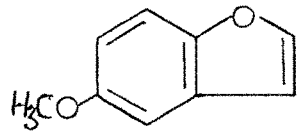
CHAPTER III

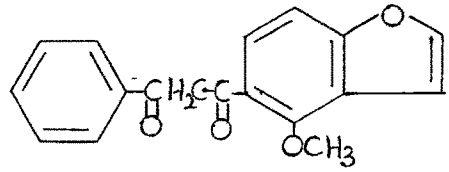
SYNTHESIS OF SOME FURONAPHTHO-α-AND γ-PYRONES

Synthesis of some Furonaphtho-α- and γ-pyrones :

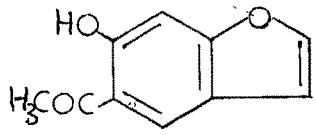
The furan derivatives are found to occur very widely in nature, either fused with a benzene nucleus as benzofurans such as, 5-Methoxybenzofuran (I), Pongamol(II), Euparin (III) and Eganol (IV),



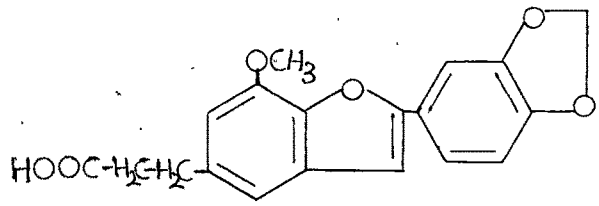
I



II

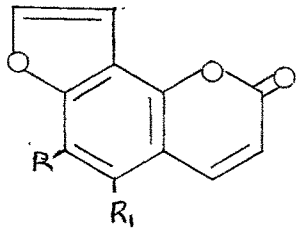


III

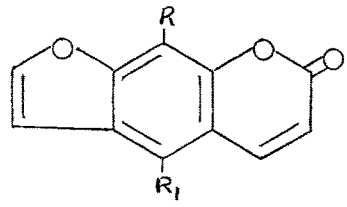


IV

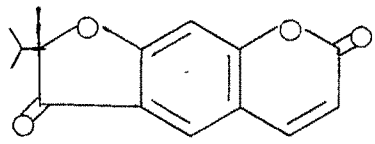
or with a coumain ring to give furocoumarins such as Angelicin (V), Pimpinellin (VI), Psoralene (VII), Bergapten (VIII), Xanthotoxin (IX), isopimpinellin (X) and Oreoselene (XI). or with a γ-pyrone ring to give furochromones such as Khellin (XII) and Visnagin (XIII). Furoflavones and furoisoflavones also occur in nature. Karanjin (XIV), Nepseudin (XV) and Netenone (XVI) are examples of such compounds.



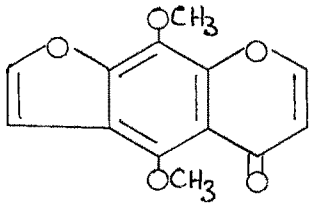
	R	R_1
V	H	H
VI	OCH_3	OCH_3



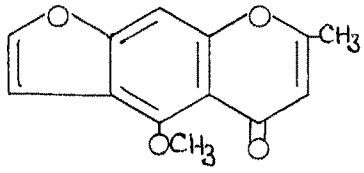
	R	R_1
VII	H	H
VIII	H	OCH_3
IX	OCH_3	H
X	OCH_3	OCH_3



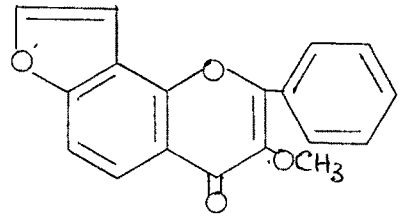
XI



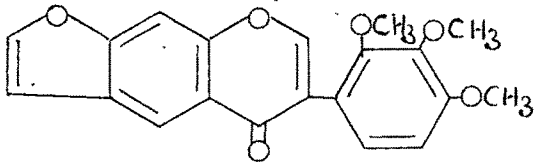
XII



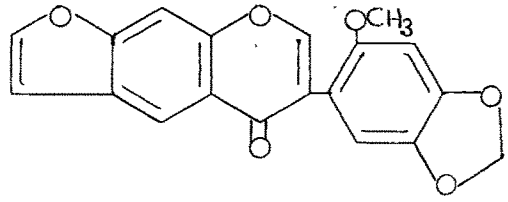
XIII



XIV

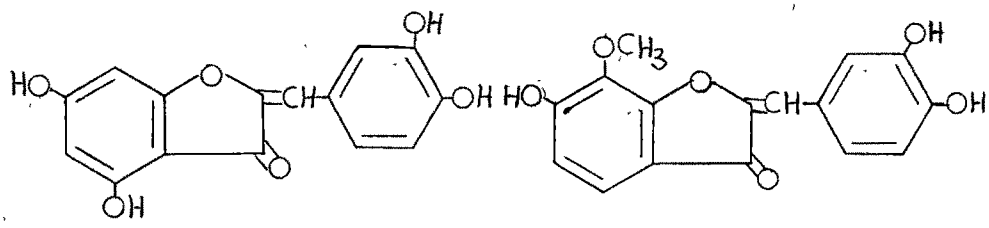


XV



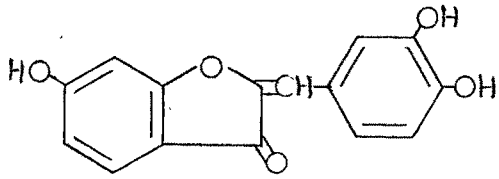
XVI

Still another group of special interest comprises aurones. They are glycosides of hydroxylated benzylidene coumaranones. Aureosidin (XVII) Leptosidin (XVIII) and Sulfuretin (XIX) are a few members of this group.



XVII

XVIII



XIX

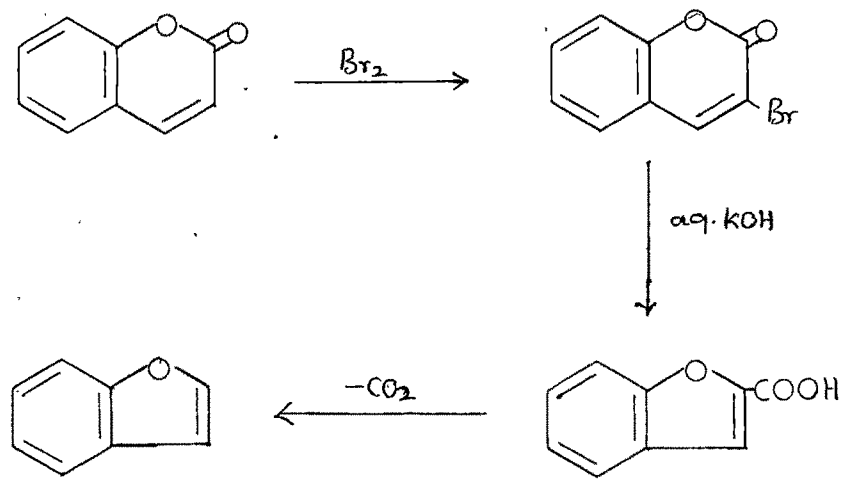
Besides these there are compounds of more complicated structures containing the furan ring system.

Synthesis of benzofuran derivatives :

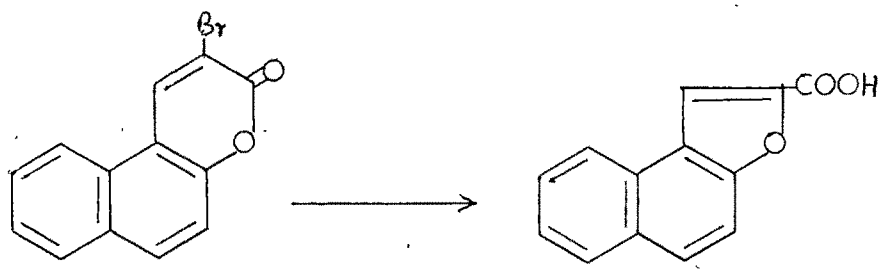
The chemistry of benzofurans has been reviewed by Mustafa[1] in his recent book entitled "Benzofurans" . There are several methods by which a furan ring can be built up on an aromatic nucleus. Some of these methods are briefly mentioned below.

(1) The classical synthesis of benzofuran involves bromination of coumarin to get 3-bromocoumarin, heating it with alkali to get a coumarilic acid derivative and its

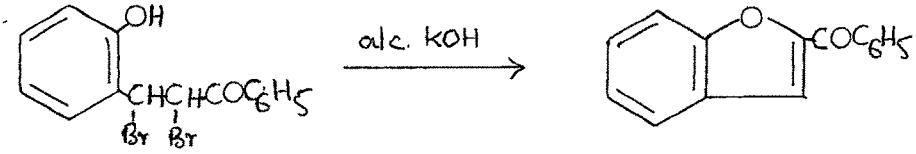
decarboxylation to a benzofuran derivative.[2,3]



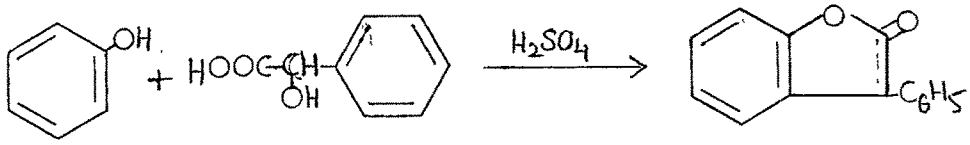
Similarly the corresponding 3-halonaphtho-α-pyrone gives the naphthofuran derivative[4]



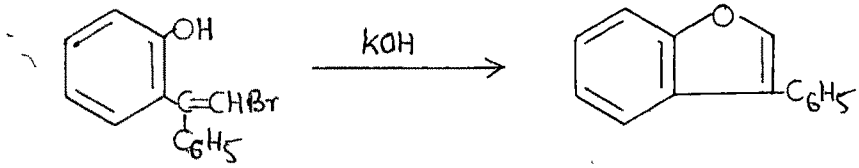
(2) Synthesis of benzofuran derivative can be accomplished from the dibromide of a chalkone by treating it with alcoholic potassium hydroxide[5].

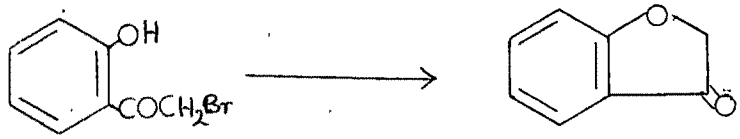


(3) α-Hydroxyphenyl acetic acid readily condenses with phenol in the presence of sulphuric acid to yield a furan derivative[6,7,8]. Thus when mandelic acid is condensed with phenol, 3-phenylcoumaran-2-one is formed.

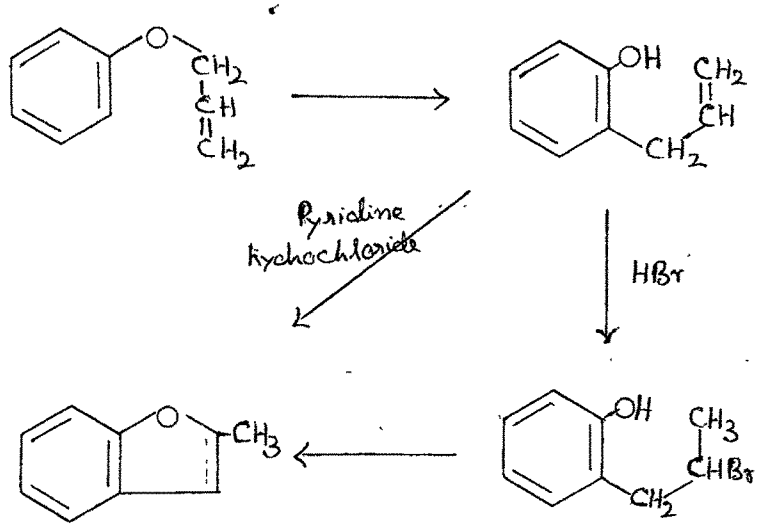


(4) A related synthesis involves the action of alkali on o-hydroxy- β-halostyrenes[9]. 3-Phenylbenzofuran can be prepared in this way, and if o-hydroxybromoacetophenone is used, 3-coumaranone results[10].

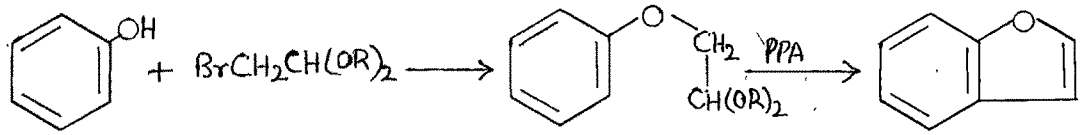


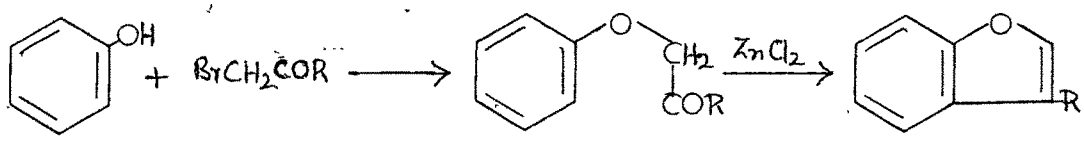


(5) Benzofuran can be obtained by the catalytic cyclodehydrogenation of o-ethylphenol[11], and 2,3-dihydrobenzofurans can be prepared by the cyclisation of o-allylphenols. The cyclisation occurs when o-allylphenol is heated with hydrobromic acid or with pyridine hydrochloride[12,13,14,15]



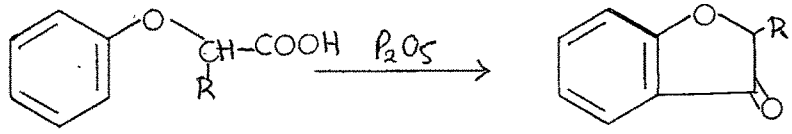
(6) Ring closure of phenoxy carbonyl compounds or their acetals can be effected with the help of reagents like conc.sulphuric acid, anhydrous zinc chloride or polyphosphoric acid to get the furan derivatives[15,17,18,19].



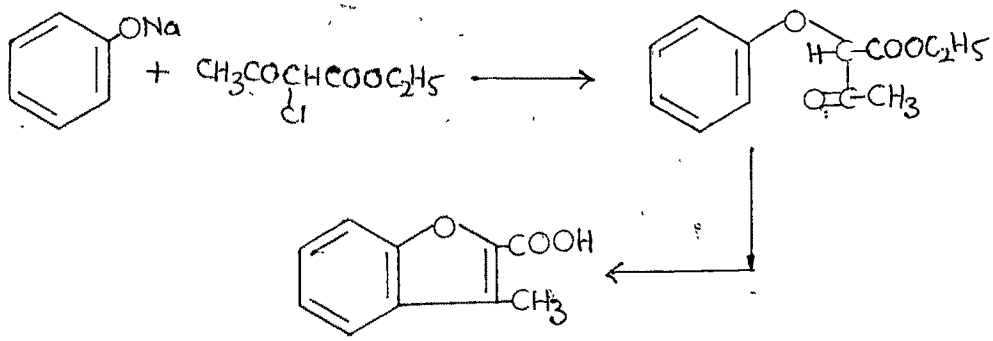


(7) Phenoxy acetic acids undergo similar cyclisation when heated with phosphorus pentoxide to

yield coumaran-3-ones[20,21,22].

