List of Research Papers

1. Studies in the syntheses of cyclohexenocoumarins. Part I. By M.G.Parekh and K.N.Trivedi. J.Indian Chem. Soc., 43, No.12, 801 (1966).

2. Studies in the syntheses of coumarino-α-pyrones and furocoumarins. Part III. By M.G.Parekh and K.N.Trivedi J.Indian Chem.Soc., 45, No. 7, 649 (1968).

3. Studies in 4-hydroxycoumarins. By V.N.Dholakia, M.G. Parekh and K.N.Trivedi. Australian J.Chem. 21, 2345-7 (1968).

[Jour. Indian Chem. Soc., Vol. 43, No. 12, 1966]

Studies in the Synthesis of Cyclohexenocoumarins. Part I

M. G. Parekh and K. N. Trivedi

β-(2:4-Dihydroxybenzoyl) propionic acid obtained from resorcinol on succinoylation and Clemmensen reduction has yielded butyric acid derivative. This on Pechmann reaction with ethyl acetoacetate, has furnished 7-hydroxy-4-methylcoumarin-6-butyric acid. The methyl ether has been cyclised to 7-methoxy-4-methyl-4'-ketocyclohexeno (5', 6'-5, 6)coumarin in poor yield using polyphosphoric acid or anhydrous aluminium chloride as cyclising agents.

Sen and Basu[1] condensed different phenols with ethyl cyclohexanone-2-carboxylate in the presence of conc. sulphuric acid and obtained corresponding cyclohexeno (1',2'-4,3)-coumarin derivatives. Chowdhry and Desai[2] prepared different cyclohexenocoumarins by the condensation of phenols with cyclic β-ketonic esters using phosphorus oxychloride, anhydrous aluminium chloride and sulphuric acid as condensing agents. It was thought of interest to synthesise different cyclohexenocoumarins in which cyclohexene ring is fused in 5,6-positions of the coumarin ring systems.

Resorcinol on succinoylation at room temperature gave β-(2,4-dihydroxybenzoyl)-propionic acid[3] which on Clemmensen reduction afforded γ-(2,4-dihydroxyphenyl)butyric acid[4,5]. The above acid on Pechamann reaction with ethyl acetoacetate and sulphuric acid gave 7-hydroxy-4-methylcoumarin-6-butyric acid and its ethyl ester. The structure of the latter was proved by esterification of the former with ethanol and sulphuric acid as also by hydrolysis. This ester on methylation gave ethyl 7-methoxy-4-methyl-coumarin-6-butyrate which on treatment with sodium hydroxide solution and excess of dimethyl sulphate furnished the corresponding cinnamic acid, thus confirming the coumarin structures assigned to these products.

This is a unique case of esterification taking place during the Pechmann condensation. The Pechmann condensation of β-resorcylic acid with ethyl acetoacetate and sulphuric acid as condensing agent gave the decarboxylated product rather than the esterfied one.[6] In order to study this esterification process further, the acid was condensed with ethyl benzoyl acetate in the presence of sulphuric acid when it gave 7-hydroxy-4-phenyl-coumarin-6-butyric acid and its ethyl ester. Similar condensation with methyl acetoacetate afforded 7-hydroxy-4-methylcoumarin-6-butyric acid and its methyl ester. The structure of the methyl ester was proved by hydrolysis to the above acid and also by esterification of the acid with methanol and concentrated sulphuric acid.

1. Sen and Basu, *this Journal*, 1928, **5**, 467.
2. Chowdhry and Desai, *Proc. Indian Acad. Sci.*, 1938, **8A**, 1.
3. Desai and Shroff, *J. Uni. Bombay*, 1941, **10**, 397.
4. Desai and Figueredo, *Proc. Indian Acad. Sci.*, 1941, **14A**, 605.
5. Brown *et al.*, *Ber.*, 1941, **74B**, 1772.
6. Shah, *et al.*, *this Journal* 1937, **14**, 717.

