CHAPTER I

BROMINATION OF SOME ALKYL COUMARINS WITH N-BROMOSUCCINIMIDE

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THEORETICAL

A survey of the literature shows that while extensive studies have been made on hydroxycoumarins studies on alkyl coumarins have been fewer. The present chapter deals with the bromination of some di- and trimethylcoumarins with N-bromosuccinimide and the utilization of the bromomethylcoumarins for further synthetic work. The bromomethyl group is capable of reaction with various reagents, for example, the bromine can be replaced by hydroxy, methoxy, acetoxy, amino, cyano and other groups by reaction with appropriate reagents. On Sommelet reaction the bromomethyl group can be replaced by the reactive formyl group which itself is capable of serving as a starting material for the synthesis of a number of oxygen heterocycles. Some of the previous work on the synthesis of the bromomethylcoumarins and their further utilization is described here.

Dey and Radhabai[1] reported the formation of two products in bromination of 7-methylcoumarin-4-acetic acid with 50 % bromine in acetic acid, viz. 7-methylcoumarin-4-bromoacetic acid and 7-methyl-4-bromomethylcoumarin. Similarly, 6-methylcoumarin-4-acetic acid also gave 6-methylcoumarin-4-bromo acetic acid and 6-methyl-4-bromomethylcoumarin. Several attempts were made by them to confirm the 4-bromomethylcoumarin

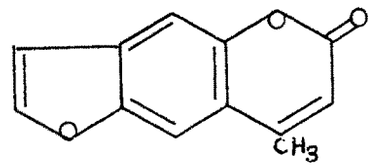
structure. Their attempts to replace the halogen by OH, NH_2 and C_6H_5NH- groups by treatment with appropriate reagents were unsuccessful. Even by heating the bromomethylcoumarin with moist silver oxide at 100° for 5 hr. the halogen was not removed. Aqueous alkali, however, eliminated the halogen completely in the course of a few minutes. This difference was explained by the fact that the alkali does not initially attack the bromine but that it is the pyrone ring which is first opened up. The subsequent rearrangement to the stable benzo dihydrofuran ring involves the interaction of the bromine and the phenolic hydrogen. The preparation of the compounds of the Grignard type with magnesium in dry ether was also attempted by the same workers without success.

7-Methyl-4-bromomethylcoumarin was reduced to 4,7-dimethylcoumarin with zinc-copper couple in acetone. Oxidation of 7-methyl-4-bromomethylcoumarin with potassium permanganate in acetone solution gave m-cresotinic acid 6-methyl-4-bromomethylcoumarin on oxidation yielded p-cresotinic acid. Dey and Sankaranarayanan[2] established the structure of 7-methyl-4-bromomethylcoumarin by its synthesis from m-cresol and γ-bromo acetoacetic ester by Pechmann condensation.

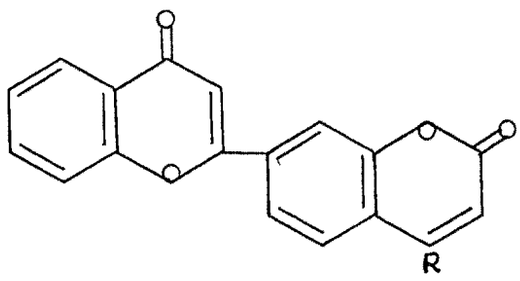
The action of N-bromosuccinimide on methylated coumarins[5] has been extensively studied by Lecocq and Buu-Hoi[3]. They observed that the N-bromosuccinimide reacts only with the methyl group in the benzene ring but not with the methyl group in the heterocyclic ring. Thus they prepared 4-methyl-7-

bromomethyl, 4-methyl-6-bromomethyl-, 6-bromomethyl- and 7-bromomethylcoumarins.

Starting with the above 4-methyl-6-bromomethyl, 4-methyl-7-bromomethyl, 6-bromomethyl and 7-bromomethyl-coumarins Jainamma and Sethna[4] in this laboratory prepared 6- and 7-formyl derivatives which were used as intermediates to synthesise compounds such as 4-methyl-furo-(5',4' : 6,7)coumarin (I) 6-(2'-chromonyl)coumarin (II), 4-methyl-6-(2'-chromonyl)coumarin (IIa), 7-(2'-chromonyl)-coumarin (III) and 4-methyl-7-(2'-chromonyl)coumarin (IIIa).

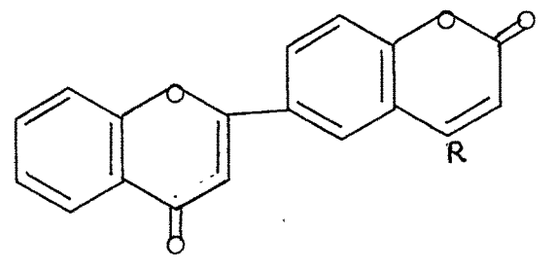


I



III R = H

IIIa R = CH_3

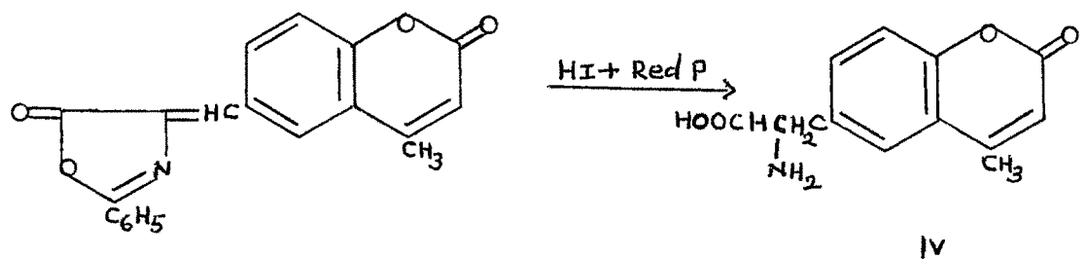


II R=H

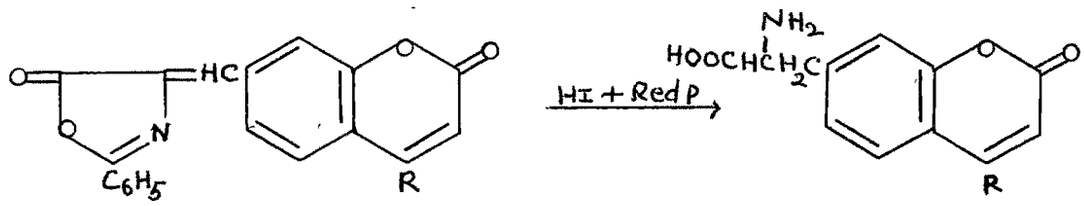
IIa R=CH_3

They also condensed the corresponding formyl-coumarins with hippuric acid to obtain the oxazolone derivatives which have been converted into β-coumarinyl alanines such as (IV, V and Va) by heating with hydriodic acid and red phosphorus.

From the corresponding bromomethyl derivatives they also synthesised different Mannich bases.



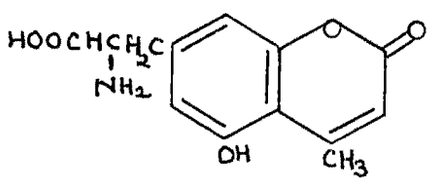
IV



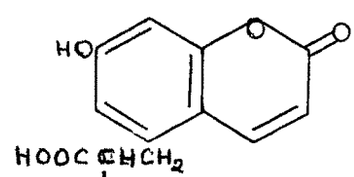
V R=H

Va R=CH_3

Trivedi and Shah[5] brominated 5-hydroxy-4,7-dimethylcoumarin and 7-hydroxy-5-methylcoumarin and obtained the corresponding 7-bromomethyl and 5-bromomethyl derivatives from which they synthesised nitrogen mustards. They also synthesised β-(5-hydroxy-4-methyl-7-coumarinyl)alanine (VI) and β-(7-hydroxy-5-coumarinyl)alanine (VII) by condensing the corresponding bromomethyl derivatives with diethyl sodioacetamidomalonate, obtained diethyl-(5-methoxy-4-methyl-7-coumarinyl-methyl)acetamidomalonate and diethyl-(7-methoxy-5-coumarinyl-methyl)acetamidomalonate which on hydrolysis with hydrobromic acid and then careful neutralisation gave the desired alanines.



VI



VII

In the course of the present work the bromination of 5,7-dimethyl-, 4,6,7-trimethyl- and 4,5,7-trimethylcoumarin with N-bromosuccinimide has been studied. As these coumarins have two methyl groups in the benzenoid part of the molecule it was thought of interest to see as to which of the methyl groups undergoes bromination when treated with one mole of N-bromosuccinimide. Further, the bromomethyl

derivatives have been utilised for further synthetical work.

Bromination of 5,7-dimethylcoumarin with N-bromosuccinimide

5,7-Dimethylcoumarin was prepared by the Pechmann condensation of 3,5-xylenol with malic acid in the presence of sulphuric acid[6]. 5,7-Dimethylcoumarin, on bromination with one mole of N-bromosuccinimide in dry benzene gave a monobromomethyl derivative in the presence of benzoyl peroxide. In order to find out as to which of the methyl groups had undergone substitution, the monobromomethyl derivative was treated with hexamine and acetic acid to get the monoformyl derivative which was characterised by the formation of a 2,4-dinitrophenyl hydrazone. This formyl derivative was oxidised by ammonical silver nitrate solution to the corresponding carboxylic acid. Attempts were made to decarboxylate this acid to get the known 5-methyl- or 7-methylcoumarin. The various methods tried, such as, decarboxylation by heating with copper and quinoline, pyridine hydrochloride or by heating the acid above its m.p. met with failure.

Another strategy was therefore tried to determine the structure of the bromomethyl derivative. The formyl derivative was subjected to Elbs persulphate oxidation. It has been shown that the Elbs persulphate oxidation of coumarins leads in all cases where the 6-position is free

to 6-hydroxycoumarins. The product obtained on Elbs persulphate oxidation was found to be different on direct comparison with the 5-formyl-6-hydroxy-7-methylcoumarin obtained by the formylation of the known 6-hydroxy-7-methylcoumarin which in turn was obtained from 7-methylcoumarin through Elbs persulphate oxidation. The same coumarin was also prepared by the condensation of 2-methylhydroquinone and malic acid in the presence of conc. sulphuric acid[7]. The mixed m.p. of the two products was depressed by over 35°. The formyl derivative has therefore been assigned the 5-methyl-6-hydroxy-7-formylcoumarin (IX_a) structure and the bromomethylcoumarin has been assigned the 5-methyl-7-bromomethylcoumarin (VIII) structure. The structure is further supported by the NMR (Fig. 1) of the 5-methyl-7-formylcoumarin (IX) taken in trifluoroacetic acid. It shows that the protons at 6- and 8-positions appear at the same place i.e. at δ 7.9, which shows that the protons are in identical environment and this is only possible when the CHO group is at 7-position and not at 5-position. The three methyl protons appear at δ 2.75 as a three proton singlet. Coumarin protons, 3-H and 4-H appear at δ 6.85 and δ 8.35 respectively as doublets of J value 9Hz. The spectrum is not screened below δ 9.0 and so the value for the formyl proton which generally appears at δ 10.0 cannot be given. However, in the NMR (Fig. 2) of the corresponding acid (X) taken in trifluoroacetic acid the carboxylic acid proton appears at δ 10.2 as a singlet. Rest of the spectrum shows a similar

