CHAPTER IV

STUDIES ON 3-(4'-HYDROXY PHENYL) COUMARIN

CHAPTER IV

Studies on 3-(4'-hydroxyphenyl)coumarin :

Considerable work has been done on the reactivity of various hydroxy coumarins with the hydroxy group in the α-pyrone ring or in the benzenoid part but hardly any work appears to have been done on 3-(4'-hydroxyphenyl)coumarin where the hydroxy group is in the side phenyl nucleus. It was therefore thought of interest to build up some heterocyclic rings such as α-pyrone, furan and γ-pyrone rings on the side phenyl nucleus.

Of the various methods available for the synthesis of 3-phenyl coumarins the Meerwein reaction[1] was found in the present study to be the most suitable for the synthesis of 3-(4'-hydroxyphenyl)coumarin.

A diazotised solution of p-anisidine was mixed with a solution of coumarin in acetone containing sodium acetate in suspension. A solution of cupric chloride in water was used as the catalyst. 3-(4'-Methoxyphenyl)coumarin was obtained in about 35 % yield. This was then demethylated by heating with aluminium chloride in dry benzene at 50° for 3 hours.

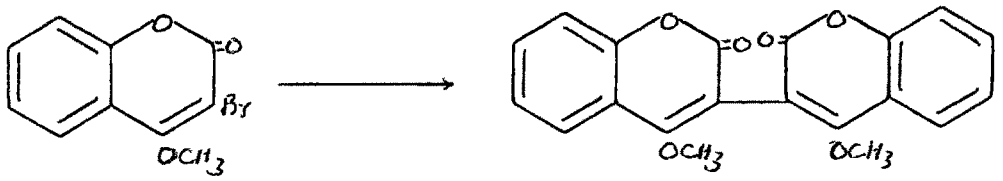
In the course of present study the following compounds have been synthesised from 3-(4'-hydroxyphenyl) coumarin.

1. 3,6'-Bicoumarinyl :
2. 3-(5'-Benzofuranyl)coumarin and its 3'-methyl derivative
3. 3-(6'-Flavonyl)coumarin and its 4''-methoxy- and 3'-benzoyl derivatives.

Bicoumarinyls :

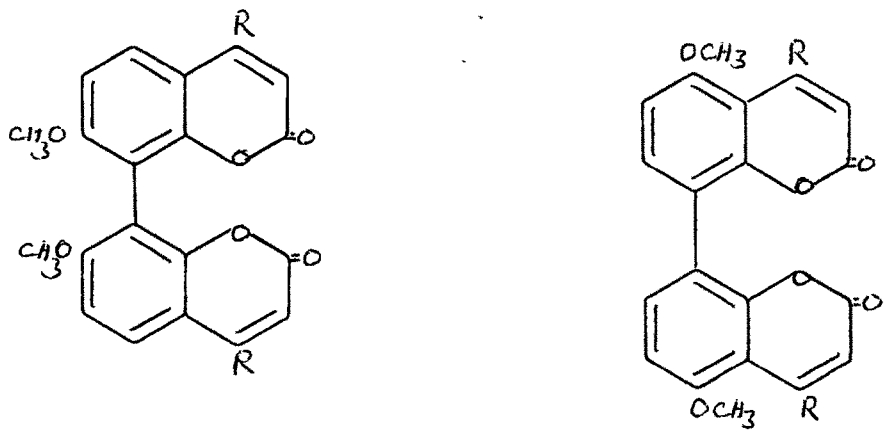
Dyson[2] synthesised 3,3'-bicoumarinyl by heating salicylaldehyde with sodium succinate and acetic anhydride in a sealed tube at 140° for 40 hours.

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



I II

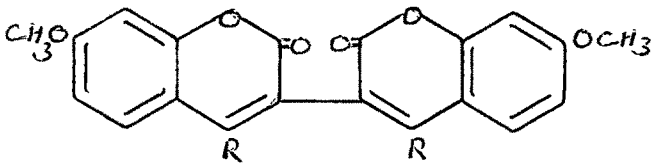
Lele et al.[4] have synthesised 8,8'-bicoumarinyl derivatives (IIIa, IIIb, IVa and IVb) and 3,3'-bicoumarinyl derivatives (Va and Vb) by the Ullmann reaction on iodocoumarins.



III IV

(a) R = H

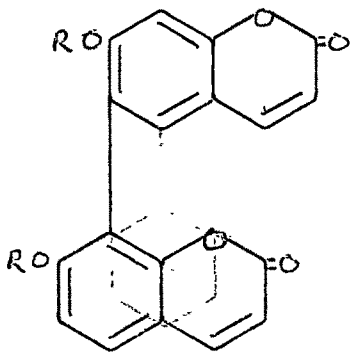
(b) R = CH_3



V (a) R = H
(b) R = CH_3

Sen and Dutt[5] obtained 6,6'-bicoumarinyl by the action of acetic anhydride and sodium acetate on 4,4'-dihydroxy-diphenyl-3,3'-dialdehyde. Harle and Lyons[6] obtained tetrahydro-4-4'-bicoumarinyl as one of the products in the reduction of coumarin using zinc and acetic acid.