7-Hydroxy-4-methylcoumarin-6-butyric acid on methylation gave methyl-7-methoxy-coumarin-6-butyrate which on hydrolysis with 6% sodium hydroxide solution yielded 7-methoxy-4-methylcoumarin-6-butyric acid. This acid on cyclisation furnished 7-methoxy-4-methyl-4'-ketocyclohexeno(5',6'-5,6)coumarin in very poor yield by using either polyphosphoric acid or by Johnson's inverse process of cyclisation with phosphorus pentachloride and anhydrous aluminium chloride[7].

EXPERIMENTAL

γ-(2,4-Dihydroxyphenyl)butyric Acid.—β-(2,4-Dihydroxybenzoyl) propionic acid was prepared by succinoylation of resorcinol according to Desai and Shroff[3].

The above acid (10 g.) was heated with zinc amalgam (30 g.) and hydrochloric acid (conc. 75 ml) for 15 hr. γ-(2,4-Dihydroxyphenyl) butyric acid was extracted with ether and crystallised from benzene as colorless crystals, m.p. 111°. Julis *et al.*[5] have reported the reduced acid as a viscous oil but Desai and Figueredo[4] have reported m p. 105°.

7-Hydroxy-4-methylcoumarin-6-butyric Acid and its Ethyl Ester.—γ-(2,4-Dihydroxyphenyl)butyric acid (6 g) was mixed with ethyl acetoacetate (6 g.) and 80% sulphuric acid (25 ml) in the cold Next day it was poured on ice water. The product was treated with bicarbonate solution and filtered. The filtrate on acidification gave an *acid* which was crystallised from acetic acid in shining needles, m p. 230°, yield 5.4 g. (Found : C, 64 25 ; H, 5.47. $C_{14}H_{14}O_3$ requires C, 64.11 ; H, 5.38%). The residue was found to be *ethyl 7-hydroxy-4-methylcoumarin-6-butyrate* which was crystallised from dil. ethanol in shining plates, m.p. 153°, yield 0.2 g. (Found : C, 66.19 ; H, 6.25. $C_{16}H_{18}O_5$ requires C, 66.2 ; H, 6.2%). The ester (0.5 g.) was hydrolysed whith 6% sodium hydroxide solution (15 ml). Next day it was filtered and acidified. It was crystallised from acetic acid in shining needles; m.p. of this acid and the acid prepared as above was identical. This ester was also prepared by refluxing the above acid with ethanol and concentrated sulphuric acid for 3 to 4 hr. M.p. and mixed m.p. were 153°. *Acetyl derivative*, prepared as usual, had m.p. 124°. (Found : C, 64.48 ; H, 5.77. $C_{18}H_{20}O_4$ requires C, 65.0 ; H, 6 0%). *Methoxy derivative*, prepared as usual, had m.p. 116°. (Found : C, 67.45 ; H, 6.45. $C_{17}H_{20}O_5$ requires C, 67.1 ; H, 6.5%).

Methyl 7-Methoxy-4-methylcoumarin-6-butyrate.—7-Hydroxy-4-methylcoumarin-6-butyric acid (1 g.) was mixed with dry acetone (30 ml), anhydrous potassium carbonate (1 g.), dimethyl sulphate (1 g.) and refluxed on a water bath for 6 to 7 hr. The residue, on evaporation of acetone, was washed with dil. sodium hydroxide solution and crystallised from ethanol in colorless plates, m.p. 118°, yield 0.6 g. (Found : C, 66.45 ; H, 6.21. $C_{16}H_{18}O_5$ requires C, 66.19 ; H, 6.25%).

7-Methoxy-4-methylcoumarin-6-butyric Acid.—Methyl-7-methoxy-4-methylcoumarin-6-butyrate (1 g.) was mixed with 6 % sodium hydroxide solution (25 ml). Next day it was filtered, acidified and crystallised from dil. ethanol in shining needles, m.p. 176°, yield 0.5 g. (Found : C, 65.48 ; H, 5.85. $C_{15}H_{16}O_5$ requires, C, 65.21 ; H, 5.84%.).

