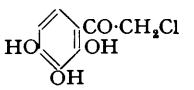
625. *Furanochromones. Part III. The Synthesis of 8-Methoxy-2-methylfurano(3′ : 2′-6 : 7)chromone and its Derivatives.**

By J. S. H. Davies and T. Deegan.

4′ : 5′-Dihydro-8-hydroxy-2-methylfurano(3′ : 2′-6 : 7)chromone and its 8-methoxy-, 8-ethoxy-, and 8-benzyloxy-derivatives (VII; R = H, Me, Et, and C_7H_7, R′ = H) have been prepared from pyrogallol *via* 6 : 7-diacetoxycoumaran (IV; R = R′ = Ac), which on Fries rearrangement gave 5-acetyl-6 : 7-dihydroxycoumaran (V; R = R′ = H). Extension of the acetyl group of appropriate ethers with ethyl acetate and sodium gave the β-diketones (as VI), and ring closure furnished the dihydrofuranochromones. The 8-methoxy-compound (VII; R = Me, R′ = H) gave 8-methoxy-2-methylfurano(3′ : 2′-6 : 7)chromone (VIII; R = H) on dehydrogenation.

Of the methoxyfuranochromones which have bene isolated from the seeds of *Ammi visnaga* (Späth and Gruber, *Ber.*, 1938, **71**, 106; 1941, **74**, 1492, 1549), two, *viz.*, 5 : 8-dimethoxy-(kellin) and 5-methoxy-2-methylfurano(3′ : 2′-6 : 7)chromone (visnagin), have been synthesised, the former by Clarke and Robertson (*J.*, 1949, 302), Baxter, Ramage, and Timson (*J.*, 1949, S30), and Murti and Seshadri (*J. Sci. Ind. Res., India*, 1949, **88**, No. 6, 112—113; *Chem. Abstr.*, 1950, **44**, 1501), and the latter by Clarke, Glaser, and Robertson (*J.*, 1948, 2260), Gruber and Hoyos (*Monatsh.*, 1948, **78**, 417), who affected a partial synthesis, and Davies and Norris (preceding paper), who succeeded in preparing an intermediate which led to the complete synthesis. The present communication deals with the synthesis of a visnagin isomer, 8-methoxy-2-methylfurano(3′ : 2′-6 : 7)chromone.

