CHAPTER-4

STUDIES IN SYNTHESES OF FURANOXANTHONES

THEORETICAL

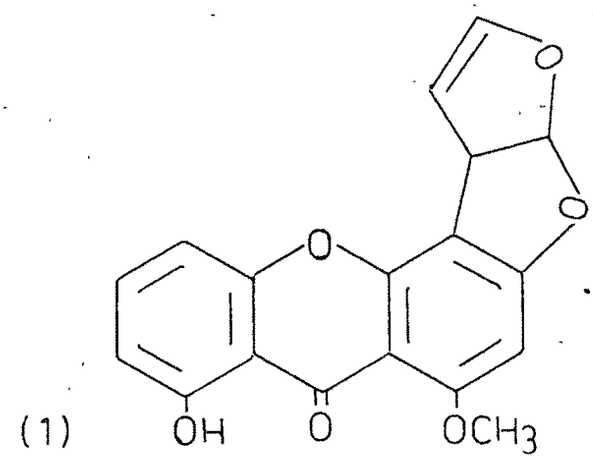
STUDIES IN SYNTHESES OF FURANOXANTHONES

Xanthones have been found in plants and in fungi. Simple furanoxanthones are not known to occur in nature, but complex furanoxanthone like sterigmatocystin[1,2] (1) (Chart 1) are isolated as a metabolite of Aspergillus verisicolor from mycelium. Recently other derivatives of sterigmatocystin[3,4,5] (2 to 7) (listed in Chart 1) have been isolated from other plants and Buchi et al[6] and Steyn et al[7] have made attempts to synthesise some of them.

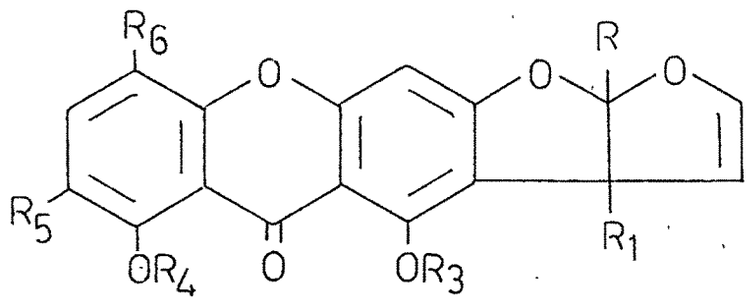
Many simple, 4'-methyl-, 4'-phenyl-, and 5'-methylfuranoxanthones have been prepared from the corresponding o-hydroxy formyl-, o-hydroxy acetyl-, o-hydroxy benzoyl-, and o-hydroxy allylxanthone. 4',5'-Diphenyl furanoxanthones were reported from hydroxyxanthones by direct condensation with benzoin. A literature survey about the syntheses of furano xanthone is presented below:

I. By Claisen or internal aldol condensation of o-hydroxy aldehyde or ketone

In this approach o-hydroxy aldehyde or ketone derivatives of xanthones are treated with bromoacetic



(1)

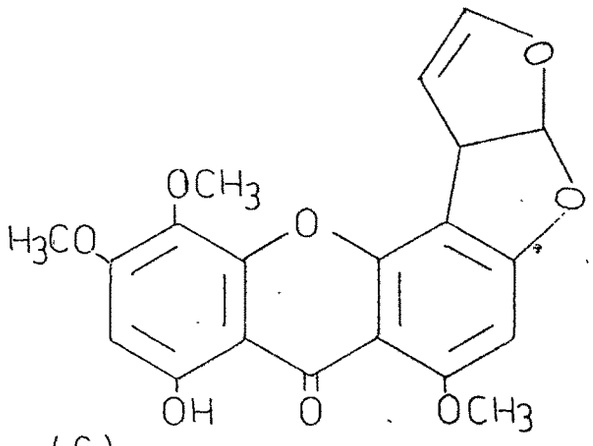


(2) $R = R_1 = R_6 = H$, $R_3 = R_4 = CH_3$, $R_5 = Cl$

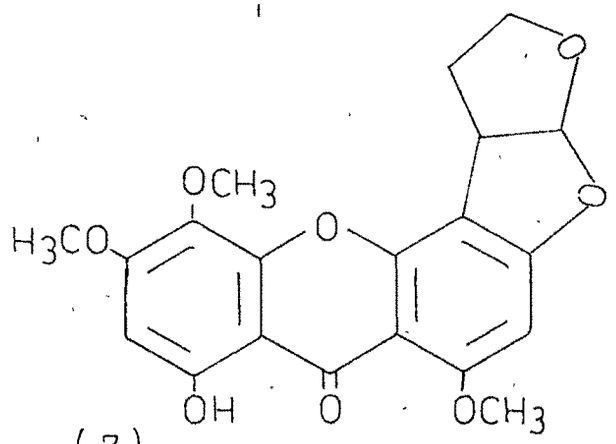
(3) $R = R_1 = R_5 = H$, $R_3 = R_4 = CH_3$, $R_6 = CH_2CH_2\overset{OH}{\overset{|}{C}}\text{-}(CH_3)_2$

(4) $R = R_3 = R_4 = R_5 = H$, $R_1 = OH$, $R_6 = CH_2CH_2\overset{OH}{\overset{|}{C}}\text{-}(CH_3)_2$

(5) $R = R_1 = OH$, $R_3 = R_4 = R_5 = R_6 = H$



(6)



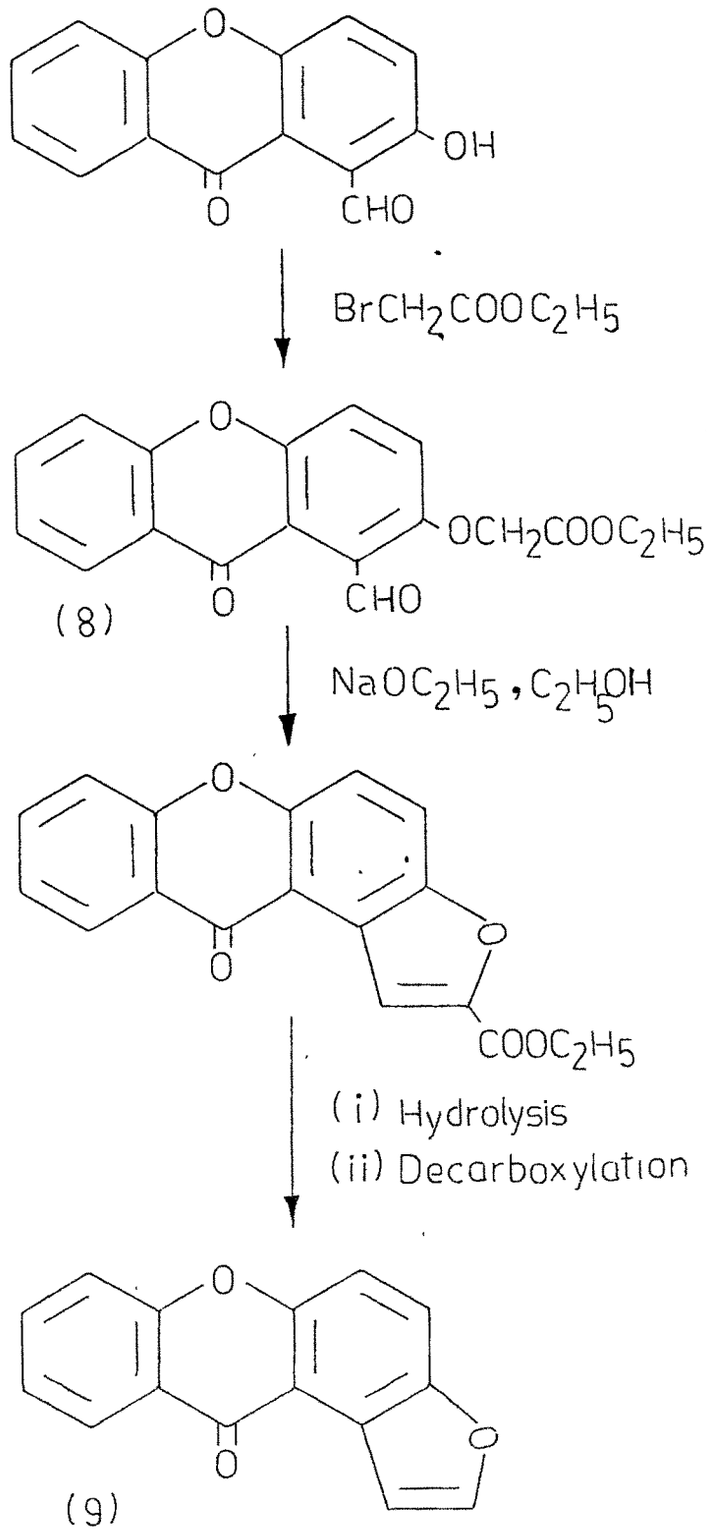
(7)

CHART - 1

or bromomalonic ester to get xanthyloxy ester, which either on hydrolysis followed by cyclization with sodium acetate and acetic anhydride or on cyclization with sodium ethoxide in ethanol followed by hydrolysis and decarboxylation give simple, 4'-methyl- or 4'-phenyl furanoxanthone.

Davies et al[8] have condensed 1-formyl-2-hydroxy xanthone with ethyl bromoacetate to obtain 1-formyl-2-xanthyloxy acetate (8). This was cyclised in ethanol with sodium ethoxide to yield 5'-carbethoxyfuro (3',2'-1,2) xanthone. Hydrolysis of this ester, followed by decarboxylation gave furano (3',2'-1,2) xanthone (9). This was also obtained by hydrolysis of (8) in alkali, followed by ring closure of acid accompanied by decarboxylation. Similarly, 4-formyl-3-hydroxyxanthones when condensed with bromomalonic ester, which effected simultaneous esterification and internal aldol condensation followed by hydrolysis and decarboxylation, yielded furano (2',3'-3,4) xanthone (10)[9].

4-Acetyl derivatives of 3-hydroxyxanthones condensed with ethyl bromoacetate to yield the corresponding 3-o-carbethoxy methyl derivatives, which on hydrolysis followed by internal Claisen condensation with sodium acetate and acetic anhydride was converted into 4'-methylfurano (2',3'-3,4) xanthone (11)[10,11].


O
OH
O
CHO
BrCH2COOC2H5
OCH2COOC2H5
(8)
NaOC2H5 , C2H5OH
COOC2H5
(i) Hydrolysis
(ii) Decarboxylation
(9)

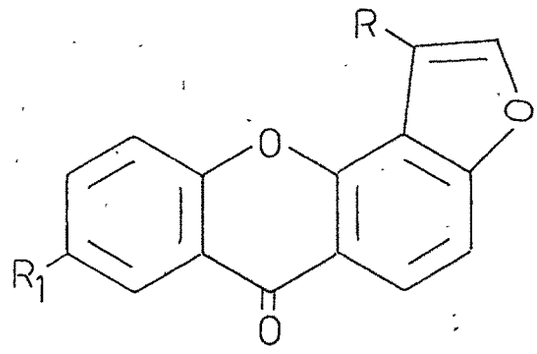
Similarly from 4-benzoyl derivatives of 3-hydroxyxanthone the synthesis of 4'-phenylfurano (2',3'-3,4) xanthones (12) is reported[12].

The synthesis of a few angular furano (2',3'-1,2) xanthone (13) carrying a methyl or phenyl group in 4'-position of furan ring, starting with a hydroxyxanthone is also reported[13].

Linear furanoxanthones viz., 4'-methylfurano (3',2'-2,3) xanthone (14), 4',7-dimethylfurano (3',2'-2,3) xanthone (15) and 4'-methyl-1-hydroxy furano (3',2'-2,3) xanthone (16)[15] was also synthesised by the above procedure.

II. From o-hydroxyallylxanthone derivatives

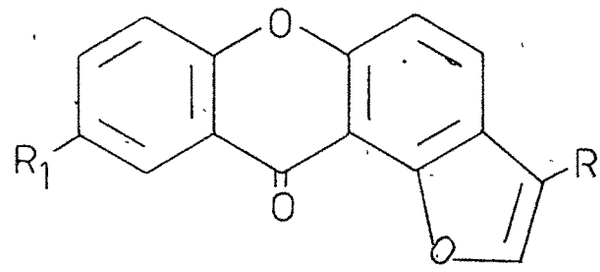
There are three different approaches leading to the formation of a furan ring. In the present work further exploration of a new approach is described. In the first approach Scheinmann and Suchitzky[16] carried out the Claisen migration of 1-allyloxy xanthone and obtained 2-allyl-1-hydroxyxanthone and reported the formation of dihydrofurano compound. It was brominated by treatment with N-bromo succinamide in presence of benzoyl peroxide and dehydrobrominated with pyridine to the corresponding 5'-methyl furano xanthone. Mustafa[17] et al. have prepared



(10) R=H , R_1=H or CH_3

(11) R=CH_3 , R_1=H or CH_3

(12) R=Ph , R_1=H or CH_3

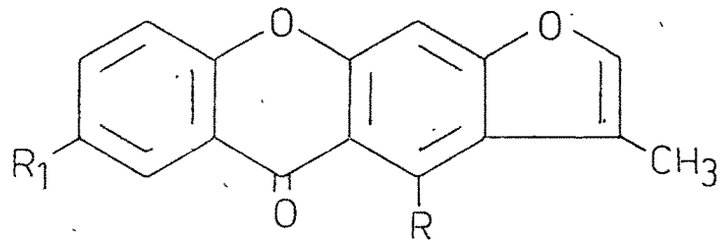


(a) R=CH_3 , R_1=H

(b) R=R_1=CH_3

(c) R=Ph , R_1=H

(d) R=Ph , R_1=CH_3



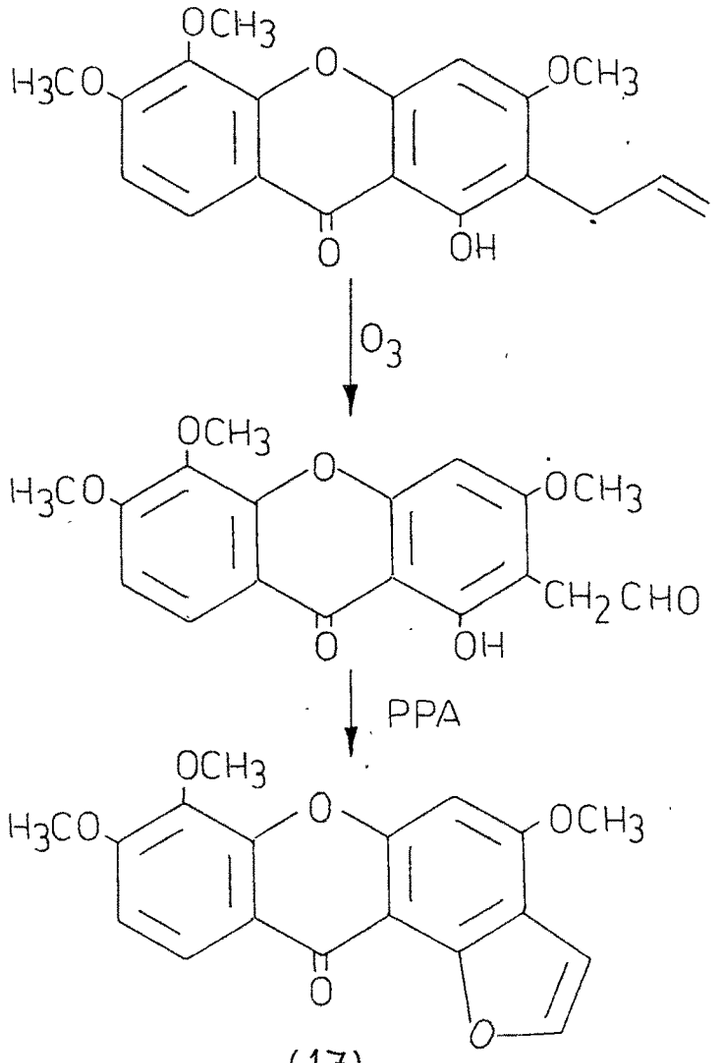
(14) R=R_1=H

(15) R=H , R_1=CH_3

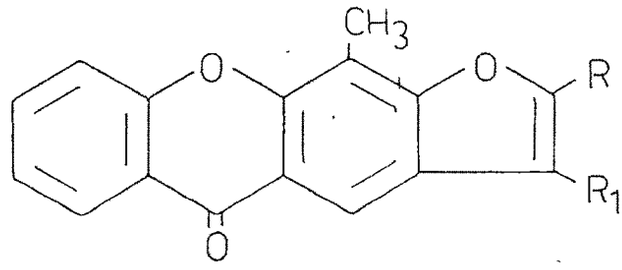
(16) R=OH , R_1=H

1-allyl-2-hydroxy-, 3-allyl-4-hydroxyxanthone from 2-allyoxy and 4-allyloxyxanthone and have reported the formation of dihydrofuranoxanthone derivatives. The second approach by Adams and Rindfusz[18] involving the addition of bromine to a o-acetoxy allyl derivative, followed by cyclisation and dehydrobromination. The third approach by Scheinmann and Coworkers[19] for the preparation of simple furanoxanthones consisted of ozonolysis of the o-hydroxy allyl derivatives followed by cyclisation with polyphosphoric acid. They have synthesised (17) from 1-hydroxy-2-allyl-3,5,6-trimethoxy xanthone.

The fourth one for the syntheses of furanoxanthones is an extension by Patolia and Trivedi[21] of the method developed by Shaikh and Trivedi[20] for the syntheses of furanocoumarins. The method consists of cyclisation of the o-hydroxyallylxanthone into dihydro furanoxanthone, by heating with conc. sulphuric acid followed by dehydrogenation with palladised charcoal. 1,5'-Dimethyl furano (2',3'-3,4) xanthone (17a), 4-methylfurano (3',2'-2,3) xanthone (18), 4,5'-dimethylfurano (3',2'-2,3) xanthone (19) 4,4'-dimethyl furano (3',2'-2,3) xanthone (20) and difuranoxanthone (3',2'-2,3) and (3",2"-5,6) xanthone (21) have been synthesised by them.



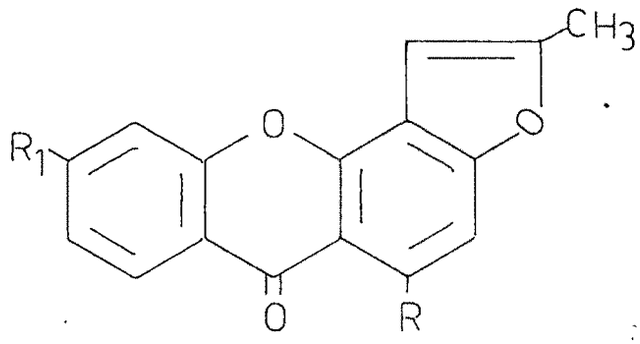
(17)



(18) $R = R_1 = H$

(19) $R = CH_3$, $R_1 = H$

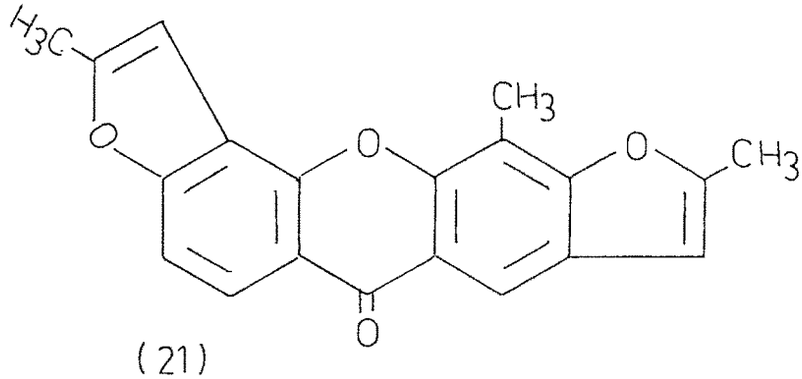
(20) $R = H$, $R_1 = CH_3$



(17a) $R = CH_3$; $R_1 = H$

(22) $R = R_1 = H$

(23) $R = H$, $R_1 = CH_3$

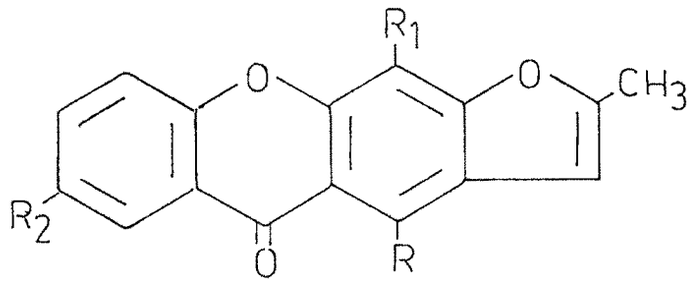


(21)

4-Allyl derivatives of 3-hydroxy-and 3-hydroxy-6-methylxanthone were obtained by Claisen migration of 3-allyloxy-and 3-allyloxy-6-methylxanthone, and converted into 5'-methylfurano (2',3'-3,4) xanthone (22) and 5',6-dimethylfurano (2',3'-3,4) xanthone (23)[22] respectively using first two approaches.

The syntheses of linear 5'-methylfuranoxanthones (24) were reported by Rajagopal and his coworkers[23,24]. Claisen migration of 3-allyloxy-4-methyl-, 3-allyloxy-4,7-dimethyl-, 3-allyoxy-4-acetyl-, and 3-allyoxy-4-acetyl-7-methylxanthone gave corresponding 3-hydroxy-2-allylderivatives, which were converted into corresponding 5'-methylfurano (3',2'-2,3) xanthones (24 R=CH_3, or $COCH_3$ R_1=H, CH_3etc.)[23,24] by adopting the method of Adams and Rindfusz[18]. They have also synthesised three different 5'-methylfuranoxanthone (25,26,27)[25] from 1-hydroxy-3-tosylxanthone by combination of allylation. Claisen migration, methylation, detosylation, acetylation, bromination and cyclisation reactions.

Rao and Rajagopal[26] have prepared 1-hydroxy-4',5'-diphenylfuranoxanthone (29) and benzoxanthone (30) and (31)[27] with possible antifertility activity by condensation of 1,3-dihydroxyxanthone (28) and benzoxanthone with benzoin in presence of PPA.



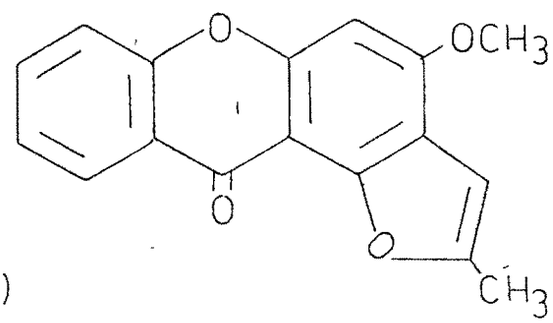
(24)a $R = R_2 = H$, $R_1 = CH_3$

b $R = H$, $R_1 = R_2 = CH_3$

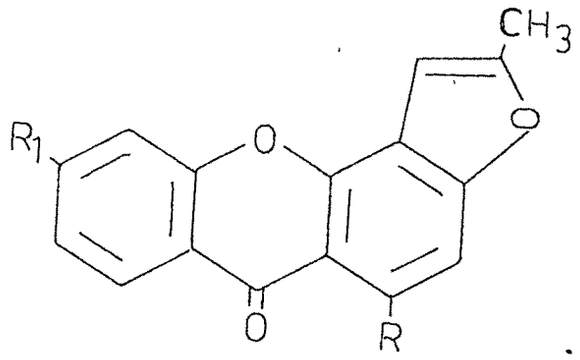
c $R = R_2 = H$, $R_1 = COCH_3$

d $R = H$, $R_1 = COCH_3$, $R_2 = CH_3$

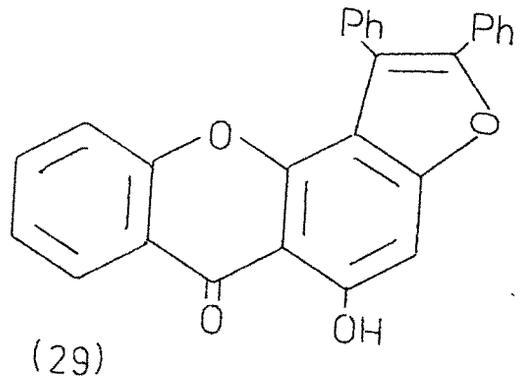
(25) $R = OCH_3$, $R_1 = R_2 = H$



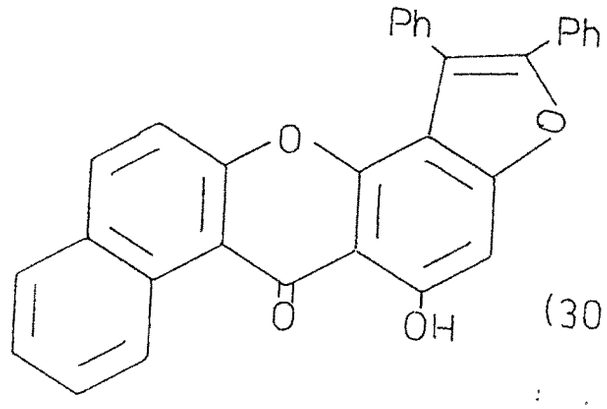
(26)



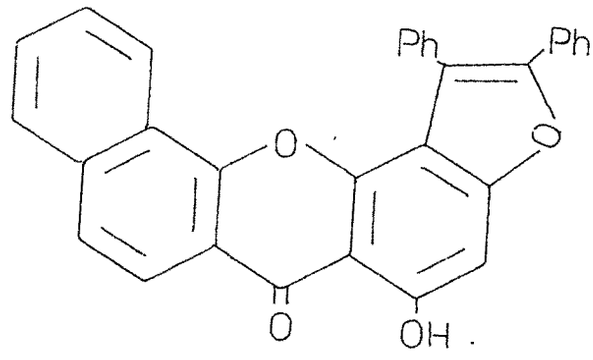
(27) $R = OCH_3$, $R_1 = H$



(29)



(30)



(31)

No attempts have been made to synthesize bromo furanoxanthones. Therefore the Claisen migration of bromoallyloxyxanthones has been studied in different solvents. Few bromofuranoxanthones have also been synthesised.

In the field of xanthones no 4'-phenylfurano xanthones have been prepared so far. The present chapter deals with syntheses of some 4'-phenylfurano xanthones by condensation of o-halo hydroxyxanthones with Cu salt of acetylinic compound, synthesis of 4'-phenyl-5'-methylfuranoxanthone and the syntheses of 5'-methyl-mono and difuranoxanthones.

PRESENT WORK

Claisen Rearrangement of 2,4-dibromo-3-allyloxy xanthone (32)

2,4-Dibromo-3-allyloxyxanthone (32) when refluxed in N,N-dimethyl aniline furnished two products: 2-bromo-3-hydroxy-4-allylxanthone (33) and 2-bromo-4', 5'-dihydro-5'-methylfurano (2',3'-3,4) xanthone (34) which was also obtained when (33) was cyclised using conc. H_2SO_4. Structure of (33) was confirmed by its mass and NMR spectral Mass m/e 332, 330 (M^+). NMR ($CDCl_3$) (Fig.1) showed a singlet in down field aromatic region at δ 8.4 for proton at position-1 suggesting that bromine at position 4 being eliminated during the reaction with simultaneous migration of allyl group to position 4. Proton at position 8 appears as doublet (J=9Hz) at δ 8.3, 7.7, td, 1H, J=8,8, 2Hz proton at position 6; 7.49, doublet, 1H, J=9Hz, proton at position 5; 7.35, td, 1H, J=8,8,2Hz proton at position 7; and three characteristic peaks for allyl group at δ 6.0, multiplet, 1H, $-CH_2\underline{C}H=CH_2$; 5.1, m, 2H, $CH_2-CH=C\underline{H}_2$; and 3.75, doublet, 2H, J=5Hz, $C\underline{H}_2CH=CH_2$. Mass of (34) m/e 332, 330 (M^+100) 304, 302 (M^+-CO).

NMR ($CDCl_3$) Fig. 2 showed an overlaping singlet and a doublet at δ 8.25 for the protons H-1 and H-8 respectively. Furthermore it exhibited a set of peaks between 7.3-7.65; m, for the three aromatic protons at positions 5,6 and 7; 5.25, m, 1H, C5'-H; 3.6, dd, 1H, J=9, 18Hz, C4'-H; 3.1, dd, 1H, J=9, 18Hz, C4'-H; 1.7, doublet, 1H, J=7Hz, C5'-CH_3. This indicates existence of dihydrofuran ring. (32), when refluxed in decalin gave (33). When heated under vacuum (0.05 mm) at 170°-180°, (32) gave two products: 2-bromo-5'-bromo methyl-4',5'-dihydrofurano (2',3'-3,4) xanthone (35) and 2-bromo-3-hydroxyxanthone (36). Structure of (35) was established on the basis of its IR, mass and NMR spectral studies. Mass spectrum of (35) m/e 412, 410, 408, 1:2:1 (M^+), 332, 330 (M^+-Br) indicates that it is a dibromoxanthone. NMR ($CDCl_3$) (Fig.3,4) showed two peaks beyond δ 8.0-ppm-one singlet at δ 8.22 for proton at position 1 and another double doublet of J value 9Hz and 2Hz at δ 8.2 due to periproton at position 8; 7.63, td, 1H, J=9,9,2Hz, H-6; 7.35, doublet, J=9Hz, H-5; 7.23, td, 1H, J=9,9,2Hz, H-7; 5.3, multiplet, 1H, C5'-H; 3.65, m, 2H,-CH_2Br; 3.4, doublet 2H, J=7Hz C4'H_2.

In the mass spectrum of compound (36) molecular ion peak appears at m/e 292, 290 (M^+) 264, 262 (M^+-CO) 235,233

246

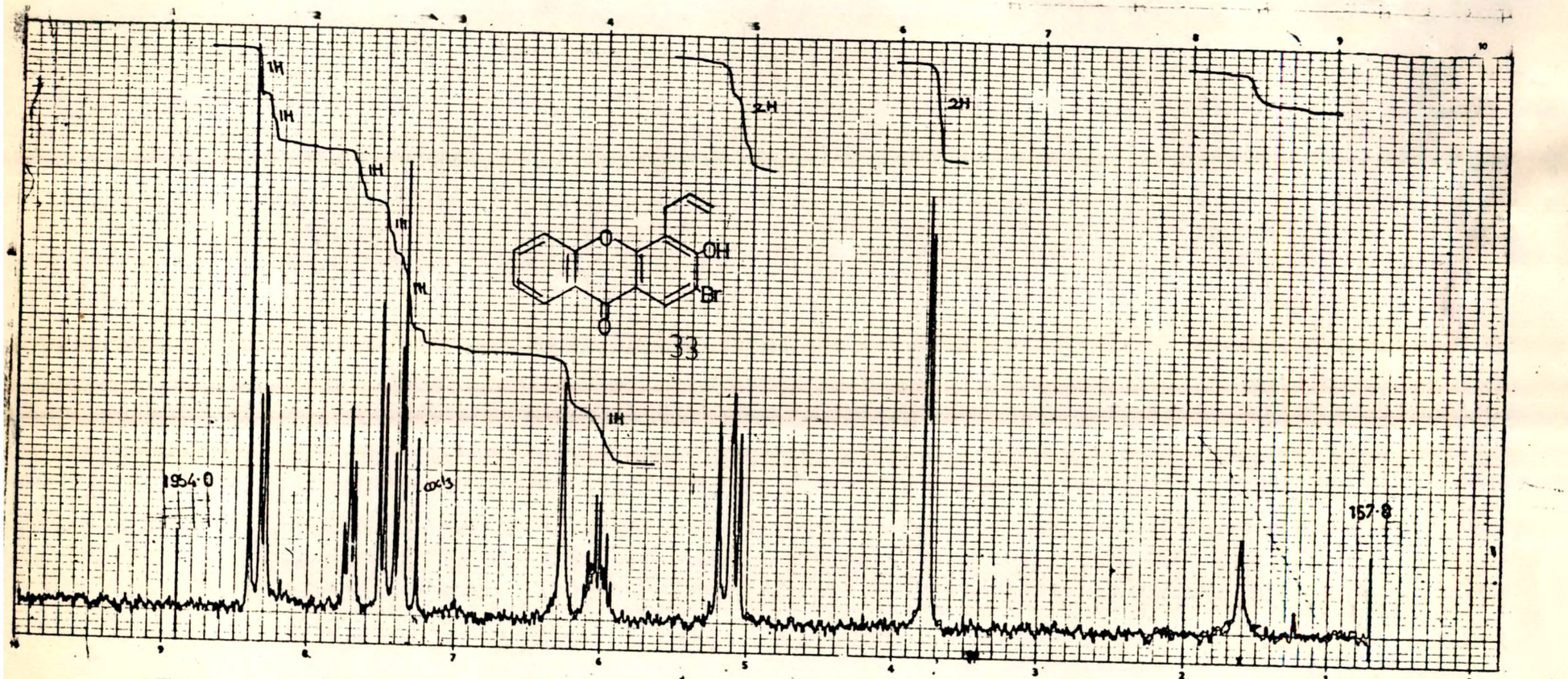


FIG 1

220MHz

247

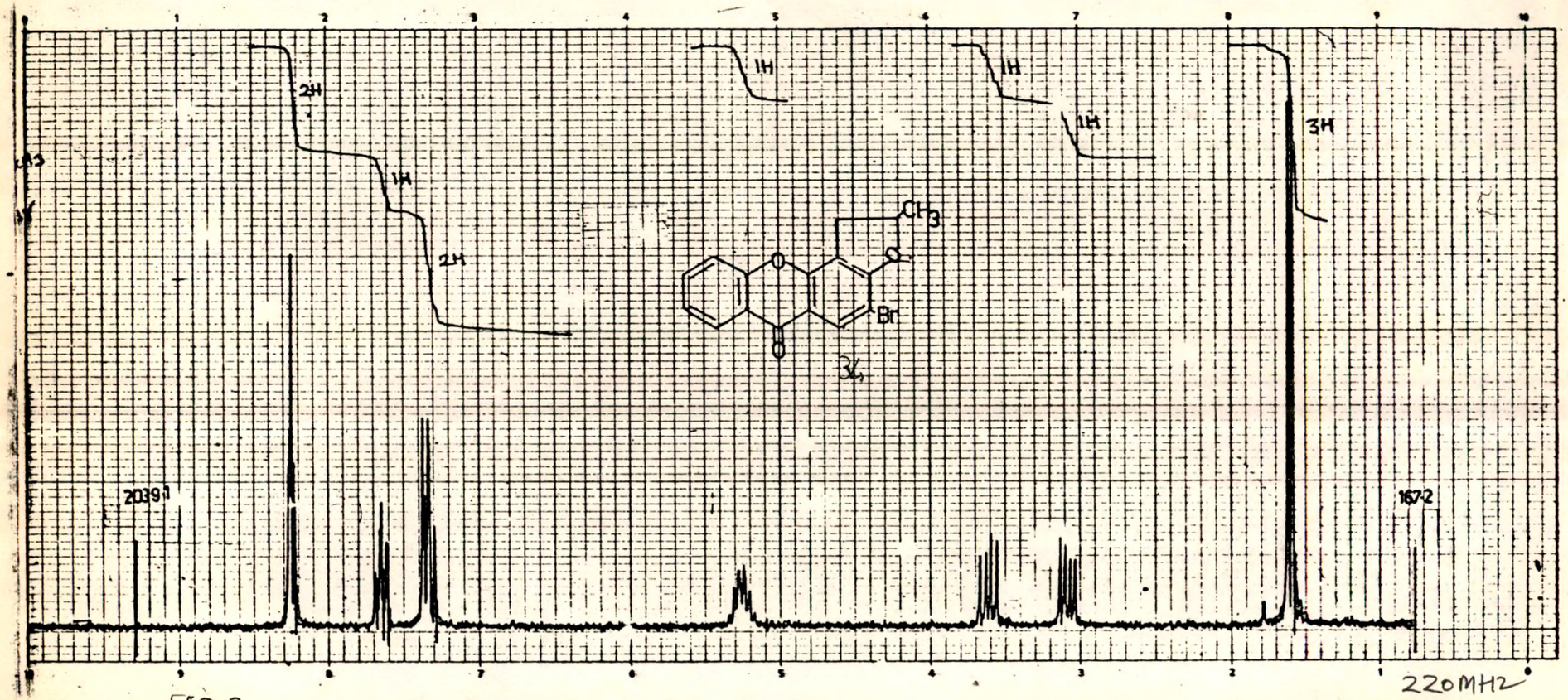


FIG 2

(M^+-CO.-CHO) suggesting that it is a monobromoxanthone. NMR ($CDCl_3/CD_3SOCD_3$) (Fig.5-7) showed the presence of a D_2O exchangeable signal at δ 11.5, singlet, 1H providing direct evidence for the free hydroxy group at position 3. Furthermore there are only two singlets in the aromatic region, one in the down field region at δ 8.25 which could be assigned to periproton at position 1 and another one, which appears at δ 7.03, is assigned to the proton at position 4. This indicates that bromine at position 4 is eliminated during heating. A single proton resonating at δ 8.15 as a double doublet J=8Hz, 2Hz due to coupling with proton H-7 ortho to it and proton H-6, is assigned to the periproton at position 8. The assignments of other three peaks were like this δ 7.4, td, 1H, J=8,8,2Hz, H-7; 7.52, doublet, 1H, J=8Hz, H-5; 7.77, td, 1H, J=8,8,$2H_z$, H-6. Thus NMR spectrum ruled out the possibility of any other rearranged product and confirmed the assigned structure (36). (32) on heating at 170-180°C, gave 2-bromo-5'-methylfurano (2',3'-3,4) xanthone (37) and (36). The structure of (37) was established on the basis of its IR, mass and NMR spectral studies IR (KBr) νmax 1650 (C=O), 1625 (C=C). Mass: m/e 330, 328 (M^+), 302, 300 (M^+-CO) suggests the presence of only one bromine in compound (37) which clearly indicates that one bromine is eliminated during reaction.