7-Methoxy-4-methyl-4'-ketocyclohexene (5', 6'-5,6) coumarin.—7-Methoxy-4-methyl-coumarin-6-butyric acid (3.0 g.) was mixed with phosphorus pentachloride (4 g.) and dry

7. Johnson and Glenn, *J. Amer. Chem. Soc.*, 1949, **71**, 1012.

benzene (20 ml). The mixture was refluxed on a water bath for 6 to 7 hr. Benzene, phosphorus pentachloride and volatile matter were removed by applying vacuum at 60° to 70°. Benzene (15-20 ml) was added and the process repeated. The acid chloride was dissolved in benzene and added slowly to the mixture of anhydrous aluminium chloride (3 g.) and dry benzene (40 ml) in cold condition. It was stirred for 2 to 3 hr. and about 50 ml of ether was added with stirring. The organic layer was washed with hydrochloric acid, sodium bicarbonate solution and potassium hydroxide solution. On evaporation of the ether the *coumarin* was obtained which was crystallised from benzene light-petroleum (m.p. 160°.) (Found: C, 69.56, H, 5.21. $C_{15}H_{14}O_4$ requires C, 69.76; H, 5.42%).

It was also prepared by heating the mixture of the acid (1 g.) and polyphosphoric acid (10 g.) at 170° for 30 min. The mixture was added to ice-water, filtered and washed with sodium hydroxide solution The compound was crystallised from benzene-light-petroleum. m p. and mixed m.p. with above sample was 160°.

7-Hydroxy-4-phenylcoumarin-6-butyric Acid and its Ethyl Ester.—γ-(2,4-Dihydroxyphenyl) butyric acid (5 g.) was mixed with ethyl benzoylacetate (5 g.) and 80% sulphuric acid (20 ml). Next day the mixture was poured on ice water, and worked up as above. The acid was crystallised from ethanol in rosey plates, m.p. 235°, yield 4.2 g. (Found: C, 70.39; H, 4 72. $C_{19}H_{16}O_5$ requires C, 70.36; H, 4.98%).

Ethyl 7-Hydroxy-4-phenylcoumarin-6-butyrate was crystallised from ethanol in shining plates, m.p. 156°, yield, 0.1 g. (Found: C, 72.2; H, 5.63. $C_{21}H_{20}O_5$ requires C, 71.9; H, 5.69%).

7-Hydroxy-4-methylcoumarin-6-butyric Acid and its Methyl Ester.—γ-(2,4-Dihydroxyphenyl) butyric acid (2 g.) was mixed with methyl acetoacetate (2 g.) and 80% sulphuric acid (10 ml) and worked up as above. 7-Hydroxy-4-methylcoumarin-6-butyric acid was crystallised from ethanol in colorless crystals, m.p. 230°, yield, 1.5 g. *Methyl-7-hydroxy-4-methylcoumarin-6-butyrate* was crystallised from ethanol in shining plates, m.p. 154°. (Found: C, 65.57; H, 5.90. $C_{15}H_{16}O_5$ requires C, 65.21; H, 5.84%).

2,4-Dimethoxy-5-carboxypropyl-β-methylcinnamic Acid.—Ethyl 7-methoxy-4-methylcoumarin-6-butyrate (0.5 g.) was heated with 5% sodium hydroxide solution (15 ml) for 15 min. Dimethyl sulphate (2 ml) was then added with constant shaking. More sodium hydroxide and dimethyl sulphate were added and the mixture was heated for a few minutes. The alkaline solution was left overnight. It is filtered and the filtrate on acidification gave the above product which was crystallised from ethanol in colorless crystals, m.p. 195°, yield, 0.1 g. (Found: C, 61.84; H, 6.42. $C_{16}H_{20}O_6$ requires C, 62.33; H, 6.49%).