On starting from pyrogallol, 6 : 7-dihydroxycoumaran-3-one (II; R = R′ = H) was prepared by a modification of the method of Feuerstein and Brass (*Ber.*, 1904, **37**, 817), the intermediate ω-chlorogallacetophenone (I) being cyclised by sodium acetate and alcohol (cf. Shriner and Grosser, *J. Amer. Chem. Soc.*, 1942, **64**, 382). Direct hydrogenation of the coumaranone to 6 : 7-dihydroxycoumaran (IV; R = R′ = H) has been reported by Späth and Pailer (*Ber.*, 1936, **69**, 767), but, as it was desired to examine the Fries rearrangement of 6 : 7-diacetoxycoumaran, acetylation of 6 : 7-dihydroxycoumaran-3-one was first investigated. Acetylation with acetic anhydride and sodium acetate was stated by Feuerstein and Brass (*loc. cit.*) to give 6 : 7-diacetoxycoumaran-3-one, m. p. 106°, but indecisive and inconsistent analytical figures led them to assign the above constitution by analogy with the product of chloroacetylation. It has now been found that, with acetyl chloride in ethyl acetate, two acetylation products are obtained, one, m. p. 106°, in much higher yield than the other, m. p. 137·5°. Elementary analyses and acetyl determinations (Freudenberg) have shown that the product, m. p. 106°, is the triacetoxycoumarone (III) : it gave a colour with Brady's reagent only after some time. The product, m. p. 137·5°, is in all probability 6 : 7-diacetoxycoumaran-3-one (II; R = R′ = Ac) and gave an immediate colour with Brady's reagent. Acetylation with acetic anhydride in pyridine gave a better yield of the triacetoxycoumarone, and no diacetoxy-compound was encountered. The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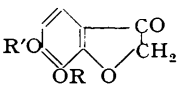
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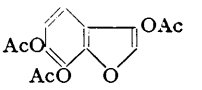
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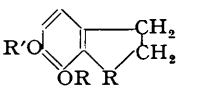
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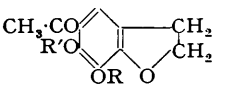
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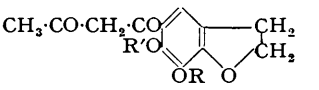
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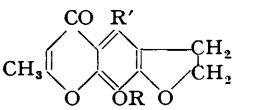
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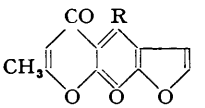
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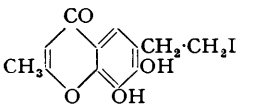
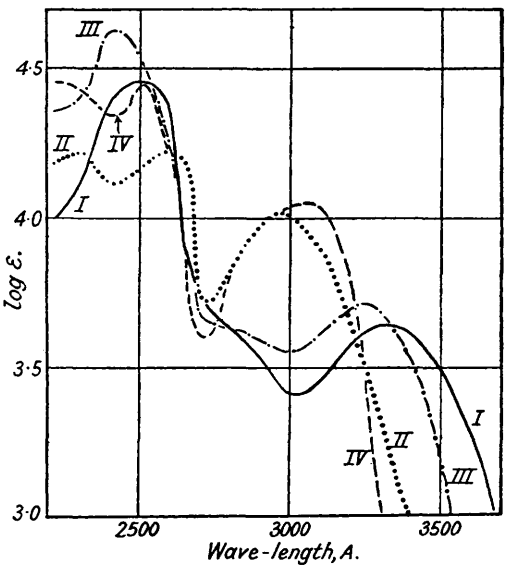

(IX.)

triacetoxycoumarone yielded 6 : 7-diacetoxycoumaran (IV; R = R′ = Ac) on hydrogenation at 60—65° and one atmosphere pressure with either palladium–charcoal, absorption of hydrogen being rapid, or with palladium–barium sulphate, absorption being less rapid. The latter catalyst appeared to be less sensitive to poisoning.

* Patent pending.

The Fries rearrangement to 5-acetyl-6 : 7-dihydroxycoumaran proceeded without difficulty with either aluminium chloride in nitrobenzene at 60° or, in slightly lower yield, with the boron trifluoride–acetic acid complex ($BF_3,2CH_3{\cdot}CO_2H$). That the acetyl group occupied the 5-position was shown by the eventual formation of a 4′ : 5′-dihydrofuranochromone. Unlike 5-acetyl-4 : 6-dihydroxycoumaran, but like the 7-acetyl isomer (cf. Part II), 5-acetyl-6 : 7-dihydroxycoumaran was stable to boiling aqueous sodium hydroxide. On monomethylation, it gave the 7-methoxy-derivative (V; R = Me, R′ = H), and with excess of methyl sulphate the dimethoxy-derivative (V; R = R′ = Me). From the latter with ethyl acetate and sodium, 6 : 7-dimethoxy-5-β-keto-butyrylcoumaran (VI; R, R′ = Me) was obtained as an oil, which with hydrobromic acid in glacial acetic acid (Heilbron, Hey, and Lowe, *J.*, 1934, 1311) gave 4′ : 5′-dihydro-8-methoxy-2-methylfurano(3′ : 2′-6 : 7)chromone (VII; R = Me, R′ = H), the 2-methyl group of which condensed with benzaldehyde to give the styryl derivative. For the preparation of 8-methoxy-2-methylfurano(3′ : 2′-6 : 7)chromone (VIII; R = H), the dihydrofuranochromone was dehydrogenated by palladium–charcoal at 250°.