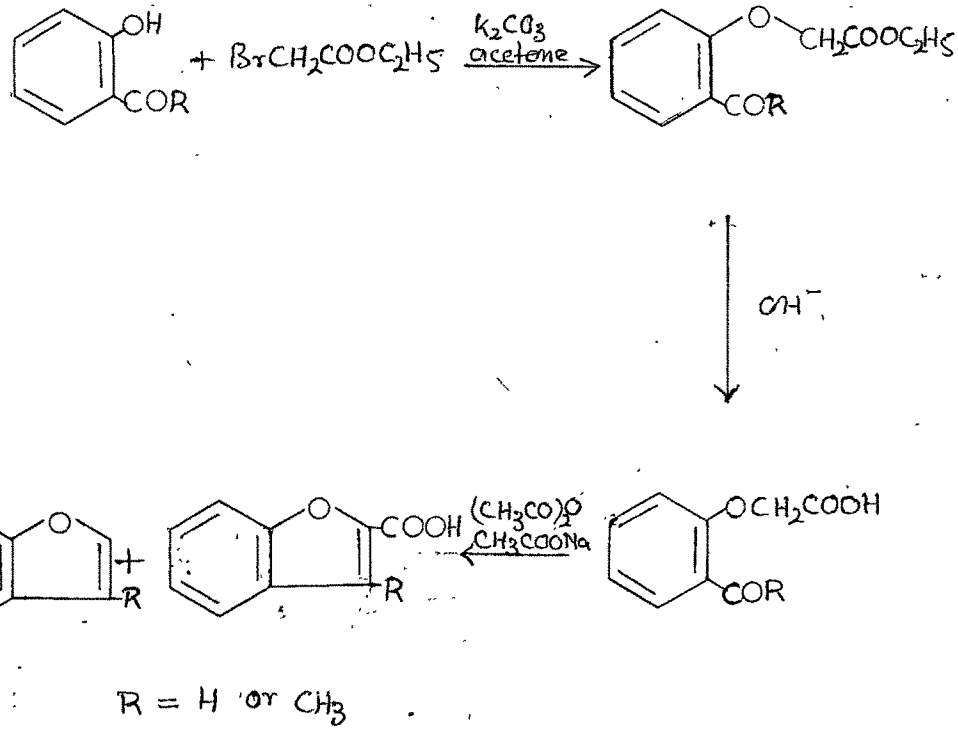


(8) This method has many variations and is examplified by the condensation of sodium phenoxide with ethyl chloro-acetoacetate to get 3-methyl benzofuran-2-carboxylic acid[23].



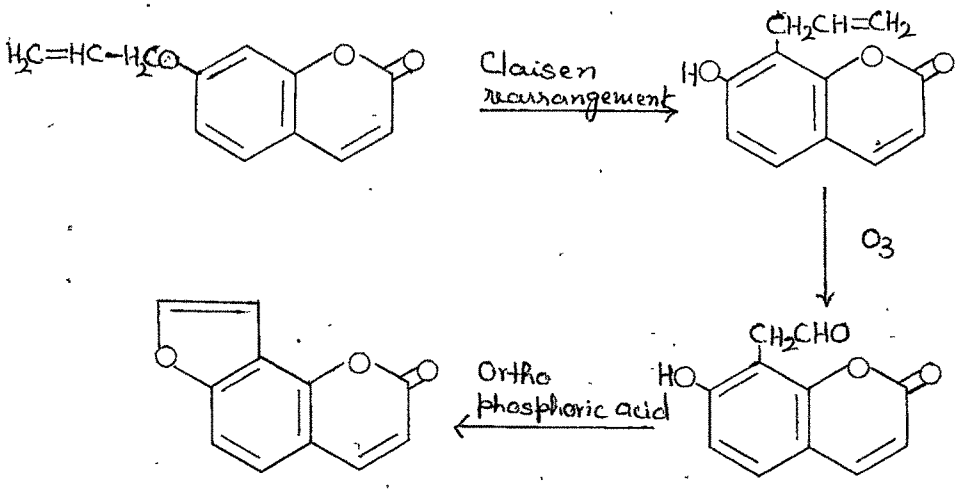
Condensations of this type are often effected with zinc chloride, sulphuric acid and similar reagents[24].

(9) A method which is extensively used for the synthesis of furan derivatives consists in the condensation of bromoacetic ester with an o-hydroxybenzaldehyde or an o-hydroxy acetophenone and subsequent hydrolysis and cyclisation of the phenoxy acetic acid derivative formed with sodium acetate and acetic anhydride. Simultaneous decarboxylation has been observed in many cases.



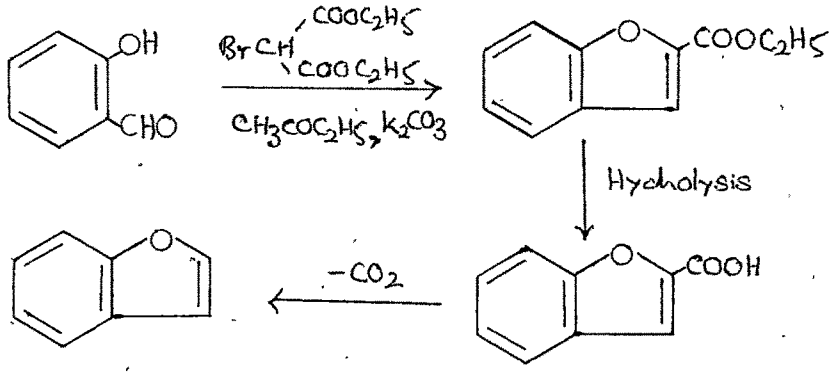
R = H or CH_3

(10) Aneja, Mukerjee and Seshadri[25] in the course of their work on the synthesis of furocoumarins developed another method in which they subjected the o-hydroxy allyl derivatives to ozonolysis and cyclised the o-hydroxy acetaldehyde derivative formed with orthophosphoric acid.

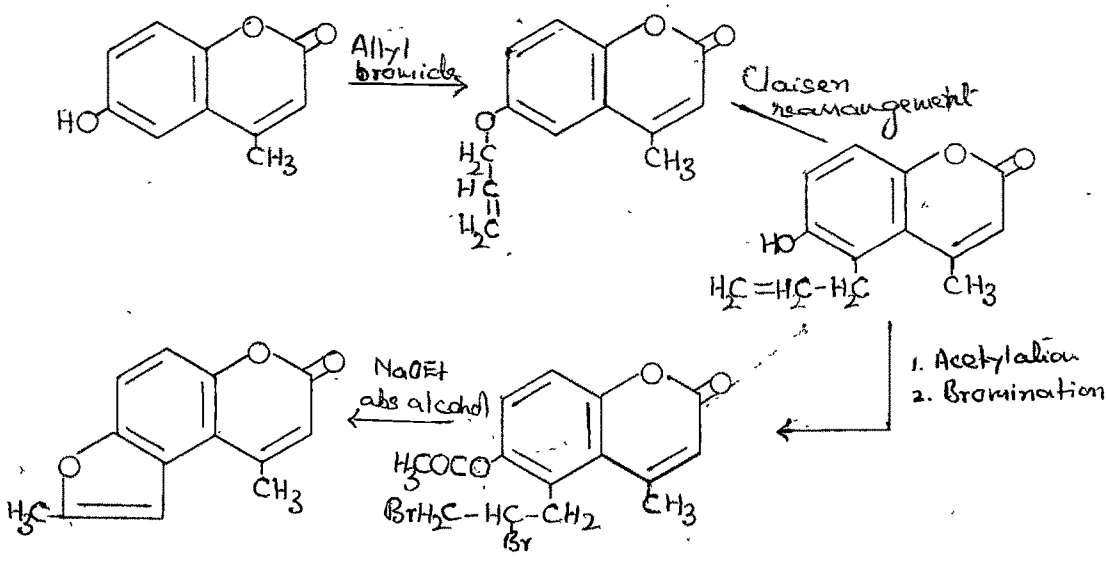


The oxidation of the allyl derivative to the formyl derivative can also be achieved with osmium tetroxide and potassium periodate[26].

(11) Tanaka's method[27] consists in the condensation of an o-hydroxyaldehyde with ethyl bromomalonate when benzofuran-2-carboxylate is obtained which on hydrolysis and decarboxylation gives the corresponding benzofuran derivative.



(12) Kaufmann et.al.[28] in their work on the synthesis of furocoumarins developed a versatile method for the synthesis of the furan derivatives from o-hydroxy allyl derivatives. It can be illustrated with the synthesis of a furocoumarin derivative.



Present work :

Of the various furan derivatives, furocoumarins which occur in nature have created a good deal of interest in recent years because of their physiological properties. Mustafa[1] has reviewed the various aspects of the naturally occurring furocoumarins in his recent book.

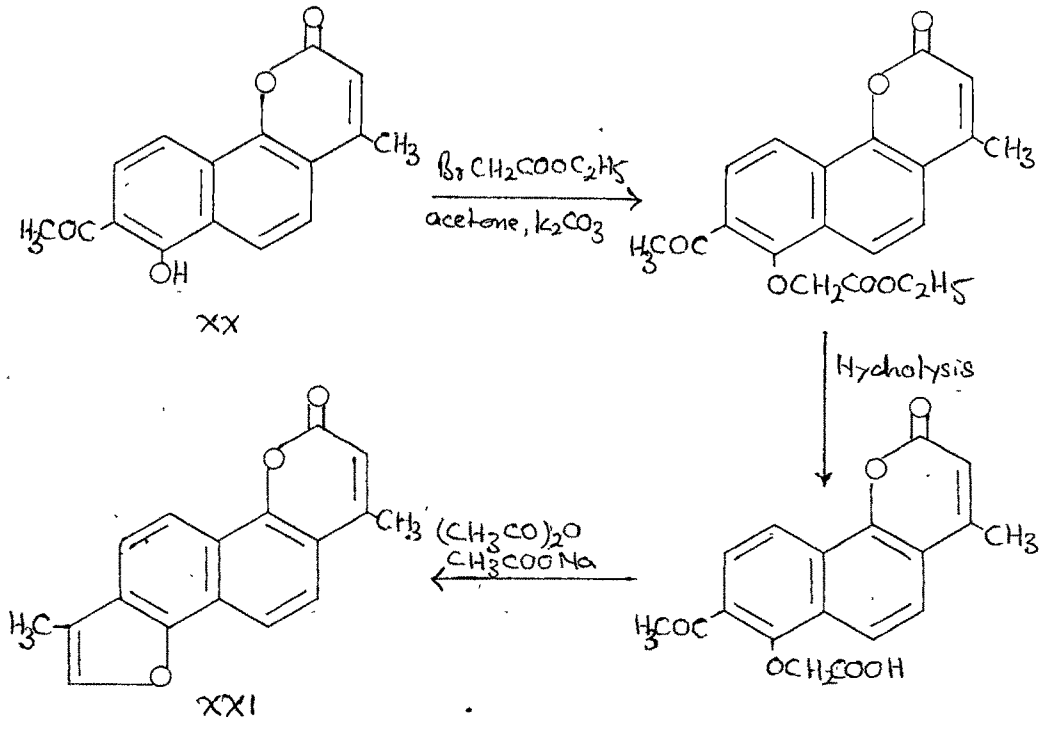
Some furocoumarins such as bergapten, pimpinellin and isopimpinellin are very good fish poisons and others such as psoralene, xanthotoxin and imperatorin are found to be photosensitising agents, which can bring about pigmentation of the depigmented skin by hastening the formation of melanin. The discovery of this unique activity of the furocoumarins stimulated further work in this field and the structure activity relationship has been studied by various workers. It has been found that the maximum photosensitising activity lies in the parent linear compound psoralene and the various structurally related compounds have more or less reduced activity. It was found that the region of activating wave lengths for photosensitising action of furocoumarins lies between 265 and 280 mu in the short ultra violet range and between 340 and 380 mu in the long ultra violet range. Furocoumarins such as psoralene and imperatorin have also been found to have antifungal activity[29]

While a large number of furocoumarins have been synthesised by the application of one or other methods described before from coumarin derivatives, the synthesis

of such compounds from benzocoumarins (naphtho-α-pyrones) have been very few. The reason probably is that the required hydroxy naphtho-α-pyrones are not readily available.

In the course of studies on dihydroxy naphthalenes going on in this laboratory, some hydroxy naphthopyrones have been synthesised and furan rings have been built up on these. Thus Mehta and Sethna[30] synthesised 4',3''-dimethyl naphtho(1,2:6',5')α-pyrone(5,6:5'',4'')furan(XXI) through the following sequence of reactions.

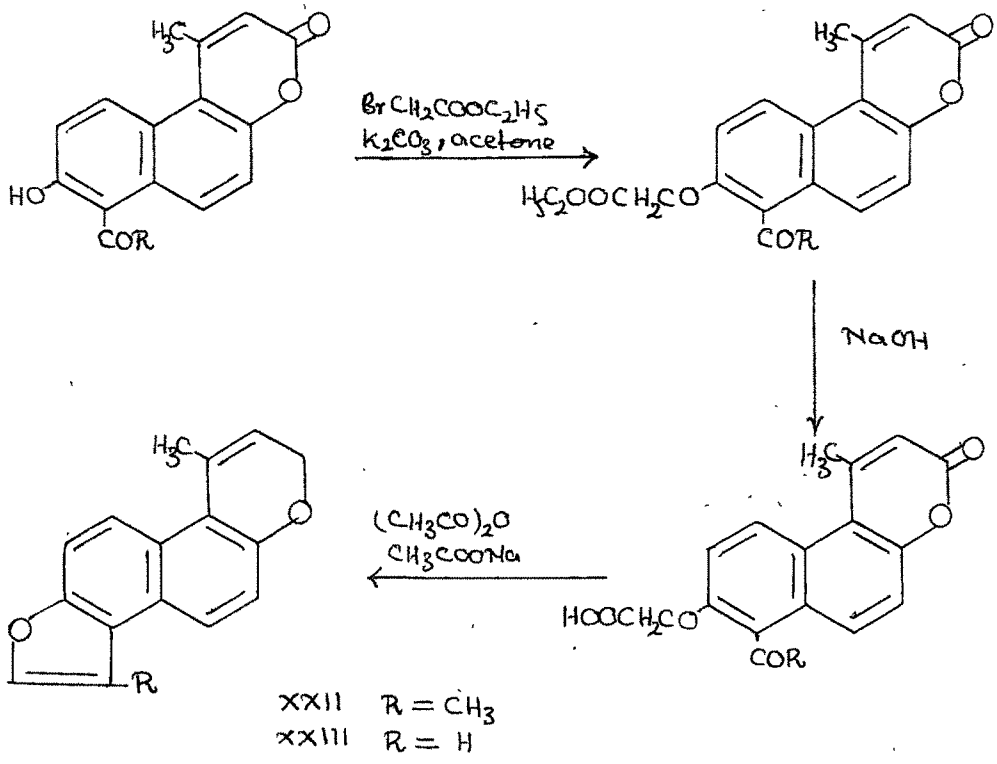
5-Hydroxy-6-acetyl-4'-methyl naphtho(1,2:6',5') α-pyrone(XX) was condensed with ethyl bromoacetate. 6-Acetyl-5-carbethoxymethoxy-4'-methyl naphtho(1,2:6',5')α-pyrone obtained was then hydrolysed to the corresponding acid. The acid on cyclisation with acetic anhydride and sodium acetate afforded the above mentioned furo naphtho-α-pyrone derivative(XXI) through simultaneous cyclisation and decarboxylation.



