732. *The Synthesis of 3-Substituted Chromones by Rearrangement of o-Acyloxyacetophenones.*

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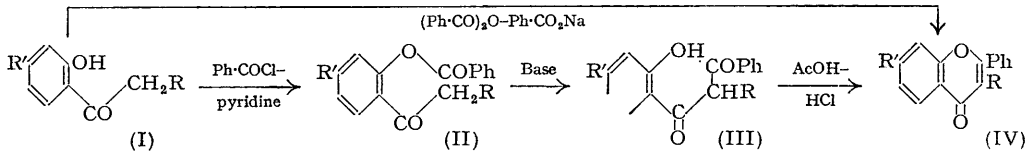
The base-catalysed rearrangement of *o*-acyloxyacetophenones (II) (the Baker–Venkataraman transformation) has been extended to ω-methyl, ω-methoxy, and ω-phenyl derivatives. The resulting 1 : 3-diketones (III) gave 3-substituted chromones (IV) with hydrochloric acid in acetic acid. Similar rearrangement and cyclisation of *o*-furoyloxy- or *o*-acetoxy-acetophenone (*e.g.*, VI) gave 2-substituted chromones (VIII).

The base-catalysed rearrangement of *o*-acyloxyacetophenones (*e.g.*, II; R = H) to *o*-hydroxydibenzoylmethanes (*e.g.*, III; R = H) (the Baker–Venkataraman transformation) (Baker, *J.*, 1933, 1381; 1934, 1953; Venkataraman *et al.*, *J.*, 1934, 1767; 1935, 868; Wheeler *et al.*, *Proc. Roy. Irish Acad.*, 1948, **24**, 291, where references to previous work are given) has been extended to ω-substituted acetophenones (*e.g.*, II; R = Me, OMe, or Ph). 3-Methoxyflavones (and thence flavonols) and *iso*flavones may thus be prepared.* These substances have usually been prepared by the Allan–Robinson synthesis (*e.g.*, I ⟶ IV), and the present work confirmed the view that the Baker–Venkataraman rearrangement is probably involved in this method.



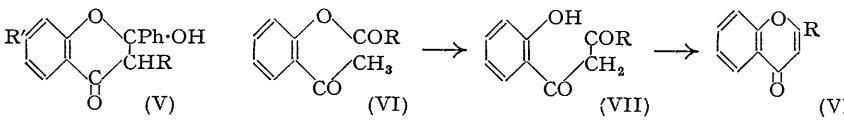
The *O*-benzoate (II; R = Me, R′ = OMe) of 2-hydroxy-4-methoxypropiophenone (I; R = Me, R′ = OMe) was smoothly rearranged by potassium hydroxide in pyridine to the 1 : 3-diketone (III; R = Me, R′ = OMe), which cyclised to 7-methoxy-3-methylflavone (IV; R = Me; R′ = OMe) when warmed with acetic–hydrochloric acids. Similarly, 2 : 4-dibenzoyloxypropiophenone (II; R = Me, R′ = Ph·CO·O) gave the diketone (III; R = Me; R′ = Ph·CO·O), and thence 7-benzoyloxy-3-methylflavone (IV; R = Me; R′ = Ph·CO·O). Demethylation of 7-methoxy-3-methylflavone, or hydrolysis of 7-benzoyloxy-3-methylflavone, gave 7-hydroxy-3-methylflavone (IV; R = Me; R′ = OH) (Canter, Curd, and Robertson, *J.*, 1931, 1264).