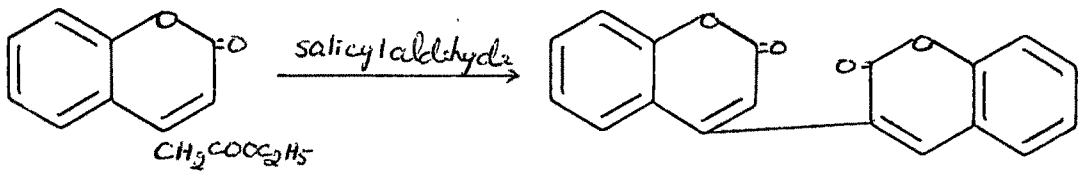
Recently some unsymmetrical bicoumarinyls have been found to occur in plants. Mihashi and co-workers[7,8] have isolated an unsymmetrical bicoumarinyl derivative and named it Matsukaze lactone. It has been assigned the 6,8'-bicoumarinyl structure (VIa)



VI (a) R = CH_3
(b) R = H

Later Spencer et al.[9] isolated bicoumol, a bicoumarinyl derivative from ladino clover and assigned the 7,7'-dihydroxy-6,8'-bicoumarinyl structure (VIb).

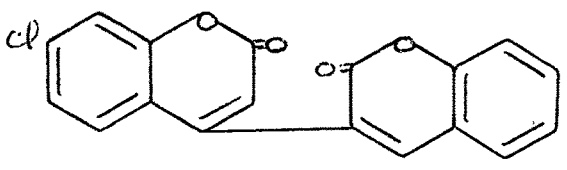
The only study in the synthesis of unsymmetrical bicoumarinyls has been reported by Dey and Row[10]. They condensed coumarin-4-acetic ester with salicylaldehyde under the conditions of Perkin reaction or Knoevenagel reaction and obtained the 4,3'-bicoumarinyl (VII) .



VII

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 (VIII) has been synthesised by Thakar[11] by the condensation of 7-chloro-coumarin-4-acetic acid with salicylaldehyde in the presence of piperidine.

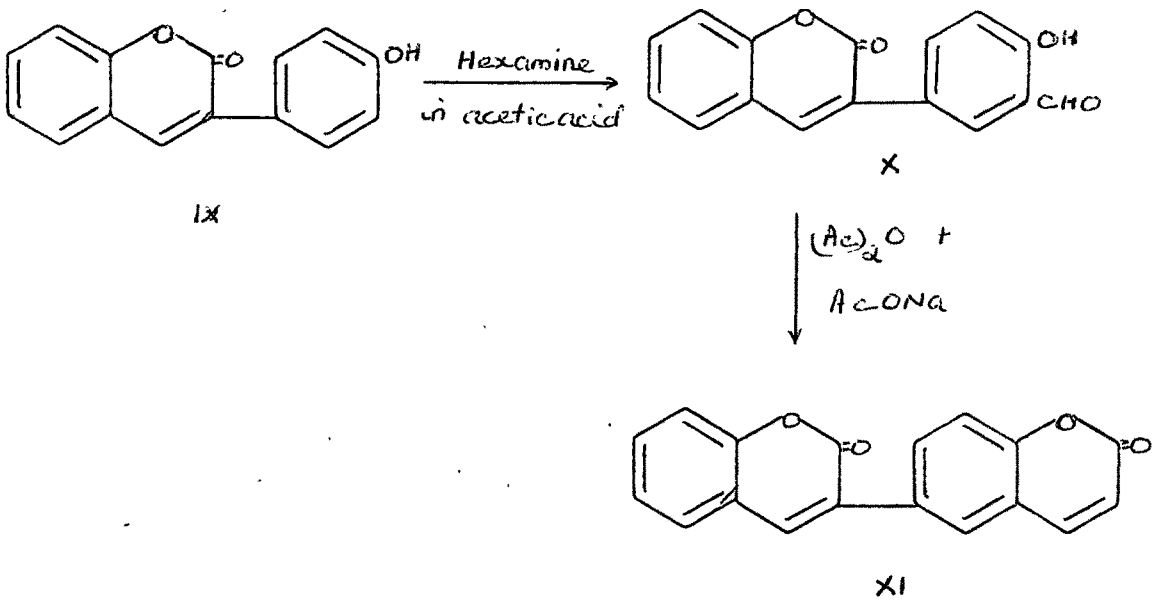


VIII

Synthesis of 3,6'-bicoumarinyl (XI) :

With a view to synthesise the unsymmetrical bicoumarinyl viz.3,6'-bicoumarinyl, the Pechmann condensation of malic acid with 3-(4'-hydroxyphenyl)coumarin in the presence of concentrated sulphuric acid was tried but the condensation did not take place and the original hydroxy coumarin was obtained back. Attempt was then made to condense the more reactive ethyl acetoacetate in the presence of sulphuric acid with the above coumarin but in this case also no condensation took place and the original coumarin was obtained back. It was therefore decided to synthesise the desired bicoumarinyl derivative through the Perkin reaction on 4'-hydroxy-3'-formylcoumarin.

3-(4'-Hydroxyphenyl)coumarin (IX) on heating with hexamine in acetic acid gave a product which gave a brown colour with alcoholic ferric chloride. 3-(3'-formyl-4'-hydroxyphenyl)coumarin structure (X) has been assigned to this product. The formyl derivative was then heated with fused sodium acetate and acetic anhydride at 170-80^{o} for 12 hours. A pale yellow product which was insoluble in sodium hydroxide solution was obtained to which the 3,6'-bicoumarinyl structure (XI) has been assigned. 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.