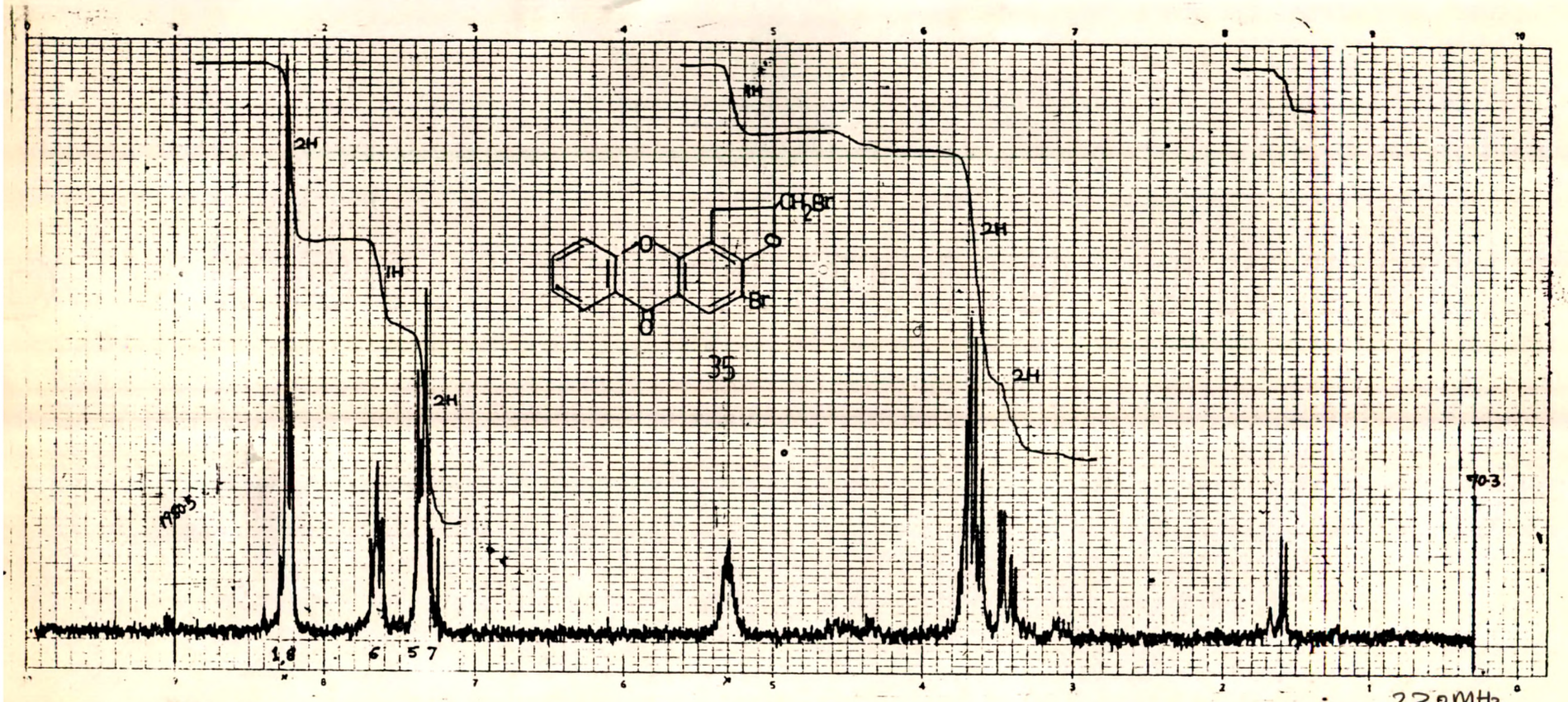


FIG 3

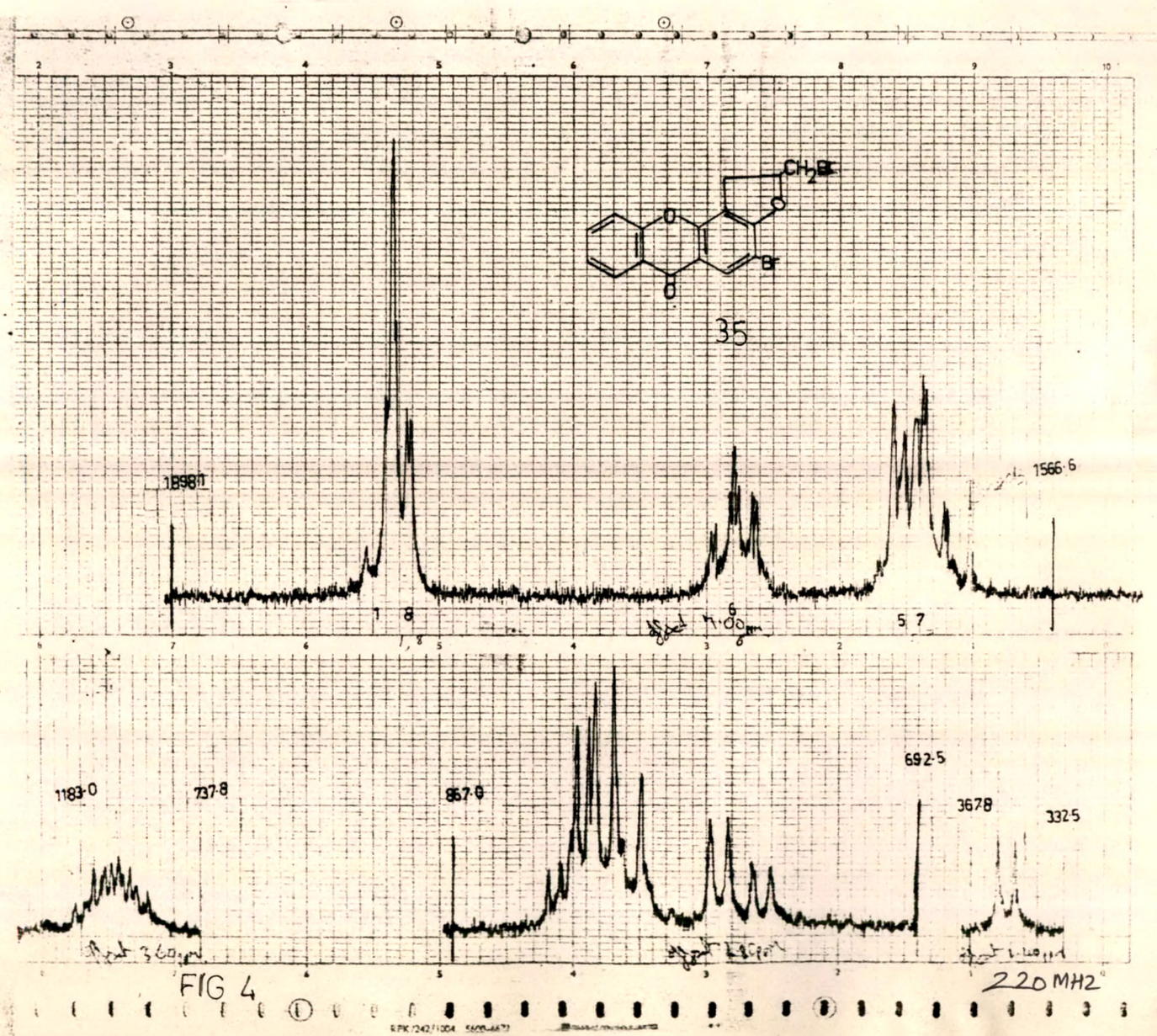

CH2Br
O
O
Br
O
35
1898·1
1566·6
1183·0
737·8
867·9
692·5
367·8
332·5
220 MHZ

FIG 4

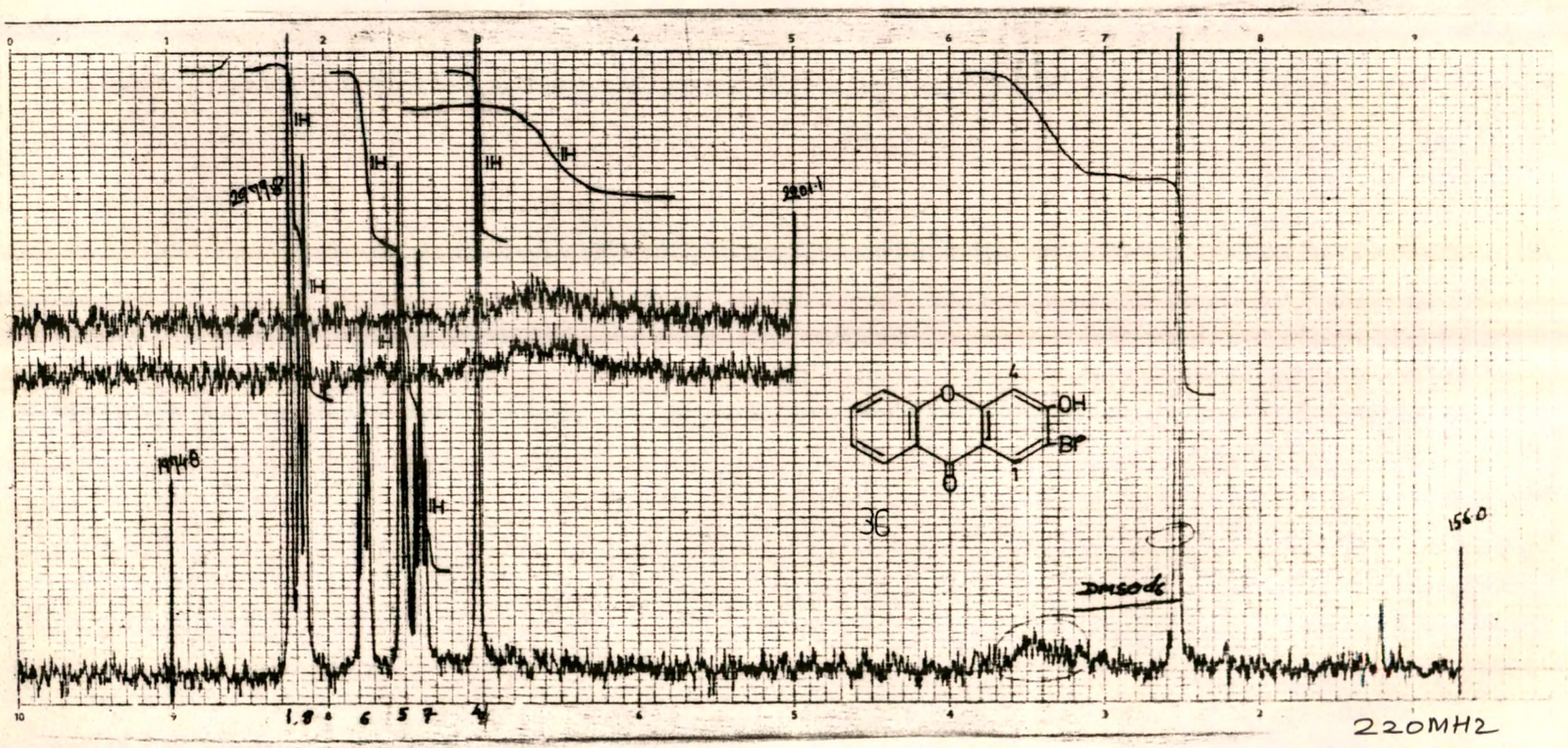


FIG 5

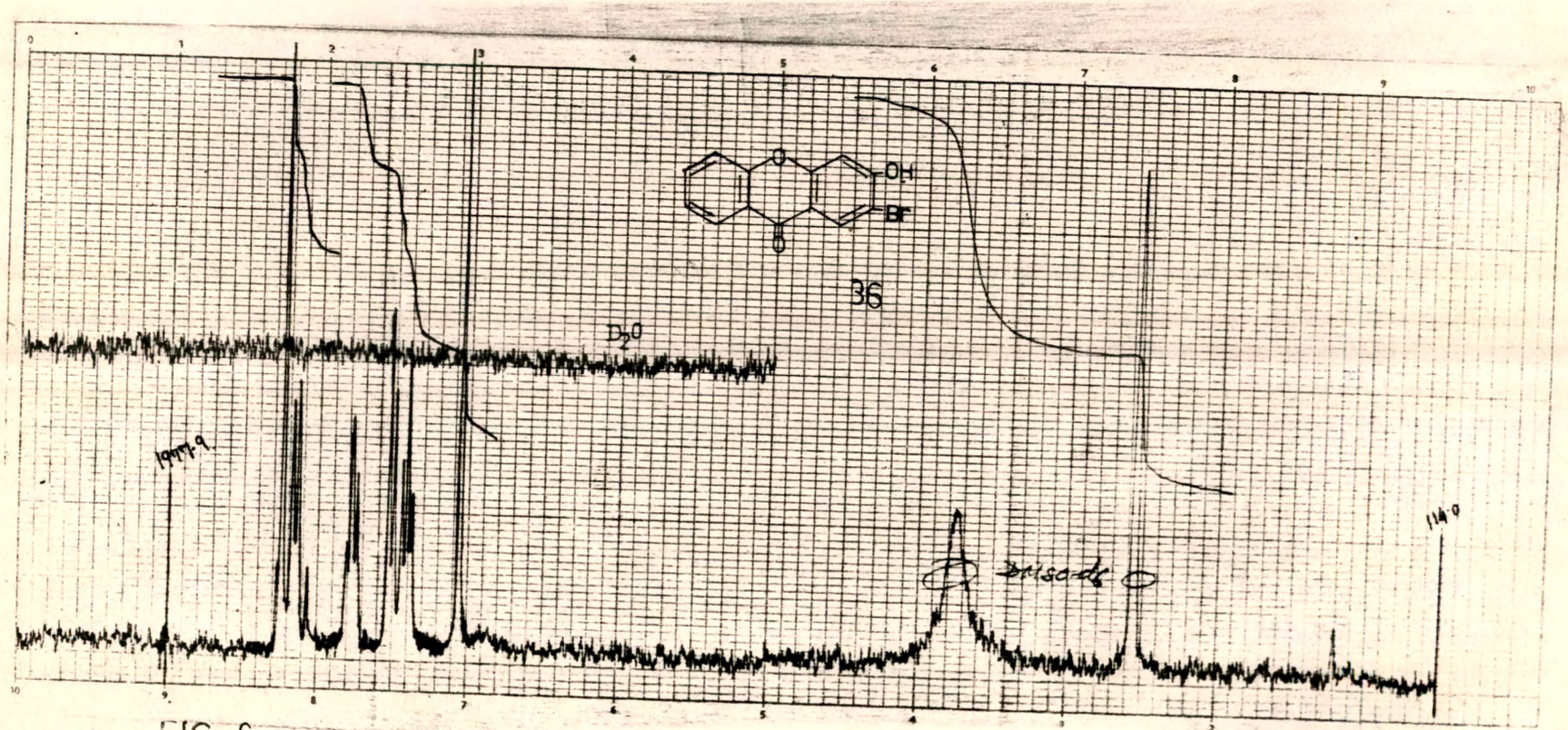


FIG 6

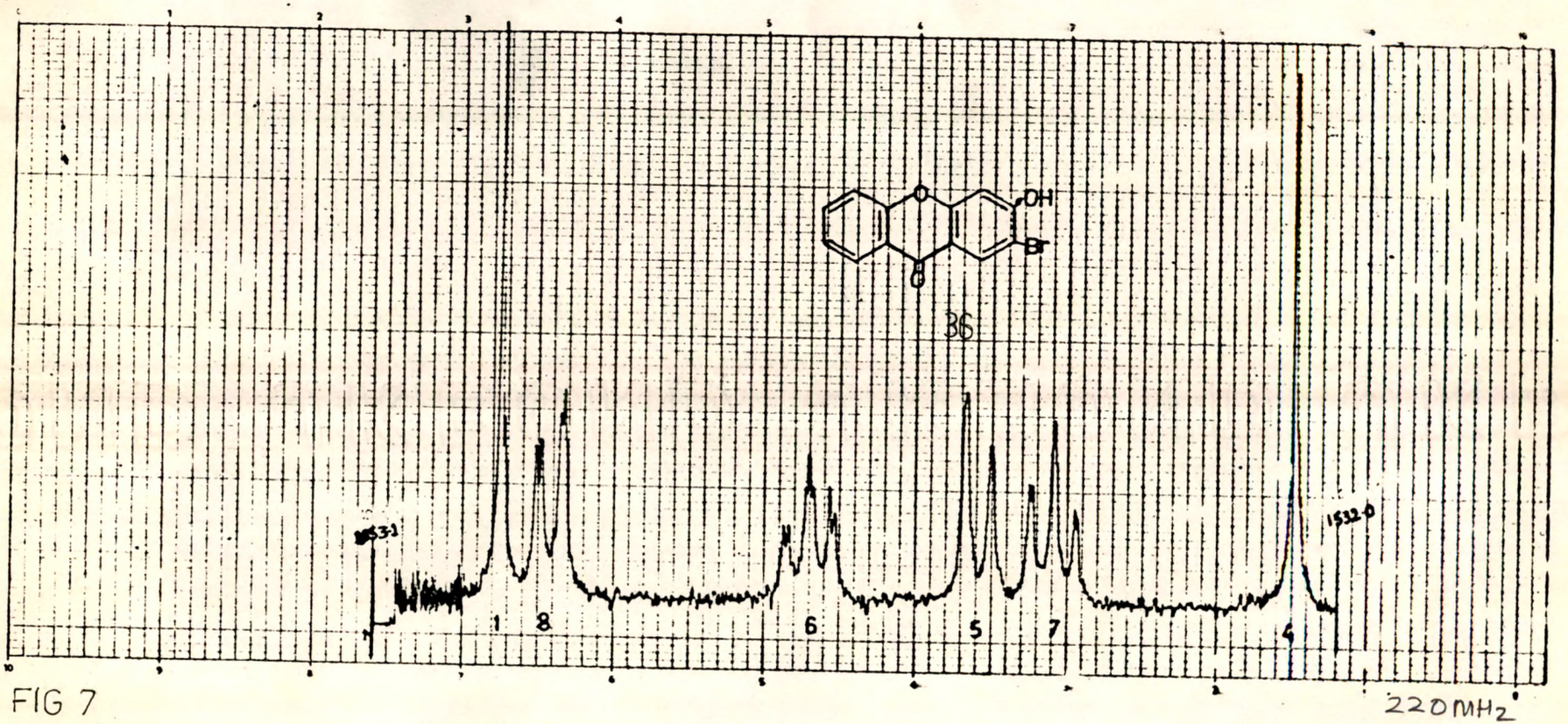


FIG 7

NMR ($CDCl_3$) (Fig.8,9) showed δ8.30, S, 1H, H-1; 8.32, dd, 1H, J=9, 2Hz, H-8; 7.76, td, 1H, J=9,9,2Hz H-6; 7.5, d, 1H, J=9Hz, H-5; 7.4, td, 1H, J=9,9,2Hz, H-7; 6.82, singlet for proton in furan ring at C_4'-H; 2.55, singlet of three protons of the methyl group at position C_5'. Thus the presence of last two signals in NMR spectrum ruled out the possibility for the dihydrofuran ring and presence of allyl group. Structure of this compound was further proved by its synthesis. Formation of compound (35) and (37) can be explained by mechanism shown in the Scheme (1). 2,4 Dibromo-3-allyloxyxanthone (32) when heated under vacuum, undergoes thermally favourable (1,3) sigmatrophic rearrangement giving rise to ketonic intermediate (38). This undergoes cyclisation involving bromine to give the product (35) which readily eliminates HBr under the thermal condition followed by prototropic shift to give (36). The formation of (35) and (37) in Claisen migration is a novel observation. The formation of dehydrogenated furan ring in (37) is possible due to the presence of bromine in the ortho position-otherwise a dihydrofuran derivative would have been obtained.

Dehydrogenation of (34) : 5'-methylfurano (2',3'-3,4) xanthone (39)

Compound (34) on dehydrogenation with palladised charcoal undergoes elimination of bromine and gives

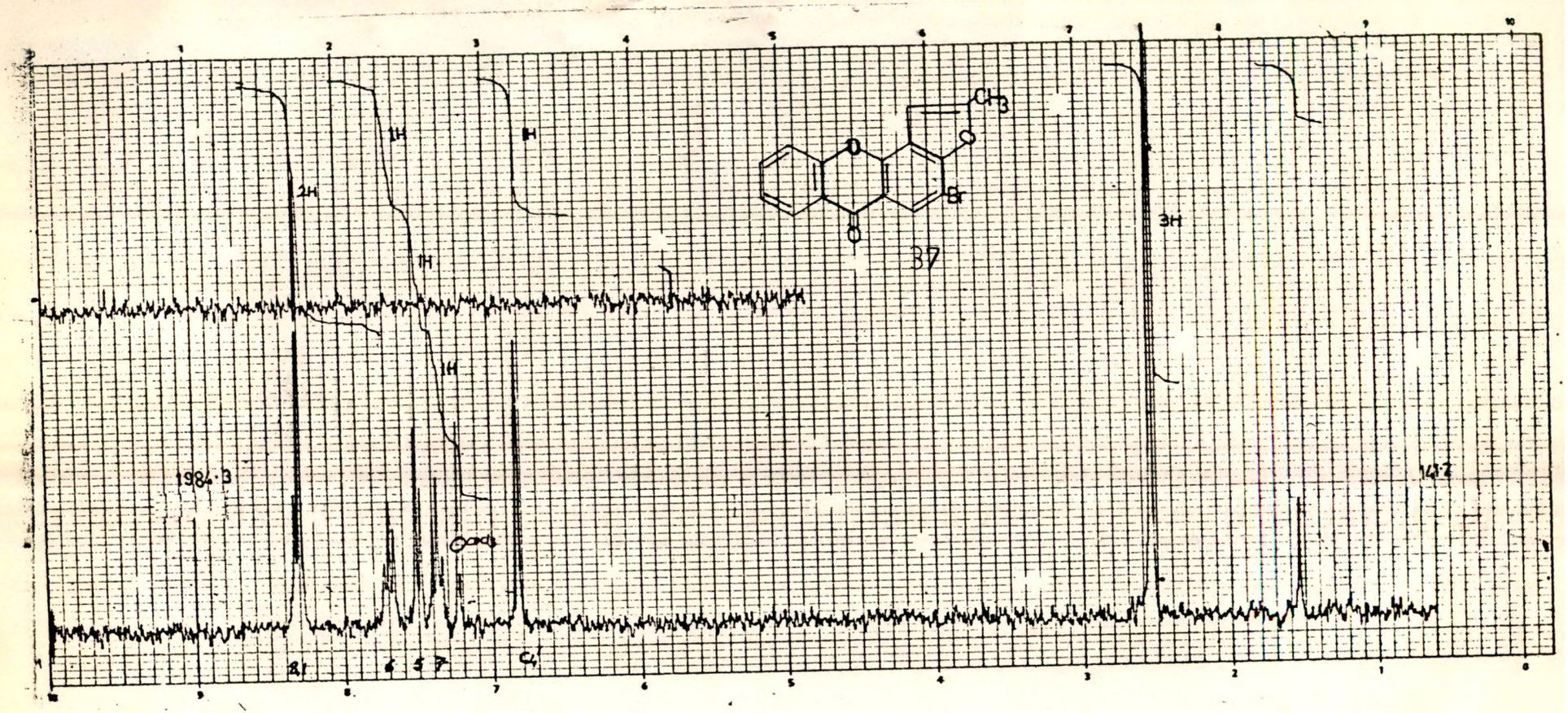


FIG 8

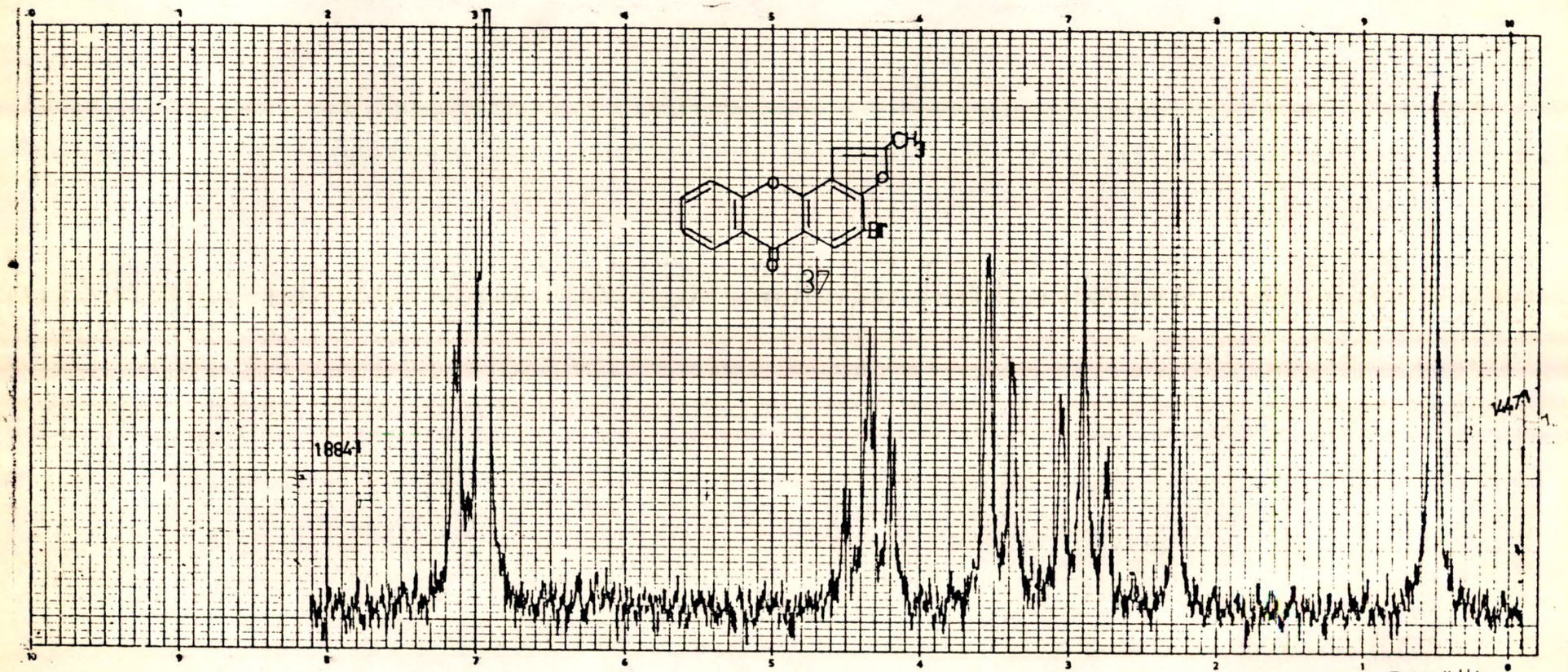
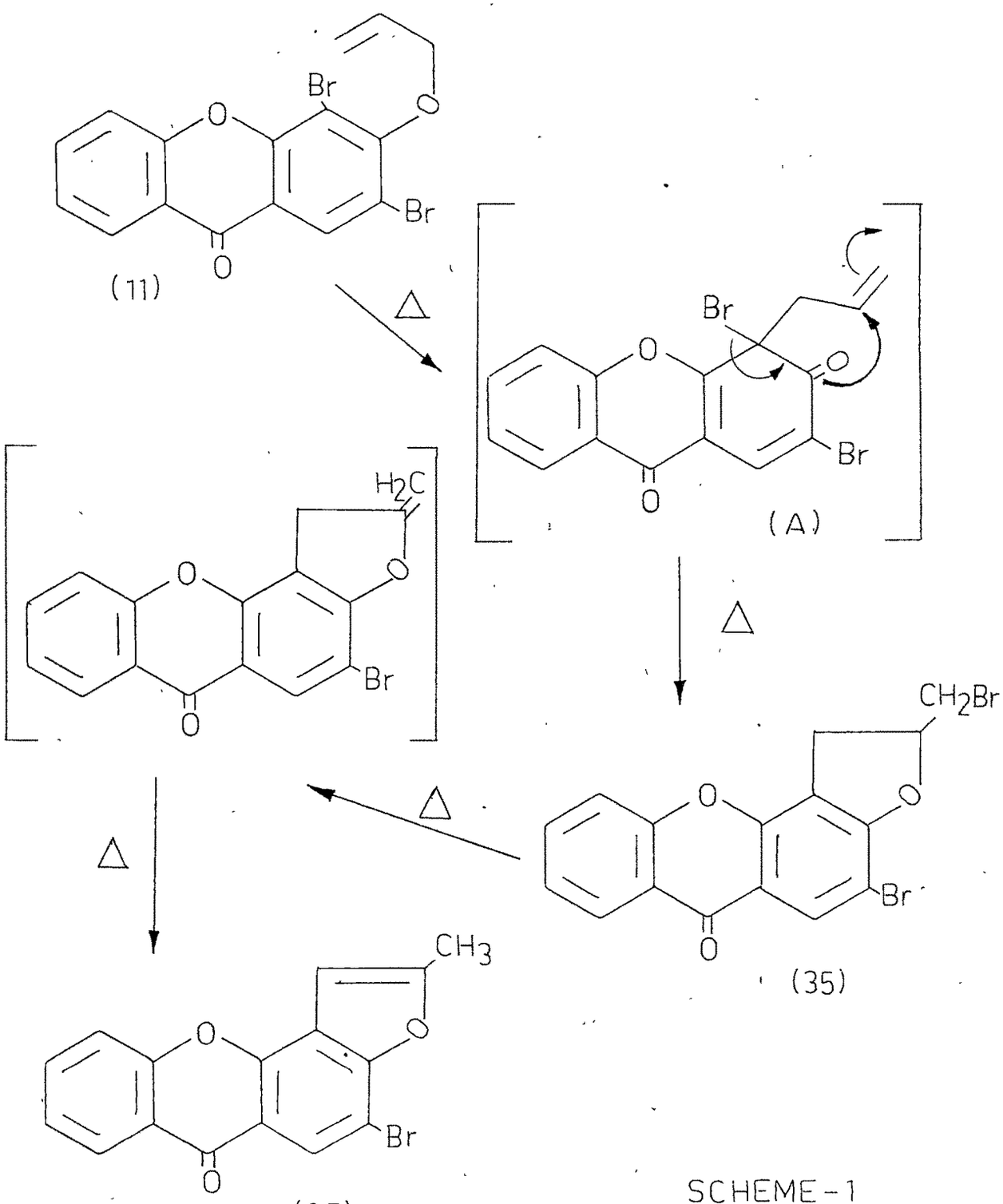


FIG 9


Br
O
O
Br
O
(11)
Δ
Br
O
O
Br
O
(A)
Δ
H2C
O
O
Br
O
Δ
CH2Br
O
O
Br
O
(35)
Δ
Δ
CH3
O
O
Br
O
(37)

SCHEME-1

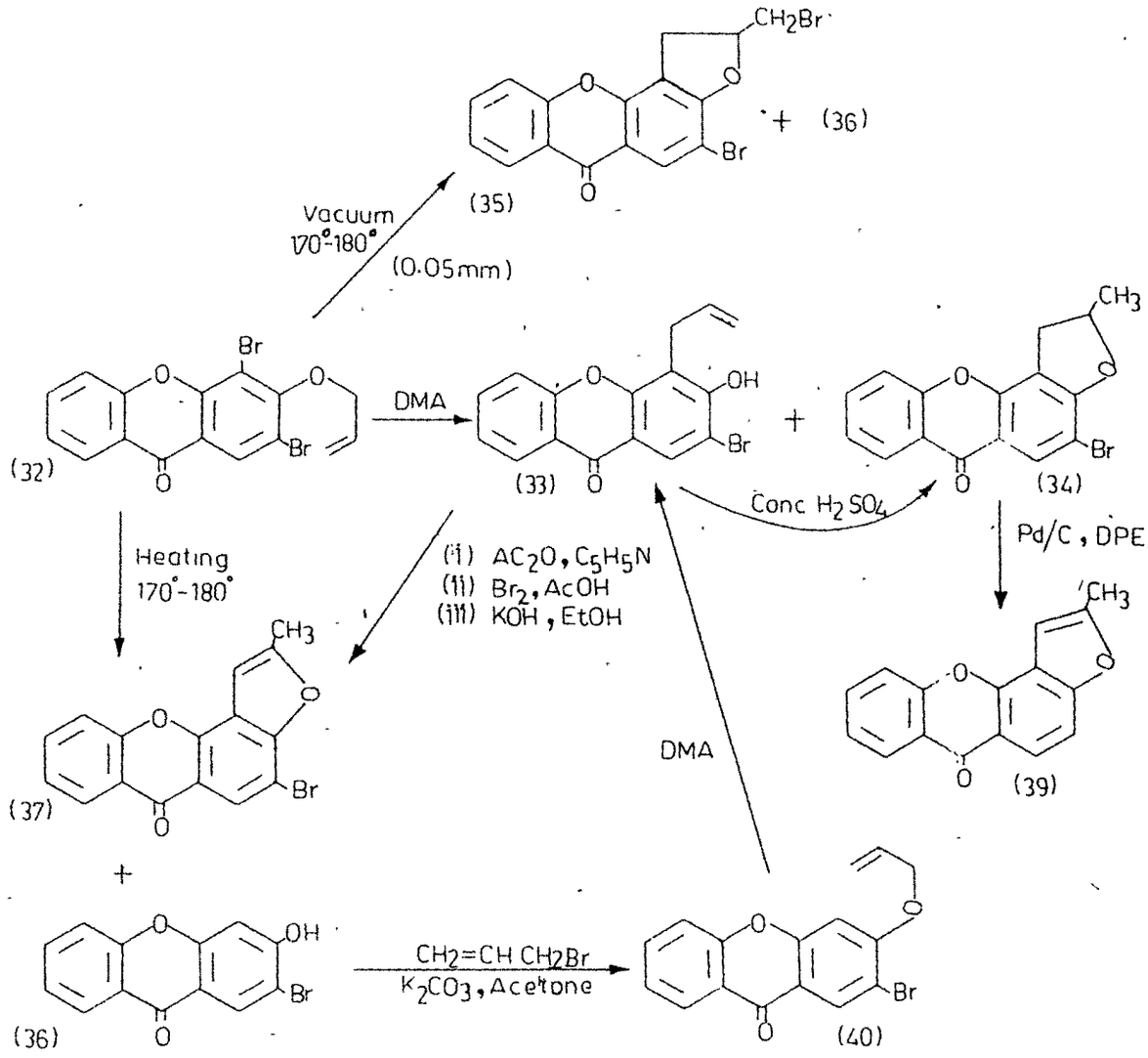
an angular furanoxanthone (39). As the NMR of (39) displays two characteristic doublets (AB pattern) at δ 8.20, 1H, J=9Hz, H-1 and at δ 7.25, 1H, J=9Hz, H-2 indicating the absence of bromine at position 2. Other signals 7.6, doublet, 1H, J=9Hz, H-5; 7.7, td, 1H, J=8,8,2Hz, H-6, 7.35, td, 1H, J=8,8,2Hz, H-7; 8.40, dd, J=9,2Hz, H-8; 6.8, S, 1H, C4'-H; 2.55, S, 3H, C5'-CH_3 confirmed the assigned structure (39). Thus NMR excludes the possibility of linear furanoxanthone and hence support the presence of bromine at position 2 in compound (33) and (34).