Rearrangement of 2-benzoyloxy-4 : ω-dimethoxyacetophenone (II; R = R′ = OMe) was not satisfactorily achieved although a variety of basic agents was used. The attempted isomerisation of 2 : 4-dibenzoyloxy-ω-methoxyacetophenone (II; R = OMe; R′ = Ph·CO·O) with potassium hydroxide in pyridine resulted in hydrolysis of the 1 : 3-diketone, but with potassium ethoxide in pyridine gave 4-benzoyloxy-2-hydroxy-ω-methoxyacetophenone (I; R = OMe, R′ = Ph·CO·O) formed by simple hydrolysis and the expected dibenzoylmethane derivative (III; R = OMe, R′ = Ph·CO·O). This 1 : 3-diketone could not be crystallised, but was readily cyclised with acetic–hydrochloric acids to 7-benzoyloxy-3-methoxyflavone (IV; R = OMe, R′ = Ph·CO·O), which on hydrolysis gave 7-hydroxy-3-methoxyflavone identical with that prepared by Allan and Robinson (*J.*, 1924, **125**, 2194). Wheeler *et al.* (*J.*, 1950, 1258) have similarly prepared 7-benzoyloxy-3-methoxyflavone by heating 2 : 4-dibenzoyloxy-ω-methoxyacetophenone in pyridine with potassium carbonate.

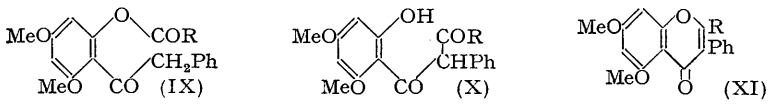
Wheeler *et al.* (*J.*, 1950, 1254) reported that *o*-acetoxyacetophenone (VI; R = Me) could not be isomerised to 2-acetoacetylphenol (VII; R = Me) by the bases usually employed, *e.g.* potassium hydroxide in pyridine or metallic sodium in toluene, but that triphenylmethylsodium was effective. We, however, found use of potassium hydroxide in

* Since this paper was submitted for publication, Lynch, O'Toole, and Wheeler (*J.*, 1952, 2063) have described the preparation of flavanol 3-methyl ethers by thermal cyclisation (involving Baker–Venkataraman transformations) of aroyl esters of ω-methoxyphloracetophenones.

pyridine as successful as that of triphenylmethylsodium. This transformation also occurs when sodium in benzene is used (Virkar and Shah, *Proc. Indian Acad. Sci.*, 1949, **30**, 58). Also *o*-2′-furoyloxyacetophenone (VI; R = 2-furyl) with potassium hydroxide in pyridine gives 2′-furoyl-*o*-hydroxybenzoylmethane (VII; R = 2-furyl), and thence 2-2′-furylchromone (VIII; R = 2-furyl), which is unaffected by boiling hydrobromic–acetic acid.



Rearrangement of 2-acyloxydeoxybenzoins has not been studied previously and is of interest in connection with the synthesis of *iso*flavones. 2-Benzoyloxy-4 : 6-dimethoxydeoxybenzoin (IX; R = Ph) was readily converted by potassium hydroxide in pyridine into the 1 : 3-diketone (X; R = Ph), which was cyclised in the usual way to 5 : 7-dimethoxy-2 : 3-diphenylchromone (XI; R = Ph). This chromone when demethylated gave 5 : 7-dihydroxy-2 : 3-diphenylchromone, identical with the compound prepared previously (Baker and Eastwood, *J.*, 1929, 2901) by fusion of 2 : 4 : 6-trihydroxydeoxybenzoin with benzoic anhydride and sodium benzoate, and subsequent hydrolysis. Baker (*J.*, 1933, 1388) described the formation of 7-hydroxy-2 : 3-diphenylchromone when 2 : 4-dihydroxydeoxybenzoin is heated with benzoyl chloride and potassium carbonate in toluene. A rearrangement is probably involved in this and the preceding experiment.



Similarly, 2-2′-furoyloxy-4 : 6-dimethoxydeoxybenzoin (IX; R = 2-furyl) gave the diketone (X; R = 2-furyl) and thence 2-2′-furyl-4 : 6-dimethoxy*iso*flavone (XI; R = 2-furyl). We failed to oxidise this to 4 : 6-dimethoxy*iso*flavone-2-carboxylic acid (X; R = CO_2H).