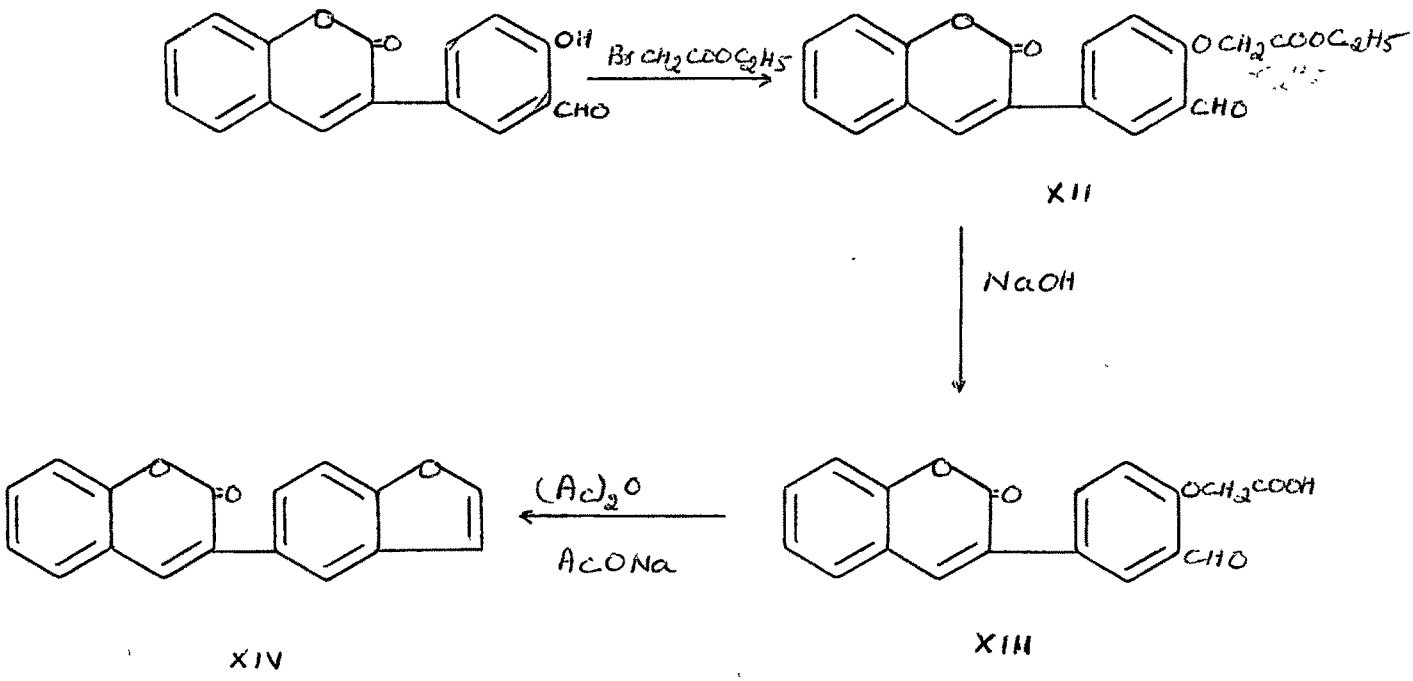
Benzofuranyl coumarins.

Even though several furocoumarins and benzofurano-coumarins have been isolated from plants and also synthesised, no work appears to have reported on the synthesis of benzofuranyl coumarins. It was therefore thought of interest to synthesise such type of compounds.

Synthesis of 3-(5'-benzofuranyl)coumarin (XIV).

3-(3'-Formyl-4'-hydroxyphenyl)coumarin (X) was condensed with ethylbromoacetate in dry acetone in the presence of anhydrous potassium carbonate to get 3-(3'-formyl-4'-carbethoxymethoxyphenyl)coumarin (XII). This on hydrolysis with 10 % sodium hydroxide solution at room temperature gave the acid (XIII), which on simultaneous cyclisation and decarboxylation on refluxing with sodium acetate and acetic anhydride gave 3-(5'-benzofuranyl)-

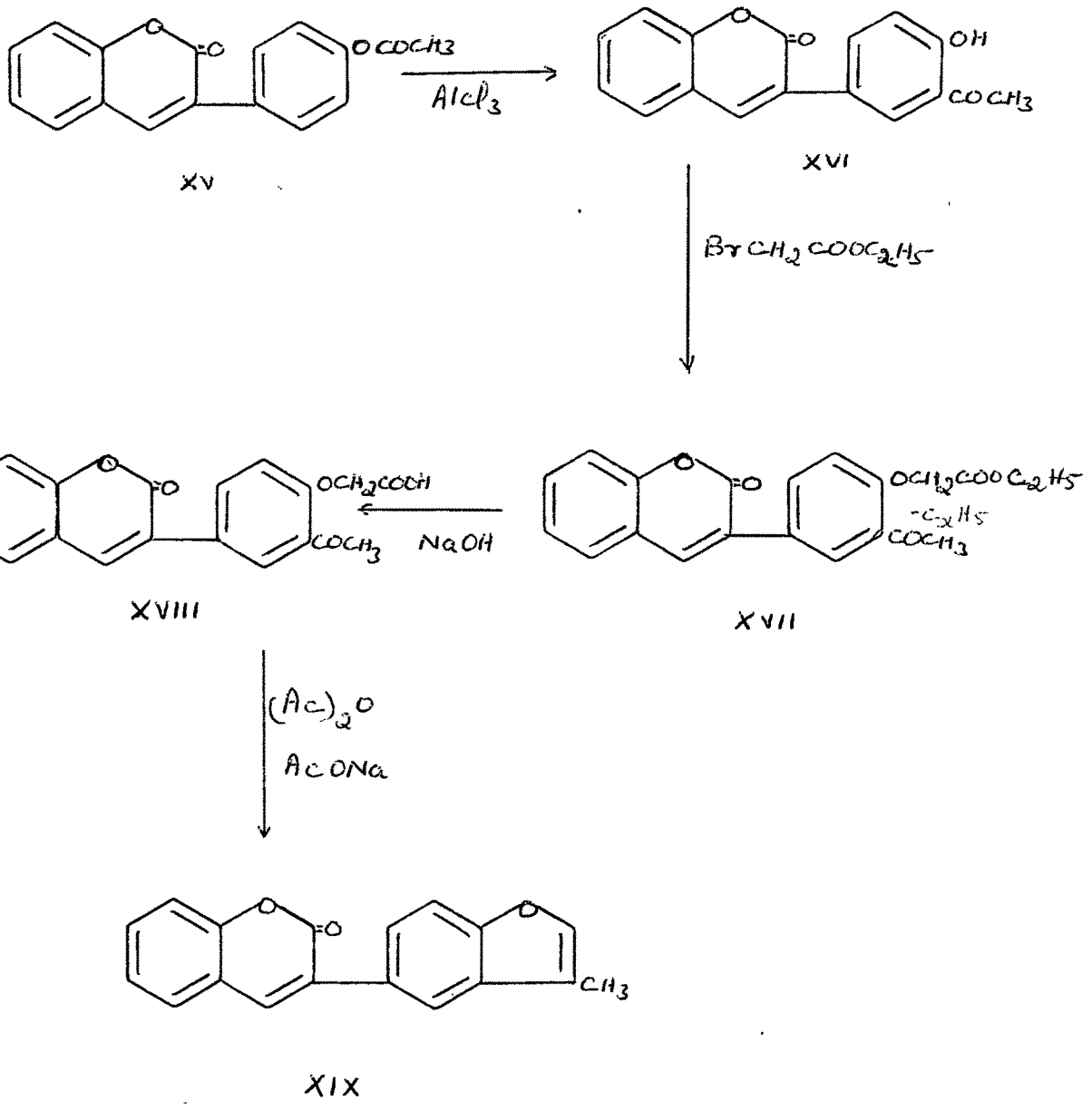
coumarin (XIV).