Absorption spectra of furanochromones.



I. (————) 5 : 8-*Dimethoxy-2-methylfurano*(3′ : 2′-6 : 7)*chromone* (*kellin*) (VIII; R = OMe).
II. (.....) 4′ : 5′-*Dihydro*-5 : 8-*dimethoxy-2-methylfurano*(3′ : 2′-6 : 7)*chromone* (*dihydrokellin* : VII; R = Me, R′ = OMe).
III. (—·—·—) 8-*Methoxy-2-methylfurano*(3′ : 2′-6 : 7)*chromone* (VIII; R = H).
IV. (– – – – –) 4′ : 5′-*Dihydro*-8-*methoxy-2-methylfurano*(3′ : 2′-6 : 7)*chromone* (VII; R = Me, R′ = H).

When heated with hydriodic acid in acetic anhydride, the dihydrofuranochromone, containing a cyclic ether grouping, suffered ring-opening and demethylation to give, probably, 7 : 8-dihydroxy-6-2′-iodoethyl-2-methylchromone (IX), though it has not been established that it is the dihydrofuran ring which undergoes fission. Many examples are known where alkoxy-γ-pyrone compounds suffer demethylation and ring-fission, followed by ring-closure in an alternative direction, on treatment with hydriodic acid, as pointed out by Clarke, Glaser, and Robertson (*loc. cit.*), but no intermediate halogen compounds were isolated. In the case of the demethylation of visnagin, however, it is the furan ring which opens, as shown by the above authors. In the present case, alternative ring-closure is precluded, and the intermediate iodo-compound readily gave 4′ : 5′-dihydro-8-hydroxy-2-methylfurano(3′ : 2′-6 : 7)chromone.

Ethylation and benzylation of 5-acetyl-6 : 7-dihydroxycoumaran gave the 7-ethoxy- and 7-benzyloxy-compounds, respectively; these on treatment with ethyl acetate and sodium gave the corresponding diketones, which were cyclised in the usual way, forming 4′ : 5′-dihydro-8-ethoxy-2-methylfurano(3′ : 2′-6 : 7)chromone and 8-benzyloxy-4′ : 5′-dihydro-2-methylfurano-(3′ : 2′-6 : 7)chromone, respectively, the former being identical with the ethylation product of 4′ : 5′-dihydro-8-hydroxy-2-methylfurano(3′ : 2′-6 : 7)chromone and the latter identical with the benzylation product.

The ultra-violet absorption curves of 5 : 8-dimethoxy-2-methylfurano(3′ : 2′-6 : 7)chromone (kellin) (VIII; R = OMe), its 4′ : 5′-dihydro-derivative (VII; R = Me, R′ = OMe), together with those of 8-methoxy-2-methylfurano(3′ : 2′-6 : 7)chromone (VIII; R = H) and its 4′ : 5′-dihydro-derivative (VII; R = Me, R′ = H) are annexed : for comments see Part IV (following paper).

Experimental.

(Carbon and hydrogen analyses and ultra-violet absorption curves are by Drs. Weiler and Strauss, Oxford; m. p.s are uncorrected.)

6 : 7-*Dihydroxycoumaran*-3-*one* (II; R = R′ = H) (cf. Feuerstein and Brass, *loc. cit.*; Shriner and Grosser, *loc. cit.*).—A stirred melt of anhydrous pyrogallol (250 g.), chloroacetic acid (200 g.), and phosphorus oxychloride (200 g.) was kept at 60—70° for 3½ hours, the mass becoming too thick to stir. Heating was continued for a further 2 hours, and then iced water (1500 c.c.) was added. The mixture was heated until the dark brown solid dissolved and, after clarification (charcoal), was kept for 24 hours at 0°; dark brown needles of nearly pure ω-chlorogallacetophenone (I) (155 g.), m. p. 166—168°, which separated were collected. A further quantity (12 g.) of less pure material separated from the mother-liquor during 3 days at 0°. Further crystallisation from water gave the pure material, m. p. 169°.