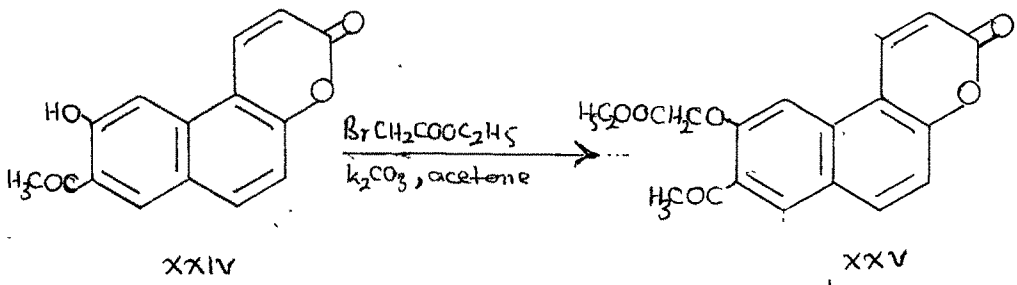
4',3''-Dimethyl naphtho (2,1:6',5')α-pyrone (6,5:5'',4'')furan (XXII) and 4'-methyl naphtho (2,1:6',5') α-pyrono(6,5:5'',4'')furan (XXIII) were synthesised through a similar sequence of reactions from 6-hydroxy-5-acetyl-4'-methyl naphtho (2,1:6',5')α-pyrone and 6-hydroxy-5-formyl-4'-methyl naphtho (2,1:6',5')α-pyrone by Kuriakose and Sethna[32]. This work has been extended further and the furan rings have been muilt up on a number of naphtho-α-pyrones. Further, the furan ring has also been built up on 5-hydroxy-2'-methyl naphtho (1,2:6',5')γ-pyrone, as no such furo naphtho-γ-pyrone appears to have been synthesised.

Synthesis of 3''-methyl naphtho (2,1:6',5')α-pyrono (7,6:5'', 4'') furan :

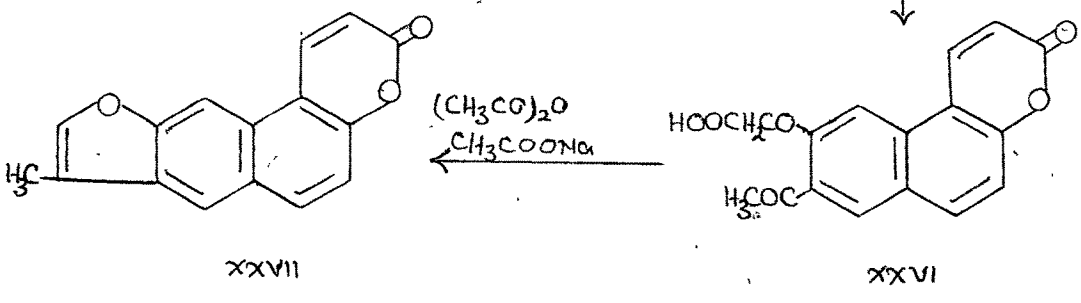
7-Hydroxy-6-acetyl naphtho (2,1:6',5')α-pyrone (XXIV) (prepared as described on p.81) was condensed with ethyl bromoacetate in the presence of anhydrous potassium carbonate in dry acetone when 7-carbethoxymethoxy-6-acetyl naphtho (2,1:6',5')α-pyrone (XXV) was obtained. It was hydrolysed by refluxing it with glacial acetic acid and hydrochloric acid mixture to the corresponding acid (XXVI). The latter when heated with sodium acetate and acetic anhydride gave on simultaneous cyclisation and decarboxylation the furan derivative (XXVII).



XXII $R = CH_3$
XXIII $R = H$



XXIV XXV



XXVII XXVI

Synthesis of 2"-methyl naphtho(2,1:6',5')α-pyrono (7,8:5",4")furan :

7-Hydroxy naphtho (2,1:6',5')α-pyrone on condensation with allyl bromide in the presence of anhydrous potassium carbonate in dry acetone gave the 7-allyloxy naphtho (2,1:6',5')α-pyrone (XXVIII). It was subjected to Claisen rearrangement by heating in dimethyl aniline for 5 hr. when an alkali soluble compound was obtained to which 7-hydroxy-8-allyl naphtho (2,1:6',5') α-pyrone (XXIX) structure was assigned on the basis of the NMR data. The NMR shows 6 doublets of AB pattern, in the region from δ 6.0 to 9.0 ppm., two doublets being overlaping with each other at δ 7.1. This confirms that the allyl group has migrated to the 8-position rather than 6-position.

The doublet situated at δ 6.3 is due to the 3'-proton, having a coupling constant J = 9.2 Hz. The other doublet with same J value of 9.2 Hz. appearing ~~downfield~~ at δ 8.42 downfield rather than having the usual value of δ 7.9, must be due to 4'-proton in the α-pyrone ring.

The remaining four aromatic protons in the positions 3,4,5 and 6 appear as doublet with J value of 9 Hz. each at δ 7.12, 7.84, 7.63 and 7.10 respectively.

Cyclisation[31] of this by triturating it with conc. sulphuric acid gave 2"-methyl naphtho (2,1: 6',5')

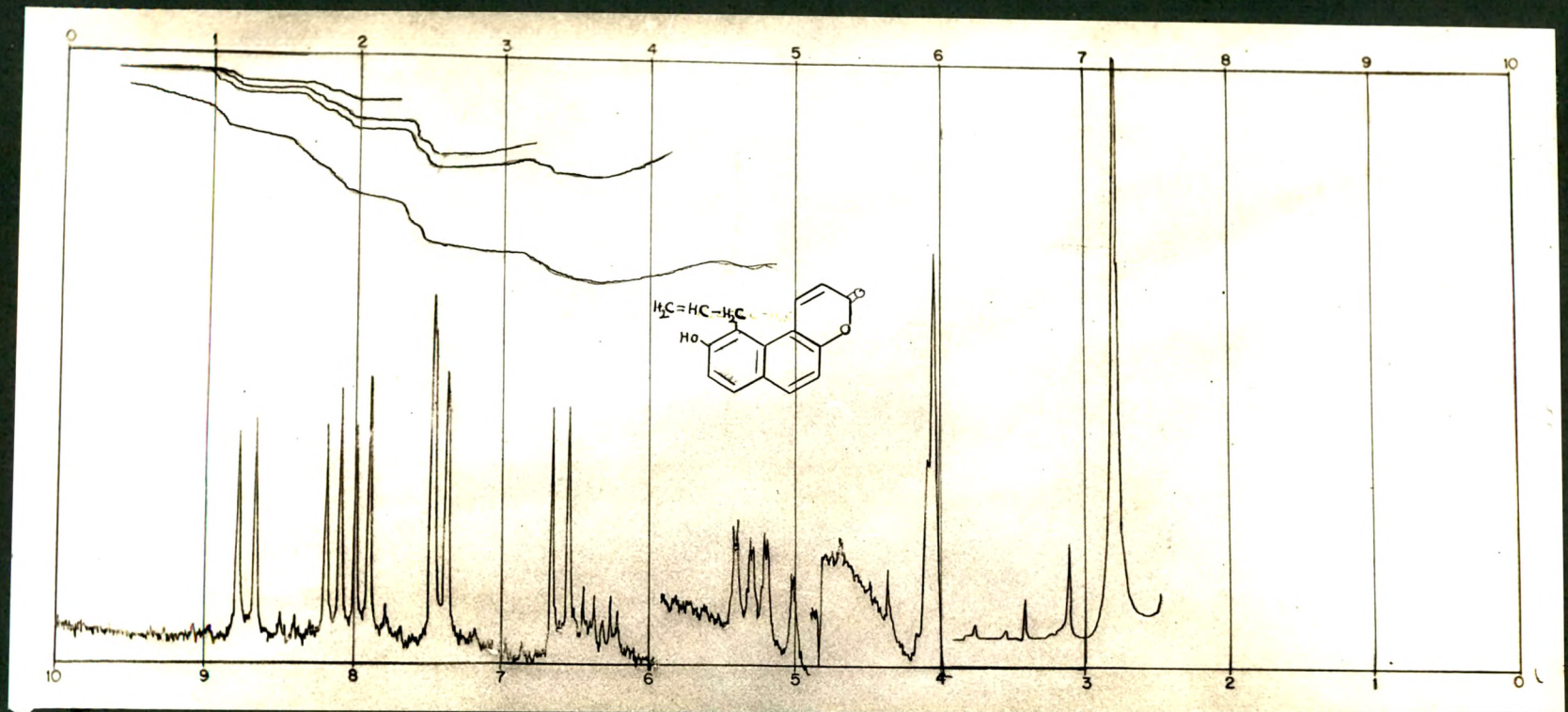
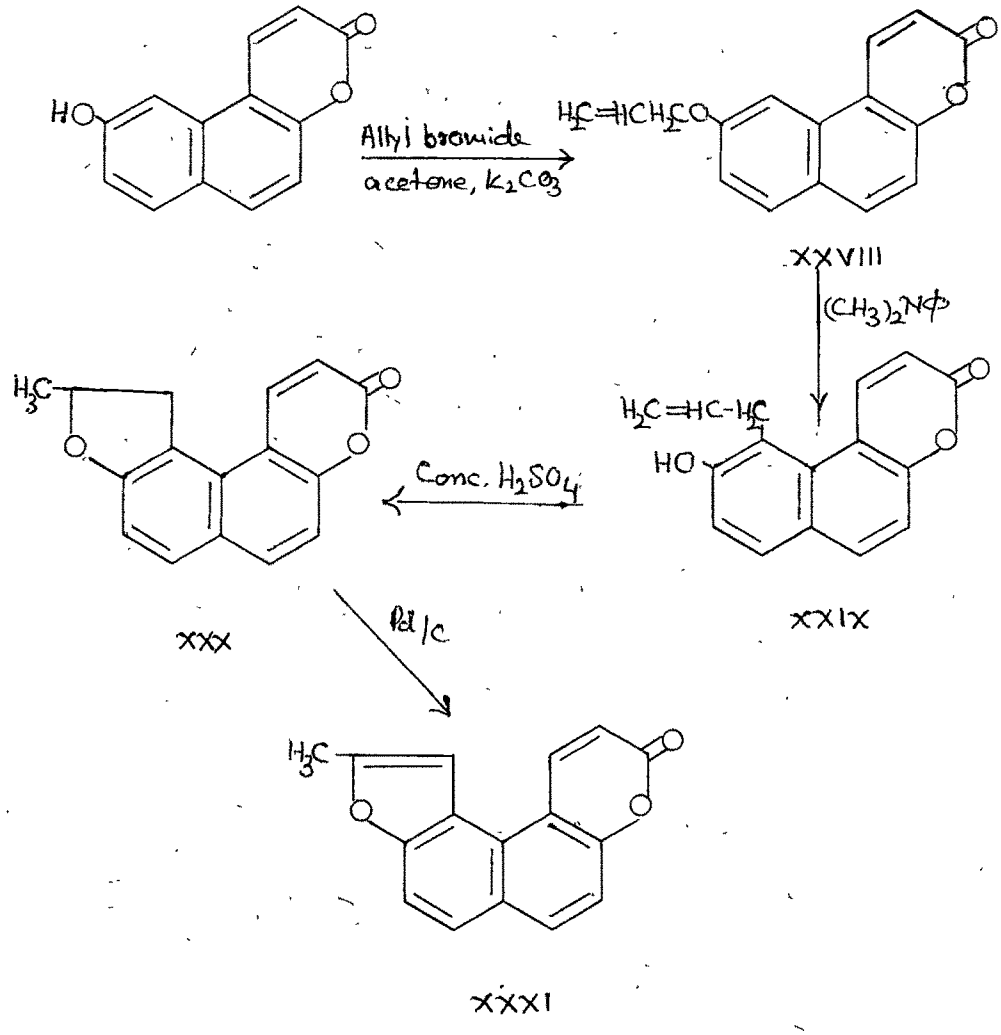


Fig. (XXIX) :- NMR spectrum of 7-hydroxy-8-allyl naphtho(2,1:6',5') α-pyrone. (DMSO)

α-pyrono(7,8:5'', 4'')$^{2'',3''}$ dihydro furan (XXX) which on dehydrogenation with palladised charcoal (10 %) afforded 2''-methyl naphtho (2,1:6',5') α-pyrono (7,8:5'', 4'') furan (XXXI).



Synthesis of 3'',4'-dimethyl naphtho (2,3:6',5') α-pyrono (7,8: 5'', 4'') furan :

7-Hydroxy-8-acetyl-4'-methyl naphtho(2,3:6',5') α-pyrone prepared as described before on condensation with ethyl bromoacetate in the presence of anhydrous

potassium carbonate in dry acetone gave 8-acetyl-7-carbethoxy methoxy-4'-methyl naphtho (2,3:6',5') α-pyrone (XXXII) which on alkaline hydrolysis (10% NaOH) gave the corresponding acid (XXXIII). This acid on refluxing with fused sodium acetate and acetic anhydride yielded 3",4'-dimethyl naphtho (2,3:6',5') α-pyrono(7,8:5",4")furan (XXXIV). The NMR spectrum of this shows two doublets and three singlets in the aromatic region. The singlet at δ7.932 due to 2"-position in furan ring[33] is quite in agreement with the inductive effect of the hetero atom. The two doublets with the coupling constant of 9.1 Hz., at δ 7.96 and 7.75 are due to H-5 and H-6 respectively. The other two aromatic singlets at δ 8.50 and 8.07 must be due to H-4 and H-1 respectively. The 3'-proton appears as a singlet at δ 6.44 while the methyl groups in the furan and the α-pyrone rings appear at δ 2.56 and 2.50 as three proton singlets respectively.

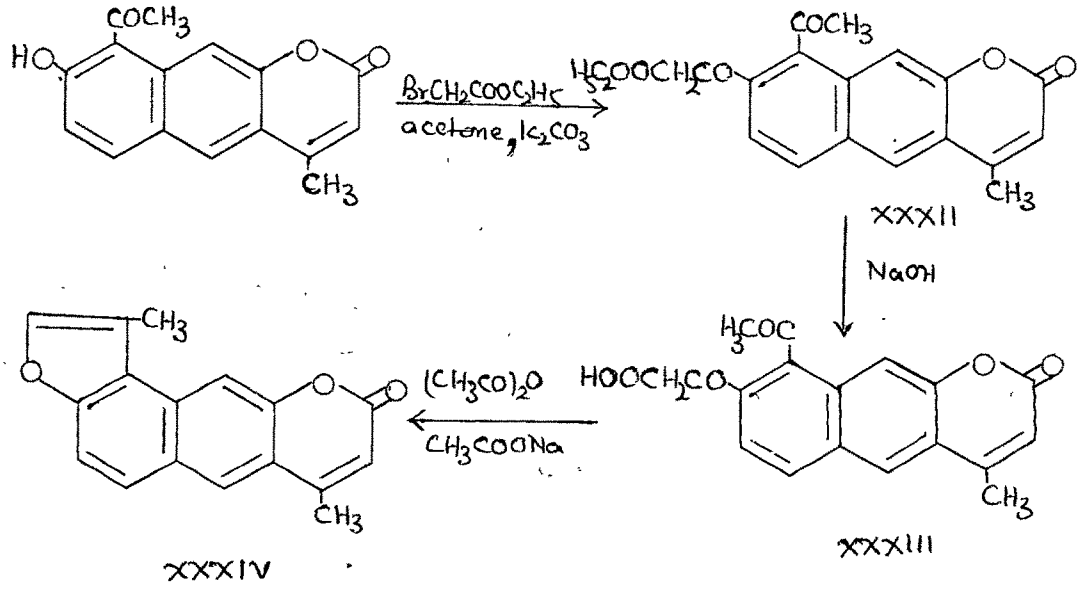


Fig. (XXXIV) :- NMR spectrum of 3'',4'-dimethyl naphtho (2,3:6',5')α-pyrono (7,8: 5 ,4)furan. (DMSO)

Synthesis of 2",4'-dimethyl naphtho(2,3:6',5')α-pyrono (7,8:5",4")furan :

7-Hydroxy-4'-methyl naphtho(2,3:6',5')α-pyrone on condensation with allyl bromide in the presence of anhydrous potassium carbonate in dry acetone afforded the corresponding allyloxy derivative (XXXV) which on Claisen rearrangement by refluxing in dimethyl aniline in an inert atmosphere of nitrogen gave o-hydroxy allyl derivative to which 7-hydroxy-8-allyl-4'-methyl naphtho (2,3:6',5')α-pyrone (XXXVI) structure was assigned on the basis of NMR spectra, which has been recorded from δ8.5 to 5.5 to get the aromatic protons only. The clear pattern of two doublets and two singlets in the aromatic region confirms the position of the allyl group to be at 8. The 6 position has clearly been rules out, as this would have given four singlets for the four isolated aromatic protons.