Synthesis of 3-(3'-methyl-5'-benzofuranyl)coumarin (XIX).

3-(4'-Acetoxyphenyl)coumarin[12] (XV) on heating with anhydrous aluminium chloride at 140-50° for 3 hours gave 3-(3'-acetyl-4'-hydroxyphenyl)coumarin (XVI). It was soluble in alkali and gave a violet colouration with alcoholic ferric chloride. On condensation with ethyl bromoacetate in dry acetone in the presence of anhydrous potassium carbonate it gave 3-(3'-acetyl-4'-carbethoxymethoxyphenyl) coumarin (XVII) which was insoluble in alkali. This ester was hydrolysed with 10 % sodium hydroxide solution at room temperature to 3-(3'-acetyl-4'-carboxymethoxyphenyl)coumarin (XVIII). The acid on heating with sodium acetate and

acetic anhydride for 3 hours gave on simultaneous cyclisation and decarboxylation, 3-(3'-methyl-5'-benzofuranyl) coumarin (XIX).



Flavonylcoumarins.

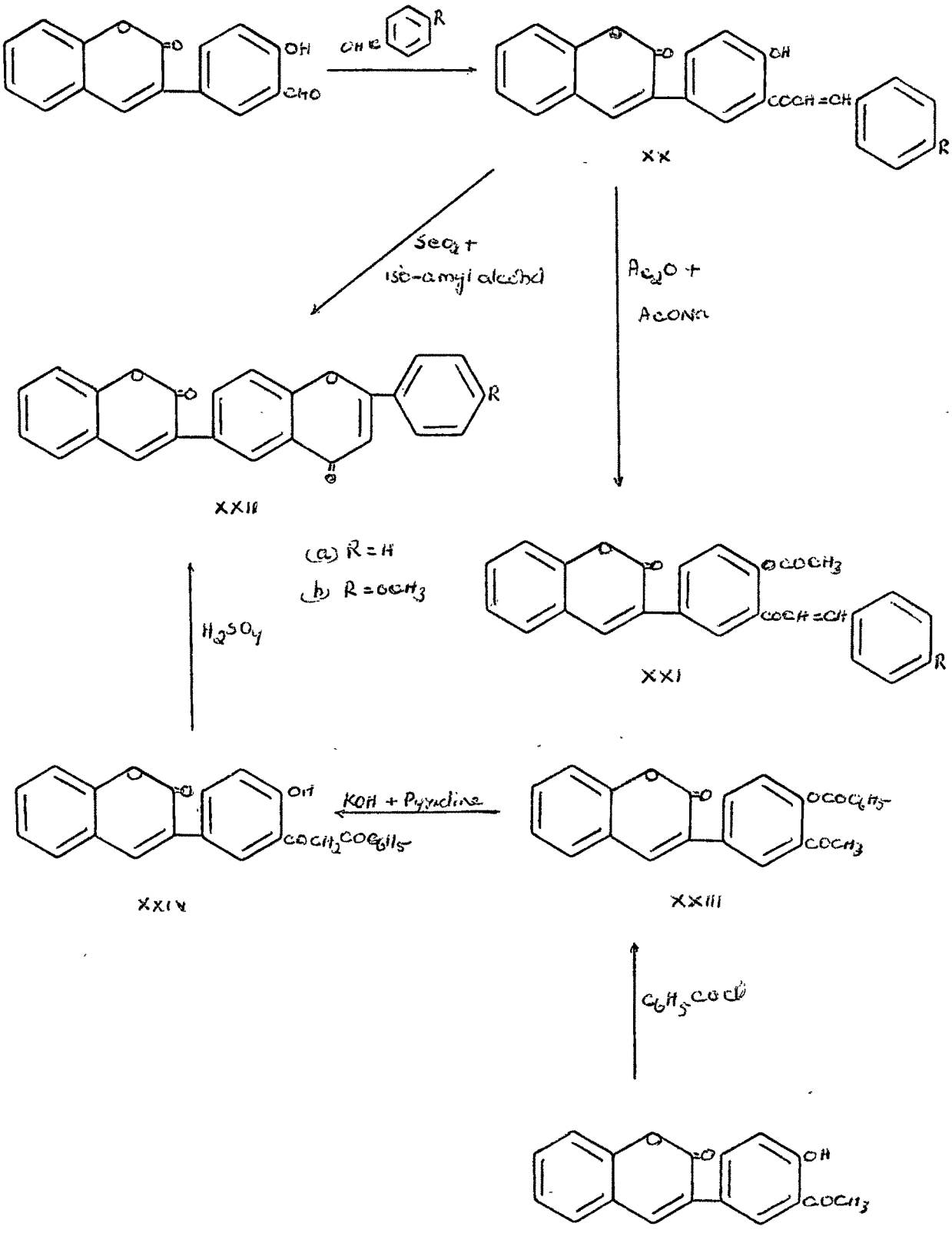
A number of methods are available for the building up of 2-phenyl-γ-pyrone ring on a suitably substituted derivative of benzene. In the present work three methods have been used viz. the chalkone method[13], the Baker-Venkataraman transformation[14] of an o-benzoyloxyacetophenone and the cyclisation of the β-diketone thus obtained and the Kostanecki-Robinson acylation method[15].