It is of interest that all the diketones of the type (III) where R = Me, OMe, or Ph are colourless, whereas those in which R = H are bright yellow. This difference may be due either to alteration in the degree of enolisation or to disturbance of the (probable) equilibrium between (III) and its hemi-acetal (V). That (V) as well as (III) is probably concerned in the actual equilibrium structure of these diketones is indicated by their relatively weak ferric chloride reactions and their slow rate of solution in alkali in some cases. In this connection, it is perhaps significant that, when first prepared, (III; R = Me; R′ =OMe) had m. p. 166°, but, on keeping or recrystallisation, the m. p. fell to 134°; similar examples are given by Baker, Ollis, and Poole (*J.*, 1952, 1505).

Experimental

M.p.s are uncorrected. Analyses are by Drs. Weiler and Strauss, Oxford, and Mr. W. M. Eno, Bristol.

2-Hydroxy-4-methoxypropiophenone (I; R = Me; R′ = OMe).—2 : 4-Dihydroxypropiophenone (50 g.), anhydrous benzene (500 c.c.), freshly roasted potassium carbonate (50 g.), and methyl sulphate (38 g.) were boiled for 10 hours, cooled, and filtered, and the solid was washed with hot benzene. Removal of the benzene left a residue which, crystallised from ethanol (30 c.c.), gave 2-hydroxy-4-methoxypropiophenone (39 g., 72%), m. p. 56° (Tahara, *Ber.*, 1892, **25**, 1298, records m. p. 58°). Methylation by Adams's procedure for the preparation of 2-hydroxy-4-methoxyacetophenone (*J. Amer. Chem. Soc.*, 1919, **41**, 260) gave a 50—55% yield, but distillation (b. p. 118—124°/0·3 mm.) was necessary to obtain a satisfactory product.

2-Hydroxy-4 : ω-dimethoxyacetophenone (I; R = R′ = OMe).—Monomethylation of 2 : 4-dihydroxy-ω-methoxyacetophenone according to Slater and Stephen (*J.*, 1920, 313) gave only a 20% yield in our hands. The following method gave a 78% yield.

2 : 4-Dihydroxy-ω-methoxyacetophenone (11·1 g.; Slater and Stephen, *loc. cit.*), anhydrous benzene (300 c.c.), freshly roasted potassium carbonate, and methyl sulphate (7·7 g.) were boiled for 10 hours, filtered, and the solid washed with hot benzene. The filtrate and washings after

concentration yielded 2-hydroxy-4 : ω-dimethoxyacetophenone (9·4 g.), m. p. 66° (Slater and Stephen gave m. p. 66°).

Preparation of ω-Substituted o-Benzoyloxyacetophenones (II).—(*a*) 2-Hydroxy-4-methoxypropiophenone (20 g.), dry pyridine (30 c.c.), and benzoyl chloride (15·6 g.) were heated on a steam-bath for 15 minutes, cooled, and poured into dilute hydrochloric acid. The precipitated oil solidified and was washed, dried (28·5 g., 90%), and recrystallised from ethanol (50 c.c.), giving 2-*benzoyloxy*-4-*methoxypropiophenone* (18 g.) as needles, m. p. 48° (Found: C, 71·6; H, 5·5; OMe, 10·9. $C_{16}H_{13}O_3$·OMe requires C, 71·8; H, 5·6; OMe, 10·9%).

(*b*) 2 : 4-Dihydroxypropiophenone (10 g.) and benzoyl chloride (16·9 g.) in anhydrous pyridine (25 c.c.) gave as in the previous case 2 : 4-*dibenzoyloxypropiophenone* (18·2 g., 86%), m. p. 92°, needles from methanol (50 c.c.) (Found: C, 73·5; H, 4·8. $C_{23}H_{18}O_5$ requires C, 73·8; H, 4·8%).

(*c*) 2-Hydroxy-4 : ω-dimethoxyacetophenone (3 g.) and benzoyl chloride (2·15 g.) in anhydrous pyridine (5 c.c.) were kept at room temperature for 2 hours and poured into dilute hydrochloric acid. The oil which solidified was collected (2·3 g., 50%) and crystallised from ethanol (10 c.c.), giving 2-*benzoyloxy*-4 : ω-*dimethoxyacetophenone* (1·8 g.) as needles, m. p. 43° (Found: C, 67·8; H, 5·2. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%). This compound could not be satisfactorily rearranged to give the corresponding diketone (see below).