The two doublets at δ7.7 and 7.15 are mainly due to H-5 and H-6. The coupling constant for these two doublets is of 9.8 Hz. The singlets at δ 8.00 , 7.5 and at 6.18 are due to H-4,H-1 and H-3' of the α-pyrone ring.

The above o-hydroxy allyl derivative was cyclised by adopting Kaufmann[27] method. It was converted to 7-acetoxy-8-allyl-4'-methyl naphtho (2,3:6',5')α-pyrone (XXXVII) by heating with acetic anhydride and sodium acetate. The acetoxy derivative was then brominated in acetic acid. The dibromo derivative (XXXVIII) obtained was subjected to cyclisation using alcoholic potassium hydroxide when the

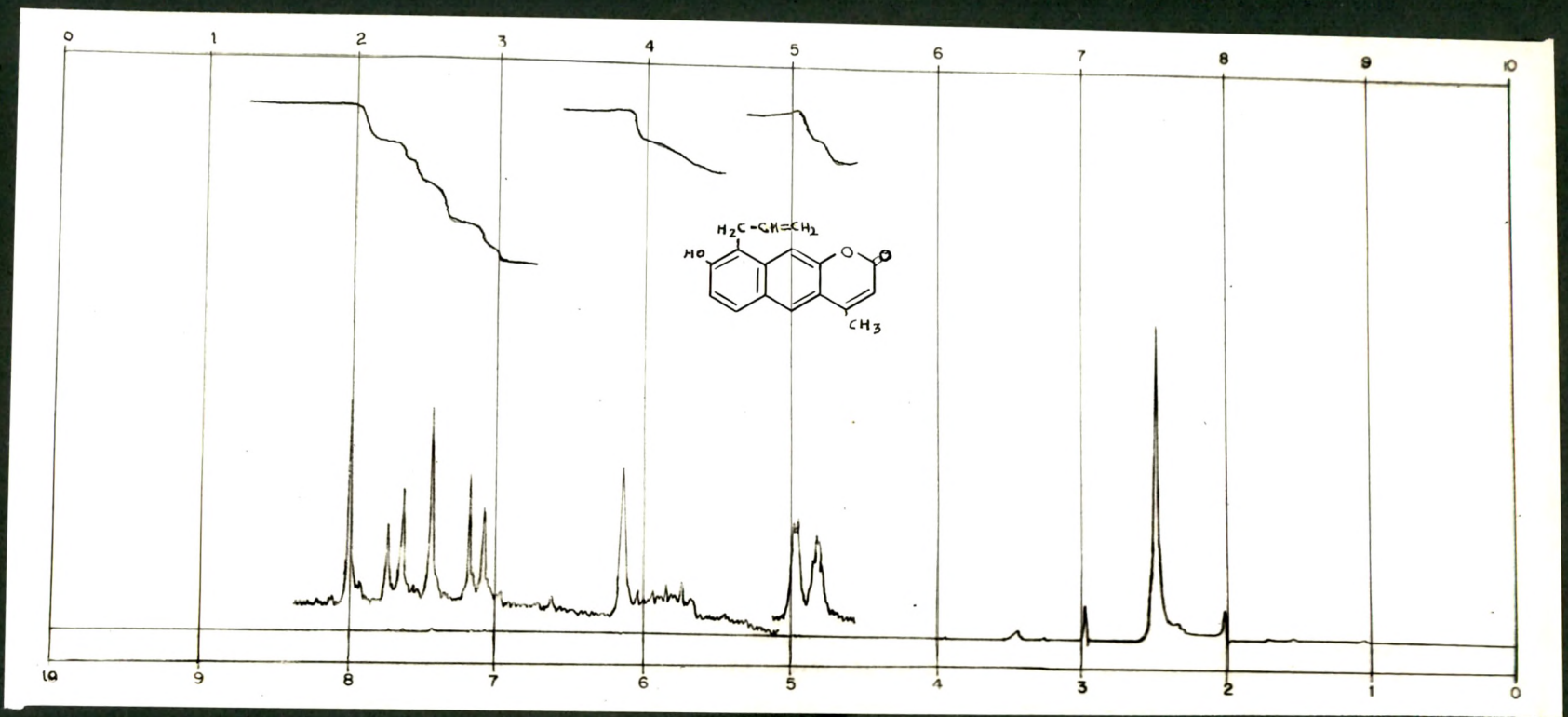
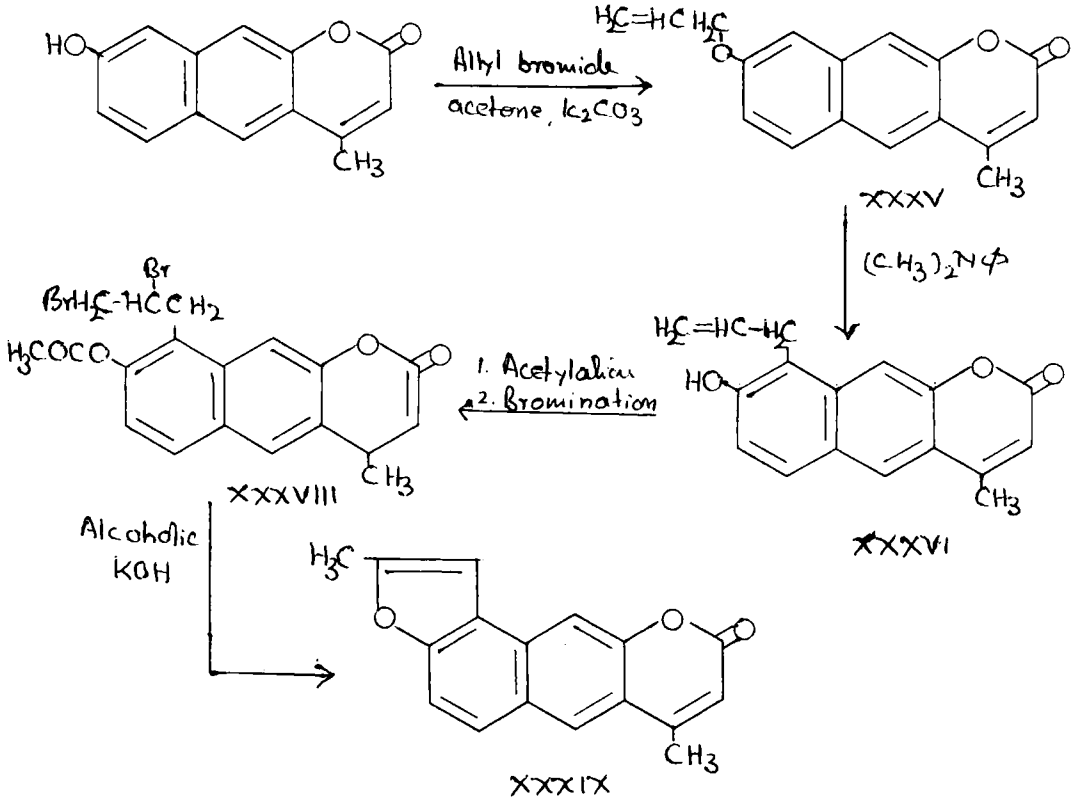


Fig. (XXXVI) :- NMR spectrum of 7-hydroxy-8-allyl-4'-methyl naphtho (2,3:6',5')α-pyrone. (DMSO)

desired furan (XXXIX) was obtained.

The NMR spectrum shows two doublets and two singlets in the aromatic region confirming the angular furan ring structure.

The two singlets at δ 8.04 and 7.76 can be assigned to H-4 and H-1. The two doublets with the coupling constant of 9.4 Hz. at δ 7.65 and 7.52 are due to two ortho protons at 5 and 6 positions respectively. The furan proton 3" appears at δ 6.77 and the α-pyrone proton 3' at δ 6.27. The methyl protons of both furan and α-pyrone rings appear as two distinct three proton singlets at δ 2.54 and 2.49 respectively. A weak peak situated at δ 7.24 is due to the chloroform impurity in $CDCl_3$.



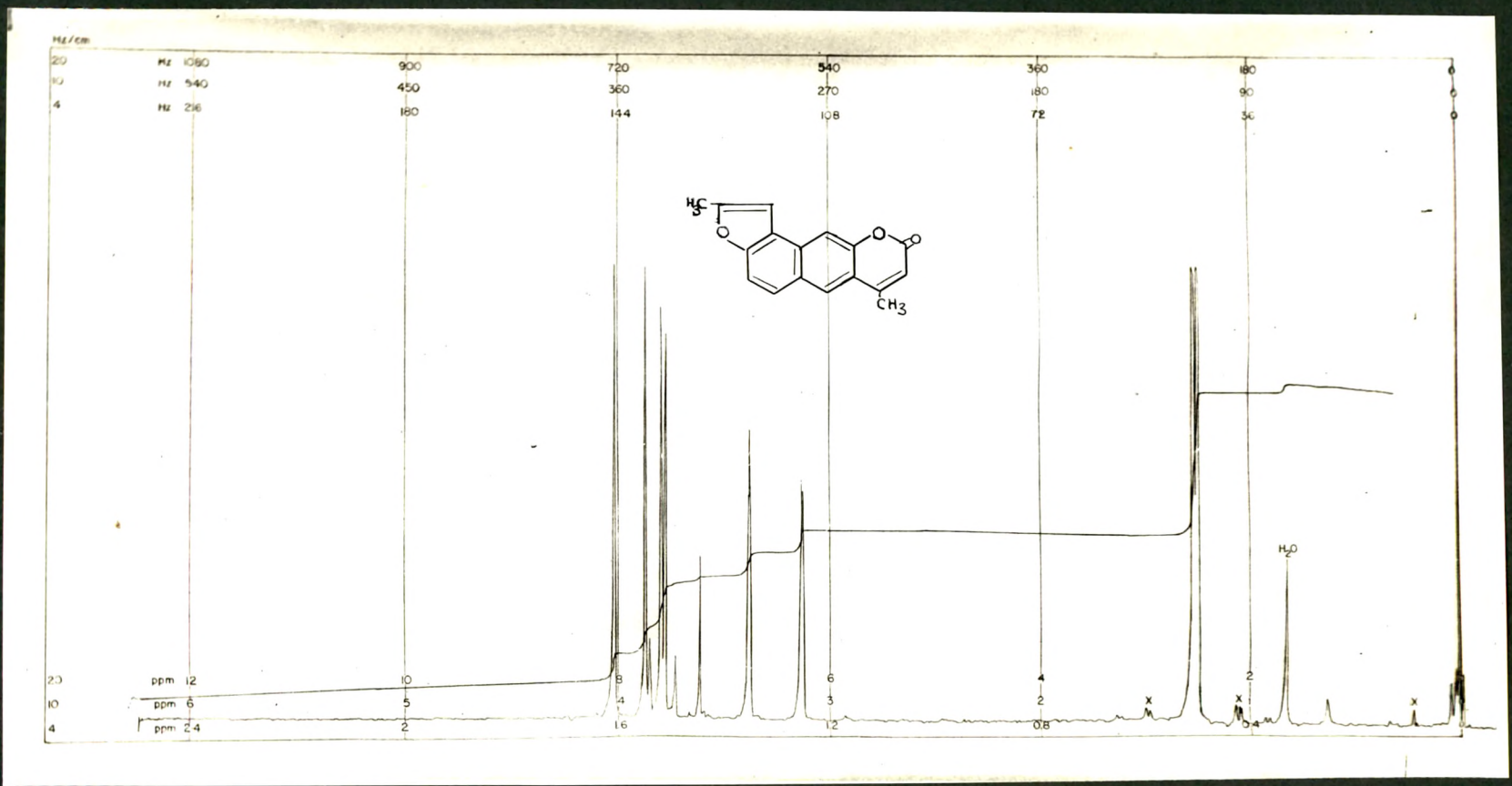
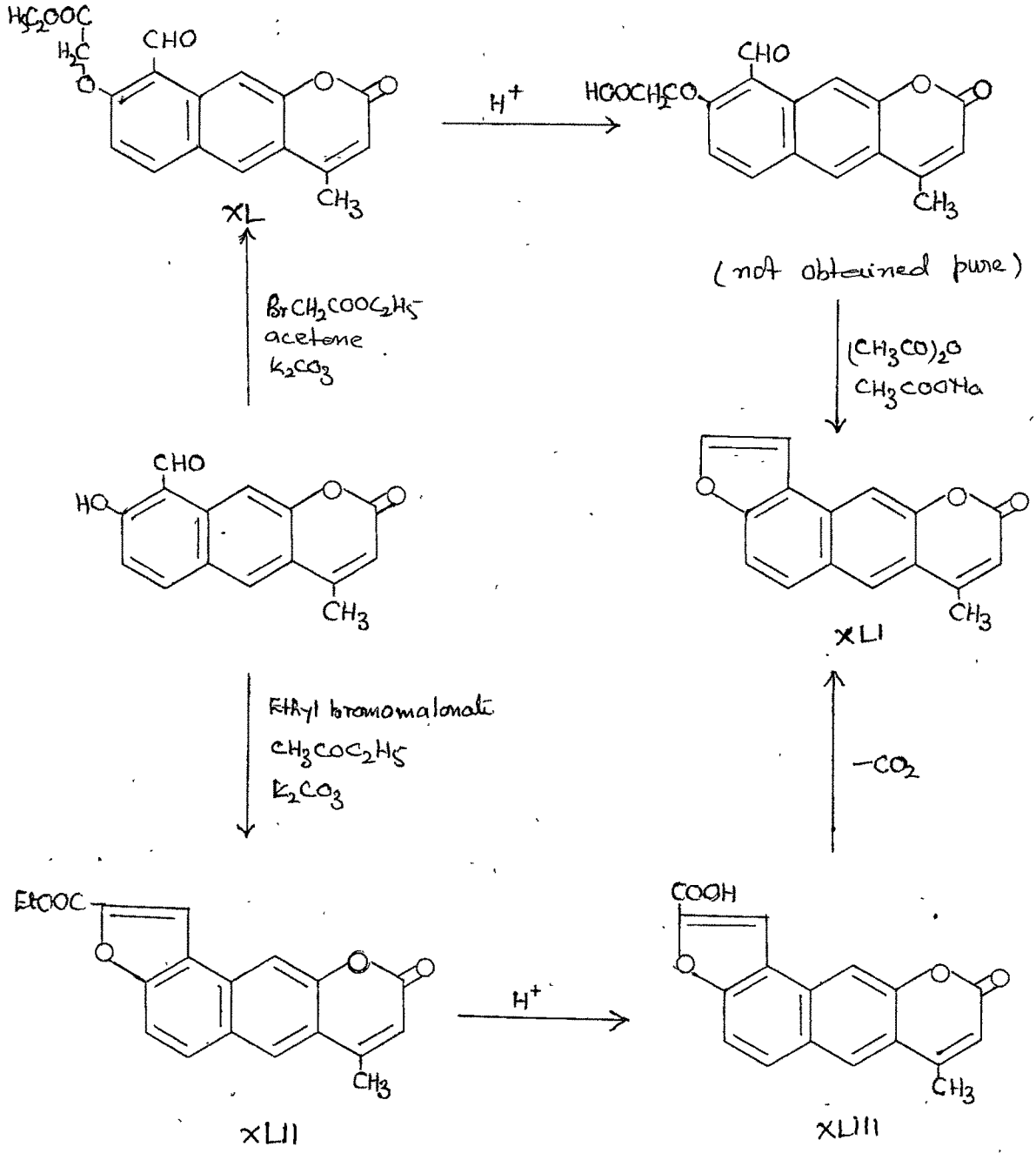


Fig. (XXXIX) :- NMR spectrum of 2",4'-dimethyl naphtho(2,3:6',5') α-pyrono (7,8:5",4") furan. ($CDCl_3$)

Synthesis of 4'-methyl naphtho(2,3:6',5')α-pyrono (7,8:5",4") furan :

7-Hydroxy-8-formyl naphtho(2,3:6',5')α-pyrone prepared as described earlier was condensed with ethyl bromoacetate in the presence of anhydrous potassium carbonate in dry acetone. The 7-carbethoxymethoxy derivative (XL)obtained was hydrolysed by refluxing with glacial acetic acid and hydrochloric acid (A.R.) mixture to the corresponding acid which could not be crystallised. It was subjected to cyclisation with acetic anhydride and sodium acetate when 4'-methyl naphtho(2,3:6',5')α-pyrono(7,8:5",4")furan (XLI) was obtained.