Claisen Rearrangement of 2-bromo-3-allyloxyxanthone (40)

2-Bromo-3-hydroxyxanthone on allylation with allyl bromide in the presence of potassium carbonate in dry acetone gave 2-bromo-3-allyloxyxanthone (40). Its structure was confirmed by NMR spectrum. Compound (40) on heating for 3 hr in dimethyl aniline gave compound (33), as its m.p. is same as that of (33) and mix m.p. with compound (33) does not show any depression in m.p.

Synthesis of 2-bromo-5'-methylfurano (2',3'-3,4) xanthone (37)

As it was not possible to get furanoxanthone (37) by dehydrogenation of (34), the compound (33) was acetylated to give 2-bromo-3-acetoxy-4-allylxanthone (41) which was brominated to yield 2-bromo-3-acetoxy-4-(2',3'-dibromopropyl) xanthone (42). This on refluxing with


CH2Br
(35)
+ (36)
Vacuum
170°-180°
(0.05mm)
Br
(32)
DMA
OH
(33)
CH3
(34)
Conc H2SO4
Pd/C , DPE
Heating
170°-180°
(i) AC2O, C5H5N
(ii) Br2, AcOH
(iii) KOH , EtOH
(37)
(39)
DMA
(36)
CH2=CH CH2Br
K2CO3, Acetone
(40)

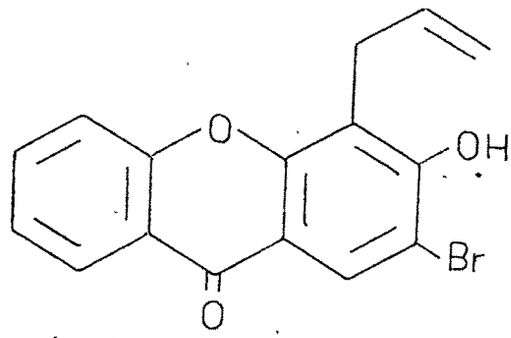
potassium hydroxide in absolute alcohol gave the title compound (37). Compound obtained during rearrangement (32) was identical in all respects (TLC. m.p. mix m.p. NMR) with the compound synthesised as above.

Synthesis of 2-bromofurano (2',3'-3,4) xanthone (44)

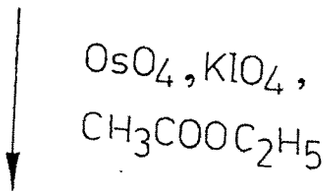
The compound (33) on oxidation with osmium tetroxide-potassium periodate in ethyl acetate-water gave corresponding 4-formylmethyl-2-bromo-3-hydroxy xanthone (43), which was cyclised using PPA to give (44). NMR (CD_3SOCD_3/CCl_4) spectrum, showed a sharp singlet at δ 8.26 for the periproton at position 1; 8.25, doublet, J=9Hz; proton at position 8; 7.72, doublet, 1H, J=1.5Hz, C5'-H; 7.02, d, 1H, J=1.5Hz, C4'-H; 7.3 to 7.8, multiplet, 3H, aromatic protons H-5, H-6 and H-7.

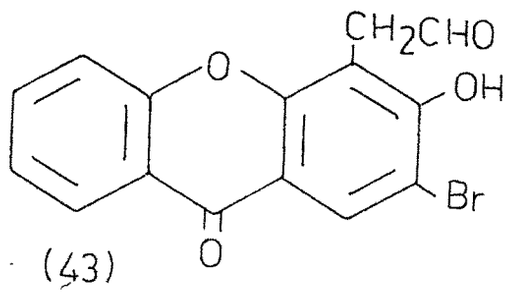
Claisen rearrangement of 3-allyloxy-4-bromoxanthone (45) 3-allyloxy-4-iodoxanthone (46):

3-Allyloxy-4-bromoxanthone (45) and 3-allyloxy-4-iodoxanthone (46) were prepared by refluxing corresponding hydroxyxanthones with allylbromide and acetone in the presence of anhydrous potassium carbonate. Claisen migration of (45) and (46) in dimethyl aniline gave three products (i) 2-allyl-3-hydroxyxanthone (47),

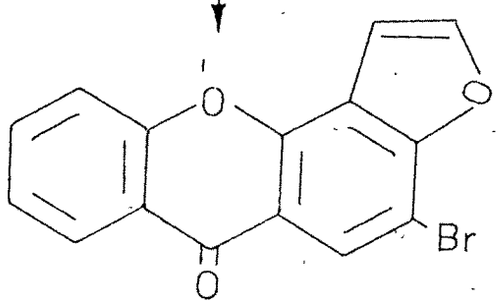


(33)





(43)



(44)

(ii) 3-hydroxy-4-allylxanthone (48), and (iii) 5'-methyl-4',5'-dihydrofurano (2',3'-3,4) xanthone (49).

The structures of compounds (47), (48) and (49) were confirmed by their mass and NMR spectra. Mass spectrum of (47) shows molecular ion peaks at 252 (M^+). The NMR ($CDCl_3$) of (47) (Fig.10) showed a singlet for one proton at δ7.85 due to the proton at position 1 and another singlet at δ6.8 due to the proton at position 4 indicating that the allyl group has migrated to position 2, along with the elimination of bromine from the compound (45), 8.12, dd, 1H, J=9,2Hz, H-8; 7.77, dd, 1H, J=9,1.5Hz, H-6; 7.57, dd, 1H, J=9,1.5Hz, H-5; 7.4, td, 1H, J=9,9,2Hz, H-7; 6.08-5.9, m, 1H, $CH_2\underline{C}H{=}CH_2$; 5.13-5.05, multiplet, 2H, $CH_2CH{=}C\underline{H}_2$; 3.35, doublet, J=7Hz, $C\underline{H}_2$-CH=CH_2. Mass spectrum of (48) shows molecular ion peak at 252 (M^+); the absence of bromine in compound (48) is easily infered. NMR of (48) in (CD_3SOCD_3) (Fig.11) exhibited two doublet of J value 9Hz, one at 7.4 due to proton at position 2 and the down field doublet which appears at δ7.99 is assigned to proton at position 1; 7.58, d, 1H, J=8Hz, H-5; 7.78, td, 1H, J=8,8, 2Hz, H-6; 7.41, td, 1H, J=8,8, 2Hz, H-7; 8.17, dd, 1H, J=8,2Hz, H-8; peaks in the upfield region clearly indicate the presence of allyl

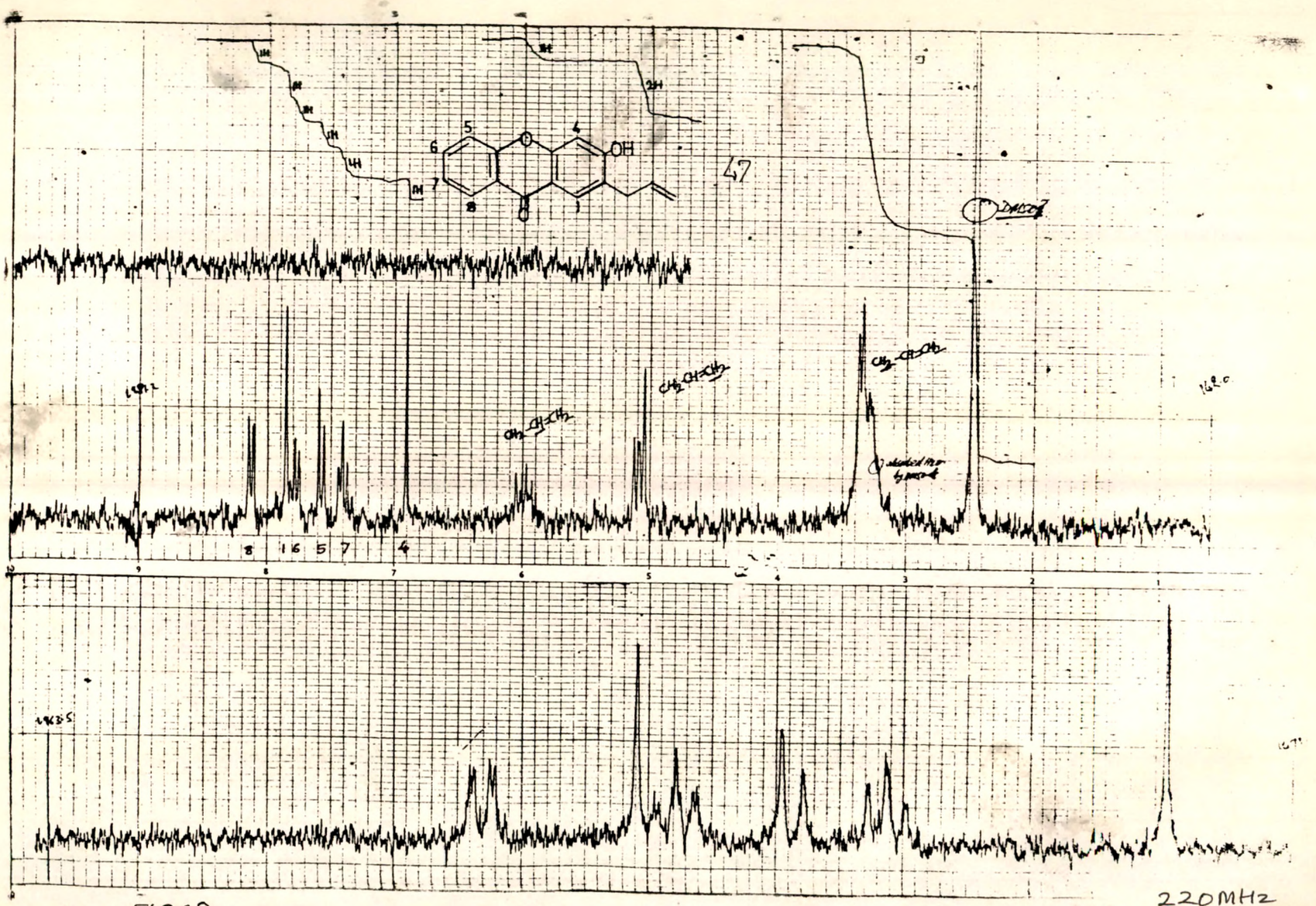


FIG 10

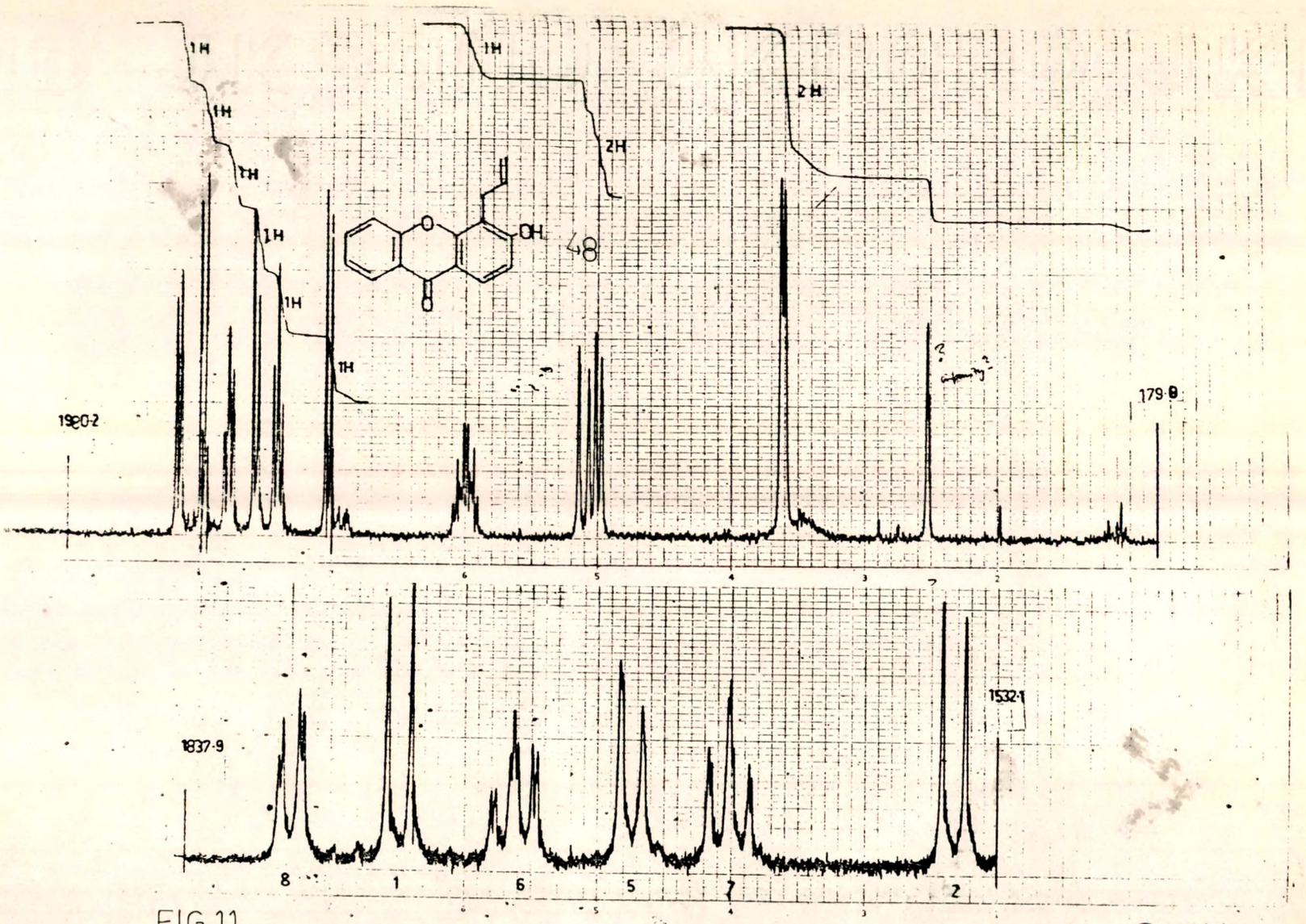

1H
1H
1H
1H
1H
1H
1H
2H
2H
OH
48
2080·2
1799·8
1837·9
1532·1
8
1
6
5
7
2
220 MHz

FIG 11

group, δ6.0, m, 1H, $CH_2\underline{CH} = CH_2$; 5.11, multiplet, 2H, $CH_2CH=\underline{CH}_2$ and 3.62, d, 1H, J=7Hz, $\underline{CH}_2CH=CH_2$. Thus compound (48) shows absence of bromine or iodine in the molecule and migration took place at position 4. The compound (49) was nothing but the cyclised product of (48) which is easily revealed by its NMR spectrum in ($CDCl_3$). The NMR (Fig.12) spectrum in the upfield region shows a single proton resonating as a multiplet at 5.15 and is due to the proton at C5'-H; 3.6, dd, 1H, J=9, 18Hz, C4'H; 2.95, dd, 1H, J=9, 18Hz, C4'H; and 1.5, doublet, 3H, J=7Hz, C5'CH_3. In the aromatic region following peaks were observed δ 8.12, doublet, 1H, J=9Hz, H-1; 7.76, doublet, J=9Hz, H-2. This indicates that it is an angular dihydrofuranoxanthone. 7.36, doublet, 1H, J=9Hz, H-5; 7.6, td, 1H, J=8,8,2Hz, H-6; 7.3, td, 1H, J=8,8,2Hz, H-7; 8.3, dd, 1H, J=9, 2Hz, H-8 confirms the assigned structure (49).

3-Allyloxy-4-iodoxanthone (46) when refluxed in decalin gave 3-allyloxyxanthone, iodine being eliminated during the reaction. While in case of 3-allyloxy-4-bromo xanthone, it gave (i) 2-allyl-3-hydroxy-4-bromoxanthone (50) (ii) 3-hydroxy-4-allylxanthone (48) and (iii) (49). Structure of (50) was established on the basis of NMR

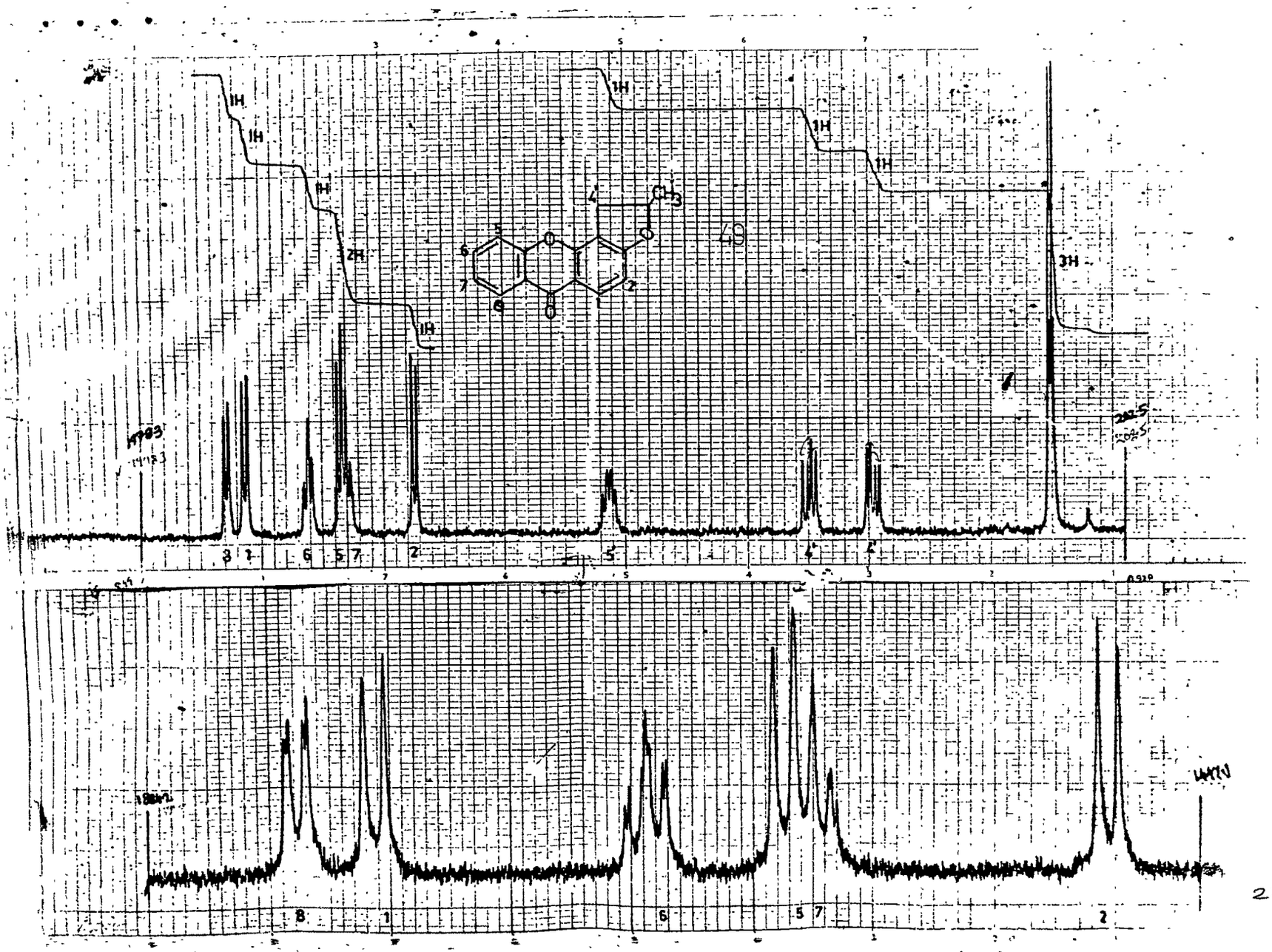
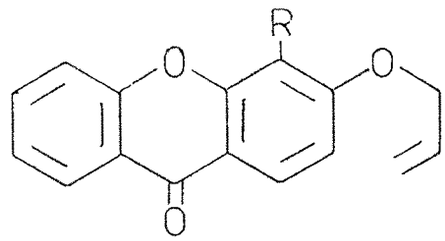


FIG 12

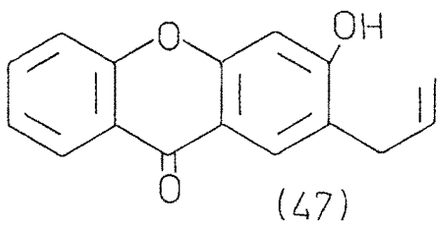
($CDCl_3$) (Fig.13,14) of its acetoxy derivative (51), which showed characteristic singlet for proton H-1 at δ 8.18 and no other singlet in the aromatic region. This indicated that allyl group has migrated to position 2 and bromine is not eliminated during the reaction, 7.5, d, 1H, J=9Hz, H-5; 7.7, td, 1H, J=8,8, 2Hz, H-6; 7.35, td, 1H, J=8,8,2Hz, H-7; 8.28, dd, 1H, J=9,2Hz, H-8; 5.9, multiplet, 1H, CH_2-$\underline{CH}$=CH_2; 5.15, m, 2H, $CH_2CH=\underline{CH_2}$; 3.4, doublet, 2H, J=5Hz, $\underline{CH_2}$-CH=CH_2; 2.4, S, 3H, $OCOCH_3$. The presence of bromine in the molecule is clearly infered from its mass spectrum m/e 374, 372 (M^+) 332, 330, (M^+-$COCH_2$).

When the rearrangement was carried out in vacuum at 140-150°C, 3-allyloxy-4-bromoxanthone (45) furnished the same products which were obtained in case of heating in decalin, yields being poorer in this case. 3-Allyloxy-4-iodoxanthone (46) when heated in vacuum at 140-150°C gave 3-allyloxyxanthone and compound (48). During the rearrangement of 3-allyloxy-4-iodoxanthone in N,N-dimethylaniline, p-iodo-N,N-dimethylaniline was isolated. Mass m/e 247 (M^+) 127, 120 indicate that it is mono iodo-N,N-dimethylaniline, NMR ($CDCl_3$) showed the pattern for para substitution δ 7.85, d, 2H, J=10Hz; 7.7, d, 2H, J=10Hz; 3.6, S, 6H, $-N\begin{matrix}CH_3\\CH_3\end{matrix}$.



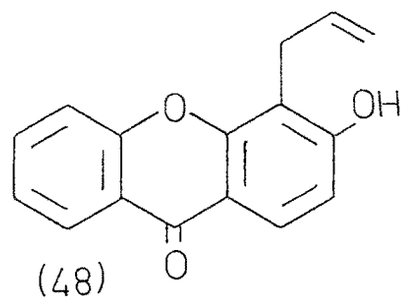
45 R=Br
46 R=I

DMA



(47)

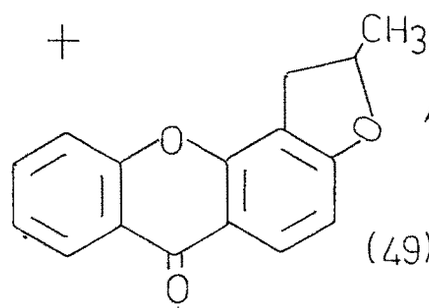
+



(48)

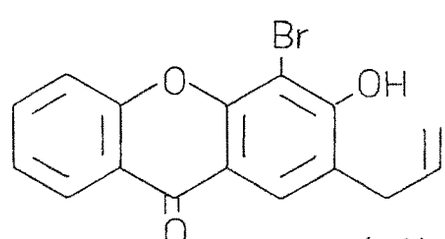
Conc. H_2SO_4

+



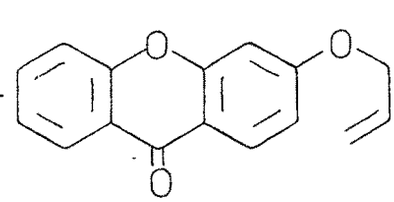
(49)

(45) —Decalin, Vacuum, 140°-150°→



(50) + (48) + (49)

(46) —Decalin→



(46) —Vacuum, 140°-150°→ » + (48)

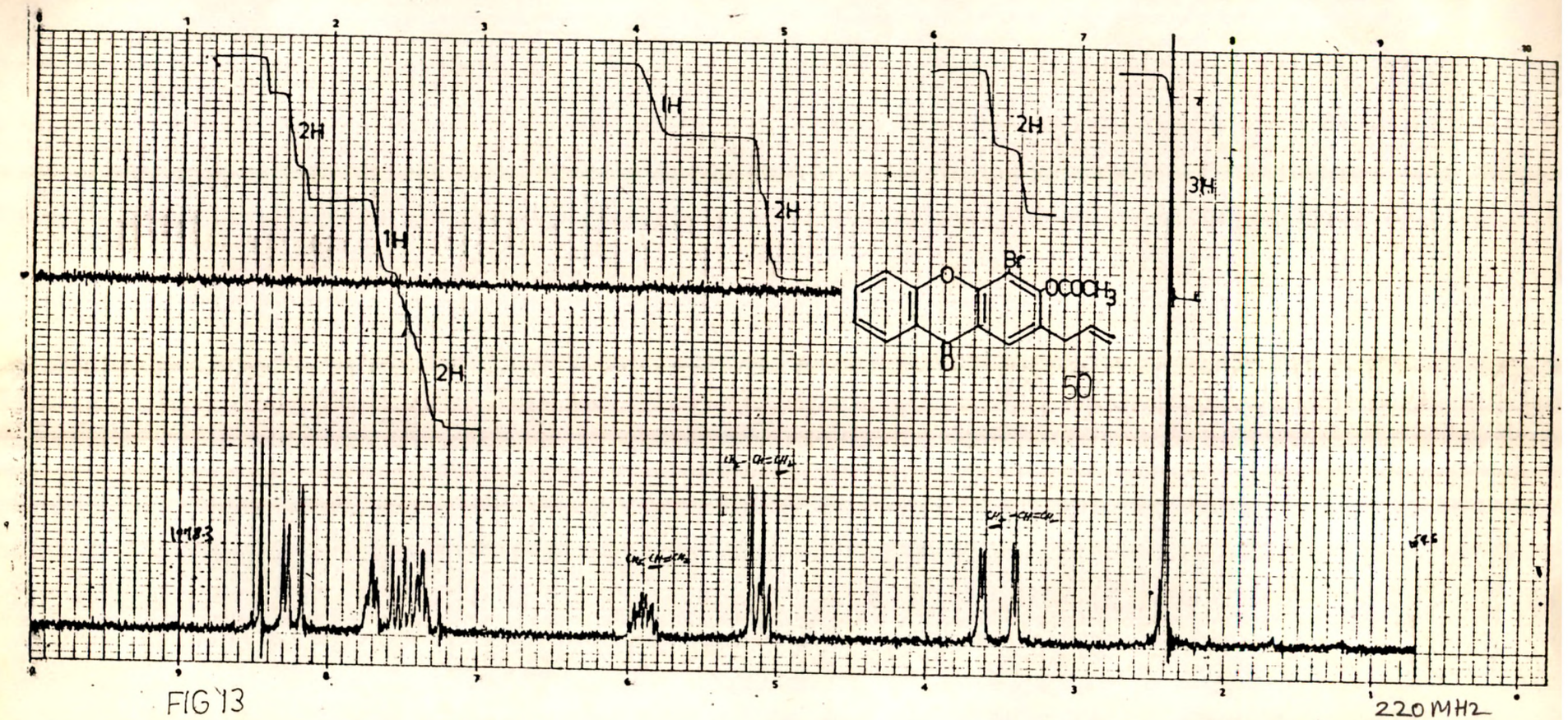


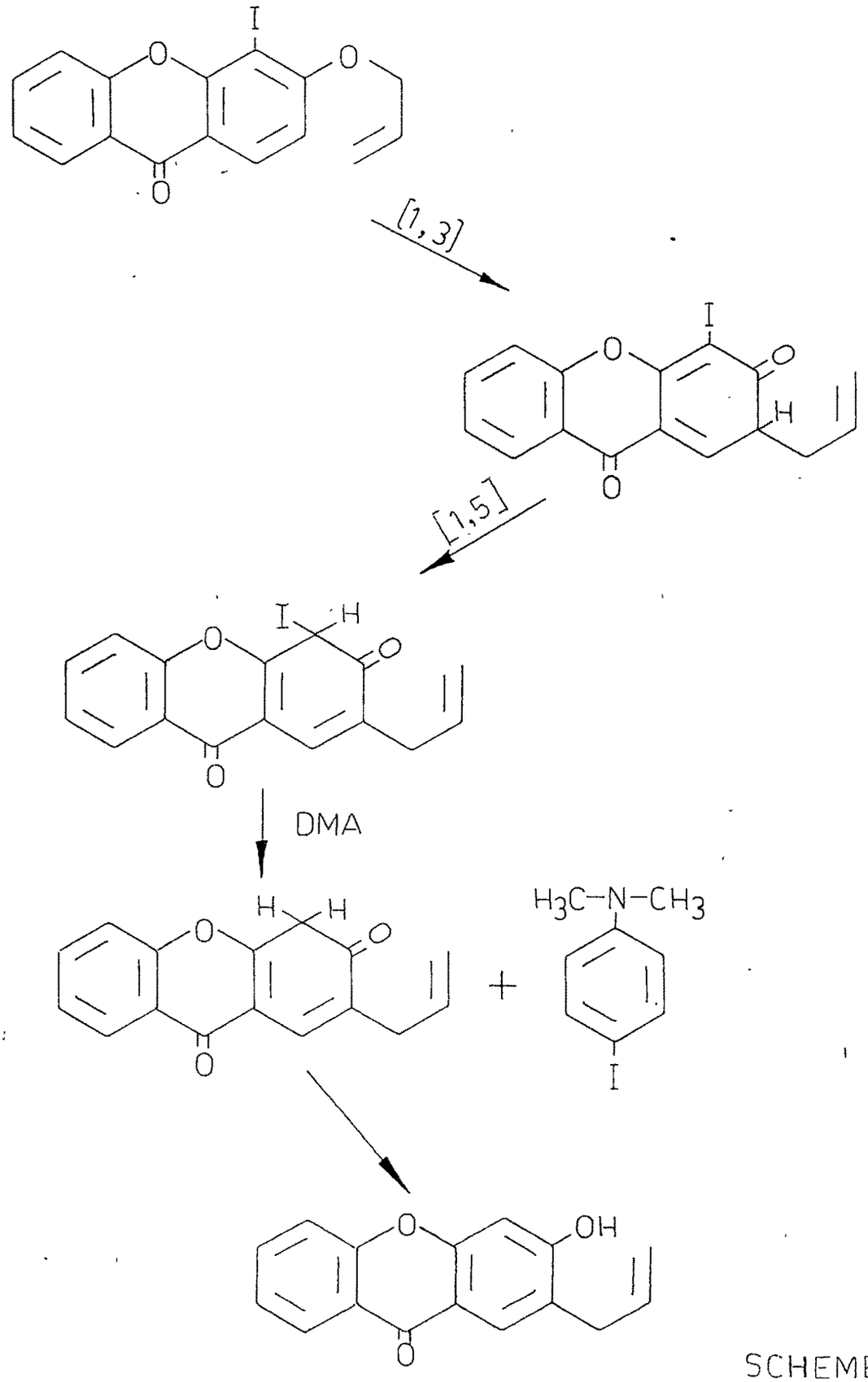
FIG 13

FIG 14

Mechanism shown in Scheme (2) is proposed to explain the formation of (47). In the first step (1,3) sigmatropic rearrangement occurs to give the ketonic structure (A) which undergoes (1,5) hydrogen shift to give rise to structure (B) which can easily liberate Iodine to displace proton from dimethyl aniline, to form p-iodo-N,N-dimethylaniline and structure(C) which undergoes keto-enol-tautomerism to give the stable phenol form (47).

Synthesis of 4-bromo-5'-methylfurano (3',2'-2,3) xanthone (53)

2-Allyl-3-acetoxy-4-bromoxanthone (51) was brominated with two moles of bromine in acetic acid to give 2-(2',3'-dibromopropyl)-3-acetoxy-4-bromo xanthone (52), which on refluxing with potassium hydroxide in absolute alcohol gave 4-bromo-5'-methyl furano (3',2'-2,3) xanthone (53). The NMR spectrum of (53) in $CDCl_3$ exhibited sharp singlet at δ 8.28 for the peri proton at position 1; doublet of J=9Hz, at 8.28 for another peri proton at position 8; 7.28 to 7.6, multiplet, 3H, protons at position 5, 6 and 7; singlet due to C4'H proton of furan ring at δ6.5; and δ2.5, singlet integrating for three proton of $-CH_3$ group at position 5'.