Synthesis of 3-(6'-flavonyl)coumarin (XXIIa).

3-(3'-Acetyl-4'-hydroxyphenyl)coumarin was condensed with benzaldehyde in the presence of alcoholic potassium hydroxide. The orange yellow product obtained on acidification gave tests for a styryl ketone derivative viz. red colouration with sulphuric acid and a positive Wilson test[16]. It gave an acetoxy derivative (XXIa) when refluxed with sodium acetate and acetic anhydride. 3-(3'-Cinnamoyl-4'-hydroxyphenyl)coumarin structure (XXa) has been assigned to this product. The above styryl ketone on refluxing with selenium dioxide in isoamyl alcohol gave a product which gave no colour with sulphuric acid. 3-(6'-Flavonyl)coumarin structure (XXIIa) has been assigned to this product.

The same flavonylcoumarin (XXIIa) was also synthesised from 3-(3'-acetyl-4'-benzoyloxyphenyl)coumarin (XXIII) through Baker-Venkataraman rearrangement as shown below.

3-(3'-Acetyl-4'-hydroxyphenyl)coumarin was refluxed with benzoyl chloride in dry acetone in the presence of


OH
CHO
CH=C
R
OH
COCH=CH
R
XX
SeO2 +
iso-amyl alcohol
Ac2O +
AcONa
R
XXII
(a) R = H
(b) R = OCH3
H2SO4
OCOCH3
COCH=CH
R
XXI
OH
KOH + Pyridine
COCH2COC6H5
OCOC6H5
COCH3
XXIV
XXIII
C6H5COCl
OH
COCH3

anhydrous potassium carbonate to get 3-(3'-acetyl-4'-benzoyloxyphenyl)coumarin (XXIII). When kept with powdered caustic potash and pyridine for 4 hours at room temperature it gave the β-diketone (XXIV) which on cyclisation by keeping it in contact with cold concentrated sulphuric acid for 4 hours gave a product which was found to be identical on direct comparison with 3-(6'-flavonyl)coumarin described before.

Synthesis of 3-(4''-methoxy-6'-flavonyl)coumarin (XXIIb).

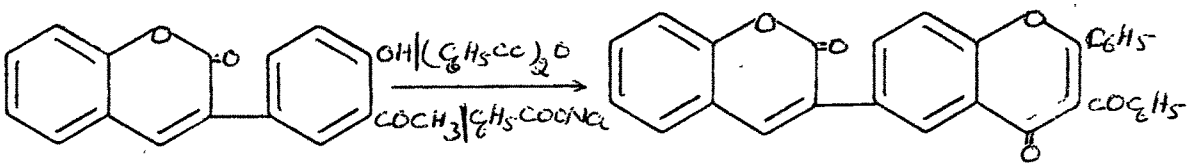
3-(3'-Acetyl-4'-hydroxyphenyl)coumarin was condensed with anisaldehyde in the presence of alcoholic potassium hydroxide. The yellow product obtained on acidification gave a red colour with sulphuric acid and a positive Wilson test. 3-[3'-(p-methoxycinnamoyl)-4'-hydroxyphenyl]coumarin structure (XXb) has been assigned to this. It gave an acetoxy derivative (XXIb) on refluxing with fused sodium acetate and acetic anhydride. The above styryl ketone was then cyclised to 3-(4''-methoxy-6'-flavonyl)-coumarin (XXIIb) by refluxing with selenium dioxide in iso-amyl alcohol for 24 hours.

3-(3'-Benzoyl-6'-flavonyl)coumarin (XXV).

3-(3'-Acetyl-4'-hydroxyphenyl)coumarin on heating with benzoic anhydride and sodium benzoate at 180-90° for 12 hours gave a product which was insoluble in alkali. On the basis of the analysis results, 3(3'-benzoyl-6'-flavonyl) coumarin structure (XXV) has been assigned to this product.

The above benzoylflavonylcoumarin was heated with alcoholic caustic potash on a steam bath. On working up the

reaction mixture the original flavonylcoumarin was obtained back. The formation of 3-acyl derivatives in the Kostanecki-Robinson acylation is a common feature[17].



XXV

Attempted synthesis of 3-(2'-methyl-6'-chromonyl)coumarin.