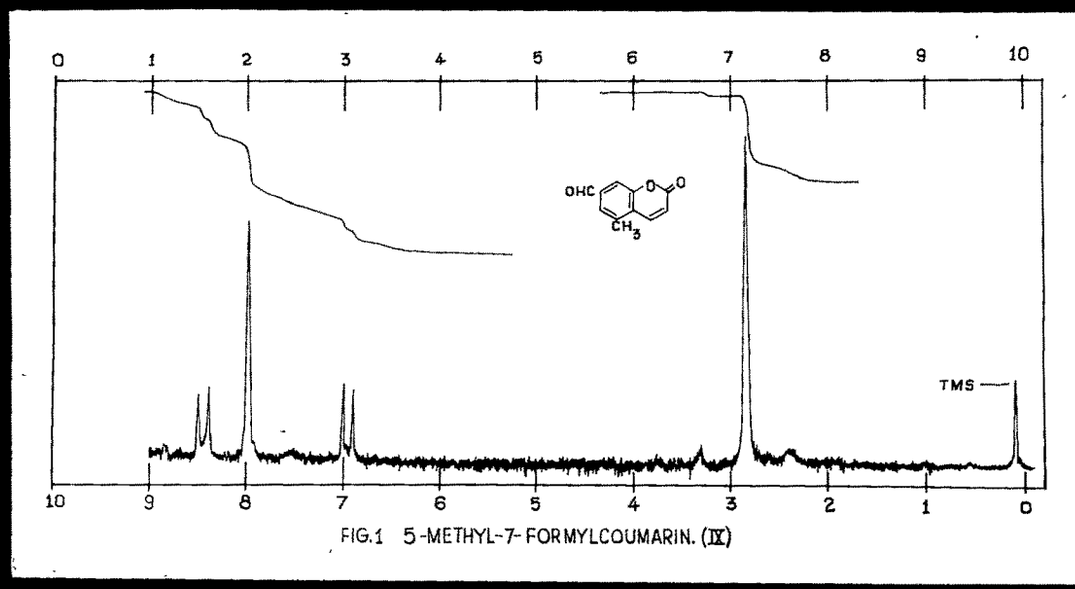
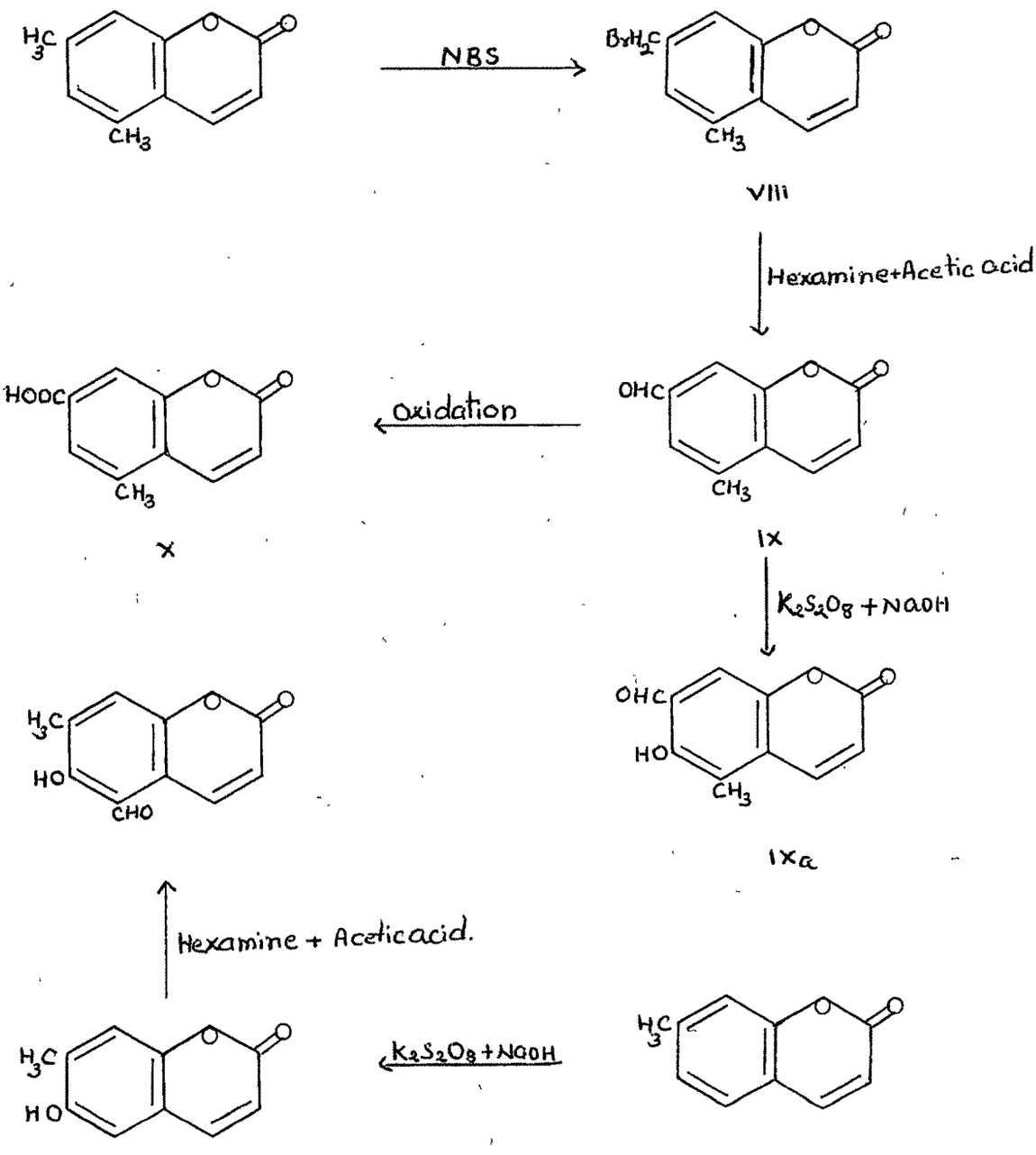


FIG.1 5-METHYL-7-FORMYLCOUMARIN. (IX)


NBS
VIII
Hexamine+Acetic acid
Oxidation
IX
X
$K_2S_2O_8$ + NaOH
IXa
Hexamine + Aceticacid.
$K_2S_2O_8$ + NaOH

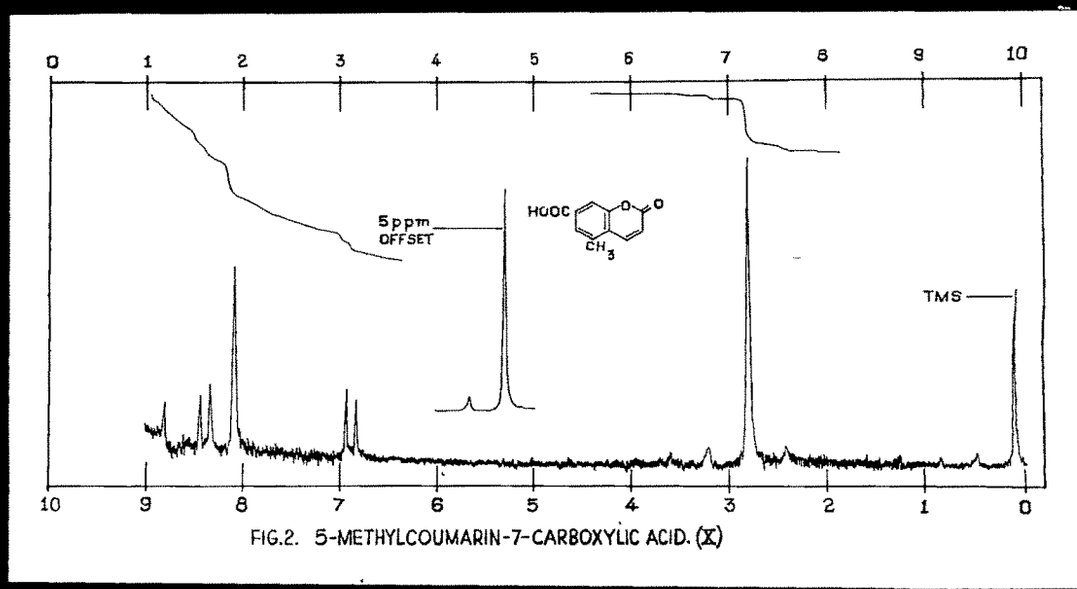


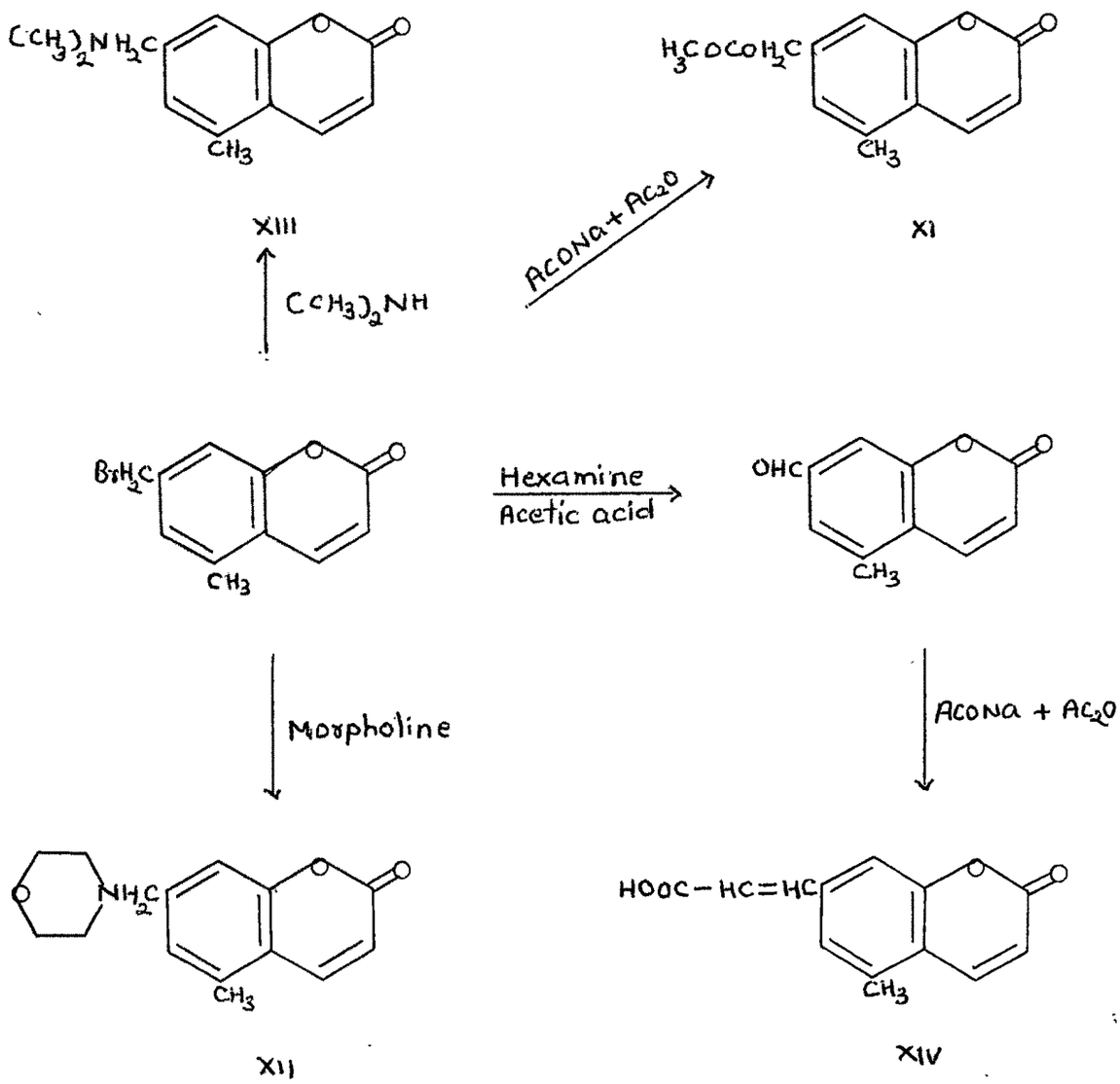
FIG.2. 5-METHYLCOUMARIN-7-CARBOXYLIC ACID. (X)

pattern of signals as that of 7-formyl-5-methylcoumarin. The three protons of 5-methyl group appear at δ 2.7. Coumarin protons 3-H and 4-H appear at δ 6.8 and δ 8.3 as doublets with coupling constant of 9Hz. Protons 6-H and 8-H appear as two proton singlet at δ 8.0. The appearance of these two protons as a singlet can be attributed to their identical environment.

5-Methyl-7-bromomethylcoumarin on heating with acetic anhydride in the presence of fused sodium acetate, gave 5-methyl-7-acetoxymethylcoumarin (XI). On condensation with secondary amines such as morpholine and dimethylamine in dry benzene it gave 5-methyl-7-morpholinomethyl- and 5-methyl-7-dimethylaminomethylcoumarins (XII and XIII) respectively.

On treating with alcoholic potassium cyanide the bromomethylcoumarin did not give a pure cyanomethyl derivative so the crude product was directly hydrolysed to obtain the corresponding acid. This acid was obtained in very poor yield so further work on this was not possible

The 5-methyl-7-formylcoumarin described earlier when treated with acetic anhydride and fused sodium acetate in an oil bath at 170-80° for 12 hr. gave β-(5-methyl-7-coumarinyl)acrylic acid (XIV). This acid decolourised neutral potassium permanganate solution and bromine water showing the presence of unsaturation.