Thanks are due to Prof. Suresh Sethna for taking keen interest in the work and also to Dr. S. S. Lele for carrying out the microanalysis of the samples.

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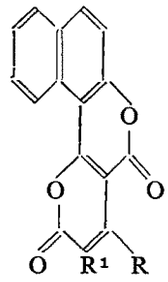
NOTES

Studies in the Synthesis of Coumarino-α-Pyrones and Furocoumarins : Part III.*

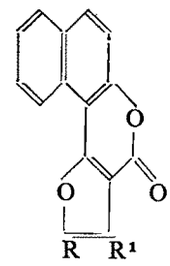
M. G. Parekh and K. N. Trivedi

In order to study the relationship between structure and anti-coagulant activity of benzopyranyl (3,2-c) pyran-2, 8-diones and 4H furo (3, 2-c) benzopyran-4-ones, it was thought of interest to synthesise benzo (3, 4) benzopyranyl (3, 2-c) pyran-2, 8-dione (Ia) and its 10-methyl derivative (Ib) and degrade them respectively to 4H-furo (3, 2-c) benzo (6,7) benzopyranyl-4-one (IIa) and its 3-methyl derivative (IIb) according to the method developed by Trivedi and Sethna[1].

4-Hydroxy-5, 6-benzocoumarin on Pechmann condensation with malic acid in the presence of 80%sulphuric acid gave (Ia) which on bromination yielded its 9-bromo derivative (Ic). This bromo derivative on hydrolysis with 10% sodium carbonate solution afforded 4H-furo (3, 2-c) benzo (6, 7) benzopyranyl-4-one-2-carboxylic acid (IIc) which was decarboxylated to (IIa).



Ia : $R=R^1=H$
b : $R=CH_3$; $R^1=H$
c : $R=H$; $R^1=Br$
d : $R=CH_3$; $R^1=Br$



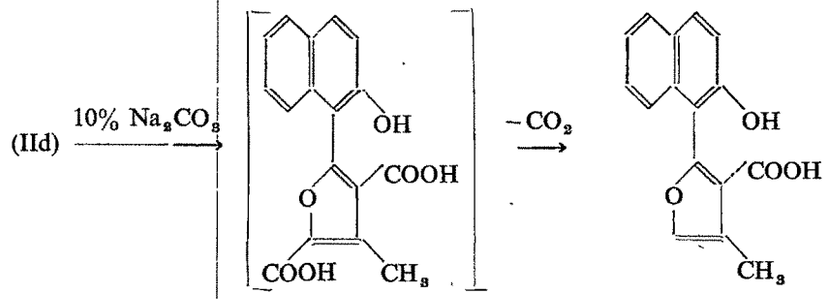
IIa : $R=R^1=H$
b : $R=H$; $R^1=CH_3$
c : $R=COOH$; $R^1=H$
d : $R=COOH$; $R^1=CH_3$

4-Hydroxy-5, 6-benzocoumarin on a similar condensation with ethyl acetoacetate gave 10-methyl benzo (3, 4) benzopyranyl (3, 2-c) pyran-2, 8-dione (Ib) as reported by Patell and Usgaonker[2]. This on bromination gave the 9-bromo derivative (Id), which on hydrolysis with 10% sodium carbonate solution afforded 2-(o-hydroxy-α-naphthyl) -4-methyl furan-3-carboxylic acid (III) and not 3-methyl-4H-furo (3, 2-c)

* Part II, *This Journal*, 1966, **43**, 804.

1. Trivedi and Sethna, *This Journal*, 1963, **40**, 563.
2. Patell and Usgaonker, *This Journal*, 1966, **43**, 536.

benzo (6, 7) benzopyranyl-4-one-2--carboxylic acid (IId). The formation of (III) from the expected (IId) is shown according to following route through the intermediate (IV), which could not be isolated.