2-*Benzoyloxy*-4 : 6-*dimethoxydeoxybenzoin* (IX; R = Ph).—2-Hydroxy-4 : 6-dimethoxydeoxybenzoin (7 g.; Badcock, Cavill, Robertson, and Whalley, *J.*, 1950, 2964) and benzoyl chloride (3·7 g.) in pyridine (12 c.c.) gave, as in the preceding cases, after 15 minutes' heating, 2-*benzoyloxy*-4 : 6-*dimethoxydeoxybenzoin* (8·45 g.; 87%) as needles, m. p. 94°, from chloroform or ethyl acetate (30 c.c.) (Found: C, 73·4; H, 5·1. $C_{23}H_{20}O_5$ requires C, 73·4; H, 5·3%).

α-*Benzoyl*-2-*hydroxy*-4-*methoxypropiophenone* (III; R = Me, R′ = OMe).—2-Benzoyloxy-4-methoxypropiophenone (2·0 g.) in anhydrous pyridine (6 c.c.) was treated at 50° with powdered potassium hydroxide (0·5 g.), and the mixture shaken vigorously for 5 minutes. The suspension of the yellow potassium salt of the diketone was added to excess of 20% acetic acid, and the solid (1·4 g., 70%) was recrystallised from ethanol, giving α-*benzoyl*-2-*hydroxy*-4-*methoxypropiophenone* (1·2 g.) as colourless cubes, m. p. 134° (Found: C, 71·7; H, 5·8; OMe, 11·1. $C_{16}H_{13}O_3$·OMe requires C, 71·8; H, 5·7; OMe, 10·9%). This compound when first prepared had m. p. 166° (cf. p. 3827); the m. p. 144° recorded for this compound by Baker, Ollis, and Poole (*loc. cit.*) was given in error for 134°. The diketone slowly dissolved in 2N-sodium hydroxide and gave a fairly weak reddish-brown colour with aqueous-alcoholic ferric chloride.

α-*Benzoyl*-4-*benzoyloxy*-2-*hydroxypropiophenone* (III; R = Me, R′ = Ph·CO·O) and 4-*Benzoyloxy*-2-*hydroxypropiophenone* (I; R = Me, R′ = Ph·CO·O).—As in the preceding experiment, 2 : 4-dibenzoyloxypropiophenone (10 g.) in pyridine (25 c.c.) with potassium hydroxide (1·6 g.) gave an oil (7·1 g.) on being poured into excess of dilute acetic acid. It could not be crystallised, but its constitution as α-benzoyl-4-benzoyloxy-2-hydroxypropiophenone follows from its ready conversion into 7-benzoyloxy-3-methylflavone by hydrochloric acid in glacial acetic acid (see below).

In an attempt to purify this diketone, a portion was distilled (b. p. 210—220°/0·4 mm.), and the product was identified as 4-*benzoyloxy*-2-*hydroxypropiophenone* (I; R = Me, R′ = Ph·CO·O), colourless needles, m. p. 80° (Found: C, 71·0; H, 5·3. $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2%). It gave a strong purple ferric chloride reaction. The distillation residue crystallised from methanol, giving 7-benzoyloxy-3-methylflavone, m. p. and mixed m. p. 127° (see below).