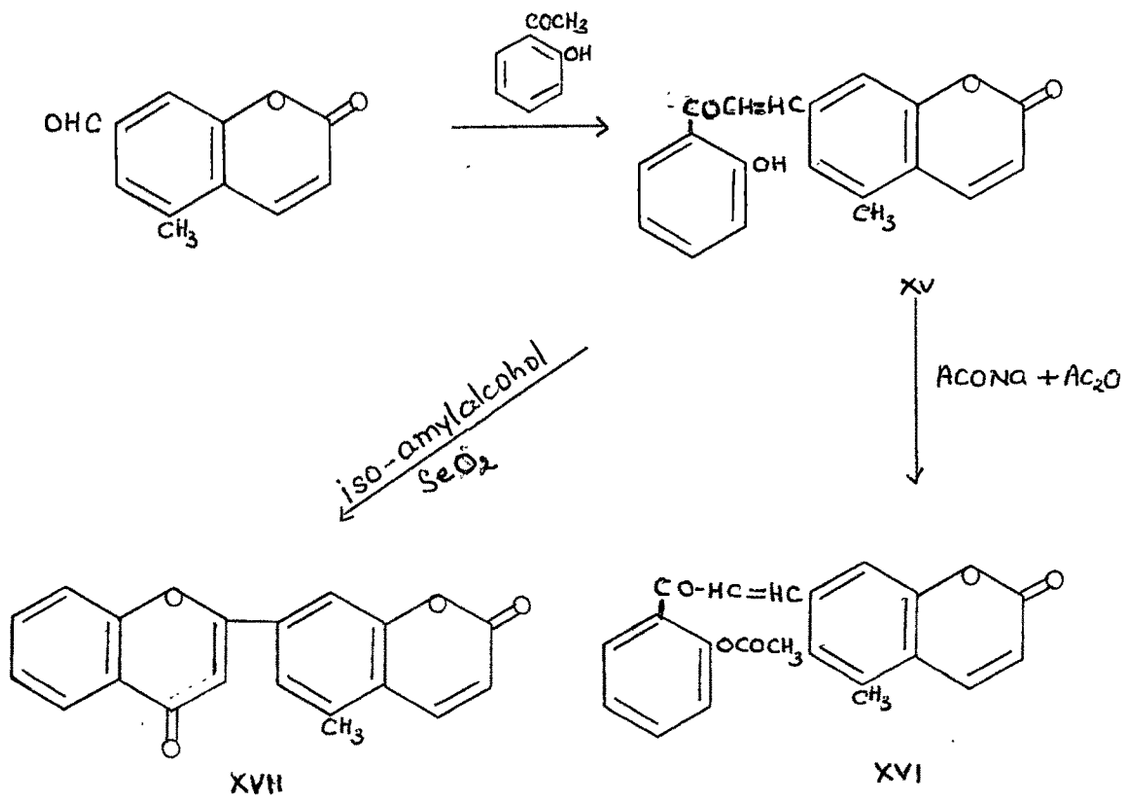


Synthesis of 5-methyl-7-(2́-chromonyl)coumarin

With a view to further exploit the synthetic possibilities of the reactive intermediate, 5-methyl-7-

formylcoumarin, it was condensed with o-hydroxyacetophenone in the presence of alcoholic potassium hydroxide and β-(5-methyl-7-coumarinyl)vinyl-o-hydroxyphenyl ketone (XV) was obtained. It gave red colouration with conc. sulphuric acid and a positive Wilson test. Moreover, it gave an acetoxy derivative, (XVI) when heated with acetic anhydride and fused sodium acetate, showing the presence of a free hydroxyl group.

The above ketone when refluxed with selenium dioxide in iso-amyl alcohol at 140-50° for 8 hr. underwent cyclisation to 5-methyl-7-(2'-chromonyl)coumarin (XVII).



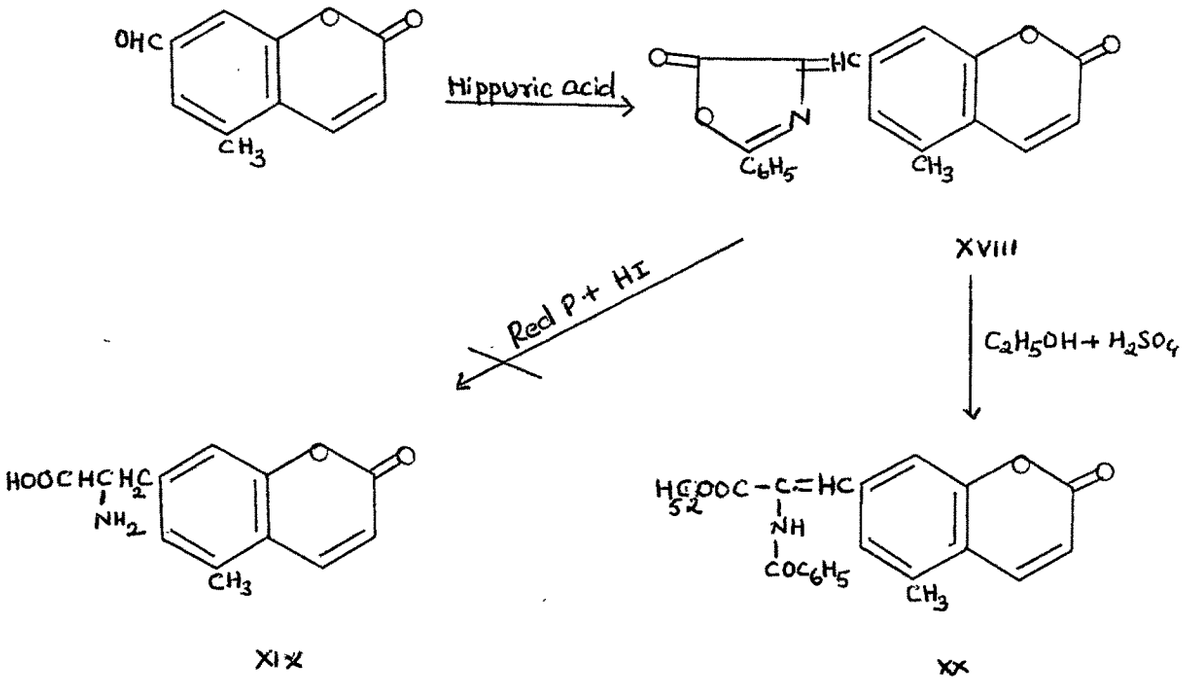
Attempted synthesis of β-(5-methyl-7-coumarinyl)alanine

The amino acids are substances of interest as many of them are found to occur in nature either in the free state or as building units of proteins. Only a few α-amino acids with oxygen heterocyclic units are known. It was therefore thought of interest to synthesise such acids.

With this view 5-methyl-7-formylcoumarin was condensed with hippuric acid in the presence of fused sodium acetate and acetic anhydride when the azlactone (XVIII) was obtained. This azlactone on heating with red phosphorus and hydriodic acid in acetic anhydride was expected to give β-(5-methyl-7-coumarinyl)alanine (XIX).

The isolation of the amino acid (XIX) met with failure as it did not crystallise out in a pure form from any of the solvents. The water extract, however, gave effervescence with sodium bicarbonate and a positive Ninhydrin test. The solid obtained by the evaporation of water extract did not melt but decomposed at 250°. It left no residue when heated on a spatula.

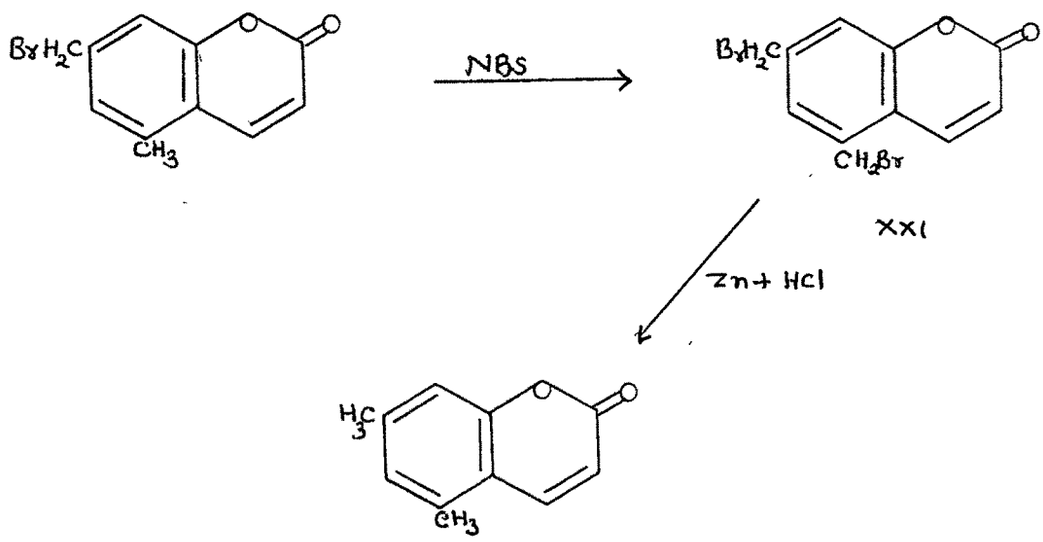
The above azlactone on hydrolysis with 10 % alcoholic sulphuric acid gave the ester (XX).



5,7-Di(bromomethyl)coumarin

Attempts were made to brominate 5,7-dimethyl-coumarin with two moles of N-bromosuccinimide in dry benzene in the presence of benzoyl peroxide when a mixture of monobromomethyl, dibromomethyl derivatives and the original coumarin was obtained. However, the monobromomethyl derivative on further bromination with one mole of N-bromosuccinimide gave a product to which the 5,7-dibromomethylcoumarin structure (XXI) is assigned as on heating with alcoholic potassium hydroxide it did not give any coumarilic acid derivative which indicated the absence of a bromine in 3-position. On reduction with

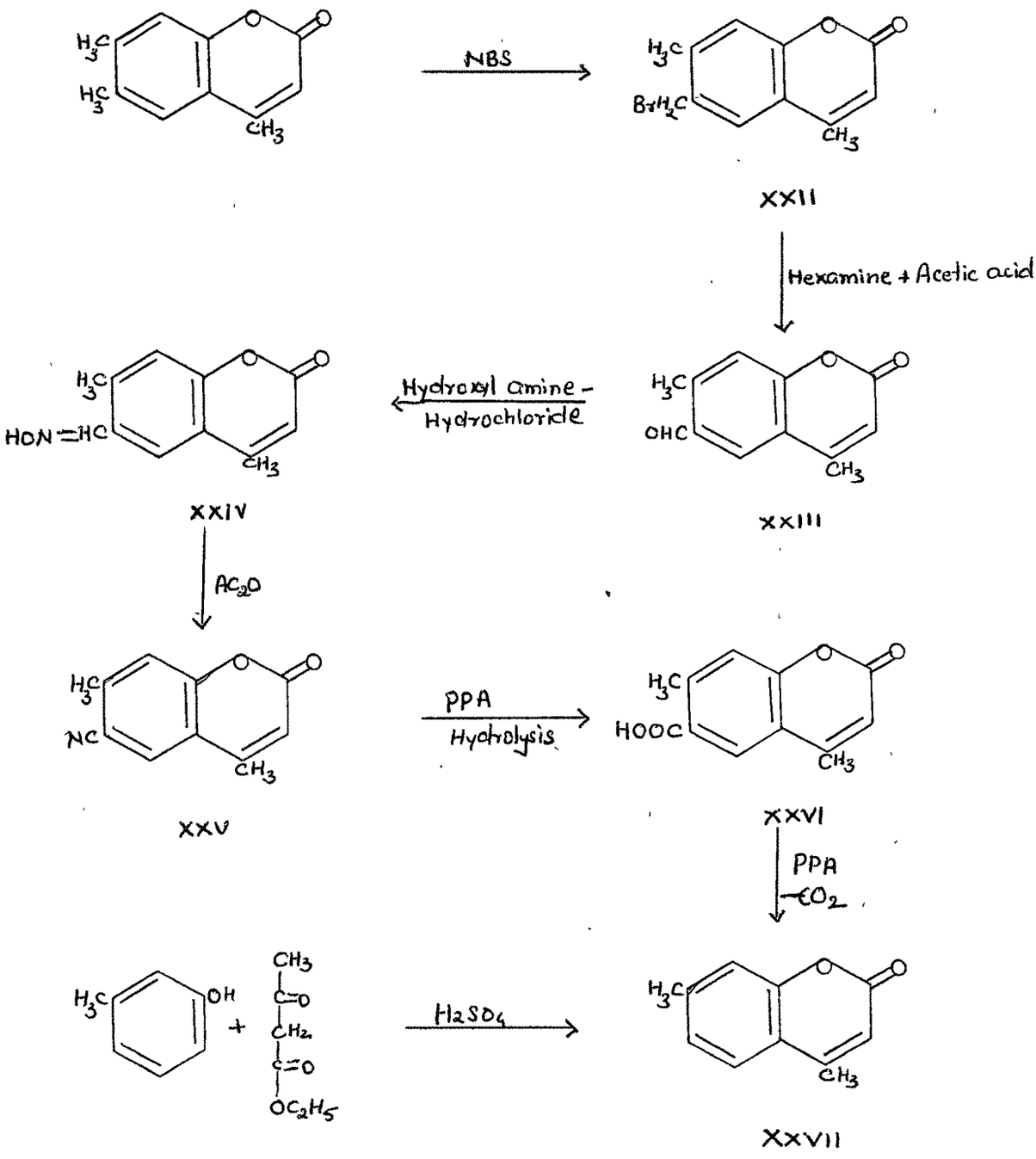
zinc and hydrochloric acid it gave the original coumarin back. With excess of N-bromosuccinimide it gave a dark brown sticky product which could not be obtained in a pure solid form by crystallisation or by chromatography. Further work on (XXI) was not possible on account of the low yield of the pure product.