A mixture of ω-chlorogallacetophenone (30 g.), ethanol (350 c.c.), and sodium acetate (35 g.) was boiled under a reflux for 5½ hours. The solvent was distilled off, and water (500 c.c.) was added to the solid residue. After about 20 hours, the precipitated 6 : 7-dihydroxycoumaran-3-one (20 g.), m. p. 226—228°, was collected; when crystallised from water it slowly formed short, pale yellow prisms (16·5 g.), m. p. 229°.

3 : 6 : 7-*Triacetoxycoumarone* (III) *and* 6 : 7-*Diacetoxycoumaran*-3-*one* (II; R = R′ = Ac).—(*a*) A mixture of 6 : 7-dihydroxycoumaran-3-one (10 g.), dry ethyl acetate (200 c.c.), and acetyl chloride (40 c.c.) was boiled under a reflux for 4 hours. The cooled solution was poured into water (300 c.c.) and neutralised with sodium hydrogen carbonate. The organic layer was separated, washed with water, and dried. The solvent was distilled off, leaving a yellow-brown oil, which set to a yellow solid. Crystallised from aqueous ethanol (50%), it gave 3 : 6 : 7-*triacetoxycoumarone* (12·5 g.) as fine, colourless needles, m. p. 105·5° (Found : C, 57·8; H, 4·1; Ac, 44·4. $C_{14}H_{12}O_7$ requires C, 57·5; H, 4·1; Ac, 44·2%). It was readily soluble in ether, acetone and glacial acetic acid, sparingly soluble in cold methanol and ethanol. The addition of Brady's reagent to the solution in methanol gave a red colour only after some time.

From acetylations of larger quantities of 6 : 7-dihydroxycoumaran-3-one (50—100 g.) by the above method, 6 : 7-*diacetoxycoumaran*-3-*one* was isolated during crystallisation. It crystallised from methanol as long, colourless needles, m. p. 137·5° (Found : C, 57·3; H, 3·8; Ac, 35·4. $C_{12}H_{10}O_6$ requires C, 57·6; H, 4·0; Ac, 34·4%). Brady's reagent gave an immediate red colour.

(*b*) Dry pyridine (50 c.c.) was added in one portion to a stirred suspension of 6 : 7-dihydroxycoumaran-3-one (32·5 g.) in acetic anhydride (130 c.c.). After 12 hours at room temperature, the red solution was poured into iced water (850 c.c.), 3 : 6 : 7-triacetoxycoumarone separating as a yellow precipitate. Purified as above, the pure material (49·1 g.) had m. p. 105—106°.

6 : 7-*Diacetoxycoumaran* (IV; R = R′ = Ac) *and* 6 : 7-*Dihydroxycoumaran* (cf. Späth and Pailer, *loc. cit.*). 3 : 6 : 7-Triacetoxycoumarone (35·5 g.) in glacial acetic acid (75 c.c.) was hydrogenated at 60—65°/1 atm. in the presence of palladium–charcoal (9 g.; 10%), previously saturated with hydrogen (*Org. Synth.*, **26**, 78; procedure D). The theoretical amount of hydrogen was rapidly absorbed. Removal of the catalyst and distillation of the solvent gave a colourless oil, which soon solidified, and, after crystallising from methanol, 6 : 7-*diacetoxycoumaran* (24·8 g.) was obtained as well defined, colourless prisms, m. p. 116° (Found : C, 61·1; H, 5·3. $C_{12}H_{12}O_5$ requires C, 61·0; H, 5·1%). When palladium–barium sulphate (5% : *Org. Synth.*, *loc. cit.*; procedure A) was used as catalyst, the theoretical amount of hydrogen was absorbed less rapidly; this catalyst, however, appeared to be less sensitive to poisoning than palladium–charcoal. It was occasionally found necessary to purify the triacetoxycoumarone by distillation (b. p. 187—188°/0·7 mm.) before hydrogenation.