It has been noted[18] that phenols which either do not react at all or react with difficulty with β-ketonic esters in the presence of sulphuric acid give chromones in the presence of phosphorus pentoxide as the condensing agent. The condensation of ethyl acetoacetate with 3-(4'-hydroxyphenyl)coumarin in the presence of phosphorus pentoxide was attempted but the original coumarin derivative was recovered unchanged.

Further, as stated in the general introduction phenols condense with β-ketonic esters either on prolonged heating at high temperature or on refluxing in a high boiling solvent to give chromones. 3-(4'-Hydroxyphenyl) coumarin was therefore refluxed with ethyl acetoacetate in diphenyl ether for 2 hours. On removal of the solvent however the original coumarin was recovered.

EXPERIMENTAL

3-(4'-Hydroxyphenyl)coumarin :

A solution of 3-(4'-methoxyphenyl)coumarin(1 g.) prepared according to Meerwein et al.[1] in dry benzene (50 ml.) was mixed with anhydrous aluminium chloride(3 g.) and heated at 50° for 3 hours. The product separating on decomposing the reaction mixture with cold hydrochloric acid was purified by taking it in sodium hydroxide solution. It crystallised from alcohol in light brown needles, m.p.202°. Yield 0.4 g. Bhandari et al.[12] give the same m.p.

3-(3'-Formyl-4'-hydroxyphenyl)coumarin :

A mixture of 3-(4'-hydroxyphenyl)coumarin (1 g.), hexamethylene tetramine (2.5 g.) and glacial acetic acid (25 ml.) was refluxed gently for 1/2 hour. Hydrochloric acid (10 ml. ; 1:1) was then added and the heating continued for further 10 minutes. The solid obtained on dilution of the reaction mixture with water crystallised from acetic acid. M.P. 238°. Yield 0.4 g. It gave a brown colouration with alcoholic ferric chloride.

Analysis : Found : C,71.88 ; H,3.68 %.

$C_{16}H_{10}O_4$ requires : C,72.18 ; H,3.76 %.

3,6'-Bicoumarinyl :

The above formyl derivative (1 g.) was refluxed with fused sodium acetate (3 g.) and acetic anhydride(10 ml.) at 170-80° in an oil bath for 12 hours. The solid obtained on pouring the reaction mixture in cold water was crystallised from acetic acid in small pale yellow

needles (0.3 g.), m.p. 218-20°.

Analysis : Found : C,74.22 ; H,3.22 %.

$C_{18}H_{10}O_4$ requires : C,74.49 ; H,3.45 %.

3-(3'-Formyl-4'-carbethoxymethoxyphenyl)coumarin :

3-(3'-Phenyl-4'-hydroxyphenyl)coumarin(0.9 g.) was refluxed on a steam bath with bromoacetic ester(0.7 g.) in the presence of anhydrous potassium carbonate (4 g.) in dry acetone for 2 hours. The acetone was then removed and water was added. The solid obtained crystallised from dilute acetic acid in white shining needles (0.8 g.), m.p.171-72°.

Analysis : Found : C,68.11 ; H,4.33 %.

$C_{20}H_{16}O_6$ requires : C,68.19 ; H,4.54 %.

3-(3'-Formyl-4'-carboxymethoxyphenyl)coumarin :

The above ester (1 g.) was heated on a steam bath with 5 % sodium hydroxide solution for 15 minutes and then kept overnight. The clear liquid on acidification gave the acid which crystallised from dilute acetic acid in white needles (0.8 g.), m.p. 218°.

Analysis : Found : C,66.19 ; H,3.26 %.

$C_{18}H_{12}O_6$ requires : C,66.68 ; H,3.70 %.

3-(5'-Benzofuranyl)coumarin :

The above acid (1 g.) was refluxed with freshly fused sodium acetate (3 g.) and acetic anhydride (10 ml.) on a wire gauze for 2 1/2 hours. The reaction mixture was then poured in water and kept overnight. The separated solid crystallised from dilute alcohol in tiny yellow needles (0.3 g.), m.p. 175-76°.

needles (0.3 g.), m.p. 175-76°.

Analysis : Found : C,77.67 ; H,4.15 %.

$C_{17}H_{10}O_3$ requires : C,77.85 ; H,3.81 %.

3-(3'-Acetyl-4'-hydroxyphenyl)coumarin :

3-(4'-Acetoxyphenyl)coumarin (1 g.) was heated with anhydrous aluminium chloride (3 g.) at 140-45° in an oil bath for 3 1/2 hours. The solid which separated on pouring the reaction mixture in ice cold hydrochloric acid (1:1) was taken in 10 % sodium hydroxide solution and crystallised from dilute acetic acid in colourless needles (0.5 g.), m.p. 168°. It gave dark violet colour with alcoholic ferric chloride solution.

Analysis : Found : C,72.85 ; H,4.18 %.

$C_{17}H_{12}O_4$ requires : C,72.85 ; H,4.28 %.

3-(3'-Acetyl-4'-carbethoxymethoxyphenyl)coumarin :

The above acetyl derivative (1 g.) was refluxed with ethylbromoacetate (0.7 g.) and anhydrous potassium carbonate (4 g.) in dry acetone on a steam bath for 2 hours. The product obtained on working up as before crystallised from dilute acetic acid in white needles (0.7 g.), m.p. 135°.

Analysis : Found : C,68.87 ; H,4.81 %.

$C_{21}H_{18}O_6$ requires : C,68.85 ; H,4.91 %.

3-(3'-Acetyl-4'-carboxymethoxyphenyl)coumarin :

The above ester (1.5 g.) was heated on a steam bath for 15 minutes with 5 % sodium hydroxide solution and then kept overnight. The solid obtained on acidification

crystallised from dilute acetic acid in white shining needles(1 g.), m.p.225-26°.