Bromination of 4,6,7-trimethylcoumarin with N-bromosuccinimide

4,6,7-Trimethylcoumarin was prepared by the Pechmann condensation of 3,4-xylenol and ethyl acetoacetate in the presence of conc. sulphuric[6].

4,6,7-Trimethylcoumarin on bromination with one mole of N-bromosuccinimide in the presence of benzoyl peroxide gave a monobromomethyl derivative in a very good yield. In order to find out as to which of the methyl groups had undergone bromination, the monobromomethyl derivative was subjected to Sommelet reaction with hexamine and acetic acid. The monoformyl derivative obtained was characterised by the formation of a 2,4-dinitrophenyl hydrazone. Attempts were then made to oxidise this formyl derivative to the corresponding carboxylic acid but it was found to be surprisingly stable towards the oxidising agents used. It has been reported[19] in the case of xylenols that the oxidation of formyl derivative is extremely difficult when the formyl group is adjacent to a methyl group. The various oxidising agents used were ammoniacal silver nitrate, hydrogen peroxide, acidic, alkaline and neutral potassium permanganate and chromic acid. An alternative method to get the carboxylic acid was tried. The above formyl derivative was condensed with hydroxylamine hydrochloride. The oxime so obtained was converted into the nitrile by refluxing it with acetic anhydride. The nitrile obtained when heated with polyphosphoric acid at 200° for 5 hr. gave a mixture of the original nitrile, carboxylic acid and a little decarboxylated product. The


NBS
XXII
Hexamine + Acetic acid
Hydroxyl amine - Hydrochloride
XXIV
XXIII
Ac_2O
PPA
Hydrolysis
XXV
XXVI
PPA
$-CO_2$
H_2SO_4
XXVII

carboxylic acid was separated from the mixture by taking it into sodium bicarbonate solution. The decarboxylation of this acid was achieved by heating it with polyphosphoric acid at 220° for 8 hr. The product obtained was found to be identical with 4,7-dimethylcoumarin (XXVII). The mixed m.p. of this product with an authentic sample of 4,7-dimethylcoumarin was not depressed. However, the mixed m.p. with the authentic 4,6-dimethylcoumarin was depressed by over 15°. These sequence of reactions (XXIII to XXVI) proves that the bromination took place at the 6-methyl group which was ultimately removed through the above reactions to give the known 4,7-dimethylcoumarin. The 6-bromomethyl-4,7-dimethylcoumarin structure (XXII) is therefore assigned to the monobromomethylcoumarin.

The NMR (Fig. 3) of 6-formyl-4,7-dimethylcoumarin (XXIII) taken in trifluoroacetic acid shows three singlets in the aromatic region. The singlet at δ 6.2 can be assigned to 3-H, the singlet at δ 7.0 to 8-H and the downfield singlet at δ 8.0 to 5-H. The formyl proton appears at δ 10.0, while the 4-methyl protons appear as three proton singlet at δ 2.25 and 7-methyl protons appear as three proton singlet at δ 2.45.

The 6-bromomethyl-4,7-dimethylcoumarin was subjected to some further reactions. Thus 6-bromomethyl-4,7-dimethylcoumarin on reaction with fused sodium acetate and acetic anhydride gave 6-acetoxymethyl-4,7-dimethylcoumarin (XXVIII).

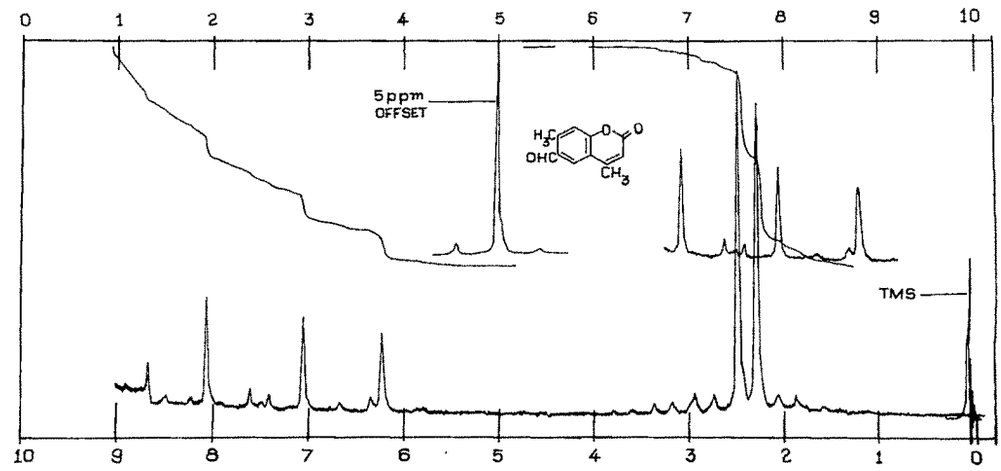
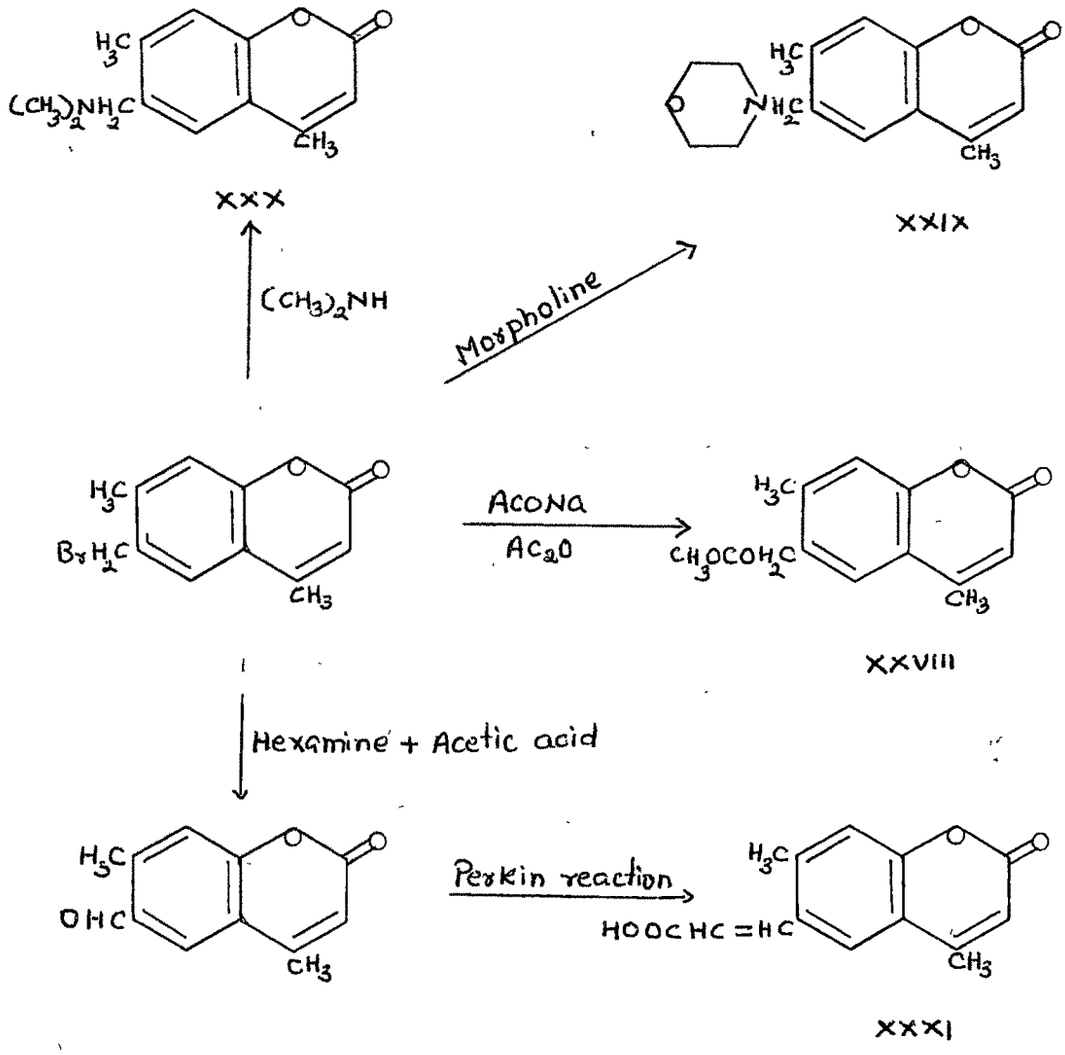


FIG.3. 6-FORMYL- 4,7-DIMETHYL COUMARIN. (XXIII)

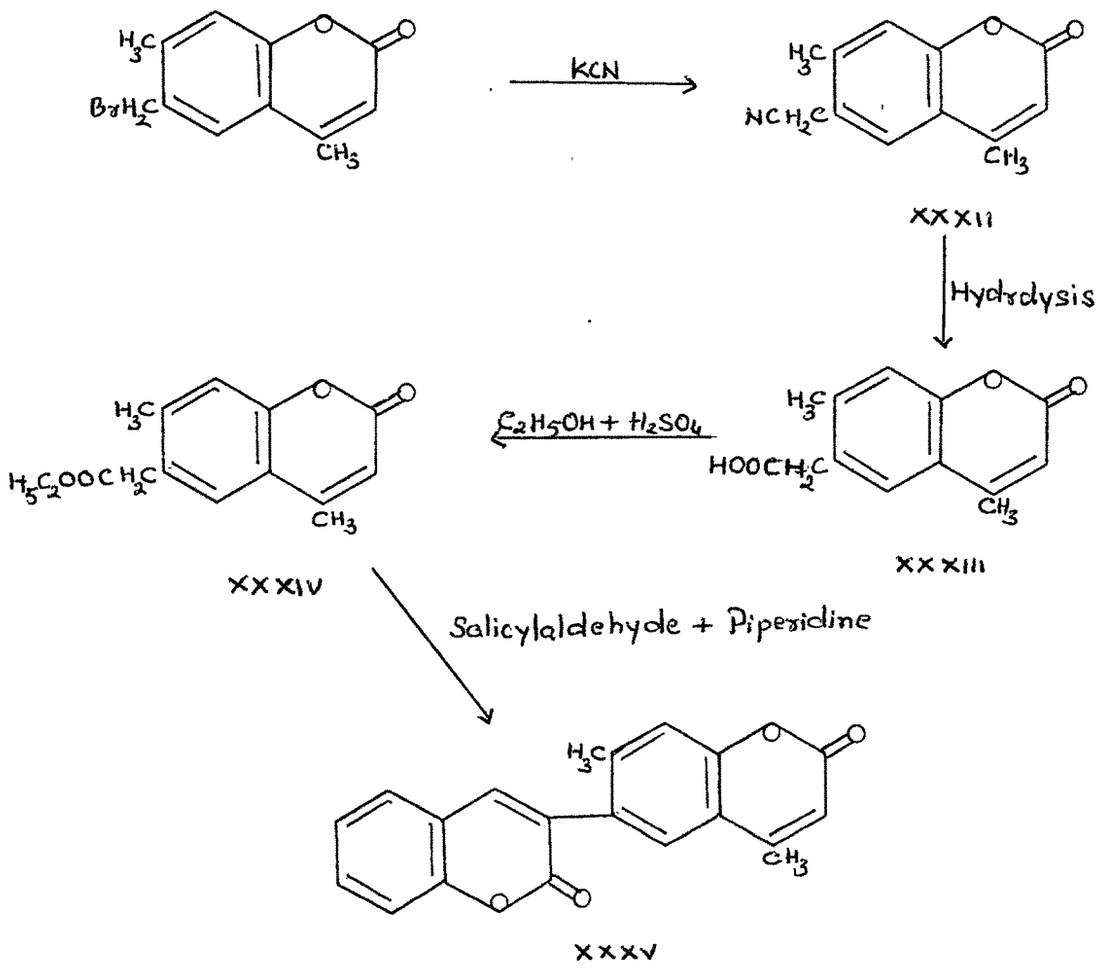


On condensation with secondary amines such as morpholine and dimethylamine 6-bromomethyl-4,7-dimethyl-coumarin gave the corresponding 6-morpholinomethyl-(XXIX)

and 6-dimethylaminomethyl- (XXX) derivatives. On Perkin reaction, 6-formyl-4,7-dimethylcoumarin described before gave β-(4,7-dimethylcoumarinyl)acrylic acid (XXXI).

