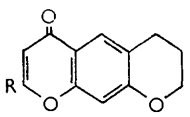
1035. *Dihydropyranochromones Derived from Quinol.*

By A. O. Fitton and G. R. Ramage.

7-Acetyl-6-hydroxychroman (III; R = H, R′ = Ac) has been prepared both by acetylation of 6-methoxychroman and by Fries rearrangement of 6-acetoxychroman. It has served to provide a new series of 2-substituted dihydropyranochromones (VII; R = H, CO_2H, or Me, etc.).

A recent paper [1] which described the preparation of a series of 2-substituted dihydropyranochromones (I) was part of a programme aimed at synthesising compounds having pharmacological activity,[2] similar to that of the naturally occurring furochromone, khellin (II). The dihydropyranochromones, like many other substances prepared as potential "khellin-like" compounds,[3,4] were derived from resorcinol, but those now reported are derived from quinol, as was a related series of furochromones.[5]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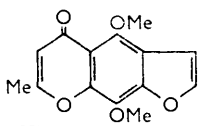
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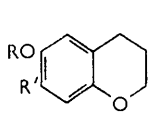
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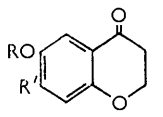
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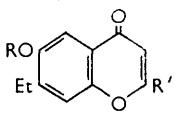
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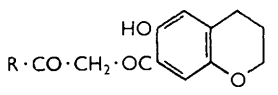
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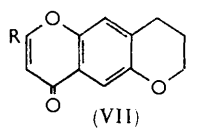
(VII)

The route chosen involved building a γ-pyrone ring on to 7-acetyl-6-hydroxychroman (III; R = H, R′ = Ac), which was prepared in two ways. β-*p*-Hydroxyphenoxypropionic acid was converted into its *O*-acetyl derivative and treated with tetraphosphoric acid to yield 6-acetoxychroman-4-one (IV; R = Ac, R′ = H). This on Clemmensen reduction and simultaneous hydrolysis gave 6-hydroxychroman (III; R = R′ = H). Failure to protect the phenolic group during ring-closure greatly reduced the yield, presumably owing to phosphate ester formation. 6-Hydroxychroman was converted in rather poor overall yield into 7-acetyl-6-hydroxychroman by *O*-acetylation and subsequent Fries rearrangement. A better route to the required chroman started with Clemmensen reduction of 6-methoxychroman-4-one, which was obtained in much higher yield by the action of tetraphosphoric acid on β-*p*-methoxyphenoxypropionic acid than by the published methods using either aluminium chloride and the corresponding acid chloride [6] or phosphorus pentoxide and the acid in toluene.[7] 6-Methoxychroman (III; R = Me, R′ = H) was treated with boron trifluoride–acetic acid, which caused demethylation as well as acetylation in the 7-position. This method was superior to acetylation by acetyl chloride and aluminium chloride in carbon disulphide solution.

The compound prepared by the above methods was shown to be the 7-isomer by reducing it to 7-ethyl-6-hydroxychroman (III; R = H, R′ = Et) which was then synthesised unambiguously. 4-Ethyl-2-hydroxy-5-methoxyacetophenone [5] was condensed with ethyl oxalate and the product was cyclised, hydrolysed, and decarboxylated to give 7-ethyl-6-methoxychromone (V; R = Me, R′ = H). The last-named compound was converted into 7-ethyl-6-hydroxychroman-4-one by demethylation and reduction (or

[1] Naylor and Ramage, *J.*, 1960, 1956.
[2] Huttrer and Dale, *Chem. Rev.*, 1951, **48**, 568.
[3] Davies, McCrea, Norris, and Ramage, *J.*, 1950, 3206.
[4] Phillips, Robertson, and Whalley, *J.*, 1952, 4951.
[5] Ramage and Stead, *J.*, 1953, 3602.
[6] Pfeiffer, Oberlin, and Konermann, *Ber.*, 1925. **58***B*, 1947.
[7] Colonge and Guyot, *Bull. Soc. chim. France*, 1958, 325.

vice versa), and the synthesis of the corresponding chroman (III; R = H, R′ = Et) was completed by further reduction by the Clemmensen method. The product of this series of reactions was identical with the ethylhydroxychroman previously prepared.