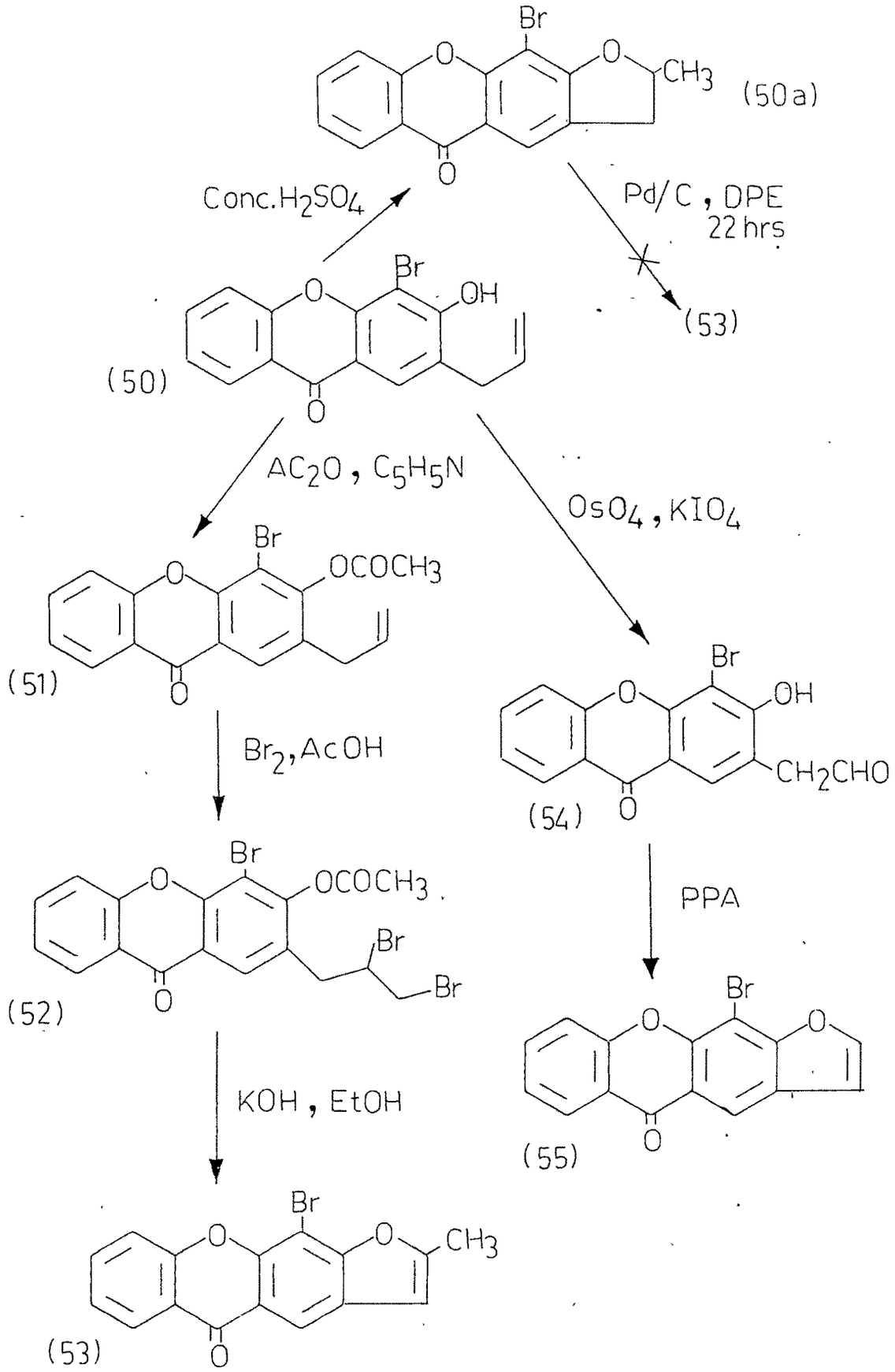
SCHEME-2

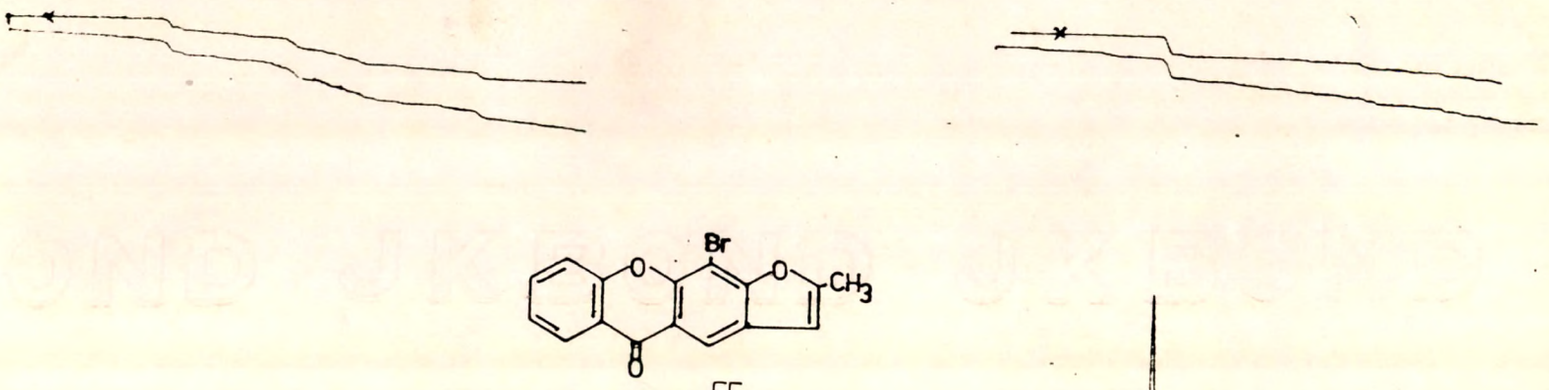
4-Bromofurano (2',3'-2,3) xanthone (55)

The compound (50) on oxidation with osmium tetroxide-potassium periodate in ethylacetate-water gave 2-formylmethyl-3-hydroxy-4-bromoxanthone (54), which was cyclised to 4-bromofurano (2',3'-2,3) xanthone (55) using PPA. The structure of (55) was confirmed on the basis of its IR, mass and NMR spectral studies. IR (KBr): 1670 (C=O γ-pyronyl), 1620 (C=C). Mass spectrum m/e 316, 314 (M^+) shows the presence of one bromine. NMR (Fig.15) in $CDCl_3$ displays singlet at δ 8.55 for the proton at position 1; 7.45, doublet, 1H, J=9Hz, H-5; 7.75, td, 1H, J=9,9,2Hz, H-6; 7.7, td, 1H, J=9,9,2Hz, H-7; 8.33, dd, 1H, J=8, 2Hz, H-8; 7.7, doublet, 1H, J=1.5Hz, C5'H; 6.99, doublet, 1H, J=1.5Hz, C4'-H.

Synthesis of 1-hydroxy-3,5'-dimethylfurano (3',2': 5,6) xanthone (61)

1,6-Dihydroxy-3-methylxanthone (56), prepared as described in Chapter (2) starting from methyl β-resorcylate and orcinol, was allylated using allybromide and potassium carbonate in dry acetone to give 6-allyloxy-1-hydroxy-3-methylxanthone (57), which was subjected to Claisen rearrangement in dimethylaniline to give 5-allyl-1, 6-dihydroxyxanthone (58). The structure of (58) was confirmed


Br
O
O
CH3
(50a)
Conc.H2SO4
Pd/C , DPE
22 hrs
(53)
(50)
Br
OH
O
AC2O , C5H5N
OsO4 , KIO4
Br
OCOCH3
(51)
Br2, AcOH
Br
OH
CH2CHO
(54)
PPA
Br
OCOCH3
Br
Br
(52)
KOH , EtOH
Br
O
O
(55)
Br
O
O
CH3
(53)



55

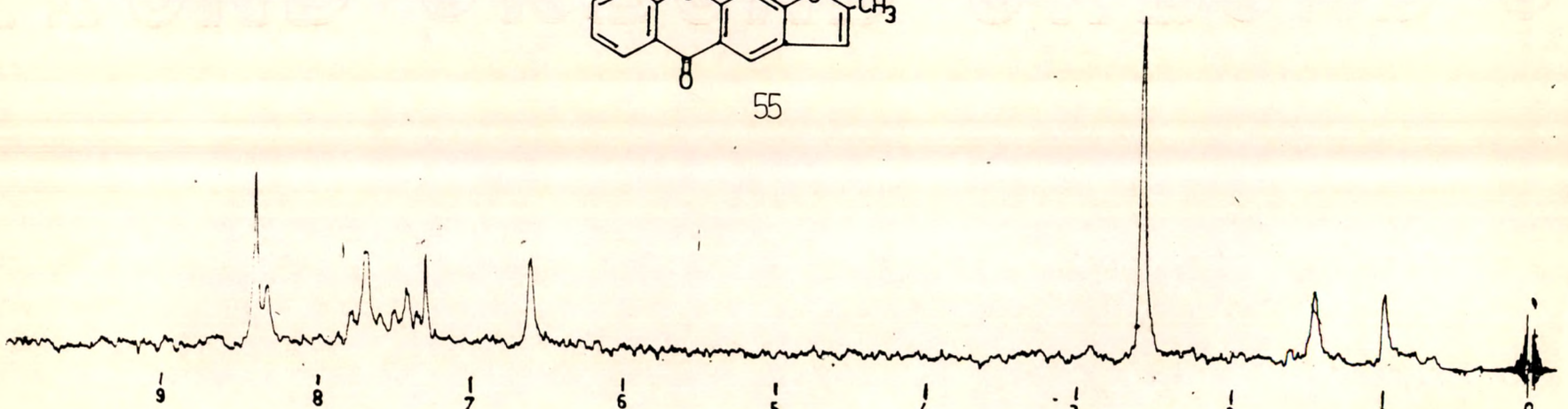
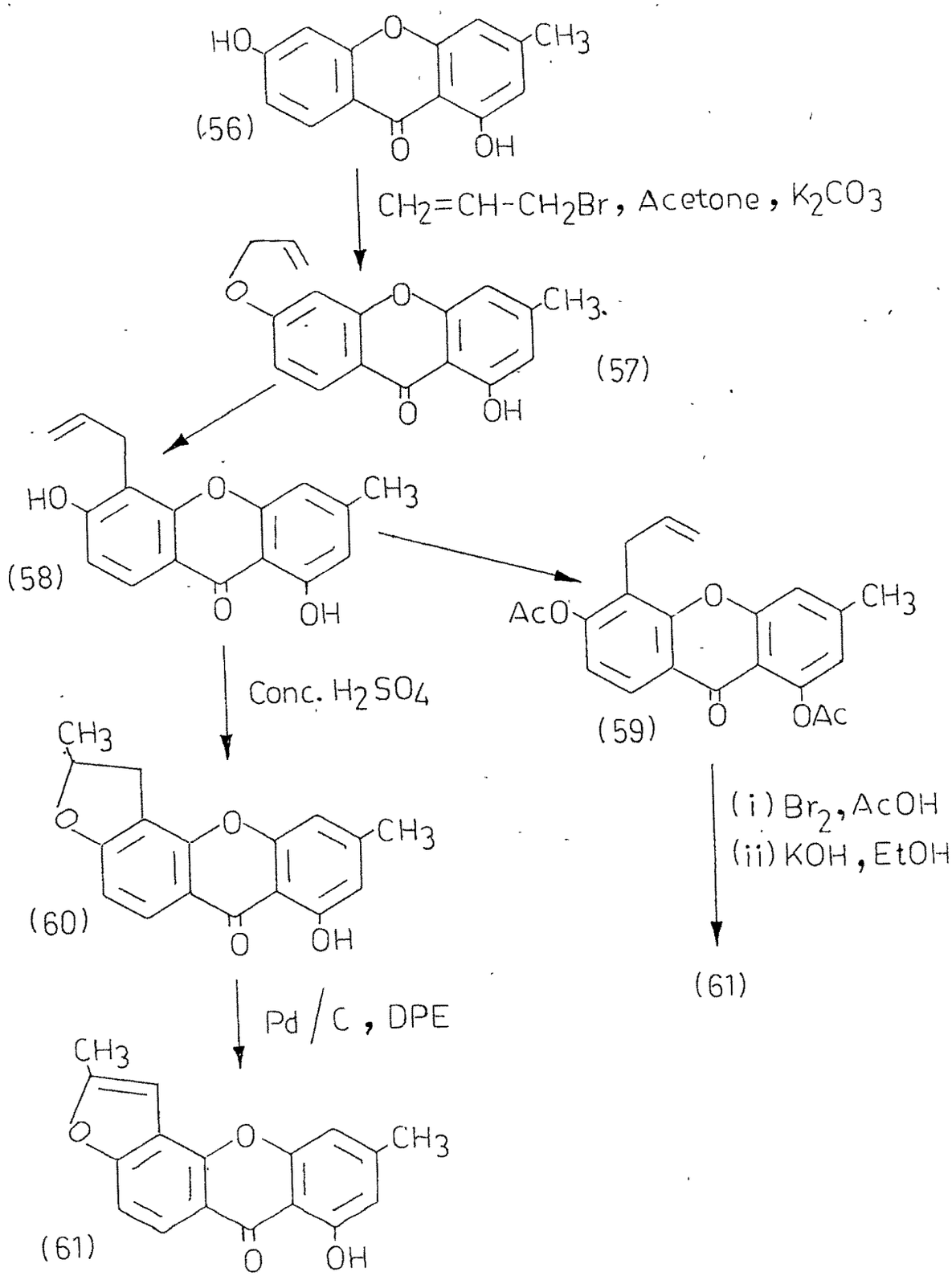


FIG 15

by NMR spectrum ($CDCl_3$) (Fig.16) of its acetoxy derivative (59). Examination of the aromatic region of the spectrum revealed the presence of two ortho coupled protons one at δ 8.05, doublet, 1H, J=9Hz proton at position 8 and the other at 7.0, doublet, 1H, J=9Hz, H-7; 7.08, singlet, 1H, H-4; 6.7, singlet 1H, H-2 which neglet the placement of allyl group at position 7; 5.6 to 6.1, multiplet, 1H, $CH_2\underline{C}H=CH_2$; 5.0, multiplet, 1H, $CH_2CH=C\underline{H}_2$; 3.5, doublet, J=9Hz, 2H, $C\underline{H}_2CH=CH_2$ presence of the last three peaks in NMR ruled out the possibility of a cyclic structure; 2.4, singlet, 3H, $ArCH_3$; 2.28, singlet, 3H, $OCOCH_3$.

The compound (58) was heated with conc. sulphuric acid to obtain a cyclised product 3,5'-dimethyl-1-hydroxy-4',5'-dihydrofurano (3',2': 5,6) xanthone (60). NMR spectrum of which in $CDCl_3$ (Fig.17) showed δ 8.0, doublet, 1H, J=9Hz, H-8; 6.7, doublet, 1H, J=9Hz, H-7; 6.55, singlet, 1H, H-4; 6.49, singlet, 1H, H-2; 5.15, multiplet, 1H, C5'H; 3.5, dd, 1H, J=9,18Hz, C4'H; 2.92, dd, 1H, J=9,18Hz, C4'H.

A signal which resonated at 2.38 for 3H was accounted for one aromatic methyl group, and a doublet at 1.55 3H, J=9Hz, was assigned to C5'-CH_3. The compound (60)


HO
CH3
O
OH
(56)
CH2=CH-CH2Br, Acetone, K2CO3
(57)
(58)
Conc. H2SO4
AcO
OAc
(59)
(i) Br2, AcOH
(ii) KOH, EtOH
(60)
Pd / C, DPE
(61)
(61)

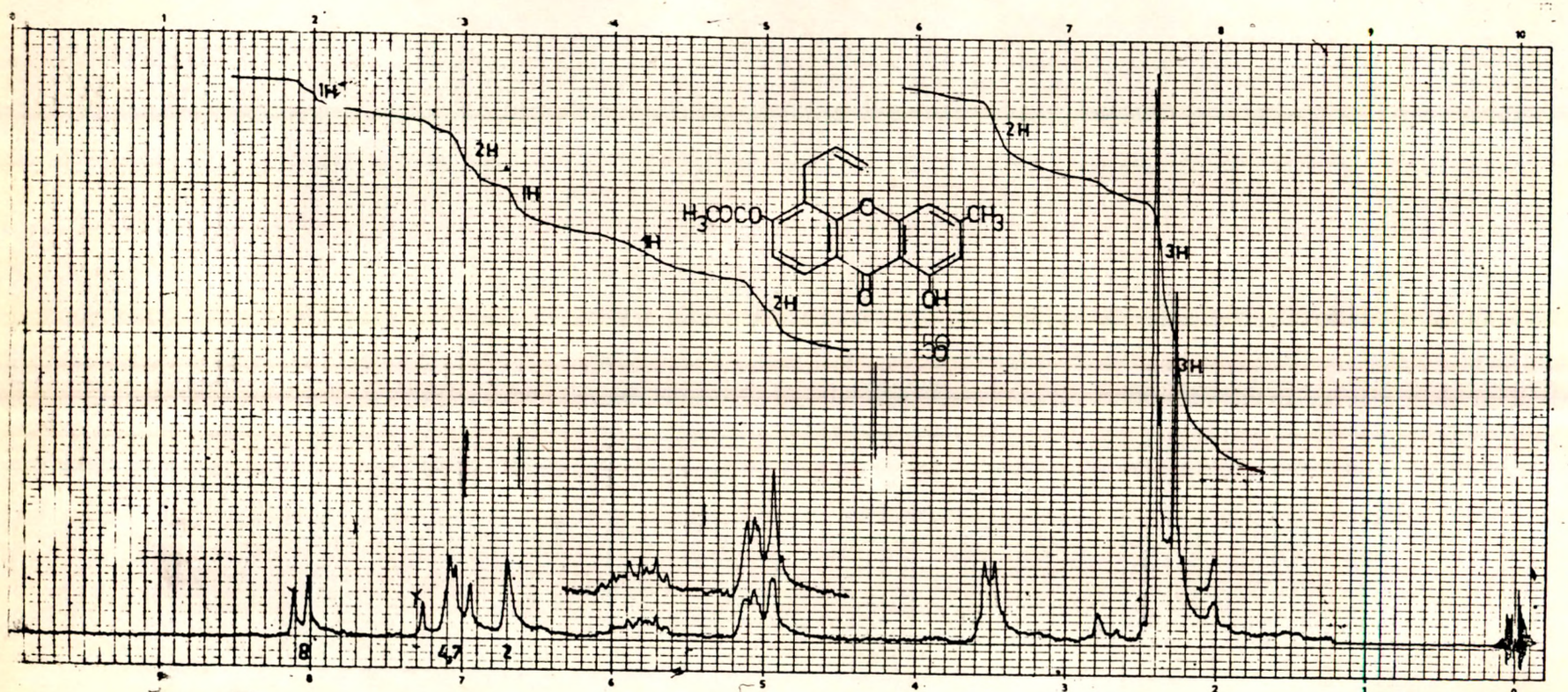


FIG 16

FIG 17

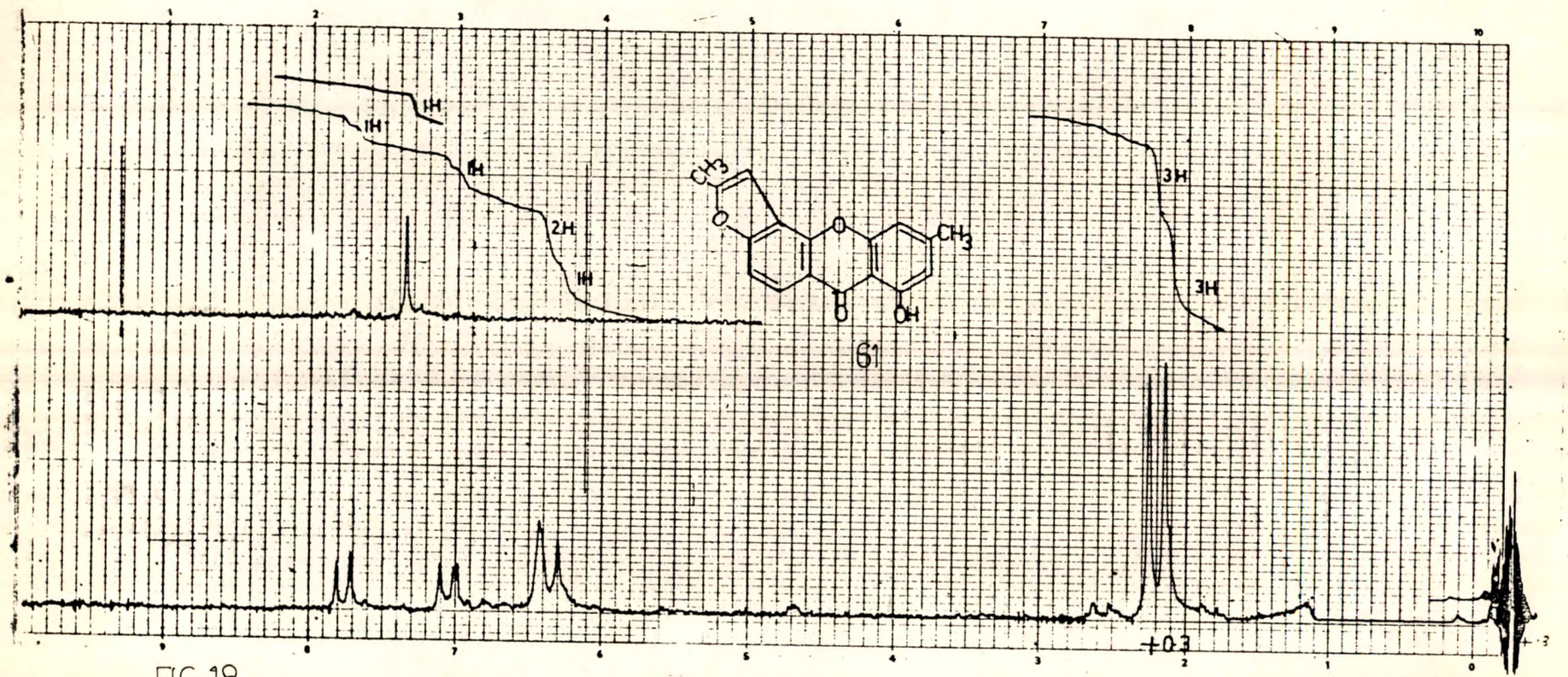


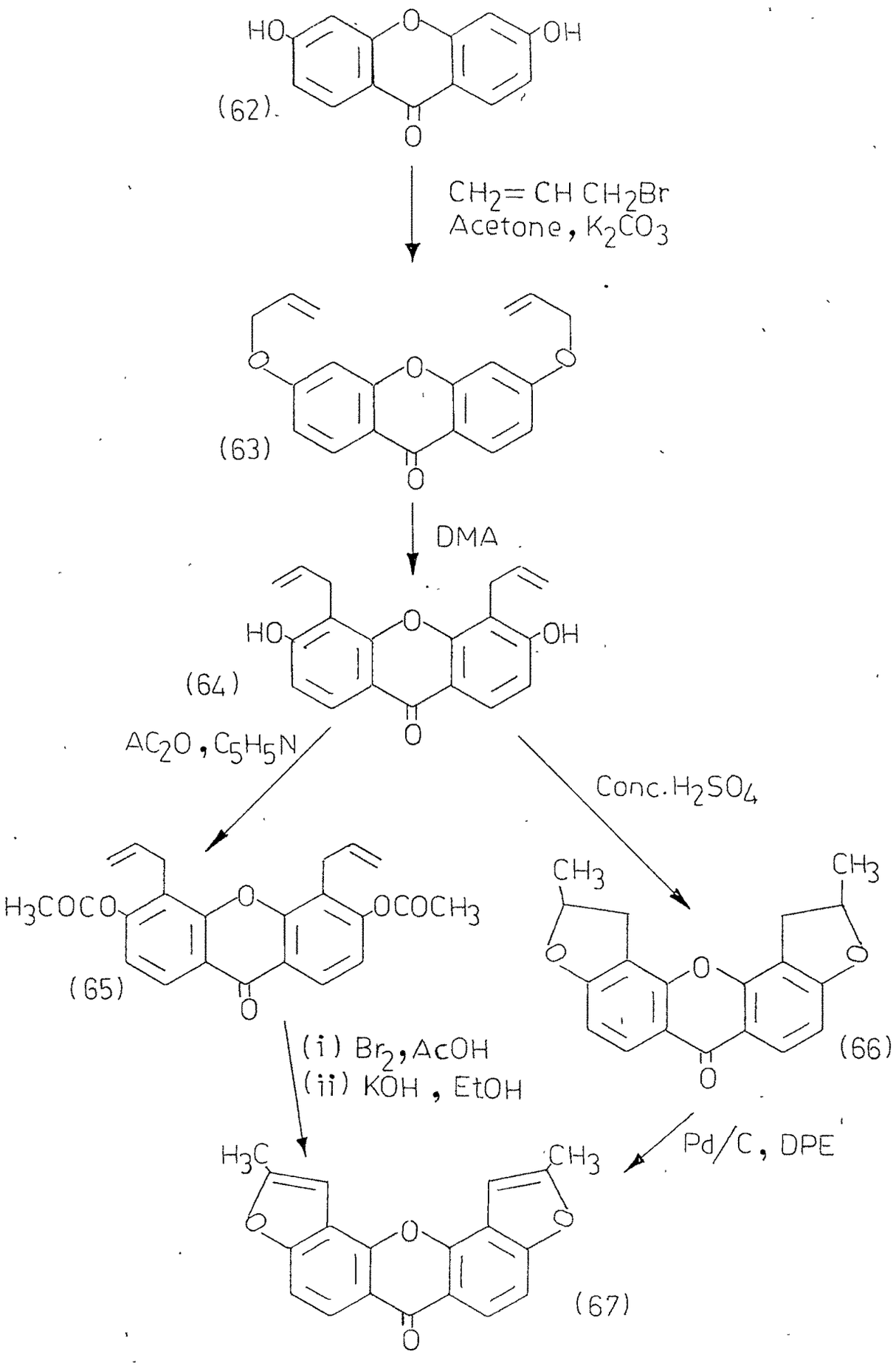
FIG 18

on dehydrogenation with palladised charcoal in diphenyl ether gave 5',3-dimethyl-1-hydroxyfurano (3',2': 5,6) xanthone (61). The structure of (61) was confirmed by its NMR spectrum in $CDCl_3$ (Fig.18) δ 8.05, doublet, 1H, J=9Hz, H-8; 7.35, doublet, 1H, J=9Hz, H-7; 6.42, singlet integrating for two protons H-4 and C4'H; 6.3, singlet, 1H,H-2. In the upfield region of NMR spectrum two singlets are observed. A singlet which resonated at δ2.55 is due to one aromatic methyl group while a second singlet at δ2.45 was identified as a methyl group at position C5' in furan ring.

Synthesis of 5',5"-dimethyldifurano (2',3'-3,4 : 3" 2"-5,6) xanthone (67)

3,6-Dihydroxyxanthone (62) was prepared as described in Chapter 2 and on allylation with allyl bromide, potassium carbonate in dry acetone, yielded 3,6-diallyloxy xanthone (63). Its NMR spectrum in ($CDCl_3$) showed only one doublet at δ8.15, 2H, J=9Hz, H-1 and H-8; 7.0 to 6.55, multiplet, 4H, H-2, H-4, H-5 and H-6; 6.0, multiplet, 2H, 2x-$OCH_2\underline{CH}=CH_2$; 5.35, multiplet, 4H, 2x-$OCH_2CH=\underline{CH}_2$, 4.65, multiplet, 4H, 2x-$O\underline{CH}_2CH=CH_2$. Compound (63) on Claisen migration in dimethylaniline yielded 4,5-diallyl-3,6-dihydroxyxanthone (64) as NMR of its acetoxy derivative(65)

showed two doublet of J=9Hz one at δ 8.2 for protons H-1 and H-8 and another at δ 7.2 for protons H-2 and H-7 indicating that migrated allyl groups are at positions 4 and 5 and not at position 2 and 7, 6.1 to 5.7, multiplet, 2H, $2x CH_2\underline{C}H=CH_2$; 5.15 to 4.9, multiplet, 4H, $2x CH_2CH=C\underline{H}_2$; 3.6, doublet, 4H, J=9Hz, $2x C\underline{H}_2CH=CH_2$; 2.35, singlet integrating for the six protons of the two $OCOCH_3$ groups. Thus the examination of NMR spectrum indicate the absence of furan type of rearranged product. (64) on cyclisation with conc. H_2SO_4, furnished 5',5"-dimethyl 4', 5', 4", 5"-tetrahydrodifurano (2',3'-3,4 : 3", 2"- 5,6) xanthone (66)-NMR spectrum ($CDCl_3$) : δ 8.08, doublet, 2H, J=9Hz, H-1 and H-8; 6.7, doublet, 2H, J=9Hz, H-2 and H-7; 5.1, m, 2H, two methine protons at C5'-H, C5"-H of furan ring; 3.4, quartet, 2H, J=18Hz, two C4'H; 2.78, quartet, 2H, J=18Hz, two C4'H; 1.65, doublet, 6H, two CH_3. The compound (66) on dehydrogenation with palladised charcoal in diphenyl ether gave 5',5"-dimethyldifurano (2',3'-3,4 : 3",2"-5,6) xanthone (67). The structure of this compound was confirmed by its NMR spectrum in($CDCl_3$) (Fig.19) : δ 8.2, doublet, 2H, J=9Hz due to two periprotons at positions 1 and 8; 7.3, doublet, 2H, J=9Hz, H-2 and H-7; 6.62, singlet, 2H, protons of furan ring C4'H and C4"H and 2.49, singlet, 6H, two $-CH_3$ groups of furan ring. Difuranoxanthone (67) was also obtained when (65) was cyclised using Adams and Rindfusz method.


HO
OH
O
(62)
CH_2= CH CH_2Br
Acetone, K_2CO_3
(63)
DMA
(64)
AC_2O, C_5H_5N
Conc. H_2SO_4
H_3COCO
$OCOCH_3$
(65)
(i) Br_2, AcOH
(ii) KOH, EtOH
CH_3
(66)
Pd/C, DPE
H_3C
(67)

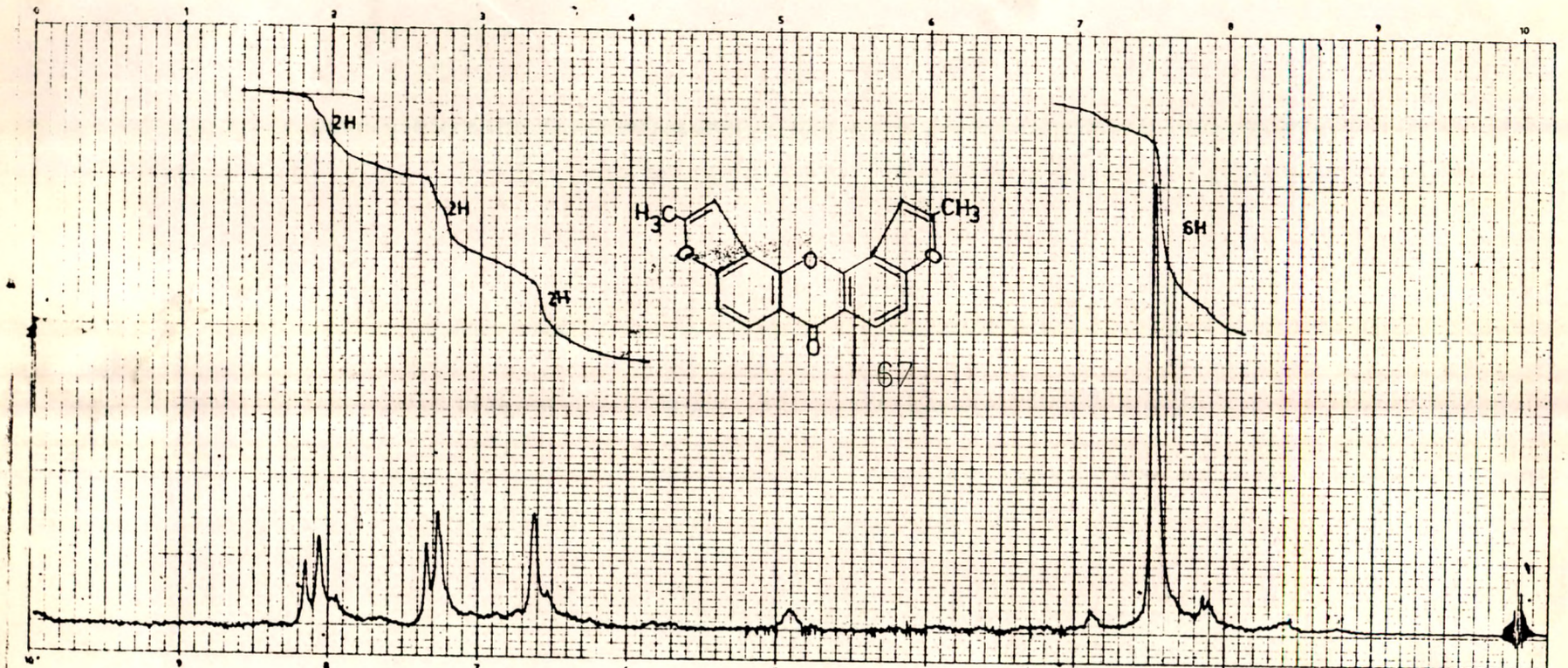
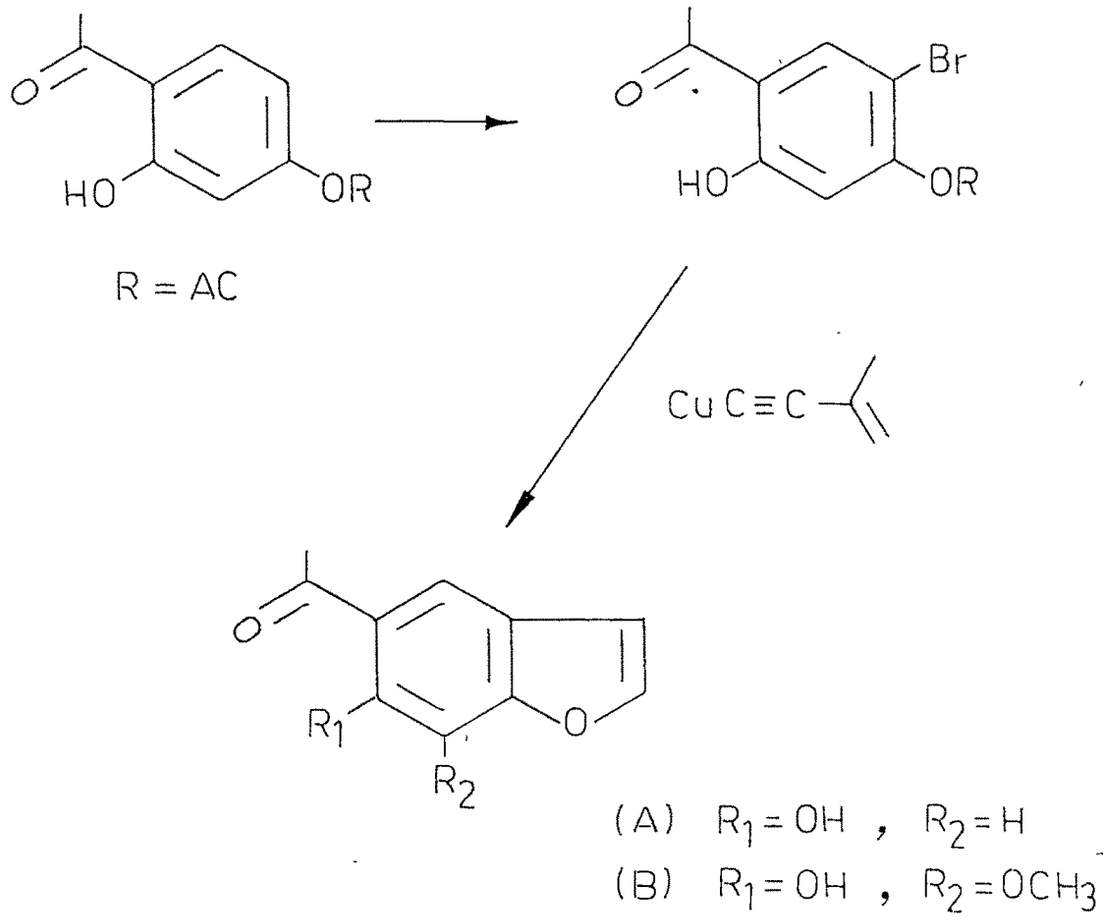


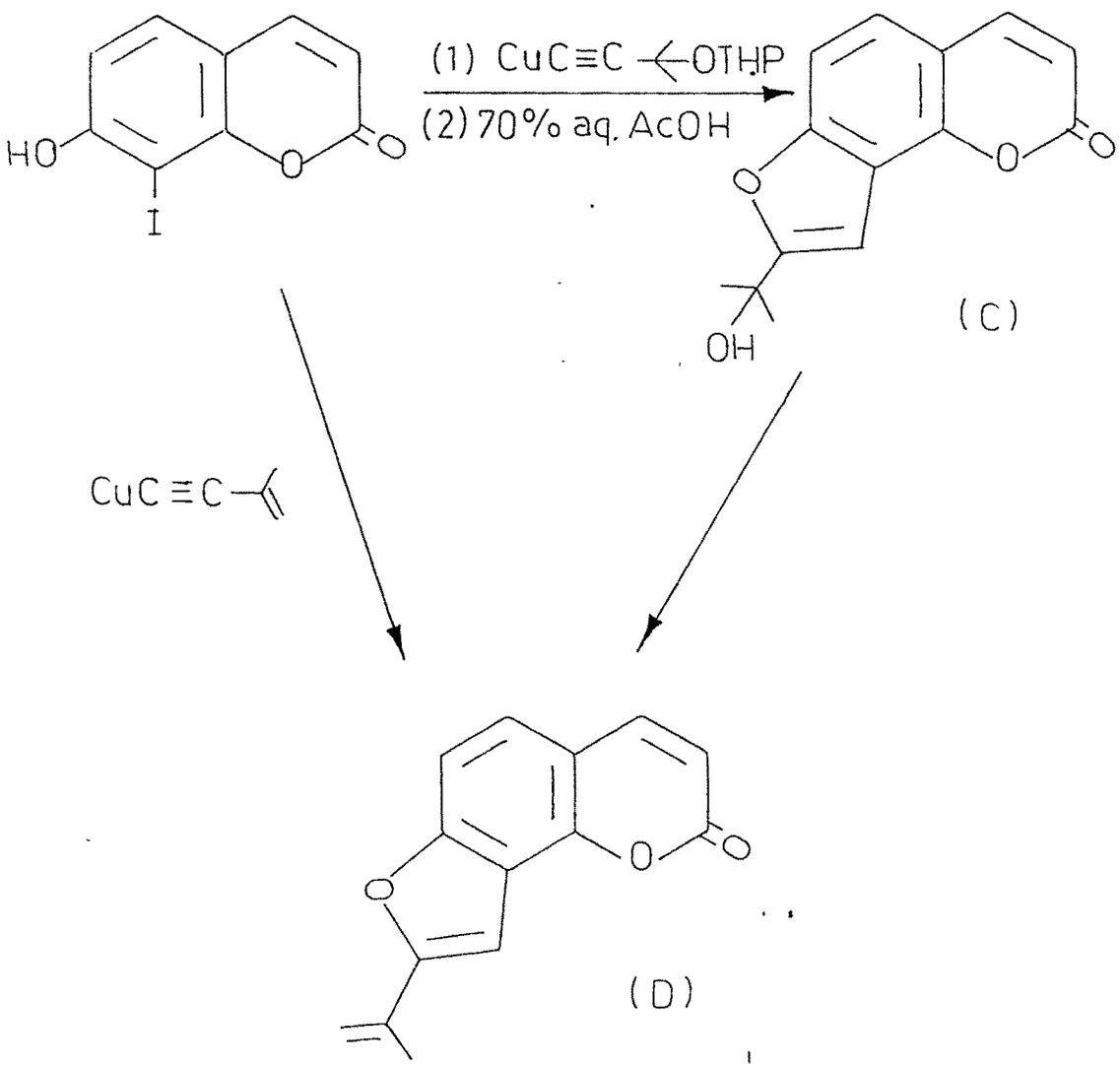
FIG 19

Naturally occuring acetophenone derivatives coumarins, isoflavones, flavones and xanthones bears an isopentenyl residue either as a side chain or as a part of heterocycle moiety. Some acetophenones like euparin (A)[28] and its methoxy derivative called methoxy euparin (B)[29] has been isolated and its synthesis was carried out by Schreiber and Stevenson[30] using short procedure involving the reaction of Copper (I) isopropenyl acetylide with an appropriate p-acetyl-o-halogenophenol as shown in Scheme (3). Angular furano coumarin, oroselol (C) was isolated[32] from the roots of Athamanta Oreoselinum L and other species[32,33] and was synthesised by Duffley and Stevenson[34]. The furano coumarin orosalone (D) have also been isolated[35], its synthesis was achieved by Stevenson et al.[35,36] by coupling of appropriate o-halogenophenol with Copper(I) isopropenyl acetylide (Scheme 4). Stevenson and coworkers have prepared naturally occuring benzofuran by coupling of substituted Copper(I) phenyl acetylide, viz. petrofuran[37], isopetrofuran[38], arylbenzofuran[39]. Synthesis of aryl benzofuran (E) is rationalised in Scheme (5).