Synthesis of 6-(3'-bicoumarinyl)-4,7-dimethylcoumarin

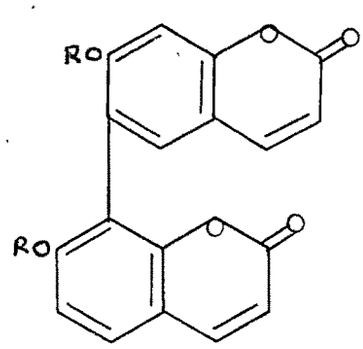
6-Bromomethyl-4,7-dimethylcoumarin in alcohol on refluxing with potassium cyanide gave a product to which the 6-cyanomethyl-4,7-dimethylcoumarin structure (XXXII) was assigned. On hydrolysis with hydrochloric acid and



XXXII XXXIII XXXIV XXXV

acetic acid it gave the 6-carboxymethyl-4,7-dimethylcoumarin (XXXIII). This acid was esterified with ethyl alcohol in the presence of sulphuric acid and the ester (XXXIV) obtained was condensed with salicylaldehyde in absolute alcohol with a few drops of piperidine, when a product was obtained which was not soluble in alkali and so was assigned 6-(3'-bicoumarinyl)-4,7-dimethylcoumarin structure (XXXV). This is an unsymmetrical bicoumarinyl in which one of the carbon atoms of the heterocyclic ring of one coumarin unit is linked to a carbon atom of the benzenoid ring of the second unit.

Some unsymmetrical bicoumarinyls have been found to occur in plants. Mihashi and co-workers[8,9] have isolated an unsymmetrical bicoumarinyl derivative and named it Matsukaze lactone. It has been assigned the 6,8'-bicoumarinyl structure (XXXVI).

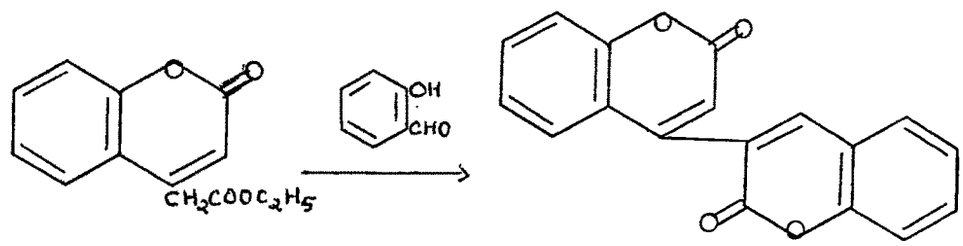


XXXVI

a - R = CH_3

b - R = H

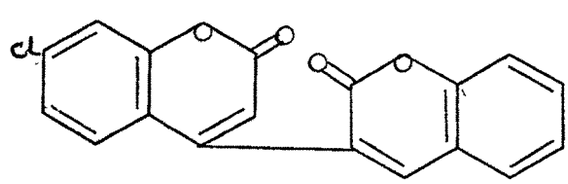
A few synthesis of unsymmetrical bicoumarinyls have been reported. For example, Dey and Row[10] condensed coumarin-4-acetic ester with salicylaldehyde under the conditions of Perkin reaction or Knoevenagel reaction and obtained the 4,3'-bicoumarinyl (XXXVII).



XXXVII

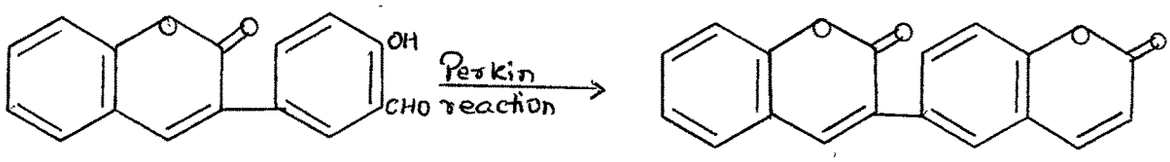
In a similar way they prepared 7-methyl-, 7-methyl-6'-bromo-, 7-methyl-6'-chloro-, 7-hydroxy-, 7-hydroxy--6'-bromo-, 6',8'-dichloro- and 7-acetoxy-6'-bromo-4,3'-bicoumarinyls.

7-Chloro-4,3'-bicoumarinyl (XXXVIII) has been prepared by Thakar[11] by the condensation of 7-chloro-coumarin-4-acetic acid with salicylaldehyde in the presence of piperidine.



XXXVIII

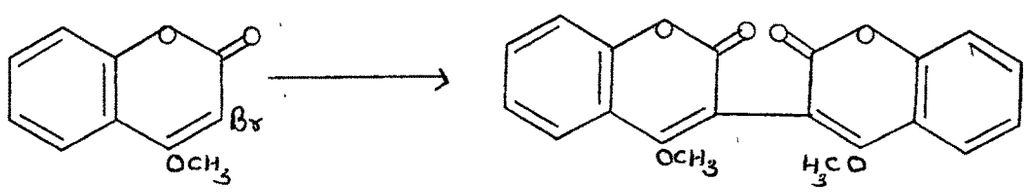
Jainamma and Sethna[12] synthesised 3,6'-bicoumarinyl (XXXIX) through the Perkin reaction on 3-(4'-hydroxy-3'-formylphenyl) coumarin.



XXXIX

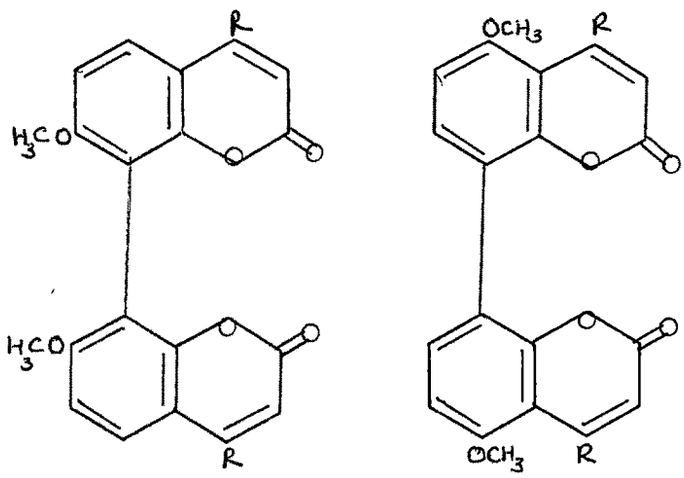
A number of symmetrical bicoumarinyls are also known. Dyson[13] synthesised 3,3'-bicoumarinyl by heating salicylaldehyde with sodium succinate and acetic anhydride in a sealed tube at 140° for 40 hr.

Huebner and Link[14] reported the formation of the 3,3'-bicoumarinyl derivative (XL) from 3-bromo-4-methoxy-coumarin.



XL

Lele et al.[15] have synthesised 8,8'-bicoumarinyl derivatives (XLIa, XLIb; XLIIa, XLIIb) and 3,3'-bicoumarinyl derivatives (XLIIIa, XLIIIb) by the Ullmann reaction on iodocoumarins.

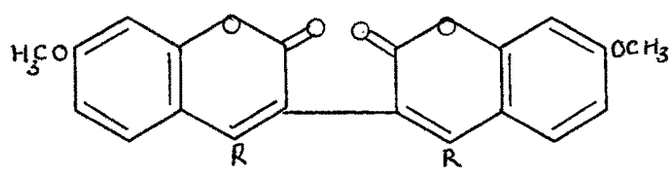


XLI

XLII

(a) R = H

(b) R = CH_3



XLIII

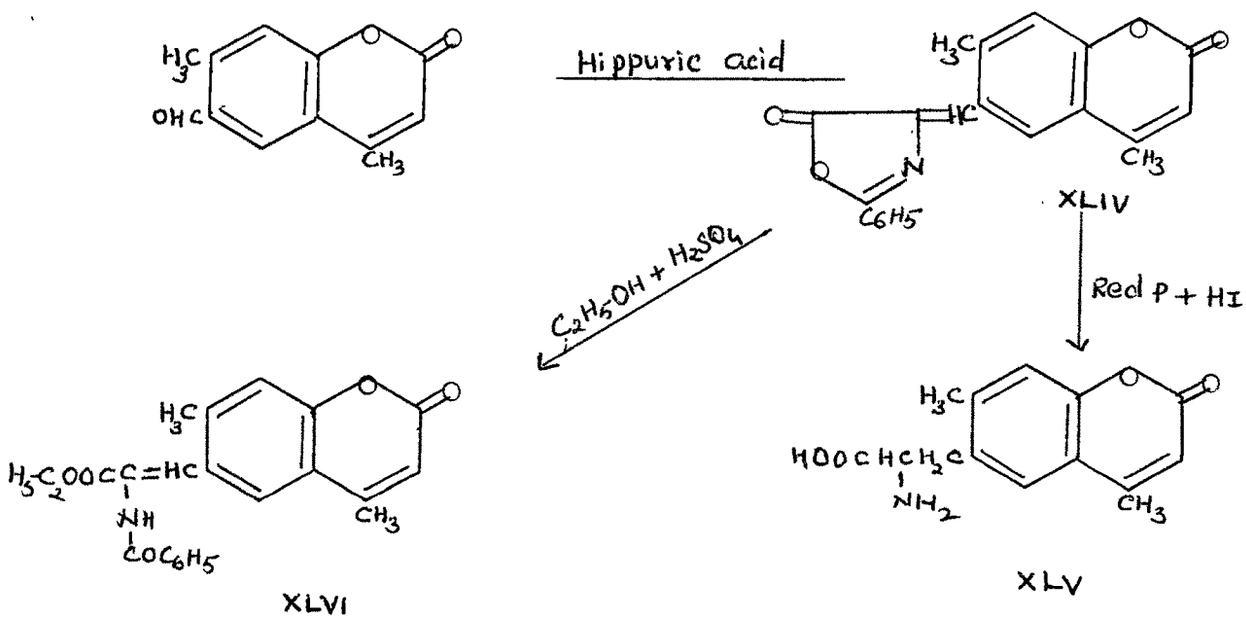
(a) R = H

(b) R = CH_3

Sen and Dutt[16] obtained 6,6'-bicoumarinyl by the action of acetic anhydride and sodium acetate on 4,4'-dihydroxydiphenyl-3,3'-dialdehyde. Harle and Lyons[17] obtained tetrahydro-4,4'-bicoumarinyl as one of the products in the reduction of coumarin using zinc and acetic acid.