The same furan was obtained when 7-hydroxy-8-formyl-4'-methyl naphtho(2,3:6',5')α-pyrone was condensed with ethyl bromomalonate in the presence of anhydrous potassium carbonate in dry methyl ethylketone which yielded 4'-methyl-2-carbethoxy naphtho (2,3:6',5')α-pyrono(7,8:5",4") furan (XLII). This was hydrolysed by refluxing it in the glacial acetic acid with hydrochloric acid. The corresponding acid (XLIII) obtained was then subjected to decarboxylation by heating with quinoline and copper powder when 4'-methyl naphtho(2,3:6',5')α-pyrono(7,8:5",4")furan (XLI) was obtained.


CHO
CH3
XL
H+
HOOCH2CO
(not obtained pure)
BrCH2COOC2H5
acetone
K2CO3
(CH3CO)2O
CH3COOHa
XLI
HO
Ethyl bromomalonate
CH3COC2H5
K2CO3
-CO2
EtOOC
COOH
H+
XLII
XLIII

Fries migration of 7-acetoxy-4'-methyl naphtho (2,1:6',5')α-pyrone : 7-Hydroxy-6-acetyl naphtho (2,1:6',5')α-pyrone :

7-Acetoxy-4'-methyl naphtho(2,1:6',5')α-pyrone (XLIV) prepared by acetylation of 7-hydroxy-4'-methyl naphtho(2,1:6',5')α-pyrone when subjected to Fries migration with anhydrous aluminium chloride gave an alkali soluble yellow compound which gave green colour with alcoholic ferric chloride. The compound also gave a 2,4-dinitro phenyl hydrazone derivative. 7-Hydroxy-6-acetyl-4'-methyl naphtho(2,1:6',5')α-pyrone structure (XLV) has been assigned to this compound on the basis of NMR data.

The NMR shows two doublets and two singlets in the aromatic region apart from a singlet at δ 6.28 which is a characteristic of H-3 of α-pyrone ring. This pattern confirms the migration of $-COCH_3$ group to the 6-position.

The upfield singlet at δ 7.74 and upfield doublet at δ 7.15 can be assigned to H-8 and H-3 respectively. Similarly the singlet at δ 8.32 and doublet at δ 7.92 can be assigned to H-5 and H-4 having a coupling constant of 9-Hz. characteristic of o-coupling.

Synthesis of 3'',4'-dimethyl naphtho (2,1:6',5') α-pyrono(7,6: 5'',4'')furan :

7-Hydroxy-6-acetyl-4'-methyl naphtho(2,1:6',5') α-pyrone was condensed with ethyl bromoacetate in the presence of anhydrous potassium carbonate in dry acetone.

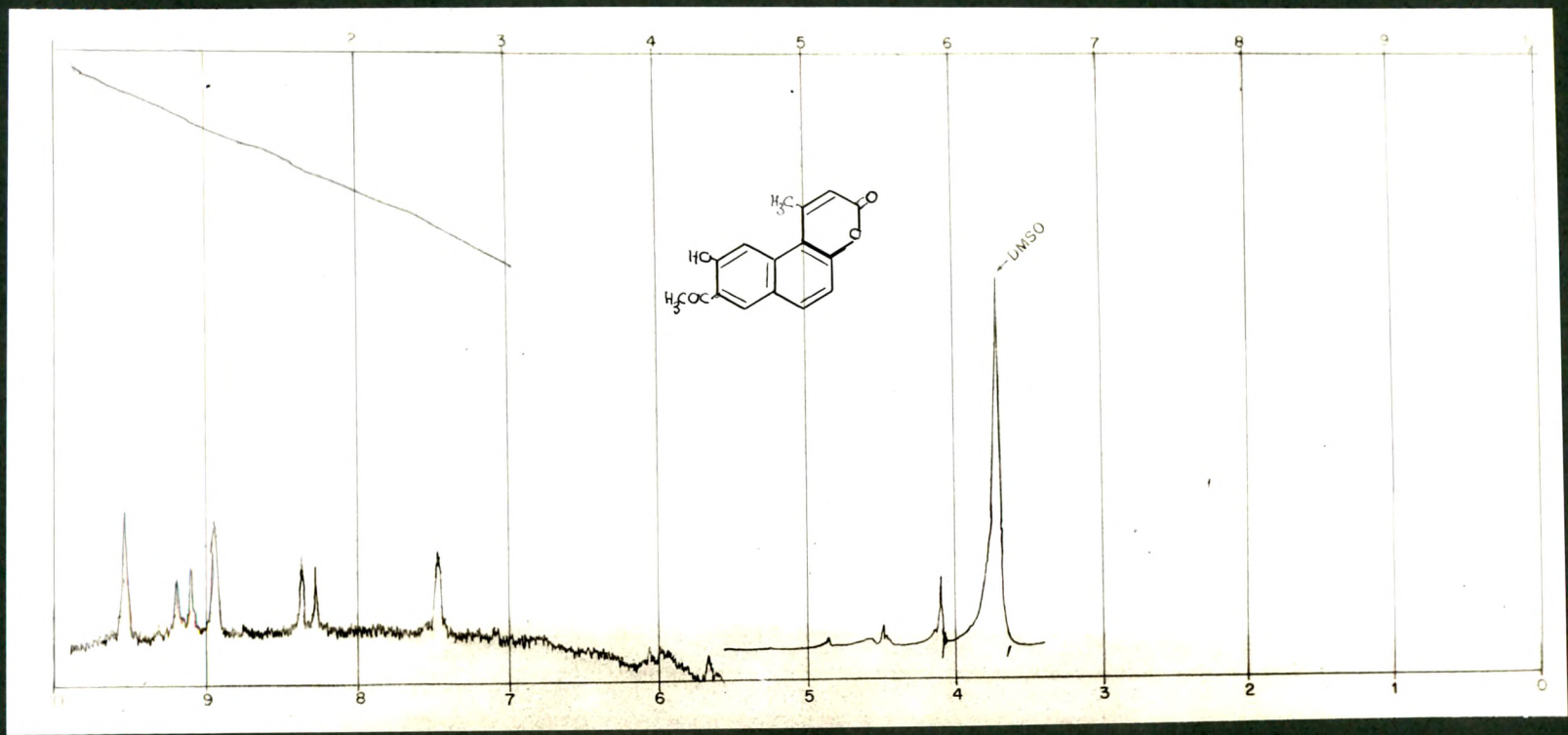
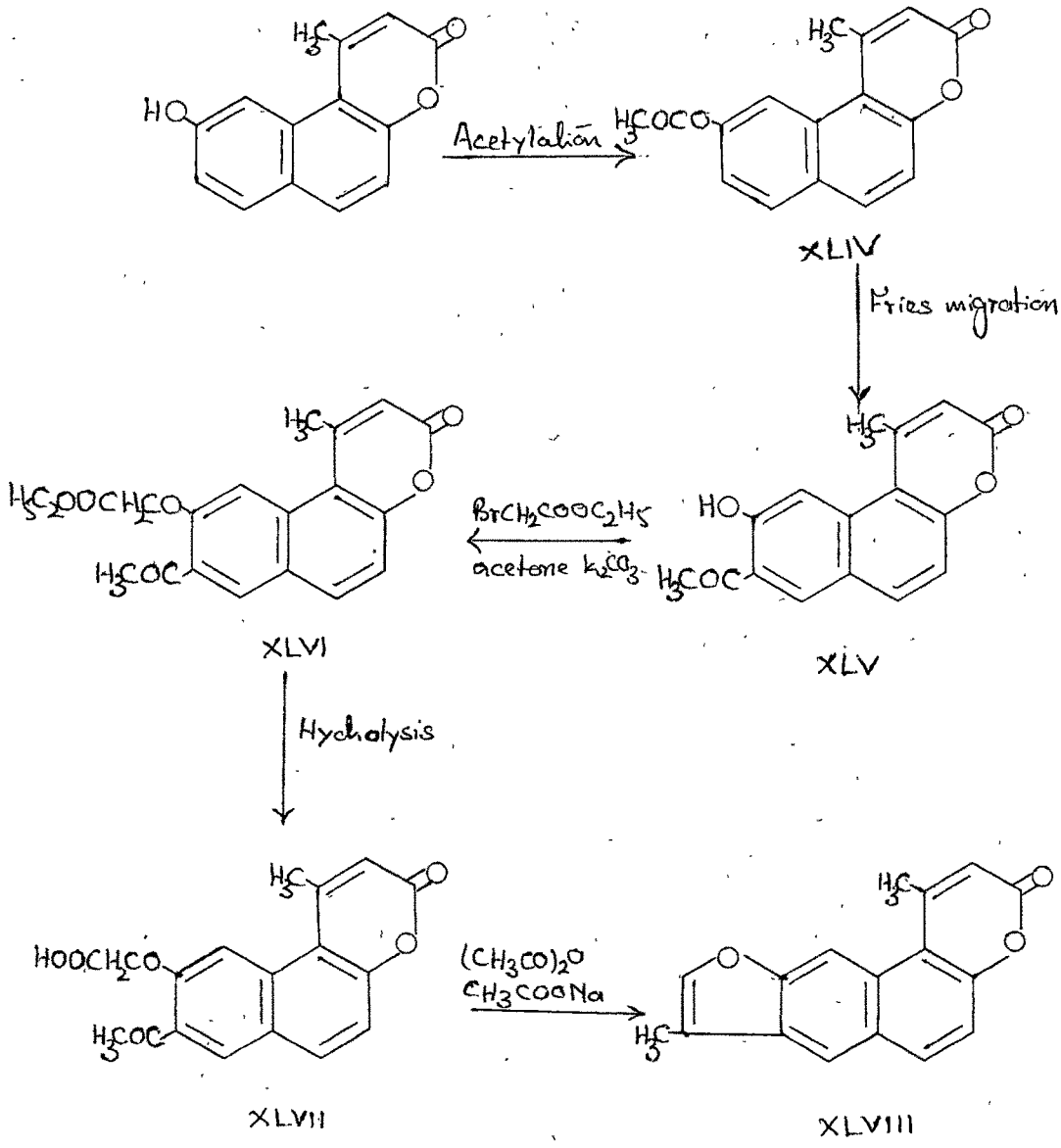


Fig. (XLV) :- NMR spectrum of 7-hydroxy-6-acetyl-4'-methyl naphtho (2,1:6',5')α-pyrone.

The ester (XLVI) obtained was hydrolysed to the corresponding acid which when refluxed with sodium acetate and acetic anhydride gave through simultaneous cyclisation and decarboxylation, the desired furan derivative (XLVIII).



Synthesis of 2",4'-dimethyl naphtho(2,1:6',5')α-pyrono (7,8:5",4") 2",3"-dihydrofuran :

7-Hydroxy-4'-methyl naphtho(2,1:6',5')α-pyrone was conddnsed with allyl bromide in dry acetone and anhydrous potassium carbonate. 7-Allyloxy-4'-methyl naphtho(2,1:6',5') α-pyrone(XLIX) obtained was then subjected to Claisen rearrangement by heating in dimethyl aniline for 6 hr. An alkali soluble compound was obtained to which 7-hydroxy-8-allyl-4'-methyl naphtho(2,1:6',5')α-pyrone structure (L) is assigned on the basis of the NMR data.

The NMR spectra shows a clear pattern of four doublets in the aromatic region, which leads to the conclusion that the allyl migration takes place at 8-position rather than the 6-position. All the four doublets have the same ortho coupling value of 9 Hz.

The doublet at δ 6.9 can be assigned to H-6 while the doublet at δ 7.02 to the H-3. The doublet at δ 7.8 and 7.5 though overlap each other are discernable and can be assigned to H-5 and H-4 respectively. The α-pyrone proton appears at δ 6.1.

Cyclisation of this by triturating it with conc. sulphuric acid gave 2",4'-dimethyl naphtho(2,1:6',5')α-pyrono (7,8:5",4")2",3"-dihydrofuran (LI).

Dehydrogenation of the above furan with palladised charcoal in diphenyl ether did not succeed.