7-Acetyl-6-hydroxychroman condensed readily with ethyl oxalate in the presence of sodium ethoxide and ethanol, and the resulting diketone (VI; R = CO_2Et) was cyclised with alcoholic hydrogen chloride to give the ester (VII; R = CO_2Et) or with a mixture of acetic and hydrochloric acids to give the carboxylic acid (VII; R = CO_2H). A third dihydropryanochromone (VII; R = H) was obtained by decarboxylation of the acid. Alternative catalysts were required for condensations with other esters, although ethyl picolinate and isonicotinate did condense with the chroman in the presence of sodium ethoxide, but only in poor yield. Ethyl acetate condensed in the presence of powdered sodium, and the resulting diketone on cyclisation gave the 2-methyl compound (VII; R = Me). Yet a third condensing agent, sodium hydride, was most effective when esters of pyridinecarboxylic acids or ethyl benzoate were used in the Claisen condensation. Other authors have found sodium hydride to be an effective catalyst for the acylation of ketones by basic esters.[8]

The basic dihydropyranochromones (VII; R = 2-, 3- or 4-pyridyl) which resulted from diketones containing a pyridine nucleus were prepared in the expectation that they would be appreciably water-soluble as their salts.

Experimental

β-p-*Acetoxyphenoxypropionic Acid.*—To β-*p*-hydroxyphenoxypropionic acid (7·28 g.) in 15% aqueous sodium hydroxide (28 ml.) was added ice (30 g.), followed by acetic anhydride (28 ml.). The solution was shaken during 3 min., then acidified with concentrated hydrochloric acid. Filtration followed by crystallisation of the residue from water (charcoal) gave β-p-*acetoxyphenoxypropionic acid* (6·22 g.) as needles, m. p. 108° (Found: C, 59·1; H, 5·5. $C_{11}H_{12}O_5$ requires C, 58·9; H, 5·4%).

6-*Acetoxychroman-4-one* (IV; R = Ac, R′ = H).—A mixture of β-*p*-acetoxyphenoxypropionic acid (5 g.) and tetraphosphoric acid (50 g.) was stirred at 40—50° during 1·5 hr., then added to ice (150 g.). The mixture was extracted with ether, and the extract was washed with aqueous sodium hydrogen carbonate and with water. Evaporation of the dried ($MgSO_4$) extract yielded a residue (3·5 g.) which on crystallisation from water gave 6-*acetoxychroman-4-one* as needles, m. p. 77—78° (Found: C, 64·4; H, 5·1. $C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%).

6-*Hydroxychroman* (III; R = R′ = H).—A mixture of 6-acetoxychroman-4-one (7 g.), amalgamated zinc (70 g.), and 5N-hydrochloric acid (100 ml.) was heated under reflux during 5 hr. The liquid was decanted from the excess of zinc and extracted with ether. After being washed with water, the dried ($MgSO_4$) extract was evaporated. Crystallisation of the residue from cyclohexane gave 6-*hydroxychroman* (1·83 g.) as plates, m. p. 99—100° (Found: C, 72·0; H, 6·9. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%).

This product (1·2 g.) and acetic anhydride (2 ml.) in 10% aqueous sodium hydroxide (15 ml.) gave 6-acetoxychroman (1·28 g.) as prisms (from aqueous ethanol), m. p. 52·5—53·5° (Found: C, 68·5; H, 6·5. Calc. for $C_{11}H_{12}O_3$: C, 68·7; H, 6·3%).

6-*Methoxychroman-4-one* (IV; R = Me, R′ = H).—A mixture of β-*p*-methoxyphenoxypropionic acid (40 g.) and tetraphosphoric acid (300 g.) was stirred at 50—60° during 2 hr., then poured into cold water (1 l.) and extracted with ether. The ethereal extract was washed with aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated. 6-Methoxychroman-4-one (34·8 g.) solidified on cooling and had m. p. 45°.[6]

6-*Methoxychroman* (III; R = Me, R′ = H).—After a mixture of 6-methoxychroman-4-one (50 g.), amalgamated zinc (500 g.), and 5N-hydrochloric acid (500 ml.) had been heated during 30 min., the liquid was decanted from the excess of zinc and extracted with ether. The extract was washed with water, then dried ($MgSO_4$), and on fractionation gave 6-*methoxychroman* (24·1 g.), b. p. 78—82°/0·2 mm. (Found: C, 73·2; H, 7·55. $C_{10}H_{12}O_2$ requires C, 73·1; H, 7·4%).

6-Methoxychroman yielded a *dinitro-derivative* (formed with concentrated nitric acid in

[8] Schmutz, Hist, Kunzle, Eichenberger, and Lauener, *Helv. Chim. Acta*, 1953, **36**, 620.

glacial acetic acid) as plates (from ethanol), m. p. 150—151° (Found: C, 47·2; H, 3·9; N, 10·7. $C_{10}H_{10}N_2O_6$ requires C, 47·25; H, 4·0; N, 11·0%).