Synthesis of β-(4,7-dimethyl-6-coumarinyl)alanine

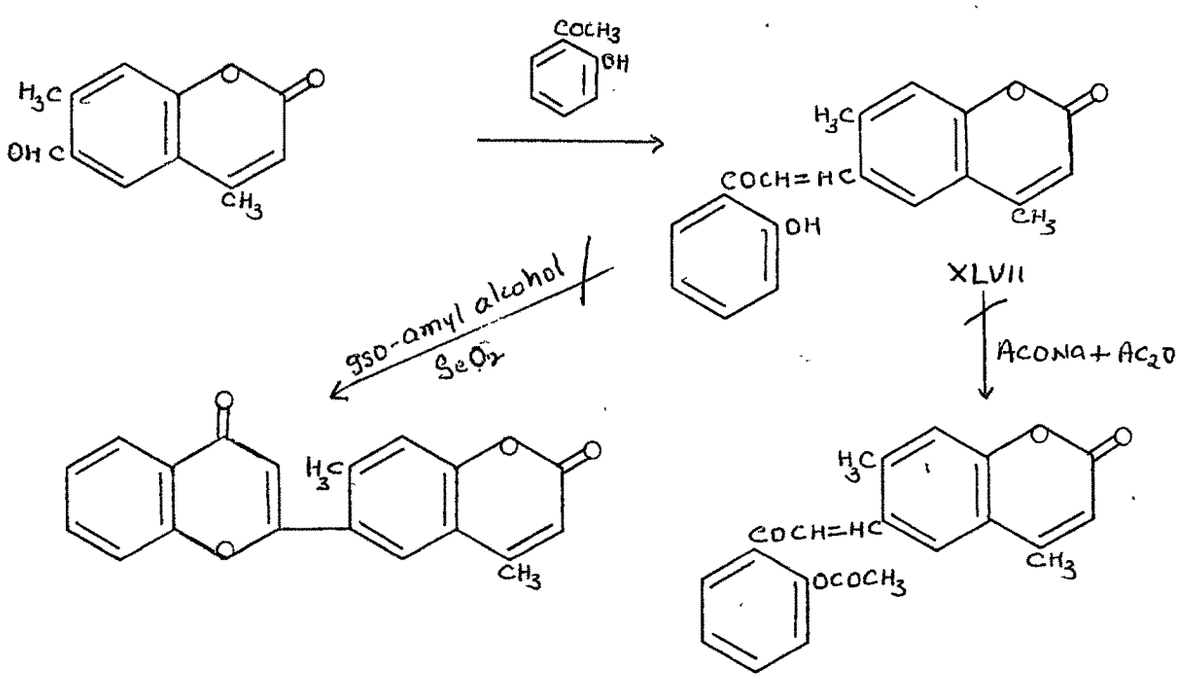
6-Formyl-4,7-dimethylcoumarin was condensed with hippuric acid in the presence of sodium acetate and acetic anhydride to get the azlactone (XLIV). The azlactone on heating on a steam bath with dry red phosphorus and hydriodic acid in acetic anhydride gave the amino acid, β-(4,7-dimethyl--6-coumarinyl)alanine (XLV). It gave a positive Ninhydrin test. The hydrolysis of azlactone with 10 % alcoholic



sulphuric acid gave the corresponding benzamido derivative (XLVI).

Attempted synthesis of 4,7-dimethyl-6-(2'-chromonyl)-coumarin

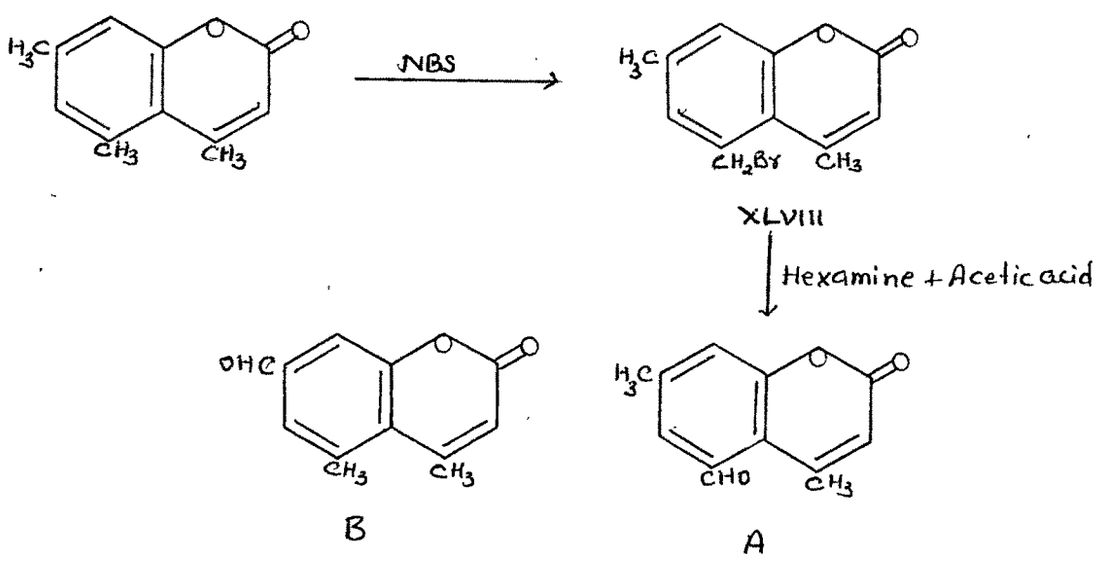
6-Formyl-4,7-dimethylcoumarin was condensed with o-hydroxy acetophenone in the presence of alcoholic potassium hydroxide. The bright yellow product which separated on acidification of the reaction mixture gave a red colouration with conc. sulphuric acid and reddish-brown colouration with ferric chloride. It also gave a positive Wilson test characteristic of chalcones. It was therefore assigned the β-(4,7-dimethyl-6-coumarinyl)vinyl-o-hydroxyphenyl ketone



structure (XLVII). The acetylation of this chalcone with fused sodium acetate and acetic anhydride, and its cyclisation and dehydrogenation with selenium dioxide in iso-amyl alcohol or its cyclisation in conc. sulphuric acid did not succeed.

Bromination of 4,5,7-trimethylcoumarin with N-bromosuccinimide

4,5,7-Trimethylcoumarin on bromination with one mole of N-bromosuccinimide in the presence of benzoyl peroxide gave a monobromomethyl derivative in a very poor



yield. This monobromomethyl derivative on heating with hexamine and acetic acid gave a monoformyl derivative which was characterised by the formation of 2,4-dinitrophenyl hydrazone derivative. Attempts were made to oxidise this formyl derivative to the corresponding carboxylic acid, which on decarboxylation could have given the known 4,7-dimethyl or 4,5-dimethylcoumarin depending upon the position of bromomethyl group, but it did not succeed. The NMR (Fig. 4) spectrum of the formyl derivative taken in trifluoroacetic acid, however, favours structure (A). The protons 6-H and 8-H are not in identical environment and so should give a separate signal for each. The NMR shows two one proton singlet at δ 7.8 and δ 7.6 in the aromatic region. These two signals can be attributed to 6-H and 8-H respectively. The coumarin proton 3-H appears as a singlet at δ 6.6, while the two methyl groups at position 4 and 5 appear as two three proton singlates at δ 2.6 and δ 2.75 respectively. The NMR spectrum of compound (B) would have shown almost similar pattern of signals to that of the NMR of 5-methyl-7-formylcoumarin (IX). The formyl derivative has, therefore, been assigned the 5-formyl-4,7-dimethylcoumarin structure (A) and the bromomethylcoumarin has been assigned the 5-bromomethyl-4,7-dimethylcoumarin structure (XLVIII), tentatively.

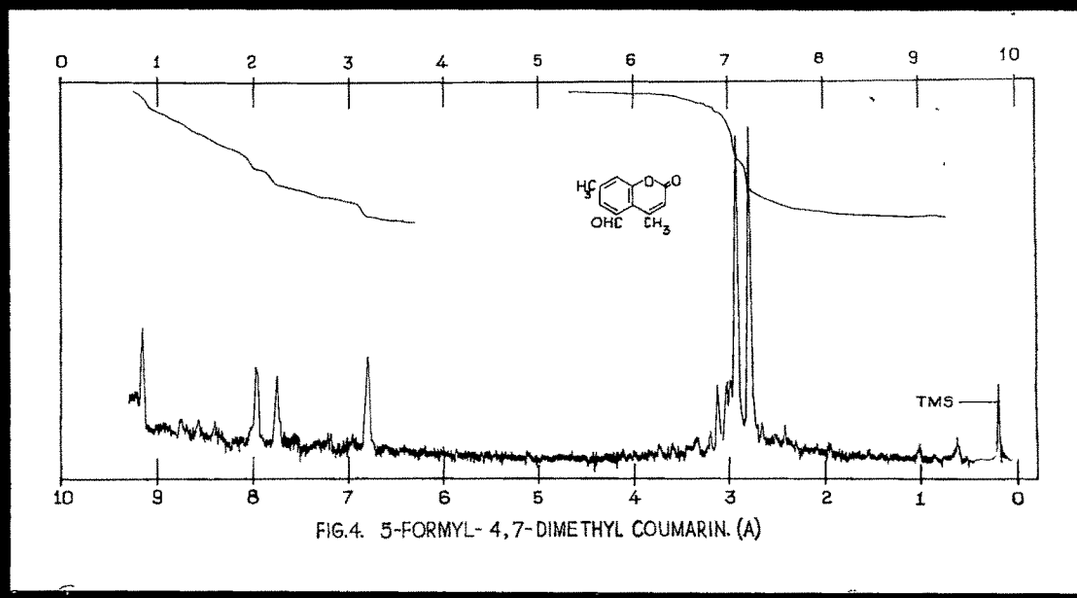


FIG.4. 5-FORMYL- 4,7-DIMETHYL COUMARIN. (A)

EXPERIMENTAL

5-Methyl-7-bromomethylcoumarin (VIII) :

N-Bromosuccinimide (6.0 g.) was dissolved in hot dry benzene and 5,7-dimethylcoumarin (6.0 g.) dissolved in dry benzene along with benzoyl peroxide (0.5 g.) was added. The reaction mixture was refluxed on a steam bath for 6 hr. till the yellow colour of the reaction mixture disappeared. The product obtained after the removal of benzene was washed with hot water and then with acetone. It crystallised from benzene in white shining needles (3.0 g.), m.p. 180°.

Analysis : Found : C, 52.13 ; H, 3.21 ; Br, 31.20 %

$C_{11}H_9O_2Br$ requires : C, 52.17 ; H, 3.55 ; Br, 31.62 %.

5-Methyl-7-formylcoumarin (IX) :

5-Methyl-7-bromomethylcoumarin (1.0 g.) was dissolved in glacial acetic acid (20 ml.) and refluxed gently with hexamine (4.0 g.) on a wire gauze till the colour of the reaction mixture changed to deep yellow (about 20 min.). Hydrochloric acid (10 ml.; 1:1) was then added to the reaction mixture and the heating continued for further 15 min. The product which separated on cooling the reaction mixture was crystallised from acetic acid in pale yellow fine needles, (0.5 g.), m.p. 225°. IR in nujol : 1725 cm^{-1} (CHO), 1695 cm^{-1} (δ lactone).

Analysis : Found : C, 70.08 ; H, 4.20 %

$C_{11}H_8O_3$ requires : C, 70.21 ; H, 4.26 %.

5-Methyl-6-hydroxy-7-formylcoumarin (IXa) :

5-Methyl-7-formylcoumarin (1.0 g.) was dissolved in sodium hydroxide solution (15 ml.; 10 %) by heating. A saturated aqueous solution of potassium persulphate (1.6 g.) was added during 4 hr. with continuous stirring and external cooling. After keeping this solution overnight, it was acidified to congo red. The precipitated unreacted substance was removed by filtration. The filtrate was treated with excess of hydrochloric acid and and heated on a steam bath for 30 min. The product obtained crystallised from acetic acid in bright yellow wooly needles (0.3 g.), m.p. 258°. It gave deep brown colouration with ferric chloride. IR in nujol : 1735 cm^{-1} (CHO) ; 1695 cm^{-1} (δ lactone).

Analysis : Found : C, 65.20 ; H, 4.08 %

$C_{12}H_8O_4$ requires : C, 64.71 ; H, 3.92 %.

Synthesis of 7-methyl-6-hydroxy-5-formylcoumarin (IXb) :

7-Methylcoumarin (5.0 g.) was subjected to Elbs persulphate oxidation as above and 7methyl-6-hydroxycoumarin was obtained. It was dissolved (1.0 g.) in acetic acid (20 ml.) and hexamine (2.5 g.) was added. The mixture was heated for 20 min. on a low flame. Hydrochloric acid (10 ml. ; 1:1) was then added and the reaction mixture was further boiled for 30 min. On cooling the reaction mixture a yellow solid separated which crystallised from xylene in yellow wooly needles (0.5 g.), m.p. 244°. It gave a deep brown colouration with alcoholic ferric chloride. The mixed m.p. with 5-methyl-6-hydroxy-7-formylcoumarin was depressed by 35°.