α-*Benzoyl*-4-*benzoyloxy*-2-*hydroxy*-α-*methoxyacetophenone* (III; R = OMe, R′ = Ph·CO·O) *and* 4-*Benzoyloxy*-2-*hydroxy*-ω-*methoxyacetophenone* (I; R = OMe, R′ = Ph·CO·O).—The rearrangement was attempted with potassium hydroxide but extensive hydrolysis occurred; use of potassium ethoxide was more successful. Potassium ethoxide (1·2 g.) was added at room temperature to a solution of 2 : 4-dibenzoyloxy-ω-methoxyacetophenone (5 g.; Fonseka, *J.*, 1947, 1683) in anhydrous pyridine (20 c.c.). A bright yellow precipitate separated and after 1 minute excess of dilute acetic acid was added. The oil was extracted with chloroform and dried ($MgSO_4$), and the solvent removed, leaving a residue (3·9 g.) which was not obtained completely crystalline. In an attempted purification it was dissolved in hot ethanol, and on cooling 4-*benzoyloxy*-2-*hydroxy*-ω-*methoxyacetophenone* (0·4 g.) separated as colourless prisms, m. p. 122° (Found: C, 67·1; H, 4·9. $C_{16}H_{14}O_5$ requires C, 67·1; H, 5·2%). It gave a strong purple ferric chloride reaction. Removal of the ethanol from the mother-liquors gave a sticky residue which was at least mainly α-benzoyl-4-benzoyloxy-2-hydroxy-α-methoxyacetophenone as it was readily cyclised to give the corresponding flavone (see below).

α-*Benzoyl*-2-*hydroxy*-4 : 6-*dimethoxydeoxybenzoin* (X; R = Ph).—Powdered potassium hydroxide (0·56 g.) was added to a solution of 2-benzoyloxy-4 : 6-dimethoxydeoxybenzoin (3·7 g.) in anhydrous pyridine (10 c.c.). The required potassium salt separated immediately. The oil

obtained by pouring the mixture into dilute hydrochloric acid solidified (3·6 g., 97%). Crystallisation from ethanol (50 c.c.) gave *α-benzoyl-2-hydroxy-4 : 6-dimethoxydeoxybenzoin* as colourless prisms, m. p. 180° [Found : C, 73·5; H, 5·5; OMe, 16·6. $C_{21}H_{14}O_3(OMe)_2$ requires C, 73·4; H, 5·3; OMe, 16·5%]. It gave a reddish-brown ferric chloride reaction, but was not soluble in 2N-sodium hydroxide.

7-Methoxy-3-methylflavone (IV; R = Me, R′ = OMe).—α-Benzoyl-2-hydroxy-4-methoxypropiophenone (6 g.), glacial acetic acid (40 c.c.), and concentrated hydrochloric acid (2 c.c.) were warmed on a steam-bath for 5 minutes, cooled, and diluted with water. The solid (5·1 g., 85%) crystallised from ethanol (25 c.c.), giving *7-methoxy-3-methylflavone* as needles, m. p. 116° (Found : C, 76·7; H, 5·4; OMe, 11·4. $C_{16}H_{11}O_2$·OMe requires C, 76·7; H, 5·3; OMe, 11·6%).

7-Benzoyloxy-3-methylflavone (IV; R = Me, R′ = Ph·CO·O).—As in the preceding experiment, crude α-benzoyl-4-benzoyloxy-2-hydroxypropiophenone (7·1 g.), acetic acid (20 c.c.), and concentrated hydrochloric acid (1 c.c.) gave 7-benzoyloxy-3-methylflavone (6·3 g., 93%), colourless needles, m. p. 127°, from methanol (150 c.c.) (Found : C, 77·4; H, 4·6. $C_{23}H_{16}O_4$ requires C, 77·5; H, 4·5%).

This and the preceding flavone were each converted into 7-hydroxy-3-methylflavone (IV; R = Me; R′ = OH) as follows. (*a*) 7-Methoxy-3-methylflavone (1 g.), glacial acetic acid (20 c.c.), and hydrobromic acid (20 c.c.; *d* 1·49) were boiled for 8 hours, then diluted with water, and the solid (0·9 g., 95%) was collected. Crystallisation from ethanol (4 c.c.) gave 7-hydroxy-3-methyl flavone as fine needles, m. p. 278°.