7-*Acetyl*-6-*hydroxychroman* (III; R = H, R′ = Ac).—(*a*) A mixture of 6-methoxychroman (3·28 g.) and boron trifluoride-acetic acid complex (40% w/w; 15 ml.) was heated during 1 hr. at 100°. The resulting solution was poured into cold water (50 ml.), made alkaline with 10% aqueous sodium hydroxide, cooled, and filtered. Acidification of the filtrate with concentrated hydrochloric acid precipitated 7-*acetyl*-6-*hydroxychroman*, which was filtered off, and then crystallised from aqueous ethanol as pale yellow plates (1·0 g.), m. p. 111—112° (Found: C, 68·4; H, 6·4. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·3%).

(*b*) A mixture of 6-acetoxychroman (0·75 g.) and resublimed anhydrous aluminium chloride (0·80 g.) was heated at 120° during 30 min. The complex was decomposed by addition to ice (20 g.) and concentrated hydrochloric acid (2 ml.), and the resulting mixture was extracted with ether. The product was removed from the ethereal layer by extraction with 10% aqueous sodium hydroxide and precipitated from the latter with concentrated hydrochloric acid. Purification as above gave 7-acetyl-6-hydroxychroman (0·1 g.), m. p. 111—112°.

7-Acetyl-6-hydroxychroman formed a 2,4-*dinitrophenylhydrazone*, deep red needles (from acetic acid), m. p. 251—252° (decomp.) (Found: C, 54·8; H, 4·4; N, 15·0. $C_{17}H_{16}N_4O_6$ requires C, 54·8; H, 4·4; N, 15·05%), and a *methyl ether* (III; R = Me, R′ = Ac), prisms [from light petroleum ether (b. p. 60—80°)], m. p. 49—50° (Found: C, 69·7; H, 6·9. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

2-(β-*Ethoxycarbonyl*-β-*oxopropionyl*)-5-*ethyl*-4-*methoxyphenol*.—To a solution of sodium (0·44 g.) in ethanol (10 ml.) was added a solution of 4-ethyl-2-hydroxy-5-methoxyacetophenone (0·97 g.) in diethyl oxalate (10 ml.). The mixture was heated at 100° during 2 hr., cooled, and added to dry ether (200 ml.). After 30 min. (see below) the precipitated sodium salt of the product was filtered off and added to 2N-hydrochloric acid (25 ml.). The liberated 2-(β-*ethoxycarbonyl*-β-*oxopropionyl*)-5-*ethyl*-4-*methoxyphenol* was filtered off and crystallised as plates (0·97 g.), m. p. 112—113°, from aqueous methanol (Found: C, 61·6; H, 6·2. $C_{15}H_{18}O_6$ requires C, 61·25; H, 6·2%).

2-*Ethoxycarbonyl*-7-*ethyl*-6-*methoxychromone* (V; R = Me, R′ = CO_2Et).—(*a*) A solution of 2-(β-ethoxycarbonyl-β-oxopropionyl)-5-ethyl-4-methoxyphenol (0·15 g.) in dry ethanolic hydrogen chloride (12% w/w; 4 ml.) was refluxed during 1 hr., cooled, and filtered. Crystallisation of the residue (0·1 g.) from ethanol gave 2-*ethoxycarbonyl*-7-*ethyl*-6-*methoxychromone* as pale yellow prisms, m. p. 128—129° (Found: C, 65·2; H, 5·6. $C_{15}H_{16}O_5$ requires C, 65·2; H, 5·8%).

(*b*) Longer storage of the ethereal filtrate in the previous preparation yielded a further precipitate which on purification as above gave 2-ethoxycarbonyl-7-ethyl-6-methoxychromone (0·2 g.), m. p. and mixed m. p. 128—129°.

2-*Carboxy*-7-*ethyl*-6-*methoxychromone* (V; R = Me, R′ = CO_2H).—A solution of 2-ethoxycarbonyl-7-ethyl-6-methoxychromone (1·74 g.) in glacial acetic acid (20 ml.) and concentrated hydrochloric acid (9 ml.) was refluxed during 1·5 hr., cooled, and filtered. Crystallisation of the residue (1·45 g.) from glacial acetic acid gave 2-*carboxy*-7-*ethyl*-6-*methoxychromone* as pale yellow needles, m. p. 213—215° (decomp., depending on rate of heating) (Found: C, 60·6; H, 5·0. $C_{13}H_{12}O_5$,½AcOH requires C, 60·4; H, 5·1%).