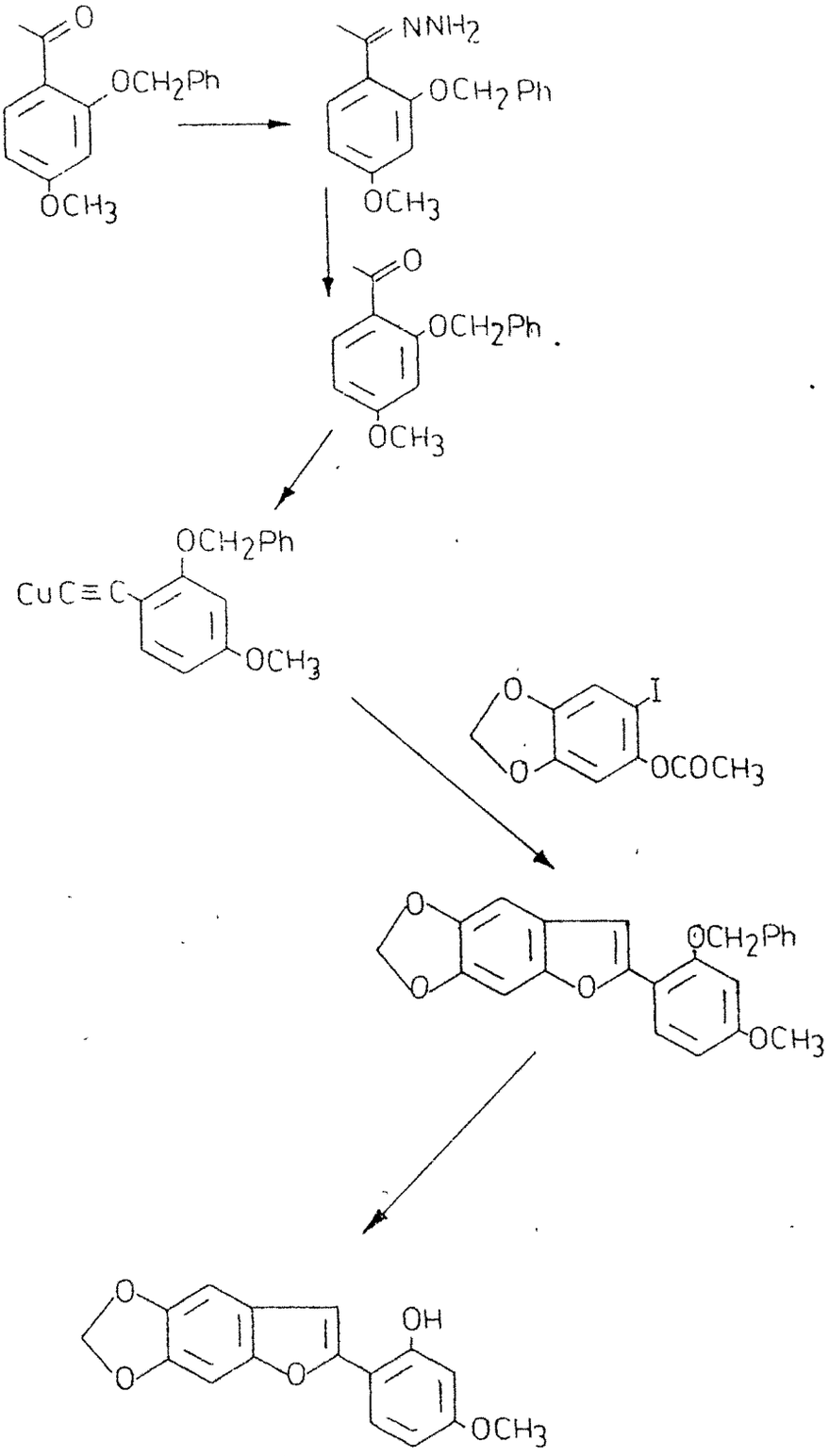
In the field of xanthones, above type of furan is not known in the nature and no one has synthesised such xanthone so it was thought of interest to prepare furano xanthone bearing 5'-isopropanol, 5'-isopropenyl and 5'-



SCHEME-3



SCHEME-4


O
OCH2Ph
OCH3
NNH2
OCH2Ph
OCH3
O
OCH2Ph
OCH3
OCH2Ph
CuC≡C
OCH3
O
O
I
OCOCH3
O
O
OCH2Ph
O
OCH3
O
O
OH
O
OCH3

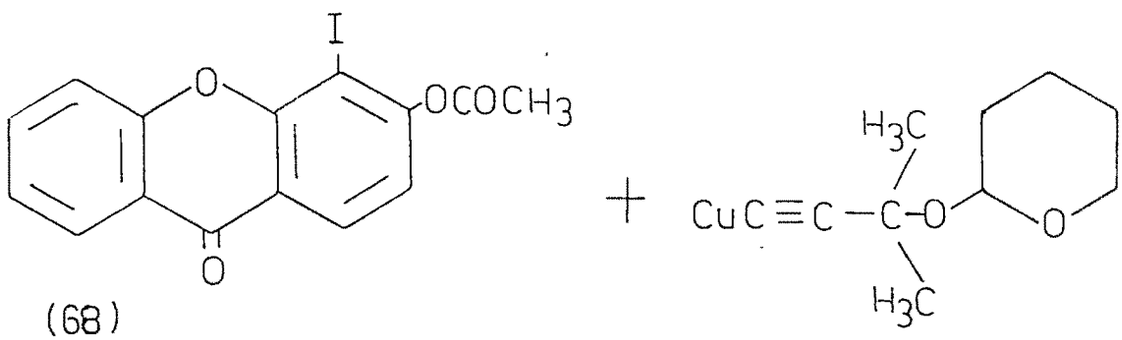
(E)

SCHEME-5

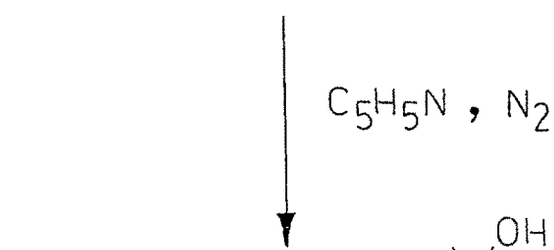
phenyl substituted xanthone, using Cu (I) acetylide derivatives and o-acetoxy or o-hydroxybromoxanthones.

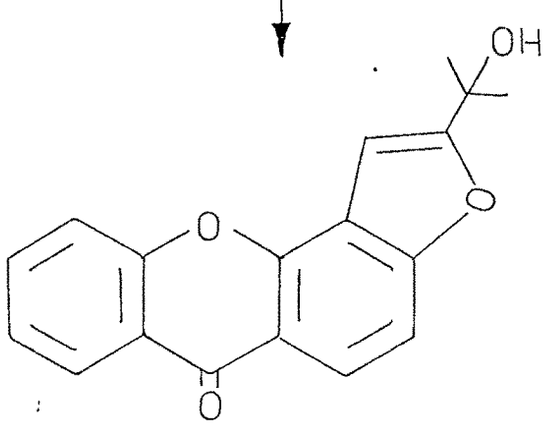
Synthesis of 5'-(1-hydroxy-1-methylethyl)-furano (2', 3' : 3,4) xanthone (70)

3-Acetoxy-4-iodoxanthone (68) on condensation with cuprous salt of THP ether of 3-hydroxy-3-methyl-2-but-1-yne (69) in pyridine gave 5'-(1-hydroxy-1-methylethyl) furano (2', 3' : 3,4) xanthone (70), the structure of which was established on the basis of its mass, IR and NMR spectral studies. mass m/e 294 (M^+), 279 (M^+-CH_3), 237, 209 indicates the absence of halogen. NMR in $CDCl_3$ (Fig.20,21) showed a singlet integrating for six protons corresponding to two methyl groups at δ 1.70; singlet at 2.75 for hydroxyl proton exchangeable with D_2O; singlet at δ 6.8 integrating for one proton is assigned to proton of furan ring at position C4' indicate that deetherification has taken place during the reaction. Moreover two doublets of J=8.5Hz (AB pattern, ortho coupling) one at δ 8.09 and another at δ 7.33 for protons at position 1 and 2 respectively, suggest that (70) is an angular furanoxanthone. 7.49, doublet, 1H, J=9Hz, H-5; 7.73, td, 1H, J=8,8,2Hz, H-6; 7.40, td, 1H, J=8,8,2Hz, H-7 and 8.37, double dublet, 1H, J=8,2Hz, H-8. The second product was indentified as 3-hydroxy-4-iodoxanthone m/e. 338 identical with authentic sample.



(68)





(70)

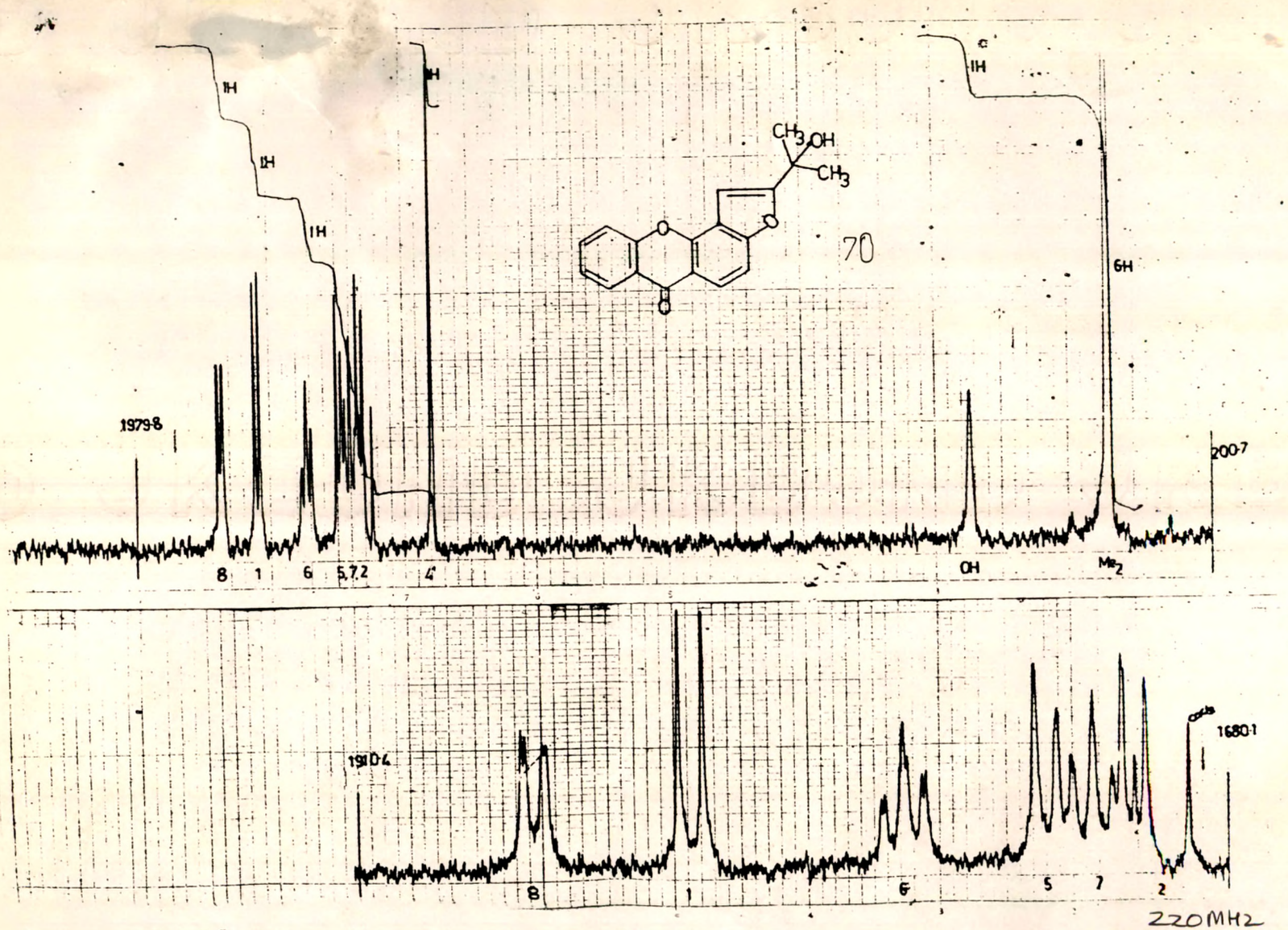

1H
1H
1H
1H
1979·8
8
1
6
5,7,2
4'
OH
Me2
6H
200·7
70
1910·4
8
1
6
5
7
2
1680·1
220MHz

FIG 20

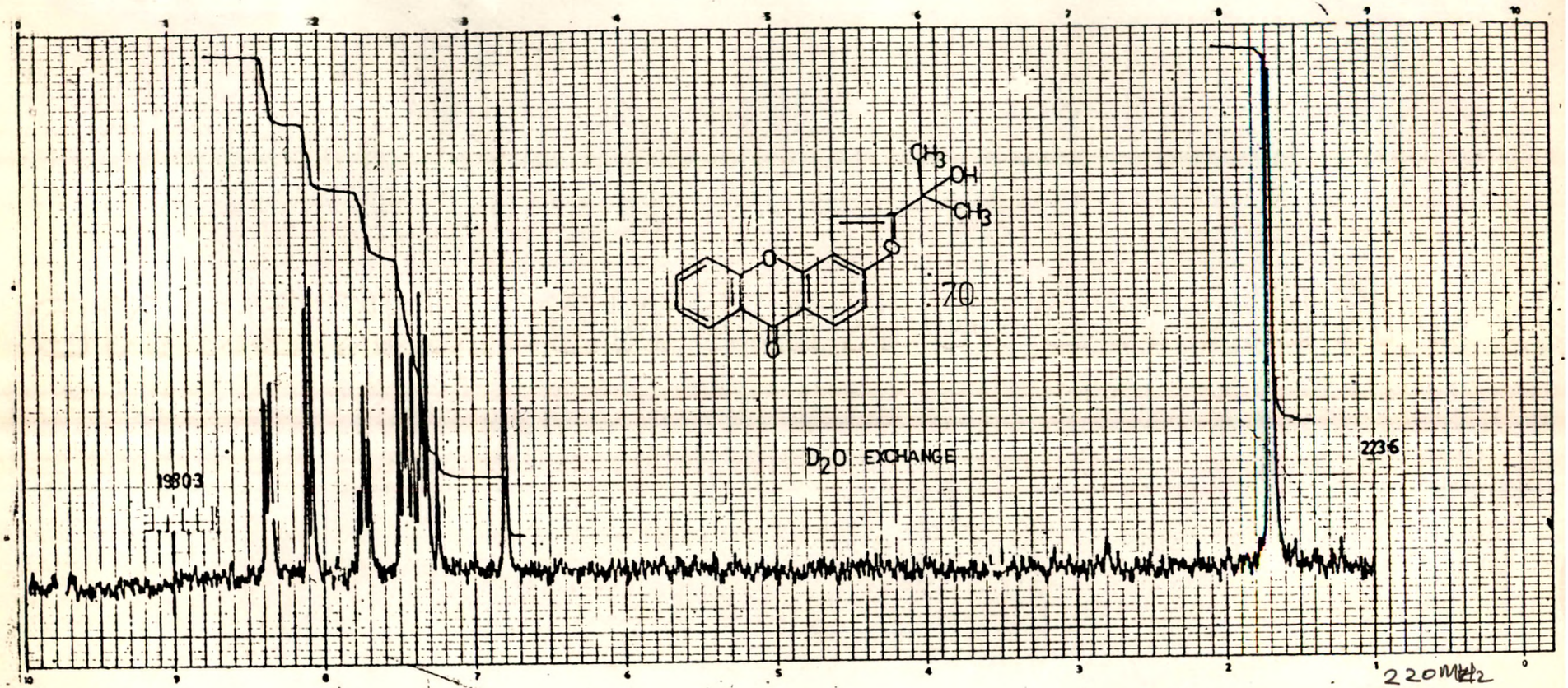


FIG 21

When condensation of (69) and 3-hydroxy-4-bromoxanthone was carried out in pyridine the compound (70) was obtained. The same reaction was also tried using dimethyl formamide as solvent but the yield was poor.

Synthesis of 5'-(1-hydroxy-1-methyl) furano (3',2': 1,2) xanthone (72)

1-Bromo-2-hydroxyxanthone (71) was prepared as described in Chapter 3, which on condensation with Cu salt (69) in pyridine, gave a mixture of two compounds which were separated by preparative tlc to give 5'-(1-hydroxy-1-methyl) furano (3',2': 1,2) xanthone (72) as major product. Its NMR spectrum in $CDCl_3$ (Fig.22) shows singlet of six protons at δ 1.7 due to two methyl groups; 3.0, broad singlet due to -OH group; 7.1 to 7.6 multiplet, 6H, H-3 to H-7 and C4'H; 8.25, dd, 1H, J=8,2Hz, H-8. The second compound was obtained in very small quantity and so no spectral studies except mass spectrum could be carried out. Mass spectrum m/e 276 (M^+), 261, 255, 242, 230, etc. suggests that it may be a dehydrogenated product 5'-isopropenylfurano (3',2' 1,2) xanthone (72a).

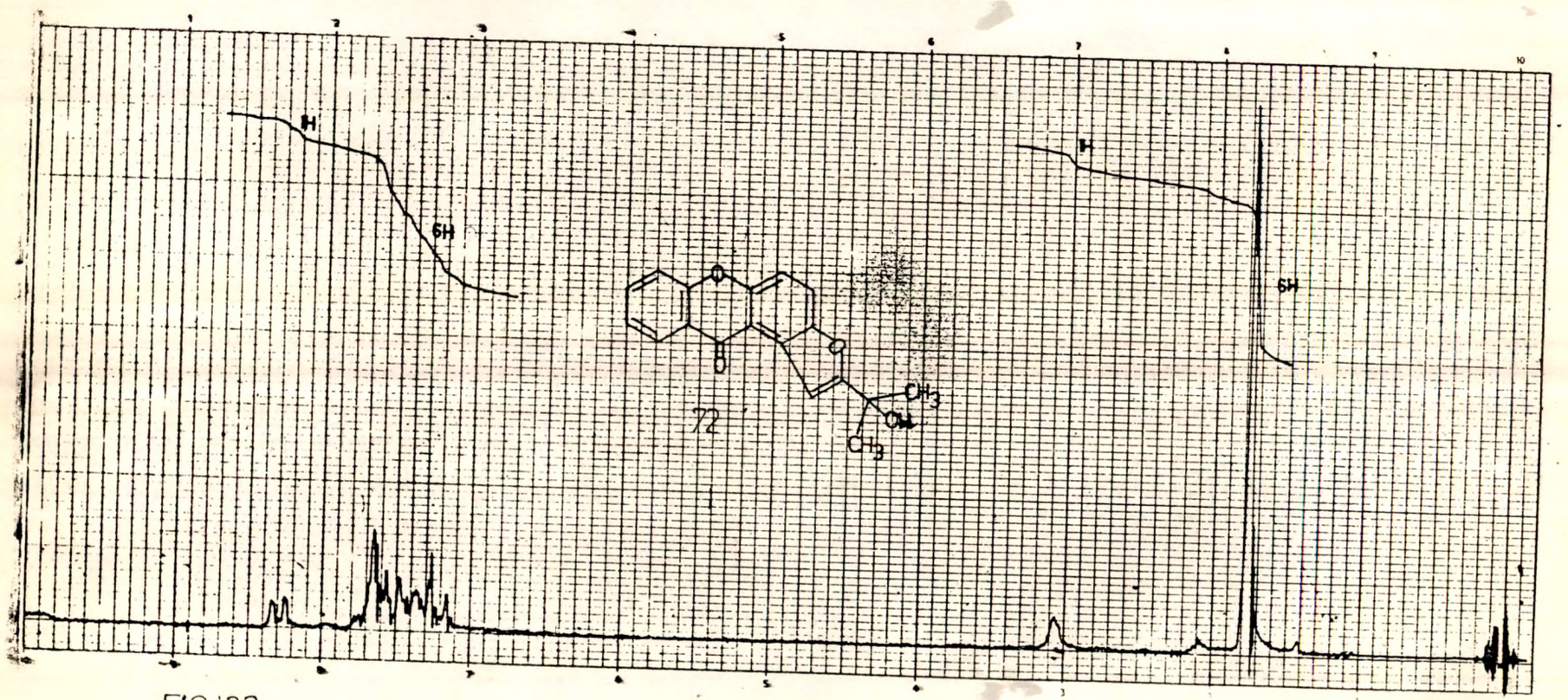
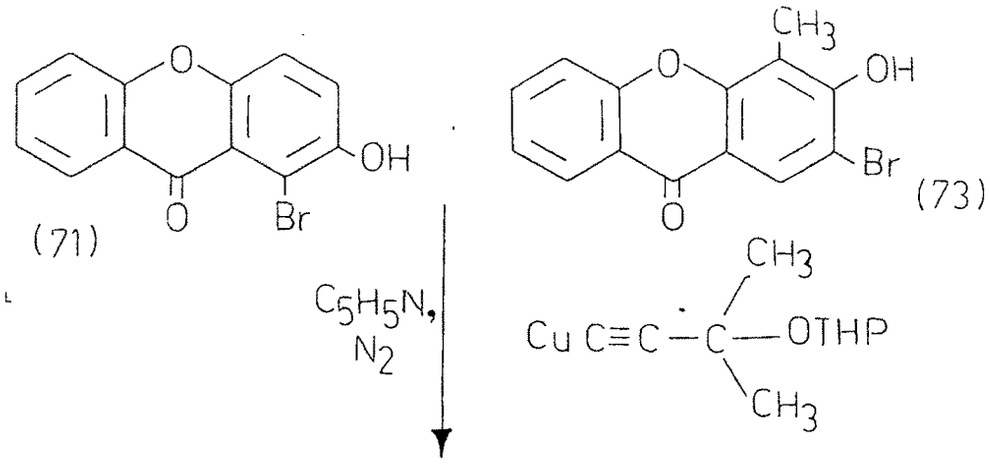
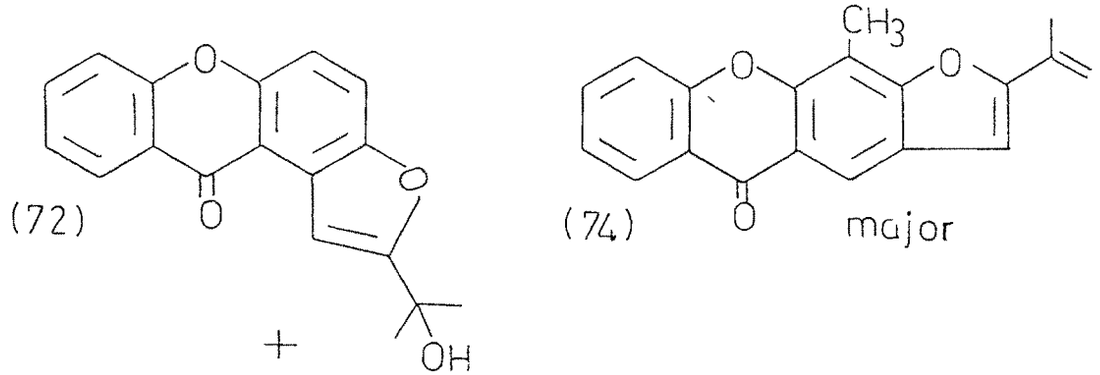


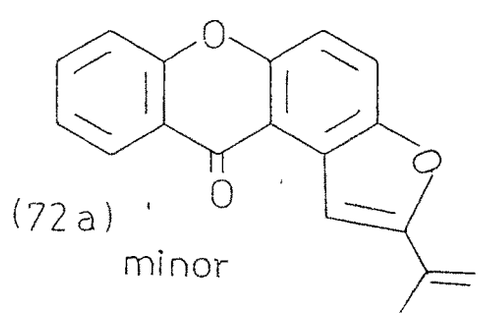
FIG 22

Synthesis of 5'-isopropenyl-4-methyl furano (3',2': 2,3) xanthone (74)

An interesting result was obtained when 2-bromo-3-hydroxy-4-methylxanthone (73) when refluxed with (69) in pyridine for 18 hr. The product obtained was characterised as 5'-isopropenyl-4-methylfurano (3',2' 2,3) xanthone (74), on the basis of its NMR spectrum in $CDCl_3$ (Fig.23) which showed a doublet of J=1Hz at δ2.18 integrating for the three protons of the vinylic CH_3 group, quartet J=1Hz and doublet J=1Hz at δ5.28 and 5.88 for two vinylic proton, δ2.7, singlet, 3H, $ArCH_3$; 6.72, singlet, one proton of furan ring at position C4'; 7.35 to 7.8, m, 3H, protons at positions 5,6 and 7; 8.32, singlet, periproton at position 1; 8.37, dd, J=8, 2Hz, another periproton at position 8. Thus compound (74) has got isopropenyl side chain instead of isopropanol side chain in the furan ring. It means that deetherification and dehydration had taken place during the reaction. This may be due to long refluxing and use of Conc. HCl during the work up of the reaction mixture.


(71)
OH
Br
O
C_5H_5N,
N_2
CH_3
OH
Br
(73)
Cu C≡C
OTHP


(72)
OH
(74)
major


(72a)
minor

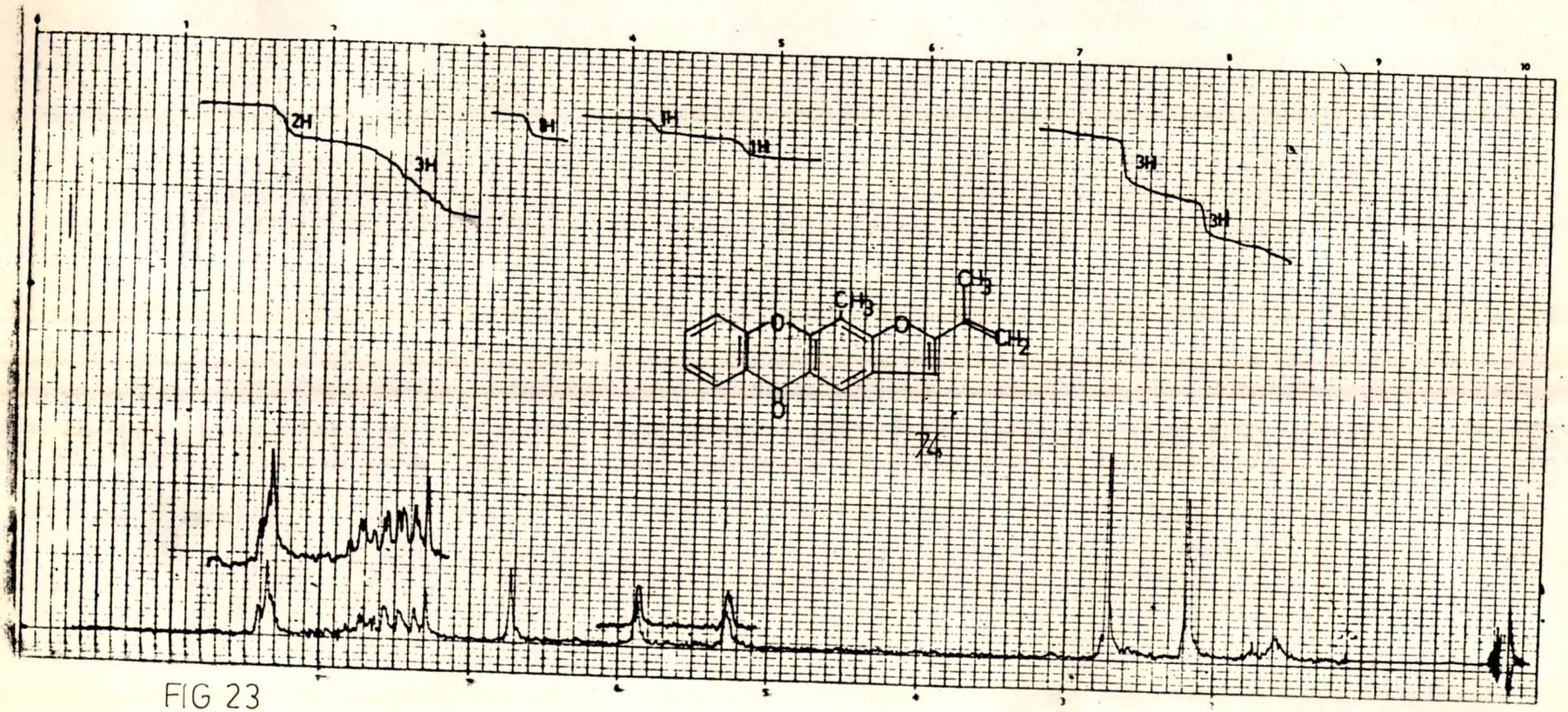


FIG 23

Synthesis of 5'-phenyl-3-methylfurano (2',3' : 1,2) xanthone (77)

The required cuprous phenylacetylide was prepared from phenyacetylene by the method of Robert stevenson. Coupling of the cuprous phenylacetylide (75) with 1-hydroxy-2-bromo-3-methyl xanthone (76), prepared as described in Chapter 3, was effected by refluxing in pyridine, which gave the desired product 5'-phenyl-3-methylfurano (2',3' : 1,2) xanthone (77), the structure of which was confirmed by its mass and NMR spectral data. Mass m/e 326. NMR spectrum ($CDCl_3$) (Fig.24) shows absence of peaks for hydroxyl group, singlet of one proton at δ 6.99 which is assigned to proton of furan ring at position c, second singlet appears at δ 7.4 due to proton at position b, 8.38, dd, J=9,2Hz, 1H, due to periproton a; 7.97, dd, J=9,2Hz, integrating for two protons e, e of phenyl group in the furan ring; 7.65, td, J=9,9,2Hz, 1H, proton d; 7.5-7.3, multiplet of 5H, protons g,g, h, i and f; and a sharp singlet resonating at 2.55 for the three protons of the methyl group on the ring.