Analysis : Found : C,67.16 ; H,3.89 %.

$C_{19}H_{14}O_6$ requires : C,67.45 ; H,4.14 %.

3-(3'-Methyl-5'-benzofuranyl)coumarin :

The above acid (0.8 g.) was refluxed on a wire-gauze with freshly fused sodium acetate (3 g.) and acetic anhydride (10 ml.) for 2 1/2 hours. The product obtained on pouring the reaction mixture in water crystallised from dilute acetic acid in white needles (0.4 g.), m.p. 151°.

Analysis : Found : C,78.16 ; H,4.06 %.

$C_{18}H_{12}O_3$ requires : C,78.27 ; H,4.34 %.

3-(3'-Cinnamoyl-4'-hydroxyphenyl)coumarin :

A solution of 3-(3'-acetyl-4'-hydroxyphenyl)coumarin (1 g.) in alcohol was mixed with benzaldehyde (0.4 g.) and potassium hydroxide solution (10 ml.; 100 %) was then added. After keeping for 24 hours the clear solution was diluted with cold water and acidified with hydrochloric acid. A yellow product separated which was washed with sodium bicarbonate solution. It crystallised from acetic acid in yellow needles (0.6 g.), m.p. 214-15°. It gave red colour with concentrated sulphuric acid and a positive Wilson test.

Analysis : Found : C,77.89 ; H,4.33 %.

$C_{24}H_{16}O_4$ requires : C,78.27 ; H,4.34 %.

3-(3'-Cinnamoyl-4'-acetoxyphenyl)coumarin :

3-(3'-Cinnamoyl-4'-hydroxyphenyl)coumarin(1 g.) was refluxed with sodium acetate (3 g.) and acetic anhydride (10 ml.) for 1 1/2 hours. The product separating on pouring the reaction mixture in water was washed with sodium hydroxide solution. It crystallised from benzene-petroleum ether. M.P. 143-44°.

Analysis : Found : C,76.50 ; H,4.39 %.

$C_{26}H_{18}O_5$ requires : C,76.10 ; H,4.39 %.

3-(6'-Flavonyl)coumarin :

3-(3'-Cinnamoyl-4'-hydroxyphenyl)coumarin (1 g.) was refluxed with selenium dioxide (3 g.) in iso-amyl alcohol (75 ml.) at 140-50° in an oil bath for 24 hours. It was then filtered hot. The product separating from the filtrate crystallised from dilute acetic acid. M.P.251°. Yield 0.4 g.

Analysis : Found : C,78.84 ; H,3.72 %.

$C_{24}H_{14}O_4$ requires : C,78.68 ; H,3.82 %.

3-(3'-Acetyl-4'-benzoyloxyphenyl)coumarin :

3-(3'-Acetyl-4'-hydroxyphenyl)coumarin (1 g.) was refluxed with benzoyl chloride (0.5 g.) and anhydrous potassium carbonate (4 g.)in dry acetone for 6 hours. The solid obtained on removal of acetone and addition of water crystallised from dilute alcohol. M.P.148°. Yield 0.7 g.

Analysis : Found : C,75.34 ; H,4.24 %.

$C_{24}H_{16}O_5$ requires : C,75.01 ; H,4.16 %.

3-[3'-(ω-Benzoylacetyl)-4'-hydroxyphenyl] coumarin :

A solution of the above benzoyl derivative(1.5 g.) in pyridine was mixed with powdered potassium hydroxide (9 g.). After keeping it at room temperature for 4 hours ice cold dilute hydrochloric acid was added. The product obtained was washed with sodium bicarbonate solution. It crystallised from benzene in yellow crystals (0.8 g.), m.p.218°.

Analysis : Found : C,74.78 ; H,4.15 %.

$C_{24}H_{16}O_5$ requires : C,75.01 ; H,4.16 %.

Cyclisation :

The above β-diketone (0.8 g.) was dissolved in concentrated sulphuric acid (5 ml.) and kept at room temperature for 4 hours. It was then poured in cold water and the solid obtained crystallised from dilute acetic acid in white needles (0.4 g.), m.p. 251°.Mixed m.p. with 3-(6'-flavonyl)coumarin described above was not depressed.

3-[3'(p-methoxycinnamoyl)-4'-hydroxyphenyl]coumarin :

To a mixture of 3-(3'-acetyl-4'-hydroxyphenyl)coumarin (2 g.) and anisaldehyde (3 ml.) in alcohol, potassium hydroxide solution (20 ml. ; 100 %) was added and the mixture was kept for 24 hours at room temperature and then diluted with water and acidified with hydrochloric acid. The yellow product obtained was washed with sodium bicarbonate solution and then crystallised from glacial acetic acid in yellow crystals(0.9 g.), m.p.205°. It gave

red colour with concentrated sulphuric acid and a positive Wilson test.

Analysis : Found : C,75.51 ; H,4.45 %.

$C_{25}H_{18}O_5$ requires : C,75.37 ; H,4.52 %.

3-[3'-(6-Methoxycinnamoyl)-4'-acetoxyphenyl]coumarin :

The above product (0.5 g.) was heated with fused sodium acetate and acetic anhydride for 1 1/2 hours. The solid obtained on pouring the reaction mixture in water was washed with sodium hydroxide solution and crystallised from acetic acid, M.P. 168°.

Analysis : Found : C,73.28 ; H,4.57 %.

$C_{27}H_{20}O_6$ requires : C,73.62 ; H,4.54 %.