5-Methyl-7-acetoxymethylcoumarin (XI) :

5-Methyl-7-bromomethylcoumarin (1.0 g.) was dissolved in acetic anhydride (5 ml.) and refluxed with freshly fused sodium acetate (2.0 g.) for 2 hr. The reaction mixture was poured in ice cold water. The solid obtained was crystallised from benzene in tiny wooly needles (0.8 g.), m.p. 135°.

Analysis : Found : C, 67.59 ; H, 4.97 %

$C_{13}H_{12}O_4$ requires : C, 67.23 ; H, 5.17 %.

5-Methyl-7-morpholinomethylcoumarin (XII) :

5-Methyl-7-bromomethylcoumarin (1.0 g.) was dissolved in minimum amount of dry benzene (5 ml.) and morpholine (1 ml.) was added. The reaction mixture was refluxed on a water bath for 2 hr. The product remaining after the removal of benzene was crystallised from petroleum ether. M.p. 128°. Yield 0.8 g.

Analysis : Found : C, 69.00 ; H, 6.75 ; N, 5.73 %

$C_{15}H_{17}O_3N$ requires: C, 69.50 ; H, 6.56 ; N, 5.40 %.

Hydrobromide of 5-methyl-7-dimethylaminomethylcoumarin (XIII) :

5-Methyl-7-bromomethylcoumarin (1.0 g.) was dissolved in minimum amount of dry benzene and dimethylamine solution (2 ml.) was added. The reaction mixture was refluxed on a steam bath for 2 hr. The product obtained on the removal of benzene was crystallised from absolute alcohol. It was found to be hydrobromide of 5-methyl-7-dimethylaminomethyl-coumarin. M.p. 252°. Yield 0.6 g.

Analysis : Found : C, 52.41 ; H, 5.57 ; N, 4.77; Br, 27.09 %

$C_{13}H_{16}O_2NBr$: requires : C, 52.31 ; H, 5.37 ; N, 4.70; Br, 26.85 %.

The 2,4-dinitrophenylhydrazone :

It was prepared by heating a mixture of the above formyl derivative in alcohol and 2,4-dinitrophenylhydrazine hydrochloride in alcohol on a steam bath for 30 min. It was crystallised from nitrobenzene in orange needles, m.p. 295°.

Analysis : Found : N, 15.06 %

$C_{17}H_{12}O_6N_4$ requires : N, 15.21 %.

5-Methylcoumarin-7-carboxylic acid (X) :

A solution of silver nitrate (3.0 g.) in water (30 ml.) was added to a solution of sodium hydroxide (3.0 g. in 30 ml. of water). The precipitate of silver oxide formed was dissolved by adding ammonia drop by drop. This freshly prepared Tollen's reagent was added to an alcoholic solution of 5-methyl-7-formylcoumarin (1.5 g. in 100 ml. of alcohol). The reaction mixture was stirred for 10 hr. and then kept overnight. Next day, it was filtered and the filtrate was acidified with hydrochloric acid. The acid separated was taken in sodium bicarbonate solution and acidified to obtain pure acid. It was crystallised from dilute alcohol in fine needles (0.5 g.), m.p. 220°. The analysis agreed with one mole of water. IR in nujol : 1745 $cm.^{-1}$ (COOH) ; 1685 $cm.^{-1}$ (δ lactone).

Analysis : Found : C, 59.61 ; H, 4.19 %

$C_{11}H_8O_4.H_2O$ requires : C, 59.45 ; H, 4.50 %.

β-(5-Methyl-7-coumarinyl)acrylic acid (XIV) :

5-Methyl-7-formylcoumarin (1.0 g.) was heated with acetic anhydride (5 ml.) and freshly fused sodium acetate (3.0 g.) in an oil bath at 170-80° for 10 hr. The product obtained on pouring the reaction mixture in water was dissolved in sodium bicarbonate solution and reprecipitated with conc. hydrochloric acid. It was crystallised from alcohol. M.p. 250°. Yield 0.7 g.

Analysis : Found : C, 67.53 ; H, 4.21 %

$C_{13}H_{10}O_4$ requires : C, 67.82 ; H, 4.35 %.

Condensation of 5-methyl-7-formylcoumarin with o-hydroxy-acetophenone : β-(5-Methyl-7-coumarinyl)vinyl-o-hydroxy-phenyl ketone (XV) :

A solution of 5-methyl-7-formylcoumarin (2.0 g.) in alcohol was kept for 24 hr. with o-hydroxy acetophenone (4 ml.) and potassium hydroxide (20 ml. ; 100 %). The yellow solid obtained on dilution and acidification of the reaction mixture was washed with sodium bicarbonate solution. It crystallised from acetic acid in yellow needles (0.8 g.), m.p. 248°.

Analysis : Found : C, 74.66 ; H, 4.55 %

$C_{19}H_{14}O_4$ requires : C, 74.50 ; H, 4.58 %.

The acetoxy derivative (XVI) :

It was prepared by heating the above ketone (0.5 g.) with fused sodium acetate (1.5 g.) and acetic anhydride (5 ml.)

for 1 1/2 hr. The solid separated on diluting the reaction mixture with water crystallised from dilute alcohol in light yellow shining prisms. M.p. 115°.

Analysis : Found : C, 71.94 ; H, 4.18 %

$C_{21}H_{16}O_5$ requires : C, 72.41 ; H, 4.59 %.

5-Methyl-7-(2'-chromonyl)coumarin (XVII) :

The above hydroxy ketone (0.6 g.) in iso-amyl alcohol was refluxed with selenium dioxide (2.0 g.) at 145-50° for 8 hr. It was filtered hot. The product separating on cooling the filtrate crystallised from alcohol in needles (0.3 g.), m.p. 290°.

Analysis : Found : C, 74.82 ; H, 3.61 %

$C_{19}H_{12}O_4$ requires : C, 74.99 ; H, 3.95 %.

4-(5-Methyl-7-coumarinal)-2-phenyl-5-oxazolone (XVIII) :

An intimate mixture of 5-methyl-7-formylcoumarin (1.5 g.), fused sodium acetate (1.5 g.), hippuric acid (3.0 g.) and acetic anhydride (15 ml.) was warmed on a wire gauze till a clear solution was obtained. The bright yellow solution was then heated on a steam bath for 1 hr. It was then cooled and ethanol (15 ml.) was added to the reaction mixture. This was again heated on a steam bath for 1/2 hr. The yellow product which separated on cooling was filtered and washed successively with boiling water and ice cold ethanol. It crystallised from xylene in yellowish orange wooly needles (1.0 g.), m.p. 242°.

Analysis : Found : N, 4.02 %

$C_{19}H_{13}O_4Cl$ requires : N, 4.39 %.

Attempted synthesis of β-(5-methyl-7-coumarinyl)alanine (XIX) :

To a mixture of the above azlactone (1.0 g.), purified red phosphorus (0.8 g.), acetic anhydride (5 ml.) and hydriodic acid (5 ml. ; sp. gr. 1.56 ; 50 %) was added in portions with stirring. The reaction mixture was heated on a steam bath for 3 hr. It was then filtered and the residue on the filter paper cone was washed with two 2 ml. portions of glacial acetic acid. The product separating from the combined filtrate was filtered and treated with sodium bisulphite solution to remove iodine. The decolourised product was then kept with ammonia (10 ml. ; 10 %) for sometime and the clear solution was then neutralised with dilute hydrochloric acid to congo red. No product separated on concentration so the whole solution was evaporated. The solid obtained was crystallised from methanol. It gave a positive Ninhydrin test. It did not melt but decomposed at 250°. When heated on a spatula, it left no residue.

Ethyl-α-benzamido-β-(5-methyl-7-coumarinyl)acrylate (XX) :

The solution of the above azlactone (1.0 g.) in alcoholic sulphuric acid 10 % ; 50 ml.) was refluxed gently on a wire gauze for 5 hr. The product obtained on dilution with water was crystallised from dilute alcohol in shining plates. It was insoluble in sodium hydroxide solution. M.p. 172°. Yield 0.6 g..

Analysis : Found : C, 69.53 ; H, 4.98 ; N, 3.65 %
$C_{22}H_{19}O_5N$ requires : C, 70.03 ; H, 5.04 ; N, 3.71 %.

Synthesis of 5,7-dibromomethylcoumarin (XXI) :

5-Methyl-7-bromomethylcoumarin (0.5 g.) was dissolved in dry benzene and mixed with N-bromosuccinimide (0.6 g.) dissolved in benzene. Benzoyl peroxide (0.1 g.) was then added and the reaction mixture was refluxed for 4 hr. The benzene was evaporated out and the residue was washed with hot water. It was then dried and crystallised from benzene into small needles (0.2 g.), m.p. 175°.
Analysis : Found : C, 40.18 ; H, 2.34 ; Br, 47.75 %
$C_{11}H_8O_2Br_2$ requires : C, 39.77 ; H, 2.41 ; Br, 48.19 %.

Action of hot alkali :

The above 5,7-dibromomethylcoumarin (0.5 g.) was refluxed with alcoholic potassium hydroxide solution (10 % ; 10 ml.) for 2 hr. The product obtained on acidification of the reaction mixture crystallised from glacial acetic acid,. m.p. 175°. Mixed m.p. with the original dibromomethylcoumarin was not depressed.

Reduction of 5,7-dibromomethylcoumarin :

The above 5,7-dibromomethylcoumarin (0.2 g.) was dissolved in minimum quantity of acetic acid and zinc dust (0.5 g.) was added. Hydrochloric acid (5. ml.) was then added portionwise and the reaction mixture was refluxed for 1 hr. It was then poured into water and the solid separated

was then crystallised from dilute alcohol. M.p. 140°. The mixed m.p. with 5,7-dimethylcoumarin was not depressed.

6-Bromomethyl-4,7-dimethylcoumarin (XXII) :

N-Bromosuccinimide (6.0 g.) was dissolved in hot dry benzene (200 ml.) and 4,6,7-trimethylcoumarin (6.0 g.) dissolved in benzene (50 ml.) along with benzoyl peroxide (0.6 g.) was added. The reaction mixture was refluxed on a steam bath for 6 hr. The product obtained after the removal of benzene was washed with hot water thoroughly, then dried and crystallised from benzene in the fine white needles (4.0 g.), m.p. 226°.

Analysis : Found : C, 53.95 ; H, 4.21 ; Br, 29.32 %

$C_{12}H_{11}O_2Br$ requires : C, 53.94 ; H, 4.02 ; Br, 29.28 %.

6-Formyl-4,7-dimethylcoumarin (XXIII) :

6-Bromomethyl-4,7-dimethylcoumarin (1.0 g.) was dissolved in glacial acetic acid (20 ml.) and refluxed gently with hexamine (2.5 g.) on a wire gauze till the colour of the reaction mixture changed to dark yellow (20 min.). Hydrochloric acid (10 ml.; 1:1) was added to the reaction mixture and the heating continued for further 10 min. The product which separated on cooling the reaction mixture was crystallised from acetic acid in pale yellow needles. M.p. 226°. The mixed m.p. with the bromomethyl derivative (m.p. 226°) was 190°. Yield 0.6 g. IR in nujol : 1745 cm^{-1} (CHO) ; 1695 cm^{-1} (δ lactone).

Analysis : Found : C, 71.11 ; H, 4.45 %

$C_{12}H_{10}O_3$ requires : C, 71.28 ; H, 4.02 %.

The 2,4-dinitrophenyl hydrazone :

It was prepared as usual and crystallised from nitrobenzene, m.p. 305° (decomp.).

Analysis : Found : N, 14.85 %

$C_{18}H_{14}O_6N_4$ requires : N, 14.66 %.

Oxime of 6-formyl-4,7-dimethylcoumarin (XXIV) :

6-Formyl-4,7-dimethylcoumarin (2.0 g.) was dissolved in ethanol (150 ml.) and pyridine (2 ml.). Hydroxylamine hydrochloride (2.0 g.) was then added and the reaction mixture was refluxed on a water bath for 30 min. The alcohol was removed by distillation and the residue obtained was thoroughly washed with water and crystallised from alcohol, m.p. 208°. Yield 1.5 g.

Analysis : Found : C, 66.59 ; H, 5.03 ; N, 6.53 %

$C_{12}H_{11}O_3N$ requires : C, 66.34 ; H, 5.07 ; N, 6.46 %.