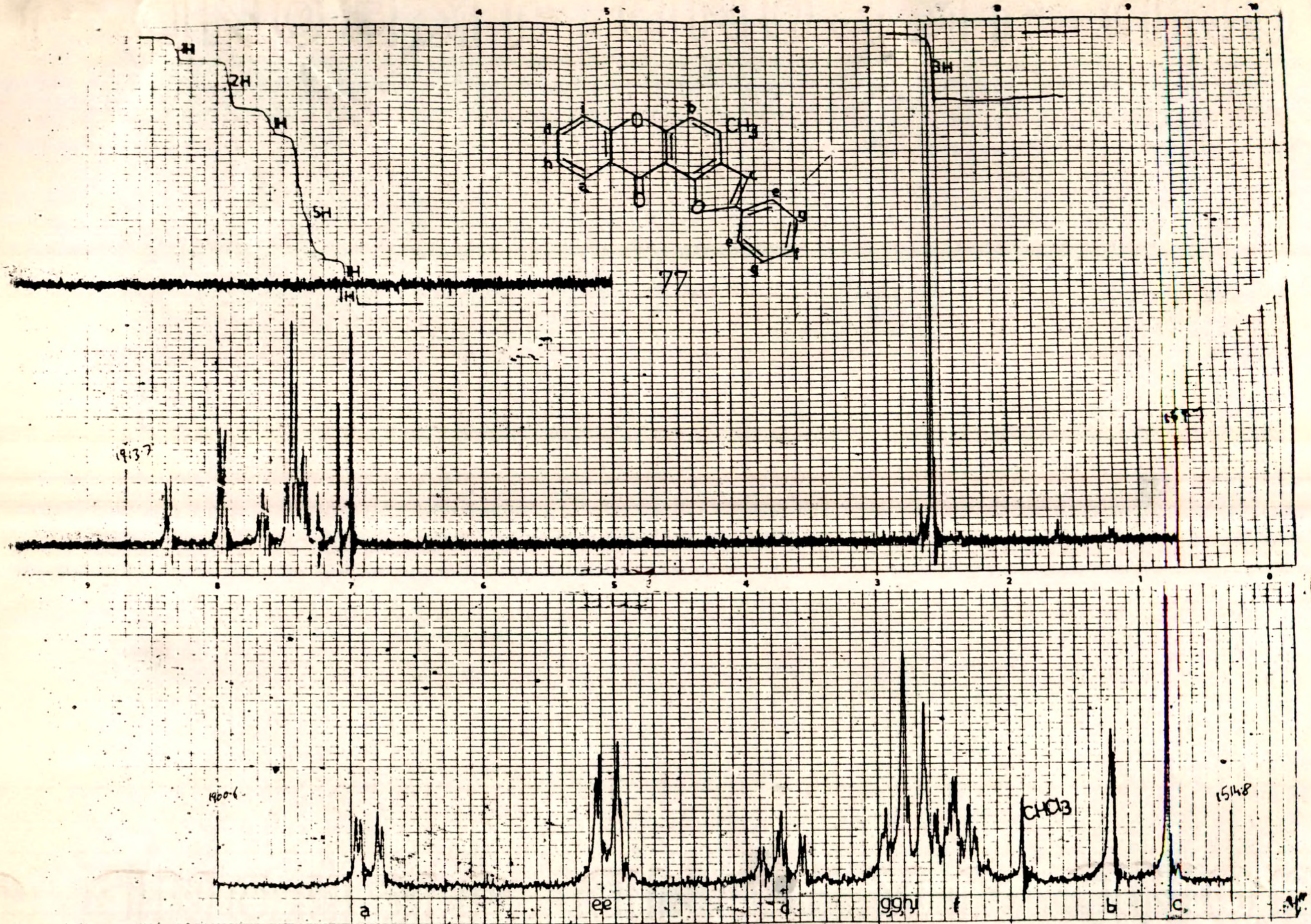

1H
2H
1H
5H
1H
1H
3H
CH3
77
19.3.7
1960.6
a
ee
d
gghi
f
CHCl3
b
c
1514.8
220MHz

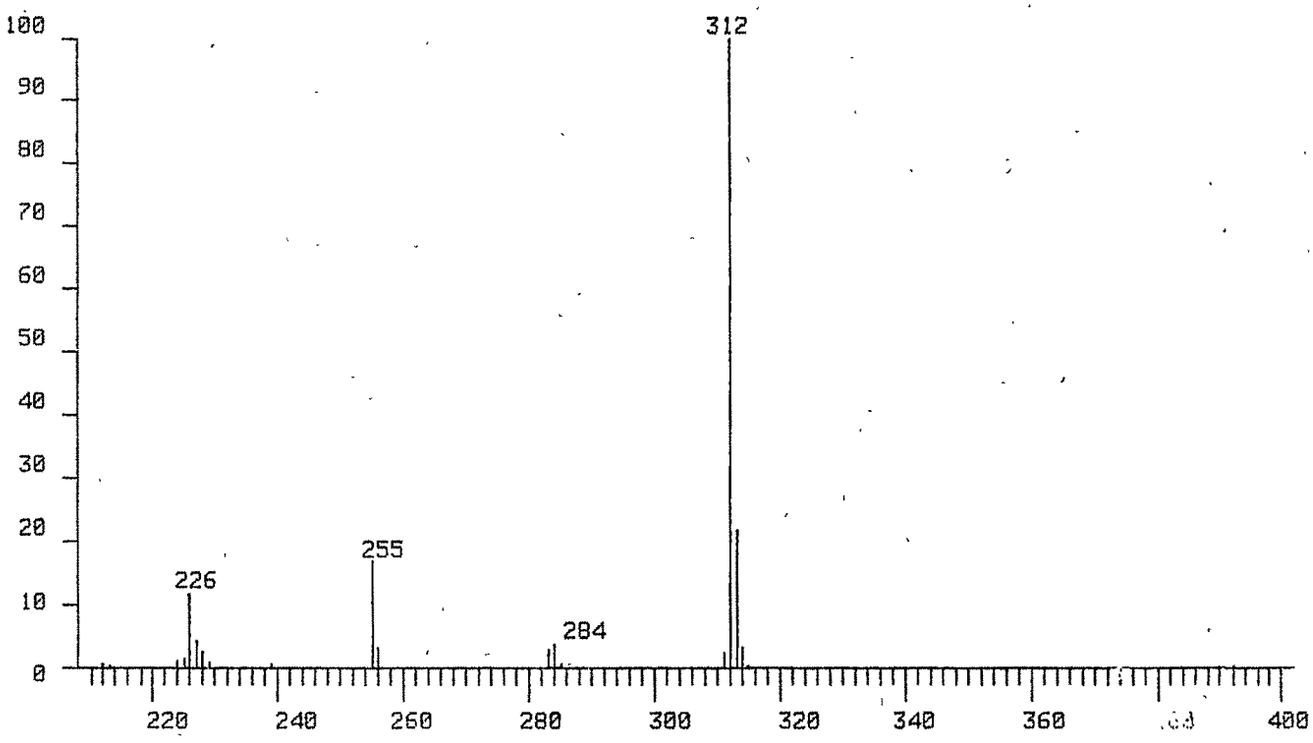
FIG 24

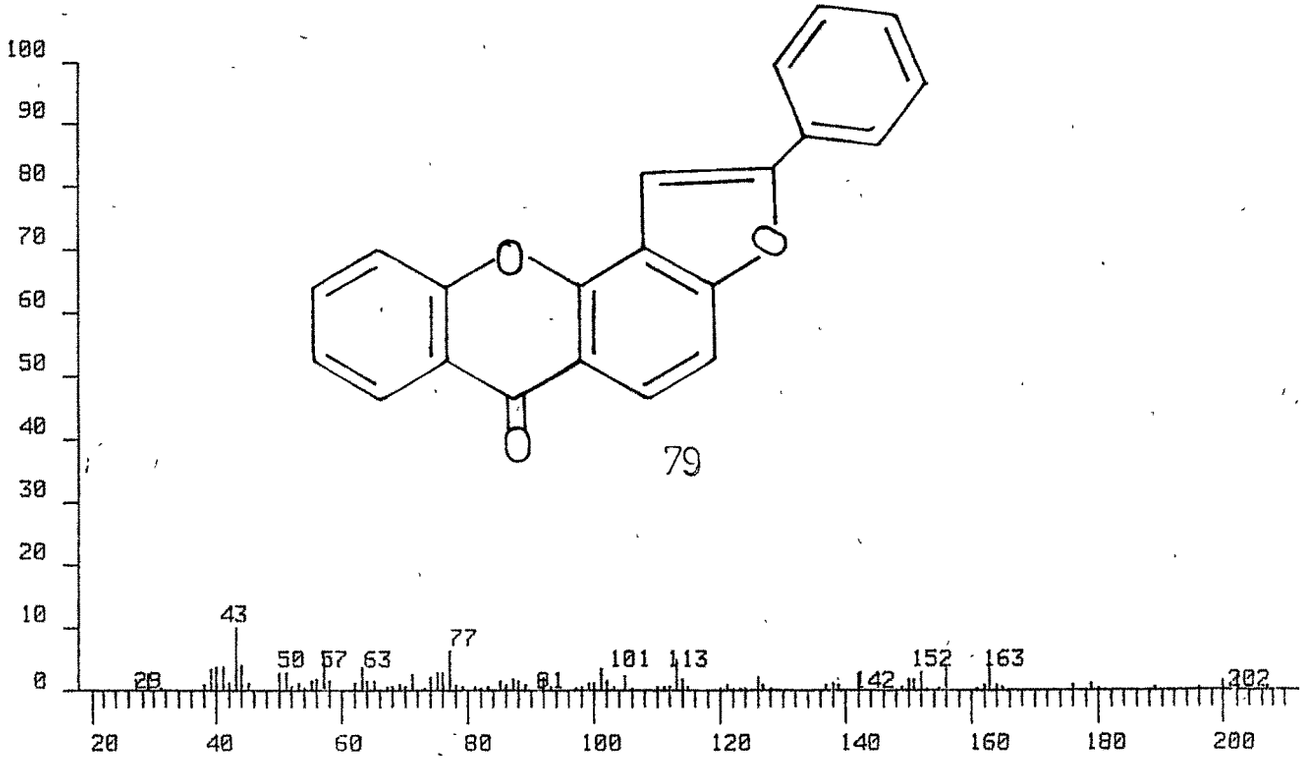
Synthesis of 5'-phenylfurano (2',3': 3,4) xanthone (79)

3-Hydroxy-4-bromoxanthone (78) and the cuprous phenyl acetylide (75) was heated in pyridine under nitrogen atmosphere for 8 hr. The product obtained was characterised as 5'-phenylfurano (2',3': 3,4) xanthone (79) on the basis of its mass and NMR spectra.
Mass m/e. 312 (M^+), 284 (M^+-CO). (Fig. 25)
NMR ($CDCl_3$) : δ 8.4, dd, J=8,2Hz, 1H, H-8; 8.28, doublet, 1H, J=9Hz, H-1; 7.9 to 7.4, multiplet, 10H, H-2, H-5 to H-7, singlet of C4'H at 7.4 and 5H of phenyl ring.

Synthesis of 2-bromo-5'-phenylfurano (2',3': 3,4) xanthone (81)

2,4-Dibromo-3-hydroxyxanthone (80) prepared as described in Chapter 3 was coupled with (75) by refluxing in pyridine under nitrogen atmosphere to give (81) the structure of which was confirmed by its IR, mass and NMR spectrum. Mass : m/e 392 (Fig.26). The NMR spectrum in $CDCl_3$ (Fig.27) showed a doublet centered at δ 8.43, J=9Hz due to periproton at position b, a singlet at 8.39 was assigned to another periproton at position a, 7.93, doublet, J=9Hz, 2H, g, g proton of phenyl ring. 7.78, t, 1H, J=9Hz, proton c, 7.4 to 7.8, multiplet, 6H, h,h,i and d,e,f, protons. This confirmed the assigned structure(81).

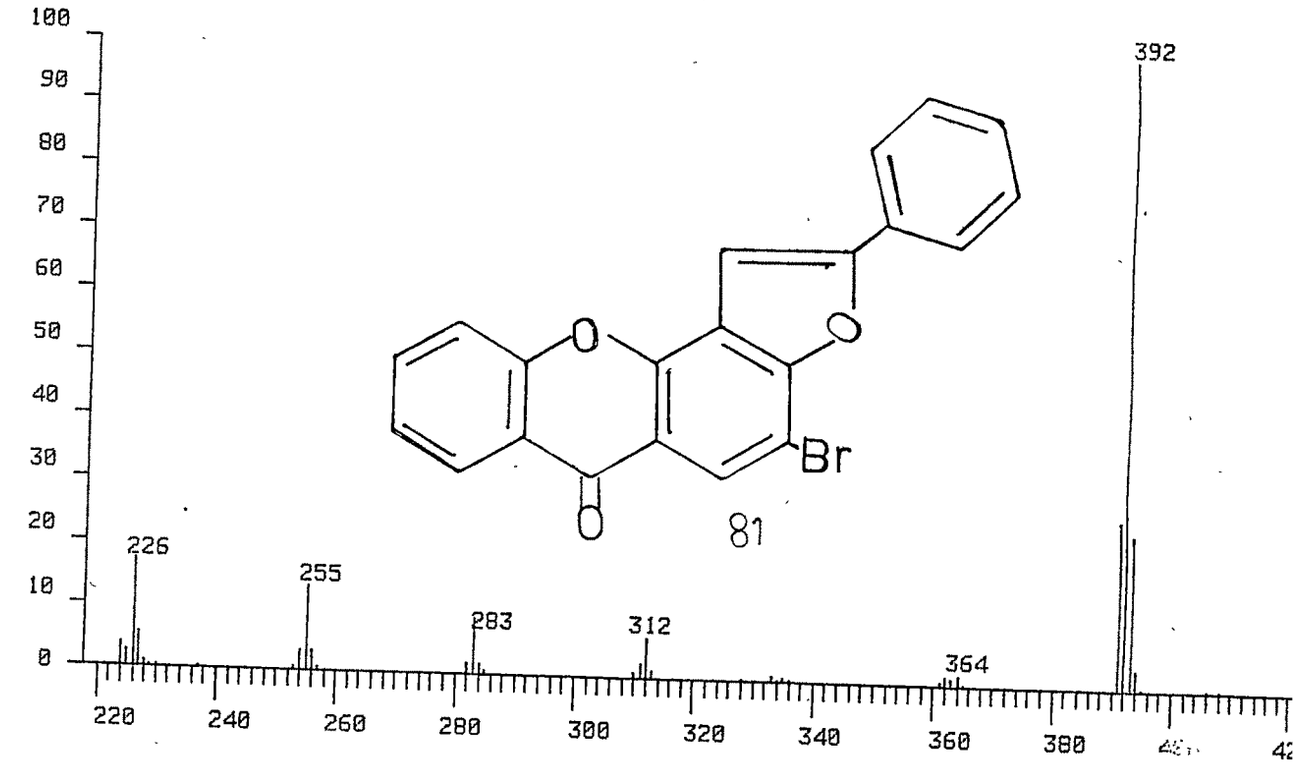

100
90
80
70
60
50
40
30
20
10
0
312
255
226
284
220
240
260
280
300
320
340
360
400


100
90
80
70
60
50
40
30
20
10
0
43
77
50
57
63
101
113
152
163
28
81
142
202
20
40
60
80
100
120
140
160
180
200

O
O
O

79

FIG 25


100
90
80
70
60
50
40
30
20
10
0
226
255
283
312
364
392
220
240
260
280
300
320
340
360
380
O
O
O
Br
81

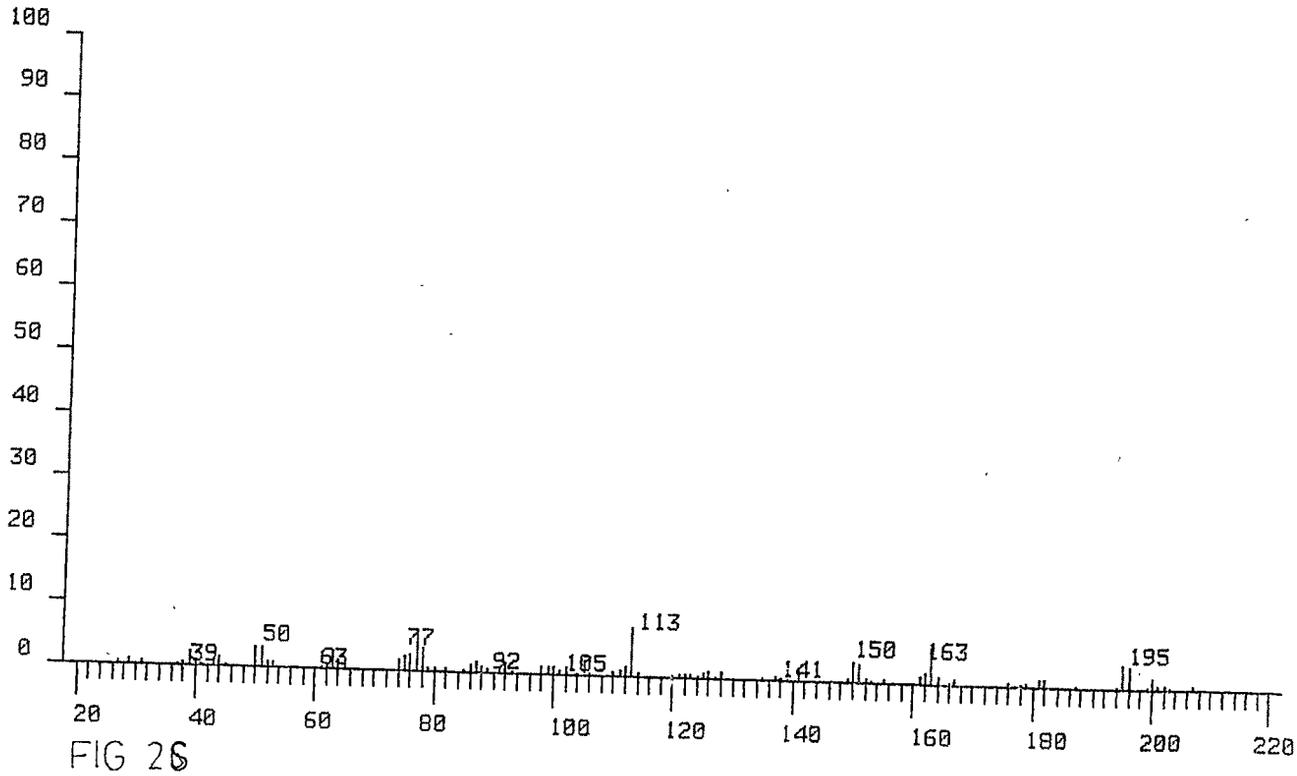
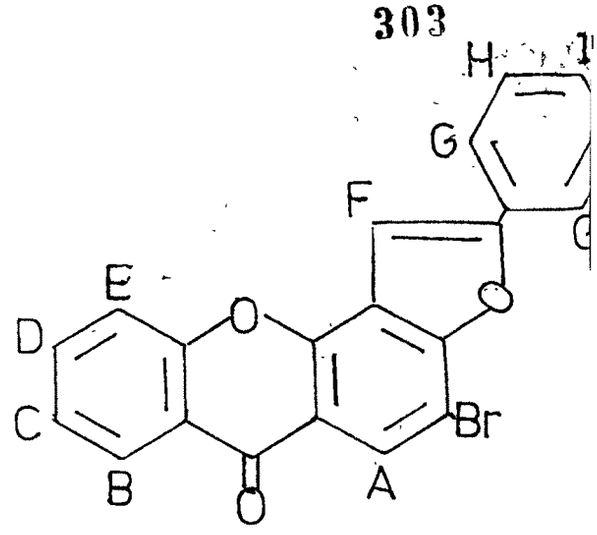

100
90
80
70
60
50
40
30
20
10
0
39
50
63
77
92
105
113
141
150
163
195
20
40
60
80
100
120
140
160
180
200
220

FIG 26

FIG 81



81

FIG 27

Synthesis of 5'-phenylfurano (2',3': 1,2) xanthone (83)

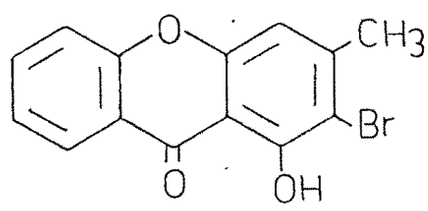
1-Hydroxy-2-bromoxanthone (82) prepared as described in Chapter 3 was coupled with (75) by heating in pyridine under nitrogen atmosphere to give 5'-phenylfurano (3',2': 1,2) xanthone (83). IR (KBr) shows no peak for hydroxyl group, moreover it shows characteristic bands, indicating the presence of furan ring. NMR ($CDCl_3$) showed δ 8.32, dd, 1H, J=9,2Hz, H-8; 6.89, doublet, 1H, J=9Hz, H-3; 8.0-7.20, multiplet, 10H, H-4 to H-7, C4'-H, 5H of phenyl ring. There were no D_2O exchangeable peaks in NMR spectrum indicating absence of free hydroxyl group and hence provided an evidence for formation of furan ring.

Synthesis of 5'-phenylfurano (3',2': 1,2) xanthone (84)

Coupling of the cuprous salt (75) with 1-bromo-2-hydroxyxanthone (71) was effected by heating in pyridine to give (84).

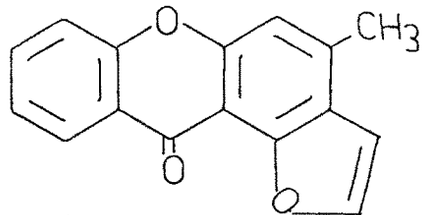
Synthesis of 4'-phenyl-5'-methylfurano (2',3': 3,4) xanthone (91)

3-Hydroxyxanthone (85), on cinnamylation with cinnamyl chloride, in presence of anhydrous potassium carbonate, and potassium iodide in dry acetone yielded 3-cinnamyloxyxanthone (86) which on Claisen

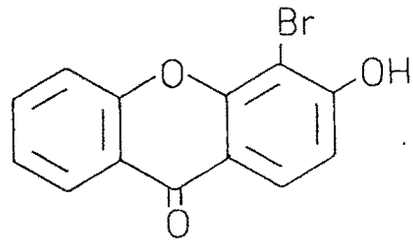


(76)

(75)

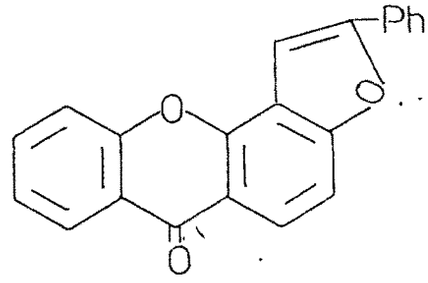


(77)

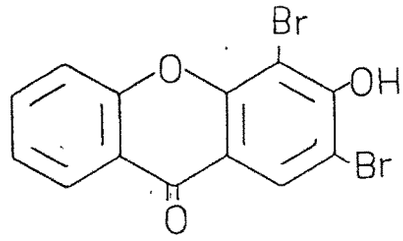


(78)

(75)

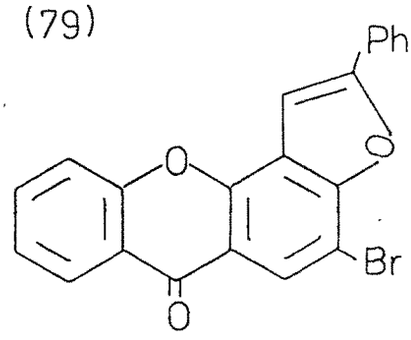


(79)

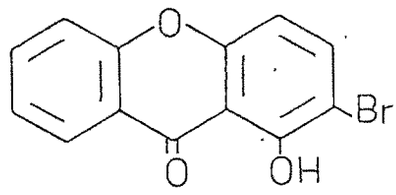


(80)

(75)

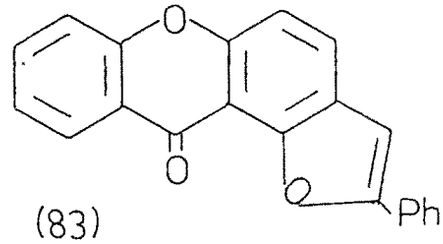


(81)

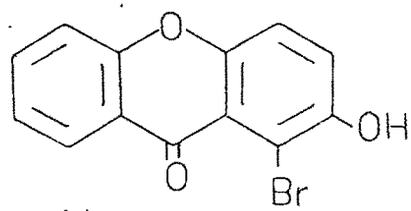


(82)

(75)

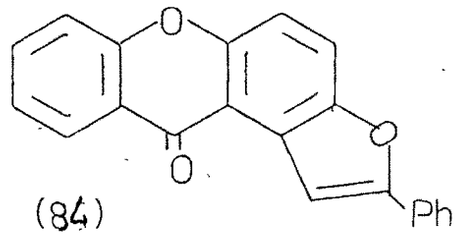


(83)



(71)

(75)



(84)

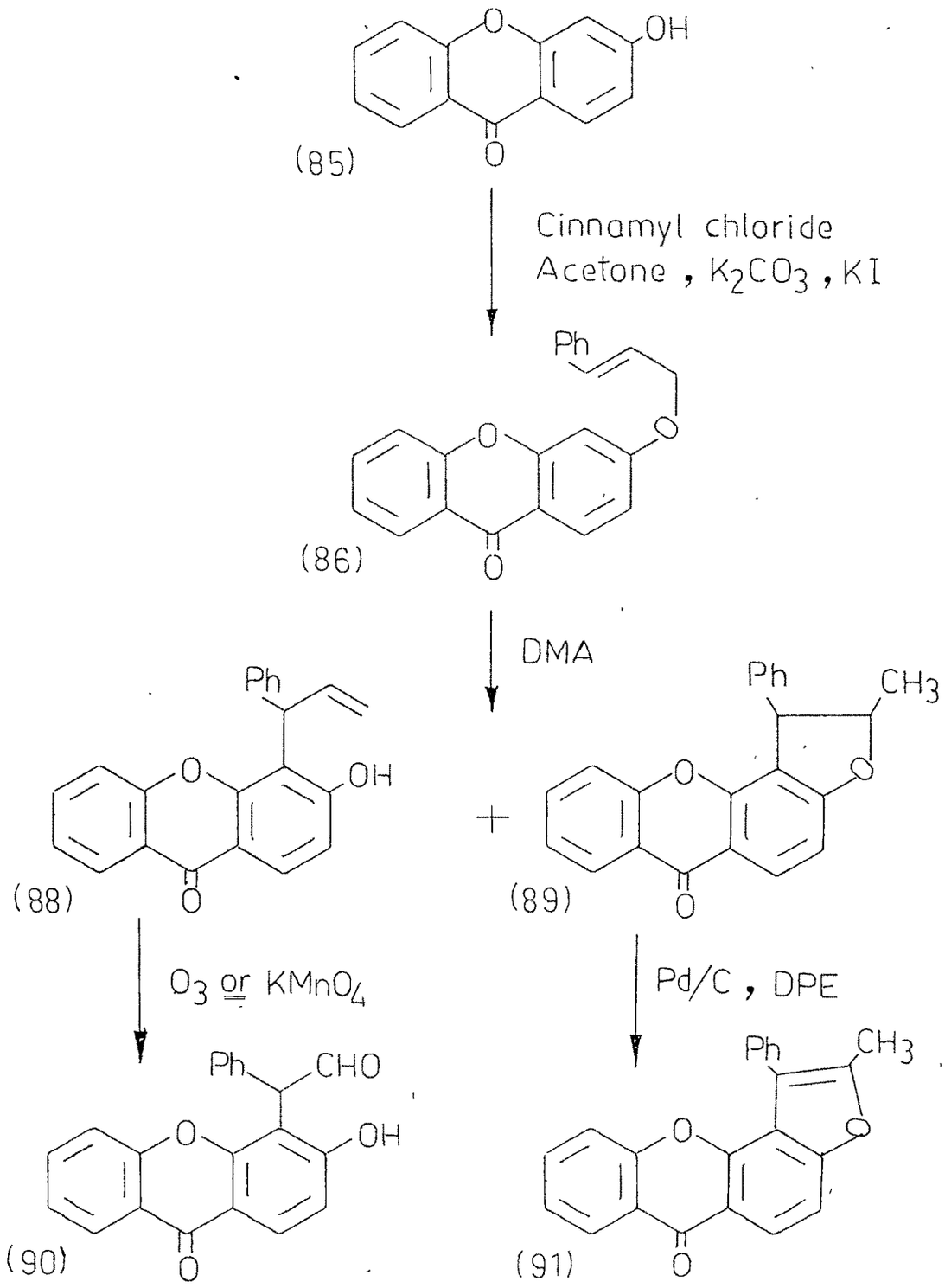
C_5H_5N , N_2 Atmosphere

migration in boiling dimethylaniline furnished two products. The first product was soluble in sodium hydroxide and was characterised as 3-hydroxy-4-cinnamylxanthone (88) on the basis of its U.V. and NMR spectral data. UV λmax. 251, 268, 277, 316, NMR spectrum (Fig.28) in CD_3SOCD_3 showed δ8.08, dd, 1H, J=9,2Hz, H-8; 7.95, doublet, J=9Hz, due to periproton 1; 7.62, td, 1H, J=9,9,2Hz, H-6; 7.35 to 7.02,multiplet, 7H, H-5, H-7 and 5 protons of phenyl ring; 6.97, doublet, 1H, J=9Hz, H-2. Examination of the upfield region of the NMR spectrum revealed that there was no CH_3 group and hence the possibility of structure (88a) could be easily ruled out; 6.8 to 6.5 multiplet, 1H, CH_2=C<u>H</u>-C<u>H</u>-Ph; 5.68 to 5.18, multiplet, 3H, C<u>H</u>$_2$=CH-C<u>H</u>-Ph. The presence of two ortho coupled doublet is a direct evidence for the placement of cinnamyl group at position 4. This confirmed the assigned structure (88). The compound (88) was subjected to oxidation by $KMnO_4$ or ozonolysis gave 3-hydroxy-4-(2'-phenyl acetaldhydo) xanthone (90) mass m/e 330. confirming the expected molecular weight.

The second product was indentified as the cyclised compound 4'-phenyl-5'-methyl-4',5'-dihydrofurano (2',3': 3,4) xanthone (89) as its NMR spectrum (Fig.29) in $CDCl_3$

showed doublet at δ 1.7 integrating for 3 protons of C5'-CH_3 group; 3.8, multiplet, 1H, J=9Hz, C5'-H; 5.5, doublet, 1H, J=9Hz, C4'-H indicated that it was a dihydrofuranoxanthone; moreover the peaks in the aromatic region suggested that it was an angular furanoxanthone δ 7.4 overlapping singlet and doublet of protons at position 2, and 5 protons of phenyl ring; 7.7, td, 1H, J=9,9,2Hz, H-6; 8.15, doublet, 1H, J=9Hz, H-1; 8.25, dd, 1H, J=9,2Hz, H-8, confirmed the structure (89), 3-Cinnamyloxy-4-bromoxanthone (87) was prepared by refluxing 3-hydroxy-4-bromoxanthone in dry acetone with cinnamyl chloride, potassium iodide and anhydrous potassium carbonate. The compound (87) on Claisen migration in boiling N,N-dimethylaniline yielded the same two products (88) and (89) as were obtained in case of migration of compound (86).

The dihydrofuranoxanthone (89) on dehydrogenation with palladised charcoal in boiling diphenyl ether yielded 5'-methyl-4'-phenylfurano (2',3': 3,4) xanthone. The structure of the compound was confirmed by its NMR spectrum (Fig.30) in ($CDCl_3$), which showed only one sharp singlet in the upfield region at δ 2.85 integrating for three protons of CH_3 group, 8.35, dd, 1H, J=9, 1.5Hz, H-8; 8.25, doublet, 1H, J=9Hz, H-1 and 7.8 to 7.3, multiplet, 9H, H-2, H-5, H-6, H-7 and 5 protons of phenyl ring.


(85)
Cinnamyl chloride
Acetone , K_2CO_3 , KI
(86)
DMA
(88)
(89)
O_3 or $KMnO_4$
Pd/C , DPE
(90)
(91)

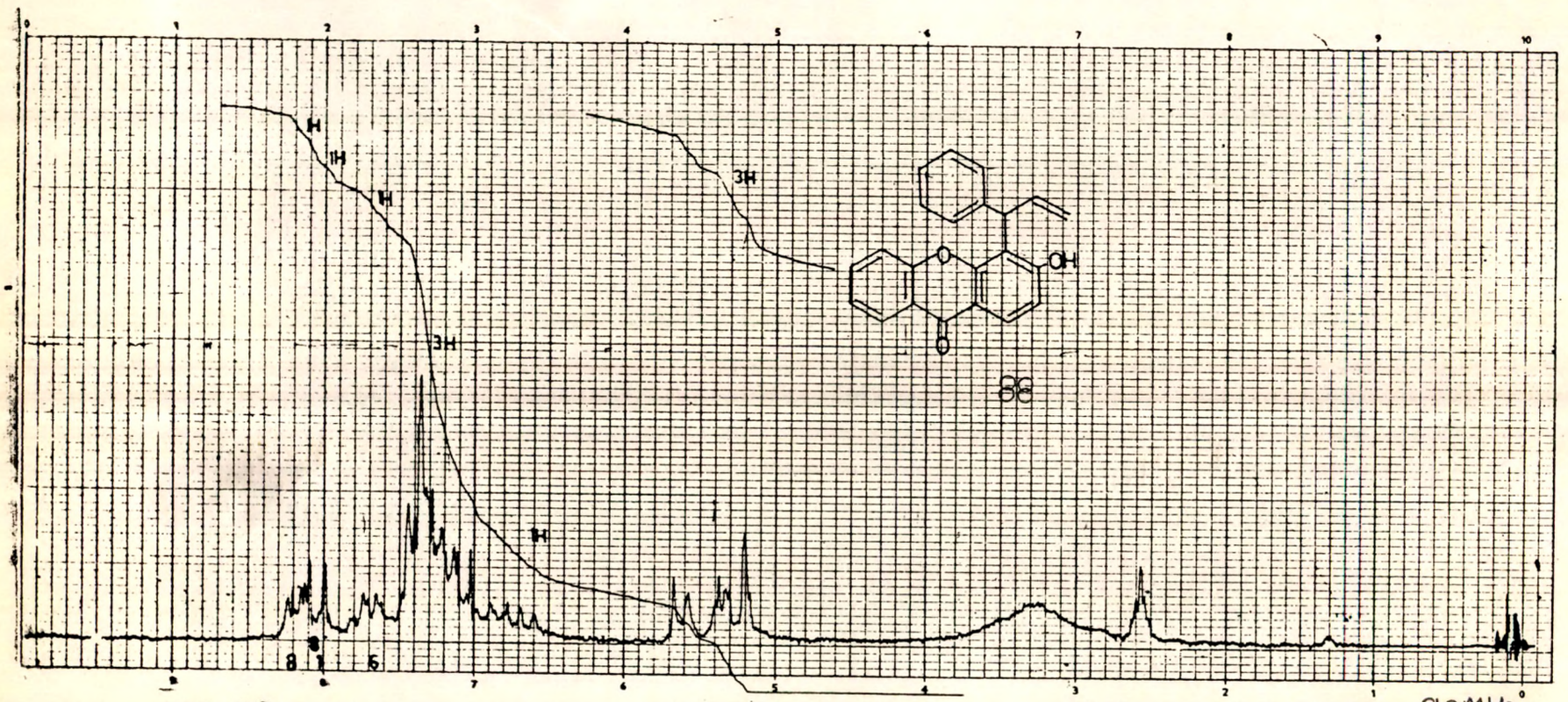


FIG 28

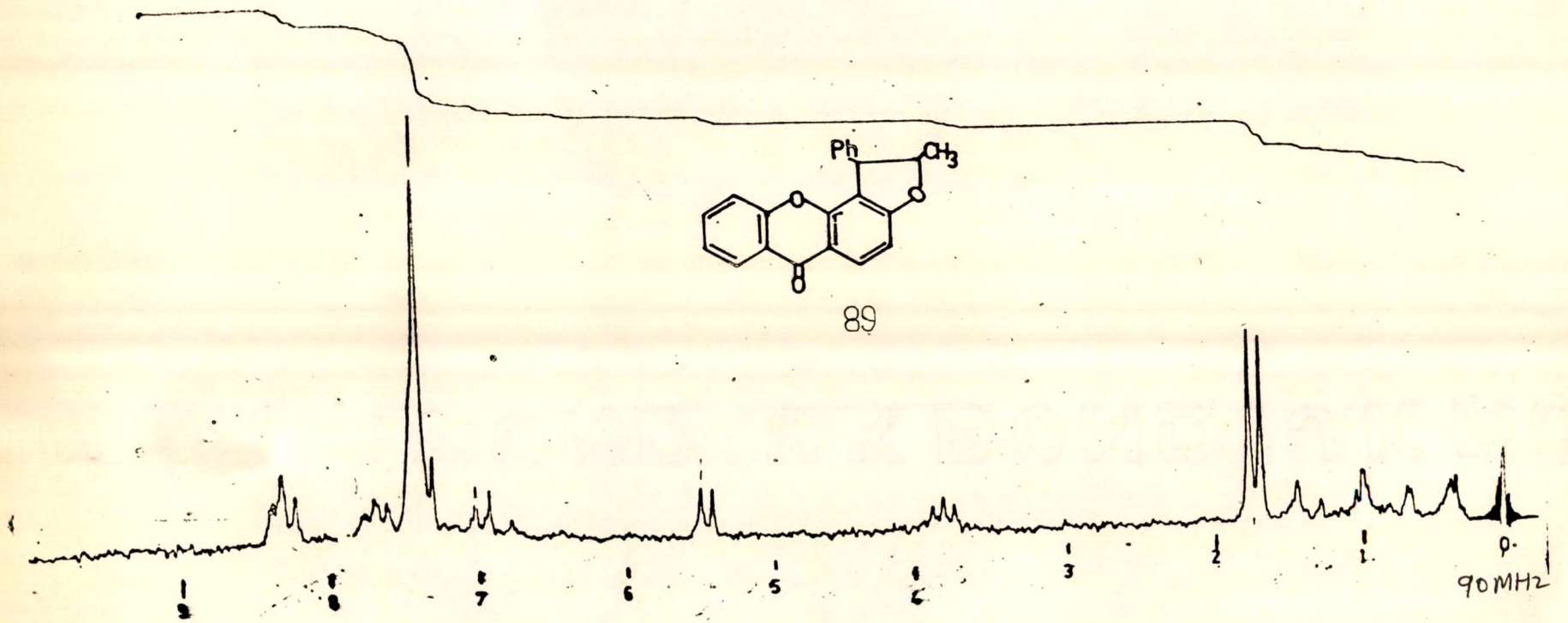


FIG 29

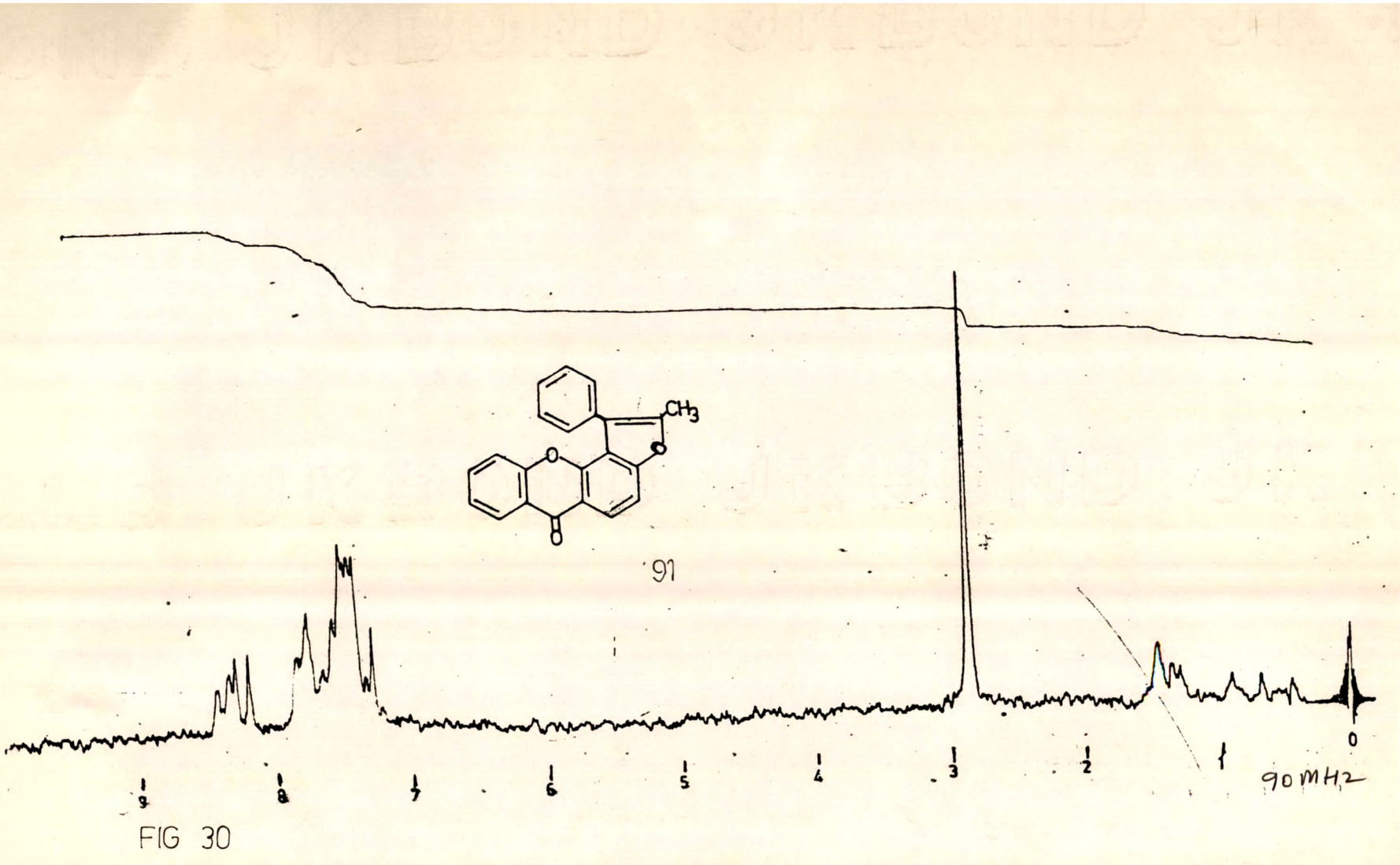


FIG 30

Synthesis of 4'-phenyl-3,5'-dimethylfurano (2',3': 1,2) xanthone (96)