6 : 7-Diacetoxycoumaran (3·6 g.) was boiled with aqueous sodium carbonate (100 c.c.; 2N.) for 50 minutes, and the solution cooled, acidified, and extracted with chloroform. 6 : 7-Dihydroxycoumaran, obtained by evaporating the chloroform layer, crystallised from a mixture (1 : 1 by vol.) of benzene and light petroleum (b. p. 60—80°) as long colourless needles (1·1 g.), m. p. 112—113° (Found : C, 63·0; H, 5·55. Calc. for $C_8H_8O_3$: C, 63·2; H, 5·3%). It dissolved readily in ether or ethanol, and gave a dark brown colour with ferric chloride.

5-*Acetyl*-6 : 7-*dihydroxycoumaran* (V; R = R′ = H).—Freshly powdered aluminium trichloride (10·5 g.) was added to a suspension of 6 : 7-diacetoxycoumaran (15 g.) in dry nitrobenzene (120 c.c.). The resulting solution was kept at 60° for 1 hour, then poured into ice–water (500 c.c.) acidified with hydrochloric acid. After 12—24 hours at room temperature, the organic layer was extracted with ethyl acetate and shaken with aqueous sodium hydroxide (2N.). Acidification of the alkaline extract gave crude 5-*acetyl*-6 : 7-*dihydroxycoumaran* as a yellow precipitate (10·6 g.), from which, after crystallisation from aqueous ethanol (50%), the pure product (9·3 g.) was obtained as long, pale yellow needles, m. p. 190° (Found : C, 61·9; H, 5·25. $C_{10}H_{10}O_4$ requires C, 61·9; H, 5·15%). It was readily soluble in acetone or warm ethanol, but sparingly soluble in ether or benzene. It gave a violet colour with alcoholic ferric chloride. It was recovered unchanged after being boiled for 1 hour with aqueous sodium hydroxide (2N.).

5-Acetyl-6 : 7-dihydroxycoumaran was also obtained on using a boron trifluoride–acetic acid complex as catalyst (cf. Part IV), but the yield was a little less.

Diacetate. Prepared by means of acetic anhydride and pyridine, the *diacetate* formed colourless prisms, m. p. 162°, from ethanol (Found : C, 60·4; H, 5·25. $C_{14}H_{14}O_6$ requires C, 60·4; H, 5·05%).

5-Acetyl-6-hydroxy-7-methoxycoumaran (V; R = Me, R′ = H).—A mixture of 5-acetyl-6 : 7-dihydroxycoumaran (0·75 g.), methyl sulphate (0·5 g.), dry acetone (30 c.c.), and anhydrous potassium carbonate (1·5 g.) was boiled under a reflux for 2 hours, then cooled and filtered. The solvent was distilled off, and a pale brown oil remained. This crystallised from aqueous ethanol and gave *5-acetyl-6-hydroxy-7-methoxycoumaran* (0·25 g.) as pale yellow prisms, m. p. 97° (Found : C, 63·4; H, 5·8. $C_{11}H_{12}O_4$ requires C, 63·3; H, 5·8%). It gave a dark blue colour with ethanolic ferric chloride.

5-Acetyl-7-ethoxy-6-hydroxycoumaran (V; R = Et, R′ = H).—5-Acetyl-6 : 7-dihydroxycoumaran (2·3 g.), ethyl sulphate (1·9 g.), anhydrous potassium carbonate (10 g.), and acetone (150 c.c.) were boiled under a reflux for 8 hours. The yellow oil obtained after removal of the solvent solidified partly on cooling, and on crystallisation from aqueous ethanol gave *5-acetyl-7-ethoxy-6-hydroxycoumaran* (0·84 g.) as colourless prisms, m. p. 111° (Found : C, 64·6; H, 6·3. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·35%).