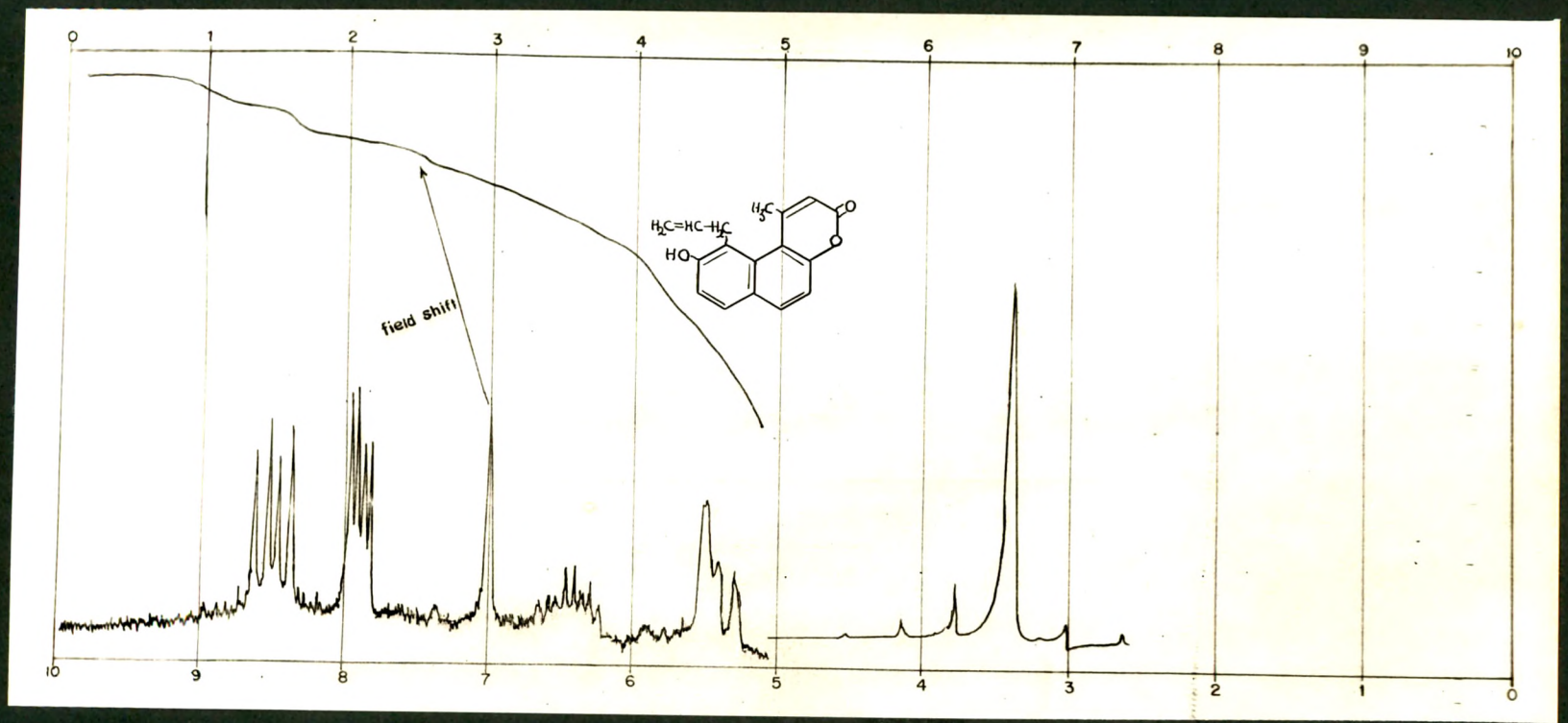
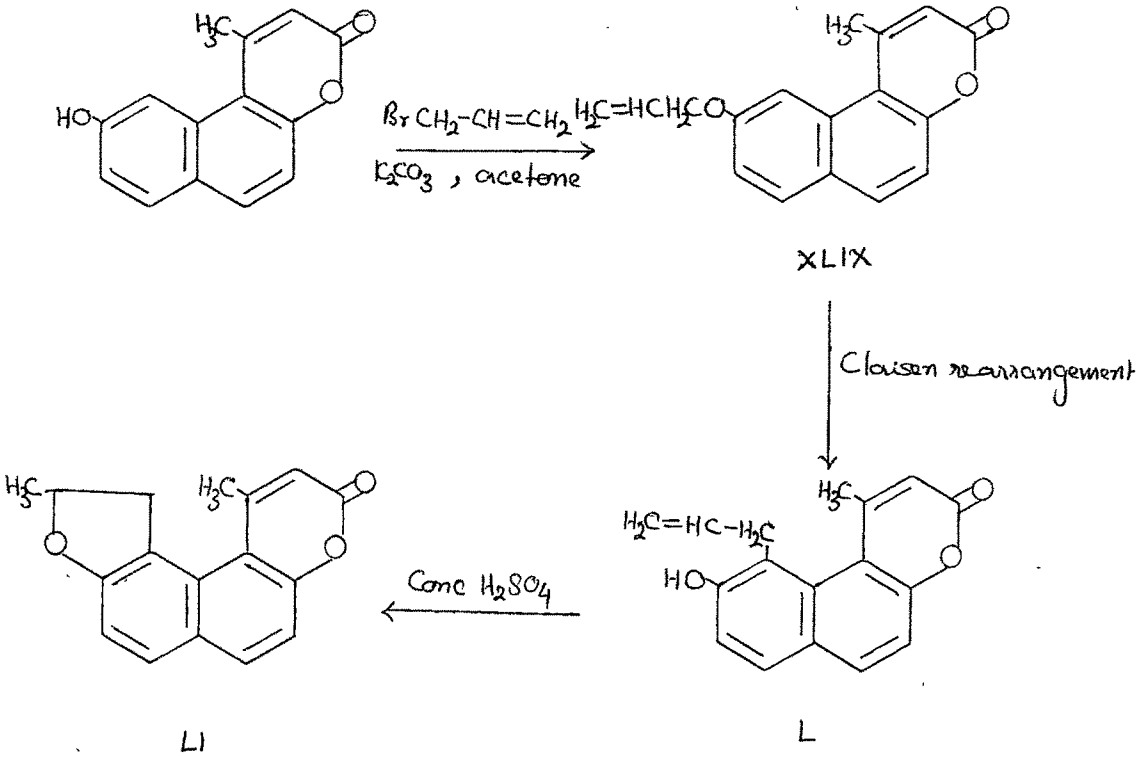
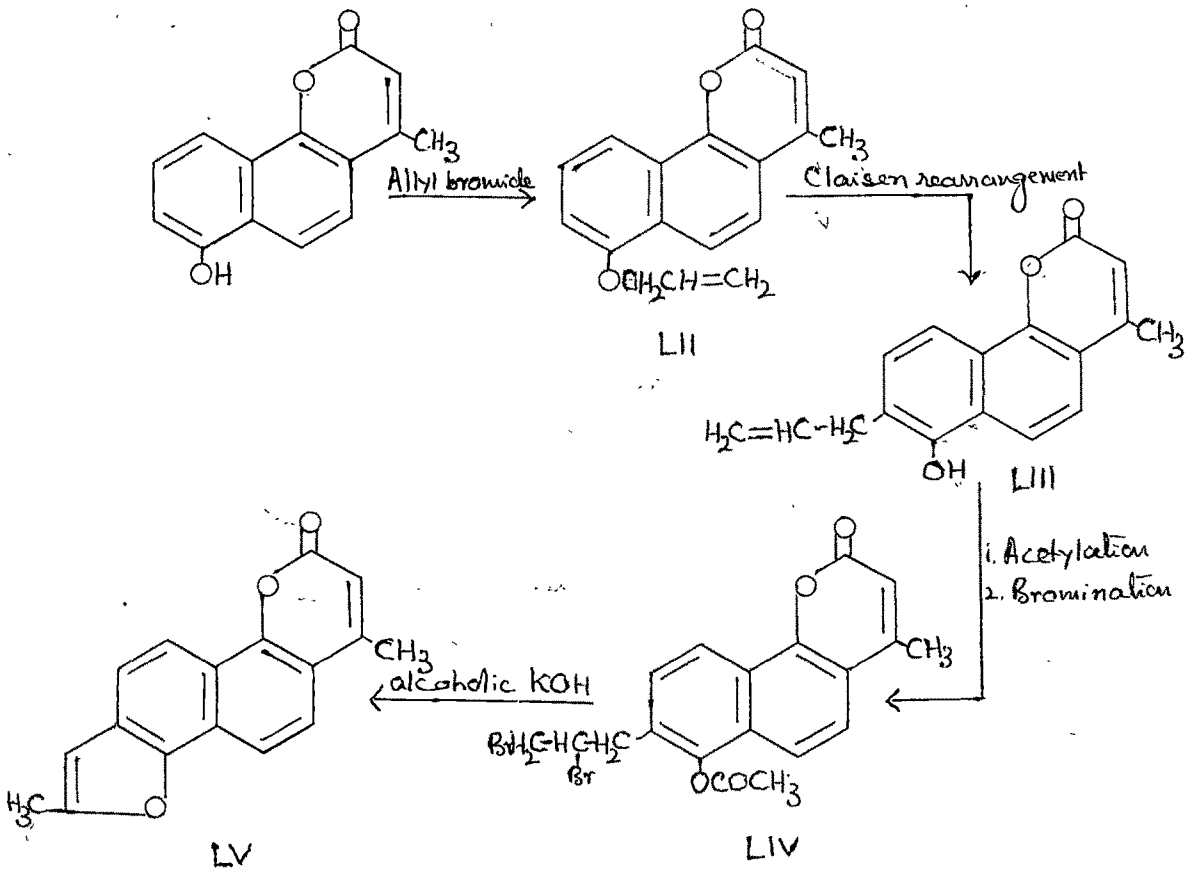


Fig. (L) :- NMR spectrum of 7-hydroxy-8-allyl-4'-methyl naphtho (2,1:6',5')α-pyrone. (DMSO)


Br CH2-CH=CH2
K2CO3 , acetone
H2C=HCH2CO
XLIX
Claisen rearrangement
H2C=HC-H2C
HO
L
Conc H2SO4
LI

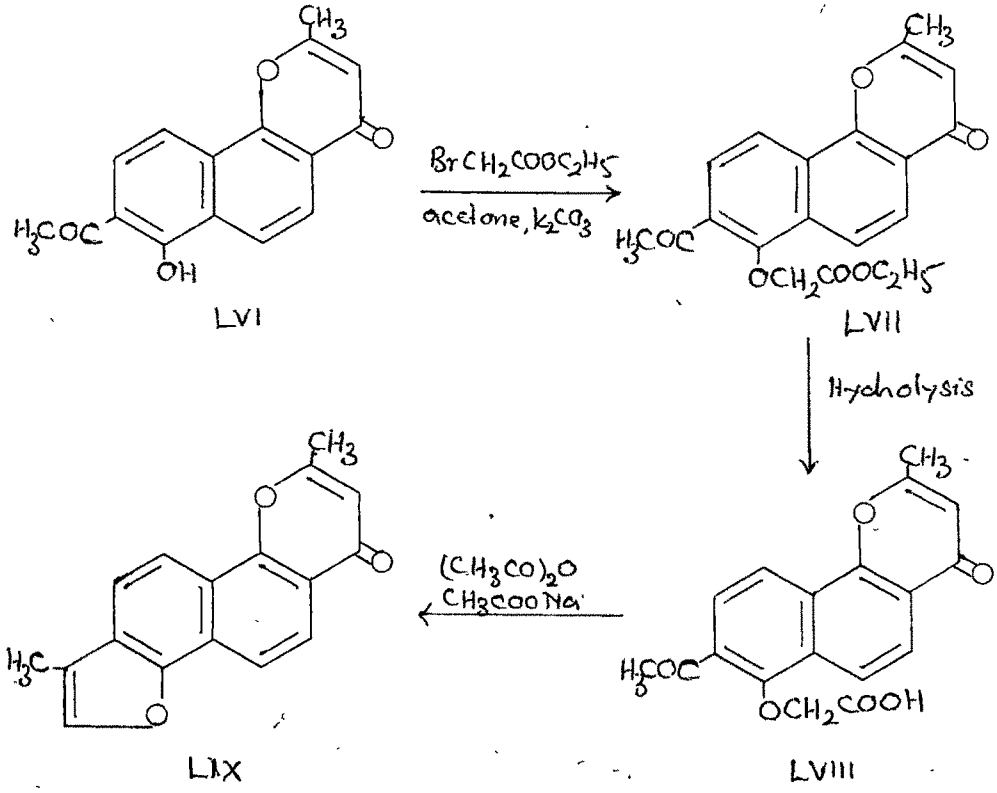
Synthesis of 2",4'-dimethyl naphtho(1,2:6',5')α-pyrono (5,6:5",4")furan :

5-Hydroxy-4'-methyl naphtho(1,2:6',5')α-pyrone was allylated by condensing with allyl bromide in the presence of anhydrous potassium carbonate in dry acetone. The allyloxy derivative (LII) on Claisen rearrangement in dimethyl aniline gave the corresponding o-hydroxy allyl derivative (LIII) which was acetylated and brominated with bromine in acetic acid. The dibromo derivative(LIV) when subjected to the action of alcoholic potassium hydroxide gave 2",4'-dimethyl naphtho(1,2:6',5')α-pyrono(5,6:5",4") furan (LV).



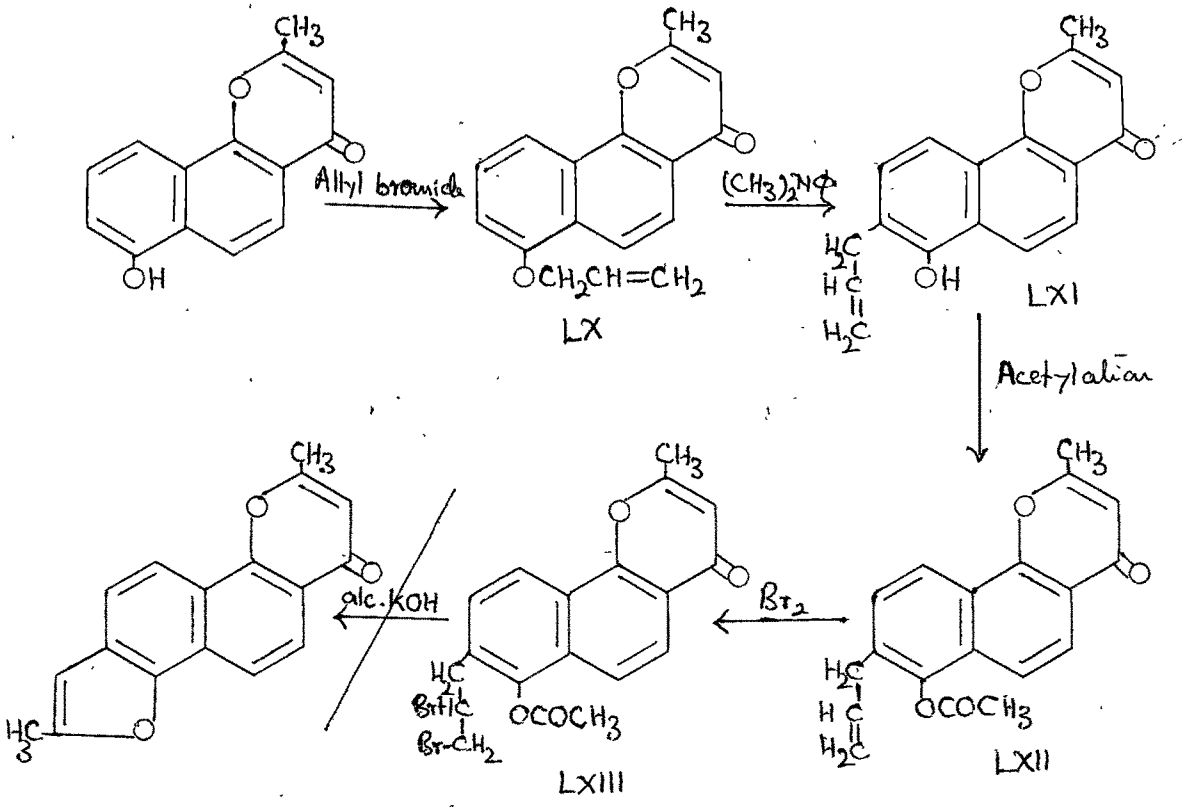
Synthesis of 2',3''-dimethyl naphtho(1,2:6',5')y-pyrono (5,6:5'',4'')furan :

5-Hydroxy-6-acetyl-2'methyl naphtho(1,2:6',5') y-pyrone(LVI) was prepared by Fries rearrangement of 5-acetoxy-2'methyl naphtho(1,2:6',5')y-pyrone as described on p. 93 . The o-hydroxy ketone on condensation with ethyl bromo acetate in the presence of anhydrous potassium carbonate in dry acetone furnished the ester derivative(LVII) which was hydrolysed by refluxing it with glacial acetic acid and hydrochloric acid mixture to the corresponding acid (LVIII) which on simultaneous cyclisation and decarboxylation with freshly fused sodium acetate and acetic anhydride afforded the 2',3''-dimethyl naphtho(1,2:6',5')y-pyrono (5,6:5'',4'')furan (LIX)



Attempted synthesis of 2',2''-dimethyl naphtho(1,2:6,5') y-pyrono(5,6:5'',4'')furan :

5-Hydroxy-2'-methyl naphtho(1,2:6,5')γ-pyrone was condensed with allyl bromide in the presence of anhydrous potassium carbonate in dry acetone. This allyloxy derivative (LX) was subjected to Claisen rearrangement with dimethyl aniline as usual. This afforded 5-hydroxy-6-allyl-2'-methyl naphtho(1,2:6,5')y-pyrone (LXI) which could not be cyclised with conc.sulphuric acid. The cyclisation by Kaufman method was also tried. It was acetylated, the acetyl derivative (LXII) was then brominated to get dibromo derivative(LXIII). This on subjecting to the action of alcoholic potassium hydroxide did not give any pure product.