7-*Ethyl*-6-*methoxychromone* (V; R = Me, R′ = H).—2-Carboxy-7-ethyl-6-methoxychromone (2 g.) was stirred at 260° during 10 min. and, after cooling, the product was dissolved in ether. The solution was treated with magnesium sulphate and charcoal, filtered, and evaporated. The resulting yellow powder was made into a slurry with aqueous sodium hydrogen carbonate solution and filtered. Crystallisation of the residue (1·2 g.) from aqueous ethanol (charcoal) gave 7-*ethyl*-6-*methoxychromone* as needles, m. p. 106—107° (Found: C, 70·8; H, 6·1. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%).

7-*Ethyl*-6-*methoxychroman*-4-*one* (IV; R = Me, R′ = Et).—7-Ethyl-6-methoxychromone (0·5 g.) in ethanol (40 ml.) was shaken with Raney nickel (1 ml.; settled suspension in ethanol) and hydrogen at room temperature until the uptake reached 66 ml. (*ca.* 3 hr.). The catalyst was filtered off and washed with ethanol and the filtrate evaporated. Crystallisation of the residue from aqueous ethanol gave 7-*ethyl*-6-*methoxychroman*-4-*one* as needles (0·38 g.), m. p. 89—90° (Found: C, 69·8; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

7-*Ethyl*-6-*hydroxychromone* (V; R = R′ = H).—A mixture of 7-ethyl-6-methoxychromone (0·95 g.) and anhydrous resublimed aluminium chloride (1·3 g.) was heated at 150° during

30 min. The resulting complex was added to ice (50 g.) and concentrated hydrochloric acid (5 ml.). 7-*Ethyl*-6-*hydroxychromone* was filtered off and crystallised from aqueous ethanol as needles (0·55 g.), m. p. 197—198° (Found: C, 69·8; H, 5·3. $C_{11}H_{10}O_3$ requires C, 69·45; H, 5·3%).

7-*Ethyl*-6-*hydroxychroman*-4-*one* (IV; R = H, R′ = Et).—(*a*) A solution of 7-ethyl-6-hydroxychromone (0·95 g.) in ethanol (40 ml.) was shaken with Raney nickel (1 ml.; settled suspension in ethanol) and hydrogen at 40—50° for *ca.* 6 hr. The catalyst was filtered off and washed with ethanol, and the combined filtrate and washings were evaporated. Crystallisation of the residue from aqueous ethanol gave 7-*ethyl*-6-*hydroxychroman*-4-*one* (0·55 g.) as pale yellow needles, m. p. 140—141° (Found: C, 68·4; H, 5·8. $C_{11}H_{12}O_3$ requires C, 68·75; H, 6·3%).

(*b*) A mixture of 7-ethyl-6-methoxychroman-4-one (1 g.) and anhydrous resublimed aluminium chloride (1·33 g.) was heated at 130° during 30 min. The complex was added to ice (50 g.) and concentrated hydrochloric acid (5 ml.). 7-Ethyl-6-hydroxychroman-4-one was filtered off and after purification as above gave needles (0·5 g.), m. p. 140—141°.

7-*Ethyl*-6-*hydroxychroman* (III; R = H, R′ = Et).—(*a*) A mixture of 7-ethyl-6-hydroxychroman-4-one (0·5 g.), amalgamated zinc (10 g.), and 5N-hydrochloric acid (20 ml.) was heated under reflux during 2 hr. The cooled solution was decanted from the excess of zinc and extracted with ether, and after being washed with water and dried ($MgSO_4$) the extract was evaporated. Crystallisation of the residue from cyclohexane (charcoal) gave 7-*ethyl*-6-*hydroxychroman* as prisms (0·2 g.), m. p. 95—96° (Found: C, 74·5; H, 7·9. $C_{11}H_{14}O_2$ requires C, 74·15; H, 7·9%).

(*b*) A mixture of 7-acetyl-6-hydroxychroman (0·3 g.), amalgamated zinc (10 g.), and 5N-hydrochloric acid (18 ml.), was heated under reflux during 1 hr. and the product isolated as in (*a*). Successive crystallisations from aqueous ethanol and cyclohexane gave 7-ethyl-6-hydroxychroman (0·05 g.), m. p. 95—96°, undepressed on admixture with the product obtained from the previous preparation.