5-Acetyl-7-benzyloxy-6-hydroxycoumaran (V; R = C_7H_7, R′ = H).—5-Acetyl-6 : 7-dihydroxycoumaran (2 g.), benzyl chloride (1·4 g.), anhydrous potassium carbonate (2 g.), sodium iodide (2 g.), and dry acetone (50 c.c.) were boiled under a reflux for 6 hours. The solvent was distilled off, leaving a yellow oil, which slowly solidified. After trituration with aqueous ethanol (20%), the solid (2·85 g.; m. p. 109—110·5°) crystallised from ethanol (50%) giving *5-acetyl-7-benzyloxy-6-hydroxycoumaran* as fine, long, pale yellow needles, m. p. 113—114° (Found : C, 71·8; H, 6·0. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·7%). It was readily soluble in chloroform, ether, or warm ethanol. It gave a purple colour with ethanolic ferric chloride.

5-Acetyl-6 : 7-dimethoxycoumaran (V; R = R′ = Me).—(*a*) (cf. Baker and Lothian, *J.*, 1935, 628). Aqueous potassium hydroxide (400 c.c.; 20%) and methyl sulphate (130 c.c.) were added alternately in 5—6 portions, with good shaking after each addition, to a solution of 5-acetyl-6 : 7-dihydroxycoumaran (10 g.) in acetone (150 c.c.) under a reflux. The addition was regulated so as to maintain boiling and took about 30 minutes; the mixture was then boiled for a further 30—45 minutes. The cooled solution was extracted with ether, and the ethereal extract washed with aqueous sodium hydroxide (2N.), then water, and dried ($MgSO_4$). Fractional distillation gave *5-acetyl-6 : 7-dimethoxycoumaran* (8 g.) as a pale yellow oil, b. p. 139—142°/1·2 mm., n_D^{20} 1·5448 (Found : C, 64·5; H, 6·6. $C_{12}H_{14}O_4$ requires C, 64·85; H, 6·35%).

(*b*) A mixture of 5-acetyl-6 : 7-dihydroxycoumaran (3 g.), methyl sulphate (6 g.), dry acetone (50 c.c.), and anhydrous potassium carbonate (6 g.) was boiled under a reflux for 4½ hours, then cooled and filtered. The solvent was distilled off, and the reddish-brown, oily residue was dissolved in ether. Fractionation of the alkali-washed and dried extract gave 5-acetyl-6 : 7-dimethoxycoumaran (2·3 g.) identical with the product formed by method (*a*).

7-Benzyloxy-6-hydroxy-5-β-ketobutyrylcoumaran (VI; R = C_7H_7, R′ = H).—5-Acetyl-7-benzyloxy-6-hydroxycoumaran (2·8 g.) in dry ethyl acetate (50 c.c.) was added to powdered sodium (0·95 g.) covered with dry ether (10 c.c.), and the mixture boiled under a reflux for 4 hours. The bulk of the solvent was distilled off, and the yellow residue of sodio-salt was decomposed by adding ice-cold, aqueous acetic acid (50 c.c.; 20%). The aqueous layer was decanted from the orange-coloured oil produced, which was then triturated successively with light petroleum (b. p. 40—60°) and ethanol. The solid product thus obtained crystallised from ethanol to give *7-benzyloxy-6-hydroxy-5-β-ketobutyrylcoumaran* (1·2 g.) as colourless, prismatic needles, m. p. 109° (Found : C, 70·0; H, 5·8. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·6%). It was readily soluble in acetone, ether, or chloroform.