I.R.and UV spectra of the furan derivatives synthesised

I.R.spectra were recorded on Beckman I.R.20 and Perkin Elmer models and UV spectra were taken on Beckman DU-2 Spectrophotometer.

Structure No.	Name of the compound	Lactonyl >C=O stretching Cm^{-1} and solvent	γ-pyronyl >C=O stretching Cm^{-1}	Furan ring breathing Cm^{-1}	λmax nm. (in chloroform)
1	2	3	4	5	6
XXVII	3"-Methyl naphtho (2,1:6',5')α-pyrono (7,6:5",4")furan	1720 nujol	-	890	226,250,286
XXXI	2"Methyl naphtho (2,1:6',5')α-pyrono (7,8:5",4")furan	1715 KBr	-	890	248,290
XXXIV	3",4'-Dimethyl naphtho (2,3:6',5')α-pyrono (7,8:5",4")furan	1710 nujol	-	880	250
XXXIX	2",4'-Dimethyl naphtho (2,3:6',5')α-pyrono (7,8:5",4")furan	1720 KBr	-	885	250,295

1	2	3	4	5	6
XLI	4'-Methyl naphtho (2,3:6,5')α-pyrono (7,8:5",4")furan	1710 nujol	-	880	226,248,304
XLVIII	3",4'-Dimethyl naphtho (2,1:6,5')α-pyrono (7,6:5",4")furan	1705 nujol	-	870	238,250
LV	2",4'-Dimethyl naphtho (1,2:6,5')α-pyrono (5,6:5",4")furan	1715 KBr	-	887	224,250,280
LIX	2',2"-Dimethyl naphtho (1,2:6,5')γ-pyrono (5,6:5",4")furan	- nujol	1630	850	

Condensation of 7-hydroxy-6-acetyl naphtho(2:1 :6',5') α-pyrone with ethyl bromoacetate : 7-Carbethoxymethoxy 6-acetyl naphtho (2,1:6',5')α-pyrone :

A solution of 7-hydroxy-6-acetyl naphtho(2,1:6',5') α-pyrone (1 g.) in dry acetone was refluxed with ethyl bromoacetate in the presence of anhydrous potassium carbonate (3 g.) on a steam bath for 5 hr. The solid obtained on removal of acetone was treated with water and washed with dil.alkali. It was crystallised from alcohol, m.p.207°. Yield 0.5 g.

Analysis : Found : C, 67.30 ; H, 5.05 %.

$C_{19}H_{16}O_6$ requires : C, 67.05 ; H, 4.70 %.

7-Carboxymethoxy-6-acetyl naphtho (2,1:6',5')α-pyrone :

The above ester (0.5 g.) in glacial acetic acid and conc.hydrochloric acid A.R.(15 ml.) was refluxed for 4 hr. and then poured into excess of ice cold water. The separated product was purified by sodium bicarbonate treatment. It crystallised from acetic acid and gave m.p.271. Yield 0.2 g.

Analysis : Found : C, 64.88 ; H, 3.45 %.

$C_{16}H_{10}O_6$ requires : C, 65.38 ; H, 3.84 %.

3''-Methyl naphtho (2,1:6',5')α-pyrono(7,6:5'',4'')furan :

The above acid (0.4 g.) was refluxed with fused sodium acetate (1.5 g.) and acetic anhydride (5 ml.) for 1 1/2 hr. on a wire gauze. A solid separated on pouring the reaction

mixture in water. It crystallised from acetic acid. M.P. 231°. Yield 0.2 g.

Analysis : Found : C, 76.45 ; H, 4.17 %.

$C_{16}H_{10}O_3$ requires : C, 76.81 ; H, 4.00 %.

Allylation of 7-hydroxy naphtho (2,1:6',5')α-pyrone : 7-Allyloxy naphtho (2,1:6',5')α-pyrone :

A mixture of 7-hydroxy naphtho (2,1:6',5')α-pyrone (2 g.), allyl bromide (2 ml.) and anhydrous potassium carbonate (8 g.) was refluxed in dry acetone (200 ml.) on a steam bath for 5 hr. After removing the acetone the residue was treated with water. The product was filtered and washed with dilute alkali to remove the unreacted compound. It crystallised from alcohol in needles (1.3 g.), m.p.165°.

Analysis : Found : C, 75.70 ; H, 4.34 %.

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

Claisen rearrangement of 7-allyloxy naphtho(2,1:6',5') α-pyrone : 7-Hydroxy-8-allyl naphtho (2,1:6',5')α-pyrone :

7-Allyloxy naphtho (2,1:6',5')α-pyrone (1 g.)was refluxed with dimethyl aniline (10 ml.) for 6 hr. The reaction mixture was poured into ice cold hydrochloric acid (1:1) in excess. The product after filtration and washing with water was taken up in alkali. The yellow solid obtained on acidification crystallised from alcohol in fine yellow needles (0.6 g.), m.p.212°.

Analysis : Found : C, 76.21 ; H, 4.53 %.

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

Cyclisation of 7-hydroxy-8-allyl naphtho (2,1:6',5') α-pyrone : 2"Methyl naphtho (2,1:6',5') α-pyrono(7,8:5",4") 2",3"-dihydrofuran :

7-Hydroxy-8-allyl naphtho (2,1:6',5') α-pyrone(0.5 g.) was triturated with conc.sulphuric acid (6 ml.) in a water bath for 15 minutes. The contents were poured into crushed ice and the separated product was filtered and washed with very dil.sodium hydroxide solution to remove uncyclised product. It crystallised from alcohol in fine needles (0.2 g.), m.p.192°.

Analysis : Found : C, 76.02 ; H, 4.68 %.

$C_{16}H_{12}O_3$ requires : C, 76.19 ; H, 4.65 %.

Dehydrogenation of 2"-methyl naphtho (2,1:6',5') α-pyrono (7,8: 5", 4") 2",3" dihydro furan : 2"Methyl naphtho(2,1:6',5') α-pyrono (7,8:5", 4") furan :

A mixture of the above dihydro furan derivative (0.25 g.), palladised charcoal (0.2 g. ; 10 %) and diphenyl ether (4 ml.) was refluxed for 6 hr. The reaction mixture was filtered hot. The product which separated was filtered and washed several times with petroleum ether (40-60°) and to the filtrate petroleum ether was added when more product separated. It crystallised from alcohol in yellowish needles (0.1 g.), m.p.212°.

Analysis : Found : C, 76.50 ; H, 3.73 %.

$C_{16}H_{10}O_3$ requires : C, 76.81 ; H, 4.00 %.

Condensation of 7-hydroxy-8-acetyl-4'methyl naphtho (2,3:6',5') α-pyrone with ethyl bromoacetate :

7-Carbethoxymethoxy-8-acetyl-4'methyl naphtho(2,3:6',5') α-pyrone :

A mixture of 7-hydroxy-8-aacetyl-4'methylnaphtho (2,1:6',5') α-pyrone (1 g.), ethyl bromoacetate (1 ml.) and anhydrous potassium carbonate (5 g.) was refluxed in dry acetone on a steam bath for 6 hr. The product obtained after distilling off the acetone, was treated with water. The product was filtered and washed with dilute sodium hydroxide to remove unreacted product. It crystallised from acetic acid, m.p.231°. Yield 0.8 g.

Analysis : Found : C, 67.75 ; H, 4.93 %.

$C_{20}H_{18}O_6$ requires : C, 67.79 ; H, 5.03 %.

7-Carboxymethoxy-8-acetyl-4'methyl naphtho(2,3:6',5') α-pyrone :

The above ester (0.5 g.) was mixed with sodium hydroxide solution (20 ml. ; 10 %) and left overnight. This was diluted, filtered and acidified. The solid separated was extracted with sodium bicarbonate solution and the bicarbonate extract on acidification afforded a product which crystallised from acetic acid in shining plates (0.2 g.), m.p.292°.

Analysis : Found : C, 66.09 ; H, 4.21 %.

$C_{18}H_{14}O_6$ requires : C, 66.27 ; H, 4.29 %.

3'',4'-Dimethylnaphtho (2,3:6',5') α-pyrono(7,8:5'',4'')furan :

The above acid (0.4 g.) was refluxed with fused

sodium acetate (1.5 g.) and acetic anhydride(5 ml.) for 2 hr. on wire gauze. The solid separating, on adding the reaction mixture to cold water, was washed with sodium bicarbonate solution. It was then crystallised from alcohol in tiny needles (0.2 g.), m.p.272°.

Analysis : Found : C, 77.43 ; H, 4.67 %.

$C_{17}H_{12}O_3$ requires : C, 77.27 ; H, 4.54 %.

Allylation of 7-hydroxy-4'methyl naphtho(2,3:6',5') α-pyrone :

A mixture of 7-hydroxy-4'methyl naphtho(2,3:6',5') α-pyrone (2 g.), allyl bromide (2 ml.) and anhydrous potassium carbonate (8 g.) was refluxed in dry acetone (150 ml.) for 5 hr. on a steam bath. The product obtained on removal of the solvent was treated with dilute sodium hydroxide and then with water. It crystallised from acetic acid in shining needles (1.3 g.), m.p. 190°.

Analysis : Found : C, 76.47 ; H, 5.06 %.

$C_{17}H_{14}O_3$ requires : C, 76.68 ; H, 5.26 %.

Claisen rearrangement of 7-allyloxy-4'methyl naphtho (2,3:6',5') α-pyrone : 7-Hydroxy-8-allyl-4'methyl naphtho (2,3:6',5') α-pyrone :

The above allyloxy derivative (2 g.) was refluxed with dimethyl aniline (15 ml.) for 6 hr. in an atmosphere of nitrogen. After cooling, the reaction mixture was poured in ice cold conc.hydrochloric acid (1:1) (200 ml.). This was left overnight. The yellow product obtained after

filtration was taken in sodium hydroxide solution. The product obtained on acidification crystallised from acetic acid in green needles (1.2 g.), m.p.252°.
(In the nitrogen atmosphere the yield is better)

Analysis : Found : C, 76.83 ; H, 5.24 %.
$C_{17}H_{14}O_3$ requires : C, 76.68 ; H, 5.26 %.

Acetylation: The above o-hydroxyallyl derivative (1 g.) was acetylated by heating with acetic anhydride (8 ml.) and freshly fused sodium acetate (2 g.) for 2 hr. The mixture was poured in ice cold water. The product obtained crystallied from alcohol in needles (0.8 g.), m.p.185°.

Analysis : Found : C, 74.49 ; H, 5.37 %.
$C_{19}H_{16}O_4$ requires : C, 74.01 ; H, 5.19 %.

Bromination: The above acetyl derivative (1 g.) was dissolved in acetic acid. Bromine (0.3 ml.) in acetic acid (10 ml.) was then added dropwise with stirring during 1 hr. The mixture was then further stirred for 1 hr. A solid separated, more of it separated on diluting the filtrate with water. It crystallised from acetic acid, m.p.235°. Yield 0.5 g.

Analysis : Found : Br, 34.33 %.
$C_{19}H_{16}O_4Br_2$ requires : Br, 34.19 %.

Cyclisation : 2"-4'-Dimethyl naphtho (2,3:6',5')α-pyrono (7,8:5",4")furan :

The above dibromo derivative (0.5 g.) in absolute

alcohol (50 ml.) was refluxed with potassium hydroxide (0.5 g.) for 2 hr. The reaction mixture turned yellow on heating. The reaction mixture was poured in ice cold water and acidified with hydrochloric acid. The product separated was extracted with ether. Removal of ether afforded a solid which was washed with dil.ammonia solution. The product after filtration was crystallised from alcohol in shining yellowish needles (0.2 g.), m.p.239°.

Analysis : Found : C, 77.07 ; H, 4.48 %.

$C_{17}H_{12}O_3$ requires : C, 77.27 ; H, 4.49 %.

Condensation of 7-hydroxy-8-formyl-4'methyl naphtho (2,3:6',5')α-pyrone with ethyl bromoacetate: 7-Carbethoxy methoxy-8-formyl-4'methyl naphtho(2,3:6',5')α-pyrone :

A mixture of 7-hydroxy-8-formyl-4'-methyl naphtho (2,3:6',5')α-pyrone (1 g.), ethyl bromoacetate (1 ml.) and anhydrous potassium carbonate (5 g.) was refluxed in dry acetone (100 ml.) for 5 hr. on a steam bath. The residue obtained after removal of acetone was treated with water. The product was filtered,washed with dilute sodium hydroxide solution and crystallised from acetic acid, m.p.297°.

Yield 0.6 g.

Analysis : Found : C, 67.54 ; H, 4.57 %.

$C_{19}H_{16}O_6$ requires : C, 67.05 ; H, 4.70 %.

Hydrolysis :

The above ester (0.5 g.) was refluxed with acetic acid and hydrochloric acid mixture for 4 hr. The product

obtained, was treated with sodium bicarbonate. A small amount dissolved. The product obtained on acidification of sodium bicarbonate extract, could not be crystallised, so this crude acid was used for further reaction. The hydrolysis was only partial. Alkaline hydrolysis gave an unworkable mass.

Cyclisation : 4'-methyl naphtho (2,3:6',5')α-pyrono (7,8:5", 4") furan :

The above acid (0.3 g.) was refluxed with acetic anhydride (5 ml.) and freshly fused sodium acetate (1 g.) for 2 hr. The reaction mixture was poured into ice cold water. The solid obtained was washed with sodium bicarbonate solution and with water. After drying, it was passed over a short column of silica gel. The product was eluted in chloroform. The white product obtained on evaporating the solvent was crystallised from acetic acid in light yellow needles (0.15 g.), m.p.274°.

Analysis : Found : C, 76.81 ; H, 3.91 %.

$C_{16}H_{10}O_3$ requires : C, 76.81 ; H, 4.00 %.

Synthesis of 2"-carbethoxy-4'-methyl naphtho(2,3:6',5') α-pyrono (7,8 : 5", 4") furan :

7-Hydroxy-8-formyl-4'-methyl naphtho (2,3:6',5')α-pyrone (prepared as described on p. 47) (1 g.) was dissolved in methyl ethyl ketone (200 ml.) by warming and refluxed with ethyl bromomalonate (1 ml.) and anhydrous potassium

carbonate (5 g.) on a steam bath for 10 hr. The solvent was then removed and the residue was treated with water and filtered. The solid obtained was run over a short column of alumina in chloroform. The product obtained on evaporation of the solvent crystallised from dimethyl formamide in needles (0.5 g.), m.p.280°.