7-(β-*Ethoxycarbonyl*-β-*oxopropionyl*)-6-*hydroxychroman* (VI; R = CO_2Et).—To a solution of sodium (0·2 g.) in ethanol (10 ml.), was added 7-acetyl-6-hydroxychroman (0·34 g.) in diethyl oxalate (6 ml.). The mixture was heated at 100° during 1 hr., then cooled and added to dry ether (200 ml.). The precipitated sodium salt was filtered off and acidified with 2N-hydrochloric acid (15 ml.). The liberated 7-(β-*ethoxycarbonyl*-β-*oxopropionyl*)-6-*hydroxychroman* was filtered and crystallised from ethanol as needles (0·23 g.), m. p. 149—150° (Found: C, 62·0; H, 5·5. $C_{15}H_{16}O_6$ requires C, 61·7; H, 5·5%).

8,9-*Dihydro*-2-*ethoxycarbonyl*-7*H*-*pyrano*[2,3-*g*]*chromone* (VII; R = CO_2Et).—A solution of 7-(β-ethoxycarbonyl-β-oxopropionyl)-6-hydroxychroman (0·6 g.) in dry ethanolic hydrogen chloride (12% w/v; 15 ml.) was refluxed during 1 hr., cooled, and filtered. Crystallisation of the residue (0·4 g.) from ethanol gave 8,9-*dihydro*-2-*ethoxycarbonyl*-7*H*-*pyrano*[2,3-*g*]*chromone* as needles, m. p. 149·5—150° (Found: C, 65·4; H, 5·0. $C_{15}H_{14}O_5$ requires C, 65·7; H, 5·1%).

2-*Carboxy*-8,9-*dihydro*-7*H*-*pyrano*[2,3-*g*]*chromone* (VII; R = CO_2H).—A solution of 7-(β-ethoxycarbonyl-β-oxopropionyl)-6-hydroxychroman (1·2 g.) in glacial acetic acid (16 ml.) and concentrated hydrochloric acid (6 ml.) was refluxed during 1·5 hr., cooled, and filtered. Crystallisation of the residue (0·95 g.) from glacial acetic acid gave 2-*carboxy*-8,9-*dihydro*-7*H*-*pyrano*[2,3-*g*]*chromone* as pale yellow needles, m. p. 285·5—286° (Found: C, 62·9; H, 4·0. $C_{13}H_{10}O_5$ requires C, 63·4; H, 4·1%).

8,9-*Dihydro*-7*H*-*pyrano*[2,3-*g*]*chromone* (VII; R = H).—2-Carboxy-8,9-dihydro-7*H*-pyrano-[2,3-*g*]chromone (0·9 g.) was stirred at 300—310° during 5 min., then cooled, and the dark product was dissolved in methanol, treated with charcoal, and filtered. The residue left on removal of the solvent was triturated with sodium hydrogen carbonate solution. 8,9-*Dihydro*-7*H*-*pyrano*[2,3-*g*]*chromone* (0·5 g.) was filtered off, dried, and crystallised from cyclohexane (charcoal) as pale yellow needles, m. p. 158—159° (Found: C, 71·2; H, 4·8. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%).

7-*Acetoacetyl*-6-*hydroxychroman* (VI; R = Me).—A solution of 7-acetyl-6-hydroxychroman (0·38 g.) in dry ethyl acetate (10 ml.) was added to powdered sodium (0·1 g.), and the whole was refluxed during 3 hr., cooled, and added to dry ether (100 ml.). Next day the sodium salt was filtered off and added to 2N-hydrochloric acid (10 ml.). 7-*Acetoacetyl*-6-*hydroxychroman* (0·25 g.) was filtered off, dried, and crystallised from carbon tetrachloride as yellow needles, m. p. 143—145° (Found: C, 66·7; H, 5·8. $C_{13}H_{14}O_4$ requires C, 66·6; H, 6·2%).

8,9-*Dihydro*-2-*methyl*-7*H*-*pyrano*[2,3-*g*]*chromone* (VII; R = Me).—A solution of 7-acetoacetyl-6-hydroxychroman (0·2 g.) in ethanolic 12% w/v hydrogen chloride (5 ml.) was refluxed during 1 hr. After addition of water (10 ml.), 8,9-*dihydro*-2-*methyl*-7*H*-*pyrano*[2,3-*g*]*chromone* (0·12 g.) was filtered off and crystallised from cyclohexane as prisms, m. p. 129·5—130° (Found: C, 72·0; H, 5·3. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%).