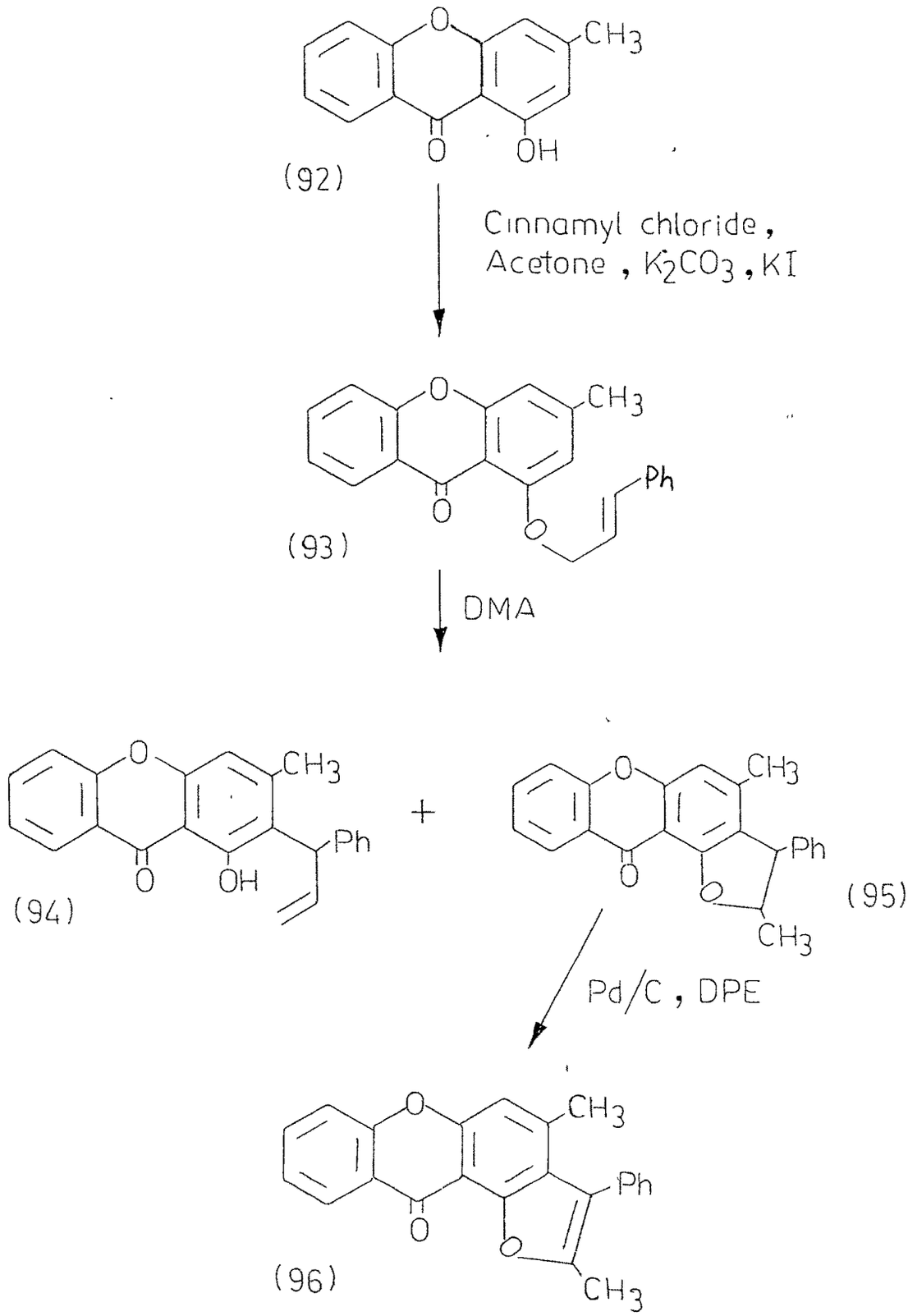
1-Hydroxy-3-methylxanthone (92) was cinnamylated using cinnamyl chloride to give 1-cinnamyloxy-3-methyl-xanthone (93) which on Claisen migration in boiling N,N-dimethylaniline yielded two products which were separated by crystallisation and preparative TLC. The first product, which gave green colour in $FeCl_3$ test, was identified as 1-hydroxy-2-cinnamyl-3-methyl xanthone (94) on the basis of its mass and NMR spectrum. Mass (Fig. 31) m/e 342 (M^+), 327 (M^+-CH_3). NMR ($CDCl_3$) (Fig.32) shows δ 8.3, dd, 1H, J=9,2Hz, H-8; 7.76, td, J=9,9,2Hz, H-6; 7.54 to 7.28, multiplet, 7H, H-7, H-5 and five aromatic protons; 6.80, singlet, 1H, H-4; 6.69-6.47, m, 1H, vinylproton $CH_2\underline{C}H=\underline{C}HPh$; 5.48 to 5.11, multiplet, 3H, 2 vinyl protons and one allylic $\underline{C}H_2=CH-\underline{C}H-Ph$; 2.3, singlet integrating for three protons of aromatic CH_3 group at position 3. This confirmed the assigned structure (94).

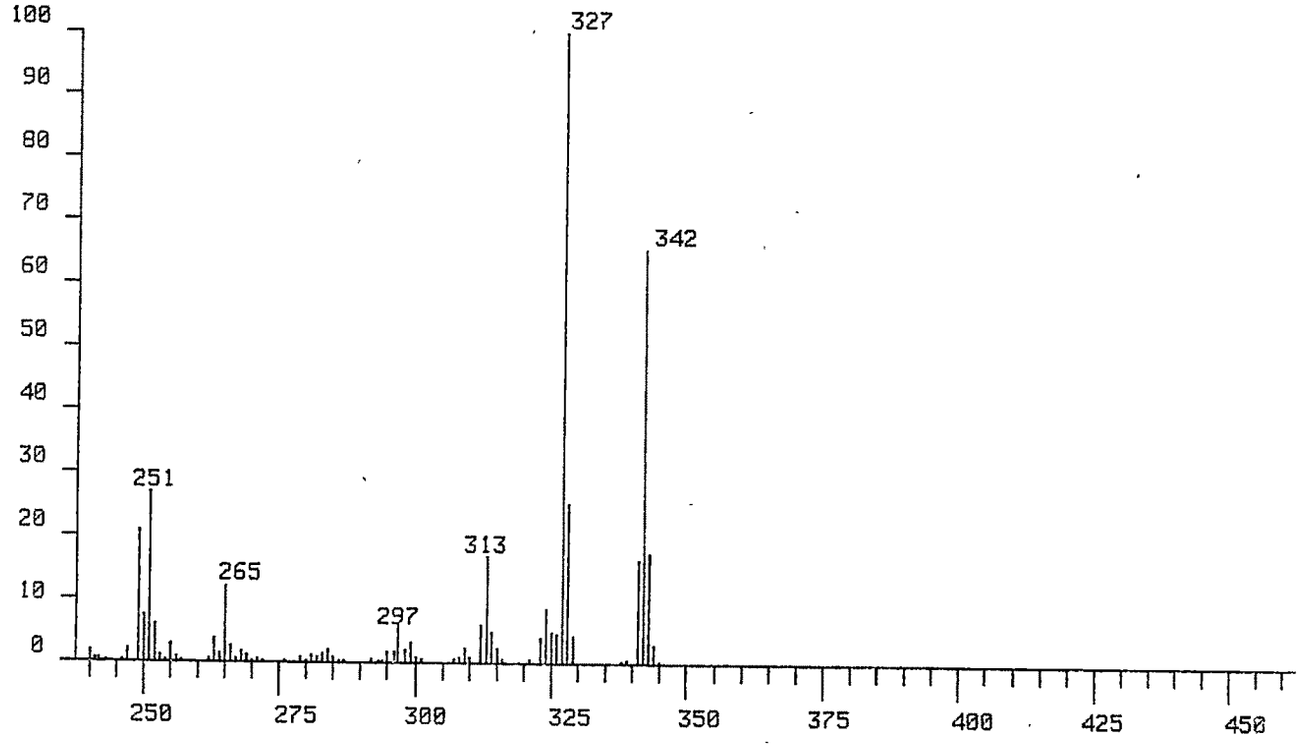
The second product was characterised as 4'-phenyl-3,5'-dimethyl-4',5'-dihydrofurano (2',3': 1,2) xanthone (95) on the basis of its NMR spectrum (Fig.33) in $CDCl_3$; δ1.22, doublet, 3H, J=9Hz, C5'-CH_3; 2.02,S, 3H, CH_3 group at position 3; 4.39, doublet, 1H, J=9Hz, C4'-H;

4.22 to 4.42, m, 1H, C5'-H, 6.72, singlet, 1H, H-4; 6.92 to 7.42, multiplet, 7H, H-5, H-7 and 5 protons of phenyl ring; 7.62, td, 1H, J=9,9, 2Hz, H-6; 8.27, dd, 1H, J=9,2Hz, H-8. Compound (95) on dehydrogenation with palladised charcoal in diphenyl ether gave the furanoxanthone, 4'-phenyl-3,5'-dimethylfurano (2',3': 1,2) xanthone (96). The structure of which was assigned on the basis of its NMR spectrum (Fig.34) in $CDCl_3$ which exhibited a sharp singlet at δ 2.17 integrating for the three protons of the CH_3 group at position C5' while a second singlet of the three protons appeared at δ 2.47 due to the aromatic CH_3 group at position 3. Appearance of the former singlet is the evidence for the dehydrogenated product. Singlet at 6.95 for one proton is assigned to proton at position 4; 7.25-7.47, multiplet, 7H, H-5, H-7 and 5 protons of phenyl ring; 7.65, td, 1H, J=9,9,2Hz, H-6; 8.30, dd, 1H, J=9,2Hz, H-8.

Synthesis of 4'-phenyl-5'-methylfurano (3',2': 1,2) xanthone (100)

2-Hydroxyxanthone (97) on cinnamylation with cinnamyl chloride in presence of potassium carbonate and potassium iodide in dry acetone yielded 2-cinnamyloxy xanthone (98) which on Claisen rearrangement in N,N-dimethylaniline furnished only cyclised product


(92)
Cinnamyl chloride,
Acetone, K_2CO_3, KI
(93)
DMA
(94)
+
(95)
Pd/C, DPE
(96)


100
90
80
70
60
50
40
30
20
10
0
327
342
251
265
313
297
250
275
300
325
350
375
400
425
450

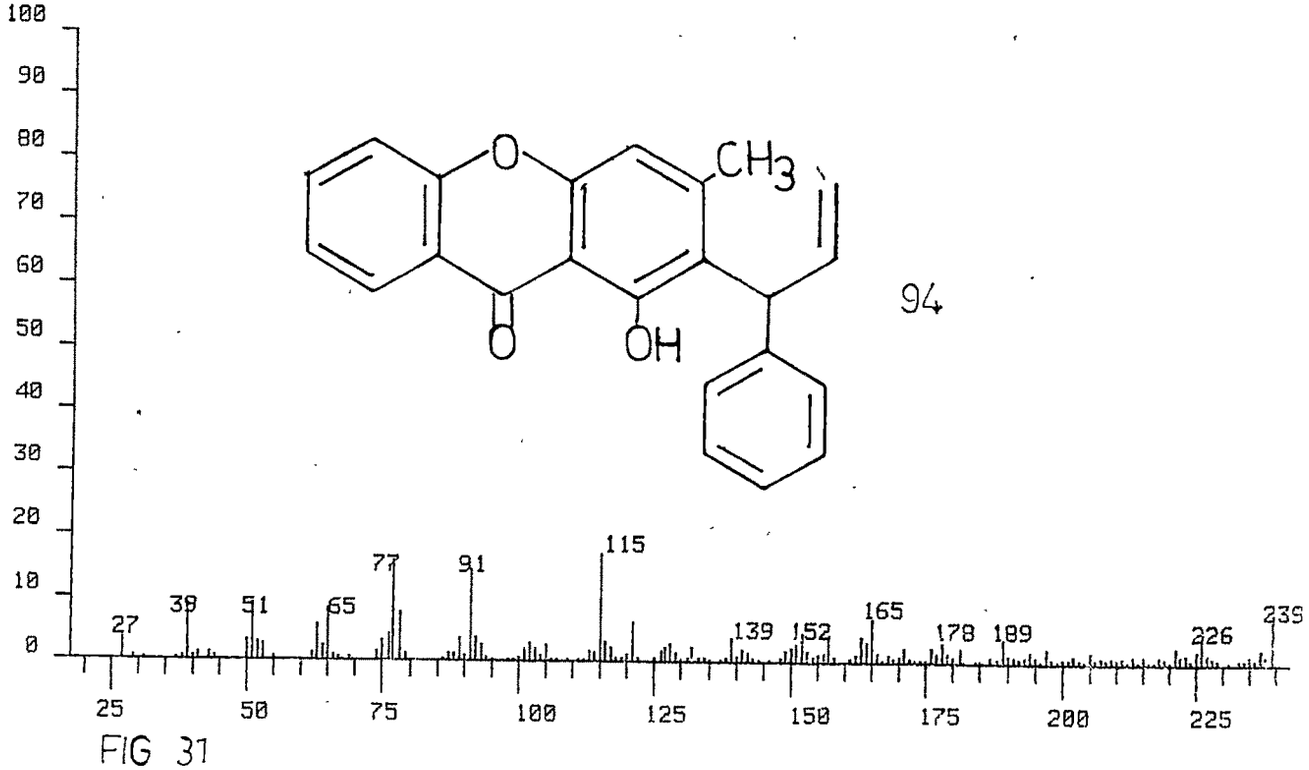
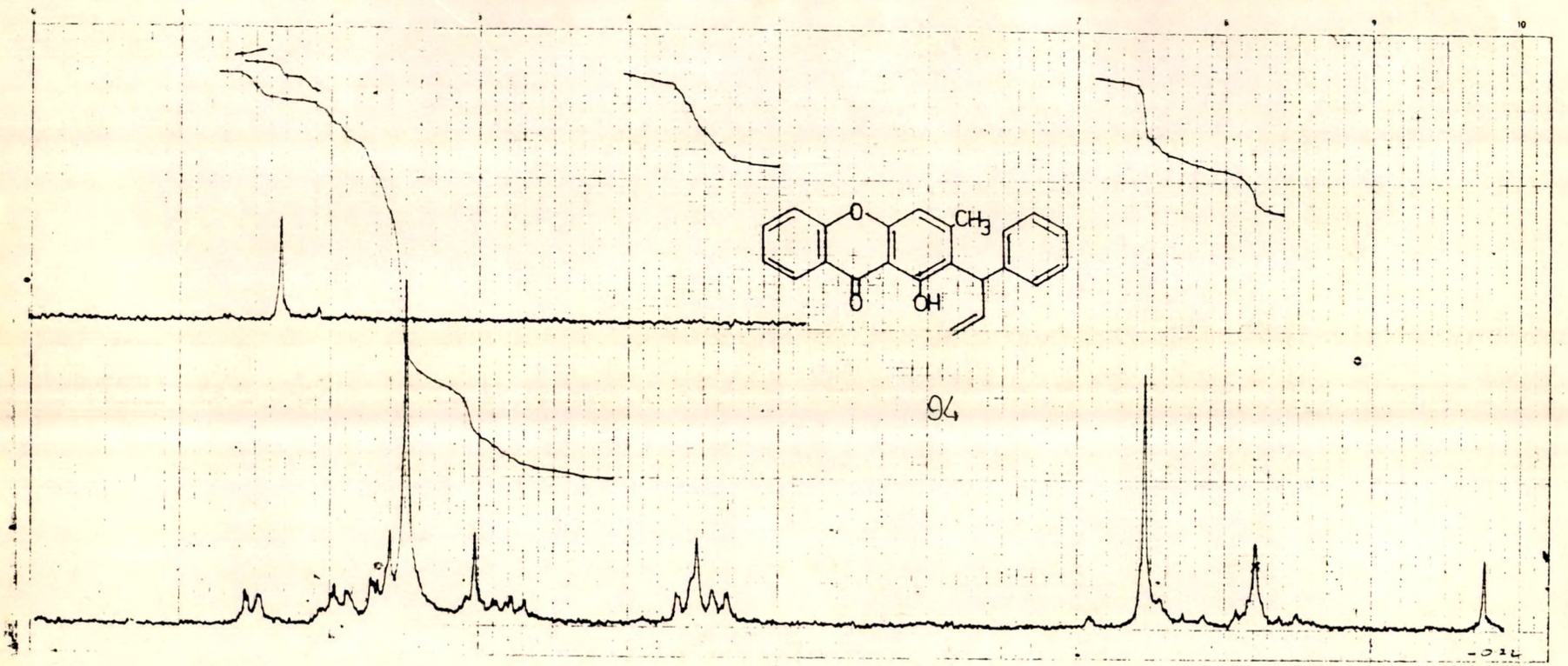

100
90
80
70
60
50
40
30
20
10
0
O
CH3
O
OH
94
115
77
91
27
39
51
65
139
152
165
178
189
226
239
25
50
75
100
125
150
175
200
225

FIG 31



94

FIG 32

90MHz

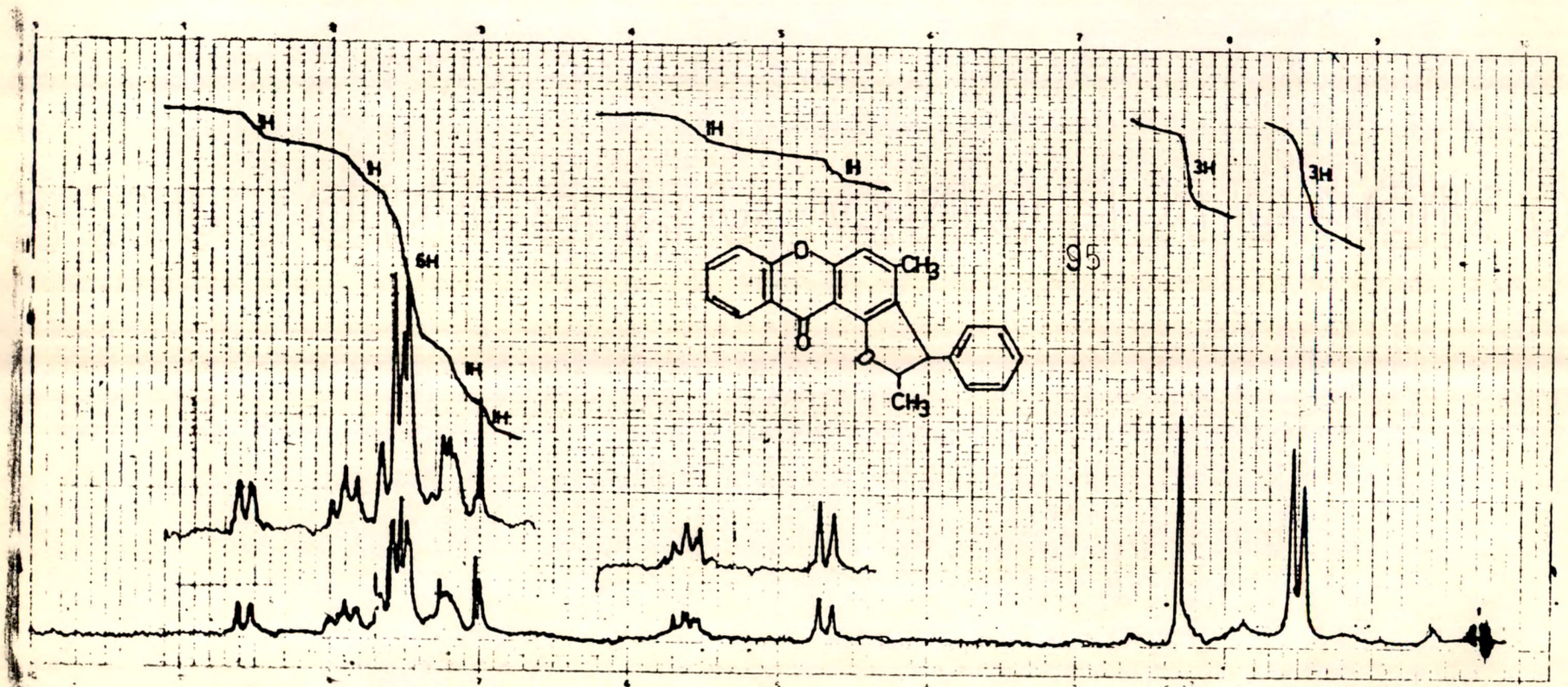


FIG 33

90MHz

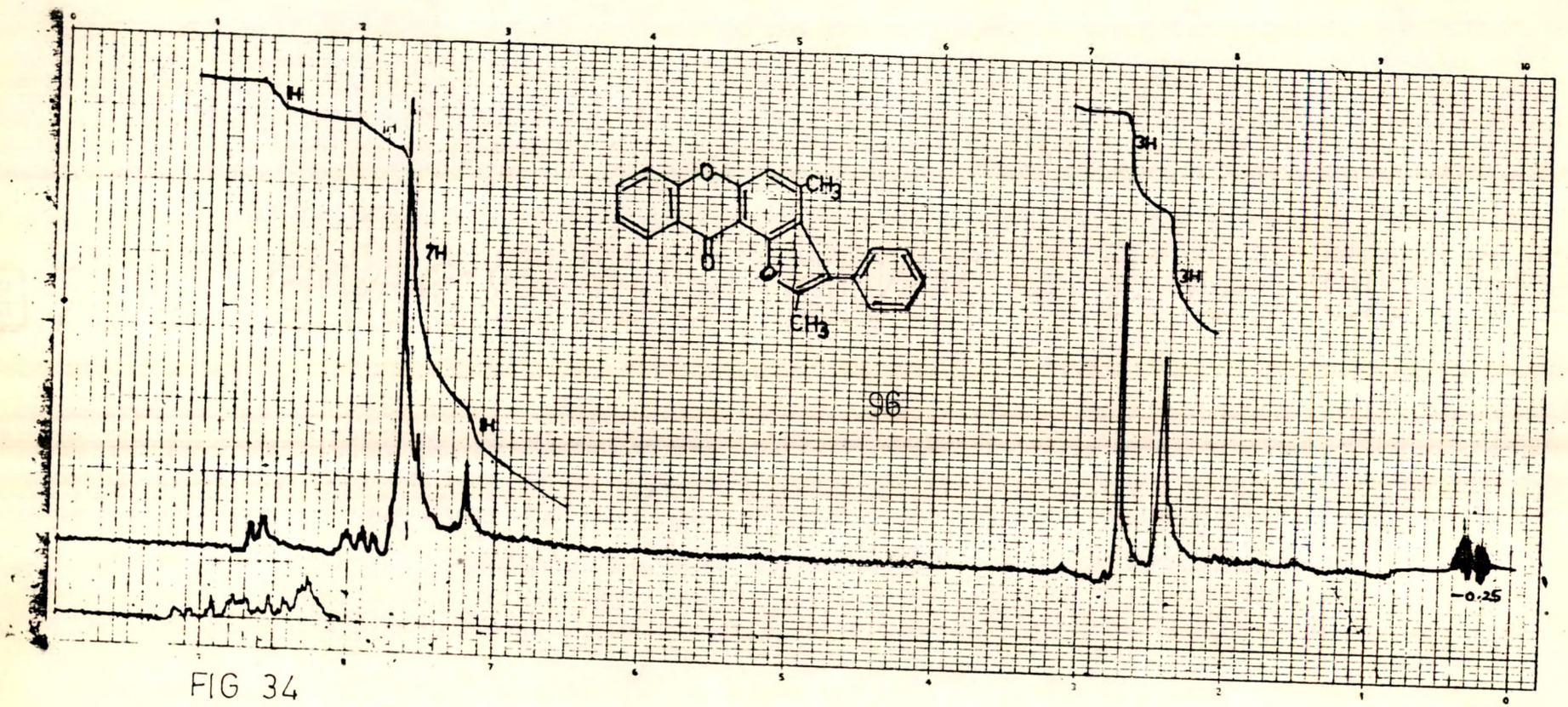
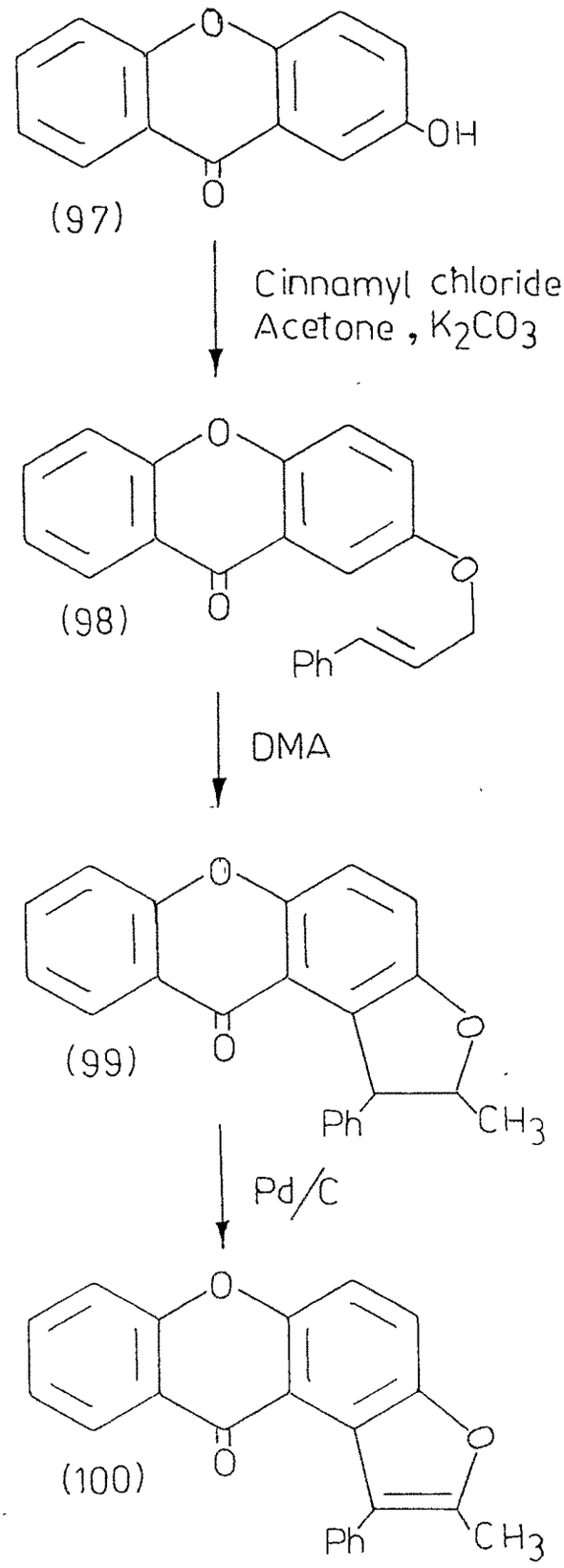


FIG 34

4'-phenyl-5'-methyl-4', 5'-dihydrofuranoxanthone (99), a sodium hydroxide insoluble product. The compound (99) on dehydrogenation with palladised charcoal in diphenyl ether gave 4'-phenyl-5'-methylfurano (3',2': 1,2) xanthone (100) as its NMR spectrum in $CDCl_3$ showed singlet at δ 2.42, 3H, for CH_3 of furan ring at position C5', 7.2 to 7.7, multiplet, 9H, H-4 to H-7 and 5 protons of phenyl ring; 7.8, doublet, 1H, J=9Hz, H-3; 8.17, dd, 1H, J=9,2Hz, H-8.


O
OH
O
(97)
Cinnamyl chloride,
Acetone, K_2CO_3
O
O
O
(98)
Ph
DMA
O
O
O
(99)
Ph
CH_3
Pd/C
O
O
O
(100)
Ph
CH_3

Experimental

For General Remarks, see Experimental, Chapter 2

2,4-Dibromo-3-allyloxyxanthone (32)

A mixture of 2,4-dibromo-3-hydroxyxanthone (10g), allyl bromide (8 ml), and anhydrous potassium carbonate (15g) was refluxed in dry acetone (200 ml) using a water bath for 10 hr. The reaction mixture was poured into water, the separated product was filtered and washed with dilute sodium hydroxide solution to remove any unreacted compound. The product crystallised from ethyl acetate to give (32) as white needles, m.p. 152° (7.0 g).

Analysis : Found : C, 46.59; H, 2.834 %.

$C_{16}H_{10}O_3Br_2$ requires : C, 47.06; H, 2.451 %.

NMR ($CDCl_3$): δ8.41, S, 1H, H-1; 8.25, 1H, J=9, 1.5Hz, H-8; 7.4 to 7.8, m, 3H, H-5, H-6 and H-7; 6.0-6.4, m, 1H, $OCH_2\underline{CH} = CH_2$; 5.28 to 5.7, m, $OCH_2CH=\underline{CH}_2$; 4.7, d, 1H, J=9Hz, $O\underline{CH}_2CH=CH_2$.

Claisen migration of 2,4-bromo-3-allyloxyxanthone (32)

(A) DMA : 2,4-Dibromo-3-allyloxyxanthone (32) (10 g) was refluxed with N,N-dimethylaniline (20 ml) for 11 hr. The reaction mixture was poured into cold dil.hydrochloric acid and extracted with solvent ether, Etheral extract was washed with water and then extracted with sodium hydroxide solution which on acidification with conc. hydrochloric acid gave the product, 2-bromo-3-hydroxy-

4-allylxanthone (33). It crystallised from ethyl acetate as white prism, m.p. 197° (2.0 g).

Analysis : Found : C, 57.98; H, 3.502 %.

$C_{16}H_{11}O_3Br$ requires : C, 58.19; H, 3.03 %.

Mass : m/e 332, 330 (100), 315, 313, 303, 301, 283, 252, 250, 235, 223, 206, 197, 165, 164, 149, 139, 121, 116, 105, 101, 92. Ether layer on evaporation gave yellow shining needles which was further crystallised from ethyl acetate to give 2-bromo-5'-methyl-4',5'-dihydrofurano (2',3': 3,4) xanthone (34) as white needles, m.p. 187° (1.4 g).

Analysis : Found : C, 58.53; H, 3.50 %.

$C_{16}H_{11}O_3Br$ requires : C, 58.19; H, 3.03 %.

Mass : m/e 332, 330 (100) 303, 301, 284, 256, 253, 252, 250, 236, 223, 185, 171, 165, 152, 139, 115, 97, 91, 83, 63.

(B) Decalin: 2,4-Dibromo-3-allyloxyxanthone (32) (2 g) was refluxed with decalin (10 ml) for 4 hr and was filtered when hot. After cooling, the separated product was isolated and then crystallised from benzene, m.p. 197° (200 mg). It was found to be identical (mixed m.p. tlc) with the compound (33).

(C) Vacuum (0.05 mm) at 170-180°C

2,4-Dibromo-3-allyloxyxanthone (32) (2.0 g) was heated under vacuum at 170-180° for 4 hr. Black mass

was extracted with chloroform and the extract upon examination on TLC showed three spots (chloroform: methanol=40:1) and hence it was chromatographed over silica gel coloumn. Elution with benzene yielded 2-bromo-5'-bromomethyl-4',5'-dihydrofurano (2',3': 3,4) xanthone (35) in the first six fractions (150-200 ml). The product (35) crystallised from benzene-petroleum ether mixture (10:1) m.p. 187-250° (200 mg).

Analysis : Found : C, 47.52; H, 2.525 %.

$C_{16}H_{10}O_3Br_2$ requires : C, 47.06; H, 2.451 %.

Mass : m/e 412, 410, 408 (M^+,100), 332, 330 (M^+-Br), 292, 290 (M^+-CH_2Br-C_2H_2) 276, 275, 250, 236, 235, 223, 222, 220, 208, 205, 194, 179, 166, 153, 139, 127, 126, 121, 102. Effluent collected after 200 ml was found to be a mixture of three compounds which were separated by preparative TLC (chloroform : methanol = 40:1) (i) product (35) R_f 0.75 (ii) 2-bromo-3-hydroxyxanthone (36) m.p. 310° (100 mg) R_f 0.47.

Analysis : Found : C, 53.64; H, 2.467 %.

$C_{13}H_7O_3Br$ requires : C, 53.79; H, 2.413 %.

Mass:m/e 292, 290 (100), 264, 262 (M^+-CO),235, 233, (M^+-CO-CHO), 211 (M^+-Br) 155 (M^+-Br-CO) 127, 126.

(D) Heating at 170°-180°

2,4-Dibromo-3-allyloxyxanthone (32) (4.0 g) was heated in an oil bath at 170-180° for 4 hr. A black mass thus obtained was extracted with chloroform and the extract on examination by TLC showed three spots (chloroform : methanol = 40:1). The crude product was passed through a column of silica gel using benzene, and then subjected to preparative TLC (chloroform : methanol = 40:1) which furnished (i) 2-bromo-5'-methyl furano (2',3' : 3,4) xanthone (37) R_f 0.8, m.p. 235° (150 mg).

Analysis : Found : C, 58.38,, H, 2.408 %.

$C_{16}H_9O_3Br$ requires : C, 58.53; H, 2.74 % identical in all respects (NMR, mass and tlc) with prepared sample and (ii) compound (36) R_f 0.5 (iii) starting material (32) R_f 0.3.