(*b*) 7-Benzoyloxy-3-methylflavone (1 g.) and potassium hydroxide (0·28 g.) were dissolved in ethanol (15 c.c.) and water (15 c.c.), boiled for ½ hour, the mixture was diluted with water and saturated with carbon dioxide, and the solid (0·59 g., 84%) collected. Crystallisation from ethanol gave 7-hydroxy-3-methylflavone, m. p. and mixed m. p. 278°. The acetyl derivative, prepared by use of acetic anhydride and pyridine, had m. p. 132° after several crystallisations from ethanol. Canter, Curd, and Robertson (*J.*, 1931, 1264) give m. p. 278° for 7-hydroxy-3-methylflavone, and m. p. 137° for its acetate.

7-Benzoyloxy-3-methoxyflavone (IV; R = OMe, R′ = Ph·CO·O).—Crude α-benzoyl-4-benzoyloxy-2-hydroxy-α-methoxypropiophenone (2·9 g.), acetic acid (10 c.c.), and concentrated hydrochloric acid (0·5 c.c.) were warmed on a steam-bath for 5 minutes. Addition of water gave an oil, and chloroform-extraction yielded a residue which, after crystallisation from ethanol, gave *7-benzoyloxy-3-methoxyflavone* as colourless needles, m. p. 131° (Found : C, 73·5; H, 4·1. $C_{23}H_{16}O_5$ requires C, 73·4; H, 4·3%).

Alkaline hydrolysis of this flavone (1 g.) as in the case of 7-benzoyloxy-3-methylflavone gave 7-hydroxy-3-methoxyflavone (0·7 g.), colourless needles, m. p. 233°, from ethanol (Allan and Robinson, *J.*, 1924, 2194, give m. p. 227°; Wheeler *et al.*, *J.*, 1950, 1258, give m. p. 233°).

5 : 7-Dimethoxy-2 : 3-diphenylchromone (XI; R = Ph).—α-Benzoyl-2-hydroxy-4 : 6-dimethoxydeoxybenzoin (0·75 g.), acetic acid (5 c.c.), and concentrated hydrochloric acid (0·3 c.c.), when heated on a steam-bath for 5 minutes, gave *5 : 7-dimethoxy-2 : 3-diphenylchromone* (0·7 g.), colourless rhombs, m. p. 195°, from ethyl acetate (3 c.c.) [Found : C, 77·1; H, 5·2; OMe, 17·5. $C_{21}H_{12}(OMe)_2$ requires C, 77·1; H, 5·1; OMe, 17·3%].

This chromone (0·3 g.), acetic acid (6 c.c.), and hydrobromic acid (6 c.c.; *d* 1·49) were boiled for 8 hours. Addition of water gave a solid (0·2 g.) which, after crystallisation from ethanol, gave 5 : 7-dihydroxy-2 : 3-diphenylchromone, m. p. 250°. It showed no depression of m. p. when mixed with a specimen prepared by the method of Baker and Eastwood (*J.*, 1929, 2901) and gave a gel with 1% aqueous sodium hydroxide (cf. Baker and Eastwood).

o-Acetoacetylphenol (VII; R = Me).—To *o*-acetoxyacetophenone (VI; R = Me) (4·2 g.; Friedländer and Neudörfer, *Ber.*, 1897, **30**, 1080) in anhydrous pyridine (10 c.c.) powdered potassium hydroxide (1 g.) was added with stirring at room temperature. After 15 minutes, dilute hydrochloric acid was added and the solution set aside in the refrigerator; the crystalline precipitate which separated was recrystallised from benzene–light petroleum (b. p. 60—80°), giving *o*-acetoacetylphenol (0·3 g., 7%) as needles, m. p. and mixed m. p. with an authentic specimen, 92° (Wittig, *Annalen*, 1926, **446**, 169, gives m. p. 90·5—91·5°). The yield is slightly higher than that obtained by Wheeler *et al.* (*J.*, 1950, 1255) who used triphenylmethylsodium. Virkar and Shah (*Proc. Indian Acad. Sci.*, 1949, **30**, 58) reported that this rearrangement may also be effected with sodium in benzene, but the yield was poor and isolation of the product *via* its copper derivative was necessary.