6 : 7-Dimethoxy-5-β-ketobyryrylcoumaran (VI; R = R′ = Me).—A solution of 5-acetyl-6 : 7-dimethoxycoumaran (5·2 g.) in dry ethyl acetate (50 c.c.) was added to powdered sodium (2·1 g.), just covered with dry ether (10 c.c.). The mixture was boiled under a reflux for 4 hours, the solvent distilled off, and ice-cold aqueous acetic acid (100 c.c.; 20%) added to the cooled residue. The mixture was extracted with ether, and the washed and dried extract was fractionated under reduced pressure, *6 : 7-dimethoxy-5-β-ketobutyrylcoumaran* (3·2 g.) being obtained as a yellow, viscous oil, b. p. 164—165°/1·2 mm., n_D^{20} 1·5956 (Found : C, 63·6; H, 6·3. $C_{14}H_{16}O_5$ requires C, 63·6; H, 6·1%).

4′ : 5′-Dihydro-8-methoxy-2-methylfurano(3′ : 2′-6 : 7)chromone (VII; R = Me, R′ = H) *and 4′ : 5′-Dihydro-8-hydroxy-2-methylfurano(3′ : 2′-6 : 7)chromone.*—A solution of 6 : 7-dimethoxy-5-β-ketobutyrylcoumaran (1·5 g.) in glacial acetic acid (25 c.c.) containing hydrobromic acid (1·5 c.c.; *d* 1·7) was boiled under a reflux for 15 minutes. The cooled solution was poured into excess of aqueous sodium hydroxide (2N.), whereupon *4′ : 5′-dihydro-8-methoxy-2-methylfurano(3′ : 2′-6 : 7)chromone* was precipitated as colourless needles, which crystallised from water as colourless, matted needles (1 g.), m. p. 158—159°, or as clusters of long colourless needles, m. p. 159°, from a mixture (1 : 1 by vol.) of light petroleum (b. p. 60—80°) and benzene (Found : C, 67·3; H, 5·2. $C_{13}H_{12}O_4$ requires C, 67·2; H, 5·2%). It dissolved in concentrated sulphuric acid to give an almost colourless solution, which became golden-yellow when warmed. Boiling the dihydrofuranochromone (0·5 g.) under a reflux for 10 minutes with benzaldehdye (0·5 g.) and a solution of sodium methoxide, derived from sodium (0·15 g.) and methanol (5 c.c.), gave the *styryl* derivative, colourless needles, m. p. 188°, from methanol (Found : C, 74·7; H, 4·9. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%). Its intense yellow solution in concentrated sulphuric acid became reddish-brown when warmed.

When the solution obtained by the cautious addition of acetic anhydride (16 c.c.) to a suspension of the 8-methoxy-compound (1·3 g.) in hydriodic acid (12 c.c.) was boiled under a reflux for 30 minutes and then poured into ice–water (100 c.c.) containing a little sodium hydrogen sulphite, a pale yellow precipitate of (probably) 7 : 8-dihydroxy-6-2′-iodoethyl-2-methylchromone (IX) separated. It formed colourless, microcrystalline prisms (1·3 g.), m. p. 193—194°, after crystallisation from aqueous ethanol (50%). It gave a bottle-green colour with ethanolic ferric chloride, and its yellow solution in concen-

trated sulphuric acid became red when warmed. The iodo-compound (1 g.) in ethanol (25 c.c.) containing anhydrous sodium acetate (2 g.) was boiled under a reflux for 4 hours, the solvent distilled off, and water (50 c.c.) added to the grey solid residue. The solid was filtered off 24 hours later and crystallised from water. 4′ : 5′-*Dihydro*-8-*hydroxy*-2-*methylfurano*(3′ : 2′-6 : 7)*chromone* (0·4 g.) separated as colourless, matted needles, m. p. 230° (Found : C, 65·7; H, 4·6. $C_{12}H_{10}O_4$ requires C, 66·0; H, 4·6%). It was readily soluble in acetone, chloroform, or ether. Its pale yellow solution in concentrated sulphuric acid became apple-green and then brown when warmed.