6-*Hydroxy*-7-(β-*oxo*-β-*phenylpropionyl*)*chroman* (VI; R = Ph).—Ethyl benzoate (1·5 ml.) was added to a mixture of 7-acetyl-6-hydroxychroman (0·57 g.) and sodium hydride (0·5 g.) in dry dioxan (25 ml.), and the whole was refluxed under dry nitrogen during 6 hr., then cooled and poured into dry ether (200 ml.). Next day the sodium salt was filtered off and added to 2N-hydrochloric acid (10 ml.). Filtration and crystallisation of the residue from methanol gave 6-*hydroxy*-7-(β-*oxo*-β-*phenylpropionyl*)*chroman* as yellow prisms (0·34 g.) m. p. 100·5—101·5° (Found: C, 72·3; H, 5·6. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%).

8,9-*Dihydro*-7*H*-*pyrano*[2,3-*g*]*flavone* (VII; R = Ph).—A solution of 6-hydroxy-7-(β-oxo-β-phenylpropionyl)chroman (0·3 g.) in dry ethanolic 12% w/v hydrogen chloride (10 ml.) was refluxed during 1 hr., cooled, and filtered. Crystallisation of the residue (0·2 g.) from ethanol gave 8,9-*dihydro*-7*H*-*pyrano*[2,3-*g*]*flavone* as needles, m. p. 196—197° (Found: C, 77·9; H, 5·1. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·1%).

6-*Hydroxy*-7-(β-*oxo*-β-2′-*pyridylpropionyl*)*chroman* (VI; R = 2-pyridyl).—Ethyl picolinate (0·75 ml.) was added to a mixture of 7-acetyl-6-hydroxychroman (0·57 g.) and sodium hydride (0·3 g.) in dry dioxan (25 ml.), and the whole was stirred under dry nitrogen at 20° during 8 hr., then poured into dry ether (200 ml.). The sodium salt was filtered off and dissolved in water (10 ml.). The resulting solution was acidified to Congo Red with concentrated hydrochloric acid, and insoluble matter was filtered off. The crude product obtained by addition of excess of sodium carbonate to the filtrate was separated and crystallised from ethanol, giving 6-*hydroxy*-7-(β-*oxo*-β-2′-*pyridylpropionyl*)*chroman* as yellow plates (0·37 g.), m. p. 146—147°.

Similar preparations with ethyl nicotinate and ethyl isonicotinate in place of ethyl picolinate gave the corresponding 3′- and 4′-*pyridyl derivatives* (see Table).

Basic diketones (VI).

R	Duration of expt. (hr.)	Temp.	Yield (%)	M. p.	Found (%) C	Found (%) H	Found (%) N	$C_{17}H_{15}NO_4$ requires (%) C	$C_{17}H_{15}NO_4$ requires (%) H	$C_{17}H_{15}NO_4$ requires (%) N
2-Pyridyl ...	8	20°	30	146°	68·6	5·3	4·9	68·7	5·1	4·7
3-Pyridyl ...	6	100	40	155	68·1	5·2	4·9			
4-Pyridyl ...	5	100	42	159	68·8	5·1	4·5			

8,9-*Dihydro*-2-2′-*pyridyl*-7*H*-*pyrano*[2,3-*g*]*chromone* (VII; R = 2-pyridyl).—A solution of 6-hydroxy-7-(β-oxo-β-2′-pyridylpropionyl)chroman (0·37 g.) in ethanolic hydrogen chloride (12% w/v; 10 ml.), was refluxed during 1 hr., cooled, and filtered. The resulting salt was washed with ethanol and then ether and dissolved in water (10 ml.), and insoluble matter filtered off. Addition of an excess of aqueous sodium hydrogen carbonate to the filtrate precipitated 8,9-*dihydro*-2-2′-*pyridyl*-7*H*-*pyrano*[2,3-*g*]*chromone* (0·3 g.) which crystallised from ethanol as needles, m. p. 180—181°.

The 3′- and 4′-pyridyl isomers were cyclised in a similar manner (cf. Table).

Basic chromones (VII).

R	Yield (%)	M. p.	Found (%) C	Found (%) H	Found (%) N	$C_{17}H_{13}NO_3$ requires (%) C	$C_{17}H_{13}NO_3$ requires (%) H	$C_{17}H_{13}NO_3$ requires (%) N
2-Pyridyl	86	180°	72·6	5·2	5·0	73·1	4·7	5·0
3-Pyridyl	95	200	73·4	5·0	5·1			
4-Pyridyl	89	214	72·6	4·9	4·9			

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