6-Cyano-4,7-dimethylcoumarin (XXV) :

The above oxime (1.0 g.) was refluxed with acetic anhydride (20 ml.) for 3 hr. The product obtained on cooling the reaction mixture was crystallised from alcohol, m.p. 280-85° (decomp.). IR in nujol : 2220 $cm.^{-1}$ (CN) ; 1790 $cm.^{-1}$ (δ lactone).

Analysis : Found : C, 72.86 ; H, 4.58 ; N, 6.86 %

$C_{12}H_9O_2N$ requires : C, 72.36 ; H, 5.52 ; N, 6.42 %.

4,7-Dimethylcoumarin-6-carboxylic acid (XXVI) :

The above cyano derivative (1.0 g. was heated with polyphosphoric acid (20 ml.) on an oil bath at 200° for 5½ hr. The reaction mixture was then poured in ice water and the product separated was treated with sodium bicarbonate solution. The carboxylic acid was reprecipitated by the acidification of the sodium bicarbonate extract with hydrochloric acid and crystallised from dilute alcohol in fine needles. M.p. 270° (effer.).

Analysis : Found : C, 66.48 ; H, 5.02 %

$C_{12}H_{10}O_4$ requires : C, 66.06 ; H, 4.59 %.

IR in nujol : 1725 cm^{-1} (COOH) ; 1710 cm^{-1} (δ lactone).

4,7-Dimethylcoumarin (XXVII) :

The above acid was heated with polyphosphoric acid on an oil bath at 220° for 8 hr. The reaction mixture was decomposed with ice cold water and the product separated was washed thoroughly with sodium bicarbonate solution and crystallised from alcohol. M.p. 140°. This was found to be identical on direct comparison with an authentic sample of 4,7-dimethylcoumarin prepared by the Pechmann condensation of m-cresol and acetoacetic ester in the presence of sulphuric acid.[18]

6-Acetoxymethyl-4,7-dimethylcoumarin (XXVIII) :

6-Bromomethyl-4,7-dimethylcoumarin (1.0 g.) was dissolved in acetic anhydride (5 ml.) and refluxed with

freshly fused sodium acetate (2.5 g.) for 2 hr. The reaction mixture was poured in ice water. The product obtained crystallised from benzene in long needles, m.p. 127°.

Analysis : Found : C, 68.28 ; H, 5.74 %

$C_{14}H_{14}O_4$ requires : C, 68.29 ; H, 6.09 %.

6-Morpholinomethyl-4,7-dimethylcoumarin (XXIX) :

6-Bromomethyl-4,7-dimethylcoumarin (1.0 g.) was dissolved in dry benzene (5 ml.) and morpholine (1 ml.) was added. The reaction mixture was refluxed on a water bath for 2 hr. The product obtained after the removal of benzene was crystallised from petroleum ether. M.p. 140-42°.

Analysis : Found : C, 70.25 ; H, 6.85 ; N, 4.74 %

$C_{16}H_{19}O_3N$ requires : C, 70.31 ; H, 6.96 ; N, 5.13 %.

6-Dimethylaminomethyl-4,7-dimethylcoumarin (XXX) :

6-Bromomethyl-4,7-dimethylcoumarin (0.5 g.) was dissolved in dry benzene (75 ml.) and dimethylamine (1 ml.) was added. The reaction mixture was refluxed on a steam bath for 2 hr. The product obtained on removal of benzene was crystallised from benzene-petroleum ether, m.p.151°.

Analysis : Found : C, 72.78 ; H, 7.35 ; N, 5.99 %

$C_{14}H_{17}O_2N$ requires : C, 73.05 ; H, 7.39 ; N, 6.09 %.

β-(4,7-Dimethyl-6-coumarinyl)acrylic acid (XXXI) :

6-Formyl-4,7-dimethylcoumarin (1.0 g.) was heated with acetic anhydride (10 ml.) and freshly fused sodium acetate (3.0 g.) in an oil bath at 170-80° for 12 hr. The

product obtained on pouring the reaction mixture in water was dissolved in sodium bicarbonate solution and reprecipitated with conc. hydrochloric acid. It crystallised from dilute acetic acid in white shining needles, M.p. 262-65° (effer.). It decolourised dilute potassium permanganate solution.

Analysis : Found : C, 68.58 ; H, 5.36 %

$C_{14}H_{12}O_4$ requires : C, 68.85 ; H, 4.92 %.

6-Cyanomethyl-4,7-dimethylcoumarin (XXXII) :

6-Bromomethyl-4,7-dimethylcoumarin (1.0 g.) was dissolved in alcohol (100 ml.) and potassium cyanide (1.0 g.) dissolved in minimum quantity of water was added. The reaction mixture was refluxed on a water bath for 3 hr. It was then poured in cold water. The separated product was crystallised from dilute alcohol in needles (0.7 g.), m.p. 190°. IR in nujol : 2235 cm^{-1} (CN) ; 1620 cm^{-1} (δ lactone).

6-Carboxymethyl-4,7-dimethylcoumarin (XXXIII) :

6-Cyanomethylcoumarin (1.0 g.) was dissolved in acetic acid (20 ml.) and hydrochloric acid (20 ml.) was added. The mixture was heated on a sand bath for 5 hr. It was then poured in ice cold water. The product which separated was taken in sodium bicarbonate solution, which was then acidified with conc. hydrochloric acid. The product obtained was crystallised from dilute alcohol, m.p. 248° (effer.). IR in nujol : 1720 cm^{-1} (COOH) ; 1625 cm^{-1} (δ lactone).

6-Carbethoxymethyl-4,7-dimethylcoumarin (XXXIV) :

6-Carboxymethyl-4,7-dimethylcoumarin (0.5 g.) was refluxed gently with alcoholic sulphuric acid (10 % ; 25 ml.) on a wire gauze for 5 hr. The product obtained on pouring the reaction mixture in water was washed with sodium bicarbonate solution. It crystallised from petroleum ether in small tiny needles, m.p. 125°.

Analysis : Found : C, 69.04 ; H, 5.75 %

$C_{15}H_{16}O_4$ requires : C, 69.23 ; H, 6.15 %.

6-(3'-Coumarinyl)-4,7-dimethylcoumarin (XXXV) :

A mixture of the above ester (0.5 g.) and salicylaldehyde (1 ml.) in absolute alcohol (5 ml.) was heated under reflux with two drops of piperidine on a steam bath. The clear brown solution was heated for 4 hr. After cooling the reaction mixture a solid separated which was washed with sodium hydroxide solution to remove the excess of salicylaldehyde. It was then washed with water and crystallised from alcohol. M.p. 274-77°. IR in nujol : 1725 cm^{-1} ; 1710 cm^{-1} (δ lactone).

Analysis : Found : C, 75.16 ; H, 4.46 %

$C_{20}H_{14}O_4$ requires : C, 75.48 ; H, 4.46 %.

4-(4',7'-Dimethyl-6'-coumarinal)-2-phenyl-5-oxazolone (XLIV) :

An intimate mixture of 6-formyl-4,7-dimethyl-coumarin (1.5 g.), fused sodium acetate (1.5 g.), hippuric acid (3.0 g.) and acetic anhydride (10 ml.) was warmed on a wire gauze till a clear solution was obtained. The bright

yellow solution was heated on a steam bath for 1 hr. It was then cooled and ethanol (15 ml.) was added to the reaction mixture. This was again heated on a steam bath for 1/2 hr. The yellow product which separated on cooling was filtered and washed successively with boiling water and ice cold ethanol. It crystallised from nitrobenzene in yellowish-orange wooly needles (0.8 g.), m.p. 230-32°.

Analysis : Found : C, 72.36 ; H, 4.08 ; N, 3.69 %

$C_{21}H_{15}O_4N$ requires : C, 73.05 ; H, 4.35 ; N, 4.06 %.

β-(4,7-Dimethyl-6-coumarinyl)alanine (XLV) :

To a mixture of the above oxazolone derivative (1.0 g.) purified red phosphorus (0.8 g.), acetic anhydride (5 ml.) and hydrochloric acid (5 ml. ; sp.gr. 1.56 ; 50 %) were added in portion with stirring. The reaction mixture was heated on a steam bath for 3 hr. It was then filtered and treated with sodium bisulphite solution to remove iodine. The decolourised product was then kept with ammonia (10 ml.; 10 %) for some time and the clear solution was then neutralised with dilute hydrochloric acid to congo red. The product obtained crystallised from distilled water. M.p. 260° (effer.). The analysis agreed with one molecule of water of crystallisation. It gave effervescence with sodium bicarbonate solution.

Analysis : Found : C, 58.05 ; H, 5.60 ; N, 4.96 %

$C_{14}H_{15}O_4N.H_2O$ requires : C, 57.50 ; H, 6.09 ; N, 5.01 %.

Ethyl-α-benzamido-β-(4,7-dimethyl-6-coumarinyl)acrylate (XLVI) :

The solution of the above oxazolone derivative (1.0 g.) in alcoholic sulphuric acid (50 ml.; 10 %) was refluxed gently on a steam bath for 5 hr. The product obtained on dilution with water was crystallised from dilute alcohol. M.p. 220°.

Analysis : Found : C, 70.57 ; H, 5.30 ; N, 3.22 %

$C_{23}H_{21}O_5N$ requires : C, 70.58 ; H, 5.37 ; N, 3.58 %.

β-(4,7-Dimethyl-6-coumarinyl)vinyl-o-hydroxyphenyl ketone (XLVII) :

A solution of 6-formyl-4,7-dimethylcoumarin (1.0 g.) in alcohol was mixed with o-hydroxyacetophenone (1 ml.) and potassium hydroxide solution (5 g. in 5 ml. water). After keeping the reaction mixture overnight, it was added to ice cold water and acidified with conc. hydrochloric acid. The product obtained crystallised from alcohol in yellow wooly needles. M.p. 240°.

Analysis : Found : C, 74.80 ; H, 4.76 %

$C_{20}H_{16}O_4$ requires : C, 75.01 ; H, 5.00 %.

Attempts to cyclise and dehydrogenate this product to 4,7-dimethyl-6-(2'-chromonyl)coumarin, by heating it with iso-amyl alcohol in the presence of selenium dioxide or cyclisation with conc. sulphuric acid did not succeed.

4,5-Dimethyl-7-bromomethylcoumarin (XLVIII) :

4,5,7-Trimethylcoumarin (5.0 g.) was dissolved in dry benzene and mixed with a solution of N-bromosuccinimide (5 g.) and dry benzoyl peroxide (0.5 g.) in dry benzene was added and the reaction mixture was refluxed on a water bath for 4 hr. After the removal of benzene the residue was washed with hot water dried and crystallised from benzene into fine needles (0.8 g.), m.p. 158°.

Analysis : Found : C, 54.11 ; H, 4.09 ; Br, 29.44 %

$C_{12}H_{11}O_2Br$ requires : C, 53.94 ; H, 4.03 ; Br, 29.28 %.

4,5-Dimethyl-7-acetoxymethylcoumarin :

The above 4,5-dimethyl-7-bromomethylcoumarin (1.0 g.) was heated with acetic anhydride (20 ml.) and fused sodium acetate (2.0 g.) for 2 hr. on a wire gauze. The reaction mixture was then poured in ice cold water and the product separated was crystallised from dilute alcohol, m.p. 148-49°.

Analysis : Found : C, 68.13 ; H, 5.47 %

$C_{14}H_{14}O_4$ requires : C, 68.29 ; H, 5.69 %.

4,5-Dimethyl-7-formylcoumarin (A) :

4,5-Dimethyl-7-bromomethylcoumarin (1.0 g.) was dissolved in acetic acid and hexamine (2.5 g.) was added. The mixture was refluxed gently on a wire gauze for 20 min. Hydrochloric acid (20 ml. ; 1:1) was then added and the reaction mixture was further heated for 30 min. On cooling

a product separated, which was crystallised from acetic acid, m.p. 200°. IR in nujol : 1735 cm^{-1} (CHO) ; 1695 cm^{-1} (δ lactone).

Analysis : Found : C, 71.29 ; H, 4.43 %

$C_{12}H_{10}O_3$ requires : C, 71.28 ; H, 4.02 %.

The 2,4-dinitrophenylhydrazone :

It was prepared as usual and crystallised from nitrobenzene in wooly orange needles, m.p. 292°.

Analysis : Found : N, 14.21 %

$C_{18}H_{14}O_6N_4$ requires : N, 14.66 %.

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