2,3,8,9-pentahydro-4H-cyclopenta[b]furo[2,3-h]-benzopyran-4-one(XCV) :

8-Allyl-7-hydroxy-1,2,3-trihydro-4H-cyclopenta[b]-benzopyran-4-one (1 g) was triturated with sulphuric acid (90 % ; 5 ml) in a water bath for 15 minutes. The content was poured into crushed ice, the separated product was filtered and washed with dilute sodium hydroxide solution. The product crystallized from ethanol, m.p. 178°, yield 0.8 g.

Analysis : Found : C, 74.36 ; H, 5.45 %

$C_{15}H_{14}O_3$ requires : C, 74.39 ; H, 5.79 % .

IR ν_{max} (nujol) : 1640 cm^{-1} (γ-pyronyl >C=O group).

UV λ_{max} (methanol) : 248 nm (log e 4.29), 256 nm (log e 4.32), 300 nm (log e 4.12), NMR ($CDCl_3$) : δ 1.52 (d, J=7Hz, 3H, C_8-CH_3),

1.95-2.29 and 2.70-3.08 (two broad multiplets, 6H, cyclopentanone ring protons), C. 2.30-3.62 (broad multiplet, 2H, C_9-H_2), 4.94-5.25 (m, 1H, C_8-H), 6.80 (d, J=10Hz, 1H, C_6-H), 8.06 (d, J=10Hz, 1H, C_5-H).

A NOVEL THERMAL DIMERIZATION REACTION OF 2-HYDROXYCHROMANONE DERIVATIVES:

Synthesis of 1-(7-allyloxy-8-methyl-3-chromonyl)-2-(2-hydroxy-3-methyl-4-allyloxybenzoyl)-ethylene (CIV) :

2-Hydroxy-7-allyloxy-8-methylchromanone (L) (1.2 g) was slowly heated in a test tube at 135° in an oil bath for 8 minutes. The evolved water vapour which condensed on the upper side of the test tube was removed and the temperature was then raised to 150° and maintained for further 10 minutes. The yellowish brown coloured solid formed in the test tube was removed and washed with sodium bicarbonate solution (8 %) and with water, dried and crystallized from n-butanol as yellow coloured shining fibrous crystals, m.p. 216°, yield 0.9 g.

Analysis :	Found	: C, 71.71 ; H, 5.09 %
$C_{26}H_{24}O_6$	requires	: C, 72.21 ; H, 5.55 %.

The title compound CIV was also prepared by a known procedure[36] described as below : 7-Allyloxy-8-methylchromone (LI) (1.0 g) was dissolved in dry ether (40 ml) and to this solution dry sodium ethoxide (from 0.6 g sodium metal) was added and the resulting red coloured solution was stirred 2 hr.

and then left overnight. The red solution was transfered into an evaporating dish and the solvent ether was removed at room temperature. The residue thus obtained was poured into ice cold water (80 ml) containing conc. hydrochloric acid (5 ml). The separated yellow coloured solid was filtered, washed with water, dried and crystallized from n-butanol as yellow fibrous crystals, m.p. 216°, yield 0.7 g. This product was identical (m.p., mixed m.p. 216°, co-TLC R_f 0.55 in chloroform and co-IR) with the above obtained product CIV.

Analysis : Found : C, 71.84 ; H, 5.76 %

$C_{26}H_{24}O_6$ requires : C, 72.71 ; H, 5.55 % .

Synthesis of 1-[2,3-dihydro-2,9-dimethyl-5-oxo-5H-furo(3,2-g) benzopyran-6-yl]-2-[2,3-dihydro-2,7-dimethyl-6-hydroxy-5-benzofuranoyl]-ethylene (CVI) :

2,9-Dimethyl-7-hydroxy-2,3,6,7-tetrahydro-5H-furo (3,2-g)benzopyran-5-one (LVI) (1.0 g) was slowly heated in a test tube at 138° in an oil bath for 10 minutes and then at 155° for further 10 minutes. The water vapour, which condensed on the side of the test tube was removed. The solid product, which formed in the test tube after cooling, was removed and washed with sodium hydrogen carbonate solution (6 %) and with water, dried and crystallized from n-butanol as yellow coloured small needles, m.p. 257°, yield 0.6 g.

Analysis : Found : C, 72.11 ; H, 6.03 %

$C_{26}H_{24}O_6$ requires : C, 72.21 ; H, 5.55 % .

The dimeric product CVI was also prepared as follows : 2,3-Dihydro-2,9-dimethyl-5H-furo(3,2-g)benzopyran-5-one (LVII) (0.8 g) was dissolved in dry ether (50 ml) and the solution was stirred with dry sodium ethoxide (from 0.5 g sodium metal) for 2 hr. It was then left overnight and the solvent was removed at room temperature. The residual pasty product was poured into ice cold water (70 ml) containing conc. hydrochloric acid (4 ml). The separated brownish yellow coloured solid was filtered, washed with water, dried and crystallized from n-butanol as yellow coloured crystals, m.p. 257°, yield 0.5 g. This product was identical (m.p., mixed m.p. 257°, co-TLC R_f 0.43 in chloroform and co-IR) with the above obtained product CVI.

Analysis : Found : C, 71.74 ; H, 5.59 %

$C_{26}H_{24}O_6$ requires : C, 72.21 ; H, 5.55 % .

Synthesis of 1-(7-allyloxy-3-chromonyl)-2-(2-hydroxy-4-allyloxybenzoyl)-ethylene (CVII) :

2-Hydroxy-7-allyloxychromanone(XLII) (1.0 g) was slowly heated at 155° in an oil bath for 10 minutes and temperature was then raised to 170° and maintained for further 10 minutes. The yellowish brown solid formed was washed with sodium bicarbonate solution (6 %) and with water, dried and crystallized from n-butanol as yellow coloured long shining needles, m.p. 198°, yield 0.75 g.

Analysis : Found : C, 71.51 ; H, 5.45 %

$C_{24}H_{20}O_6$ requires : C, 71.28 ; H, 4.95 % .

IR ν_{max} (nujol) : 1630 cm^{-1} (γ-pyronyl >C=O group), 1652 cm^{-1} (carbonyl >C=O group), and a weak band at 3080 cm^{-1} (-OH group).

The yellow dimeric product was also synthesised as described below : 7-Allyloxychromone(XLIV) (0.7 g) was dissolved in dry ether (35 ml) and to this solution dry sodium ethoxide (from 0.45 g sodium metal) was added and the resulting red coloured solution was shaken for some times and left overnight. Solvent ether was removed at room temperature and the residue was poured into ice cold water (60 ml) containing conc.hydrochloric acid (4 ml). The separated solid was filtered, washed with water, dried and crystallised from n-butanol as yellow coloured needles, m.p. 198°, yield 0.5 g. This product was identical (m.p., mixed m.p. 198°, co-TLC R_f 0.64 in chloroform and co-IR) with the above obtained product CVII.

Analysis : Found : C, 71.37 ; H, 5.36 %

$C_{24}H_{20}O_6$ requires : C, 71.28 ; H, 4.95 % .

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