(IV) (III)

The acid (III) was cyclised to (IIb) when refluxed with hydrochloric acid.

EXPERIMENTAL

Benzo (3,4) benzopyranyl (3, 2-c) pyran-2, 8-dione (Ia) : A mixture of 4-hydroxy-5, 6-benzocoumarin (4 g) and malic acid (4 g) was heated on a steam bath with gradual addition of 80% sulphuric acid (40 ml) in 45 min. period. Heating was continued for further 4 hr. The reaction mixture was added to ice and the product filtered, washed with sodium bicarbonate solution, dried and crystallised from benzene in shining crystals, 310°. Yield 1 g. (Found : C, 72.38 ; H, 3.31. $C_{16}H_8O_4$ requires C, 72.73 ; H, 3.03%).

9-Bromo benzo (3, 4) benzopyranyl (3, 2-c) pyran-2, 8-dione (Ic) : (Ia) (0.66 g) was dissolved in minimum amount of acetic acid and bromine, dissolved in acetic acid (9 ml ; 20% ; 4 mole) was added and the mixture heated on a water bath for 3 hr. The reaction mixture was then added to ice and the bromo derivative filtered, dried and crystallised from benzene m. p. 282°. Yield 0.5 g. (Found : Br, 23.68. $C_{16}H_7O_4Br$ requires Br, 23.32%).

4H-Furo (3,2-c) benzo (6, 7) benzopyranyl-4-one carboxylic acid (IIc) : (Ic) (0.5 g) was mixed with sodium carbonate solution (10 ml ; 10%) and was refluxed for 4 hr. The solution was allowed to cool and filtered. The filtrate on acidification gave the product which was crystallised from acetic acid in yellowish crystals, m.p. 318°. Yield 0.1 g. (Found : C, 68.47 ; H, 2.50. $C_{16}H_8O_5$ requires C, 68.57 ; H, 2.85%).

4H-Furo (3, 2-c) benzo (6, 7) benzopyranyl-4-one (IIa) : (IIc) (0.4) was heated on a sand bath with quinoline (5 ml) and copper bronze (0.2 g) for 1 hr. The reaction mixture was filtered hot, acidified with hydrochloric acid and filtered again. The filtrate was diluted with water and extracted with ether. The product

obtained after evaporation of ether was washed with sodium bicarbonate solution and crystalli-sed from dil. acetic acid in colourless needles, m.p. 181°. Yield 0.1 g. (Found : C, 76.51 ; H, 3.16. $C_{15}H_8O_3$ requires C, 76.27 ; H, 3.41%).

9-Bromo-10 methyl benzo (3, 4) benzopyranyl (3, 2-c) pyran-2, 8-dione (Id) : (Ib) (1.5 g) was dissolved in minimum amount of acetic acid and bromine dissolved in acetic acid (18 ml ; 20% ; 4 mole) was added slowly with constant stirring and the mixture was heated on a water bath for 3 hr. The compound separated was filtered, dried and crystallised from benzene in yellow shining needles, m.p. 235°. Yield 1 g. (Found : Br, 22.67 ; $C_{17}H_9O_4Br$ requires Br, 22.4%).

2-(o-*Hydroxy-α-naphthyl)-4-methyl furan-3-carboxylic acid (III)* : (Ic) (0.8 g) was refluxed with sodium carbonate solution (15 ml ; 10%) for 2 hr. The reaction mixture was allowed to cool, filtered and acidified. The product was purified by dissolving it in sodium carbonate solution reprecipitated and crysttllised from hot water in colourless crystals, m.p. 182°. Yield 0.1 g. (Found : C 17.94 ; H, 4.75. $C_{16}H_{12}O_4$ requires C, 71.-61 ; H, 4.48%).