2-Bromo-4',5'-dihydro-5'-methylfurano (2',3' - 3,4) xanthone (34)

2-Bromo-3-hydroxy-4-allyxanthone (33) (100 mg) was titurated with conc.sulphuric acid on a water bath for 15 min, the contents were poured onto crushed ice, the separated product was filtered and washed with dil.sodium hydroxide solution to remove uncyclised compound, if any.

The residue was crystallised from ethyl acetate, m.p. 187° (80 mg) identical in all respects (mixed m.p., tlc) with compound (34) obtained earlier in case of rearrangement (32) in DMA.

Dehydrogenation of (34)

5'-Methylfurano (2',3': 3,4) xanthone (39)

A mixture of 2-bromo-4', 5'-dihydro-5'-methyl furano (2',3': 3,4) xanthone (34) (0.5 g), palladised charcoal (10%,0.6g) and diphenyl ether (20 ml) was refluxed for 18 hr. The reaction mixture was filtered hot and diphenyl ether was removed by steam distillation. The separated product crystallised from alcohol as white needles m.p. 165°-8° (lit[21]; 170°, lit[20]; 172°) (0.2 g).

Analysis : Found : C, 76.91; H, 4.525 %.

$C_{16}H_{10}O_3$ requires : C, 76.80; H, 4.0 %.

2-Bromo-3-allyloxyxanthone (40)

2-Bromo-3-hydroxyxanthone (2.0 g), allylbromide (1.8 ml), and anhydrous potassium carbonate (5 g) were refluxed in dry acetone (100 ml) on a water bath for 10 hr. The reaction mixture was worked up as described before. The product crystallised from aqueous alcohol as white needles m.p. 115° (1.5 g).

Analysis : Found : C, 58.60; H, 3.791 %.

$C_{16}H_{11}O_3Br$ requires : C, 58.18; H, 3.333 %.

NMR ($CDCl_3$): δ 8.48, S, 1H, H-1; 8.28, dd, 1H, J=9,2,Hz, H-8; 7.7, td, 1H, J=9,9,2Hz, H-6; 7.29-7.45, m, 2H, H-7 and H-5; 6.85, S, 1H, H-4; 5.9 to 6.3, m, 1H, $OCH_2\underline{CH} = CH_2$; 5.3 to 5.65, m, 2H, $OCH_2CH = \underline{CH_2}$; 4.67 to 4.75, m, 2H, $O\underline{CH_2}\ CH{=}CH_2$.

Claisen rearrangement of (40)

The compound (40) (1.0 g) was refluxed with N,N-dimethyl aniline (3 ml) for 2 hr. The reaction mixture was cooled and poured onto ice cold hydrochloric acid. The separated product was filtered, washed with water, dried and crystallised from alcohol to obtain (33) as white needles.m.p. 197° (mix m.p. 196° with compound obtained in the case of rearrangement of (32) does not show any depression in m.p.).

2-Bromo-3-acetoxy-4-allylxanthone (41)

A mixture of compound (33), (0.5 g), acetic anhydride (7 ml) and pyridine (2 ml) was heated on a water bath for 11 hr. The reaction mixture was worked up as before. The product obtained was crystallised from alcohol to obtain (41) as cremish white needles m.p. 180° (0.3 g). IR (KBr) νmax 1770 (C=0 ester), 1665 (C=0 γ-pyronyl).

2-Bromo-3-acetoxy-4-(2',3'-dibromopropyl) xanthone (42)

The compound (41) (0.4 g) was dissolved in acetic acid (50 ml) and to this bromine was added in glacial acetic acid (10 ml, 1% v/v). The reaction mixture was stirred for 2 hr and poured into water. The separated product crystallised from aqueous acetic acid m.p. 190° (300 mg). Mass m/e 534, 532, 492, 490, 452, 450, 410, 388, 386, 384, 372, 370, 368, 335, 332, 305, 303, 292, 290, 264, 262, 235, 233, 211, 183, 155, 127, 126, 92, 77, 63, 43.

2-Bromo-5'-methylfurano (2',3'-3,4) xanthone (37)

Above compound (42) (10 mg) was refluxed with alcoholic potassium hydroxide (10 %,40 ml) for 8 hr. and poured into water. The separated product crystallised from alcohol + benzene mixture as white needles m.p. 235° (80 mg).

Analysis:Found : C, 58.98; H, 2.916 %.

$C_{16}H_9O_3Br$ requires : C, 58.53; H, 2.74 %.

IR (KBr) νmax 1650 (C=O γ-pyronyl), 1625 (C=C), 1600, 1580, 1470, 1450, 1340, 1330, 1220, 1110, 765.

Mass:m/e 330, 328 (100), 304, 303, 302, 301, 250, 249, 221, 220, 212, 193, 192, 165, 163, 150, 139, 125, 101,92, 85, 75, 63, 43.

2-Bromo-3-hydroxy-4-formylmethylxanthone (43)

2-Bromo-3-hydroxy-4-allylxanthone (33) (1.0 g) in ethyl acetate (100 ml) and osmium tetroxide (60 mg) in water (60 ml) were vigorously stirred for 15 minutes. Potassium periodate (2.0 g) was then added in small quantities to the dark black solution over a period of 2 hr. The reaction mixture was stirred for another 4 hr and then the ethyl acetate layer was separated, washed with water, dried over sodium sulphate and distilled. The product thus obtained crystallised from alcohol, m.p. 232-30° (500 mg).

Analysis : Found : C, 53.81; H, 3.191 %.

$C_{15}H_9O_4Br$: requires : C, 54.05; H, 2.70 %.

2-Bromofurano (2',3' - 3,4) xanthone (44)

The above product (43) was taken in PPA (8 ml), heated in an oil bath for 2 hr at 110° and then poured over crushed ice. The separated product was washed with dil. sodium hydroxide and crystallised from alcohol or alcohol-benzene mixture (50:50) to obtain (44) as white needles, m.p. 225-30° (150mg).

Analysis : Found : C, 58.64; H, 2.619 %.

$C_{15}H_7O_3Br$ requires : C, 58.53; H, 2.74 %.

3-Allyloxy-4-bromoxanthone (45)

A mixture of 3-hydroxy-4-bromoxanthone (10 g), allybromide (7 ml) and anhydrous potassium carbonate (10 g) was refluxed in dry acetone (200 ml) on a water bath for 12 hr. The reaction mixture was worked up as described before. The product crystallised from aqueous alcohol to give (45) as light yellow needles, m.p. 121° (5 g).

Analysis : Found : C, 58.26; H, 3.80 %.

$C_{16}H_{11}O_3Br$ requires : C, 58.18; H, 3.39 %.

NMR ($CDCl_3$) δ 8.25, dd, 1H, J=9,2Hz, H-8; 8.15, d, 1H, J=9Hz, H-1; 7.7 to 7.5, m, 2H,H-6, H-5; 7.35, d, 1H, J=9Hz, H-2; 6.75-6.95, m, H-7; 5.9 to 6.3, m, 1H, $OCH_2\underline{C}H=CH_2$; 5.28 to 5.65, m, 2H, $OCH_2CH=\underline{C}H_2$; 4.6 to 4.8, m, 2H, $O\underline{C}H_2CH=CH_2$.

3-Allyloxy-4-iodoxanthone (46)

A mixutre of 3-hydroxy-4-iodoxanthone (25) (5 g), allyl bromide (3 ml) and anhydrous potassium carbonate (6 g) was refluxed in dry acetone (150 ml) on a water bath for 10 hr. The reaction mixture was worked up as described earlier. The product (46) crystallised from ethyl acetate as pale yellow needles, m.p. 142° (3 g).

Analysis : Found : C, 50.35; H, 3.40 %.

$C_{10}H_{11}O_3I$ requires : C, 50.79; H, 2.91 %.

NMR ($CDCl_3$) δ 8.28, dd, 1H, J=9,2Hz, H-8; 8.25, d, 1H, J=9Hz, H-1; 7.35 to 7.72, m, 3H, H-5, H-6, H-7; 6.85, d, 1H, J=9Hz, H-2; 5.9 to 6.3, m, 1H, $OCH_2\underline{C}H=CH_2$; 5.3 to 5.7, m, 2H, $OCH_2CH=\underline{C}H_2$; 4.7 to 4.8, m, 2H, $OC\underline{H}_2CH=CH_2$.

Claisen migration of 3-allyloxy-4-bromoxanthone (45)

(A) DMA : 3-Allyloxy-4-bromoxanthone (45) (10 g) was refluxed with N,N-dimethylaniline (25 ml) for 8 hr. After cooling, the reaction mixture was poured into cold dil.hydrochloric acid the separated product was filtered and stirred with sodium hydroxide solution and again filtered. Solid thus obtained was crystallised from ethylacetate to obtain 5'-methyl-4',5'-dihydro furano (2',3' : 3,4) xanthone (49) as white needles m.p. 180° (lit[20]; 180°; lit[21]; 181°) (0.2 g).

Analysis : Found : C, 75.78; H, 4.740 %.

$C_{16}H_{12}O_3$ requires : C, 76.19; H, 4.76 %.

IR : (KBr) νmax 1645 (C=O, γ-pyronyl). Mass : m/e 252, 237, 225, 212, 209, 197, 181, 168, 165, 152, 139, 126, 115, 105, 92, 87, 77,63. The filterate on acidification with conc.hydrochloric acid gave a solid (2 g) which showed two spots on TLC (chloroform: methanol=40:1) R_f 0.77 and 0.45.

The crude product was chromatographed over silica gel using benzene and the material thus obtained was then subjected to preparative TLC (chloroform : methanol= 40:1), to isolate (i) 2-allyl-3-hydroxyxanthone (47) as white seeds from alcohol m.p. 233° (50 mg). IR (KBr) ν_{max} 3000-3200 (br.OH) 1640 (C=O), 1615, 1600, 1580, 1560, 1465, 1320, 1255. Mass : m/e 252, 237, 235, 224, 209, 205, 197, 181, 165, 152, 139, 121, 115, 102, 92,87, 77, 63, 50. Analysis : Found : C, 75.70; H, 4.486 %. $C_{16}H_{12}O_3$ requires : C, 76.19; H, 4.76 %.
(ii) 4-allyl-3-hydroxyxanthone (48) crystallised from aqueous alcohol m.p. 245° (lit[22] 253 lit[21]; 240°) (120 mg) Mass : m/e 252, 237, 236, 225, 212, 209, 208, 197, 184, 181, 168, 152, 141, 139, 121, 115, 102, 92, 82, 77, 65. Further elution with chloroform eluted the compound (48).

(B) Decalin : 3-Allyloxy-4-bromoxanthone (45) (7.0 g) was refluxed with decalin (35 ml) for 3 hr. After cooling the separated product was filtered and dissolved in sodium hydroxide solution, and again filtered. The filterate on acidification with conc.hydrochloric acid gave the product (1.7 g) which showed two spots on TLC (chloroform : methanol=40:1) R_f 0.07, 0.45.

The product was chromatographed over a silica gel column. Elution with benzene gave 2-allyl-3-hydroxy-4-bromoxanthone (50) m.p. 167° (400 mg).

Analysis : Found : C, 58.37; H, 3.507 %.

$C_{16}H_{11}O_3Br$ requires : C, 58.19; H, 3.03 %.

Further elution with chloroform gave (1.2 g) of (48).

(C) VACUUM : 3-Allyloxy-4-bromoxanthone (45) (2 g) was heated under vacuum at 140° to 150° C for 5 hr. The product was extracted with acetone. Acetone was distilled off, residue was dissolved in sodium hydroxide solution and filtered. The filtrate on acidification with conc.hydrochloric acid gave the product which showed the same pattern on TLC as in the case of decalin. The alkali insoluble portion gave the starting material and a cyclised product (49).

4-Bromo-4',5'-dihydro-5'-methylfurano (2',3'- 2,3) xanthone (50a)

2-Allyl-3-hydroxy-4-bromoxanthone (50) (200 mg) was heated with conc.sulphuric acid on water bath for 15 minutes, the contents were poured onto crushed ice, the separated product was filtered and washed with dilute sodium hydroxide solution to remove

uncyclised compound. The solid crystallised from benzene alcohol mixture (50:50) to give (50a) as yellow needles, m.p. 190° (120 mg).

Analysis : Found : C, 57.73; H, 3.189 %.

$C_{16}H_{10}O_3Br$ requires : C, 58.19; H, 3.03 %.

NMR ($CDCl_3$) : δ 8.12, S, 1H, H-1; 8.02, d, 1H, J=9Hz, H-8; 7.0-7.6, m, 4H, ArH; 5.1, m, 1H, C5'-H, 3.45, dd, 1H, J=9,18Hz, C4'-H; 3.29, dd, 1H, J=9,18Hz, C4'-H; 1.35, d, 1H, J=7Hz, C5'-CH_3.

2-Allyl-3-acetoxy-4-bromoxanthone (51)

A mixture of compound (50) (0.5 g), acetic anhydride (6 ml) and pyridine (2 ml) was heated on a water bath for 10 hr. The reaction mixture was worked up as usual. The product upon crystallisation from alcohol gave pure (51) m.p. 140° (0.4 g).

IR (KBr) ν_{max} 1760 (C=O ester), 1670 (C=O, γ-pyronyl).

Mass : m/e 374, 372, 332, 330 (100), 318, 303, 301, 292, 290, 252, 251, 250, 236, 223, 222, 221, 205, 196, 195, 176, 166, 152, 139, 121, 102, 92, 87, 63.

2-(2',3'-Dibromopropyl)-3-acetoxy-4-bromoxanthone (52)

The compound (51) (180 mg) was dissolved in acetic acid (30 ml). To this bromine in glacial acetic acid (5 ml; 1% V/V) was added. The reaction mixture was

Analysis : Found : C, 53.62; H, 3.115 %.

$C_{15}H_9O_4Br$ requires : C, 54.05; H, 2.70 %.

4-Bromofurano (3',2' - 2,3) xanthone (55)

The above product (54) was taken in PPA (10 g), heated in an oil bath for 2 hr. at 115° and was then poured over ice. The separated solid was washed with dilute sodium hydroxide and extracted with benzene-alcohol mixture. This solution was percolated through a column of silica gel and eluted with benzene-alcohol (50:50) (80 mg). The isolated product crystallised from benzene as yellow needles, m.p. 240°.

Analysis : Found : C, 57.60; H, 2.482 %.

$C_{15}H_7O_3Br$ requires : C, 57.15; H, 2.22 %.

IR (KBr) ν_{max} 1670 (C=O, γ-pyronyl), 1620 (C=C),

m/e, 316, 314 (100), 288, 286, 256, 236, 235, 207, 179, 151, 150, 143, 126, 92, 88, 77, 63, 43.

1-Hydroxy-3-methyl-6-allyloxyxanthone (57).

A mixture of 3-methyl-1,6-dihydroxyxanthone (56) (2.0 g), allyl bromide (3.0 ml) and anhydrous potassium carbonate (6 g) was refluxed in dry acetone (200 ml) on a water bath for 20 hr. The reaction mixture was worked up as usual. The product crystallised from ethyl acetate to give (57) m.p. 176°.

Analysis : Found : C, 71.90; H, 4.991 %.

$C_{17}H_{14}O_4$ requires : C, 72.34; H, 4.96 %.

stirred for 2 hr. and poured into water. The separated product was crystallised from aqueous alcohol or acetic m.p. 170° (180 mg) m/e 534, 532, 499, 492, 490, 488, 413, 411, 409, 332, 330, 305, 303 (100) 250, 223, 196, 165, 139, 121, 102, 92, 82, 43.

4-Bromo-5'-methylfurano (3',2' - 2,3) xanthone (53)

Above compound (52) (150 mg) was refluxed in alcoholic potassium hydroxide (10 %, 40 ml) for 8 hr. and poured into water. The separated product was washed with dil.sodium hydroxide solution and crystallised from alcohol-benzene to give (53) as white needles, m.p. 243-245° (50 mg).

Analysis : Found : C, 58.98; H, 2.916 %.

$C_{16}H_9O_3Br$ requires : C, 58.53; H, 2.74 %.

2-Acetaldehydro-3-hydroxy-4-bromoxanthone (54)

2-Allyl-3-hydroxy-4-bromoxanthone (50) (1.0 g) in ethyl acetate (100 ml) and osmium tetroxide (1.0 g) in water (60 ml) were vigourously stirred for 15 minutes. Potassium periodate (2.0 g) was added in small quantities to the dark black solution, over a period of 2 hr. The reaction mixture was stirred for 4 hr. more and then the ethyl acetate layer was separated, washed with water, dried with sodium sulphate and distilled. The residue crystallised from alcohol or benzene petroleum ether mixture, m.p. 200° (650 mg).

3-Methyl-5-allyl-1,6-dihydroxyxanthone (58)

Above compound (57) (2.0 g) was refluxed in dimethylaniline (10 ml) for 10 hr. The reaction mixture was cooled, poured into cold dil.hydrochloric acid. The separated product was crystallised to isolate (58) as yellow needles from acetic acid m.p. 240° (1.2 g). The compound gave green colour with alcoholic $FeCl_3$.

Analysis : Found : C, 72.83; H, 5.315 %.

$C_{17}H_{14}O_4$ requires : C, 72.34; H, 4.96 %.

1-Hydroxy-3-methyl-5-allyl-6-acetoxyxanthone (59)

A mixture of compound (58) (0.2 g), acetic anhydride (1 ml) and pyridine (2 ml) was heated on a water bath for 5 hr. The reaction mixture on usual work up gave the product, which crystallised from aqueous acetic acid as buff colour needles m.p. 155° (1.7 g).

Analysis : Found : C, 69.8; H, 5.4 %.

$C_{19}H_{16}O_5$ requires : C, 70.4; H, 4.9 %.

1-Hydroxy-3, 5'-dimethyl-4',5'-dihydrofurano (3',2'-5,6) xanthone (60)

The compound (58) (0.5 g) was heated with conc. H_2SO_4 on a water bath for 15 minutes. The reaction

mixture was worked up as usual. The product crystallised from aqueous acetic acid to give (60) as brown needles m.p. 160° (0.25 g).

Analysis : Found : C, 71.8; H, 5.4 %.

$C_{17}H_{14}O_4$ requires : C, 72.3; H, 4.9 %.

1-Hydroxy-3,5'-dimethylfurano (3',2' : 5,6) xanthone (61)

Above compound (60) (0.2 g), palladised charcoal (10%, 0.5 g) and diphenyl ether (10 ml) were refluxed for 10 hr. The product was isolated as usual and crystallised from aqueous alcohol m.p. 195° (0.12 g).

Analysis : Found : C, 72.68; H, 4.567 %.

$C_{17}H_{12}O_4$ requires : C, 72.85; H, 4.285 %.

3,6-Diallyloxyxanthone (63)

A mixture of 3,6-dihydroxyxanthone (2.0 g), allyl bromide (3 ml) and anhydrous potassium carbonate (5 g) was refluxed in dry acetone (100 ml) for 12 hr. The reaction mixture was worked up as usual. The sodium hydroxide insoluble solid thus obtained was crystallised from alcohol to obtain pale yellow needles m.p. 140°.

Analysis : Found : C, 74.15; H, 5.336 %.

$C_{19}H_{16}O_4$ requires : C, 74.02; H, 5.194 %.

3,6-Dihydroxy-4,5-diallylxanthone (64)

Above compound (63) (2.0 g) was refluxed in N,N-dimethylaniline (10 ml) for 6 hr. The reaction mixture on usual worked up gave a solid product which crystallised from aqueous alcohol m.p. 222° (1.2 g).

Analysis : Found : C, 73.69, H, 5.417 %.

$C_{19}H_{16}O_4$ requires : C, 74.02; H, 5.194 %.

3,6-Diacetoxy-4,5-diallyxanthone (65)

3,6-Dihydroxy-4,5-diallylxanthone (64) (0.5) was dissolved in pyridine (3 ml). To this was added acetic anhydride (4 ml) and the reaction mixture was heated on a water bath for 8 hr. The product obtained after usual work up, crystallised from alcohol m.p. 160° (0.3 g).

Analysis : Found : C, 70.57; H, 5.039 %.

$C_{23}H_{20}O_6$ requires : C, 70.40; H, 5.14 %.

5',5"-Dimethyl-4',5',4",5"-tetrahydrofurano (2',3'-3,4 : 3",2"- 5,6) xanthone (66)

The compound (64) (0.6 g) was dissolved in sulphuric acid and heated on a water bath for 15 minutes. The reaction mixture was worked up as before to obtain the product, which crystallised from aqueous alcohol as brown needles m.p. 180° (0.3 g).

Analysis : Found : C, 73.82; H, 5.592 %.

$C_{19}H_{16}O_4$ requires : C, 74.02; H, 5.194 %.

5',5"-Dimethyldifurano (2',3'-3,4 : 3",2"-5,6) xanthone (67)

A mixture of the above compound (66) palladised charcoal (10 %, 0.5 g) and diphenyl ether was refluxed for 10 hr. The reaction mixture was worked up as described before. The product crystallised from aqueous acetic acid m.p. 256-259° (0.15 g).

Analysis : Found : 75.21; H, 4.19 %.

$C_{19}H_{12}O_4$ requires : 74.99, H, 3.97 %.

5'-(1-Hydroxy-1-methylethyl) furano (2',3' : 3,4) xanthone (70)

A solution of 3-acetoxy-4-iodoxanthone (68) (1.2 g) in pyridine (10 ml) was added to the cuprous salt[28] (69) (0.8 g) in the same solvent (20 ml) and the mixture was refluxed under nitrogen for 22 hrs. Pyridine was removed by steam distillation. When a a brown solid residue (1.0 g) was obtained. It was boiled with benzene and filtered. The filtrate on concentration gave a solid (0.4 g), which was found to be a mixture of two products by TLC. Hence it was subjected to coloumn chromatography. Elution with benzene (5x50 ml) gave an unidentified oil further elution with benzene (500 ml) yielded 5'-(1-hydroxy-1-

methylethyl) furano (2',3': 3,4) xanthone (70) as white needles (0.15 g) from ethanol, m.p. 175°; IR (KBr) ν max. 3400 (br-OH), 1635 (C=O, γ-pyronyl). Analysis : Found : C, 73.35; H, 5.157 %. $C_{18}H_{14}O_4$ requires : C, 73.47; H, 4.762 %. Elution with benzene and chloroform yielded 3-hydroxy-4-iodoxanthone (0.15 g) m.p. 230°. mass m/e 338, 310, 246, 212, 195, 184, 155, 128, 102.

Synthesis of 5'-(1-hydroxy-1-methylethyl) furano (3',2'- 1,2) xanthone (72)

A solution of cuprous 2-methylbut-3-yne-2-ol tetrahydropyranyl ether (69)[28] (0.5 g) and 1-bromo-2-hydroxyxanthone (71) (0.6 g) in pyridine (30 ml) was heated under reflux for 20 hr. under nitrogen atmosphere, then reaction mixture was poured into cold dil.HCl (1:1) a solid obtained was filtered off. The brown solid thus obtained was dissolved in chloroform, washed with sodium hydroxide solution to remove starting material and passed through silica gel coloumn to remove the colour. The product thus obtained shows two spots on TLC. So it was subjected to preparative TLC which furnished 5'-(1-hydroxy-1-methyl ethyl) furano (3',2'-1,2) xanthone (72), which crystallised in pale yellow needles from petroleum ether m.p. 126-130°.

Analysis : Found : C, 73.90; H, 5.212 %.

$C_{18}H_{14}O_4$ requires :C, 73.47; H, 4.762 %.

Mass : m/e 294 (M^+), 279 (M^+-CH_3) and (~ 5 mg) of (72a) m.p. 114° Mass m/e 276 (M^+) 261 (M^+-15).

Synthesis of 5'-isopropenyl-4-methylfurano (3',2': 2,3) xanthone (74)

A solution of cuprous 2-methylbut-3-yne-2-ol tetrahydropyranyl ether (69) (0.35 g) and 2-bromo-3-hydroxy-4-methylxanthone (73) (0.5 g) in pyridine (15 ml) was heated under reflux for 18 hr. The reaction mixture was worked up as above to give a yellow solid which was purified by preparative TLC to obtain 5'-isopropenyl-4-methylfurano (3',2': 2,3) xanthone (74) as yellow needles from benzene, m.p. 206° (0.2 g).

Analysis : Found : C, 78.63; H, 4.724 %.

$C_{19}H_{14}O_3$ requires : C, 78.60; H, 4.82 %.

Synthesis of 5'-phenyl-3-methylfurano (2',3': 1,2) xanthone (77)

A mixture of cuprous phenylacetylide[29] (75) (0.33g) and 1-hydroxy-2-bromo-3-methylxanthone (76) (0.6 g) in pyridine (25 ml) was refluxed under nitrogen atmosphere for 7 hr. The reaction mixture after cooling

was poured into cold dil. hydrochloric acid (1:1). The separated solid was filtered off. The residue on purification by TLC gave (77) as golden yellow shining needles from alcohol m.p. 210° (100 mg).

Analysis : Found : C, 80.30; H, 4.51%.

$C_{22}H_{14}O_3$ requires : C, 80.73; H, 4.58 %.

Mass : m/e 316, 288, 275, 273, 260, 231, 155, 127.

Synthesis of 5'-phenylfurano (2',3' : 3,4) xanthone (79)

A mixture of cuprous salt (75) (0.850 g) and the 3-hydroxy-4-bromoxanthone (78) (1.5 g) in pyridine (30 ml) was heated under reflux (nitrogen atmosphere) for 8 hr. The reaction mixture was poured into the cold dil. hydrochloric acid (1:1), the separated solid was filtered off, washed with dil.sodium hydroxide solution and crystallised from alcohol to obtain (79) as a pale yellow needles m.p. 235°-36° (0.6 g).

Mass : m/e 312, 284, 255, 226, 202, 163, 152, 142, 113, 101, 77, 63, 57, 50, 43. IR (KBr) νmax 1650, 1615, 1600, 1460, 1450, 1340, 1225, 1145, 1060, 755, 685.

Analysis : Found : C, 80.91; H, 4.162 %.

$C_{21}H_{12}O_3$ requires : C, 80.76; H, 3.846 %.

2-Bromo-5'-phenylfurano (2',3': 3,4) xanthone (81)

A mixture of the cuprous phenylacetylide (75) (0.5 g) and 2,4-dibromo-3-hydroxyxanthone (80) (1.1 g) in pyridine (40 ml) was refluxed under nitrogen atmosphere for 8 hr. The reaction mixture was worked up as above to obtain (81), which crystallised from alcohol gave pale yellow needles (0.8 g) m.p. 240°.

Mass m/e 392, 390 (100), 364, 362, 311, 382, 252, 253, 254, 223, 224, 199, 162, 149, 141, 113, 105, 92, 77, 63, 50, 39. IR (KBr) νmax 1650 (C=C), 1595, 1460, 1450, 1405, 1335, 1300, 755.

Analysis : Found : C, 64.80; H, 3.260 %.

$C_{21}H_{11}O_3Br$ requires : C, 64.45; H, 2.813 %.

Synthesis of 5'-phenylfurano (2',3': 1,2) xanthone (83)

A mixture of the cuprous phenylacetylide (75) (0.5 g) and 1-hydroxy-2-bromoxanthone (82) (0.88 g) in pyridine (25 ml) was heated under nitrogen atmosphere for 7 hr. The reaction mixture was worked up as earlier to isolate a solid which showed two spots on TLC. Preparative TLC of the solid gave (i) the starting material (82) and furanoxanthone (83)

m.p. 165° (0.1 g). IR (KBr) ν_{max} 1650, 1600, 1580, 1450, 1430, 1340, 1060, 1045, 885, 820, 760, 690.

Analysis : Found : C, 80.96; H, 3.398 %.

$C_{21}H_{12}O_3$ requires : C, 80.76; H, 3.846 %.

Synthesis of 5'-phenylfurano (3',2' : 1,2)xanthone (84)

A mixture of the cuprous salt (75) (0.330 g) and 1-bromo-2-hydroxyxanthone (71) (0.580 g) in pyridine (25 ml) was heated under reflux in a nitrogen atmosphere for 8 hr. the reaction mixture was poured into dil.hydrochloric acid (1:1) and extracted with ether. The ethereal extract was washed with dil.sodium hydroxide solution and water. The ether layer on evaporation gave a brown solid, which on crystallisation from alcohol and benzene mixture (90:10) gave (84) as yellow needles m.p. 210° (0.2 g).

Analysis : Found : C, 80.30; H, 4.141 %.

$C_{21}H_{12}O_3$ requires : C, 80.76; H, 3.846 %.

3-Cinnamyloxyxanthone (86)

3-Hydroxyxanthone (85) (2.0 g), cinnamyl chloride (1.5 ml), anhydrous potassium carbonate (2.0 g) and potassium iodide (2.0 g) which refluxed in dry acetone (100 ml) for 7 hr. After distilling off the acetone,

water was added to this residue, the separated product was filtered off, and washed with dil. sodium hydroxide solution. The product thus obtained was crystallised from acetone to furnish (86) as white tiny needles m.p. 145° (2.0 g).

Analysis : Found : C, 80.43; H, 5.048 %.

$C_{22}H_{16}O_3$ requires : C, 80.487; H, 4.878 %.

3-Cinnamyloxy-4-bromoxanthone (87)

3-Hydroxy-4-bromoxanthone (2.0 g), cinnamyl chloride (1.5 ml), potassium carbonate (2.0 g) and potassium iodide (2.0 g) were refluxed in dry acetone (150 ml) for 6 hr. The reaction mixture was worked up as above. The product crystallised from alcohol-benzene mixture (50:50) m.p. 173° (1.0 g). The starting material (0.5 g) was also recovered from the reaction mixture.

Analysis : Found : C, 65.32; H, 4.158 %.

$C_{22}H_{15}O_3Br$ requires : C, 64.864; H, 3.685%.

Claisen rearrangement of 3-cinnamyloxyxanthone (86)

3-Cinnamyloxyxanthone (1.0 g) was refluxed with N,N-dimethyl aniline (5 ml) for 5 hr. The reaction mixture was cooled, poured into cold dil.hydrochloric

acid and extracted with solvent ether. The ether layer was washed with dil.sodium hydroxide solution, which on acidification with dil.hydrochloric acid gave 4-cinnamyl-3-hydroxyxanthone (88) which crystallised from aqueous alcohol in white tiny needles m.p.240° (0.32 g).

Analysis : Found : C, 80.90; H, 5.046 %.

$C_{22}H_{16}O_3$ requires : C, 80.487; H, 4.878 %.

U.V. λmax (251,268,277,316). The ether layer (after washing with sodium hydroxide) on evaporation gave a solid product, which crystallised from aqueous alcohol to give 4'-phenyl-5'-methyl-4',5'-dihydrofurano (2',3' : 3,4) xanthone (89) as white needles m.p. 163° (0.62 g).

Analysis : Found : C, 80.35; H, 4.989 %.

$C_{22}H_{16}O_3$ requires : C, 80.487; H, 4.878 %.

4'-Phenyl-5'-methylfurano (2',3' : 3,4) xanthone (91)

The compound (89) (0.2 g), palladised charcoal (10% 0.3 g) and diphenyl ether (5 ml) were refluxed for 14 hr. The product was isolated as usual and crystallised from alcohol-benzene mixture (50:50) to obtain compound (91) as yellow shining needles m.p. 215° (90 mg).

Claisen rearrangement of (87)

3-Cinnamyloxy-4-bromoxanthone (87) (0.8 g) was refluxed with N,N-dimethylaniline (5 ml) for 5 hr. The reaction mixture on usual work up gave sodium hydroxide insoluble product (230 mg) (89) and sodium hydroxide soluble compound (0.1 g) m.p. 240° which is nothing but compound (88).

Ozonolysis of (88)

The compound (88) (0.5 g) was taken in ethyl acetate and to this ozonised oxygen was bubbled for about 30 minutes. Then palladised charcoal (10 % 0.3 g) was added and the solution was made saturated with hydrogen gas. After filtering off the charcoal, ethyl acetate solution on distillation gave compound (90), which crystallised from ethyl acetate-petroleum ether as white needles, m.p. 220°.

Analysis : Found : 76.86; H, 4.68 %.

$C_{21}H_{14}O_4$ requires : 76.36; H, 4.24 %.

Mass : m/e 330 (331 M^++1, 332, M^++2) 301, 283, 273, 255, 224, 215, 196, 152, 139, 121, 113, 105, 91, 63, 51, 39, 29.

1-Cinnamyloxy-3-methylxanthone (93)

A mixture of 1-hydroxy-3-methylxanthone (92) (5 g), cinnamyl chloride (5 ml), potassium carbonate (10 g) and potassium iodide (2g) was refluxed in dry acetone (250 ml) for 50 hr. (till no green colour observed with alcoholic ferric chloride solution). The acetone was distilled off, and water was added. The separated product crystallised from acetone to give (93) as yellowish white needles m.p. 143° (4.2g).

Analysis : Found : C, 80.63; H, 5.439 %.

$C_{23}H_{18}O_3$ requires : C, 80.70; H, 5.26 %.

Claisen rearrangement of (93)

1-Cinnamyloxy-3-methylxanthone (93) (1.0 g) was refluxed with N,N-dimethylaniline (5 ml) for 5 hr. The reaction mixture was worked up as usual. The solid product thus obtained was crystallised from alcohol-benzene mixture (50:50) to give single spotted compound, 1-hydroxy-2-cinnamyl-3-methylxanthone (94) m.p.198°(0.5g).

Analysis : Found : C, 80.98; H, 5.374 %.

$C_{23}H_{18}O_3$ requires : C, 80.70; H, 5.26 %.

Mass m/e 342, 327, 313, 297, 265, 251, 239, 226, 189, 176, 165, 152, 139, 115,91, 77, 65, 51, 39, 27.

The mother liquor on TLC examination showed two spots.

So it was concentrated and subjected to preparative tlc (chloroform) to isolate (94) and the cyclised product 4'-phenyl-3,5'-dimethyl-4',5'-dihydrofurano (2',3': 1,2) xanthone (95) which crystallised from chloroform in white needles m.p. 232° (0.25 g).

Analysis : Found : C, 80.58; H, 5.01 %.

$C_{23}H_{18}O_3$ requires : C, 80.70; H, 5.26 %.

4'-Phenyl-3,5'-dimethylfurano (2',3': 1,2) xanthone(96)

The compound (95) (0.2 g), palladised charcoal (10% 0.6g) and diphenyl ether (10 ml) were refluxed for 16 hr. The product, obtained after usual work up, crystallised from aqueous alcohol or benzene to give (96) as brown prismatic crystals, m.p. 200°(0.1g).

Analysis : Found : C, 81.14; H, 4.863 %.

$C_{23}H_{16}O_3$ requires : C, 80.70; H, 5.26 %.

2-Cinnamyloxyxanthone (98)

2-Hydroxyxanthone (97) (1.8 g), cinnamyl chloride (2 ml), anhydrous potassium carbonate (5 g) and potassium iodide (2 g) were refluxed in dry acetone (100 ml) for 10 hr. The reaction mixture was worked up as usual. The product crystallised from acetone as white needles m.p. 145° (1.5 g).

Analysis : Found : C, 80.86; H, 4.933 %.

$C_{22}H_{16}O_3$ requires : C, 80.487; H, 4.878 %.

4'-Phenyl-5'-methyl-4',5'-dihydrofurano (3',2' : 1,2) xanthone (99)

2-Cinnamyloxyxanthone (98) (1.2 g) was refluxed with N,N-dimethylaniline (15 ml) for 7 hr. The reaction mixture on usual work up gave only one product, which crystallised from aqueous alcohol as pale yellow needles m.p. 175° (0.5 g).

Analysis : Found : C, 80.01; H, 4.961 %.

$C_{22}H_{16}O_3$ requires : C, 80.487; H, 4.878 %.

4'-Phenyl-5'-methylfurano (3',2' : 1,2) xanthone (100)

The above compound (99) (0.2 g), palladised charcoal (10% 0.4g), and diphenyl ether (10 ml) were refluxed for 16 hr. The reaction mixture was worked up as usual. The product crystallised from alcohol-benzene mixture (10:90) to give yellowish brown needles m.p. 208-10° (0.150 g).

Analysis : Found : C, 80.90; H, 5.191 %.

$C_{22}H_{14}O_3$ requires : C, 80.487; H, 4.878 %.

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