Analysis : Found : C, 71.08 ; H, 4.36 %.

$C_{19}H_{14}O_5$ requires : C, 70.79 ; H, 4.34 %.

2"- Carboxy-4'-methyl naphtho (2.3:6',5')α-pyrono (7.8: 5", 4")furan :

The above ester (0.5 g.) was dissolved in glacial acetic acid (100 ml.) and conc.hydrochloric acid (A.R.) (25 ml.) was added to it. The whole mixture was refluxed for 4 hr. and then poured into ice cold excess of water. The separated product was purified by sodium bicarbonate treatment and crystallised from acetic acid, m.p.320°. Yield 0.3 g.

Analysis : Found : C, 68.90 ; H, 3.46 %.

$C_{17}H_{16}O_5$ requires : C, 69.39 ; H, 3.40 %.

Decarboxylation : 4'-methyl naphtho(2.3:6',5')α-pyrono (7.8:5",4") furan :

The above acid (0.4 g.) was refluxed with copper powder (0.2 g.) in quinoline (15 ml.) for an hour and the solution was filtered hot. The solid separating on cooling was washed with hydrochloric acid (1:1) and then with water.

The separated product crystallised from acetic acid in shining needles (0.2 g.), m.p.274°. Mixed m.p.with the furan obtained by ethyl bromoacetate method was not depressed.

Analysis : Found : C, 76.81 ; H, 4.00 %.

$C_{16}H_{10}O_3$ requires : C, 77.08 ; H, 3.89 %.

7-Acetoxy-4'methyl naphtho (2,1:6',5')α-pyrone :

7-Hydroxy-4'methyl naphtho (2,1:6',5')α-pyrone (2 g.) was refluxed with acetic anhydride (10 ml.) and freshly fused sodium acetate (3 g.) for 2 hr. The product obtained on pouring the reaction mixture in cold water was filtered and crystallised from xylene in fine needles (1.3 g.). M.P. 164°.

Analysis : Found : C, 71.52 ; H, 4.21 %.

$C_{16}H_{12}O_4$ requires : C, 71.64 ; H, 4.47 %.

Fries rearrangement of 7-acetoxy-4'methyl naphtho (2,1:6',5')α-pyrone : 7-Hydroxy-6-acetyl-4'methyl naphtho (2,1:6',5')α-pyrone :

An intimate mixture of 7-acetoxy-4'methyl naphtho (2,1:6',5')α-pyrone (2 g.) and anhydrous aluminium chloride (5 g.) was heated at 140° for 3 hr. in an oil bath. The reaction mixture was decomposed with ice cold hydrochloric acid (1:1). The solid separated was taken in sodium hydroxide. The yellow product obtained on acidification of the alkaline solution was filtered,dried and crystallised from acetic acid

in yellow needles (1.1 g.). It gave green colour with alcoholic ferric chloride. M.P.238°.

Analysis : Found : C, 71.80 ; H, 4.11 %.

$C_{16}H_{12}O_4$ requires : C, 71.64 ; H, 4.47 %.

The 2,4-dinitrophenyl hydrazone :

It was prepared from 7-hydroxy 6-acetyl-4'methyl naphtho (2,1:6',5')α-pyrone as usual and crystallised from dimethyl formamide in tiny orange needles. M.P.312-15°.

Analysis : Found : N, 12.47 %.

$C_{22}H_{16}O_7N_4$ requires : N, 12.50 %.

Condensation of 7-hydroxy-6-acetyl-4'methyl naphtho (2,1:6',5')α-pyrone with ethyl bromoacetate :

7-Carbethoxy methoxy-6-acetyl-4'methyl naphtho(2,1:6',5') α-pyrone :

A mixture of 7-hydroxy-6-acetyl-4'methyl naphtho (2,1:6',5')α-pyrone (1 g.), ethyl bromoacetate (1 ml.) and anhydrous potassium carbonate (5 g.) was refluxed in dry acetone on a steam bath for 6 hr. The product obtained after removal of acetone was taken in water, filtered and washed with dilute sodium hydroxide and then water. It crystallised from acetic acid, m.p.158°. Yield 0.5 g.

Analysis : Found : C, 67.33 ; H, 4.96 %.

$C_{20}H_{16}O_6$ requires : C, 67.79 ; H, 5.08 %.

Hydrolysis :

The above ester (0.5 g.) was dissolved in glacial acetic acid (75 ml.) and conc.hydrochloric acid (25 ml.) was added to it. The reaction mixture was refluxed for 4 hr. and then poured into excess of ice cold water. The separated product was purified by sodium bicarbonate treatment and crystallised from acetic acid, m.p.261°. Yield 0.3 g.

Analysis : Found : C, 66.56 ; H, 3.87 %.

$C_{18}H_{14}O_6$ requires : C, 66.27 ; H, 4.29 %.

3", 4'-Dimethyl naphtho (2,1:6',5')α-pyrono(7,6:5",4") furan :

The above acid (0.4 g.) was refluxed with fused sodium acetate (1.5 g.) and acetic anhydride (5 ml.) for 1 1/2 hr. The reaction mixture was poured in cold water. The solid separated was washed with sodium bicarbonate solution and then water. The cyclised product crystallised from acetic acid in light yellow needles (0.2 g.),m.p.241°.

Analysis : Found : C, 77.03 ; H, 4.27 %.

$C_{17}H_{12}O_3$ requires : C, 77.27 ; H, 4.54 %.

Allylation of 7-hydroxy-4'-methyl naphtho (2,1:6',5') α-pyrone :

A mixture of 7-hydroxy-4'-methyl naphtho(2,1:6',5') α-pyrone (2 g.),allyl bromide (25 ml.) and anhydrous potassium bicarbonate (8 g.) was refluxed in dry acetone for 5 hr. on a steam bath. The product obtained on removal of the solvent

was treated with dilute sodium hydroxide and then with water. It crystallised from dilute acetic acid, m.p.105°. Yield 1.3 g.

Analysis : Found : C, 76.58 ; H, 5.14 %.

$C_{17}H_{14}O_3$ requires : C, 76.68 ; H, 5.26 %.

Claisen rearrangement of 7-allyloxy-4'-methyl naphtho (2,1:6',5')α-pyrone : 7-Hydroxy-8-allyl-4'-methyl naphtho (2,1:6',5')α-pyrone :

The above allyloxy derivative (2 g.) was refluxed with dimethyl aniline (15 ml.) for 6 hr. The reaction mixture was poured into excess of ice cold hydrochloric acid and left overnight. The product after filtration was taken in sodium hydroxide solution. The yellow solid obtained on acidification was filtered, dried and passed over a short column of aluminia in benzene. It crystallised from benzene, m.p.195°. Yield 1.2 g.

Analysis : Found : C, 76.92 ; H, 5.14 %.

$C_{17}H_{14}O_3$ requires : C, 76.68 ; H, 5.26 %.

Cyclisation : 2'',4'-Dimethyl naphtho (2,1:6',5')α-pyrono (7,8:5'',4'')2'',3''-dihydro furan :

7-Hydroxy-8-allyl-4'-methyl naphtho (2,1:6',5') α-pyrone (0.5 g.) was triturated with conc.sulphuric acid (5 ml.) in a water bath for 10 minutes. The reaction mixture was poured over crushed ice and the separated product was filtered and washed with very dilute sodium hydroxide solution and then with water. It crystallised

from benzene in fine

from benzene in fine yellow needles (0.2 g.) after passing over a short column of alumina in chloroform, m.p.155°.

Analysis : Found : C, 76.49 ; H, 4.98 %.

$C_{17}H_{14}O_3$ requires : C, 76.68 ; H, 5.26 %.

Allylation of 5-hydroxy-4'-methyl naphtho(1,2:6,5') α-pyrone :

A mixture of the above hydroxy compound (2 g.), allyl bromide (2 ml.) and anhydrous potassium carbonate (8 g.) was refluxed in dry acetone (150 ml.) on a steam bath for 6 hr. The product obtained on removal of the solvent was washed with water and crystallised from alcohol in fine needles (1.3 g.), m.p.137°.

Analysis : Found : C, 76.42 ; H, 5.01 %.

$C_{17}H_{14}O_3$ requires : C, 76.68 ; H, 5.26 %.

Claisen rearrangement of 5-allyloxy-4'-methyl naphtho (1,2:6,5') α-pyrone : 5-Hydroxy-6-allyl-4'-methyl naphtho(1,2:6,5') α-pyrone :

The allyloxy derivative (2 g.) was heated in dimethyl aniline (15 ml.) for 6 hr. The reaction mixture after cooling was poured in cold hydrochloric acid (1:1). The mixture was left overnight. The solid which separated was filtered and taken in sodium hydroxide solution. On acidification yellow solid separated. It crystallised from alcohol in yellow plates (1.2 g.), m.p.223°.

Analysis : Found : C, 76.35 ; H, 5.05 %.

$C_{17}H_{14}O_3$ requires : C, 76.68 ; H, 5.26 %.

Acetylation :

The above allyl derivative (1 g.) was acetylated with acetic anhydride (5 ml.) and sodium acetate as usual. It crystallised from alcohol. M.P.175°. Yield 0.7 g.

Analysis : Found : C, 73.65 ; H, 5.07 %.

$C_{19}H_{16}O_4$ requires : C, 74.01 ; H, 5.19 %.

Bromination :

To the above acetyl derivative (1 g.) dissolved in acetic acid and bromine (0.3 ml.) in acetic acid (10 ml.) was slowly added with stirring. The addition of bromine solution was completed during 1 hr. The reaction mixture was further stirred for 1 hr. and then diluted with cold water. The yellowish solid which separated was filtered and crystallised from acetic acid, m.p.200°. Yield 0.6 g.

Analysis : Found : Br, 34.57 %.

$C_{19}H_{16}O_4Br_2$ requires : Br, 34.19 %.

2'' 4'-Dimethyl naphtho (1.2:6',5')α-pyrono(5.6:5'',4'') furan :

The above dibromo derivative (0.5 g.) in absolute alcohol (50 ml.) was refluxed with potassium hydroxide (0.5 g.) for 2 hr. The reaction mixture was acidified with dil.hydrochloric acid then extracted with ether. The solid obtained on removal of ether was washed with dil.ammonia (1:1). The insoluble product was washed with water and crystallised from alcohol, m.p.220°. Yield 0.2 g.

Analysis : Found : C, 77.71 ; H, 4.70 %.

$C_{17}H_{12}O_3$ requires : C, 77.27 ; H, 4.54 %.

Condensation of 5-hydroxy-6-acetyl-2'-methyl naphtho (1,2:6',5')γ-pyrone with ethyl bromoacetate: 5-Carbethoxy methoxy-6-acetyl-2'-methyl naphtho (1,2:6',5')γ-pyrone :

5-Hydroxy-6-acetyl-2'-methyl naphtho(1,2:6',5') γ-pyrone (1 g.) was refluxed with ethyl bromoacetate(1 ml.) and anhydrous potassium carbonate (5 g.) in dry acetone for 6 hr. on a steam bath. After removal of acetone the reaction mixture was treated with water. The solid obtained was filtered,washed with dilute sodium hydroxide solution and then with water. It crystallised from alcohol,m.p.148°. Yield 0.7 g.

Analysis : Found : C, 67.82 ; H, 5.53 %.

$C_{20}H_{18}O_6$ requires : C, 67.79 ; H, 5.08 %.

5-Carboxymethoxy-6-acetyl-2'-methyl naphtho(1,2:6',5') γ-pyrone :

The above ester (0.75 g.) was refluxed with the mixture of glacial acetic acid (75 ml.) and hydrochloric acid (20 ml.) for 4 hr. The reaction mixture was poured in excess of water and the separated solid was purified by extraction with sodium bicarbonate. The acid obtained was crystallised from acetic acid, m.p.284°. Yield 0.4 g.

Analysis : Found : C, 66.65 ; H, 3.97 %.

$C_{18}H_{14}O_6$ requires : C, 66.27 ; H, 4.29 %.

Cyclisation : 2',3''-dimethyl naphtho(1,2:6,5') γ-pyrono(5,6:5'',4'')furan :

The above acid (0.4 g.) was refluxed with acetic anhydride (5 ml.) and fused sodium acetate (1 g.) for 1 1/2 hr. The reaction mixture was poured in ice cold water. The separated solid was washed with sodium bicarbonate. It crystallised from alcohol in white crystalline plates (0.2 g.), m.p.251°.

Analysis : Found : C, 76.80 ; H, 4.76 %.

$C_{17}H_{12}O_3$ requires : C, 77.27 ; H, 4.54 %.

Allylation of 5-hydroxy-2'-methyl naphtho(1,2:6,5') γ-pyrone : 5-Allyloxy-2'-methyl naphtho (1,2:6,5') γ-pyrone :

A mixture of 5-hydroxy-2'-methyl naphtho(1,2:6,5') γ-pyrone (2 g.), allyl bromide (2 ml.) and anhydrous potassium carbonate (8 g.) in dry acetone was refluxed for 6 hr. The product obtained on removal of the solvent was treated with water and washed with dil.sodium hydroxide solution. It crystallised from alcohol in cream coloured needles(1.5 g.), m.p.136°.

Analysis : Found : C, 76.60 ; H, 5.29 %.

$C_{17}H_{14}O_3$ requires : C, 76.68 ; H, 5.26 %.

Claisen rearrangement of 5-allyloxy-2'-methyl naphtho (1,2:6',5')γ-pyrone : 5-Hydroxy-6-allyl-2'-methyl naphtho (1,2:6',5')γ-pyrone :

The above allyloxy derivative (2 g.) was refluxed in dimethyl aniline (20 ml.) for 6 hr. It was then poured into conc.hydrochloric acid (1:1). The solid separating on keeping overnight was filtered and taken in sodium hydroxide solution. The alkaline solution on acidification gave a yellow solid. This was purified by passing over a short column of alumina in ethyl acetate. The solid obtained on removing the solvent crystallised from acetic acid in tiny needles (0.8 g.), m.p.231°.

Analysis : Found : C, 76.32 ; H, 4.83 %.

$C_{17}H_{14}O_3$ requires : C, 76.68 ; H, 5.26 %.

Acetylation :

5-Hydroxy-6-allyl-2'-methyl naphtho(1',2:6',5') γ-pyrone (1 g.) was refluxed with acetic anhydride (6 ml.) and fused sodium acetate (2 g.) for 2 hr. The reaction mixture was poured into cold water. The separated product was crystallised from alcohol, m.p.197°. Yield 0.6 g.

Analysis : Found : C, 73.87 ; H, 5.28 %.

$C_{19}H_{16}O_4$ requires : C, 74.01 ; H, 5.19 %.

Bromination :

The above acetoxy derivative (1 g.) in acetic acid (40 ml.) was treated with bromine (0.3 ml.) in acetic acid dropwise with stirring over 2 hr. After diluting with

excess of cold water, the separated product was crystallised from benzene in fine needles (0.6 g.), m.p.217°.

Analysis : Found : Br, 34.67 %.

$C_{17}H_{16}O_4Br_2$ requires : Br, 34.19 %.

Attempted synthesis of 2',2''-dimethyl naphtho (1,2:6',5')γ-pyrono (5,6:5'',4'')furan :

The above dibromo derivative (0.5 g.) in absolute alcohol (50 ml.) was refluxed with potassium hydroxide (0.5 g.) for2 hr. It was then diluted with water and acidified with dilute hydrochloric acid then extracted with ether. On removal of ether, it did not give any pure product.

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