3-*Methyl-4H-furo (3, 2-c) benzopyranyl-4-one (IIb)* : 2-(*o*-Hydroxy-α-naphthyl)-4-methyl furo-3-carboxylic acid (0.5 g) was dissolved in ethanol and refluxed with hydrochloric acid (5 ml) for 4 hr. The separated product was filtered and crystallise from acetic acid in shining needles, m.p. 247°. Yield 0·1 g. (Found : C, 74.72 ; H, 4.27. $C_{14}H_{10}O_3$ requires C, 74.33 ; H, 4.43%).

Thanks are due to Professor Sethna for taking keen interest in the work and also to Dr. Lele for carrying out the microanalysis of the samples.

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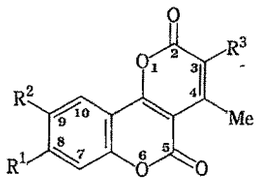
STUDIES IN 4-HYDROXY COUMARINS*

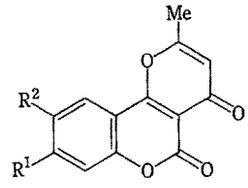
II.† α- AND γ-PYRONES FROM 4-HYDROXY COUMARINS

By V. N. Dholakia,‡ M. G. Parekh,‡ and K. N. Trivedi‡§

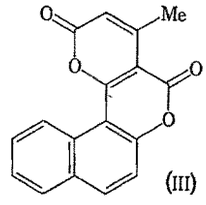
Arora and Mathur[1] reported that a methyldioxophenylpyranobenzopyran (Ia) possesses anticoagulant activity comparable to that of dicoumarol. It was thought of interest to prepare α- and γ-pyrones having different groups in the benzenoid part of the coumarin ring system and to study their anticoagulant activity.



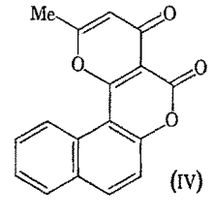
	R^1	R^2	R^3
(Ia)	H	H	Ph
(Ib)	H	H	H
(Ic)	H	Me	H
(Id)	OMe	H	H



	R^1	R^2
(IIa)	H	H
(IIb)	H	Me
(IIc)	OH	H



(III)



(IV)

Woods[2] condensed 4-hydroxycoumarin with ethyl acetoacetate in the presence of trifluoroacetic acid and claimed to have obtained 2-methyl-4,5-dioxo-4*H*,5*H*-pyrano[3,2-c]benzopyran (IIa), m.p. 252°, principal absorption bands in the i.r. region, 3344, 1727, 1631, 1613 cm^{-1}. Mustafa *et al.*[3] synthesized (IIa), yellow crystals, m.p.

* Manuscript received March 19, 1968.

† Part I, *J. scient. ind. Res.* B, 1962, **21**, 402.

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[1] Arora, R. B., and Mathur, C. N., *Brit. J. Pharmac. Chemother.*, 1963, **20**, 29.

[2] Woods, L. L., *J. org. Chem.*, 1962, **27**, 696.

[3] Mustafa, A., Hsihmat, O. H., Zayed, S. M. A. D., and Ahmed Nawar, A., *Tetrahedron*, 1963, **19**, 1831.

246°, carbonyl stretching frequencies, 1754 cm^{-1} and 1667 cm^{-1}, by different routes and claimed that it was identical in all respects with the compound prepared according to Woods.[2] On repeating Woods's work, it has now been found that 4-methyl-2,5-dioxo-2*H*,5*H*-pyrano[3,2-*c*]benzopyran (Ib), colourless crystals, m.p. 243°, carbonyl stretching frequency in the i.r. region, 1740 cm^{-1}, is the only isolable product when the condensation is carried out in the presence of trifluoroacetic acid. The mixed m.p. with an authentic sample of (Ib) prepared by using either concentrated sulphuric acid[3,4] or anhydrous aluminium chloride[4] was not depressed; but the mixed m.p. with an authentic sample of (IIa), yellow crystals, m.p. 246°, carbonyl stretching frequencies in the i.r. region, 1760 cm^{-1} and 1670 cm^{-1}, prepared according to Mustafa *et al.*[3] was depressed by 20°.