3-(4''-Methoxy-6'-flavonyl)coumarin :

The above hydroxy ketone (0.5 g.) was refluxed with selenium dioxide (1.5 g.) in isoamyl alcohol at 140-50° in an oil bath for 24 hours. The product obtained on working up the reaction mixture as before crystallised from nitrobenzene in pale yellow needles (0.2 g.),m.p.298°.

Analysis : Found : C,75.61 ; H,4.02 %.

$C_{25}H_{16}O_3$ requires : C,75.75 ; H,4.04 %.

3-(3'-Benzoyl-6'-flavonyl)coumarin :

A mixture of 3-(3'-acetyl-4'-hydroxyphenyl)coumarin (1 g.),fused sodium benzoate (3 g.) and benzoic anhydride (5 g.) was heated in an oil bath at 180-90° for 12 hours. The solid obtained on dilution of the reaction mixture with water was washed with sodium bicarbonate solution. It

crystallised from glacial acetic acid in tiny yellow needles (0.3 g.), m.p. 263-64°.

Analysis : Found : C,78.72 ; H,3.86 %.

$C_{31}H_{18}O_5$ requires : C,79.14 ; H,3.82 %.

Attempted debenzoylation :

The above 3-(3'-benzoyl-6'-flavonyl)coumarin (0.5 g.) was refluxed with alcoholic potassium hydroxide solution (10 % ; 10 ml.) for 2 hours. The product obtained on acidification of the reaction mixture crystallised from glacial acetic acid. M.P. 262°. Mixed m.p. with the original flavonyl coumarin was not depressed.

Attempted condensation of 3-(4'-hydroxyphenyl)coumarin with (i) malic acid in the presence of sulphuric acid and (ii) ethylacetoacetate in the presence of (a) sulphuric acid (b) phosphorus pentoxide (c) in boiling diphenyl ether without any condesning agent.

(i) Condensation wwith malic acid in the presence of sulphuric acid :

A mixture of 3-(4'-hydroxyphenyl)coumarin (1 g.), malic acid (1 g.) and concentrated sulphuric acid (90 % ; 3 ml.) was heated at 140-50° until the effervescence ceased. The solid separating on adding the reaction mixture to water was found to be identical with the original coumarin on direct comparison.

(iia) Condensation with ethylacetoacetate in the presence of concentrated sulphuric acid :

3-(4'-Hydroxyphenyl)coumarin (1 g.) was mixed with

ethyl acetoacetate (1 g.) and sulphuric acid (2 ml. ; 80 %) was added slowly. The reaction mixture was kept for 24 hours. and then poured in ice. The product obtained crystallised from dilute alcohol in white needles, m.p. 201°. Mixed m.p. with the original coumarin was not depressed.

(iib) Condensation with ethyl acetoacetate in the presence of phosphorus pentoxide :

A mixture of 3-(4'-hydroxyphenyl)coumarin (0.5 g.), ethyl acetoacetate (0.5 g.), absolute alcohol (10 ml.) and phosphorus pentoxide (1.8 g.) was heated on a steam bath for 2 hours. The product separating on pouring the reaction mixture in water was found to be the original coumarin.

(iic) Condensation with ethyl acetoacetate in boiling diphenyl ether :

A solution of 3-(4'-hydroxyphenyl)coumarin (0.8 g.) in diphenyl ether (5 ml.) was refluxed with ethyl acetoacetate (0.8 g.) for 4 hours. The product obtained on removal of the solvent was the original coumarin.

REFERENCES

1. H.Meerwein,E.Buchner and K.V.Emster., J.Prakt.Chem., 152, 237 (1939).
2. G.Dyson., J.Chem.Soc.Trans., 51, 62 (1887).
3. C.F.Huebner and K.P.Link., J.Amer.Chem.Soc., 67, 99 (1945).
4. S.S.Lele, M.G.Patel and S.Sethna., J.Chem.Soc., 969 (1961).
5. R.N.Sen and S.Dutt., J.Indian Chem.Soc., 8, 223 (1931).
6. A.J.Earle and L.E.Lyons., J.Chem.Soc., 1575 (1950).
7. J.Miyazaki and S.Mihashi., Chem.Pharm.Bull., Tokyo., 12, 1232 (1964).
8. J.Miyazaki, S.Mihashi and K.Okabayashi., Chem.Pharm. Bull., Tokyo., 12, 1236 (1964).
9. R.R.Spencer, S.C.Witt, R.E.Lundin and E.M.Bickoff., Agr. and Food Chem., 15, 536 (1967).
10. B.B.Dey and K.K.Row., J.Indian Chem.Soc., 1, 107 (1924).
11. K.A.Thakar., J.Indian Chem.Soc., 40, 397 (1963).
12. P.R.Bhandari, J.L.Bose and S.Siddiqui., J.Sci.Ind. Res., India. 8B, No.11, 189 (1949).
13. St.V.Kostanecki and G.Rossbach., Ber., 29, 1488 (1896).
14. W.Baker., J.Chem.Soc., 1386 (1933).
15. H.S.Mahal and K.Venkataraman, Current Sci., 4, 214 (1933); J.Chem.Soc., 1767 (1934).
15. V.Kostanecki and A.Rozycki., Ber., 34, 102 (1901). ; J.Allan and R.Robinson., J.Chem.Soc., 2192 (1924).
16. C.L.Wilson., J.Amer.Chem.Soc., 61, 2303 (1939).

17. P.L.Trivedi, S.Sethna and R.C.Shah., J.Indian Chem. Soc., 20, 171 (1943).;

18. S.Sethna and R.Phadke., Organic Reactions., Vol.VII (Wiley) New York., 1-58 (1953).