o-2′-Furoyloxyacetophenone (VI; R = 2-furyl).—2-Furoyl chloride (5·5 g.) was added to *o*-hydroxyacetophenone (5·6 g.) in dry pyridine (10 c.c.), and after 1 hour the whole was poured into dilute hydrochloric acid. The solid (9·4 g., 99%) crystallised from ethanol, giving *o-2′-*

furoyloxyacetophenone as colourless plates, m. p. 92° (Found : 67·8; H, 4·2. $C_{13}H_{10}O_4$ requires C, 67·8; H, 4·3%).

2-2′-*Furoyloxy*-4 : 6-*dimethoxydeoxybenzoin* (IX; R = 2-furyl).—Similarly, 2-furoyl chloride (2·5 g.) and 2-hydroxy-4 : 6-dimethoxydeoxybenzoin (5 g.) in pyridine (20 c.c.) gave the 2-2′-*furoyloxy*-4 : 6-*dimethoxydeoxybenzoin* (6·1 g., 91%), as colourless platelets, m. p. 116°, from ethanol (Found : C, 68·9; H, 4·8. $C_{21}H_{18}O_6$ requires C, 68·8; H, 4·9%).

2-*Furoyl*-o-*hydroxybenzoylmethane* (VII; R = 2-furyl).—Powdered potassium hydroxide (4·4 g.) was slowly added to *o*-2′-furoyloxyacetophenone (15·2 g.) in dry pyridine (40 c.c.). After 5 minutes, excess of dilute acetic acid was added, and the oil which solidified was collected (9·9 g., 65%) and crystallised from ethanol, giving 2-*furoyl*-o-*hydroxybenzoylmethane* (8·8 g.) as yellow needles, m. p. 76° (Found : C, 67·8; H, 4·2. $C_{13}H_{10}O_4$ requires C, 67·8; H, 4·3%). It gave a yellow solution in aqueous sodium hydroxide and an intense reddish-brown colour with aqueous-alcoholic ferric chloride.

α-2″-*Furoyl*-2-*hydroxy*-4 : 6-*dimethoxydeoxybenzoin* (X; R = 2-furyl).—Similarly, powdered potassium hydroxide (0·7 g.) and 2-2″-furoyloxy-4 : 6-dimethoxydeoxybenzoin (4·4 g.) in pyridine (20 c.c.) after 5 minutes at 50° gave α-2″-*furoyl*-2-*hydroxy*-4 : 6-*dimethoxydeoxybenzoin* (4·1 g., 93%) as colourless prisms, m. p. 139°, from ethanol (15 c.c.) (Found : C, 68·5; H, 5·2. $C_{21}H_{18}O_6$ requires C, 68·8; H, 4·9%). It gave a deep-red ferric chloride reaction and gave a yellow solution in 2N-sodium hydroxide.

2-2′-*Furylchromone* (VIII; R = 2-furyl).—α-2′-Furoyl-*o*-hydroxybenzoylmethane (2·5 g.), acetic acid (10 c.c.), and concentrated hydrochloric acid (0·5 c.c.) gave, after 5 minutes at 100°, 2-2′-*furylchromone* (2·1 g., 91%). This forms colourless needles, m. p. 135°, from ethanol (10 c.c.) (Found : C, 73·3; H, 3·7. $C_{13}H_8O_3$ requires C, 73·6; H, 3·8%).

2-2′-*Furyl*-5 : 7-*dimethoxy*isoflavone (XI; R = 2-furyl).—Similarly α-2″-furoyl-2-hydroxy-4 : 6-dimethoxydeoxybenzoin (2 g.) gave 2-2′-*furyl*-5 : 7-*dimethoxy*isoflavone (1·9 g.), fine, colourless needles, m. p. 195°, from ethanol (10 c.c.) (Found : C, 72·4; H, 4·5. $C_{21}H_{16}O_5$ requires C, 72·4; H, 4·6%).

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