This observation is further supported when three substituted 4-hydroxycoumarins are condensed with ethyl acetoacetate in the presence of trifluoroacetic acid: they yield the same known compounds (Ic), (Id), and (III) which were obtained by using either conc. sulphuric acid or anhydrous aluminium chloride as condensing agent. 3-Acetyl-4-hydroxy-6-methylcoumarin, 3-acetyl-4-hydroxy-7-methoxycoumarin, and 3-acetyl-4-hydroxybenzo[*f*]coumarin when subjected to Claisen condensation followed by cyclization with 25% sulphuric acid gave (IIb), (IIc), and (IV) respectively; demethylation took place during cyclization to yield (IIc). (Ic) and (III) differed considerably from the corresponding (IIb) and (IV) in i.r. spectra and melting point. The carbonyl stretching frequencies in the i.r. region of the above compounds are (Ic), 1745; (Id), 1740; (III), 1745; (IIb), 1760, 1672; (IIc), 1760, 1672; and (IV), 1760, 1670 cm^{-1}.

Experimental

Infrared spectra ($CHCl_3$) were determined with a Perkin–Elmer 237 grating spectrophotometer. All melting points were uncorrected.

*4,9-Dimethyl-2,5-dioxo-2*H,5H*-pyrano[3,2-c]benzopyran (Ic)*

4-Hydroxy-6-methylcoumarin (1 g) was heated with ethyl acetoacetate (1 ml) in trifluoroacetic acid (5 ml) on a sand-bath for 15 hr. After the completion of the reaction, a few millilitres of ethanol were added and the mixture kept overnight. The product which separated was filtered off and washed with sodium bicarbonate solution. The residue was crystallized from acetic acid, colourless crystals, m.p. 197–198° (lit.[4] 197–198°), yield 0·3 g. Mixed m.p. with an authentic sample prepared by using conc. sulphuric acid as condensing agent was not depressed.

*8-Methoxy-4-methyl-2,5-dioxo-2*H,5H*-pyrano[3,2-c]benzopyran (Id)*

4-Hydroxy-7-methoxycoumarin was condensed with ethyl acetoacetate in the presence of trifluoroacetic acid using the above procedure. M.p. of the colourless crystals and mixed m.p. with an authentic sample was 237° (lit.[5] 237°).

*4-Methyl-2,5-dioxo-2*H,5H*-pyrano[3,2-c]benzo[f]benzopyran (III)*

4-Hydroxybenzo[*f*]coumarin was condensed with ethyl acetoacetate in the presence of trifluoroacetic acid using the above procedure. M.p. and mixed m.p. with an authentic sample was 246° (lit.[6] 245–246°).

[4] Patell, J., and Usgaonker, R. N., *J. Indian chem. Soc.*, 1965, **42**, 217.
[5] Dholakia, V. N., and Trivedi, K. N., *J. Indian chem. Soc.*, 1966, **43**, 804.
[6] Patell, J., and Usgaonker, R. N., *J. Indian chem. Soc.*, 1966, **43**, 536.

3-Acetoacetyl-4-hydroxy-6-methylcoumarin

A solution of 3-acetyl-4-hydroxy-6-methylcoumarin (1 g) in freshly distilled ethyl acetate (25 ml) was added to pulverized sodium (1 g). The reaction mixture was heated on a water-bath for 6 hr. It was then decomposed with ice and extracted with ether. The aqueous layer on acidification gave *3-acetoacetyl-4-hydroxy-6-methylcoumarin*, which crystallized from dil. acetic acid, yellow needles, m.p. 153°, yield 0·7 g (Found: C, 64·5; H, 4 7. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·65%).