4′ : 5′-*Dihydro*-8-*ethoxy*-2-*methylfurano*(3′ : 2′-6 : 7)*chromone* (VII; R = Et, R′ = H).—(*a*) 5-Acetyl-7-ethoxy-6-hydroxycoumaran (0·64 g.) was condensed with dry ethyl acetate (30 c.c.) in the usual way, using powdered sodium (0·25 g.) just covered with ether (10 c.c.) and boiling under a reflux for 4 hours. The yellow sodio-salt was decomposed with ice-cold, aqueous acetic acid (30 c.c.; 20%). The crude diketone, obtained as a red oil, was boiled under a reflux for 15 minutes with glacial acetic acid (10 c.c.) containing 1 drop of concentrated hydrochloric acid. Addition of water and extraction with chloroform furnished a red oil, which solidified on trituration with light petroleum (b. p. 60—80°) to give pink crystals. On crystallisation from water, 4′ : 5′-*dihydro*-8-*ethoxy*-2-*methylfurano*(3′ : 2′-6 : 7)*chromone* (0·2 g.) was obtained as colourless, matted needles, m. p. 130° (Found : C, 68·3; H, 6·0. $C_{14}H_{16}O_4$ requires C, 68·3; H, 5·7%). It was readily soluble in acetone, ether, or warm ethanol. The colourless solution in concentrated sulphuric acid became yellow, then brown, when warmed.

(*b*) 4′ : 5′-Dihydro-8-hydroxy-2-methylfurano(3′ : 2′-6 : 7)chromone (0·18 g.) was boiled for 17 hours under a reflux with ethyl sulphate (2 c.c.), potassium carbonate (2 g.), and acetone (25 c.c.); the 8-ethoxy-compound obtained (0·1 g.) was identical with the above.

8-*Benzyloxy*-4′ : 5′-*dihydro*-2-*methylfurano*(3′ : 2′-6 : 7)*chromone* (VII; R = C_7H_7, R′ = H).—(*a*) 7-Benzyloxy-6-hydroxy-5-β-ketobutyrylcoumaran (0·55 g.) in glacial acetic acid (5 c.c.) containing 1 drop of concentrated hydrochloric acid was boiled under a reflux for 15 minutes. The solution was poured into hot water (100 c.c.), and an oil separated, which slowly solidified on cooling and stirring. Crystallised from aqueous ethanol (50%), it gave 8-*benzyloxy*-4′ : 5′-*dihydro*-2-*methylfurano*(3′ : 2′-6 : 7)*chromone* (0·38 g.) as colourless needles, m. p. 110° (Found : C, 73·7; H, 5·2. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%). It was readily soluble in ether, chloroform, or warm ethanol. The yellow solution in concentrated sulphuric acid became dark brown when warmed.

(*b*) Benzylation of 4′ : 5′-dihydro-8-hydroxy-2-methylfurano(3′ : 2′-6 : 7)chromone (0·3 g.) by boiling it under a reflux for 3 hours with benzyl chloride (0·3 g.) in dry acetone (50 c.c.) containing anhydrous potassium carbonate (0·6 g.) also gave the 8-benzyloxy-compound (0·1 g.), m. p. 109·5°.

8-*Methoxy*-2-*methylfurano*(3′ : 2′-6 : 7)*chromone* (VIII; R = H).—The corresponding 4′ : 5′-dihydro-compound (0·8 g.) was heated at 240—250° with palladium–charcoal (0·1 g.) (Linstead and Thomas, *J.*, 1940, 1127) for 24 hours in a slow stream of carbon dioxide. The product, isolated by means of chloroform, was crystallised from methanol, and 8-*methoxy*-2-*methylfurano*(3′ : 2′-6 : 7)*chromone* (0·2 g.) separated as pale yellow needles, m. p. 196—197° (Found : C, 67·5; H, 4·5. $C_{13}H_{10}O_4$ requires C, 67·8; H, 4·4%). Its solution in concentrated sulphuric acid became golden-yellow and finally red-brown when warmed.

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