*2,9-Dimethyl-4,5-dioxo-4*H,*5*H-*pyrano*[*3,2*-c]*benzopyran* (*IIb*)

A solution of 3-acetoacetyl-4-hydroxy-6-methylcoumarin (0·5 g) in 50 ml dil. sulphuric acid (25%) was heated on a sand-bath for 1 hr. The cooled reaction mixture was neutralized with sodium carbonate solution, the separated product was crystallized from dil. acetic acid, yellow needles, m.p. 248°, yield 0·2 g (Found: C, 69·7; H, 3·8. $C_{14}H_{10}O_4$ requires C, 69·4; H, 4·2%).

3-Acetoacetyl-4-hydroxy-7-methoxycoumarin

A solution of 3-acetyl-4-hydroxy-7-methoxycoumarin (1 g) in ethyl acetate (25 ml) was added to pulverized sodium (1 g) and the reaction mixture refluxed on a water-bath for 6 hr. The reaction mixture was worked up as before. *3-Acetoacetyl-4-hydroxy-7-methoxycoumarin* crystallized from dil. acetic acid, yellow needles, m.p. 153°, yield 0·8 g (Found: C, 60·9; H, 4·2. $C_{14}H_{12}O_6$ requires C, 60·9; H, 4·4%).

*8-Hydroxy-2-methyl-4,5-dioxo-4*H,*5*H-*pyrano*[*3,2*-c]*benzopyran* (*IIc*)

A solution of 3-acetoacetyl-4-hydroxy-7-methoxycoumarin (0·7 g) in 75 ml dil. sulphuric acid (25%) was refluxed on a sand-bath for 1 hr. The cooled reaction mixture was basified with sodium hydroxide solution and filtered. The filtrate on acidification gave *8-hydroxy-2-methyl-4,5-dioxo-4*H,*5*H-*pyrano*[*3,2*-c]*benzopyran*, which crystallized from dil. acetic acid, yellow needles, m.p. 221° (Found: C, 63·4; H, 3·8. $C_{13}H_8O_5$ requires C, 63·9; H, 3·3%).

3-Acetyl-4-hydroxybenzo[f]*coumarin*

4-Hydroxybenzo[*f*]coumarin (1 g) was dissolved in acetic acid (5 ml) and phosphorus oxychloride (2 ml) and the reaction mixture was gently refluxed for 40 min and then added to ice-water. *3-Acetyl-4-hydroxybenzo*[f]*coumarin* crystallized from acetic acid, m.p. 201°, yield 0·68 g. It developed a red coloration with alcoholic ferric chloride solution (Found: C, 70·4; H, 4·1. $C_{15}H_{10}O_4$ requires C, 70·8; H, 4·0%).

3-Acetoacetyl-4-hydroxybenzo[f]*coumarin*

3-Acetyl-4-hydroxybenzo[*f*]coumarin (0·5 g) dissolved in ethyl acetate (15 ml) was added to pulverized sodium (0·6 g) and refluxed for 6 hr. On working up the reaction mixture as before, *3-acetoacetyl-4-hydroxybenzo*[f]*coumarin* crystallized from benzene, yellow needles, m.p. 166°, yield 0·2 g (Found: C, 68·9; H, 4·5. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·1%).

*2-Methyl-4,5-dioxo-4*H,*5*H-*pyrano*[*3,2*-c]*benzo*[f]*benzopyran* (*IV*)

3-Acetoacetyl-4-hydroxybenzo[*f*]coumarin (0·4 g) was refluxed with 25 ml of dil. sulphuric acid (25%) on a sand-bath for 2 hr. On working up the reaction mixture as before, *2-methyl-4,5-dioxo-4*H,*5*H-*pyrano*[*3,2*-c]*benzo*[f]*benzopyran* crystallized from acetic acid, yellow needles, m.p. 282°, yield 0·1 g (Found: C, 73·1; H, 3·9. $C_{17}H_{10}O_4$ requires C, 73·4; H, 3·6%).

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